The 7th International Conference on

Advanced Nanoparticle Generation and Excitation by Lasers in Liquids (ANGEL)

May 26th -30th, 2024
Charlottesville, Virginia, USA
https://angel-conference.org

Conference Program
and
Book of Abstracts

Table of Contents

Welcome

Dear ANGEL Conference participants,

We are pleased to welcome you to the 7th International Conference on Advanced Nanoparticle Generation and Excitation by Lasers in Liquids (ANGEL), which makes its debut in the United States at the end of May of 2024. The conference continue the tradition initiated at the 2010 Conference in Engelberg, Switzerland, and strengthened at successive meetings in Taormina (Sicily, Italy) in 2012, Matsuyama-shi (Japan) in 2014, Essen (Germany) in 2016, Lyon (France) in 2018, and Hefei (China) in 2021.

ANGEL is the main international conference focused on synthesis of nanoparticles and nanomaterials by laser ablation and processing in liquid environment. It bring together researchers involved in experimental, theoretical, and computational investigations in the general area of laser-materials interaction in liquids. Broad representation of researchers from different countries and active interdisciplinary discussions are characteristics of ANGEL meetings. The conference provides a forum for sharing the results of both application-oriented work and studies of fundamental mechanisms related to laser synthesis and processing of nanoparticles, as well as the utilization of laser-generated particles in catalysis, energy conversion, additive manufacturing, and optics.

The program of the conference consist of four days of oral and poster sessions. To increase the visibility of poster presentations, flash-talk sessions are scheduled before each of the two poster sessions. A full-day pre-conference tutorial on the generation of nanoparticles by laser ablation in liquids is conducted on Sunday preceding the conference. The tutorial includes a hands-on component demonstrating the laser synthesis of nanoparticles in real time.

Conference participants are invited to contribute to Special Issues of the of Physical Chemistry C and Beilstein Journal of Nanotechnology.

Several ANGEL awards are established to recognize the most notable achievements and creative ideas, particularly by young researches entering the field. These includes the best oral and poster student presentation awards, the Fojtik-Henglein Prize, named after the inventors of the laser-based synthesis of nanoparticle colloids, as well as a newly established Shafeev Award, named after one of the most daring pioneers in the field of laser-based synthesis of nanoparticles, Dr. Georgy Shafeev.

ANGEL-7 Conference Chairs:

Katharine Tibbetts, Virginia Commonwealth University, USA

Leonid Zhigilei, University of Virginia, USA

Sponsors

We gratefully acknowledge and appreciate sponsorship and support by

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- Department of Materials Science and Engineering
- School of Engineering and Applied Science
- Office of the Vice President for Research

Virginia Commonwealth University

- College of Engineering
- Office of the Vice President for Research & Innovation

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Leonid Zhigilei, University of Virginia, USA

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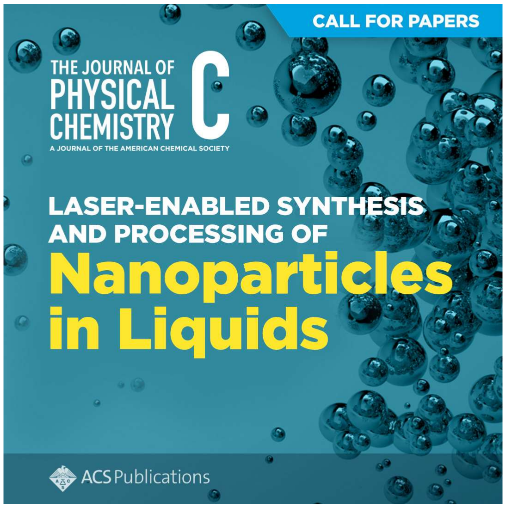
Special Journal Issues

ANGEL participants are invited to contribute to the Special Issues of *The Journal of Physical Chemistry C* and *Beilstein Journal of Nanotechnology*.



Guest Editors:

Prof. Katharine Tibbetts
Virginia Commonwealth University, USA

Prof. Dr. Stephan Barcikowski
University of Duisburg-Essen, Germany

Dr. Anna Ziefuß
University of Duisburg-Essen, Germany

Laser-enabled synthesis and processing of nanoparticles in liquids

https://axial.acs.org/physical-chemistry/call-for-papers-laser-enabled-synthesis-and-processing-of-nanoparticles-in-liquids

Contributions focused on physical chemistry aspects of the laser-material or nanoparticle interactions are invited to this Special Issue. Topics of interest include defect engineering through highly nonequilibrium synthesis conditions, the effect of defects, size and ligands on electron-phonon relaxation, optical properties and chemical activity of nanoparticles, time-resolved probing of laser-induced phase transformations (both in laser ablation and in laser-nanoparticle interactions), and nanoscale phase separation in multicomponent nanoparticles.

BEILSTEIN JOURNAL OF NANOTECHNOLOGY
Diamond Open Access journal

Laser-material interactions in liquids applied to nanoparticles and nanocomposites

https://www.beilstein-journals.org/bjnano/series/110

Guest Editors:

Dr. Carlos Doñate Buendía,
University Jaume I, Spain

Prof. Bilal Gökce,
University of Wuppertal, Germany

Prof. Leonid V. Zhigilei,
University of Virginia, USA

Contributions focused on nanoparticle synthesis and characterization, productivity of nanoparticle synthesis, manufacturing of nanoparticle-based nanocomposites, and related topics are invited to contribute to this Special Issue.

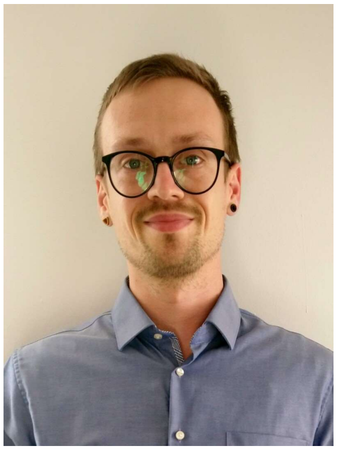
Topics of interest include new developments in laser-based nanoparticle synthesis and processing in liquids, applications of laser-generated nanoparticles and nanocomposites in catalysis, energy conversion, additive manufacturing, biomedicine, and other areas, integration of nanoparticles in advanced nanocomposite materials, biomedical applications of laser–nanoparticle interactions, fundamental studies of laser-materials interaction in liquids.

Tutorial

Pre-conference tutorial on the generation of nanoparticles by laser ablation in liquids will take place Sunday, May 26, at the University of Virginia Rotunda (*see Venue and Locations for directions*). The tutorial will be conducted by leading experts in the field and will include a hands-on component.

Prof. Vincenzo Amendola
University of Padova, Italy

Prof. Stephan Barcikowski



Dr. Friedrich Waag

University Duisburg-Essen, Germany

Schedule of the Tutorial

8:45: Registration and light breakfast (Multipurpose Room in the southwest wing of the Rotunda)

9:30: Tutorial starts in the Lower West Oval Room

9:30: Welcome by Conference Chairs (Tibbetts and Zhigilei)

9:40: Outline of the tutorial (Barcikowski)

9:45: Optimal laser and processing strategies for ablation, fragmentation, and melting (Barcikowski)

11:15: Unique nanoparticle properties and functionalities accessible by laser synthesis and processing of colloids (Amendola)

12:45: Lunch break and preparation for Science Slam (with brief Tips and Tricks from Friedrich Waag)

13:45: Science Slam (2 min oral pitch talk from each student) (Waag)

14:45: Practical course and demonstration of automated laser synthesis (Waag)

16:15: Discussion: Matching study design with unique goals of the project (Amendola, Barcikowski, Waag)

16:45: Wrap-up, flashback-round

17:30: Participants move to the ANGEL Welcome Reception (The Dome Room of the UVA Rotunda)

Venue and Locations

Tutorial on Sunday, May 26, 8:45 – 17:15

Tutorial starts with registration and light breakfast in the Multipurpose Room in the southwest wing of the Rotunda (8:45 – 9:30 am) and takes place in the Lower West Oval Room of the Rotunda starting from 9:30 am.

Enter Rotunda from the Lawn, ANGEL signs will be posted

Directions from the Dorm where many of the tutorial participants are staying (Watson - Webb House, 561 McCormick Rd) to the UVA Rotunda

Rotunda

Watson - Webb

One mile, about 20 minute walk

Follow McCormick Rd., cross bridge above Emmet St., turn right after you pass Minor Hall, and then turn left to the Lawn. Go along the Lawn and enter Rotunda.

Venue and Locations

ANGEL Welcome Reception, Sunday, May 26, 17:30 – 20:00

The ANGEL Welcome Reception is in the Dome Room of the UVA Rotunda.

On Sunday, the last free trolley departs from Downtown Transit Station at 5:05 pm and arrives to Chapel (close to Rotunda) at 5:30 pm. It is also possible to use Uber, or take a long walk (1.2 miles, 30 min) from Omni hotel to the Rotunda.

Enter Rotunda from the Lawn, ANGEL signs will be posted

ANGEL Conference, Monday - Thursday, May 27-30

The conference is held at the Charlottesville Omni Hotel adjacent to the historic downtown pedestrian mall, with many restaurants and shops located in the immediate vicinity of the hotel.

Charlottesville is located in the foothills of the Blue Ridge Mountains in Central Virginia, 110 miles south from the capital, Washington, DC (2.5 hours driving).

Regional airport in Charlottesville (CHO) is 8 miles from downtown, 50 non-stop flights to/from Charlotte, Chicago, Philadelphia, New York, Washington D.C., Atlanta.

Dulles International Airport (IAD) just outside Washington, D.C. + 2-3 hours by rental car or taxi to Charlottesville.

Train Amtrak daily routes from Union Station in Washington, D.C. (~2h 30 min).

Social Program

Wednesday, May 29, 14:00 – 22:00: Excursion to Monticello and Banquet

Excursion to Monticello - the house, gardens, and plantation of Thomas Jefferson (3rd president of the United States (1801- 1809), the principal author of the Declaration of Independence, and founder of UVA.

Conference banquet at The Wool Factory – the place of a mill complex, founded in 1868. The historic Woolen Mills was founded on a site of the Charlottesville Factory, built in 1840. The Factory produced cloth and uniforms during the Civil War and was burned by the Union Army in 1865. The Woolen Mills was known nationally for military fabrics and uniforms it produced, furnishing cloth for the majority of railroad workers and military schools. During World War II, the factory also provided uniform cloth. It was closed in 1962 and restored into an industrial event venue.

Conference Program – Sunday – Tutorial & Reception

Pre-conference tutorial at the UVA Rotunda

8:45: Registration and light breakfast
(Multipurpose Room in the southwest wing of the Rotunda)

9:30: Tutorial starts in the Lower West Oval Room

9:30: Welcome by Conference Chairs

9:40: Outline of the tutorial

9:45: Optimal laser and processing strategies for ablation, fragmentation, and melting

11:15: Unique nanoparticle properties and functionalities accessible by laser synthesis and processing of colloids

12:45: Lunch break and preparation for Science Slam

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17:30: Participants move to the ANGEL Welcome Reception
(The Dome Room of the UVA Rotunda)

ANGEL Welcome Reception at the Dome Room of the UVA Rotunda

17:30 – 19:30: Welcome Reception

Conference Program – Monday – Session 1

08.30-09.00: **Registration** (Omni Charlottesville Hotel Lobby)

08:30-09:00: **Light breakfast/snacks** (Salon AB, Jefferson Ballroom)

09.00-09.10: **Introductory Remarks** (Jefferson Ballroom)

Co-Chairs: Katharine Tibbetts, Virginia Commonwealth University, USA and Leonid Zhigilei, University of Virginia, USA

09.10-10.40: **SESSION 1: Fundamentals: Time-resolved probing of laser-induced processes**

Chair: Patrick Hopkins, University of Virginia, USA

09.10-09.40: **Changyong Song**, POSTECH, Korea (*invited talk*)

Direct observation of nanoparticle melting at femtosecond and nanometer scale with the XFEL

Co-authors: Chulho Jung, Yungok Ihm, Junha Hwang, Eunyoung Park, Jaeyong Shin, Daewoong Nam

09.40-10.00: **Anton Plech**, Karlsruhe Institute of Technology, Germany

Dynamics and mechanism of picosecond laser fragmentation of gold colloids in liquid

Co-authors: Meike Tack, Hao Huang, Mikhail Arefev, Anna R.Ziefuss, Matteo Levantino, Yogesh Pokhrel, Chaobo Chen, Leonid Zhigilei, Sven Reichenberger

10.00-10.20: **Mianzhen Mo**, SLAC National Accelerator Laboratory, USA

Ultrafast visualization of femtosecond laser-induced structural changes in liquid water

Co-authors: M. Arefev, C. Chen, S. Liang, D. Deponte, C. Crissman, Z. Chen, A. Descamps, M. Kozina, M.-F. Lin, J.P.F. Nunes, X. Na, B. Ofori-Okai, D. Pemmaraju, X. Shen, J. Yang, L.V. Zhigilei, X. J. Wang, S. H. Glenzer

10.20-10.40: **Heinz Huber**, Munich University of Applied Sciences, Germany

How can time-resolved experiments contribute to a validated model of ultrashort pulse laser ablation in liquids?

Co-authors: Maximilian Spellauge, David Redka, Meike Tack, Tina Friedenauer, Christoph Rehbock, Sven Reichenberger, Anna Rosa Ziefuss, Stephan Barcikowski, Carlos Doñate-Buendía, Bilal Gökce, Chaobo Chen, Leonid Zhigilei

10.40-11.10: **Coffee break**

Conference Program – Monday – Session 2

11.10-12.30: **SESSION 2: Fundamentals: Time-resolved probing and modeling**
Chair: Anton Plech, Karlsruhe Institute of Technology, Germany

11.10-11.30: **David Amans**, Université Claude Bernard Lyon 1, France
Unravelling bubbles formation in laser ablation in liquids
Co-authors: Vito Coviello, Vincenzo Amendola, Arnaud Sollier, Laurent Berthe, Bratislav Lukic, Alexander Rack

11.30-11.50: **Eunyoung Park**, POSTECH, Korea (student presentation)
Direct observation of localized surface plasmon-induced ultrafast melting in Au nanorods
Co-authors: Junha Hwang, Jaeyong Shin, Sung Yun Lee, Heemin Lee, Seung Phil Heo, Daewoong Nam, Sangsoo Kim, Min Seok Kim, In Tae Eom, Do Young Noh, Changyong Song

11.50-12.10: **Patrick Hopkins**, University of Virginia, USA
Specular vs. diffusive nature of heat transfer between acoustic phonons in a solid and gas molecules at interfaces
Co-authors: Ashutosh Giri, John A. Tomko

12.10-12.30: **Mohammad Sadegh Shakeri**, Institute of Nuclear Physics, Polish Academy of Sciences, Poland
Pulsed laser induced solvent-nanoparticle chemo-physical interaction: An effective approach toward creation of submicron heterostructures
Co-authors: Zaneta Swiatkowska-Warkocka

12.30-14.30: **Lunch** (Salon C, Jefferson Ballroom and James Monroe Room)

Conference Program – Monday – Sessions 3 and 4

14.30-16.00: **SESSION 3: Synthesis of nanoparticles: Biomedical & other applications**
Chair: Vincenzo Amendola, University of Padova, Italy

14.30-15.00: **Grégory Guisbiers**, University of Arkansas at Little Rock, USA (*invited talk*)
Designing nano-drugs by pulsed laser ablation in liquids

15.00-15.20: **Marcella Dell'Aglio**, Institute for Photonics & Nanotechnologies, CNR-IFN, Italy
Synthesis and characterization of boron nanoparticles produced by ns-laser ablation in water
Co-authors: Alessandro De Giacomo, Daniela Manno, Antonia Mallardi, Chiara Provenzano, Marcella Marra, Francesco Nocito, Antonio Serra, Gianluca Quarta, Anna Paola Caricato

15.20-15.40: **Francis Rey Cortes**, Universitat Jaume I, Spain (student presentation)
Pulsed laser fragmentation synthesis of carbon quantum dots (CQDs) as fluorescent probes in non-enzymatic glucose detection
Co-authors: Eva Falomir, Jesus Lancis, Gladys Mínguez-Vega

15.40-16.00: **Dana Krenz**, University of Duisburg-Essen, Germany (student presentation)
Is there a structural "sweet spot" for different ferrites treated with single laser pulses to engineer defects?
Co-authors: Soma Salamon, Joachim Landers, Sven Reichenberger, Stephan Barcikowski

16.00-16.30: **Coffee break**

16.30-17.30: **SESSION 4: Advances in pulsed laser ablation in liquids**
Chair: Tsuyoshi Asahi, Ehime University, Japan

16.30-16.50: **Meike Tack**, University of Duisburg-Essen, Germany (student presentation)
Inhibition of particle growth during single-pulse laser fragmentation by barrierless in-situ adsorption of the just-formed gold nanoparticles on a GO support
Co-authors: Anton Plech, Stephan Barcikowski, Sven Reichenberger

16.50-17.10: **Alejandro Crespo-Sosa**, Universidad Nacional Autónoma de México, Mexico
Laser ablation of metallic thin layers in liquids with wide irradiation spots
Co-author: Samuel Sánchez-Torres, Brenda-Lizeth Pérez-García, Juan-Gabriel Morales-Morales, Samuel Tehuacanero Cuapa

17.10-17.30: **Marcello Condorelli**, University of Study of Catania, Italy
Nanoparticles generated by laser ablation in liquids of Mount Etna volcanic rock
Co-authors: Antonio Brancato, Lucrezia Catanzaro, Matteo Barcellona, Maria Elena Fragalà, Luisa D'urso, Giuseppe Compagnini

Conference Program – Monday – Poster Session 1

17.30-18.00: FLASH TALKS for Poster Session 1

Chair: David Green, University of Virginia, USA

Flash talks by Nadine Stratmann, Marcello Condorelli, Sergio Molina-Prados, Chaobo Chen, Cory Trout, Mikhail Arefev, Samuel Harris, Sabila Kader Pinky, Wei Ran, and Zachary LaFaver

18.10-20.00: POSTER SESSION 1

Chair: Katharine Tibbetts, Virginia Commonwealth University, USA

P1 **Nadine Stratmann**, University of Duisburg-Essen, Germany (student presentation)

Influence of laser parameters and surface chemistry on the fragmentation of NIR absorbing LaB_6 microparticles for powder bed fusion with diode lasers

Co-authors: Michael Willeke, Matthias Miertz, Simon Leupold, Anna Ziefuß, Michael Schmidt, Stephan Barcikowski

P2 **Giuseppe Compagnini**, University of Catania, Italy

Random lasing using laser generated and modified silver nanoparticles

Co-authors: Luca Salemi

P3 **Marcello Condorelli**, University of Catania, Italy

AgNFs/2D hybrid nanomaterials as multi-wavelength SERS active and flexible platforms for chemical sensing applications

Co-authors: Antonio Brancato, Matteo Barcellona, Maria Elena Fragalà, Giuseppe Compagnini, Luisa D'Urso

P4 **Sergio Fernández Molina-Prados**, Universitat Jaume I, Spain (student presentation)

Co-localized scanning probe microscopy-Raman scattering studies of hybrid plasmonic substrates for SERS

Co-authors: Ana Cros, Gladys Minguez-Vega, Nuria Garro

P5 **Chaobo Chen**, University of Virginia, USA (student presentation)

Multiphysics modeling for laser-material interaction

Co-authors: Leonid V. Zhigilei

P6 **Cory Trout**, Rutgers University - Camden, USA (student presentation)

The influence of alkanethiols on the production of hydrophobic gold nanoparticles via pulsed laser ablation in liquids

Co-authors: Paul Kumpf, Karli Sipps, Julianne C. Griepenburg, Sean M. O'Malley

P7 **Yoshie Ishikawa**, National Institute of Advanced Industrial Science and Technology (AIST), Japan

Zn-Mg-O alloying in pulsed laser melting in liquid

Co-authors: Koichiro Saito, Takeshi Tsuji, Naoto Koshizaki

P8 **Chae Eun Park**, Gyeongsang National University, Korea (student presentation)

RuPdIrPtAu high-entropy alloys on carbon nanotube for hydrazine electrolysis via in situ Raman spectroscopy

Co-authors: Yeryeong Lee, Jayaraman Theerthagiri, Myong Yong Choi

Conference Program – Monday – Poster Session 1

P9 **Robert Stuckert**, University of Duisburg-Essen, Germany (student presentation)
Structure of Cantor and platinum group metal high-entropy alloy nanoparticles produced by laser ablation in liquid
Co-authors: Felix Pohl, Ulrich Schürmann, Lorenz Kienle, Christoph Rehbock, Stephan Barcikowski

P10 **Mikhail Arefev**, University of Virginia, USA (student presentation)
Molecular dynamics modeling of heat transfer and nanobubble formation around a rapidly heated gold nanoparticle in water
Co-authors: Hao Huang, Leonid V. Zhigilei

P11 **Yogesh Pokhrel**, Karlsruhe Institute of Technology, Germany (student presentation)
Ultrafast in situ visible-light diagnostics of laser fragmentation in liquids
Co-authors: Meike Tack, Anna R. Ziefuss, R. Streubel, S. Reichenberger, Anton Plech

P12 **Nicholas G. Simpson**, Virginia Commonwealth University, USA (student presentation)
Visualizing crystal defects in copper nanoparticles using precession illumination-hollow cone dark field imaging
Co-authors: Katharine Moore Tibbetts

P13 **Jianping Chen**, Virginia Commonwealth University, USA (student presentation)
Laser-synthesized metal phyllosilicate nanoparticles for efficient CO_2 reduction
Co-authors: Chamari Weththasingha, Katharine Moore Tibbetts, Wei-Ning Wang

P14 **Chamari Weththasingha**, Virginia Commonwealth University, USA (student presentation)
Preparation of copper phyllosilicate (Cu-PS) nanocatalysts by laser ablation method in liquid
Co-authors: Katharine Moore Tibbetts

P15 **Samuel Harris**, Virginia Commonwealth University, USA (student presentation)
Exploring the trends of laser ablation of organic solvents
Co-authors: Ella Kaplan, Chamari Weththasingha, Katharine Moore Tibbetts

P16 **Sabila Kader Pinky**, North Carolina State University, USA (student presentation)
Role of solvents and surfactants in controlling polyfluorene film morphology deposited by RIR-MAPLE: An atomistic approach
Co-authors: Buang Zhang, Albert L. Kwansa, Adrienne D. Stiff-Roberts, Yaroslava G. Yingling

P17 **Ran Wei**, University of Rochester, USA (student presentation)
Simultaneous solar photovoltaic conversion and water desalination via quad-band superwicking fano-resonant optical coatings
Co-authors: Tianshu Xu, Mingjiang Ma, Mohamed Elkabbash, Chunlei Guo

P18 **Zachary R. LaFaver**, University of Virginia, USA (student presentation)
Predicting the effect of core size on ligand self-assembly in chemically mismatched alkyl thiol monolayers and reverse Monte Carlo fitting to MALDI-MS with ultrasmall nanoparticles
Co-authors: Kateri H. DuBay

Conference Program – Tuesday – Session 5

08:30-09:00 **Light breakfast/snacks** (Salon AB, Jefferson Ballroom)

09.00-10.30: **SESSION 5: Fundamentals: Time-resolved probing and modeling**
Chair: David Amans, Université Claude Bernard Lyon 1, France

09.00-09.30: **Hiroshi Yoshikawa**, Osaka University, Japan (*invited talk*)
Fabrication of single crystals by laser ablation in supersaturated/supercooled liquids
Co-authors: Hozumi Takahashi

09.30-09.50: **Tina Friedenauer**, University of Duisburg-Essen, Germany (student presentation)
The mechanisms of low degradation pulsed laser processing of organic microparticles in liquids
Co-authors: Maximilian Spellauge, Lucie K. Tintrop, Dana Krenz, Anna R. Ziefuss, Christoph Rehbock, Heinz P. Huber, Torsten C. Schmidt, Stephan Barcikowski

09.50-10.10: **Sara Makarem**, University of Virginia, USA (student presentation)
Measurement of thermal relaxation time of vibrational modes in glycerol using pump-probe spectroscopy
Co-authors: William D. Hutchins, Saman Zare, Patrick E. Hopkins

10.10-10.30: **Maximilian Spellauge**, Munich University of Applied Sciences, Germany (student presentation)
Significant reduction of ablation efficiency by spallation layer redeposition during ultrashort pulse laser ablation in liquid
Co-authors: Doñate-Buendia, Bilal Gökce, Stephan Barcikowski, Heinz P. Huber

10.30-11.00: **Coffee break**

Conference Program – Tuesday – Session 6

11.00-12.30: **SESSION 6: Laser-nanoparticle interactions: Melting, fragmentation, defect generation**

Chair: Sean O'Malley, Rutgers University - Camden, USA

11.00-11.30: **Anna Ziefuß**, University of Duisburg-Essen, Germany (*invited talk*)

Breaking boundaries: Laser-driven nanoparticle formation and microparticle crushing in liquids

Co-authors: Tina Friedenauer, Heinz Huber, Christoph Rehbock, Sven Reichenberger, Max Spellauge, Nadine Stratmann, Meike Tack, Michael Willeke, Stephan Barcikowski

11.30-11.50: **David Green**, University of Virginia, USA

Integrating laser desorption and simulation to predict monolayer structure on metallic nanoparticles

Co-authors: Kateri Dubay, Xu Wang

11.50-12.10: **Pooja Raveendran Nair**, Universidad Autónoma de Nuevo León, Mexico (student presentation)

Plasmonic hybrids of laser-modified TiO_2 for enhanced photoelectrochemical applications

Co-authors: Claudia Rosa Santiago Ramirez, Miguel Angel Gracia Pinilla, Bindu Krishnan, David Avellaneda Avellaneda, Josue Amilcar Aguilar Martinez, Sadasivan Shaji

12.10-12.30: **Sven Reichenberger**, University Duisburg-Essen, Germany

How surface defects and related local charge distributions control the adsorption of surfactant-free, electrostatically-stabilized colloidal nanoparticles under diffusion-controlled conditions

Co-authors: Kinran Lau, Manuel Matten, Brian Giera, Kai S. Exner, Stephan Barcikowski

12.30-14.10: **Lunch** (Salon C, Jefferson Ballroom and James Monroe Room)

14.10-14.30: **Special Presentation from NSF**

Chair: Leonid Zhigilei, University of Virginia

14.10-14.30: **Khershed P. Cooper**, National Science Foundation, Division of Civil, Mechanical and Manufacturing Innovation, USA

NSF support for ANGEL-related research: Advanced Manufacturing, Future Manufacturing and related programs, national and international collaborations, and new calls for proposals

Conference Program – Tuesday – Sessions 7 and 8

14.30-15.50: **SESSION 7: Reactive processes in synthesis of nanoparticles**
Chair: Vittorio Scardaci, University of Catania, Italy

14.30-14.50: **Rikuto Kuroda**, Illuminus Inc., Japan
Effect of additives on efficiency of gold nanoparticles formation by laser-induced reduction method
Co-authors: Shuhei Shibata, Hideki Ina, Takahiro Nakamura

14.50-15.10: **Runpeng Miao**, University of Padova, Italy (student presentation)
Data-driven predetermination of Cu oxidation state in copper nanoparticles: Application to the synthesis by laser ablation in liquid
Co-authors: Michael Bissoli, Andrea Basagni, Ester Marotta, Stefano Corni, Vincenzo Amendola

15.10-15.30: **Theo Fromme**, University of Duisburg-Essen, Germany (student presentation)
Chemical reaction pathways during laser fragmentation in organic solvents through chemical and physical by-product analysis
Co-authors: Rutger R. Müller, Lucie K. Tintrop, Torsten C. Schmidt, Sven Reichenberger, Stephan Barcikowski

15.30-15.50: **Morihisa Saeki**, National Institutes for Quantum Science & Technology, Japan
Time-resolved XAFS study on the laser-induced particle formation of a Pd(II) and Rh(III) ions in an aqueous/ethanol solution
Co-authors: D. Matsumura, R. Nakanishi, T. Yomogida, T. Tsuji, Y. Kurosaki, H. Saitoh, H. Ohba

15.50-16.20: **Coffee break**

16.20-17.40: **SESSION 8: Synthesis of nanoparticles: Applications in catalysis, HEA**
Chair: Stephan Barcikowski, University of Duisburg-Essen, Germany

16.20-16.40: **Theerthagiri Jayaraman**, Gyeongsang National University, Korea
Pulsed laser-driven high-entropy materials for electrocatalytic water splitting
Co-authors: Chae Eun Park, Yeryeong Lee, Cheol Joo Moon, Myong Yong Choi

16.40-17.00: **Astrid Müller**, University of Rochester, USA
Pulsed laser in liquids made electrocatalysts for sustainability applications

17.00-17.20: **Bibek Singh**, Sikkim University, India (student presentation)
Structural evolution and Cu-Ni nanoprecipitate formation in Al-rich high entropy alloy nanoparticles through laser processing
Co-authors: Rajesh Rawat, Ajay Tripathi

17.20-17.40: **Zaneta Swiatkowska-Warkocka**, Institute of Nuclear Physics, Poland
Cu-based composite particles with enhanced electrocatalytic performance
Co-authors: M. Sadegh Shakeri

Conference Program – Tuesday – Poster Session 2

17.40-18.10: **FLASH TALKS for Poster Session 2**

Chair: Zaneta Swiatkowska-Warkocka, Institute of Nuclear Physics, Polish Academy of Sciences, Poland

Flash talks by Ella Kaplan, Chaobo Chen, Rafael A. Gonzalez Rosario, Ozcan Seslikaya, Vittorio Scardaci, Jan Söder, Madeleine Wilsey, Michael Ritch

18.10-20.00: **POSTER SESSION 2**

Chair: Leonid Zhigilei, University of Virginia, USA

P19 **William McMahon-Puce**, Swinburne University of Technology, Australia (student presentation)

Size separation of femtosecond pulsed laser ablated silicon nanoparticles

Co-authors: Christopher Nahon, Daniel Smith, Saulius Juodkazis, James W. M. Chon

P20 **Yeryeong Lee**, Gyeongsang National University, Korea (student presentation)

Dual-laser pulse-patterned α-$Co(OH)_2$/rGO heterointerface for accelerated water oxidation

Co-authors: Chae Eun Park, Jayaraman Theerthagiri, Myong Yong Choi

P21 **Stefano Faubel**, SLAC National Accelerator Laboratory, USA

Developing a highly stable liquid sheet with solvated nanoparticles for laser fragmentation studies

Co-authors: S. H. Glenzer, M. Z. Mo

P22 **Tina Hesabizadeh**, University of Arkansas at Little Rock, USA (student presentation)

Synthesis of selenium nanoparticles by pulsed laser ablation in liquids: Amorphous versus trigonal

Co-authors: Grégory Guisbiers

P23 **Rajendra Subedi**, University of Arkansas at Little Rock, USA (student presentation)

Synthesis of Bi_2Te_3 quantum dots by pulsed laser ablation in liquids

Co-authors: Grégory Guisbiers

P24 **Sepideh Khalili**, Tulane University, USA (student presentation)

Laser ablation of 2D layered materials to synthesize metastable nanostructures for energy storage applications

Co-authors: Najma Khatoon, Majed Ibrahim, Grégory Guisbiers, Michael Naguib, Mark Sulkes, Douglas B. Chrisey

P25 **Ella Kaplan**, Virginia Commonwealth University, USA (student presentation)

Laser synthesis of nickel-carbon-oxygen composites as catalysts for the oxygen reduction reaction

Co-authors: Chamari Weththasingha, Ashish Nag, Katharine M. Tibbetts

P26 **Chaobo Chen**, University of Virginia, USA (student presentation)

Thermodynamic maps and nanoparticle cooling rates in laser ablation of FeNi in liquid

Co-authors: Leonid V. Zhigilei

Conference Program – Tuesday – Poster Session 2

P27 **Rafael A. Gonzalez Rosario**, Virginia Commonwealth University, USA (student presentation)

Identifying unique de novo proteins for nanoparticle synthesis using LSPC synthesized metal oxide nanoparticles

Co-authors: Vivian Payne, Chamari Weththasingha, Katharine Tibbetts, Leah C. Spangler

P28 **Ozcan Seslikaya**, University of Virginia, USA (student presentation)

Spatially and size resolved maps of nanoparticle generation and energy partitioning in laser ablation in liquid

Co-authors: Rishika Deshmukh, Vivian Feng, Chaobo Chen, Leonid V. Zhigilei

P29 **Vittorio Scardaci**, University of Catania, Italy

Tuning the aggregation of metal nanoparticles prepared by laser ablation with halide salt solutions

Co-authors: Lucrezia Catanzaro, Marcello Condorelli, Luisa D'Urso, Mario Scuderi, Vittorio Scardaci, Giuseppe Compagnini

P30 **Rafael Torres-Mendieta**, Technical University of Liberec, Czech Republic

Reactive laser ablation in liquids as a promising approach for repurposing wastewater

Co-authors: Sabrin Abdallah

P31 **Jan Söder**, University Duisburg-Essen, Germany (student presentation)

How to tailor the mass loading and productivity during continuous single-step in-situ deposition of laser-generated nanoparticles

Co-authors: Bastian Mei, Stephan Barcikowski, Sven Reichenberger

P32 **Madeleine K. Wilsey**, University of Rochester, USA (student presentation)

Selective electrooxidation of toluene to benzyl alcohol by laser-made mixed-metal hydroxide nanocatalysts

Co-authors: Astrid M. Müller

P33 **Michael Ritch**, Virginia Commonwealth University, USA (student presentation)

Reducing temperature constraints of carbon monoxide oxidation utilizing 1,3,5-bezenetricarboxylate metallic organic framework derivative catalysts and laser assisted reduction

Co-authors: Abdallah Zedan, Michael Moody, Natalie Herring, Samy El-Shall

P34 **Tobias Wrubel**, University of Duisburg-Essen, Germany (student presentation)

Pulsed laser surface melting of micrometer particles

Co-authors: Emily Schönenberg, René Streubel, Leonid Zhigilei, Stephan Barcikowski, Anna R. Ziefuss

P35 **Antonios S. Valavanis**, University of Virginia, USA (student presentation)

Atomistic simulations of nanoparticle generation by fs laser ablation of thin Ag films

Co-authors: Cheng-Yu Shih, Costas P. Grigoropoulos, Leonid V. Zhigilei

P36 **Elaina Truhart**, University of Virginia, USA (student presentation)

Light-matter Interactions inside a transmission electron microscope: A new paradigm for studying laser ablation at the atomic scale

Co-authors: Kory Burns

Conference Program – Wednesday – Session 9

08:30-09:00 **Light breakfast/snacks** (Salon AB, Jefferson Ballroom)

09.00-10.30: **SESSION 9: Laser ablation for surface modification and nanoparticle synthesis**
Chair: Sadasivan Shaji, Universidad Autónoma de Nuevo León, Mexico

09.00-09.30: **Costas Grigoropoulos**, University of California at Berkeley, USA (*invited talk*)
Fundamental studies of femtosecond laser ablation by single and GHz train of pulses
Co-authors: Minok Park, Matthew Eliceiri, Runxuan Li, Vasileios Korakis, Vassilia Zorba

09.30-09.50: **Vittorio Scardaci**, University of Catania, Italy
Tuning wettability of graphene oxide by laser induced reduction in liquids
Co-authors: Sonia Zappalà, Luca Pulvirenti, Guido Condorelli, Antonella Sciuto, Giuseppe D'arrigo, Giuseppe Compagnini

09.50-10.10: **Jan Lino Kricke**, University of Wuppertal, Germany (student presentation)
Incorporating laser-synthesized $Fe_{50}Ni_{50}$ nanoparticles in photo-sensitive polymers for 4D printing of miniaturized magneto-responsive actuators
Co-authors: Inna Y. Khairani, Natalia Shkodich, Michael Farle, Carlos Doñate-Buendía, Bilal Gökce

10.10-10.30: **Sean O'Malley**, Rutgers University - Camden, USA
Formation of bismuth oxide nanostructures via laser ablation in water
Co-authors: Cory J. Trout, Julianne C. Griepenburg

10.30-11.00: **Coffee break**

11.00-12.40: **SESSION 10: Synthesis of nanoparticles for biomedical and other applications**

Chair: Carlos Doñate-Buendía, Universitat Jaume I, Spain

11.00-11.20: **Tsuyoshi Asahi**, Ehime University, Japan

Fabrication of organic nanoparticle colloids toward bio and medical applications

Co-authors: Taisei Himeda, Yuto Uchida , Ryosuke Nabeya, Tamotsu Zako

11.20-11.40: **Christoph Rehbock**, University of Duisburg-Essen, Germany

The therapy enhancing effect of laser-fabricated metal and alloy nanoparticles in proton therapy is driven by surface chemistry

Co-authors: Sandra Zwiehoff, Jacob Johny, Astrid Hensel, Shirley Knauer, Carina Behrends, Christian Bäumer, Kevin Kröninger, Beate Timmermann, Stephan Barcikowski

11.40-12.00: **Vincenzo Amendola**, University of Padova, Italy

Laser ablation synthesis of biodegradable and multifunctional nanoalloys for nanomedicine

12.00-12.20: **Sadasivan Shaji**, Universidad Autónoma de Nuevo León, Mexico

Plasmonic nanoparticles synthesized by laser ablation in liquid for SERS sensors with high enhancement in sensitivity and stability

Co-authors: Jithin Kundalam Kadavath, Bindu Krishnan, David Avellaneda Avellaneda, Rene Fabian Cienfuegos Pelaes, Nora Aleyda Garcia Gomez, Selene Sepulveda Guzman

12.20-12.40: **Mahantesh Khetri**, University of Virginia, USA (student presentation)

Laser generation of silver nanoparticles from recycled solar cells

Co-authors: Pawan K. Kanaujia, Mool C. Gupta

12.40-13.30: **Lunch** (Salon C, Jefferson Ballroom and James Monroe Room)

13.45-17.15: **Excursion to Monticello** - the house, gardens, and plantation of Thomas Jefferson

18.45-22.00: **Conference banquet at The Wool Factory**

Conference Program – Thursday – Session 11

08:30-09:00 **Light breakfast/snacks** (Salon AB, Jefferson Ballroom)

09.00-10.30: **SESSION 11: Special online session**

Chair: Bilal Gökce, University of Wuppertal, Germany

09.00-09.30: **Yunyu Cai**, Institute of Solid State Physics, Hefei Institutes of Physical Sciences, China (*invited talk*)

Laser-generated metal oxide nanodots for magnetic resonance imaging

Co-authors: Xiaohu Cheng, Sihan Ji, Changhao Liang

09.30-10.00: **Emmanuel Stratakis**, Institute of Electronic Structure and Laser, FORTH, Greece (*invited talk*)

Application of pulsed laser ablation in liquids in photovoltaic devices

10.00-10.30: **Natalie Tarasenka**, Ulster University, UK (*invited talk*)

Electric field assisted laser ablation in liquids: Main features and application for the controlled synthesis of nanocomposites

Co-authors: Vladislav Kornev, Davide Mariotti, Nikolai Tarasenko

10.30-11.00: **Coffee break**

11.00-12.20: **SESSION 12: Pulsed-laser ablation in liquids: Quest for productivity in synthesis of nanoparticles**

Chair: Marcella Dell'Aglio, Institute for Photonics and Nanotechnologies, CNR-IFN, Italy

11.00-11.20: **Carlos Doñate-Buendía**, Universitat Jaume I, Spain

Spatial and temporal beam control for laser ablation in liquids productivity increase and nanoparticle size modification

Co-authors: F. Riahi, I. Y. Khairani, A. Bußmann, S. Adami, M. Spellauge, R. Streubel, H. P. Huber, N. Adams, S. Barcikowski, B. Gökce

11.20-11.40: **Alexander Bulgakov**, HiLASE Centre, Institute of Physics of the Czech Academy of Sciences, Czech Republic

Beam splitting as a way to increase the nanoparticle production by laser ablation in liquids

Co-authors: Oleksandr Gatsa, Carlos Doñate-Buendía, Shabbir Tahir, Miroslava Flimelová, Farbot Riahi, Bilal Gökce

11.40-12.00: **Shuhei Shibata**, Illumines Inc., Japan

Improving the production efficiency of gold nanoparticles in the laser-induced reduction method by optical system modulation

Co-authors: Rikuto Kuroda, Hideki Ina, Takahiro Nakamura

12.00-11.20: **Bilal Gökce**, University of Wuppertal, Germany

Laser-generated FeRh nanoparticles inks for laser-assisted direct writing of custom magnetocaloric

Co-authors: S. Tahir, C. Doñate-Buendía, J. Landers, S. Salamon, H. Wende

12.20-12.50: **AWARD CEREMONY, CLOSING REMARKS**

12.50-14.00: **Lunch** (Salon C, Jefferson Ballroom and James Monroe Room)

Abstracts

Monday – Oral Sessions 1 – 4

Monday – Poster Session 1

Tuesday – Oral Sessions 5 – 8

Tuesday – Poster Session 2

Wednesday – Oral Sessions 9 – 10

Thursday – Oral Session 11 – 12

Direct observation of nanoparticle melting at femtosecond and nanometer scale with the XFEL

Changyong Song,[1,2,*] **Chulho Jung**,[1,2] **Yungok Ihm**,[3] **Junha Hwang**,[1,2] **Eunyoung Park**,[1,2] **Jaeyong Shin**,[1,2] **Daewoong Nam**[4]

1- Department of Physics and Photon Science Center, POSTECH, Pohang 37673, Korea
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Intense femtosecond-laser pulses drive material phase transitions via kinetic reactions otherwise hidden in equilibrium measurements, which stimulates a strong interest in revealing the reaction dynamics of individual atoms prompted by photo-depleted bonding electrons. However, the field of ultrafast atomic dynamics has been limited by the challenges involved in resolving the accompanying irreversible processes at the relevant space–time resolution. By establishing single-pulse time-resolved experimental technique using an X-ray free-electron laser, we overcome this to directly observe the kinetic processes accompanied during the nonequilibrium phase transitions. In this talk, we will introduce recent experimental observations of exotic melting reaction forbidden in thermodynamic (near) equilibrium condition together with physical interpretation guided by the two-temperature molecular dynamics.

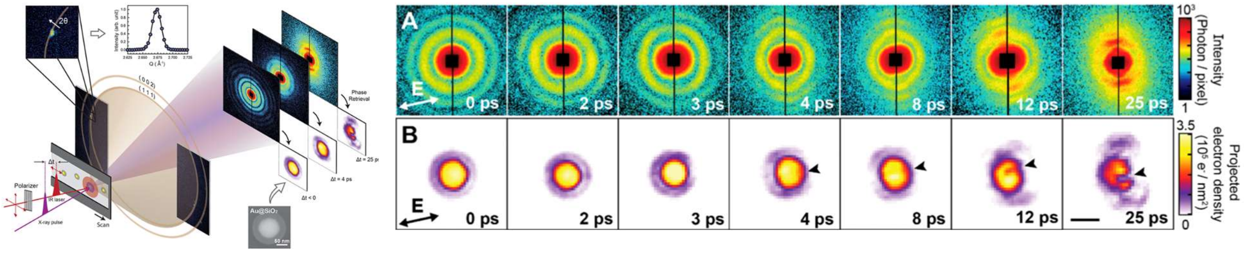

Figure 1. XFEL single pulse time-resolved imaging and diffraction experiments (left). Femtosecond photoinduced melting of the Au@SiO_2 single nanoparticles observed by single XFEL pulses (Right). Top panel displays XFEL diffraction patterns and bottom panel display specimen images as projected electron densities on ultrafast melting [1].

References

[1] Jaeyong Shin, Chulho Jung, Yungok Ihm, Seung-Phil Heo, Daewoong Nam, Sangsoo Kim, Minseok Kim, Intae Eom, Ji Hoon Shim, Do Young Noh, and Changyong Song*, "*Ultrafast energy transfer process in confined Au nanospheres revealed by femtosecond X-ray imaging and diffraction*", Nano Letters 23:1481 (2023).

[2] C. Jung, Y. Ihm, D.-H. Cho, H. Lee, D. Nam, S.-S. Kim, I.-T. Eom, J. Park, C. Kim, Y. Kim, J. Fan, N. Ji, J. R. Morris, S. Owada, K. Tono, J-H Shim, H. Jiang, M. Yabashi, T. Ishikawa, D.-Y. Noh, and C. Song*, "*Inducing thermodynamically blocked atomic ordering via strongly driven nonequilibrium kinetics*", Science Advances 7:eabj8552 (2021)

[3] Y. Ihm, D. Cho, D. Sung, D. Nam, T. Sato, C. Jung, S-S. Kim, J. Park, S-N. Kim, M. Gallagher-Jones, Y. Kim, R. Xu, S. Owada, J. H. Shim, K.Tono, M. Yabashi, T. Ishikawa, J. Miao, D.-Y. Noh, and Changyong Song*, *"Direct observation of picosecond melting and disintegration of metallic nanoparticles"*, Nature Communications 10:2411 (2019).

Dynamics and mechanism of picosecond laser fragmentation of gold colloids in liquid

Anton Plech,[1*] **Meike Tack,**[2] **Hao Huang,**[3,4] **Mikhail Arefev,**[3] **Anna R. Ziefuss,**[2] **Matteo Levantino,**[5]
Yogesh Pokhrel,[1] **Chaobo Chen,**[3] **Leonid Zhigilei,**[3] **Sven Reichenberger**[2]

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Nanoparticle synthesis by pulsed laser ablation in liquids has been widely studied [1]. Multi-modal size distributions of the produced nanoparticles are linked to inherent mechanisms during ablation [2]. Therefore, a second step of laser processing by laser fragmentation is required that produces ultra-small particles with novel properties for photonics or catalysis. We have studied the fragmentation process both by large-scale molecular dynamics simulations [3, 4] and by picosecond-pump probe experiments with x-rays [5-7]. The results show a remarkable agreement (Fig. 1), that allows describing fragmentation of gold nanoparticles in the 10-60 nm range excited by pulses of 1 ps or longer as a thermal process. The energy deposition defines several regimes of nanoparticle fragmentation, including evaporation, mild phase explosion with reformation of a core particle by the inverse Leidenfrost effect, and a strong phase explosion at a multiple of the energy required for melting of the nanoparticle [7].

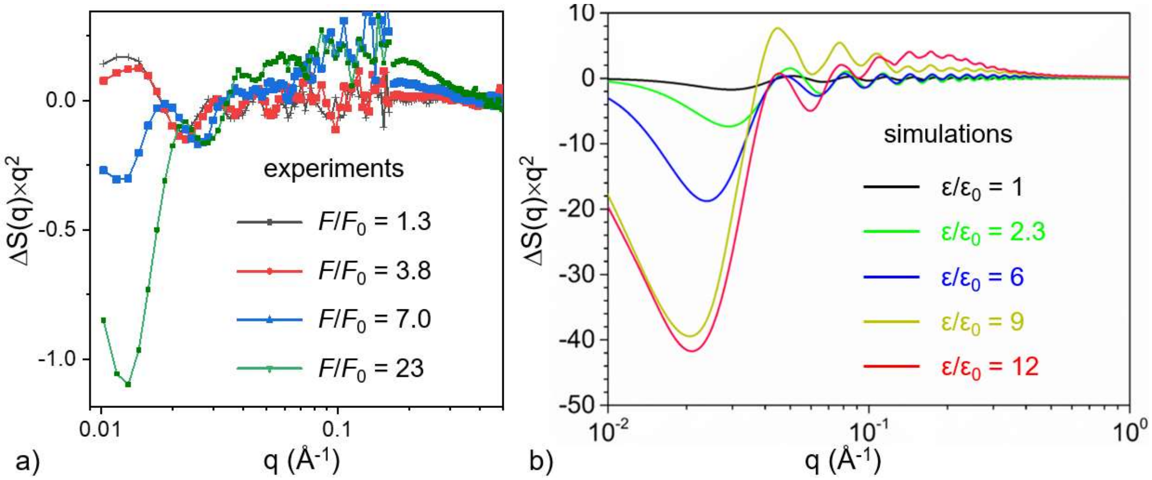

Figure 1. Scattering profiles of a pump-probe experiment with 400 nm, 1-ps laser pump and 100-ps x-ray probe pulses at a delay of 1 μs of a gold colloid with initial 44 nm spheres at selected fluence values $\boldsymbol{F}$ relative to the melting fluence $\boldsymbol{F_0}$ (a) and computed scattering profiles obtained from large-scale, hybrid computer simulations of 20 nm spheres at selected excitation energies ε relative to the energy for reaching the melting point ε_0 (b). [7]

[1] D. Zhang, B. Gökce, and S. Barcikowski, *Chem. Rev.* **117**, 3990-4103 (2017).
[2] S. Reich *et al*., *Nanoscale* **11,** 6962 (2019).
[3] H. Huang and L. V. Zhigilei, *J. Phys. Chem. C* **125**, 13413-13432 (2021).
[4] H. Huang and L. V. Zhigilei, *Sci. China: Phys. Mech. Astron.* **65**, 274206 (2022).
[5] A. Ziefuß, S. Reich, S. Reichenberger, M. Levantino, A. Plech, *PCCP* **22,** 4993 (2020).
[6] A. Plech et al., *ACS Photonics* **9,** 2981 (2022).
[7] A. Plech, M. Tack, H. Huang, M. Arefev, A. R. Ziefuss, M. Levantino, H. Karadas, C. Chen, L. V. Zhigilei, and S. Reichenberger, *ACS Nano* **18**, 10527-10541 (2024).

Ultrafast visualization of femtosecond laser-induced structural changes in liquid water

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A. Descamps,[1] M. Kozina,[1] M.-F. Lin,[1] J.P.F. Nunes,[3] X. Na,[1] B. Ofori-Okai,[1] D. Pemmaraju,[1]
X. Shen,[1] J. Yang,[1] L.V. Zhigilei,[2] X. J. Wang,[1]and S. H. Glenzer [1]

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Understanding the structural dynamics of liquid water under strongly excited conditions is important to a wide range of applications including radiotherapy, water disinfection, and laser fragmentation in liquids. Here we report the results of using femtosecond electron diffraction to directly image the structural changes of liquid water induced by intense fs laser excitation. In this study, we focus 266 nm, 100 fs laser pulses onto a free-standing 650-nm-thick liquid water sheet jet, with the maximum excitation energy density reaching ~5.4 MJ/kg. We probe the structural change of the excited water using the technique of time-resolved electron scattering with femtosecond temporal and Angstrom spatial resolutions. We perform the analysis of differential pair distribution function (ΔPDF) on the electron scattering data to unravel the dynamics of intermolecular O···O and O···H bonds of water. The ΔPDF results show that the structural change is dominated by OH(H_3O^+) radical-cation pairs within 0.5 ps, followed by a steady state up to 50 ps and a transition to phase explosion regime on a 100-ps time scale. Molecular Dynamics simulations are performed and show good agreement with the experimental data, hence providing a complete atomic-level description of the structural evolution in strongly excited liquid water.

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How can time-resolved experiments contribute to a validated model of ultrashort pulse laser ablation in liquids?

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Meike Tack,[2] Tina Friedenauer,[2] Christoph Rehbock,[2] Sven Reichenberger,[2] Anna Rosa Ziehfuss,[2] Stephan Barcikowski[2]

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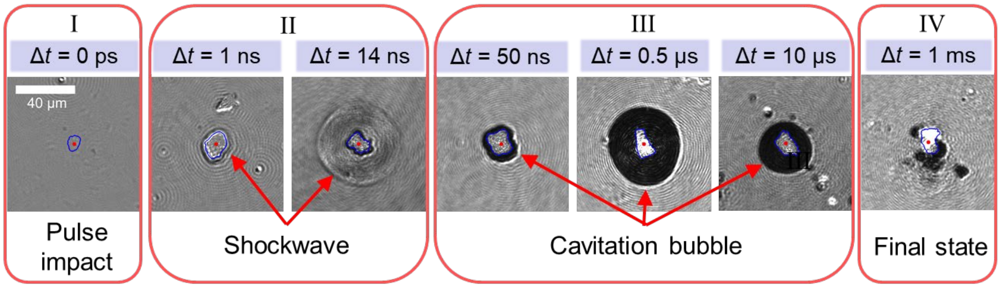
In recent decades, laser-matter interactions in ultrafast laser ablation have been extensively studied. Numerous simulations exist today that combine two-temperature modeling with subsequent lattice response, including phase transitions. These simulations primarily provide a qualitative understanding of laser ablation with single pulses, while the precise quantitative prediction of final state and time-resolved observables remains challenging. Final state observables that may be predicted by simulations include ablation threshold, efficiency and morphology [1,2]. Pump-probe techniques can measure time-resolved observables with a femtosecond temporal resolution up to the final state within several hundreds of µs [3]. When pressure waves become visible in pump-probe microscopy (II), such as during laser ablation in liquids, also pressure amplitudes can be measured [4,5]. Here, we present new experimental findings to test theoretical models and gain insight how pulse duration, separation, and fluence affect the efficiency of ablation and how photo-mechanical and photo-thermal mechanisms contribute to the process.



[1] C. Chen, L. Zhigilei, Atomistic modeling of pulsed laser ablation in liquid: spatially and time-resolved maps of transient nonequilibrium states and channels of nanoparticle formation, Appl. Phys. A **129** 288 (2023)

[2] D. Redka, J. Winter, C. Gadelmeier, A. Djuranovic, U. Glatzel, J. Minár, H.P. Huber, Control of ultrafast laser ablation efficiency by stress confinement due to strong electron localization in high-entropy alloys, Appl. Surf. Sci. **594** 153427 (2022)

[3] S. Rapp, M. Kaiser, M. Schmidt, H.P. Huber, Ultrafast pump-probe ellipsometry setup for the measurement of transient optical properties during laser ablation, Opt. Expr. **24** 17572 (2016)

[4] M. Spellauge, C. Doñate-Buendía, S. Barcikowski, B. Gökce, H. Huber, Comparison of ultrashort pulse ablation of gold in air and water by time-resolved experiments, Light Sci. Appl. **11** 68 (2022)

[5] M. Spellauge, M. Tack, R. Streubel, M. Miertz, K. Exner, S. Reichenberger, S. Barcikowski, H. Huber and A. Ziefuss, Photomechanical Fragmentation of IrO_2 Microparticles for the Synthesis of Active and Redox-Sensitive Colloidal Nanoclusters, Small 2206485 (2023)

Unravelling bubbles formation in laser ablation in liquids

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A great deal of effort has gone into characterizing the thermodynamic conditions in laser ablation in liquids as well as to understand the formation of nanoparticles in these conditions [1]. Most of the experimental methods used only provide access to characteristic times longer than 100 ns. These times seem too long compared to the characteristic times of particle formation mechanisms derived from molecular dynamics [2]. The latter suggests that particle formation, including bimodal size distributions, occurs at a nanosecond timescale. Moreover, the interaction between the plasma and the liquid, as well as the bubble formation mechanism remain open questions. We have conducted experiments on the ID 19 beamline at the European Synchrotron Radiation Facility (ESRF), combining high-resolution multi-channel framing camera to observe the short times, and x-ray phase contrast imaging (PCI) using synchrotron radiation.

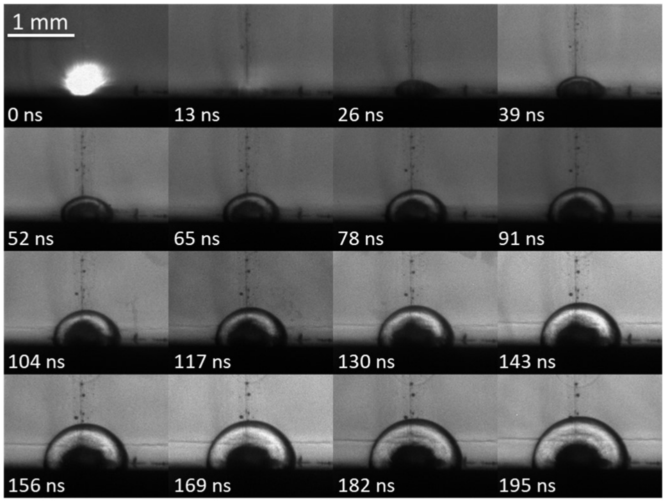

Figure 1. Laser ablation of a gold surface in water. Shadowgraph imaging shows the propagation of the laser-generated shock wave and the nucleation of the vapor bubble. The sixteen-frame movie is obtained with a *SIMX* camera, a high-resolution multi-channel framing camera (16 combined iCCD cameras). The gating is 5 ns and the delay between two frames is 8 ns. The Nd:YAG laser parameters are 5 ns pulse duration, 100 mJ per pulse, 532 nm.

We find that whatever the liquid used (water, ethanol, solution of H_2O_2, PDMS), the bubble formation is triggered by the propagation of the shock wave. It suggests that the bubble formation is not induced by heat transfer from the plasma to the liquid, but by a standard cavitation phenomenon, i.e. a negative peak pressure following the shock propagation. The pressure reached at the shock front range from a few GPa to tens of GPa [3]. It also suggests that the plasma is isolated from the liquid phase after a few tens of nanoseconds, but the characteristics time of vapor formation appears a bit longer than the one predicted by molecular dynamics. Finally, from radiography, we observed that liquid can enter into the bubble when its maximum size is reached.

[1] A. Kanitz, M. R. Kalus, E. L. Gurevich, A. Ostendorf, S. Barcikowski and D. Amans, *Plasma Sources Sci. Technol.* **28**, 103001 (2019).

[2] C.-Y. Shih, R. Streubel, J. Heberle, A. Letzel, M. V. Shugaev, C. Wu, M. Schmidt, B. Gökce, S. Barcikowski and L. V. Zhigilei, *Nanoscale* **10**, 6900 (2018).

[3] A. Chemin, M.W. Fawaz, and D. Amans, *Appl. Surf. Sci.* **574**, 151592 (2022).

Direct observation of localized surface plasmon-induced ultrafast melting in Au nanorods

Eunyoung Park[1], Junha Hwang[1], Jaeyong Shin[1], Sung Yun Lee[1], Heemin Lee[1], Seung Phil Heo[1],
Daewoong Nam[2], Sangsoo Kim[2], Min Seok Kim[2], In Tae Eom[2], Do Young Noh[3], Changyong Song[1]

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Ultrafast light–matter interaction invigorates research activities on light induced quantum control of materials properties by providing routes to explore new phases of matters in nonequilibrium states. With the exclusive excitations of electrons through femtosecond IR laser pulses, various physical processes can be accessed mode selectively, which enables the way to tackle fundamental science issues including the role of electrons in driving crystal phase changes [1]. Au nanorod, are elongated gold single nanoparticle that has longitudinal localized surface plasmon (LSP). Understanding this surface plasmons in Au nanorod is essential, which enables to control optical properties in metal nanostructures. Despite the significance of surface plasmons in the light-matter interaction in metallic nanoparticles, the role of the localized surface plasmon in ultrafast melting has remained elusive. We studied the impact of surface plasmons dynamics in ultrafast phase transition of Au nanoparticle using femtosecond pump-probe X-ray imaging at PAL-XFEL [2]. To study further, we directly imaged the reaction dynamics of photoinduced Au nanorod with femtosecond X-ray pulses. Shape distortion caused by LSP and further investigation of laser fluence and polarization direction dependence was carried out to result in various melting reaction in reaction in response to the surface plasmon excitations in metallic nanoparticles.

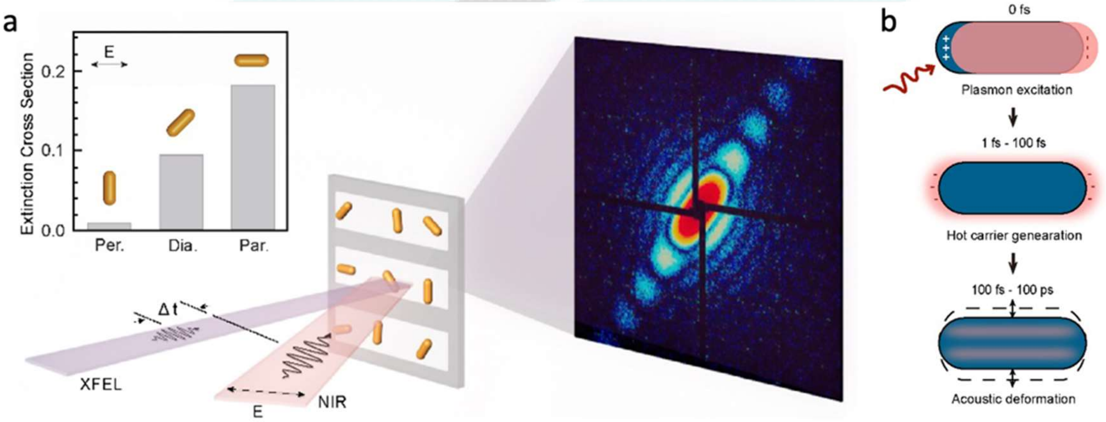

Figure 1. (a) Schematics of time-resolved single-pulse XFEL imaging experiments. Bar graph show the extinction cross section of the three groups with the laser polarization parallel (Par), diagonal (Dia) and perpendicular (Per) to the long axis of the nanorod. (b) Schematics of acoustic deformation due to localized surface plasmon.

CONFERENCE

[1] Nasu, K. Photoinduced Phase Transitions; World Scienctific Pub. Co. :2004; pp 1−69.

[2] Ihm, Y. et al. Direct observation of picosecond melting and disintegration of metallic nanoparticles. Nature Communications 10, 2411 (2019).

Specular vs. diffusive nature of heat transfer between acoustic phonons in a solid and gas molecules at interfaces

Patrick E. Hopkins,[1,2,3,*] **Ashutosh Giri**,[4] **John A. Tomko**[2]

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The interfacial interactions between acoustic waves in a solid and those in vapors and gases are the fundamental processes that drive energy exchange across surfaces of different phases of matter. The conversion of the coupled lattice motion in the solid to the energetic particles in the gas involves a conversion mechanism that relies on ability of the acoustic phonons in the solid to transduce its energy across the heterogeneous interface, which can occur on nanometer dimensions dictated by adsorbates, geometries and carrier length scales. Laser-based photoacoustic techniques have proven useful for experimentally probing the acoustic wave transmission across interfaces, and when coupled with ultrafast laser sources, provide the necessary temporal sensitivity to resolve these nanoscale interfacial conversion mechanisms. These approaches, rooted in picosecond ultrasonic generation and detection [1], have been commonly applied to measure acoustic transmission across nanoscale solid interfaces, and due to their nanoscale sensitivity, can provide insight into how nanometer changes in roughness [2], defect distributions [3], and bonding [4] can impact acoustic phonon coupling between two solids. Related techniques have been used to study how acoustic waves couple at interfaces between solids and liquids [5, 6], and more recently, with the adoption of ellipsometry configurations or plasmonic sensing, solid/gas interfaces [7, 8]. Notably, these studies on solid/gas coupling have demonstrated that monitoring of temporal changes in photoacoustic-driven absorption can also be related to changes in heat transport. In this work, we theoretically and experimentally study the scattering nature of how acoustic phonons in a solid transmit energy to molecules in a gas. Specifically, we seek to answer the question, do acoustic phonons in a solid transmit their energy to gas molecules via specular or diffusive surface interactions? We derive new models based on semi-classical phonon interfacial transmission theories that predict the transmission probability of acoustic waves across a solid/gas interfaces assuming either specular or diffusive interactions between the long wavelength phonon modes in a solid with the energetic particles in the gas. We then study the validity of these theories through our recently modified picosecond ultrasonic measurement platform to monitor the change in photo-thermally-excited acoustic wave transmission in a gold film in argon atmospheres with varying temperatures and pressures. We demonstrate clear evidence that diffusive rather than specular scattering between the acoustic phonons in the solid and molecules in the gas drives interfacial energy trans- mission across the gold/Ar interface. The temperature and pressure dependence on this phononic energy transmission into the gas also provide experimental validation to previous theoretical and computational findings on the thermal boundary conductance across solid/gas interfaces and thermal accommodation of gas molecules on heated surfaces [9].

[1] C. Thomsen, J. Strait, Z. Vardeny, H. J. Maris, J. Tauc, and J. J. Hauser, Physical Review Letters 53, 989 (1984).
[2] J. C. Duda, C.-Y. P. Yang, B. M. Foley, R. Cheaito, D. L. Medlin, R. E. Jones, and P. E. Hopkins, Applied Physics Letters 102, 081902 (2013).
[3] C. S. Gorham, K. Hattar, R. Cheaito, J. C. Duda, J. T. Gaskins, T. E. Beechem, J. F. Ihlefeld, L. B. Biedermann, E. S. Piekos, D. L. Medlin, and P. E. Hopkins, Physical Review B 90, 024301 (2014).
[4] M. D. Losego, M. E. Grady, N. R. Sottos, D. G. Cahill, and P. V. Braun, Nature Materials 11, 502 (2012).
[5] G. Tas and H. J. Maris, Physical Review B 55, 1852 (1997).
[6] J. A. Tomko, D. H. Olson, A. Giri, J. T. Gaskins, B. F. Donovan, S. M. O'Malley, and P. E. Hopkins, Langmuir 35, 2106 (2019).
[7] C.-K. Min, D. G. Cahill, and S. Granick, Review of Scientific Instruments 81, 074902 (2010).
[8] J. Park, X. Xie, D. Li, and D. G. Cahill, Nanoscale and Microscale Thermophysical Engineering 21, 70 (2017).
[9] A. Giri, J. L. Braun, and P. E. Hopkins, Journal of Physical Chemistry C 120, 24847 (2016).

Pulsed laser induced solvent-nanoparticle chemo-physical interaction; an effective approach toward creation of submicron heterostructures

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Creating heterostructures has been a brilliant solution to address the increasing need for innovative materials in high-tech applications. Heterostructures possess distinct attributes that render them highly promising for the development of sustainable and environmentally friendly energy systems with a diverse range of applications across multiple fields, such as catalysis, energy storage, and solar energy harvesting. In this study, we aim to investigate a promising and innovative approach for producing heterostructures involving the use of pulsed laser irradiation on suspended nanoparticles. Our main focus lies in understanding the chemo-physical interactions that occur at the interface between the solvent and the nanoparticles when they are adjusted to the laser pulses. When the nanoparticles are exposed to the laser pulses, they absorb the energy from the pulses, causing the solvent molecules in contact with them to gain kinetic energy. This increase in energy is sufficient for the solvent molecules to dissociate and diffuse into the molten nanoparticle, leading to the formation of different phases [1]. The formation process involves both physical phase transitions and chemical oxidation/reduction reactions, which are highly influenced by the chemical environment and temperature of the reaction [2]. These variables were adjusted accordingly based on the suspension and laser parameters to achieve the desired heterostructures. An example of the formation of copper quantum dot on the surface of Fe_3O_4 using laser irradiation has been illustrated in Figure 1a. The particle growth mechanism is also depicted schematically in Figure 1b. Further exploration of the process by which phases were created is being studied through the application of atomistic modeling techniques. In this study, density functional theory (DFT) calculations were employed to determine the reactive bond force fields. These force fields are subsequently utilized to investigate the breaking and formation of bonds in the respective systems, employing molecular dynamics (MD) simulations. This work is supported by the Polish National Science Center under programs No. 2018/31/B/ST8/03043 and 2022/06/X/ST3/01743. The calculations were also performed in the Prometheus Cluster, Cyfronet, under grant number PLG/2022/015573. We thank the Polish National Synchrotron Center (SOLARIS) and Elettra Synchrotron, Trieste, Italy for their efforts toward this project.

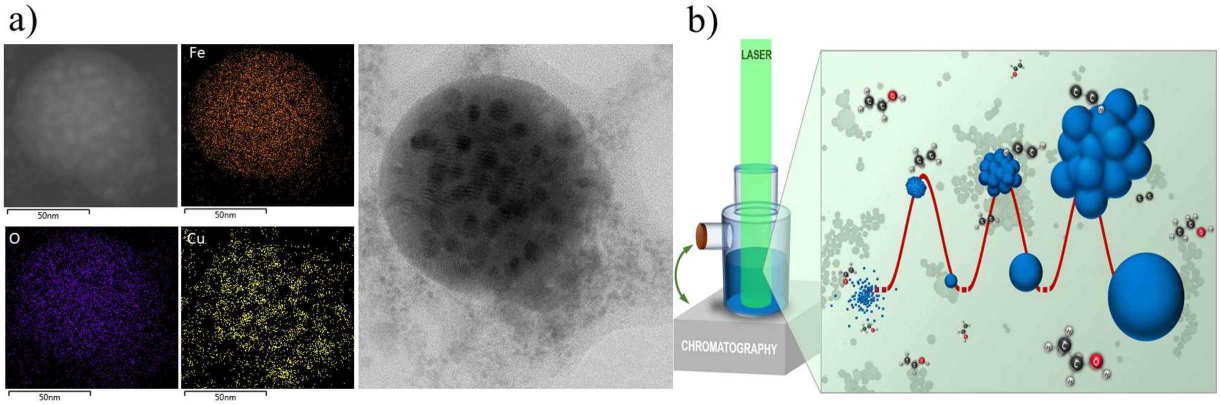

Figure 1. (a) Formation of copper quantum dot on magnetite nanoparticles, and (b) schematic of growth mechanism during pulsed laser irradiation of suspended nanoparticles

[1] M.S. Shakeri, O. Polit, B. Polakowska, A. Pyatenko, K. Suchanek, M. Dulski, Z. Swiatkowska-Warkocka, "*Studies on solvent-particles chemical interactions during composite particles formation by pulsed laser melting of α-Fe_2O_3*", Scientific Reports, Nature Publication, 12 (2022) 11950.

[2] Mohammad Sadegh Shakeri, Zaneta Swiatkowska-Warkocka, Oliwia Polit, Tatiana Itina, Alexey Maximenko, Joanna Depciuch, Jacek Gurgul, Marzena Mitura-Nowak, Marcin Perzanowski, Andrzej Dziedzic, Jarosław Nęcki, "*Alternative local melting-solidification of suspended nanoparticles for heterostructure formation enabled by pulsed laser irradiation*", Advanced Functional Materials, 2023, 2304359.

Designing Nano-Drugs by Pulsed Laser Ablation in Liquids

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Currently, antibiotic resistance and cancer are the two of the most important public health problems killing more than ~1.5 million people annually, showing that antibiotics and current chemotherapeutics are not as effective as they were in the past. Nanotechnology is presented here as a potential solution. However, current protocols for the traditional physicochemical synthesis of nanomaterials are not free of environmental and social drawbacks, often involving the use of toxic catalysts. This talk will present a novel process called « Pulsed Laser Ablation in Liquids » (PLAL) that synthesize nanostructures free of any surface contamination. The effect of the pulse duration, wavelength, repetition rate, solvent and target on the synthesized nanoparticles will be determined. And finally, the biomedical properties of the nanoparticles synthesized by PLAL will be discussed.

References

- T. Hesabizadeh, K. Sung, M. Park, S. Foley, A. Paredes, S. Blissett, G. Guisbiers, Synthesis of antibacterial copper oxide nanoparticles by pulsed laser ablation in liquids: potential application against foodborne pathogens, Nanomaterials vol. 13 (2023) 2206. https://doi.org/10.3390/nano13152206
- L. D. Geoffrion, D. Medina-Cruz, M. Kusper, S. Elsaidi, F. Watanabe, P. Parajuli, A. Ponce, T. Ba Hoang, T. Brintlinger, T. J. Webster, G. Guisbiers, Bi_2O_3 nano-flakes as a cost-effective antibacterial agent, Nanoscale Advances vol. 3 (2021) 4106-4118. https://doi.org/10.1039/D0NA00910E
- L. D Geoffrion, T. Hesabizadeh, D. Medina-Cruz, M. Kusper, P. Taylor, A. Vernet-Crua, J. Chen, A. Ajo, T. J Webster, G. Guisbiers, Naked Selenium Nanoparticles for Antibacterial and Anticancer Treatments, ACS Omega vol. 5 (2020) 2660-2669. http://dx.doi.org/10.1021/acsomega.9b03172

Synthesis and characterization of boron nanoparticles produced by ns-laser ablation in water

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Boron nanoparticles (BNPs) are attractive nanomaterials for their employment in many applications, such as neutron detection, boron neutron capture therapy, proton boron capture therapy, combustion, nuclear fusion. Depending on the specific application, ^{10}B or ^{11}B isotopes can be used.

Nevertheless, there are significant challenges in developing suitable BNPs. For instance, the chemical synthesis routes often lead to complex processes, resulting in the introduction of harmful by-products like carbon and chlorine into the nanoparticles (NPs) or in difficult size control, etc.

In this study, we report BNPs directly synthesized in water by pulsed Laser Ablation in Liquid (PLAL). In particular, nanoparticles of elemental boron have been generated by laser ablation of a sintered ^{10}B target in MilliQ water by employing ns laser pulse. With the aim of understanding the process and at the same time of characterizing the produced BNPs, several diagnostic techniques have been applied.

The structure has been investigated with High-Resolution Transmission Electron Microscopy (HR-TEM) and a crystalline structure has been revealed (Figure1), instead the elemental content and their distribution were analyzed with electron energy loss spectroscopy (EELS). A novel analytical methodology based on Laser Induced Breakdown Spectroscopy (LIBS) has been proposed for estimating the BNP concentration and the amount of boron subproducts as the boric acid directly from the produced colloidal solution. Moreover, for understanding the chemical reactions occurring during the laser ablation, the analysis of the produced gas has been performed with gas-chromatography. Using as a reference the PLAL process of AuNPs generation, that is well-known, the routes of mechanisms occurring during BNP production are investigated. It emphasizes the importance of the chemistry of water species with boron within the PLAL physical processes occurring during the synthesis.

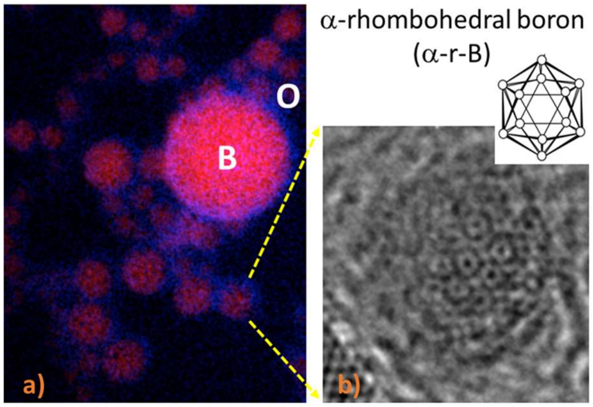

Figure 1. a) TEM composite map for boron and oxygen co-localization, b) crystal structure of an NP from HRTEM image and SAED data, using a crystallographic image processing.

Pulsed laser fragmentation synthesis of carbon quantum dots (CQDs) as fluorescent probes in non-enzymatic glucose detection

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Over the past few decades, diabetes has been one of the leading causes of blindness, kidney failure, stroke, heart attack, and amputation. To minimize these serious health complications, early diagnosis and self-intervention are critical in monitoring glucose levels [1]. Up to this day, glucose levels are determined through well-established electrochemical-based methods. The drawback of this method is the usage of glucose-binding enzymes (e.g. glucose oxidase) which are costly and sensitive to environmental conditions (e.g. pH, temperature, etc.). To resolve this, fluorescent-based glucose sensors using carbon quantum dots (CQDs) as fluorescent probes have been extensively studied to develop a low-cost and non-enzymatic glucose sensor with rapid response characteristics. As a new emerging class of carbon nanomaterials, CQDs exhibit distinct and unique properties such as high biocompatibility, low cytotoxicity, abundant and cheap sources, excellent photostability, and most importantly, their intrinsic fluorescence emission and broad emission range [2]. In this study, we synthesized CQDs by employing a pulsed laser fragmentation technique which was carried out through Nd: YAG nanosecond laser [3]. Carbon black powder and ethanol were used as the carbon precursor and liquid medium, respectively. The laser-synthesized CQDs were modified and functionalized with boronic acid compound derivatives as the glucose molecule receptors via the EDC/NHS conjugation process. Figure 1a shows a TEM image of CQDs-functionalized with APBA (CQDs-APBA) having a spherical-like morphology with an average size of 3 nm. Figure 1b shows that CQDs-functionalized with APBA (CQDs-APBA) fluorescence decreases as the concentration of glucose increases with a wide range between 0 – 40 mM. Thus, the fabricated CQDs-APBA could be a promising candidate for glucose determination in clinical diagnostics.

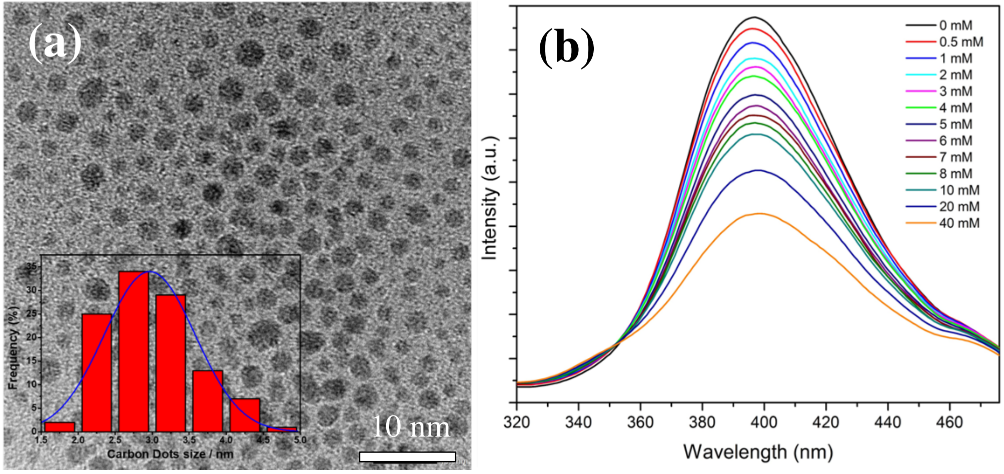

Figure 1. (a) TEM image of CQDs-APBA (Inset: Size distribution of CQDs) and (b) Fluorescence curve of CQDs-APBA as glucose concentration increases.

[1] E. Makrantonaki, D. Jiang, A.M. Hossini, G. Nikolakis, M. Wlaschek, K. Scharffetter-Kochanek, C.C. Zouboulis, *Rev Endocr Metab Disord* **17**, 269 (2016).
[2] Y.L. Thi Ngo, J.S. Chung, S.H. Hur, *Dyes and Pigments* **168**, 180 (2019).
[3] C. Doñate-Buendia, R. Torres-Mendieta, A. Pyatenko, E. Falomir, M. Fernández-Alonso, G. Mínguez-Vega, *ACS Omega* **3**, 2735 (2018).

Is there a structural ‘sweet spot’ for different ferrites treated with single laser pulses to engineer defects?

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Spinels are interesting catalysts that contribute to the development of sustainable technological progress because they exhibit different cation occupations of tetrahedral and octahedral sites, for which it has been shown that the parameter correlates with the catalytic activity.[1] The inversion parameter varies between zero (normal spinel) and one (inverse spinel). A subgroup of spinels are the ferrites, which are made of iron and have a huge application potential in technical, catalytical and medical applications due to their magnetic and catalytic properties.[2]

To tailor the magnetic properties and simultaneously improve the catalytic activity, we recently employed a method called <u>Pu</u>lsed laser <u>D</u>efect <u>E</u>ngineering in <u>L</u>iquid (PUDEL) in a flat liquid jet setup (Fig. 1a), which allowed us to precisely control the cation occupancy of the octa- and tetrahedral sites in $CoFe_2O_4$ (quantified by the degree of inversion) with single laser pulses of increasing laser intensity, Fig. 1b.[3] In this study, we observed that when PUDEL-processing $CoFe_2O_4$ with different initial degrees of inversion (red/black trend vs blue trend in Fig. 1b) with a single laser pulse causes a trend towards a ‘sweet spot’ of cation occupancy inversion at higher laser intensities. However, there are still questions to be answered.[1] This talk will present new results and insights into this phenomenon, where a wider range of ferrites and initial degrees of inversion have been studied to find out if there is an universal or material-dependent ‘sweet spot’ at higher laser intensities (Fig. 1c), by single-pulse PUDEL (s-PUDEL). The inversion parameter will be measured by Mössbauer spectroscopy, while the role of s-PUDEL-induced formation of additional phases will then be studied by XRD. Throughout this talk, possible mechanistic correlations related to the observed trends will be discussed. Ultimately, this talk will provide a new perspective of s-PUDEL for the precise design of phase-pure magnetic and catalytic material properties.

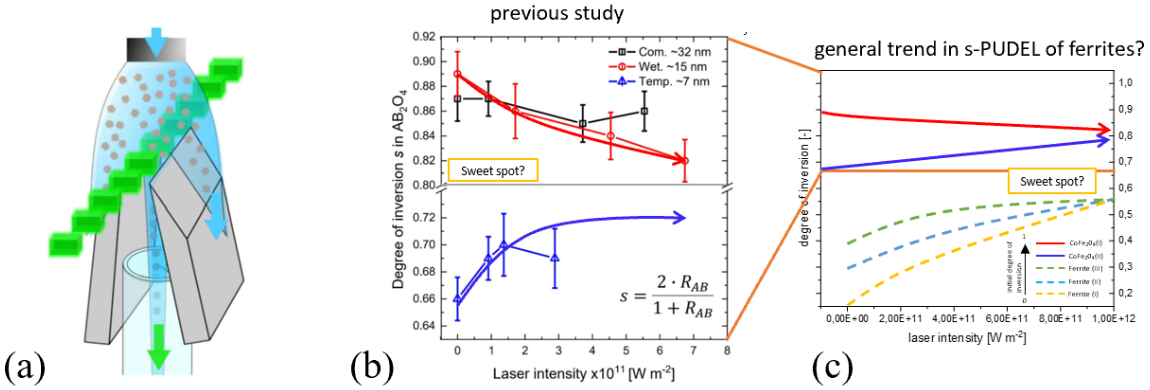

Figure 1: Study on pulsed laser defect engineering in liquid with single laser pulses (s-PUDEL) at defined laser intensity, a) gradually tuning the structural inversion parameter of a catalyst b) Experimental set-up; study of the inversion parameter of gradually laser-modified ferrites c).[1]

[1] S. Zerebecki; S. Salamon; J. Landers; Y. Yang; Y. Tong; E. Budiyanto; D. Waffel; M. Dreyer; S. Saddeler; T. Kox*; et al. ChemCatChem* **2022**.

[2] S. J. Salih; W. M. Mahmood. *Heliyon* **2023**, e16601.

[3] S. Zerebecki; S. Reichenberger; S. Barcikowski. *The journal of physical chemistry. A* **2020**, 11125–11132.

Inhibition of particle growth during single-pulse laser fragmentation by barrierless *in-situ* adsorption of the just-formed gold nanoparticles on a GO support

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Due to growth processes, the particle size distributions of laser-generated and electrostatically stabilised colloidal nanoparticles evolve over a broad range of time scales. Time-resolved *in-situ* pump-probe SAXS measurements as well as *ex-situ* UV-Vis spectroscopy have shown that particle ripening can occur already within pico- and up to microseconds [1] and can continue on a scale of hours [2], respectively. Therefore, the stabilisation of the generated fragments must occur as early as possible to harvest even the smallest particle sizes which are potentially characteristic of the respective fragmentation mechanisms [3]. Inspired by previous publications on the *in-situ* stabilisation of nanoparticles by support materials present during laser ablation in liquid (LAL) [4,5], this talk will demonstrate that the *in-situ* size quenching using support material is also applicable to laser fragmentation in liquid (LFL). Prior to the laser fragmentation, AuNPs were uniformly adsorbed on the GO nanosheets (Figure 1a) by a kinetically driven, barrierless adsorption process which can be adopted independent of the isoelectric point (zeta potential) of the respective materials. To demonstrate that the GO support can successfully prevent particle growth *in-situ*, laser fragmentation of the same initial ~70 nm AuNPs was performed with and without GO support. As a result, a significantly higher number of particles < 3 nm was observed when using the *in-situ* stabilisation of the Au fragments by GO (see Figures 1b and c). Thus, this method offers the possibility of mechanistic LFL studies which are potentially less dependent on the nanoparticle growth processes during and after LFL.

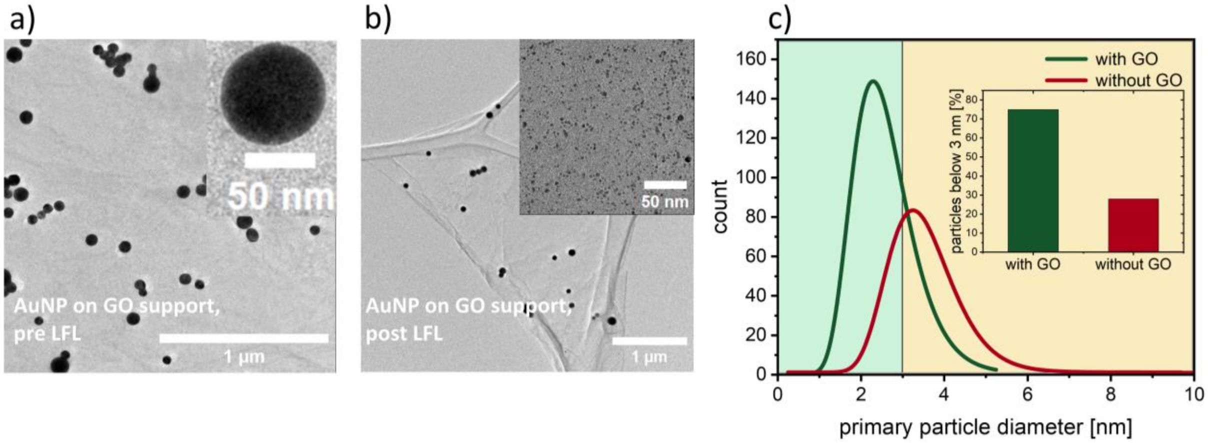

Figure 1. *In-situ* size quenching during laser fragmentation of GO-supported AuNPs. (a) initial ~70 nm AuNPs supported on GO nanosheets, before LFL, (b) resulting AuNPs, still supported on GO nanosheets, after LFL, (c) size distribution of the nanoparticles after LFL with and without pre-LFL adsorption on GO for *in-situ* size quenching.

[1] A. R. Ziefuss, S. Reich, S. Reichenberger, M. Levantino, A. Plech. Phys. Chem. Chem. Phys. **22**, 4993 (2020).
[2] S. Jendrzej, B. Gökce, V. Amendola, S. Barcikowski. J. Colloid Interface Sci. **463**, 299 (2016).
[3] H. Huang, L. V. Zhigilei. Sci. China Phys. Mech. Astron. **65**, 274206 (2022).
[4] R. Torres-Mendieta, D. Ventura-Espinosa, S. Sabater, J. Lancis, G. Mínguez-Vega, J. A. Mata. Sci. Rep. **6**, 30478 (2016).
[5] I. Haxhiaj, S. Tigges, D. Firla, X. Zhang, U. Hagemann, T. Kondo, J. Nakamura, G. Marzun, S. Barcikowski. Appl. Surf. Sci. **469**, 811 (2019).

Laser Ablation of Metallic Thin Layers in Liquids with Wide Irradiation Spots

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The nanoparticle production process via laser ablation of materials immersed in liquids has been thoroughly investigated, primarily focusing on thick targets [1, 2]. In this process, the laser beam is sharply focused on a small spot and scanned across a larger area. This method has successfully generated spherical nanoparticles, although it may display multimodal Gaussian distributions.

In this experimental research, we evaporated films of 100 nm thickness on glass substrates using various metals, including Au, Ag, and pure Pt, as well as double AgPt and Au/Ag films. As depicted in Figure 1(a), the samples were vertically positioned and irradiated with 6 ns laser pulses at full width at half maximum (FWHM). The liquid colloidal solution was analyzed using *High-Resolution Transmission Electron Microscopy* (HRTEM) and *High-angle annular dark-field* imaging (HAADF) mode.

Contrary to prior studies, this research emphasizes using fewer pulses with broad area spots (6 × 5 mm^2) while maintaining the energy density or fluency low. Due to the expanded interaction area, the effects during the liquid phase are more noticeable than when irradiating a small spot.

The resulting Au and Ag-Au structures (Fig.1(b)) suggest that these structures formed within microseconds under superfluid conditions, similar to those previously identified in Ref.[3]. Preliminary numerical solutions of the Euler equations for the corresponding fluid phase evolution confirm this claim.

Moreover, the Au-Ag system is entirely miscible, while the Ag-Pt system exhibits a significant miscibility gap with a hard-to-detect intermetallic phase. Understanding the formation and characteristics of these intermetallic phases is critical for developing new materials with improved properties.

The authors thank Francisco Jaimes--Bernstein and Diego Quiterio Vargas at the Pelletron accelerator and LCM (Microscopy Laboratory), respectively. DGAPA-UNAM (IN108921) principally funded this project. .

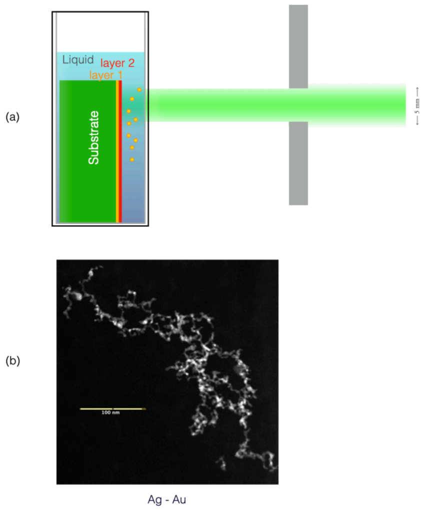

Figure 1. (a) Geometry of the experimental setup. (b) HAADF image of the Ag-Pt structures formed by the laser irradiation.

References

[1] V. Amendola, M. Meneghetti, What controls the composition and the structure of nanomaterials generated by laser ablation in liq- uid solution?, Phys. Chem. Chem. Phys. **15** (2013) 3027–3046

[2] A. H. Attallah, F. S. Abdulwahid, Y. A. Ali, A. J. Haider, Effect of liq- uid and laser parameters on fabrication of nanoparticles via pulsed laser ablation in liquid with their applications: A review, Plasmonics **18** (2023) 1307–1323.

[3] K. ichi Saitow, T. Yamamura, T. Minami, Gold nanospheres and nano- necklaces generated by laser ablation in supercritical fluid, The Journal of Physical Chemistry C **112** (2008) 18340–18349

Nanoparticles generated by laser ablation in liquids of Mount Etna volcanic rock

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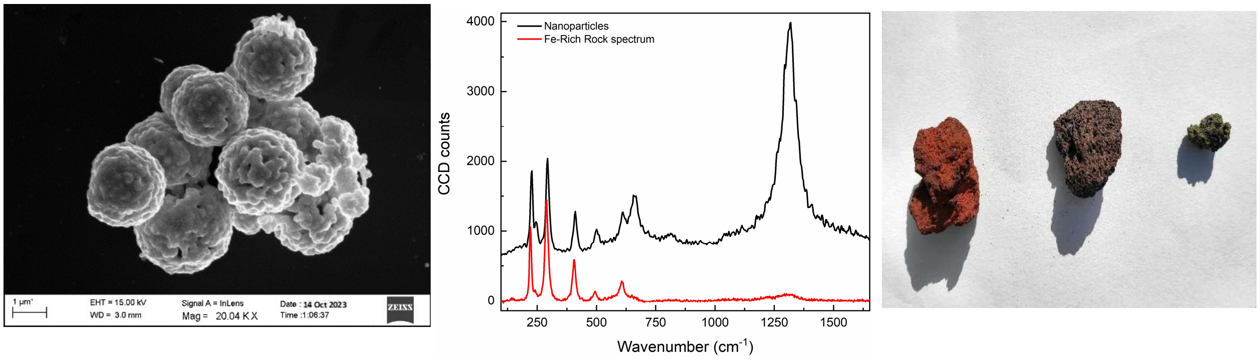
Mount Etna is the highest and most active volcano in Europe. Thanks to its volcanic activity, every year several tons of magmatic materials are spilled on the volcano's slope. It is well known in the literature that such magmatic material after cooling down became rocks rich in metals such as Fe, Co, Vn, Cu, Zn, Si but also non-metal, S, B, and so on [1]. These elements are not easy to recover from the rocks with classic methods. In this work, we show that a proper procedure in which laser ablation of different rocks has been conducted in water, leads to the generation of nanoparticles with high porosity and interesting magnetic properties given by the presence of Fe and Co oxides. In detail, 3 volcanic rocks (fig1 c) picked up at 3000 m from the sea level have been ablated in water by using a nanosecond pulsed laser at fluences around 4.4 J/cm^2 and characterized by SEM (fig.1 a), Raman spectroscopy (fig.1 b) and Laser-Induced Breakdown Spectroscopy (LIBS). It has been found that the most interesting nanostructure has been obtained by the ablation of the Fe-richest rock which presents a high response when exposed to an intense magnetic field. These findings are particularly compelling as they demonstrate the generation of nanostructures featuring both significant porosity and magnetic properties, derived from a plentiful and easily accessible source. The notable porosity renders these nanostructures an ideal platform for the absorption of pollutants, including dispersed organic molecules in water, in addition, due to the high responsiveness to the magnetic field, it is possible to selectively separate the nanoparticles containing the absorbed pollutants from the water by applying a magnetic field. Furthermore, with appropriate functionalization, these nanoparticles could serve for both characterizing and degrading the absorbed pollutants. [3].



(a) (b) (c)

Figure 1. (a) SEM image of hematite nanoparticle obtained from Fe-rich rock, (b) Raman spectrum of the obtained nanostructure compared with that of the bulk rock. (c) The three rocks studied.

This work has been partially funded by the European Union (NextGeneration EU), through the MUR- PNRR project SAMOTHRACE (ECS00000022).

[1] Aiuppa, Alessandro, et al. "Mobility and fluxes of major, minor and trace metals during basalt weathering and groundwater transport at Mt. Etna volcano (Sicily)." *Geochimica et Cosmochimica Acta* 64.11 (2000): 1827-1841. [2]

[2] Melo, T. F. O., et al. "Investigation of surface passivation process on magnetic nanoparticles by Raman spectroscopy." *Surface science* 600.18 (2006): 3642-3645

[3] Chen, Juhong, et al. "Highly sensitive and selective detection of nitrite ions using Fe3O4@ SiO2/Au magnetic nanoparticles by surface-enhanced Raman spectroscopy." *Biosensors and Bioelectronics* 85 (2016): 726-733.

Influence of laser parameters and surface chemistry on the fragmentation of NIR absorbing LaB_6 microparticles for powder bed fusion with diode laser

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Laser-based powder bed fusion of polymer powders (PBF-LB/P) has become a mature additive manufacturung technique for fabricating 3D components with high design freedom.[1] However, the prevailing use of CO_2 laser sources in this process presents certain limitations, such as low energy efficiency and beam shaping restrictions. To provide a more cost-effective and energy-efficient solution, there is the need for the development of desktop PBF-LB machines [2] equipped with dynamic beam delivery systems based on diode lasers operating in the near-infrared range (NIR > 800 nm). However, the standard polymers used in this process do not absorb NIR wavelengths effectively enough to enable diode-PBF-LB/P procedure, necessitating material modifications for NIR absorbance.

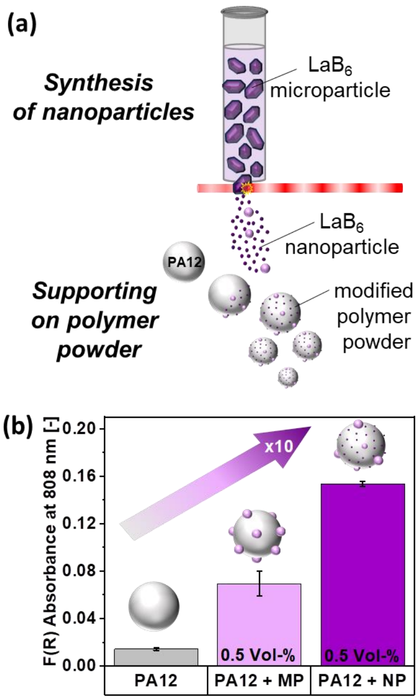

Figure 1: (a) Schematic illustration of the LaB_6 nanoparticle generation via laser fragmentation in liquids followed by dielectrophoretic deposition on PA12 and (b) the influence of the additivated LaB_6 NPs or MPs on the defuse reflection of the PA12 particles.

Therefore, we modify the absorbance behavior of the industrial standard polymer powder material PA12 by nano-additivation with LaB_6 nanoparticles (NP), which enhance the NIR absorbance, thereby refining the precision of energy input control in both temporal and spatial dimensions within the process zone.

We fabricated surfactant-free NPs with NIR-absorbing properties by utilizing the scalable laser fragmentation in a liquid jet process (Fig. 1a) downsizing LaB_6 feedstock microparticles (MP). This process results in substantial throughput with a significantly increased NIR absorbance depending on the laser parameters and surface chemistry, while the highest fragmentation efficiency was achieved with one cycle and a micropowder concentration of 500 mg/L.

As illustrated in Figure 1a, the NIR-sensitizing NPs are surface-loaded onto the PA12 MP surface using the dielectrophoretic deposition method [3]. This nano additive leads to an increase in NIR absorbance by a factor of 10 compared to the non-additivated polymer powder and doubled absorbance compared to the MP additive before laser fragmentation into NPs (Figure 1b), consequently leading to a significant decrease in the required laser energy for NIR-PBF-LB/P.

[1] T. Wohlers; R.I. Campbell; O. Diegel; J. Kowen; N. Mostow, In *Wohlers Report 2021 – 3D Printing and Additive Manufacturing: Global State of the Industry*, (Wohlers Associates, Colorado, 2021).

[2] T. Hupfeld; A. Wegner; M. Blanke; C. Doñate-Buendia; W. Scharow; S. Nieskens; M. Piechotta; M. Giese; S. Barcikowski; B. Gökce, *Advanced Optical Materials* **8**, 2000473 (2020).

[3] T. Hupfeld; A. Sommereyns; T. Schuffenhauer; E. Zhuravlev; M. Krebs; S. Gann; O. Keßler; M. Schmidt; B.Gökce; S. Barcikowski, *Additive Manufacturing* **36**, 101419 (2020).

Random lasing using laser generated and modified silver nanoparticles

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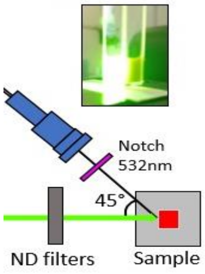
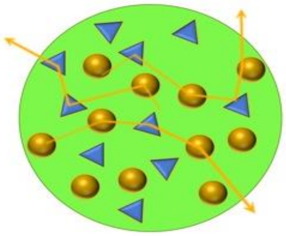
We have compared the use of silver nanoprisms[1] and laser melted spherical silver nanoparticles to generate random laser light[2] in a rhodamine 6G dye, used as an active medium.

In both cases the prepared colloids pumped at fluences above 1mJ/cm^2 emit a narrow fluorescence peak that dominates the spectrum (see figure below). The bandwidth of the emission decreases rapidly increasing the pumping fluence and a sigmoidal defines a lasing threshold of about 2.6mJ/cm^2 for the nanospheres and 1.0 mJ/cm^2 for the nanoprisms, having plasmon resonances close to the R6G fluorescence.

This means that a better overlap between the plasmonic resonance of the anisotropic nanoparticles and the dye's fluorescence defines improved performances in terms of a reduced lasing threshold and lower optimal silver concentration when compared to the nanospheres, with similar spectral behavior.

However, we have also demonstrated that tuning the plasmonic resonance close to the pump wavelength leads to a reduced resistance of the particles to melting during the laser action, which limits the range of operation and might prevent random lasing altogether, whereas the spherical particles are much more stable. The optimal approach to choosing plasmonic nanoparticles for random lasing must therefore take the stability aspect into serious consideration, as the random lasing thresholds reported in previous literature are sometimes higher than the damage threshold.





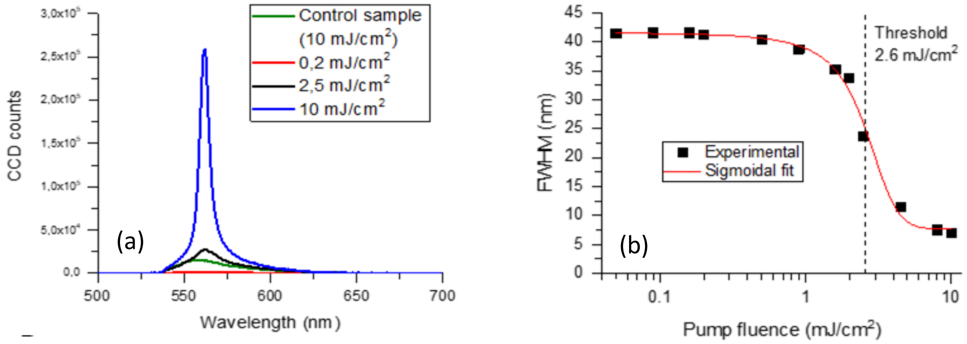


Figure 1. Emission spectrum before and after the threshold (a). Signal FWNM as a function of the pump fluence (b)

[1] V.Scardaci, M.Pulvirenti, M.Condorelli, G.Compagnini "Monochromatic light driven synthesis and growth of flat silver nanoparticles and their plasmon sensitivity" J. Mater. Chem. C, vol. 8, p. 9734 (2020)

[2] D. S. Wiersma, "The physics and applications of random lasers" Nature Phys, vol. 4, p. 359 (2008)

AgNFs/2D hybrid nanomaterials as multi-wavelength SERS active and flexible platforms for chemical sensing applications.

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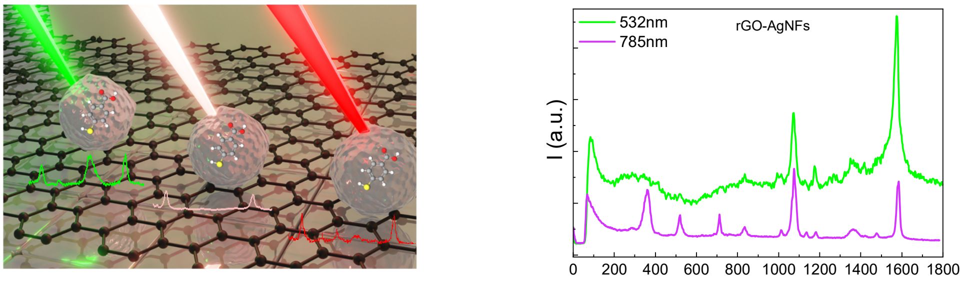
Silver nanoflowers (AgNFs) are plasmonic materials offering a huge surface area for enhanced molecular interactions, enabling high sensitivity and extremely low detection limits in sensing applications. Active sites (so called hot spots) on their surface easily immobilize target species by chemical and electrostatic interactions, facilitating the detection by Surface Enhanced Raman Spectroscopy (SERS). The possibility to amplify Raman signals is also strongly linked to the excitation wavelength [1] of the laser interacting with the SER active substrate. In order to explore novel functional nanomaterials with high enhancement in a wide range of excitation wavelengths, we propose AgNFs anchorated to 2D materials (r-GO, MoS_2, h-BN) with properties from semiconductors to insulators. Due to the metal morphology and to the large surface of the hybrid platforms, it was possible to create a numberless of hot spot regions with intense electromagnetic fields between particle and in the nanogaps at the AgNFs/2D interface. While silver nanostructures were prepared by a chemical method (one-pot chemical synthesis), 2D layers were obtained by laser irradiation of commercial materials. This last is a defect-induced physical procedure modifying their chemical-physics properties, promoting the interaction with AgNFs and boosting the sensitivity at a nanomolar concentration. SERS properties of the hybrid materials were studied using a standard molecule 4-mercaptobenzoic acid (4-MBA) and glucose as probe analytes at nanomolar concentration. We were able to study the enhancement in a laser wavelength range between 532 and 785 nm, finding very high enhancement factors [2]. This suggests that AgNFs-2D materials could be excellent SERS substrates in the entire visible and near infrared spectral region, opening the possibility to investigate several biological and medical interest analytes, without the interference of unwanted optical phenomena such as luminescence.



(a) (b)

Figure 1. Schematic representation of multi-wavelength SERS active platforms (a) SERS measurements at different excitation wavelengths on AgNFs/r-GO platforms (b).

This work has been partially funded by the European Union (NextGeneration EU), through the MUR-PNRR project SAMOTHRACE (ECS00000022).

[1] A. D. McFarland, M. A. Young, J. A. Dieringer, and R. P. Van Duyne, Wavelength-Scanned Surface-Enhanced Raman Excitation Spectroscopy, *J. Mater. Chem. A,* 2, 4534 (2014).

[2] E. C. Le Ru, E. Blackie, M. Meyer, and P. G. Etchegoin, Surface Enhanced Raman Scattering Enhancement Factors: A Comprehensive Study, J. Phys. Chem. C 111, 13794 (2007)

Co-localized scanning probe microscopy-Raman scattering studies of hybrid plasmonic substrates for SERS.

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Surface Enhanced Raman Scattering (SERS) improves Raman signal intensity up to 9 orders of magnitude by coupling light with plasmons in metallic nanostructures [1]. However, SERS suffer from inconsistency in intensities and the occurrence of spurious peaks. Yet, a promising solution is the use of graphene as SERS substrates. The hybrid structure of graphene and metal nanoparticles (NPs) is called the G-SERS substrate. Thus, we propose using a GO-SERS substrate based on graphene oxide (GO) sheets decorated with colloidal gold NPs synthesized by the pulsed laser ablation in liquid (PLAL) technique [2].

This study developed efficient GO-SERS substrates for highly sensitive molecule detection via Raman spectroscopy. NPs synthesized through PLAL demonstrate exceptional signal enhancement capabilities as well as commercially purified NPs and surpassing precursor-grown NPs, which exhibit significantly weaker signals, shown in Figure. 1a)-d). PLAL technique enables rapid, pure, and cost-effective synthesis of NPs for GO-SERS substrates. Characterization using Atomic Force Microscopy (AFM) and Kelvin Probe Force Microscopy (KPFM) [3] elucidated the influence of GO in stabilizing SERS. Intense regions were detected on GO films decorated with NPs, which are essential for detecting MB, the signal is absent without the presence of NPs. Raman intensity and reproducibility have been shown to increase using GO-SERS substrates. AFM-Raman co-localized studies linked NP positioning and electrical coupling to enhanced Raman scattering efficiency, see Figure. 1e)-g). Regions with dense NPs on GO exhibited lower surface potential values, correlating with intense MB Raman spectra. In this way, we can characterize the substrates by obtaining the most significant SERS enhancement.

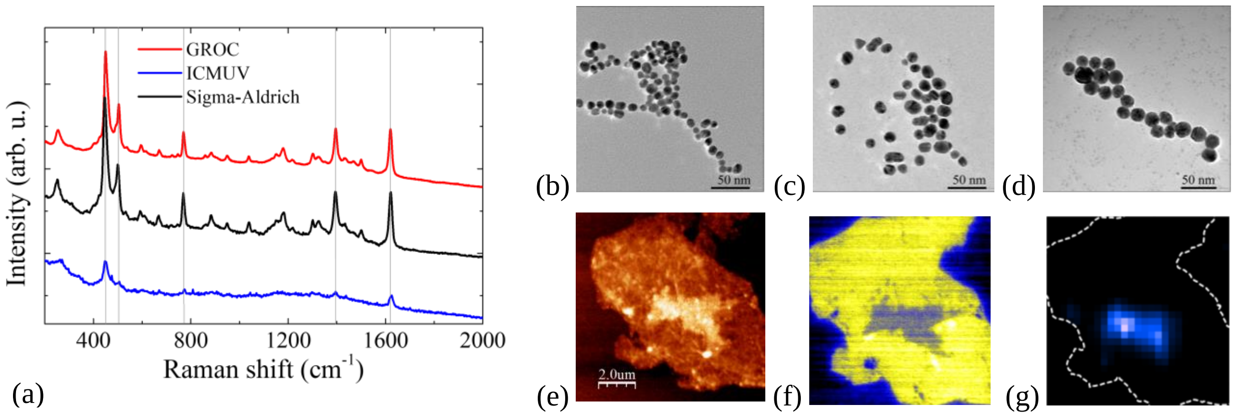

Figure 1. a) SERS spectra using Au NPs synthesized by PLAL technique (GROC), growth with precursors (ICMUV) and Commercial NPs (Sigma-Aldrich). TEM images of NPs synthesized in **b)** GROC, **c)** ICMUV and **d)** Sigma-Aldrich. **e)** Image of the surface topography of a GO film decorated with Au NPs, scaled from 0 to 60 nm. **f)** Image of the surface potential, scaled from 10 to 60 mV. **g)** SERS intensity due to the existence of hot spots.

[1] M.A.Tahir, N.E.Dina, H.Cheng, V.K.Valev, L.Zhang. Nanoscale **13**, 11593 (2021).

[2] R.Torres-Mendieta, S.Sabater, J.Lancis, G. Mínguez-Vega, J.A.Mata. *Scientific Reports*, **6**, 30478 (2016).

[3] L.Z.Cheong, W.Zhao, S.Song, C.Shen. *Acta Biomaterialia*, **99**, 33 (2019).

Multiphysics Modeling for Laser-Material Interaction

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Ultrashort pulse laser ablation in liquids (LAL) forms the basis for a number of important practical applications, from surface nanostructuring [1] to the synthesis of chemically pure colloidal nanoparticles. The colloidal nanoparticles, in particular, are in high demand across biomedicine and catalysis [2,3]. The inherently multiphysics nature of laser ablation highlights the critical need for advanced modeling to deepen our understanding of the involved complex processes.

We have developed a comprehensive computational framework that integrates multiple modeling approaches: the two temperature model (TTM) for simulation of the excitation and relaxation of conduction-band electrons, atomistic molecular dynamics (MD) for capturing laser-induced phase transformations within metal targets, a coarse-grained (CG) MD representation of the liquid environment, and non-reflecting boundary (NRB) conditions to effectively mimic the propagation of laser-induced pressure waves across computational boundaries. We have also incorporated a compressible hydrodynamic (HD) model for simulation of the long-range shockwave propagation in the liquid caused by rapid plume expansion. Additionally, an electromagnetic wave model (EM) that directly solves Maxwell's equations and accounts for temperature-dependent material properties enables the simulation of the optical properties of the laser-induced plume and laser absorption by rough surfaces.

This presentation outlines the implementation of these models and their interconnections. Several case studies that demonstrate the application of the multiphysics model to practically relevant systems are provided.

1. E. Stratakis, V. Zorba, M. Barberoglou, C. Fotakis, and G. A. Shafeev, Laser writing of nanostructures on bulk Al via its ablation in liquids, *Nanotechnology* **20**, 105303 (2009).
2. G. W. Yang, Laser ablation in liquids: Applications in the synthesis of nanocrystals, *Prog. Mater. Sci.* **52**, 648-698 (2007).
3. D. Zhang, B. Gökce, and S. Barcikowski, Laser synthesis and processing of colloids: Fundamentals and applications, *Chem. Rev.* **117**, 3990-4103 (2017).

The Influence of Alkanethiols on the Production of Hydrophobic Gold Nanoparticles via Pulsed Laser Ablation in Liquids

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The ability to suspend plasmonic metal nanoparticles in apolar environments is crucial for leveraging their optical properties in amphiphilic biological settings. Pulsed Laser Ablation in Liquids (PLAL) is a well-known technique for producing gold nanoparticles (AuNPs) in aqueous environments. However, ablation in organic liquids for synthesizing hydrophobic AuNPs still presents challenges, particularly regarding the relationship between colloidal stability and the ligand shell. In this study, hydrophobic AuNPs were generated by PLAL of gold in a 1-alkanethiol/n-decane solution and further processed with laser fragmentation, Figure 1. The results showed that longer chain length alkanethiols (ATs) led to smaller average particle sizes; however, there was no significant correlation between AT concentration and particle size. Stability was assessed by monitoring changes in the extinction spectra, indicating that lower AT concentrations stabilized the colloids, while higher concentrations led to faster particle aggregation. Moreover, longer chain length ATs exhibited enhanced stability. Vibrational spectroscopy was also used to analyze the AuNP surface chemistry, revealing the presence of oxidized carbon species and graphitic carbon. [1]

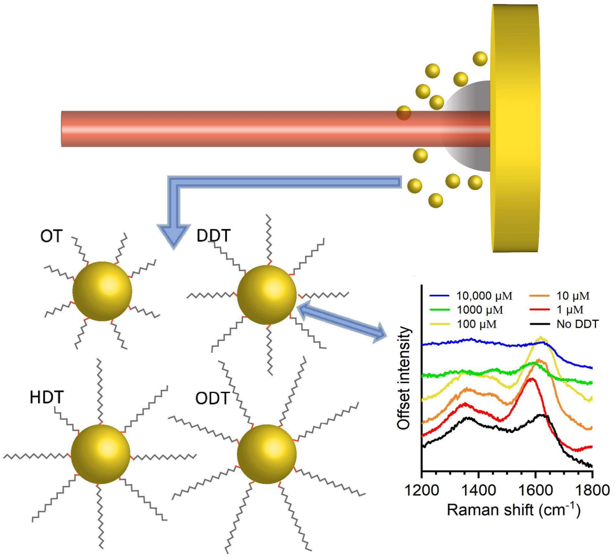

Figure 1. Graphical abstract depicting the PLAL process along with identification of the alkanethiol ligands examined in the study.

[1] Cory J. Trout, Paul Kumpf, Karli Sipps, Julianne C. Griepenburg, Sean M. O'Malley, The Influence of Alkanethiols on the Production of Hydrophobic Gold Nanoparticles via Pulsed Laser Ablation in Liquids, *nanomanufacturing* **1(3)**, 98 (2021).

Zn-Mg-O Alloying in Pulsed Laser Melting in Liquid

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Pulsed laser melting in liquid (PLML), which is a fabrication technique of submicrometer-sized spherical particle (SMPs), have been examined using particles of two or more components as starting materials. Spheronization of raw particles without optical absorption can be achieved by mixing the carbon particles as assisting optical absorption reagent (e.g., Al_2O_3, MgO and ZrO_2, etc.) [1]. We have also reported on the synthesis of Au-Fe alloy systems using the fast heating and cooling characteristic of the PLML process [2,3]. In this study, we focused on $Zn_{1-x}Mg_xO$ as an oxide material and investigated the effect of various parameters (mixing method of starting materials and irradiation conditions) in the PLML process on the ZnO-MgO solid solution state. Wurtzite $Zn_{1-x}Mg_xO$, Mg dissolved in ZnO with high concentration, is a promising material for solar blind sensors.

Mechanical mixing using a planetary ball mill and co-precipitation from ionic aqueous solution of Zn^{2+} and Mg^{2+} by alkali solution addition were examined to obtain starting mixture of ZnO and $MgO/Mg(OH)_2$. Obtained mixture particles were dispersed in deionized water and irradiated with a Nd:YAG laser (wavelength: 266 nm, pulse frequency: 10 Hz, pulse width: 5 ns).

Figure 1 shows the UV-vis diffuse reflectance spectra of pure ZnO, the irradiated mixture particles obtained by the mechanical mixing, and by the co-precipitation process. The blue shift in absorption due to the dissolution of MgO into ZnO was observed more clearly in particles obtained from the co-precipitation than in particles from the mechanical milling. This is probably due to that the contact points between ZnO and $MgO/Mg(OH)_2$ are more frequent for the mixed particles obtained by the co-precipitation method.

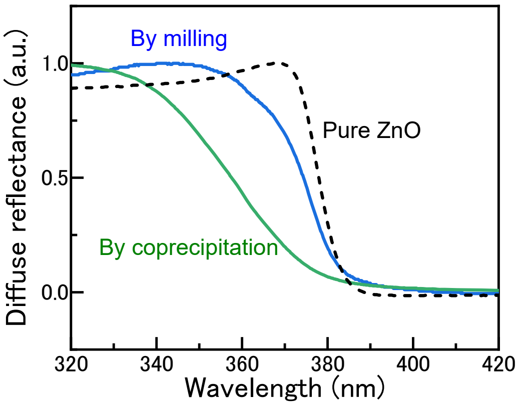

Figure 1. UV-vis spectra of pure ZnO and particles after irradiation at 100 mJ cm^{-2} $pulse^{-1}$ for 45 min.

[1] X. Li, Y. Shimizu, A. Pyatenko, H. Wang, N. Koshizaki, *J. Mater. Chem.* **21**, 14406 (2011).

[2] Z. Swiatkowska-Warkocka, K. Kawaguchi, Y. Shimizu, A. Pyatenko, H. Wang, N. Koshizaki, *Langmuir* **28**, 4903 (2012).

[3] H. Fuse, N. Koshizaki, Y. Ishikawa, Z. Swiatkowska-Warkocka, *Nanomaterials* **9**, 198 (2019).

RuPdIrPtAu high-entropy alloys on carbon nanotube for hydrazine electrolysis via in situ Raman spectroscopy

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In recent years, the quest for efficient and sustainable energy conversion technologies has led to the exploration of novel materials with exceptional catalytic properties. High-entropy alloys (HEAs), characterized by their unique atomic arrangements and composition, have emerged as promising candidates for electrocatalytic applications. Herein, we successfully design carbon nanotubes (CNT) embedded with HEA nanoparticles via pulsed laser irradiation coupled with hydrazine oxidation (HzOR)-enhanced water electrolysis. The electrochemical results revealed that the HEA/CNT-10 exhibited remarkable hydrogen and oxygen evolution reactions (HER and OER) performance with small overpotentials of 30.7 and 330 mV at 10 mA cm^{-2}, correspondingly, with low Tafel slope and exceptional stability in an alkaline medium. By replacing OER with HzOR, HEA/CNT-10 required lower potential of 0.1 V to desire 10 mA cm^{-2} compared with OER (1.56 V vs. RHE). The hydrazine splitting electrolyzer required a small cell voltage of 0.242 V to attain 10 mA cm^{-2} with outstanding stability. An optimal HEA/CNT-10 with cocktail effects strongly influences the efficiency of parallel HER||HzOR, highlighting the energy-saving sustainable hydrogen production. The real-time monitoring of H_3O^+ during HER via in situ electrochemical Raman spectroscopy revealed an acidic environment.

Composition and Size Dependent Elemental Segregation in Cantor and Platinum Group Metal High-Entropy Alloy Nanoparticles Produced by Laser Ablation in Liquid

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High Entropy Alloy (HEA) nanoparticles (NP) represent a relatively new class of nanomaterials composed of at least five elements at near-equimolar ratio, which tend to form crystal structures (mainly fcc) that may deviate from those of the single elements. Thus, the tunability of used elements and atomic ratios is limitless, which offers multiple opportunities for nanomaterial design e.g. tuning surface potentials in electrocatalysis.[1]

The synthesis of HEA NP by Laser Ablation in Liquid (LAL) has already been reported in the literature at the example of Cantor Alloy (CoCrFeMnNi) where homogeneous distributed particles with fcc-structures as well as segregated structures were reported.[2] Moreover, it is known that segregation of binary (AuFe) LAL-generated NP is very sensitive to size and element ratio.[3] However, to which extent the internal phase structure of HEA NP can tolerate the excess and depletion of an element is underexplored.

In this work we investigate to which extent crystal structure and elemental distribution of Cantor Alloy and AgAuCuPdPt HEA NPs change, affected by deviation of equimolarity and particle size. The colloidal HEA NPs were synthesized by LAL of the bulk targets using both picosecond- and nanosecond-pulsed lasers in organic solvents. Particle characterization was conducted by TEM/EDS as well as XRD. In preliminary experiments AgAuCuPdPt HEA NPs showed a homogeneous distribution of the elements in the particle (Figure 1A) as well as a notable similarity in the lattice structure between NP and bulk target (Figure 1B).

The aspired composition and size dependent differences in the particles´ structure could aid in the development of design criteria for HEA NP synthesis by LAL and may also help to elucidate particle formation mechanisms.

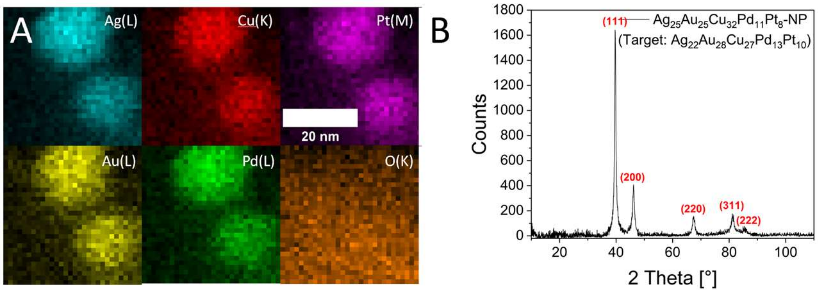

Figure 1. LAL-generated HEA-nanoparticle EDS/TEM mapping (A) and XRD pattern (B).

[1] Löffler, T., Waag, F., Gökce, B., Ludwig, A., Barcikowski, S and Schuhmann, W. Comparing the Activity of Complex Solid Solution Electrocatalysts Using Inflection Points of Voltammetric Activity Curves as Activity Descriptors, *ACS Catal*. 11, 3. (2021)
[2] Waag, F., Li, Y., Ziefuß, A. R., Bertin, E., Kamp, M., Duppel, V., Marzun, G., Kienle, L., Barcikowski, S. and Gökce, B. Kinetically controlled laser-synthesis of colloidal high-entropy alloy nanoparticles. *RCS Advances* 9, 32, 18547-18558. (2019)
[3] Tymoczko, A., Kamp, M., Prymak, O., Rehbock, C., Jakobi, J., Schürman, U., Kienle, L. and Barcikowski, S. How the crystal structure and phase segregation of Au-Fe alloy nanoparticles are ruled by the molar fraction and size, Nanoscale., 10, 16434-16437. (2018)

Molecular Dynamics modeling of heat transfer and nanobubble formation around a rapidly heated gold nanoparticle in water

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Understanding the heat transfer mechanism from metallic nanoparticles (NPs) undergoing rapid laser heating to surrounding water is necessary for the advancement of cancer therapy [1], laser processing of colloidal solutions [2, 3], and multiple other areas. The rapid heating to higher temperatures is known to result in the explosive boiling of liquid adjacent to the hot NP [4], which causes the formation of a cavitation nanobubble [5]. The subsequent heat transfer from the NP to the surrounding liquid is strongly affected by the thermal conductance of the metal/supercritical water interface and nanobubble dynamics [6,7].

The mechanisms and channels of heat transfer at the NP-liquid interface are investigated in this work using two sets of atomistic simulations. First, we use nonequilibrium molecular dynamics (MD) to study the interfacial thermal conductance (ITC) at the interface between supercritical water and gold under steady-state conditions. We found that ITC drops by approximately a factor of two when the temperature of the water reaches the supercritical state as compared to heat transfer to normal water (50 MW m^{-2} K^{-1} vs 114 MW m^{-2} K^{-1}).

In the second part, we use large-scale MD simulations to study the formation of the cavitation bubble around a rapidly heated 20-nm Au NP. As has been shown in earlier MD simulations performed with a coarse-grained (CG) representation of water, the heat transfer from the NP is almost completely interrupted by the onset of nanobubble formation [6,7]. On the other hand, the nanobubble dynamics is defined by the heat transfer rate from the metal to water right after the laser irradiation. Here, we focus on the influence of heat transfer at the water/gold interface and the dynamics of the initial supercritical water expansion on the nanobubble dynamics and the NP temperature evolution. We compare the results of MD modeling with CG and atomistic water to see how they capture the effect of heat transfer and the initial nanobubble dynamics.

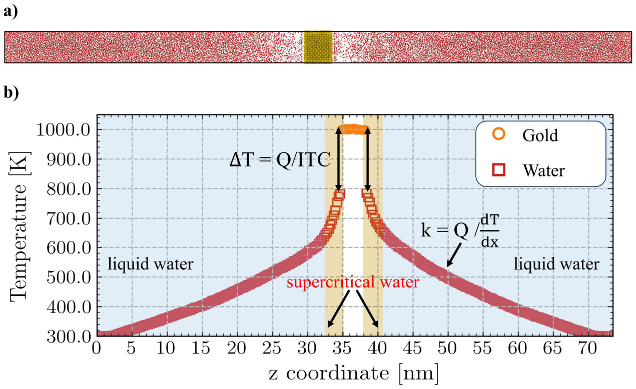

Figure 1. Results of a nonequilibrium MD simulation used to calculate the ITC on a supercritical H_2O/Au interface:

a) Snapshot of atomic configuration in a steady state. Red atoms – oxygen, orange atoms – gold.

b) Temporally averaged temperature profile for water and gold. Orange circles – gold, red squares – water. Arrows and ΔT are used to indicate the magnitude of temperature jump at the interface.

[1] D. Jaque *et al.*, *Nanoscale* **6**, 9494 (2014).
[2] A. Takami, H. Kurita, and S. Koda, *J. Phys. Chem. B* **103**, 1226 (1999).
[3] A. R. Ziefuss, S. Reich, S. Reichenberger, M. Levantino, and A. Plech, *Phys. Chem. Chem. Phys.* **22**, 4993 (2020).
[4] Y. Dou, L. V. Zhigilei, N. Winograd, and B. J. Garrison, *J. Phys. Chem. A* **105**, 2748 (2001).
[5] V. Kotaidis and A. Plech, Appl. *Phys. Lett.* **87**, 213102 (2005).
[6] H. Huang and L. V. Zhigilei, *J. Phys. Chem. C* **125**, 13413 (2021).
[7] H. Huang and L. V. Zhigilei, *Sci. China: Phys. Mech. Astron.* **65**, 274206, (2022).

Ultrafast in situ visible-light diagnostics of laser fragmentation in liquids

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Laser fragmentation in liquid can employed to produce nanoclusters < 3 nm, e.g. for gold to be used in selected applications in catalysis [1] or photonics [2] starting from colloids of poorly defined sizes. The goal is to fragment particles with high efficiency at a given laser setup. The *in situ* diagnostics of the process, however, is challenging due to competing energy deposition and structure evolution at nanosecond time scales [3, 4]. We demonstrate an optical pump-record setup to detect laser-induced changes of the colloid by optical absorption spectroscopy. In order to map both the excitation energy scale and relaxation times scales, the optical transmission is recorded by a continuous probe laser. A balanced detector connected to a storage oscilloscope allows detecting small changes of transmission. Thus, many excitation events can be collected rapidly to map the excitation pulse energy and delay after excitation.

The goal is to quantify typical threshold processes during fragmentation that have been described earlier. The most prominent change in the liquid is the formation of vapor bubbles around heated nanoparticles that is related to reaching the spinodal temperature of the surrounding liquid. We evaluate the possibility to detect particle melting or fragmentation. The results will be discussed in terms of efficiency of laser excitation [5] and influences of possible stabilizers to quench particle ripening.

[1] S. Reichenberger, G. Marzun, M. Muhler, and S. Barcikowski, *ChemCatChem*. **11**, 4489 (2019).
[2] A. R. Ziefuss, T. Steenbock, D. Benner, A. Plech, J. Göttlicher, M. Teubner, B. Grimm-Lebsanft, C. Rehbock, C. Comby-Zerbino, R. Antoine, D. Amans, I. Chakraborty, G. Bester, M. Nachev, B. Sures, M. Rübhausen, W. J. Parak, and S. Barcikowski, *Adv. Mat.* 2101549 (2021).
[3] A. R. Ziefuß, S. Reich, S. Reichenberger, M. Levantino, and A. Plech, *PCCP* **22,** 4993 (2020).
[4] A Siems, S Weber, J Boneberg and A. Plech: *New. J. Phys*. **13** , 043018 (2011).
[5] A. Plech, A. R. Ziefuss, M. Levantino, R. Streubel, S. Reich, and S. Reichenberger, *ACS Photonics* **9,** 2981 (2022).

Visualizing Crystal Defects in Copper Nanoparticles Using Precession Illumination-Hollow Cone Dark Field Imaging

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Nanoparticle catalysts are employed in a variety of chemical reactions throughout the chemical industry, including the water–gas shift reaction, synthesis of fatty alcohols from fatty acid methyl esters, and in methanol synthesis. While these catalysts are effective in increasing reaction rates, alternate reaction pathways with lower activation energies are required to increase chemical efficiency and meet sustainability needs. Therefore, there is increased demand to explore ways to enhance the activities of NP catalysts. One common way to increase their catalytic activity is to introduce defects in their crystalline structure. As shown in prior studies, introducing geometrical defects (such as kinks and steps on a catalyst surface) can expose the active sites for adsorption and surface reaction processes, force bond breaking, and enhance reactivity and selectivity [1]. While introducing nanoparticle defects using traditional chemical synthesis routes is well studied, pulsed laser ablation in liquid (PLAL) has emerged as a unique method to further increase the density of defects in NP catalysts. PLAL is characterized by highly nonequilibrium conditions including ultrafast quench rates of NPs and NP growth under extreme supersaturation [2,3]. As a result, NPs synthesized using this technique have been shown to contain a high concentration of defects and metastable phases [4]. Additionally, laser-generated NPs do not require additives such as capping ligands or surfactants, which increases the available surface area for catalysis [5]. Typically, planar defects in NPs are visualized using bright-field HRTEM. While this technique can reveal crystal defects in individual NPs, it can be difficult to quantify defect density across multiple NPs from the bright-field image alone. Furthermore, crystalline material in the resulting image appears dark in color, making it difficult to distinguish one large particle from a conglomeration of smaller ones. Here, we present an alternative method to aid in the visualization of crystal defects in copper NPs using precession illumination-hollow cone dark field (PI-HCDF) imaging.

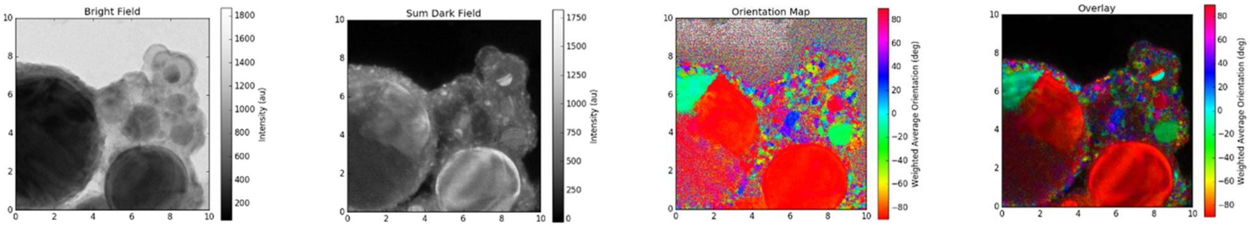

Figure 1. Bright-field and dark-field HRTEM images, as well as orientation mapping which displays planar defects in Cu NPs synthesized in acetone using PLAL.

[1] Kopač, D.; Likozar, B.; Huš, M. Catalysis of material surface defects: Multiscale modeling of methanol synthesis by CO_2 reduction on copper. Applied Surface Science 2019, 497, 143783.

[2] Reichenberger, S. Freezing crystallographic defects into nanoparticles: The development of pulsed laser defect engineering in liquid (PUDEL). Sci. China Phys. Mech. Astron. 2022, 65, 274208.

[3] Shih, C.-Y.; Streubel, R.; Heberle, J.; Letzel, A.; Shugaev, M. V.; Wu, C.; Schmidt, M.; Gökce, B.; Barcikowski, S.; Zhigilei, L. V. Two mechanisms of nanoparticle generation in picosecond laser ablation in liquids: the origin of the bimodal size distribution. Nanoscale 2018, 10, 6900–6910.

[4] Lin, Q.; Nadarajah, R.; Hoglund, E.; Semisalova, A.; Howe, J. M.; Gökce, B.; Zangari, G. Towards synthetic $L1_0$-FeNi: Detecting the absence of cubic symmetry in Laser-Ablated Fe-Ni nanoparticles. Applied Surface Science 2021, 567, 150664

[5] Zhang, D.; Liu, J.; Li, P.; Tian, Z.; Liang, C. Recent Advances in Surfactant-Free, Surface-Charged, and Defect-Rich Catalysts Developed by Laser Ablation and Processing in Liquids. ChemNanoMat 2017, 3, 512–533.

Laser-Synthesized Metal Phyllosilicate Nanoparticles for Efficient CO_2 Reduction

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Catalytic conversion of carbon dioxide (CO_2) into value-added carbon-containing chemicals is an important approach to combat climate change, which is also a critical component of circular carbon economy. Developing cost-effective, sustainable solutions to synthesize catalysts is a constant goal in this area. In this work, we present a facile laser approach to design and synthesize metal phyllosilicate nanoparticles for efficient CO_2 reduction.

Laser synthesis is a versatile, green strategy using high energy photons to create various types of nanomaterials. Laser synthesis enables fine-tuning of the properties of catalysts, which directly affects the selectivity and efficiency of CO_2 reduction. Metal phyllosilicates, produced through the laser approach (Figure 1a), exhibit distinctive chemical and structural properties (Figure 1b).[1] As shown in Figure 1b, the crinkly morphology of the samples is consistent with the morphology of metal phyllosilicates from previous reports. XRD pattern of ps-Cu-PS (ps: picosecond) in Figure 1b contains fcc-silicon peaks, Cu_2O, and poorly crystallized copper-phyllosilicate. The characterization results confirm the laser-synthesized products have adjustable metal loading and species distributed throughout a matrix of amorphous silica and metal phyllosilicates. Exploring modification method in phyllosilicate particles and tuning the laser ablation condition allows us to improve the faradaic efficiency (Figure 1c) in CO_2 reduction. As shown in Figure 1c, ps-Cu-PS exhibits higher selectivity towards the CO_2 reduction to ethylene reaction than ps-Cu_1Zn_1-PS. Femtosecond (fs) laser particle fs-Cu-PS offers further enhanced selectivity towards ethylene, as compared to low ethylene production on AE-Cu-PS prepared by wet chemistry literature method.

In conclusion, modulation of metal species could enhance the high-performance CO_2 reduction to C_2 product on metal phyllosilicates. In laser synthesis, laser pulse reduction also enhances the catalytic activity, leading to more efficient conversion of CO_2 into ethylene. This highlights the potential of this approach in producing highly effective and tailored catalysts for CO_2 reduction.

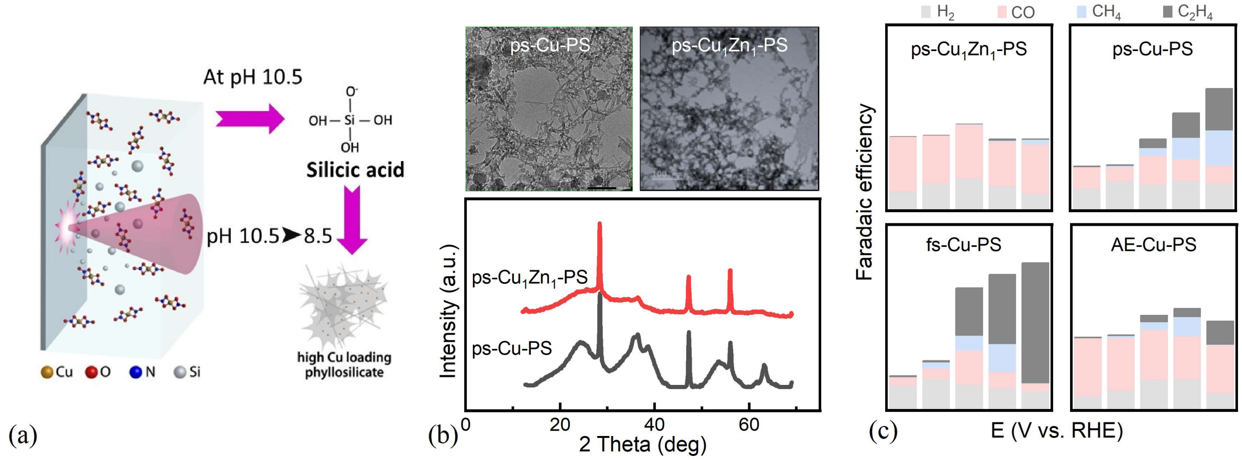

Figure 1. (a) Formation mechanism of phyllosilicate (PS) particles. (b) TEM images and XRD patterns of PS particles. (c) Faradaic efficiency of PS particles for CO_2 reduction.

[1] John, M.G. and K.M. Tibbetts, Mechanism of Nickel Phyllosilicate Formation by Laser Ablation in Liquid. J. Phys. Chem. C, vol. 124, pp. 13273-13282 (2020).

Preparation of copper phyllosilicate (Cu-PS) nanocatalysts by laser ablation method in liquid

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Abstract

In the last two decades, exponential urbanization and the industrial revolution have contributed substantially to global warming. The conversion of CO_2 into value-added products offers a promising solution to the global climate crisis caused by CO_2 emissions. Many nanocatalysts have been developed for CO_2 conversion. However, it remains incredibly challenging to achieve high product selectivity although many supported metal-oxide heterogeneous catalysts are effective at CO_2 conversion. Metal phyllosilicate nanocatalysts often exhibit higher CO_2 hydrogenation rates than conventional catalysts due to their unique structural properties. In contrast to conventional catalysts, phyllosilicates have a high surface area, allowing metal atoms to disperse finely. The phyllosilicates could thus have more active sites than conventional catalysts with a similar weight loading but greater dispersion. This work aims at the synthesis of copper phyllosilicates (Cu-PS) using Reactive Laser Ablation in Liquid (RLAL), a "green" technique that is becoming increasingly popular due to its ability to create nanostructures with exotic metastable phases. Two different composite nanomaterials were produced by focusing femtosecond (fs) and picosecond (ps) laser pulses onto a silicon wafer immersed in an aqueous copper (II) nitrate solution, and by adjusting the pH. The prepared catalysts have been characterized by XRD, FTIR, SEM, XPS, TEM, and Raman. Cu-PS synthesized by fs-RLAL has a higher Cu^+ percentage than Cu-PS synthesized by ps-RLAL. In ps-RLAL Cu-PS, the Cu^+ content is 47%, while in fs-RLAL Cu-PS has 58% of Cu^+. According to the TEM Cu-PS generated by the fs-RLAL and ps-RLAL display similar morphology and contain small Cu_2O NPs within a matrix of long nanoneedles and amorphous structures, along with larger spherical Si particles. Cu-PS catalysts produced by femtosecond RLAL are expected to demonstrate greater catalytic activity than those produced by picosecond RLAL.

References
[1] M. G. John, K. M. Tibbetts, Mechanism of Nickel Phyllosilicate Formation by Laser Ablation in Liquid. *J. Phys. Chem. C,* **124**, 13273-13282, 2020.
[2] M. G. John, K. M. Tibbetts, Controlling the Morphology of Copper-Silica Nanocomposites from Laser Ablation in Liquid. *Applied Surface Science*, **510**, 145037, 2020.

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Laser ablation has become an increasingly utilized method of nanoparticle generation in recent years, with applications in both materials and medical sciences [1]. Even though ablation is often aimed at a solid target, organic solvents may be utilized to prevent oxidation of metals and modify properties of produced nanoparticles, such as in the generation of carbon nanoparticle shells. The Tibbetts Lab has explored the effects of using a 4 ps pulse width and a 30 fs pulse width on the ablation of organic solvents, the latter of which is the shortest pulse width a typical Titanium-Sapphire laser is capable of. The lab has found that solvents produce products slower with shorter pulse widths, but also do not produce as many oxidized products. [2] Raw kinetics information was obtained with UV-Vis Spectrometry, and further product information was obtained using Gas Chromatography – Mass Spectrometry. The observed trend was found to have varying degrees of intensity dependent on the solvent used, as shown in Figure 1 below, leading to recent attempts to identify and explain these trends.

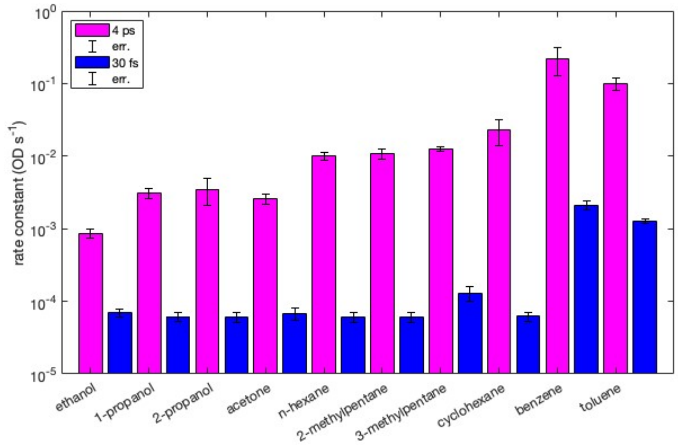

Figure 1. Kinetics Data for Irradiation of Organic Solvents at different Pulse Widths.

It was found that under 4 ps pulse width conditions, a molecule's carbon content generally positively correlates with an increase in product formation, though this trend does not it explain differences between different isomers of molecules with the same carbon content. Ongoing research seeks to evaluate the validity of the carbon-dependence hypothesis by testing more solvents, while also testing samples under vacuum conditions, and examining the difference between 2-methylpentane and 3-methylpentane specifically, which were found to have very different product profiles despite their isomer relationship.

[1] L. M. Frias Batista, A. Nag, V. K. Meader, K. M. Tibbetts, Generation of Nanomaterials by Reactive Laser-Synthesis in Liquid, Sci China Chem **65**, 274202 (2022)

[2] L. M. Frias Batista, E. Kaplan, C. Weththasingha, B. Cook, S. Harris, A. Nag, K. M. Tibbetts, How Pulse Width Affects Laser Ablation of Organic Solvents, J. Phys. Chem. B **127**, 6441 (2023)

Role of Solvents and Surfactants in Controlling Polyfluorene Film Morphology Deposited by RIR-MAPLE: An Atomistic Approach

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The morphology of conjugated polymer thin films deposited by the resonant infrared matrix-assisted pulsed laser evaporation (RIR-MAPLE) process is related to the emulsion characteristics. However, a fundamental understanding of how and why the emulsion characteristics control the film properties and device performance, particularly polyfluorene (PFO) light-emitting diodes (LEDs) deposited by RIR-MAPLE is yet unclear. We performed all-atom molecular dynamics simulations of emulsions containing a mixture of PFO polymer, different primary solvents, different surfactants, secondary solvent, and water. The emulsion properties were then examined as a function of variable primary solvent and surfactant and correlated with the morphology of deposited PFO thin films. The examination of the explicit interactions between all components of the emulsion indicated that using a primary solvent with a lower solubility-in-water and a higher non-bonded interaction energy ratio, between the solvent, polymer, and water in the emulsion recipe, produced the best result with smoother and denser films. Additionally, in the RIR-MAPLE deposition process, the thin film morphology exhibits a strong correlation to the density of the droplet which varies with the type of surfactant used. Moreover, our simulation results are consistent with the AFM experimental results, indicating that interactions driven by trichlorobenzene (TCB) primary solvent within the emulsion are responsible for high-quality, smooth, and continuous thin film surfaces. Overall, this study can support the choice of a suitable primary solvent and surfactant and provide the computational framework for predictions of new recipes for polymeric emulsion systems.

Simultaneous Solar Photovoltaic Conversion and Water Desalination via Quad-band Superwicking Fano-Resonant Optical Coatings

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Solar energy provides clean and sustainable energy solutions alternative to traditional energy sources. The deployment of solar panels, engineered to capture and convert sunlight into electricity through photovoltaic (PV) systems [1], has garnered immense popularity across residential, commercial, and industrial sectors due to its scalability, cost-efficiency, and minimal environmental impact. For a solar cell, however, only photons with energy around the bandgap of the PV cell can be converted into electrical energy, while the remaining photons will lead to excessive heat. This represents an insufficient use of solar energy as well as limited operating efficiency and reduced lifetime due to the elevated temperature. Alternatively, solar hybrid photovoltaic/thermal (HPT) systems represent a significant advancement in renewable energy, capable of converting solar energy to both electricity and heat. Nevertheless, there has been no device that can effectively separate the PV spectrum while directly harness the thermal component from sunlight.

In this work, we report on a novel and highly compact solar HPT system (**Fig. 1(a)**) by synergistically combining two pioneer technologies developed by our lab, a Fano-resonant optical coating (FROC, **Fig. 1(b)**) [2] and a femtosecond laser-induced superwicking surface for water purification (**Fig. 1(c)**) [3]. This superwicking-FROC HPT system nearly eliminates the overheating of solar cells, with the superwicking-FROC serves the dual purpose of both a spectrum splitter and a thermal receiver. This leads to a 335.7% improvement in photoelectric conversion efficiency, as well as efficient water desalination with an ultrahigh water evaporation rate of 2 $kgm^{-2}h^{-1}$. Besides the ultrahigh performance, the superwicking FROC HPT is compact, cost-effective, and easy to scale.

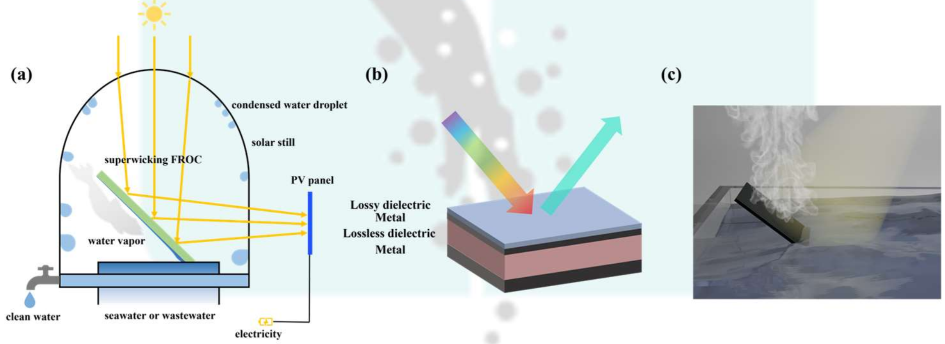

Figure 1. (a) Schematics of our proposed superwicking-FROC HPT system. (b) Schematics of a FROC structure, which will lead to a narrowband reflection. (c) Schematics of a femtosecond laser-induced superwicking surface for water purification.

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Reference

1. Al-Ezzi, A.S. and M.N.M. Ansari, *Photovoltaic Solar Cells: A Review.* Applied System Innovation, 2022. **5**(4): p. 67.
2. ElKabbash, M., et al., *Fano-resonant ultrathin film optical coatings.* Nature Nanotechnology, 2021. **16**(4): p. 440-446.
3. Singh, S.C., et al., *Solar-trackable super-wicking black metal panel for photothermal water sanitation.* Nature Sustainability, 2020. **3**(11): p. 938-946.

Predicting the Effect of Core Size on Ligand Self-Assembly in Chemically Mismatched Alkyl Thiol Monolayers and Reverse Monte Carlo Fitting to MALDI-MS with Ultrasmall Nanoparticles

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Nanoparticles with self-assembled monolayers (SAMs) have a wide range of applicability due to tunability of the monolayer composition. However, being able to precisely tune the monolayer for a desired application depends on accurately characterizing the SAMs, which present difficulties in nanoparticles smaller than 10 nm. We have previously developed a configurationally biased Monte Carlo (CBMC) model that agrees with experimental matrix assisted laser desorption ionization mass spectrometry (MALDI-MS) results and can aid in the elucidation of the SAMs morphology. This model revealed that ligand chain length and chemical functionality differences promote phase separation in binary monolayers. In this work, we explore the influence of nanoparticle core size on ligand self-assembly in four chemically mismatched binary monolayers with varying chain length differences. We observe that increased core size does not significantly influence the degree of phase separation as reported by the SSR. Interestingly, the average patch size is seen to decrease for both alkane and alcohol ligands in all 4 monolayers examined, and a unique “fencing” morphology emerges for certain systems where one ligand type localizes toward the center of the facet and is surrounded by the other. We have also refined a reverse Monte Carlo (RMC) approach which can rapidly generate a monolayer morphology consistent with experimental MALDI-MS data by adding a with tunable core size, non-spherical nanoparticle shapes, and variable ligand ratios, and surface densities. In addition, we have used the RMC model to estimate the baseline of the SSR value to be 0.015 ± 0.02 which reveals that the 0.1 SSR threshold used as a benchmark in the field is significant enough to report on phase separation. We also observe that both icosahedral and spherical nanoparticles can reproduce ideal configurations of Janus, patchy, and striped to similar extents. This work provides complementary surface morphology characterization methods and a better understanding of the driving forces of ligand phase separation on the surface of ultrasmall nanoparticles.

Fabrication of single crystals by laser ablation in supersaturated/supercooled liquids

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Fabrication of single crystals with desired size, shape, and structures is indispensable in various scientific and industrial fields such as material science, electronics, and structural biology. However, production of such crystals of organic/biological materials by conventional crystallization methods alone (e.g., adjusting temperature and concentration) often fails because of their weak intermolecular interactions (e.g., van der Waals force). To solve the problem, we have discovered that laser ablation via the focused irradiation with a pulsed laser can act as a three-dimensional external stimulus to various crystallization processes (e.g., nucleation and growth) [1-9] in supersaturated/supercooled liquids. In this presentation, we introduce the overview of the laser ablation-based crystallization control methods.

Firstly, focused irradiation with a pulsed laser into a supersaturated/supercooled liquid can be a spatiotemporal trigger for crystal nucleation of various materials (e.g., chemical compounds, proteins, and water) from liquids. Interestingly, the crystal nucleation efficiency is highly dependent on not only laser energy but also pulse duration, which implies photothermal/photomechanical process of laser ablation of liquids is involved in the underlying mechanisms of crystal nucleation. So far, we expect that the positive factor for enhancing crystal nucleation is cavitation bubbles that are generated by laser ablation of liquids. On the other hand, the laser irradiation should also cause temperature increase of liquids, which negatively affect crystal nucleation, but its degree should be highly dependent on pulse duration. Secondly, we also demonstrated the control of crystal growth induced by laser ablation of crystals, which provides crystal defects (e.g., dislocations) and/or fragments that can act as new sites for crystallization process in a supersaturated/supercooled liquid [5-9]. In this method, we also found that laser energy and pulse durations are crucial parameters for the production of single crystals. We foresee that these laser ablation-based methods will be useful means for the production of single crystals with desired properties and in-situ monitoring of spatiotemporal dynamics of various crystallization processes.

[1] H. Y. Yoshikawa et al. Laser ablation for protein crystal nucleation and seeding, *Chem. Soc. Rev.*, **Vol**. 43, pp. 2147-2158 (2014).

[2] H. Takahashi, Y. Hosokawa, H. Y. Yoshikawa et al., Spatiotemporal Control of Ice Crystallization in Supercooled Water via an Ultrashort Laser Impulse, *J. Phys. Chem. Lett.*, **Vol**. 14, pp. 4394-4402, (2023).

[3] H. Takahashi, H. Y. Yoshikawa et al., Crystallization from Glacial Acetic Acid Melt via Laser Ablation, *Appl. Phys. Exp.*, **Vol**. 14, 045503 (4 pages), (2021).

[4] Y. Turi, M. Maruyama, H. Y. Yoshikawa et al., Effects of pulse duration on laser-induced crystallization of urea from 300 fs to 1200 fs: impact of cavitation bubbles on crystal nucleation, *Appl. Phys. A*, **Vol**. 128, Article Number: 803 (2022).

[5] Y. Tominaga, M. Maruyama, H. Y. Yoshikawa et al. Promotion of protein crystal growth by actively switching crystal growth mode via femtosecond laser ablation, *Nat. Photon.*, **Vol**. 10, 723-726 (2016).

[6] D. Suzuki, H. Y. Yoshikawa et al. Control of Organic Crystal Shape by Femtosecond Laser Ablation, *Cryst. Growth Des.*, **Vol**. 18, pp. 4829-4833 (2018).

[7] C-S. Wu, H. Y. Yoshikawa et al. Growth Promotion of Targeted Crystal Face by Nano-Processing via Laser Ablation, *J. Phys. Chem. C*, **Vol**. 123, pp. 24919-24926 (2019).

[8] H. Takahashi, M. Yamaji, H. Y. Yoshikawa et al. Growth Enhancement of Organic Nonlinear Optical Crystals by Femtosecond Laser Ablation, *J. Phys. Chem. C*, **Vol**. 125, pp. 8391-8397 (2021).

[9] H. Takahashi, M. Shiraiwa, H. Y. Yoshikawa et al. Production of single crystalline seeds of organic nonlinear optical materials via laser ablation, *J. Phys. Chem. C*, **Vol**. 127, pp. 14005-14012 (2023).

The Mechanisms of Low Degradation Pulsed Laser Processing of Organic Microparticles in Liquids

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Laser processing of organic microparticles (MP) in liquids has been addressed in the literature, focusing on size reduction and solubilization of drug particles.[1] This laser-based comminution process is commonly referred to as laser fragmentation in liquids (LFL) and takes place in a comparatively high fluence regime, depending on the material and laser system.[2] In contrast to most frequently studied inorganic materials, organic microparticles are more susceptible to heat effects which can cause chemical degradation, particularly undesirable in pharmaceuticals and food ingredients. Consequently, laser energy intake must be particularly well controlled during laser processing of organic particles, which necessitates an in depth understanding of the fragmentation process.[1] In this work, LFL was used for particle size reduction of curcumin, cannabidiol (CBD), and naproxen in an optimized flow-through flat-jet reactor at a fluence of 428 mJ/cm² to obtain insights into the underlying fragmentation mechanisms after only two pulses per volume (PPV). Particle size analyses shows quantitative transformation to nano and sub-micrometer particles, while chemical degradation studied via HPLC, ATR-FTIR, H-NMR and XRD was minimal (<< 0.5 wt.%). Pump-probe microscopy experiments (Fig. 1 G-J), measuring shockwave and bubble expansion rates, allowed further elucidations of the fragmentation mechanisms, which are believed to be based on photomechanical fragmentation under stress confinement conditions (Fig. 1 A and B), cracking by thermally induced stress gradients due to inhomogeneous heating (Fig. 1 C and D), and degradation-free ablation enabled by evaporation and expansion of residual water within the organic MP. In addition to LFL, the hitherto underexplored method of laser processing in the low fluence range, known as Pulsed Laser Diffusion Enhancement in Liquids (PuDEL), was studied.[3] During laser cold extraction of coffee powder in a flow-through reactor, it was demonstrated via headspace-GC that flavor attributes typical for both hot and cold brew coffee were also present in laser coffee, using only a laser fluence <20 mJ/cm², however, fluences >40 mJ/cm² went along with chemical degradation. The PuDEL mechanism could thus pave the way for laser extraction as a new process in the food industry.

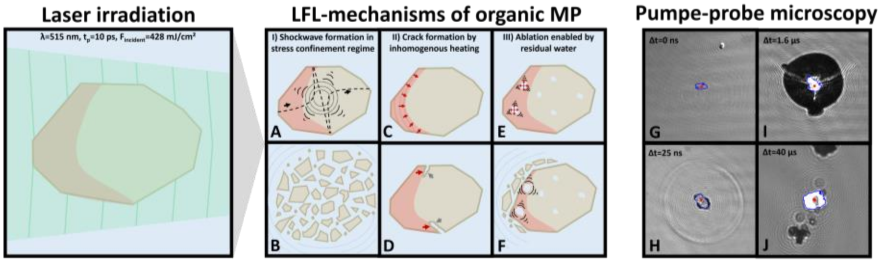

Figure 1. Potential mechanisms of organic MP induced by LFL [1] and pump-probe results

[1] T. Friedenauer, K. Buck, M. Eberwein, A.-L. Bünte, C. Rehbock, S. Barcikowski, *Part. Part. Syst. Charact*, 2300034 (2023).

[2] V. Amendola, D. Amans, Y. Ishikawa, N. Koshizaki, S. Scirè, G. Compagnini, S. Reichenberger, S. Barcikowski, *Chem. - A Eur. J.*, 26, 9206–9242 (2020).

[3] A. R. Ziefuss, T. Hupfeld, S. W. Meckelmann, M. Meyer, O. J. Schmitz, W. Kaziur-Cegla, L.K. Tintrop, T. C. Schmidt, B. Goekce, S. Barcikowski, *Npj Science of Food*, 6 (1) (2022).

Measurement of Thermal Relaxation Time of Vibrational Modes in Glycerol Using Pump-Probe Spectroscopy

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The energetic coupling and dissipation of vibrational modes in liquids play a pivotal role in various applications, including photothermal therapy for cancer treatment [1], thermal management in electronic packages, and heat dissipation in nanoparticle generation and manufacturing [2]. In particular, the molecular vibrational dynamics of glycerol is of interest due to its significance in biomedical applications, owing to its biocompatibility and low toxicity. In addition, the well-studied IR-active modes facilitates navigating the vibrational landscape, aiming to expand glycerol's role in biomedical applications and ensuring effective heat transfer in therapies.

In this work, we utilize a pump-probe method to study the vibrational dynamics of liquids after short-pulsed laser heating. Using glycerol as an exemplar system, we aim to understand the role of different vibrational modes on energy dissipation. Our experiment employs a sub-picosecond, wavelength-tuneable mid-infrared pulse specifically tuned to target distinct vibrational modes of the glycerol liquid (C-O stretching mode and O-H bending mode). We monitor the relaxation of these modes after excitation of the glycerol with a sub-picosecond visible pump pulse at 520 nm as our thermal source. Through direct resonance of the IR probe pulses with these vibrational modes, we systematically investigate energy transfer processes within the molecular structure. This comprehensive molecular probing not only elucidates intricate details of glycerol's thermal behaviour but also serves as a gateway to gain further insight into the nuanced interplay between vibrational modes and heat transfer dynamics. Such understanding is crucial for the success of photothermal therapies.

The analysis of the FTIR spectrum of glycerol has provided valuable insights into the molecular vibrational dynamics within the 6.0 -8.5 μm wavelength range. Our pump-probe spectroscopy measuring lifetimes of these modes reveal that the spectral width of the vibrational peaks can relax on the nanosecond timescale. Notably, our results demonstrate a distinction in lifetimes between bending and stretching modes. Specifically, bending modes exhibit a shorter relaxation time, lasting between 1000-1500 ns, while stretching modes endure for a more extended period, with lifetimes exceeding 2500 ns. This detailed understanding of the vibrational dynamics and lifetimes of glycerol's molecular modes is crucial for tailoring its applications in various fields, including biomedical applications, where precise control of energy transfer is paramount.

[1] M. Chen, X Zhang, J. Liu, F Liu, R. Zhang, P. Wei, H. Feng, M. Tu, A. Qin, J. W. Y. Lam, D. Ding, B. Z. Tang, Evoking Photothermy by Capturing Intramolecular Bond Stretching Vibration- Induced Dark-State Energy, *ACS Nano* **14,** 4265 (2020).

[2] A. Giri, S. G. Walton, J. Tomko, N. Bhatt, M. J. Johnson, D. R. Boris, G. Lu, J. D. Caldwell, O. V. Prezhdo, P. E. Hopkins, Ultrafast and Nanoscale Energy Transduction Mechanisms and Coupled Thermal Transport across Interfaces, *ACS Nano 2023* **17**, 14253 (2023).

Significant reduction of ablation efficiency by spallation layer redeposition during ultrashort pulse laser ablation in liquid

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Ultrashort laser ablation is governed by two main ablation mechanisms, namely spallation and phase explosion. The former of the two only occurs when the stress confinement condition is met, which states that the heating time of the material must be shorter than the acoustic relaxation time τ_{ac}. While both mechanisms significantly contribute to the ablation volume during laser ablation in air, simulations predict that a large amount of material ejected via spallation during laser ablation in liquid (LAL) is redeposited to the target surface [1]. As this mechanism would reduce the ablation volume during LAL, a profound understanding of the significance of material redeposition is crucial to understand LAL efficiency and further upscale the process. In this study we aim to experimentally verify spallation layer redeposition and quantify the magnitude of redeposited material. For this, pump-probe microscopy experiments (PPM) are carried out [2]. Additionally, the pulse duration dependent ablation efficiency η for ablation of Au in air and water is determined (see figure 1). By varying the pulse duration to be either smaller or larger than the acoustic relaxation time τ_{ac}, the condition of stress confinement and thus the spallation mechanism can be controlled. The time-resolved PPM experiments clearly demonstrate spallation layer redeposition, which up until now was only shown by computational methods. Furthermore, the control of stress confinement allows us to determine the significance of spallation layer redeposition, amounting to more than 80 % of the ablated material. Our results clearly show that spallation layer redeposition during LAL is the main mechanism limiting ablation efficiency. Based on this fundamental finding, strategies beyond utilizing stress confinement, such as increasing fluence or employing double pulses may be formulated to reduce redeposition, increase ablation efficiency, and further scale up the LAL process.

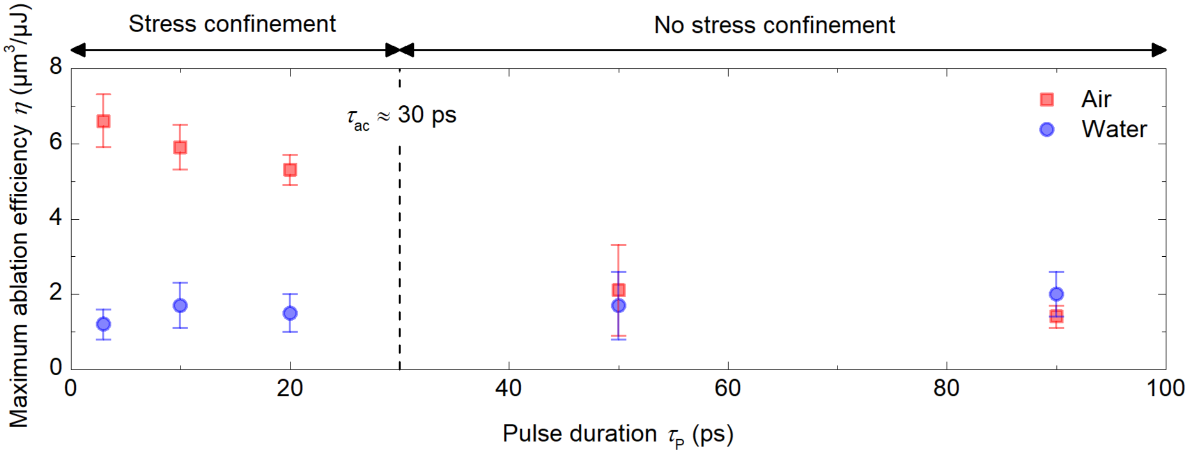

Figure 1. a) Maximum ablation efficiency η of Au in air and water for different pulse durations τ_P. The dashed vertical line shows the acoustic relaxation time τ_{ac}.

[1] C. Chen, L. Zhigilei, Appl. Phys. A 129, 288 (2023)

[2] M. Spellauge, C. Doñate-Buendía, S. Barcikowski, B. Gökce, H. Huber, Light Sci. Appl. 11, 68 (2022)

Breaking Boundaries: Laser-Driven Nanoparticle Formation and Microparticle Crushing in Liquids

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As the most important laser-based synthesis and processing methods, pulsed laser ablation (LAL) and pulsed laser fragmentation (LFL) in liquids allow the synthesis of colloidal nanoparticles [1-3]. While LAL has demonstrated productivities close to 10 g/h, LFL, though still exhibiting one order of magnitude lower throughput, gives access to far smaller nanoparticles in the nanocluster size range (<3 nm) [4] via laser-induced phase explosion of nanoparticles [5]. In contrast, microparticle LFL is driven by a totally different mechanism (Fig. 1) that reminds us of particle crushing rather than their total evaporation, still giving access to the same nanocluster. From the application viewpoint, the LFL of microparticles has the potential to surpass even advanced LAL efficiencies by one order of magnitude [6]. So, the question arises about the mechanisms, driving forces, and application potentials of this LFL variant. This presentation unveils current developments in scaling microparticle-LFL, with examples of NIR-absorbing materials, metal oxide, food, and drug microparticles in water. The most important scaling possibility is a precise matching to the efficiency "sweet spot" number of pulses per volume element (PPV), adjustable by matching the laser repetition rate with the flat jet flow velocity. The presented results showcase a scalable and continuous particle-crushing method, with application examples ranging from Laser Powder Bed Fusion (NIR absorbing LaB6 for desktop 3D printing) over Catalysis (water splitting by IrOx [6]) to Pharma (solubilization of the drug naproxen [7]) and even Food (dispersing the nutraceutical curcumin).

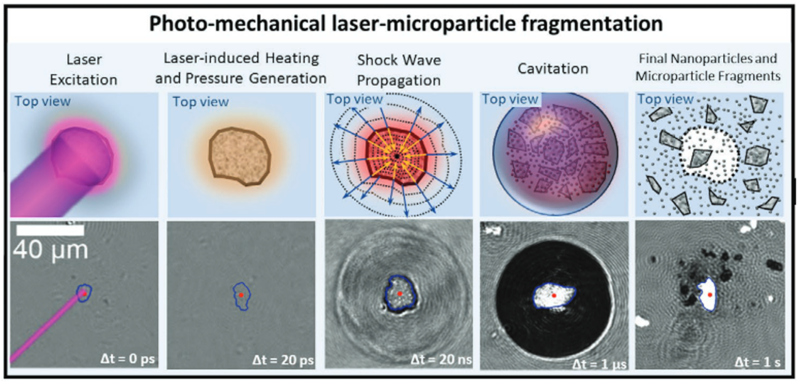

Figure 1: Mechanistic summary of the ps-laser pulse induced IrO_2 microparticle-LFL mechanism (adapted from [6]).

[1] V. Amendola, D. Amans, Y. Ishikawa, N. Koshizaki, S. Scirè, et al.: Room-Temperature Laser Synthesis in Liquid of Oxide, Metal-Oxide Core-Shells, and Doped Oxide Nanoparticles Vincenzo, Chem. Eur.J. 2020, 26, 9206 –9242

[2] S. Reichenberger, G. Marzun, M. Muhler, S. Barcikowski, Perspective of Surfactant-free Colloidal Nanoparticles in Heterogeneous Catalysis; ChemCatChem 2019, 11, 4489–4518.

[3] D. Zhang, B. Gökce, S. Barcikowski, Laser Synthesis and Processing of Colloids: Fundamentals and Applications, ChemRev, 2017, 117, 5, 3990 - 4103

[4] A. R. Ziefuss, T. Steenbock, D. Benner, A. Plech, J. Göttlicher et al. Photoluminescence of Fully Inorganic Colloidal Gold Nanocluster and Their Manipulation Using Surface Charge Effects, Adv. Mater, 2021, 2101549

[5] H. Huang, L. Zhigilei, Computational study of laser fragmentation in liquid: Phase explosion, inverse Leidenfrost effect at the nanoscale, and evaporation in a nanobubble, Sci. China Phys., 2022, 65, 274206

[6] M. Spellauge, M. Tack, R. Streubel, M. Miertz, K. Steffen Exner et al., Photomechanical Laser Fragmentation of IrO2 Microparticles for the Synthesis of Active and Redox-Sensitive Colloidal Nanoclusters, 2023, 19, 10, 2206485

[7] T. Friedenauer, K. Buck, M. Eberwein, A.Bünte, C. Rehbock, S. Barcikowski, Efficient Synthesis of Submicrometer-Sized Active Pharmaceuticals by Laser Fragmentation in a Liquid-Jet Passage Reactor with Minimum Degradation, 2023, 40, 12, 2300034

Integrating Laser Desorption and Simulation to Predict Monolayer Structure on Metallic Nanoparticles

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In this work, we combine matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) and atomistic simulation to predict and visualize the structure of binary, mixed-ligand monolayers on ultrasmall silver and gold nanoparticles (smaller than 10 nm), which impede the detection of monolayer morphology by traditional visualization techniques. In principle, monolayers can include a mixture of ligand types with multiple chemical functionalities and may also self-assemble into advantageous patterns (e.g., Figure 1). Previous work has shown that both chemical and length mismatches among the surface ligands influence phase separation [1-2]. To examine the interplay between these driving forces, we first use MALDI-MS to experimentally probe the surface morphologies of a series of two-ligand mixtures, and then use our previously-developed configurationally-biased Monte Carlo (CBMC) algorithm to quantitatively predict the MALDI-MS results for the ligand mixtures, while providing atomic scale details of the equilibrated ligands structures. We also discuss the challenges for further adapting MALDI-MS and simulation for mapping the nanoparticle ligand shell morphology.

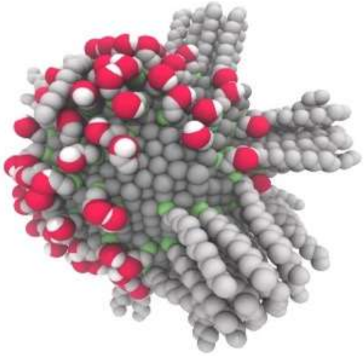

Figure 1. Visualization of a silver (Ag) nanoparticle (in gray, diameter, *d* = 4 nm) functionalized with a binary, mixed-ligand monolayer of mercaptoethanol (red) and dodecanethiol (gray). The atomistic simulations of the ligand distributions consistently matched the corresponding MALDI-MS spectra of the functionalized nanoparticles of core diameter, *d*=4 nm, confirmed by transmission electron microscopy (TEM) [1-2].

[1] S. N. Merz, Z. J. Farrell, J. Pearring, E. Hoover, M. Kester, S. A. Egorov, D. L. Green, and K. H. DuBay, ACS Nano **12**, 11031 (2018).

[2] S. N. Merz, E. Hoover, S. A. Egorov, K. H. DuBay, and D. L. Green, Soft Matter **15**, 4498 (2019).

Plasmonic Hybrids of Laser-Modified TiO_2 for Enhanced Photoelectrochemical Applications

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Defect-induced titanium dioxide, characterized by intentional introduction of structural imperfections, opens avenues for tailoring the electronic and optical properties of the material, thereby offering unique opportunities for applications in photocatalysis, energy conversion, and advanced materials science[1]. The photoelectrochemical performance of TiO_2 is often hindered by its limited absorption of visible light. To address this challenge, plasmonic metal nanoparticles, Ag and Au, are strategically integrated by the above-mentioned laser assisted processes, aiming to enhance light absorption and promote efficient charge separation. This research explores the development of photoelectrochemical materials for heightened energy conversion efficiency by incorporating plasmonic nanoparticles (silver (Ag), gold (Au), and bimetallic Ag/Au) into titanium dioxide (TiO_2) with laser-induced defects (355/532 nm Nd:YAG laser). Laser ablation in liquids was used to synthesize plasmonic nanoparticles, while laser irradiation for their incorporation to defects rich TiO_2 nanoparticles. Laser-induced defects serve a crucial role in augmenting the material's photoelectrochemical activity by providing additional active sites for charge transfer[2]. Characterization techniques such as XRD, TEM (figure1), SEM, XPS, PL, Raman spectroscopy, EDS and UV-Vis spectroscopy are employed to assess the structural and optical properties of the hybrid nanomaterials. The bimetallic Ag/Au nanoparticles are designed to exploit synergistic effects, potentially resulting in superior photoelectrochemical properties compared to individual metal nanoparticles. The photoelectrochemical performance is evaluated through systematic studies of the materials' current-voltage characteristics and photoconversion efficiencies. This research contributes to the advancement of photoelectrochemical materials, showcasing the potential of bimetallic Ag/Au nanoparticles incorporated into laser modified TiO_2 matrices as a promising avenue for efficient solar energy conversion.

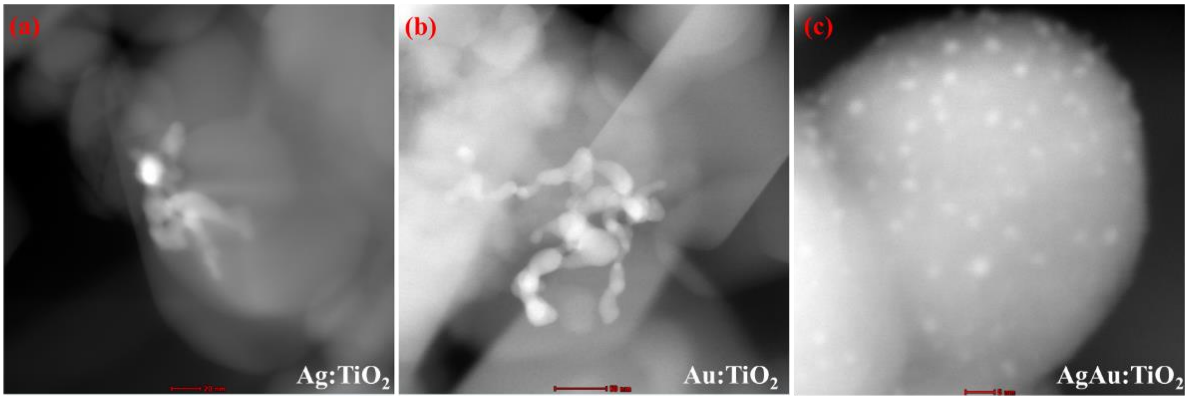

Figure 1: TEM images of titanium dioxide incorporated with Ag(a), Au(b) and bimetallic AgAu(c).

[1] X. Chen, L. Liu, P. Y. Yu, and S. S. Mao, "Increasing solar absorption for photocatalysis with black hydrogenated titanium dioxide nanocrystals," *Science*, vol. 331, no. 6018, pp. 746–750, Feb. 2011, doi: 10.1126/science.1200448.

[2] P. Raveendran Nair *et al.*, "Black titanium dioxide nanocolloids by laser irradiation in liquids for visible light photo-catalytic/electrochemical applications," *Appl. Surf. Sci.*, vol. 623, p. 157096, Jun. 2023, doi: 10.1016/j.apsusc.2023.157096.

How surface defects and related local charge distributions control the adsorption of surfactant-free, electrostatically-stabilized colloidal nanoparticles under diffusion-controlled conditions

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A controlled nano integration is essential for the preparation of nano-functionalized materials like heterogeneous catalysts. The DLVO theory hereby successfully models the colloidal interaction between (nano-) particles.[1] Yet, in the past, we reported first deviations from the DLVO predictions and suggested that these were caused by local features such as surface-near defects and crystal facets that naturally occur in real nanoparticle systems.[2] This talk aims to discuss our newest insights on how local features and surficial defects tailor the adsorption properties under electrostatically controlled conditions. Within the first part, the latest simulation results will be summarized where the non-linear Poisson Boltzmann equation was solved for over 5000 adsorption conditions showing that a high defect density can significantly lower the interaction energy barrier in line with the previous hypothesis. Hereby, the term “defect” attributes any local structure deviation that alters the local charge distribution. In the second part of the talk, a new surface characterization technique using pH-dependent fluoride substitution [3] will be presented at the example of laser-modified oxides which indeed will verify that such local charge distribution features that were assumed in the theoretical model exist in real oxides. Further, the preferential nanoparticle adsorption on respective crystal phases will be verified and discussed from the perspective of a combined strategy of precise single pulse laser processing (s-PUDEL[4]) and surface-site selective nano functionalization as well as related opportunities for mechanistic studies in heterogeneous catalysis.

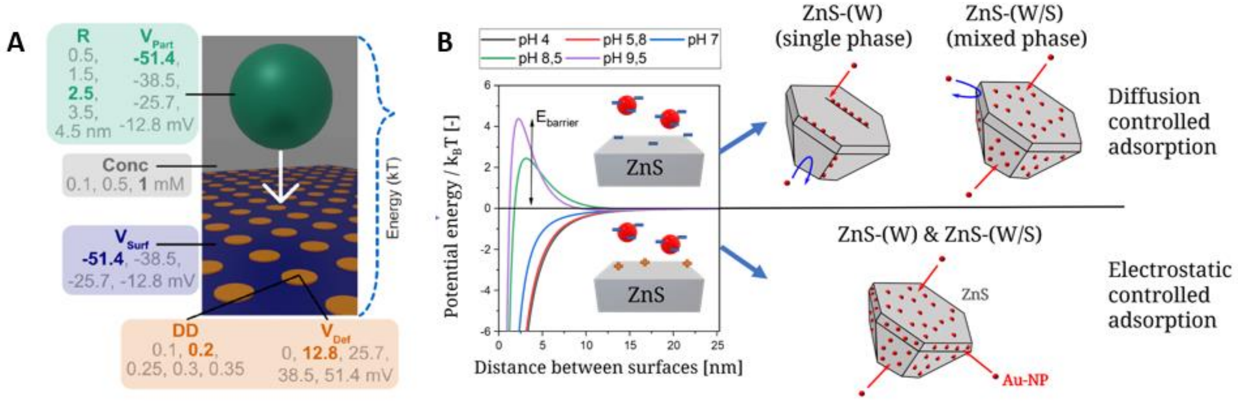

Figure 1. A) Schematic representation of the simulation model used to evaluate the role of local defect sites in the nanoparticle adsorption. B) Schematic representation of the energy barriers and related site selectivity under diffusion- (electrostatic repulsion) and electrostatic-controlled (electrostatic attraction) adsorption

[1] H. Ohshima, Electrical Phenomena at Interfaces and Biointerfaces, John Wiley & Sons, Inc., 2012.
[2] S. Reichenberger, G. Marzun, M. Muhler and S. Barcikowski, *ChemCatChem*, **2019**, 11, 4489–4518.
[3] K. Lau, F. Niemann, K. Abdiaziz, M. Heidelmann, Y. Yang, Y. Tong, M. Fechtelkord, T. C. Schmidt, A. Schnegg, R. K. Campen, B. Peng, M. Muhler, S. Reichenberger and S. Barcikowski, *Angew. Chem. Int. Ed.*, **2023**, 62, e202213968.
[4] Reichenberger, S., *Sci. China Phys. Mech. Astron.*, **2022**, 65, 274208

Effect of Additives on Efficiency of Gold Nanoparticles Formation by Laser-Induced Reduction Method

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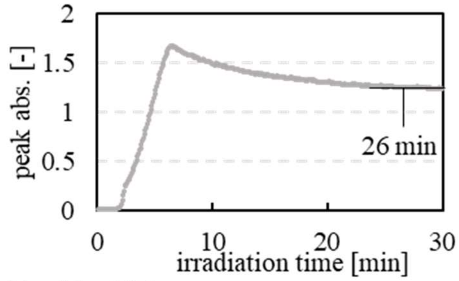
We demonstrate formation of metal[1] and alloy[2] nanoparticles (NPs) in solvent containing metallic ions by laser-induced reduction method. Active species such as hydrogen radicals ($H^{\bullet}$), hydroxyl radicals ($OH^{\bullet}$) and solvated electrons (e^{-}) are produced by decomposition of solvent molecules by high-intensity laser irradiation in solution. Among them, solvated electrons act as a strong reducing agent for metallic ions, resulting in formation of NPs[3]. On the other hand, hydroxyl radicals behave as oxidizing agents which can inhibit the reduction reaction of metallic ions. Therefore, the efficiency of NPs formation could be improved by addition of a scavenger for hydroxyl radicals.

An aqueous solution of gold ions was prepared by dissolving hydrogen tetrachloroaurate (III) tetrahydrate ($HAuCl_4 \cdot 4H_2O$) in pure water at a concentration of 5.0×10^{-4} mol/dm^3. Femtosecond laser pulses (wavelength: 800 nm; pulse energy: 7 mJ; pulse width: 100 fs; repetition rate: 250 Hz) were irradiated for 30 minutes through an aspheric lens (focal length: 8 mm; numerical aperture: 0.5) into a fused silica cuvette filled with 3 ml of the gold aqueous solution without and with an alcohol at the concentration of 5 vol% as a scavenger for the hydroxyl radicals. The UV-visible absorption spectra were measured every 5 seconds during laser irradiation. The reaction of gold NPs formation was evaluated by transition of peak absorbance of surface plasmon resonance (SPR) of gold NPs.

Figure 1(a) shows time variation of peak absorbance of SPR during laser irradiation of gold solution without an alcohol. The peak absorbance increases with laser irradiation time, reaches a maximum after 7 minutes and then slowly decreases to a constant after about 26 minutes. We had reported that NPs are formed by the reduction of ions and then fragmented by the ablation reaction by laser irradiation of the fabricated NPs[4]. On the other hand, the transition of peak absorbance became constant only after 5 minutes irradiation in the solution with alcohol (Fig. 1(b)). This indicates that the reduction reaction was accelerated and single-digit gold NPs were formed without fragmentation process. Consequently, the formation of gold NPs could be shortened to about one-fifth by addition of alcohol to the aqueous solution.

(a) without additive



(b) with additive

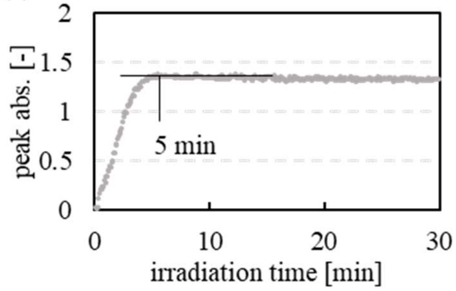


Figure 1. Time variation of peak absorbance in the UV-visible absorption spectra for gold solutions (a) without and (b) with alcohol.

Generally, alcohol is oxidized by an oxidizing agent to form aldehyde, carboxylic acid or ketone. Since the alcohol radical generated during the oxidation process of alcohol by $OH^{\bullet}$ has a reducing effect, the alcohol not only acts as a scavenger of $OH^{\bullet}$, but promotes NPs formation through the reduction reaction by decomposition products of alcohol in laser-induced reduction method. We will show further improve of formation efficiency of NPs by optimization of kinds and concentrations of additives.

[1] T. Nakamura et al., *Appl. Phys. A*, **104**, 1021–1024, (2011).

[2] Y. Herbani et al., *J. Phys. Chem. C*, **115**, 21592–21598, (2011).

[3] J. P. Sylvestre et al., *J. Phys. Chem. B*, **108**, 16864–16869, (2004).

[4] T. Nakamura et al., *AIP Adv*, **3**, 082101, (2013).

Data-Driven Predetermination of Cu Oxidation State in Copper Nanoparticles: Application to the Synthesis by Laser Ablation in Liquid

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Copper-based nanocrystals play a pivotal role as reference nanomaterials in the integration of emerging green technologies.[1] Notably, the synthesis of these nanocrystals is effectively achieved through laser ablation in liquid (LAL), highlighting its significance as a distinctive technique.[2]In this investigation, we initially conducted a bibliographic analysis of the LAL synthesis of Cu-based nanocrystals. The purpose was to identify relevant physical and chemical characteristics and to organize an extensive literature database for the training of Machine Learning (ML) models aimed at predicting the oxidation state of copper. The compiled database comprises 36 features that may influence the oxidation state of synthesized copper nanoparticles, along with one output variable representing the weighted average value of the relative mass of each phase of copper nanoparticles. Subsequently, various feature selection techniques, including single feature analysis, super feature analysis, and genetic algorithm, were employed to uncover correlations between the features and identify influential variables for the construction of a linear regression model. Results indicated that, across all techniques, the highest R^2 scores were found to be below 0.6394, underscoring the ineffectiveness of linear regression models in handling the complexity of the dataset.

Given the limitations of linear regression, we adopted a machine learning (ML) approach, specifically employing a permutation-based feature ranking method. This reduced the initial 36 features to a subset of 9, 10, or 11 features. The validity of this method was substantiated by the consistent performance across various ML models. Following this reduction, we employed the ensemble method, specifically the Voting Regressor, to amalgamate the predictive capabilities of all utilized models and trained it for optimal predictive accuracy. Results demonstrated that the Voting Regressor model exhibited excellent performance on both the training and testing datasets under 9 influential features, yielding R2 scores of 0.95 and 0.91, respectively. Additionally, five typical LAL setup features were fixed based on specific laboratory conditions. The well-trained Voting Regressor model was then employed to reverse predict the different oxidation states of copper nanoparticles under various LAL parameter combinations. The impact of the remaining four features, including the percentage of O+Cl+CN+S in the solvent, the number of atoms in the solvent, the percentage of O+Cl+CN+S in the solute, and the mass fraction in the solution, on the oxidation state of copper nanoparticles was explored. Finally, guided by ML maps, a series of new LAL experiments were conducted to target various oxidation states of Cu, including the challenging Cu(I) compounds. The agreement between experimental outcomes and ML predictions resulted in an R2 of 0.9, leading to the identification of three distinct sets of experimental conditions yielding Cu-based NPs with a copper oxidation state close to 1. This underscores the general applicability of the ML approach to other nanomaterials and opens new perspectives for understanding the chemical pathways of nanomaterials generated by LAL.[3]

[1] S. F. Hansen *et al.*, ‘Nanotechnology meets circular economy’, *Nature Nanotechnology*, vol. 17, no. 7. 2022. doi: 10.1038/s41565-022-01157-6.

[2] D. A. Goncharova, T. S. Kharlamova, I. N. Lapin, and V. A. Svetlichnyi, ‘Chemical and Morphological Evolution of Copper Nanoparticles Obtained by Pulsed Laser Ablation in Liquid’, *Journal of Physical Chemistry C*, vol. 123, no. 35, 2019, doi: 10.1021/acs.jpcc.9b03958.

[3] R. Miao, M. Bissoli, A. Basagni, E. Marotta, S. Corni, and V. Amendola, ‘Data-Driven Predetermination of Cu Oxidation State in Copper Nanoparticles: Application to the Synthesis by Laser Ablation in Liquid’, *J Am Chem Soc*, Oct. 2023, doi: 10.1021/jacs.3c09158.

Chemical Reaction Pathways during Laser Fragmentation in Organic Solvents through Chemical and Physical By-product Analysis

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Laser synthesis and processing of colloids (LSPC) is accompanied by extreme conditions that lead to the decomposition of the liquid and reactions with the processed material resulting in chemical reactions that greatly affect the properties of the nanomaterials. These reactions and their effect on oxidation and productivity of the nanoparticles have mostly been studied in water, in particular the role of the redox potential of the material and the formation of hydrogen, oxygen, and hydrogen peroxide[1]. In contrast, LSPC in organic liquids has been found to be dominated by pyrolysis behavior[2] leading to carbon shells[3] and volatile as well as non-volatile by-products[4,5]. This contribution will provide insight into the chemical reactions occurring during laser fragmentation of metal microparticles in organic solvents through quantification of gaseous decomposition products and by-product analysis. In addition, the influence of atmospheric oxygen and the redox potential of the metal on the gas and hydrogen yield will be discussed. Significant differences between nitrogen-saturated and ambient atmosphere will be highlighted as the hydrogen content of the laser fragmentation in liquid (LFL)-generated gas produced differs. For example, the LFL of Au microparticles in cyclohexane using ambient atmosphere (with O_2) resulted in 6 vol% hydrogen, whereas the LFL in nitrogen-saturated cyclohexane yielded about 40 vol% hydrogen, while the total gas formed is comparable (Fig. 1a and 1b). The determinants and pathways of liquid decomposition will be explained (exemplified in Fig. 1c), possible intermediates suggested, and chemical reaction schemes for nanoparticle formation by reactive LFL are drawn.

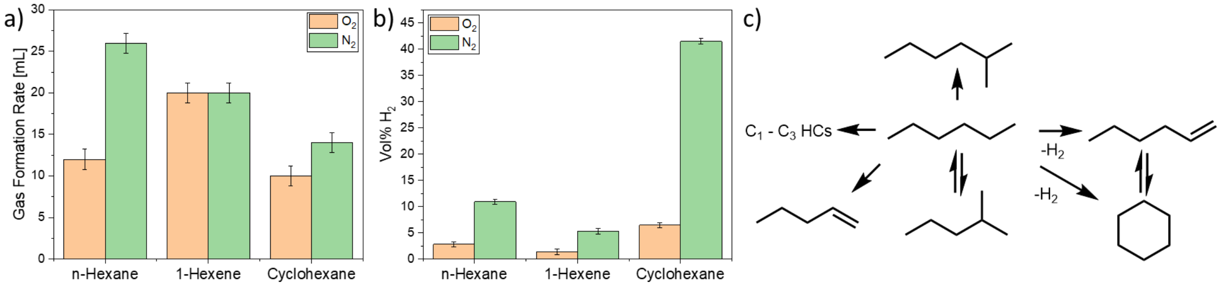

Figure 1. Gas formation during reactive LFL of Au microparticles in organic solvents. a) Total gas formation rates. b) Vol% of H_2 in the total gas formed. c) Scheme of characterized decomposition products for the LFL of metal microparticles in *n*-hexane. HCs: hydrocarbons

[1] M.-R. Kalus, R. Lanyumba, N. Lorenzo-Parodi, M. A. Jochmann, K. Kerpen, U. Hagemann, T. C. Schmidt, S. Barcikowski, B. Gökce, Phys. Chem. Chem. Phys., 21, 18636-18651 (2019).
[2] T. Fromme, L. K. Tintrop, T. C. Schmidt, S. Reichenberger, S. Barcikowski, ChemPhysChem, 24, e202300089 (2023).
[3] D. Zhang, C. Zhang, J. Liu, Q. Chen, X. Zhu, C. Liang, ACS Appl. Nano Mater., 2, 28-39 (2019).
[4] P. Marabotti, S. Peggiani, A. Vidale, C. S. Casari, Chin. Phys. B, 31, 125202 (2022).
[5] L. F. Frias Batista, M. Moody, C. Weththasingha, E. Kaplan, I.S. Faruque, S. El-Shall, K. M. Tibbetts, Phys. Chem. Chem. Phys., 25, 18844-18853 (2023).

Time-Resolved XAFS Study on the Laser-Induced Particle Formation of a Pd(II) and Rh(III) Ions in an Aqueous/Ethanol Solution

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When a pulsed UV laser is irradiated to the aqueous/ethanol solution including precious metals (PM: Pd, Rh and so on), the photo-excited PM^{n+} ions react with ethanol and are reduced to PM neutrals. The PM neutrals form particles in the solution because electronic repulsion forces between the ions are lost in the neutrals. A series of reactions is called laser-induced particle formation (LIPF) and is used for PMs from industrial waste (Fig. 1) [1].

Previously, we showed that the LIPF technique can selectively recover Pd from the solution of a spent nuclear fuel [2], and investigated the LIPF mechanism in the Pd(II) ion by time-resolved X-ray fine structure (XAFS) [3]. The time-resolved XAFS study in the Pd ion showed that (i) the LIPF process is described by contribution of only two species (Fig. 2a), (ii) in the first stage the LIPF is dominated by laser-induced reduction of Pd(II) to Pd(0), (iii) in the second stage the Pd(0) neutrals form the Pd nanoparticle, and (iv) in the third stage the Pd nanoparticle behaves as a catalyst and promotes the reduction of Pd(II) (autocatalytic reduction). In addition, relationship between the reaction coefficient and the laser fluences elucidated that the autocatalytic reduction is accelerated by the laser irradiation.

More recently, we performed the time-resolved XAFS measurement in the Rh(III) ion, which is neighboring to the Pd(II) ion in the 4d transition metal series, in the aqueous/ethanol solution [4]. Temporal change of XAFS spectra during the LIPF in Rh(III) does NOT show presence of the isosbestic point, which was clearly observed in the Pd(II) ion (Fig. 2b). It means that more than three Rh species contribute to the LIPF. Thus, to identify the Rh species we analyzed the time-resolved XAFS data by using multivariate curve resolution (MCR), which is one of the chemometrics. The MCR analysis elucidates that the photoreduction proceeds in the order of Rh(III) → Rh(I) → Rh(0) in early stage in the LIPF. We also succeeded in explaining the LIPF mechanism based on the reaction model, which involves photoreductions of Rh(III) and Rh(I), photoinduced autocatalytic reductions of Rh(III) and Rh(I), and photooxidation of Rh(I).

In my presentation, the LIPF mechanism of the PM ions is discussed by comparing the time-resolved XAFS data between the Pd(II) and Rh(III) ions.

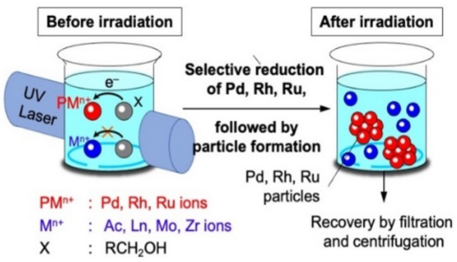

Figure 1. Recovery of precious metals using LIPF

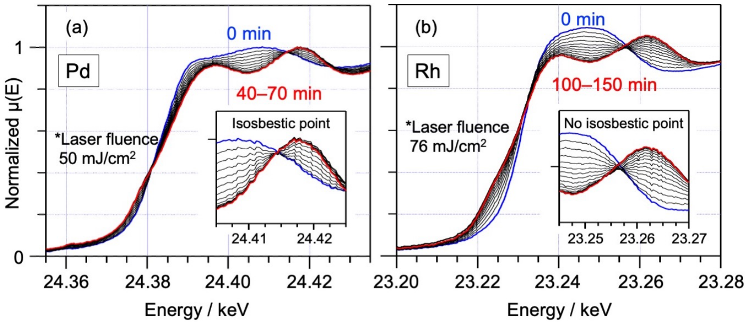

Figure 2. Temporal change of the XAFS spectra during the LIPF in (a) Pd(II) ion [3] and (b) Rh(III) ion [4]. Appearance of isosbestic point in Pd indicates that only two species contribute to the LIPF.

[1] M. Saeki, In *High-Energy Chemistry and Processing in Liquids*, Y. Ishikawa, T. Nakamura, M. Saeki, T. Sato, T. Sugiyama, H. Wada, T. Yatsuhashi Eds. (Springer Singapore: Singapore, 2022), p33-55
[2] S. Asai et al., Anal. Chem. 88, 12227 (2016).
[3] M. Saeki et al., J. Phys. Chem. C 123, 817 (2019).
[4] M. Saeki et al., J. Phys. Chem. C 126, 5607 (2022).

Pulsed Laser-driven high-entropy materials for electrocatalytic water splitting

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High purity and functionality-driven nanomaterials demand diverse applications in energy and environment-related fields, which have become an intensive research topic of interest. The production of novel electro- and photo-active nanomaterials is significantly subjected to the synthetic routes that make the development of surface and crystalline-tuned advanced materials possible. The significant size and tailored textural properties of materials synthesized by the interaction of laser with matter have emerged as a promising synthetic technique. Pulsed laser-assisted synthesis of nanomaterials in liquids, powered by high-power laser, offers many degrees of parameter control (i.e., pulsed laser power, wavelength, reaction time duration, laser pulse repetition rate, and solvent) and owns numerous advantages over traditional physical and chemical synthetic methods such as high purity, no byproducts, simple, non-toxic, no need of surfactants and reducing agents. Thus, the fundamental insights into the mechanism of pulsed laser techniques in depth by considering various experimental conditions to accelerate hypotheses that are appropriate for the production of high entropy materials for electrocatalytic water splitting applications.

High-entropy materials (HEMs), characterized by their unique atomic arrangements and composition, have emerged as promising candidates for electrocatalytic applications. The composition/structure complexity and adjustability endow them with a huge design space to adjust electronic structure, geometric configuration as well as catalytic activity through constructing reaction active sites with optimal binding energies of different reaction intermediates. The presentation will commence with a brief introduction to the pulsed laser-synthesis methods employed to fabricate high-entropy electrocatalysts. Subsequently, the role of HEM in enhancing key electrochemical reactions, such as the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER), and small molecule oxidation reaction coupled water electrolyzer will be discussed in detail.

Pulsed Laser in Liquids Made Electrocatalysts for Sustainability Applications

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Electrocatalysis has the potential to transform the manufacturing of chemicals and consumer goods in a sustainable way by replacing existing fossil-fuel-based processes by energy-saving successor technologies that utilize renewable energy [1]. Likewise, advanced electrocatalytic redox processes for environmental remediation of halogenated organic water pollutants are emerging as globally scalable, viable technologies if they consist solely of nonprecious materials, work in aqueous media, have low energy consumption, and enable complete destruction of harmful chemicals [2]. Functional electrocatalytic processes require the development of a quantitative understanding of mechanisms and rationally designed nanomaterials with controlled properties, for which pulsed laser in liquids synthesis is an ideal technique [3].

Selective hydrocarbon oxidations to alcohols have the ultimate goal of gas-to-liquid conversion of methane to methanol without energy-intensive steam reforming. Better catalysts, reaction control, and understanding of electrocatalytic processes are needed to achieve high selectivity for single alcohol products at high activity. We developed earth-abundant mixed-metal nanocatalysts that were synthesized by pulsed laser in liquids synthesis [3] and employed them on high-surface-area carbon supports [4] to selectively electrooxidize toluene to benzyl alcohol. We show how electrolyte engineering and concomitant accessibility of different mechanistic pathways led to 100 % selectivity for benzyl alcohol with high activity.

Per- and poly-fluoroalkyl substances (PFAS) are a class of highly toxic synthetic chemicals with extremely high chemical stability, necessitating the development of advanced remediation strategies [2]. We used electrocatalysis to mineralize the PFAS compound perfluorooctane sulfonate (PFOS) in aqueous electrolyte. Bimetallic nanocatalysts made by pulsed laser in liquid synthesis [3] were immobilized on hydrophilic carbon fiber paper [4] anodes, allowing us to achieve complete defluorination of PFOS. Systematic variation of electrocatalysis process parameters provided mechanistic insights into the aqueous defluorination of PFOS.

[1] T. Taseska, W. Yu, M. K. Wilsey, Z. Meng, C. P. Cox, S. S. Ngarnim, A. M. Müller, Analysis of the Scale of Global Human Needs and Opportunities for Sustainable Catalytic Technologies, *Top. Catal.* **66**, 338-374 (2023).

[2] M. K. Wilsey, T. Taseska, Z. Meng, W. Yu, A. M. Müller, Advanced Electrocatalytic Redox Processes for Environmental Remediation of Halogenated Organic Water Pollutants, *Chem. Commun.* **59**, 11895-11922 (2023).

[3] R. C. Forsythe, C. P. Cox, M. K. Wilsey, A. M. Müller, Pulsed Laser in Liquids Made Nanomaterials for Catalysis, *Chem. Rev.* **121**, 7568-7637 (2021).

[4] M. K. Wilsey, K. R. Watson, O. C. Fasusi, B. P. Yegela, C. P. Cox, P. R. Raffaelle, L. Cai, A. M. Müller, Selective Hydroxylation of Carbon Fiber Paper for Long-Lasting Hydrophilicity by a Green Chemistry Process, *Adv. Mater. Interfaces* **10**, 2201684 (2023).

Structural Evolution and Cu-Ni Nanoprecipitate Formation in Al-rich High Entropy Alloy Nanoparticles through Laser Processing

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This study presents the synthesis of Al-rich non-equiatomic high entropy alloy nanoparticles (HEA NPs) through laser ablation of an AlSiCrMnFeNiCu target in deionized water, employing a nanosecond Nd:YAG pulsed laser with a wavelength of 1064 nm and an 8 ns pulse duration. The resulting NPs maintain the composition and structural phases (B2 type AlFe and Cr_5Si_3) of the target material. A secondary laser at 532 nm was used to further process the colloidal solution, leading to systematic investigations of compositional and structural changes using electron microscopy (Figure 1a) and spectroscopic techniques. During laser processing, cyclic reheating induces the formation of Cu-Ni nanoprecipitates on the processed NPs [1]. This can be attributed to the similar ionic sizes and FCC structural phase of Cu and Ni, causing them to segregate together during the molten stage and subsequently form precipitates upon solidification. Thermodynamically, Cu-Ni phases are favoured among all binary combinations of the elements present in the HEA NPs. Based on our experimental findings, we discuss a plausible growth mechanism for the Cu-Ni enriched nanoprecipitates (Figure 1b). This work sheds light on the controlled synthesis and unique structural evolution of HEA NPs, offering insights into their potential applications.

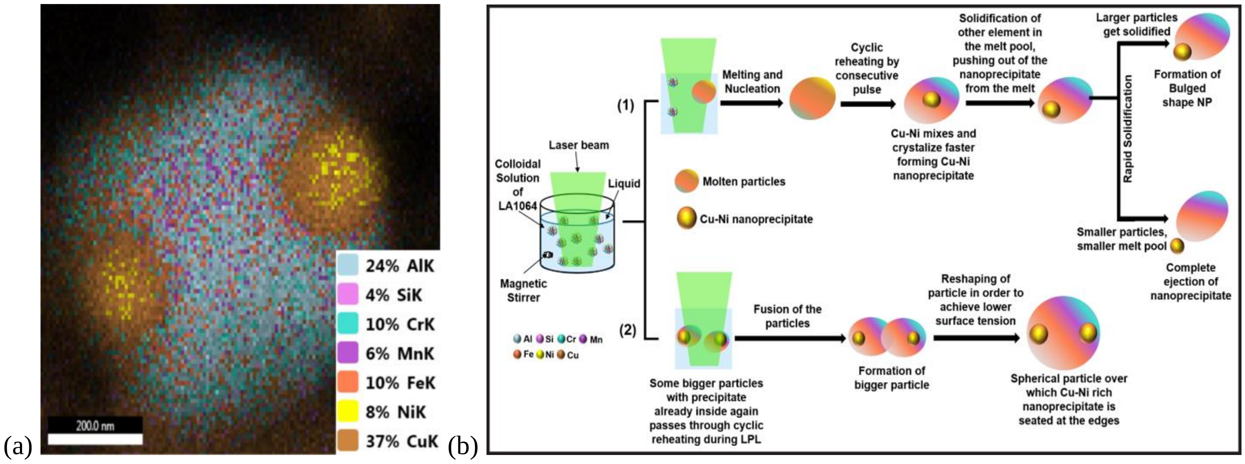

Figure 1. (a) Elemental overlay and, (b) Schematic for morphological changes for processed particles.

[1] R. Rawat, B. K. Singh, A. Tiwari, N. Arun, A. P. Pathak, Y. Shadangi, N. K. Mukhopadhyay, S. V. Rao, A. Tripathi, “Formation of Cu-Ni enriched phases during laser processing of non-equiatomic AlSiCrMnFeNiCu high entropy alloy nanoparticles”, J. Alloys Compd Vol 927, 166905 (2022).

[2] X.Q. Rong, H. Guo, M. Enomoto, C. J. Shang,“Enhancement of Cu nano-precipitation by Al addition in a Cu-Ni bearing alloy steel”, Mater. Lett.Vol 284, Part 2, 128938 (2021)

Cu-based composite particles with enhanced electrocatalytic performance

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Transition metal and metal oxide particles are attracting much scientific and application interest due to their low price, adaptability, and thermal stability, which often depend on bulk and surface characteristics. They are often referred to as the most miscellaneous group of materials because of their exceptional features ranging from optical, electrical, electronic, magnetic, catalytic, and photoelectronic factors that cover almost all of the areas of physics and materials sciences. The combination of metal oxides or metal oxide with metal in one particle can unlock new sets of properties such as enhanced surface area, enhanced surface activities, enhanced porosity, and increase in conductivities, or can improve the effectiveness, efficiency, and durability of the practical application of these materials [1].

Composite particles based on (Ag, Au, Cu)-Cu-oxides were successfully produced and tailored by using the pulsed laser melting method with various experimental parameters; laser fluence, irradiation time, raw material, or solvent [2,3]. During irradiation reduction and oxidation could occur. Due to the size distribution of agglomerates in the solvent, the particles are heated up to various temperatures allowing them to crystallize in different structures. The influence of changes in the irradiation parameters on changes in oxidation states and the change in the coordination number were investigated to understand the mechanism of particle formation in this complex system. We analyzed the bond breaking/formation of (Au, Ag)-Cu-O formation applicable as an electrocatalyst in ethanol oxidation fuel cells. For this, a series of both experimental and theoretical studies were performed. The structure, phase composition, size, morphology, optical properties, and oxidation state were confirmed by UV-vis, XRD, SEM, TEM, EDS, XPS, and X-ray absorption spectroscopy (Fig.1). Moreover, we studied the evaluation of the electrocatalytic activity of obtained composites, and how it depends on the composition, structure details, and surface of particles. We believe, that understanding of the structure details supports the elaboration of the synthesis procedure towards more efficient composites used for advanced fuel cells of the future.

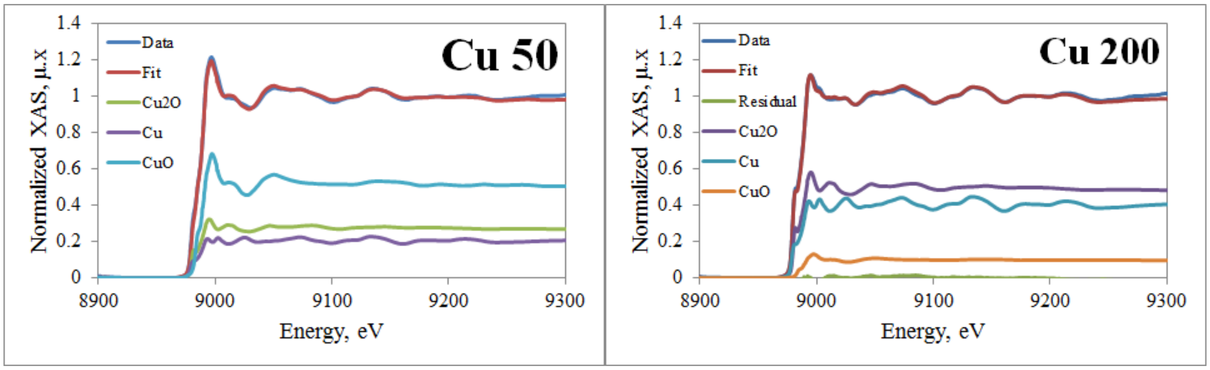

Figure 1. XANES spectra and linear combination of Cu, CuO, and Cu_2O pure phases for Cu-ethanol samples irradiated by 50 and 200 mJ/cm^{2}·pulse nanosecond laser pulses

[1] T. Hassan, A. Salam, A. Khan, A. et al. Functional nanocomposites and their potential applications: A review. J Polym Res 28, 36 (2021).

[2] D. Zhang, B. Gökce, S Barcikowski, Laser Synthesis and Processing of Colloids: Fundamentals and Applications, Chem. Rev., 117, 3990–4103, (2017).

[3] M. Sadegh Shakeri, Z. Swiatkowska-Warkocka, O. Polit, T. Itina, A. Maximenko, J.Depciuch, J. Gurgul, M. Mitura-Nowak, M. Perzanowski, A. Dziedzic, J. Nęcki, Alternative Local Melting-Solidification of Suspended Nanoparticles for Heterostructure Formation Enabled by Pulsed Laser Irradiation, Adv. Funct. Mater. 2304359 (2023).

Size Separation of Femtosecond Pulsed Laser Ablated Silicon Nanoparticles

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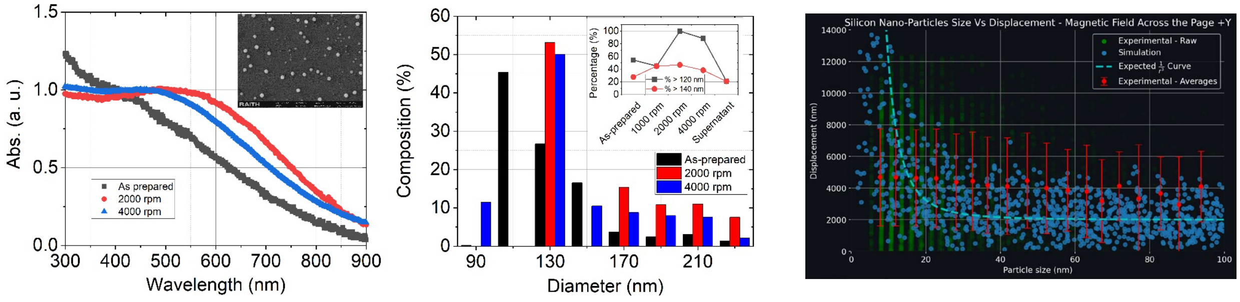
Due to the unique optical properties, silicon nanoparticles (SiNPs) could have a diverse range of potential applications including their use in medical imaging [1]. Pulsed laser ablation synthesis is currently the best method for efficient, high-throughput synthesis of SiNPs, but broad size distribution is one of the challenges preventing its full application. Here we investigate and compare two different methods of size separation in pulsed laser ablation synthesis of SiNPs - differential centrifugation and magnetic-field based separation [2]. The later was conducted to see if magnetic field could be used as a method of particle filtration.

In the first design, an amplified pulsed laser (Spitfire, Spectra-Physics) with λ = 800 nm, 100 fs pulse width and pulse intensity 1.4 TW/cm^2 was used to ablate a silicon wafer in liquid. This was followed by differential centrifugation to sequentially filter the particles, and then the sample spectra were analysed using UV-Vis spectroscopy and electron microscopy (Fig. 1a). An optimisation model based on Mie theory was used to calculate the distributions of particle sizes from the extinction spectra (Fig. 1b). In the second design, a single laser pulse with intensity 70 TW/cm^2, was used to ablate silicon in the presence of a magnetic field (~ 0.1T). The effects of the magnetic field were also simulated and compared to the experimental results (Fig.1c).

Both methods created varying degrees of size separation. In the differential centrifugation method, percentage of large particles (Diameter > 120 nm) separated after sequential centrifugation up to 2000 rpm could be reached up to 100 percent in the pellets (inset, Fig.1b). After sequential 4000 rpm centrifugation, it produced 80% of the particles less than 120 nm in the supernatant solution. However the separation of narrow size bins (i.e., 100 – 120 nm) was difficult to achieve prompting further development of the method. The presence of external magnetic field did not show any clear signs of influencing SiNP distributions, apart from the fact that the small particles (<20 nm) were predicted to fly further away from the single pulse crater. Such could be due to low level of charging of synthesised nanoparticles, and varying the laser pulse energy beyond Coulomb explosion regime could induce more charging. Alternate experimental designs for the magnetic field experiment could also yield different results.



(a) (b) (c)

Figure 1. (a) Extinction spectrum of laser ablated SiNP solutions after differential centrifugation. Change in spectrum indicate composition change. Inset: SEM image of supernatant solution. (b) Particle diameter distribution extracted based on the absorption spectrum, showing higher percentage of larger particle sizes from centrifugation of 2000 and 4000 rpms. (c) Particle size separation measured from the centre of single pulse crater (red points). Overlaid are the simulated (blue dots) and theoretical (blue dashed line).

[1] A. I. Kuznetsov et al., et al., *Sci., Rep.*, **2**, 492 (2012).

[2] J. Maximovic et al, *Nanomaterials*, **10**, 182 (2020).

Dual-laser pulse-patterned α-$Co(OH)_2$/rGO heterointerface for accelerated water oxidation

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The dynamic surface reconstruction of electrodes is a legible sign to understand the deep phase-transition mechanistic and electrocatalytic origin during the oxygen evolution reaction (OER). Herein, we report a dual-laser pulse-patterned heterointerface of α-$Co(OH)_2$ and reduced graphene oxide (rGO) nanosheets via pulsed laser irradiation in liquid (PILL) to accelerate OER kinetics. α-$Co(OH)_2$ was formed from the OH^- ions generated during the PILL of GO at neutral pH. Co^{2+} modulation in tetrahedral coordination sites benefits as an electrophilic surface for water oxidation. Few *d*-vacancies in Co^{2+} increase its affinity toward oxygen, lowering the energy barrier and generating many CoOOH and CoO_2 active sites. rGO with an ordered π-conjugated system aids the surface adsorption of OOH*, O*, and OH* during OER. α-$Co(OH)_2$ surface phase-transition and OER mechanistic steps occurred via phase-reconstruction to CoOOH and CoO_2 reactive intermediates, uncovered using in situ electrochemical–Raman spectroscopy. Our findings in the dual-laser pulse strategy and the surface reconstruction correlation in active OER catalysts pave the path for paramount in multiple energy technologies.

Developing a highly stable liquid sheet with solvated nanoparticles for laser fragmentation studies

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Laser-induced fragmentation has a wide variety of applications towards the nanoparticle field including the fragmentation of colloidal nanoparticles [1] and the synthesis of ultra-small nanoparticles [2]. Liquid sheets offer the capability of delivering high-repetition rate targets with the potential to match the increasing speed of high repetition rate laser drivers [3]. By combining these two techniques, we outline a strategy to probe the structure dynamics of femtosecond laser fragmentation of nanoparticles using the technique of ultrafast electron diffraction (UED) [4]. Recently, UED has emerged as a means of probing structural changes in liquids within the femtosecond regime [3]. The approach of solvated nanoparticles in cylindrical liquid jet systems has been extensively used in laser fragmentation studies [1]. Building on the benefits of this approach, flat liquid sheets provide variable thickness between 250 nm and 2.5 µm along the length of the sheet and a wide lateral cross-section for consistent laser interactions [3] making them ideal for UED experiments. However, high-intensity laser interactions in these experiments could degrade the stability of liquid sheet targets over the course of multiple repetitions. This degradation is caused by the laser-liquid interaction producing shockwaves and ionizing particles that would gradually deteriorate the structure of the glass nozzle used in producing the liquid sheets. We are developing a stainless-steel nozzle resistant to these degradation mechanisms that would potentially fix this problem. This would enable the use of higher intensity lasers in conjunction with UED to explore transient behaviour of laser-nanoparticle interactions at elevated fluence regimes.

[1] A. R. Ziefuß, *The Journal of Physical Chemistry* Vol 122, Issue 38 (2018)

[2] O. Havelka, *Nanomaterials* Vol 11, Issue 6 (2021)

[3] C.J Crissman, *Lab Chip*, Vol 7, Issue 22 (2022)

[4] M. Mo, *Science,* Vol 360, Issue 6396 (2018)

Synthesis of Selenium Nanoparticles by Pulsed Laser Ablation in Liquids: Amorphous versus Trigonal

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Selenium nanoparticles (Se NPs) were synthesized by Pulsed Laser Ablation in Liquids (PLAL) at 10.5 W and 3 kHz (Figure 1). The phase of the Se NPs was controlled post-synthesis by using a heating treatment. Indeed, after synthesis, the Se NPs were amorphous after undergoing a heating treatment for 60 minutes at 121 degrees Celsius, there was a phase transition taking place from amorphous to trigonal. The colloids containing amorphous or trigonal Se NPs displayed an orange or grey color, respectively. The two types of Se NPs were then tested against various anti-microbial resistant bacteria. The results will be discussed in detail.

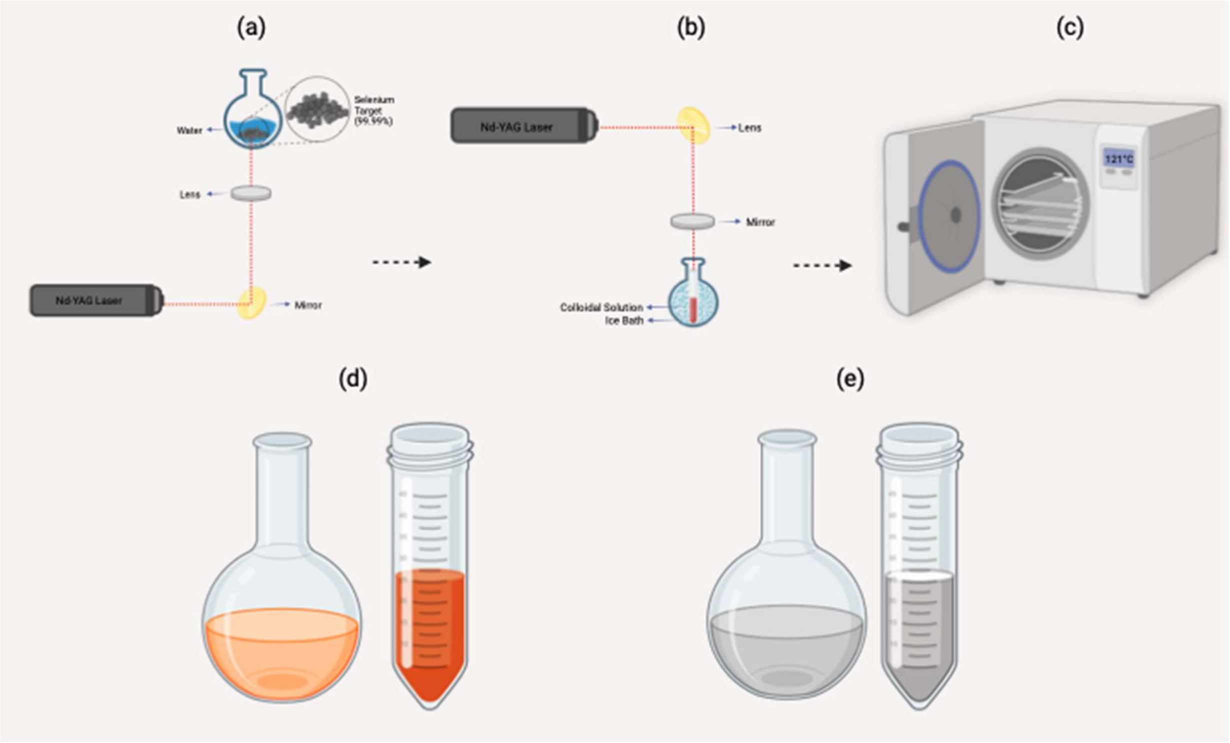

Figure 1. Synthesis protocol of Se NPs by PLAL: 1st set of irradiations using a bottom-up set-up (a), 2nd set of irradiations using a top-down set-up (b), autoclave treatment to induce phase transition (c), Amorphous phase (orange) Se NPs (d), Trigonal phase (grey) Se NPs (e).

[1] X. Zhou, P. Gao, S. Sun, D. Bao, Y. Wang, X. Li, T. Wu, Y. Chen, P. Yang, Amorphous, Crystalline and Crystalline/Amorphous Selenium Nanowires and Their Different (De)Lithiation Mechanisms, *Chemistry of Materials,* **Vol. 27**, 6730-6736 (2015).
[2] L. D. Geoffrion, T. Hesabizadeh, D. Medina-Cruz, M. Kusper, P. Taylor, A. Vernet-Crua, J. Chen, A. Ajo, T. J. Webster, G. Guisbiers, Naked Selenium Nanoparticles for Antibacterial and Anticancer Treatments, *ACS Omega,* **Vol. 5**, 2660-2669 (2020).

Synthesis of Bi_2Te_3 Quantum Dots by Pulsed Laser Ablation in Liquids

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Bismuth Telluride (Bi_2Te_3) is an important thermoelectric material [1,2] and topological insulator [3]. In this project, Bi_2Te_3 quantum dots (QDS) were synthesized for the very first time by Pulsed Laser Ablation in Liquids (PLAL) using a bottom-up synthesis protocol. Acetone was used as a solvent and the repetition rate was fixed at 1 kHz. The size and the energy band gap of Bi_2Te_3 QDs were determined to be around ~ 18 nm and ~ 1.72 eV respectively. Quantum confinement of those Bi_2Te_3 nanoparticles was confirmed by Raman spectroscopy.

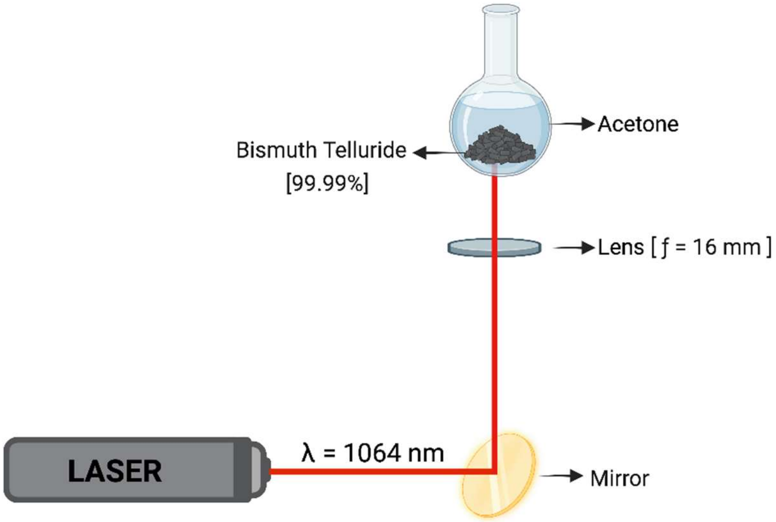

Figure 1. Bottom-up PLAL synthesis protocol

1. I.T. Witting, T. C. Chasapis, F. Ricci, M. Peters, N. A. Heinz, G. Hautier, G. J. Snyder, The thermoelectric properties of bismuth telluride, *Advanced Electronic Materials*, **Vol. 5**, 1800904 (2019).
2. H. J. Goldsmid, Bismuth telluride and its alloys as materials for thermoelectric generation, *Materials*, **Vol. 7**, 2577-2592 (2014).
3. Y. L. Chen, J. G. Analytis, J. H. Chu, Z. K. Liu, S. K. Mo, X. L. Qi, H. J. Zhang, D. H. Lu, X. Dai, Z. Fang, S. C. Zhang, I. R. Fischer, Z. Hussain, Z. X. Shen, Experimental realization of a three-dimensional topological insulator, Bi2Te3, *Science*, **Vol. 325**, 178-181 (2009).

Laser Ablation of 2D Layered Materials to Synthesize Metastable Nanostructures for Energy Storage Applications

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Synthesis and tuning of nanomaterials constitute expansive research domains that present diverse techniques for producing these materials. Numerous methods, such as chemical approaches (e.g., Brust–Schiffrin method, Turkevich method), physical techniques (sputtering, lithography, etc.), and gas-phase methods like pulsed laser deposition, have been employed for synthesizing nanomaterials (NMs). In recent years, laser ablation in liquid has garnered significant attention due to its distinctive outcomes and characteristics. Among its notable features is the ability to synthesize metastable nanophases and nanoparticle colloids characterized by exceptional stability and purity. Pulsed laser ablation in liquids (PLAL) stands out as a technique that offers an almost limitless array of potential materials and solvents. A key advantage of employing PLAL over conventional NMs production processes lies in its capacity to produce ligand-free NMs, which leads to devoid of impurities originating from additives and precursor reaction products. Titanium carbide (Ti_3C_2 -T_x), where T_x represents surface terminations, is a member of the relatively recent class of two-dimensional materials known as "MXenes." MXenes exhibit intrinsic conductivity and exceptional volumetric capacitance due to their composition of molecular sheets derived from carbides and nitrides of transition metals, such as titanium. The intriguing aspect of this material class lies in its potential to encompass millions of unique arrangements involving transition metals (e.g., molybdenum or titanium), carbon, and nitrogen.

In this study, we conducted PLAL of Ti_3C_2 -T_x and their parent MAX phase; titanium aluminum carbide (Ti_3AlC_2), to achieve multi-metallic nanostructures. Ti_3AlC_2 and Ti_3C_2 -T_x were synthesized using traditional solid-state synthesis and chemical etching processes, respectively. Pulsed LAL was performed using a UV laser (193 nm, 248 nm, and 266 nm) for the as-synthesized materials. During PLAL, the temperature inside the cavitation bubble is estimated to be 1000 K with 10^7- 10^8 Pa or even higher pressure. This elevated temperature facilitated the oxidation of target materials, and subsequent rapid quenching trapped the metastable states of the nanomaterials, resulting in unique characteristics. We used deionized water and diluted potassium hydroxide and dodecyl sulfate dispersant as medium for PLAL of Ti_3AlC_2 and Ti_3C_2 -T_x, the laser ablation was carried out at 300 mJ and 150 mJ energies focused to 2-4 J/cm^2 for 30 minutes. The results revealed distinct morphologies at various stages of the process, emphasizing the strong dependence of nanostructures on the energy and time of laser ablation. We aim to investigate the impact of ablation time, energy, and laser wavelength on the laser ablation of MAX and MXenes, presenting a straightforward, environmentally friendly, versatile, and high-production-rate approach for efficiently generating nanomaterials in a condensed timeframe.

Laser Synthesis of Nickel-Carbon-Oxygen Composites as Catalysts for the Oxygen Reduction Reaction

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Carbon-based metal nanomaterials are versatile materials with applications spanning from energy storage to biomedical devices.[1,2] An important application is their use as catalysts for reactions relevant to renewable energy such as the hydrogen evolution reaction, oxygen evolution reaction, and oxygen reduction reaction (ORR).[3,4] Common metal nanocomposite materials used for these purposes often utilize metals such as palladium, gold, or iridium, which are costly and have limited abundance.[5] Less expensive metals, such as nickel, are of interest due to their high durability, good catalytic ability, and high energy storage. However, there are currently very few environmentally friendly techniques for the synthesis of these materials. In this work, nickel-carbon nanocomposites are synthesized with high controllability and on a short time scale using laser reduction in liquid (LRL), a reactive laser techniques that uses non-equilibrium chemistry to synthesize very small nanomaterials with uniform size distribution.[6] LRL differs from laser ablation in liquid in that it uses picosecond or femtosecond laser pulses to produce an electron dense plasma, easily reducing metal precursor ions in solution. In LRL, the laser is able to induce decomposition of the liquid producing solvated electrons, radicals, and various reactive species without the use of surfactants, capping ligands, and toxic reducing agents –overall limiting the chemical waste produced.[1,6] Nickelocene in hexanes was irradiated using unfocused picosecond pulses to generate a supercontinuum, causing the solution to undergo a fast conversion that followed first order kinetics. Unfocused light irradiation resulted in the formation of composites with highly dispersed nickel species, which can be attributed to the low-density plasma formed that prevents the coalescence of these species into larger nickel nanoparticles. Small composites with a high surface area consisting of Ni, C, and O co-localized throughout the product were seen using SEM-EDX and STEM-EDS. The onset and half wave potential of this material for ORR in basic medium was investigated and found to be similar to that of platinum, meaning these composites hold promise as electrocatalysts for ORR in fuel cells.[1] Transient absorption spectroscopy has been used to investigate how nickelocene influences the electron dynamics of hexane. Understanding these dynamics aids in the identification of intermediate species formed during laser irradiation. Gas chromatography supports the existence of a nickelocene anion intermediate, as indicated by the presence of a hydrogenated nickelocene species in the chromatogram.

(1) Nag, A.; Frias Batista, L. M.; Tibbetts, K. M. Synthesis of Air-Stable Cu Nanoparticles Using Laser Reduction in Liquid. *Nanomaterials* **2021**, *11* (3), 814.

(2) Fritea, L.; Banica, F.; Costea, T. O.; Moldovan, L.; Dobjanschi, L.; Muresan, M.; Cavalu, S. Metal Nanoparticles and Carbon-Based Nanomaterials for Improved Performances of Electrochemical (Bio)Sensors with Biomedical Applications. *Materials (Basel)* **2021**, *14* (21), 6319.

(3) Jahan, M.; Liu, Z.; Loh, K. P. A Graphene Oxide and Copper-Centered Metal Organic Framework Composite as a Tri-Functional Catalyst for HER, OER, and ORR. *Advanced Functional Materials* **2013**, *23* (43), 5363–5372.

(4) Wang, X.; Li, Z.; Qu, Y.; Yuan, T.; Wang, W.; Wu, Y.; Li, Y. Review of Metal Catalysts for Oxygen Reduction Reaction: From Nanoscale Engineering to Atomic Design. *Chem* **2019**, *5* (6), 1486–1511.

(5) McCrory, C. C. L.; Jung, S.; Peters, J. C.; Jaramillo, T. F. Benchmarking Heterogeneous Electrocatalysts for the Oxygen Evolution Reaction. *J. Am. Chem. Soc.* **2013**, *135* (45), 16977–16987.

(6) Frias Batista, L. M.; Nag, A.; Meader, V. K.; Tibbetts, K. M. Generation of Nanomaterials by Reactive Laser-Synthesis in Liquid. *Science China Physics, Mechanics & Astronomy* **2022**, *65* (7), 274202.

Thermodynamic Maps and Nanoparticle Cooling Rates in Laser Ablation of FeNi in Liquid

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The pulsed laser ablation in liquid (PLAL) shows strong potential in synthesis of chemically-clean nanoparticles with high efficiency [1]. In the PLAL, the fast laser energy deposition can bring the irradiated target material to the supercritical state and trigger a sequence of far-from-equilibrium processes leading to the nanoparticle formation. Large-scale molecular dynamics simulations, e.g., [2, 3], are capable of providing valuable information on the initial dynamic processes occurring during the first nanoseconds of PLAL. In this study, the simulations of laser ablation occurring in different parts of a laser spot are performed for a FeNi target irradiated by a 10 ps laser pulse in a liquid environment. The results of the simulations are presented in the form of time and spatially resolved thermodynamic maps showing the conditions realized in different regions of the emerging cavitation bubble at the initial stage of PLAL. The conditions leading to the nanoparticle generation are related to the solidification mechanisms and the nanostructure of nanoparticles produced in different parts of the laser spot.

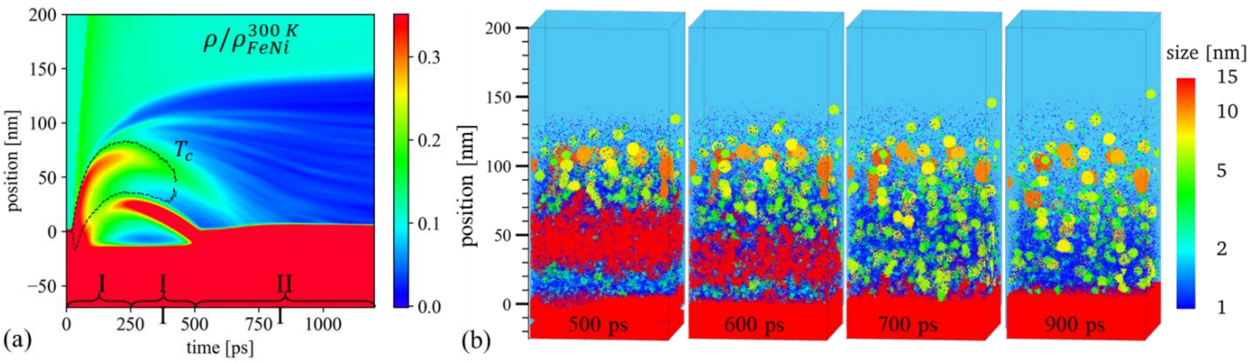

Figure 1. Density profile (a) and snapshots of the ablation products colored by nanoparticle size (b) predicted in a simulation of laser ablation of a FeNi target irradiated by a 10 ps laser pulse in water at an absorbed fluence of 1500 J/m^2.

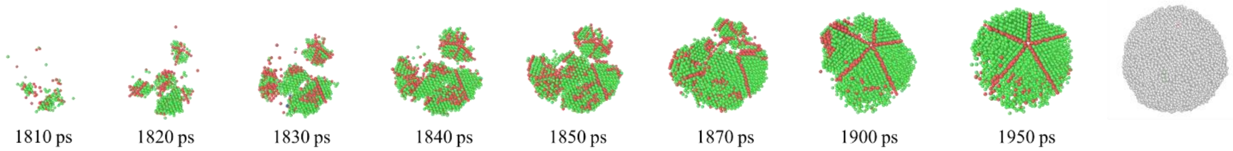

Figure 2. A series of snapshots illustrating the generation of a twinned pentagonal nanoparticle in PLAL of a FeNi target by a 10 ps laser pulse at an absorbed fluence of 3000 J/m^2. In all but the last frame, the atoms with local face-centered cubic (fcc) and hexagonal close packed (hcp) structure are colored green and red, respectively, while all other atoms are blanked. All atoms in the nanoparticle are shown in the last frame.

[1] D. Zhang, B. Gökce and S. Barcikowski, Laser synthesis and processing of colloids: fundamentals and applications, *Chem. Rev.* **117**, 3990-4103, 2017.

[2] C.-Y. Shih, C. Chen, C. Rehbock, A. Tymoczko, U. Wiedwald, M. Kamp, U. Schuermann, L. Kienle, S. Barcikowski and L. V. Zhigilei, Limited elemental mixing in nanoparticles generated by ultrashort pulse laser ablation of AgCu bilayer thin films in a liquid environment: Atomistic modeling and experiments, *J. Phys. Chem. C* **125**, 2132-2155, 2021.

[3] C. Chen and L. V. Zhigilei, Atomistic modeling of pulsed laser ablation in liquid: spatially and time-resolved maps of transient nonequilibrium states and channels of nanoparticle formation, *Appl. Phys. A* **129**, 288, 2023.

Identifying Unique De Novo Proteins for Nanoparticle Synthesis using LSPC Synthesized Metal Oxide Nanoparticles

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Biomineralization, the process organisms use to produce materials, uses proteins that bind to material surfaces influencing the size, shape, and morphology. Because biomineralization is performed under ambient temperatures and pressures, this method is ideal for producing semiconductor nanoparticles for photocatalysts and photovoltaics in a sustainable way. However, synthetizing highly efficient semiconductors, like zinc oxide (ZnO) and ceria (CeO_2), through biomineralization remains challenging because natural proteins do not produce such materials. To overcome this limitation, we have developed *de novo* proteins that are carefully designed with strong metal-binding amino acid groups, capable of interacting with the semiconductor surface. Here, we present preliminary results demonstrating the binding of several *de novo* proteins to ligand-free ZnO and CeO_2 semiconductor nanoparticles synthesized using laser synthesis and processing of colloids (LSPC). Producing highly stable nanoparticles with LSPC is crucial for screening protein binding strength as it ensures that the nanoparticles are ligand-free prior to protein addition. ZnO and CeO_2 ligand-free nanoparticles were successfully synthesized to be approximately 50-100 nm and 5 nm, respectively. Initial binding experiments were performed with the protein S824, designed, and produced following a heptad polar-nonpolar motif, as well as two protein mutations (G52C and G78C) modified with extra cysteine at specific locations to enable stronger particle binding. The binding strength was quantified by tracking the protein concentration in solution before and after binding to the semiconductors using spectroscopic measurements.

Preliminary results show that a higher percentage of protein remained bound with ZnO than with CeO_2, likely attributed to the difference in size of the particles, with ZnO having a larger surface area. Other possibilities could be that the morphology of ZnO favors the binding of the protein, or that other metal binding sites, like histidine, have a stronger affinity for Zn than Ce. The results obtained also indicate different binding strengths to the same material between each protein. For ZnO, S824 resulted in the strongest binding, followed by G52C and then G78C. However, G52C showed the strongest binding with CeO_2, while G78C and S824 had a weaker binding with the particle. These findings suggest that even minor protein mutations have an influence in binding strength, and that the strength of the binding heavily depends on the material of interest. Future work will test additional de novo proteins to collect binding data that can be used to develop a machine learning model that can guide protein design for semiconductor materials.

Spatially and Size Resolved Maps of Nanoparticle Generation and Energy Partitioning in Laser Ablation in Liquid

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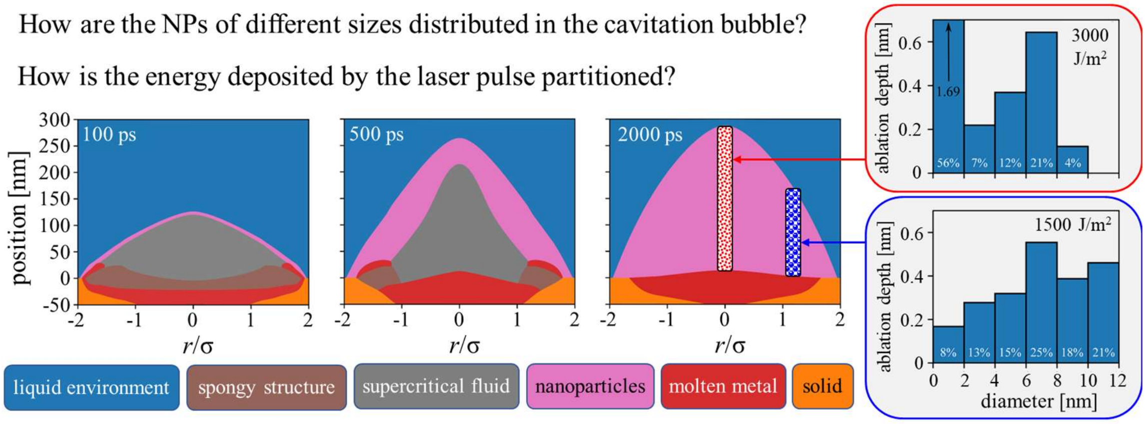
Laser ablation in liquid (LAL) is a promising technique for synthesis of chemically clean nanoparticles (NPs) [1]. Tuning the characteristics of NPs produced by LAL to the needs of practical applications, however, still presents a significant challenge and calls for detailed analysis of processes that control the size distribution and internal structure of the NPs. The mechanisms of LAL have been investigated in a series of large-scale atomistic simulations performed for FeNi targets irradiated by 10 ps laser pulses [2]. The results of the simulations have been mapped to the conditions realized in different parts of the laser spot, where different ablation regimes are activated simultaneously. The spatially and time-resolved maps of the transient nonequilibrium states predicted in the simulations provide a foundation for interpretation of the results of time-resolved experimental probing of the initial stage of LAL [3]. A number of outstanding questions, however, remain and are the subjects of the analysis reported in this presentation. In particular, the contributions of different locations within the Gaussian laser spot to the total yield of the NPs, as well as to the different parts of the NP size distribution are evaluated. Additionally, the fractions of energy deposited by the laser pulse that goes into (1) formation of new surface area associated with the NP generation, (2) heating the metal target, (3) heating and vaporization of the liquid environment, and (4) emission of pressure waves in the target and the liquid environment are investigated and related to the energy efficiency of the NP synthesis by laser ablation.



How are the NPs of different sizes distributed in the cavitation bubble?

How is the energy deposited by the laser pulse partitioned?

Figure 1. The maps of the phase states (left panels) and the nanoparticle size distributions (right panels) in different parts of the cavitation bubble predicted in large-scale atomistic simulations of FeNi alloy targets irradiated in water by 10 ps laser pulses. The research questions in the focus of this presentation are listed in the top part of the figure.

[1] D. Zhang, B. Gökce, and S. Barcikowski, Laser synthesis and processing of colloids: Fundamentals and applications, *Chem. Rev.* **117**, 3990 (2017).

[2] C. Chen and L. V. Zhigilei, Atomistic modeling of pulsed laser ablation in liquid: spatially and time-resolved maps of transient nonequilibrium states and channels of nanoparticle formation, *Appl. Phys. A* **129**, 288 (2023).

[3] M. Spellauge, C. Doñate-Buendía, S. Barcikowski, B. Gökce, and H. P. Huber, Comparison of ultrashort pulse ablation of gold in air and water by time-resolved experiments, *Light.: Sci. Appl.* **11**, 68 (2022).

Tuning the Aggregation of Metal Nanoparticles prepared by Laser Ablation with Halide Salt solutions

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The localized surface plasmon resonance (LSPR) of metal nanoparticles is strongly dependent on geometrical and environmental factors, as well as the nanoparticle aggregation phenomena, which are exploited in a range of applications. In this work we investigate the LSPR of gold nanoparticles, produced by laser ablation in liquid (LAL), and their agglomeration induced by halides after LAL. We study the aggregation process under a range of factors like bromide concentration, temperature, and different halides. By absorption spectroscopy and electron microscopy we show that increasing bromide concentration leads to longer and more complex aggregates, with consequent red-shift and broadening of the LSPR. Simulations, in agreement with experiments (Figure 1), show that a redshift of the LSPR is expected as AuNP linear chains become longer and validate this trend for different particle size and gap between particles. By using real-time absorption spectroscopy, we observe immediate growth of nanoparticles after salt addition. We also demonstrate that higher temperatures tend to suppress the aggregation process, while lower temperatures promote it. We then observe that a heavier halide like iodide tends to form a very broad LSPR indicating complex nanoparticle architectures. Finally, we show that the aggregates are disrupted by re-irradiating the colloid. These findings provide an expanded understanding into the factors ruling the aggregation phenomena, and will help developing existing applications while stimulating new ones [1].

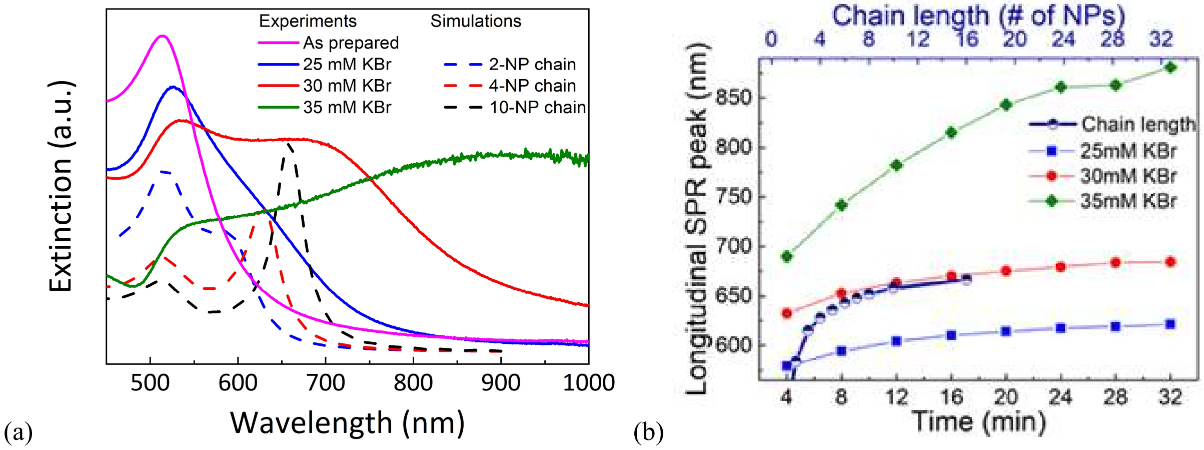

Figure 1. Comparison a) between experimental extinction spectra obtained from the addition of KBr at different concentrations and simulated spectra of Au NP chains of different lengths and (b) between the evolution in time of the experimental longitudinal LSPR peak and of longitudinal SPR value of simulated linear chains (from 2 to 16NPs).

This work has been partially funded by the European Union (NextGeneration EU), through the MUR-PNRR project SAMOTHRACE (ECS00000022).

[1] L.Catanzaro, V. Scardaci, M. Scuderi, M. Condorelli, L. D'Urso, G. Compagnini, Mat. Chem. and Phys**. Vol. 308**, 128245 (2023).

Reactive Laser Ablation in Liquids as a Promising Approach for Repurposing Wastewater

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Efficient wastewater management is essential for safeguarding the environment and human well-being. Repurposing wastewater can reduce the need for fresh water sources and minimize pollution. However, traditional wastewater treatment methods are often energy-intensive and can have negative environmental impacts, including the release of pollutants and greenhouse gases [1]. Therefore, it is vital to explore alternative wastewater treatment approaches. In this context, our current work introduces the use of reactive laser ablation in liquids (RLAL) as a promising method to support sustainable water management, as it can incorporate valuable resources found in wastewater such as nutrients, metals, and organic matter into nanoparticles (NPs). Herein, we employed wastewater sourced from a critical mineral mining site within the Czech Republic's territory as the liquid medium for generating Au NPs doped with various elements. The wastewater was utilized in its untreated form, and based on inductive-coupled plasma mass spectrometry (ICP-MS) analysis, it was found to contain 11,19 mg/L of Al, 21,60 mg/L of Ca, 1,48 mg/L of Cu, 14,20 mg/L of Fe, 1,44 mg/L of K, 13,55 mg/L of Mg, 1,91 mg/L of Mn, 2,62 mg/L of Na and 16,70 mg/L of Zn. During the RLAL process, 40 mL of this mineral-rich wastewater served as the liquid medium while ablating an Au (99.99%, Sigma-Aldrich) foil. The ablation process was performed employing an industrial femtosecond pulsed laser (ORIGAMI XP-S; NKT Photonics), delivering 400 fs pulses at 1 MHz and 1030 nm. The employed average power was set to 5.1 W, so after deflecting the laser beam by a 2D galvanometer mirror scanner (intelliSCAN 14; ScanLab) moving it in a raster-like pattern at a velocity of 2 m/s, and focussing it by a 160 mm F-Theta lens on the surface of the Au foil, enabled it's ablation (see Figure 1).

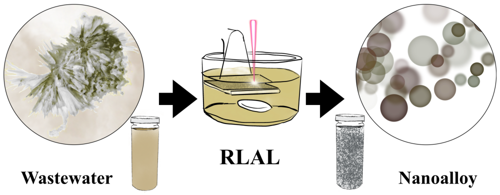

Figure 1. Artwork depicting the utilization of wastewater sourced from a critical mineral mining site in RLAL to produce Au NPs doped by Al and Fe; an ideal element combination to form strong catalytic magnetic NPs.

Upon the ablation process, minerals present in the wastewater that adhere to the Hume-Rothery rules, predicting their combination into a substitutional solid alloy with Au, were successfully integrated into the final NPs [2]. This resulted in a colloidal suspension containing NPs with an average size of 66 nm. After undergoing a magnetic separation for purification, the NPs exhibited a composition of 57.1 wt% Fe, 24.7 wt% Au, and 18.2 wt% Al. Considering the resulting element composition, with Al forming stable high oxidation state oxides, Fe producing oxides of intermediate stability with the ability to provide the final nanosystem magnetophoretic motility, and the noble metal Au, it is possible anticipating the formation of magnetic NPs with the potential to exhibit strong metal-support interactions (SMSI), one of the last tools allowing the improvement of recyclable heterogeneous catalysts [3]. This contribution, therefore, represents a long-term, forward-thinking solution to the escalating water resource management crisis we are currently facing while promoting technological advancements and interdisciplinary collaboration.

[1] X. Hao, et.al. Environmental impacts of resource recovery from wastewater treatment plants. *Water Research*, **Vol.** 160, p. 268 (2019).

[2] W.D. Callister Jr, William D. *Materials science and engineering an introduction*. (Wiley Publishers, USA, 2007), pp. 832.

[3] H. Tang, et.al. Strong metal–support interactions between gold nanoparticles and nonoxides. *Journal of the American Chemical Society*, 2016, vol. 138, no 1, p. 56-59.

How to tailor the mass loading and productivity during continuous single-step *in-situ* deposition of laser-generated nanoparticles

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Nearly 10 years ago, Mafune et al. have shown that a nanoparticle size quenching and simultaneous fabrication of a heterogeneous catalyst can be achieved when dispersing the inorganic support material in the liquid prior to laser ablation[1]. On the downside, controlling or predicting the mass load of the metal nanoparticles on the support particles is hampered due to the superposition of nanoparticle productivity and the initial support concentration in the feed stream of the ablation chamber. Therefore, the aim of this work is to develop a prediction tool based on experimental data to predict both the productivity of the NPs and the mass loading. At the example of the ablation of a catalytically-relevant quinternary noble metal alloy, the nanoparticle mass productivity will be investigated at different concentrations and incident laser powers (pulse energies at constant repetition rate) in an Al_2O_3 suspension. Given the previous laser ablation work of Neuenschwander et al.[2] in air, verified by Streubel el al. in liquid [3], we propose that the ablation rate is predicted by the effective fluence on the target where the latter is directly correlated with the incident laser fluence applied to the ablation process which will be attenuated by the liquid layer containing the support particles following Lambert-Beer Law (Fig. 1a). Indeed, it will be shown that for the given parameter space the nanoparticle mass productivity is linearly correlated with the predicted incident fluence that reaches the target after attenuation by the support particle dispersion (Fig. 1b). The validity of the physical determinants and their correlation will be validated for other supports. Further, the impact of supporting the laser-generated nanoparticles *in situ* (Fig. 1a) and *ex situ* (mixing with support after ablation) on the catalytic activity will be discussed.

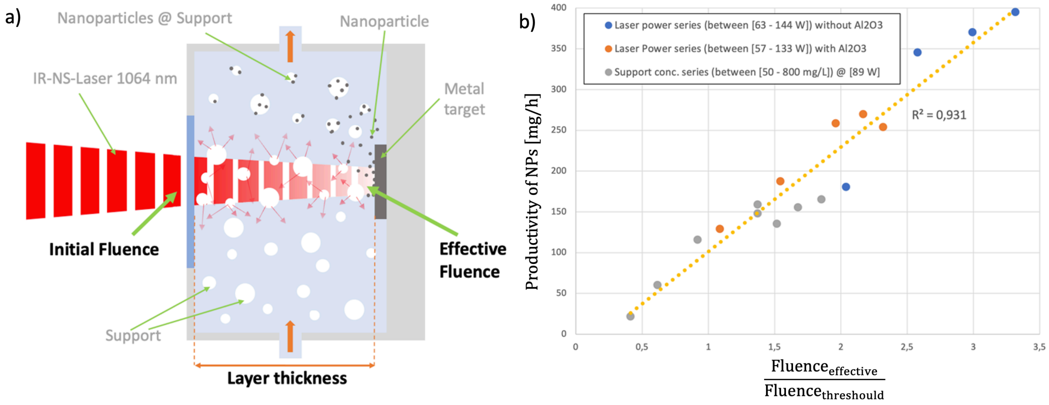

Figure 1: a) Scheme of the flow-through *in-situ* deposition of laser-generated nanoparticles on dispersed supports and **b)** Correlation of mass ablation rate (productivity of NPs) within the support particle dispersion for different effective fluences predicted from attenuation of the laser-beam by following Lambert-Beer Law.

[1] F. Mafuné, T. Okamoto, and M. Ito, *Chem Phys Lett*, vol. **591**, pp. 193–196 (2014)
[2] B. Neuenschwander, B. Jaeggi, M. Schmid, and G. Hennig, *Physics Procedia*, pp. 1047–1058 (2014).
[3] S. Streubel, S. Barcikowski, and B. Gökce, *Optics Letters*, pp. 1486-1489 (2016).

Selective Electrooxidation of Toluene to Benzyl Alcohol by Laser-Made Mixed-Metal Hydroxide Nanocatalysts

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The electrocatalysis of hydrocarbons to selectively produce alcohols holds the promise of revolutionizing the production of chemicals and consumer goods in a sustainable manner by replacing current fossil-fuel-based processes with energy-efficient technologies that harness renewable energy sources [1]. Selective hydrocarbon oxidations to alcohols have the ultimate goal of the gas-to-liquid conversion of methane to methanol without energy-intensive steam reforming. Better catalysts, reaction control, and understanding of electrocatalytic processes and mechanisms are needed to achieve high selectivity for single alcohol products at high activity. Arresting the oxidation of hydrocarbons at alcohols without the generation of overoxidized products is challenging because the first oxidation is thermodynamically most difficult and further oxidations are energetically downhill.

The unique advantages of pulsed laser in liquids synthesis make this technique particularly powerful for the preparation of electrosynthesis nanocatalysts [2]. Laser-made materials have been shown to be intrinsically more active than analogs prepared by conventional chemical equilibrium methods [2, 3], opening new mechanistic pathways for hydrocarbon to alcohol conversions. Additionally, the laser method enables the rapid synthesis of uniform, multicomponent, nonequilibrium nanomaterials with independently and precisely controlled properties, such as size, composition, morphology, defect density, and atomistic structure within the nanoparticle and at its surface [2].

We developed laser-made, earth-abundant, mixed-metal hydroxide nanocatalysts and employed them on high-surface-area carbon supports [4] to selectively electrooxidize toluene to benzyl alcohol. We show how electrolyte engineering and concomitant accessibility of different mechanistic pathways led to 100 % selectivity for benzyl alcohol with an unprecedentedly high toluene conversion efficiency of >85 %. We also revealed the mechanistic underpinnings of this remarkable performance of laser-made nanocatalysts for the electrooxidation of toluene to benzyl alcohol.

[1] T. Taseska, W. Yu, M. K. Wilsey, Z. Meng, C. P. Cox, S. S. Ngarnim, A. M. Müller, Analysis of the Scale of Global Human Needs and Opportunities for Sustainable Catalytic Technologies, *Top. Catal.* **66**, 338-374 (2023).

[2] R. C. Forsythe, C. P. Cox, M. K. Wilsey, A. M. Müller, Pulsed Laser in Liquids Made Nanomaterials for Catalysis, *Chem. Rev.* **121**, 7568-7637 (2021).

[3] B. M. Hunter, H. B. Gray, A. M. Müller, Earth-Abundant Heterogeneous Water Oxidation Catalysts, *Chem. Rev.* **116**, 14120-14136 (2016).

[4] M. K. Wilsey, K. R. Watson, O. C. Fasusi, B. P. Yegela, C. P. Cox, P. R. Raffaelle, L. Cai, A. M. Müller, Selective Hydroxylation of Carbon Fiber Paper for Long-Lasting Hydrophilicity by a Green Chemistry Process, *Adv. Mater. Interfaces* **10**, 2201684 (2023).

Reducing Temperature Constraints of Carbon Monoxide Oxidation utilizing 1,3,5-Bezenetricarboxylate Metallic Organic Framework Derivative Catalysts and Laser Assisted Reduction

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Carbon monoxide (CO) is a known toxin and a hazardous gas pollutant. It is also an indirect greenhouse gas produced from incomplete combustion from vehicles, heating, and various industrial processes.[1] Catalytic oxidation of CO over transition metal oxides is an efficient mechanism for the direct removal of CO from flue gas of any of the above-mentioned processes.[2] The development of cost-effective, yet active catalysts for the catalytic conversion of CO into carbon dioxide (CO_2) are in demand[1]. Copper (Cu) and cobalt (Co) are inexpensive and earth-abundant transition metals.[3,4] In recent years, metal-organic frameworks (MOFs) have been extensively studied for different applications in catalysis.[5] In this work, MOF-derived Cu and Co nano catalysts were developed based on MOF pyrolysis in an inert atmosphere followed by calcination in air. The catalytic activity of the unsupported Cu and Co catalysts for CO oxidation was studied and compared as well as the effect of silicon-doped alumina (SDA) as a support on the Co and Cu catalyst's performance were evaluated. Finally, laser assisted reduction was used to deposit palladium (Pd) nanoparticles onto the binary MOF derived metal oxide SDA. Namely, cobalt oxide SDA (CoO-SDA) and copper oxide SDA (CuO-SDA) to form Pd/CoO-SDA and Pd/CuO-SDA. The catalytic activity of these different materials was then measured for CO oxidation and were compared.

References

(1) Farrag, M.; Das, M. K.; Moody, M.; Samy El-Shall, M. Ligand-Protected Ultrasmall Pd Nanoclusters Supported on Metal Oxide Surfaces for CO Oxidation: Does the Ligand Activate or Passivate the Pd Nanocatalyst? *ChemPhysChem* **2021**, *22* (3), 312–322. https://doi.org/10.1002/cphc.202000656.
(2) Medical Research Council (Great Britain). Institute for Environment and Health.; Humfrey, Charles.; Shuker, Linda.; Harrison, P. *IEH Assessment on Indoor Air Quality in the Home: Nitrogen Dioxide, Formaldehyde, Volatile Organic Compounds, House Dust Mites, Fungi, and Bacteria*; Institute for Environment and Health, 1996.
(3) U.S. Geological Survey. *Mineral Commodity Summaries 2022 - Cobalt*; 2022.
(4) Flanagan, D. M.; Merchant, S. *Mineral Industry Surveys*; 2022.
(5) Han, W.; Huang, X.; Lu, G.; Tang, Z. Research Progresses in the Preparation of Co-Based Catalyst Derived from Co-MOFs and Application in the Catalytic Oxidation Reaction. *Catalysis Surveys from Asia*. Springer New York LLC June 1, 2019, pp 64–89. https://doi.org/10.1007/s10563-018-9258-1.

Pulsed Laser Surface Melting of Micrometer Particles

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Over the years, researchers have been fascinated by the interaction between pulsed lasers and matter. Depending on the laser fluence (typically over several J·pulse^{-1}·cm^{-2}) and target dimension [1], this interaction can lead to laser ablation in liquid (LAL) or laser fragmentation in liquid (LFL), resulting in the production of nanoparticles (NPs), observable by a clear size change of matter [2]. Laser melting in liquid (LML) differs significantly from LAL and LFL methods. Unlike LAL and LFL, LML operates at much lower laser fluences, typically ranging from several tens to hundreds of mJ·pulse^{-1}·cm^{-2} [3], one to two orders of magnitude less than fluences required for LAL and LFL. LML has shown promise in generating sub-micrometer spheres [4] in a volume-conserving process [5]. However, the LML of micrometer particles dispersed in pure water remains underexplored. However, the full extent of this capability remains unexplored and will be the primary focus of this study.

Here, we demonstrate that under full melting conditions (0.41 J/cm^2, calculated according to Ref [3]), the LML process is a one-pulse event (see Fig. 1). However, melting can also be reached with fluences one order of magnitude lower requiring multiple pulses. It is crucial to note that heat accumulation during processing is avoided due to the chosen interpulse time in the microsecond range, ensuring complete particle cooling before the next pulse arrives. Therefore, we hypothesize that the particle shape change may occur gradually at fluences below the threshold for complete particle melting. In addition, we found that even LFL can occur below the calculated full melting conditions, necessitating multiple pulses per volume element. This surprising observation calls for further experimental verification and computational/theoretical efforts focused on the mechanistic interpretation of the results.

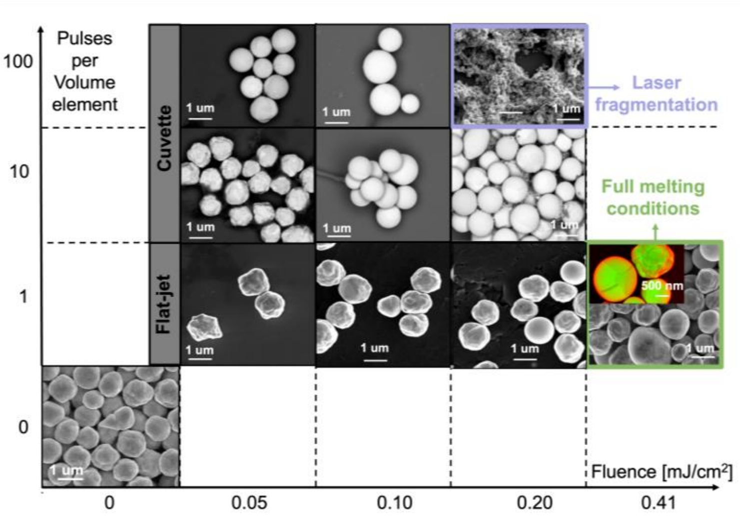

Fig. 1: SEM of the gold microparticles before and after irradiation using different laser fluences (Nd:YAG, 7ns, 9250 Hz, 0.00 – 0.41 J/cm^2) and increased pulses per volume element (0 - 100). Green highlights the fluence at full melting conditions are adjusted, according to Pyatenko et al. [3]. Purple highlights the area in which laser fragmentation was observed. Note that 1 PPV conditions were adjusted using a flat-jet set-up, while a batch-set up was used for multi-pulse conditions.

[1] D.Zhang; B.Gökce;S.Barcikowski, Chem. Rev. Vol. 117, 2017, Nr. 5, 3990-4103
[2] A.R.Ziefuß; S.Reichenberger;C.Rehbock; I.Chakraborty; M.Gharib; W.J.Parak; S.Barcikowski, J. Phys. Chem. C, 2018, Vol.122, 38, 22125–22136
[3] A.Pyatenko; H.Wang; N. Koshizaki T. Tsuji, Laser Photonics Rev. 7, 2013, No. 4, 596–604
[4] Y.Ishikawa; N.Koshizaki; A.Pyatenko; N.Saitoh; N.Yoshizawa; Y.Shimizu, J. Phys. Chem. C, 2016, Vol.120, 2439–2446
[5] M.Lau; A.Ziefuss; T.Komossa; S.Barcikowski, Phys. Chem. Chem. Phys., 2015,17, 29311-29318

Atomistic simulations of nanoparticle generation by fs-laser ablation of thin Ag films

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The interaction of ultrashort pulse lasers with thin metal films is a phenomenon of high practical importance, with applications ranging from the generation of chemically clean nanoparticles to laser high-precision micro/nanomanufacturing of multi-layered systems in microelectronics. At the same time, strong laser excitation makes it possible to access the extreme states of electronic, mechanical, and thermodynamic nonequilibrium, thus providing unique opportunities for investigation of material behavior and properties far from the equilibrium conditions. In this work, we use molecular dynamics simulations of femtosecond laser interactions with silver thin films to obtain a detailed microscopic picture of the underlying mechanisms responsible for nanoparticle generation. The simulations are performed for a broad range of laser fluence and different film thicknesses, from 5 nm to the bulk targets. Four distinct regimes of laser – film interactions are established in the simulations and mapped to the space of film thickness and absorbed fluence. For a fixed film thickness, the increase in fluence results in sequential transitions from melting with no ejection of the film, to film splitting or spallation, to an explosive decomposition of the top part of the film and generation of a residual layer in the lower part of the ablation plume, and to a complete phase decomposition of the film into small droplets and vapor. The nanoparticle distributions are analysed at different regimes and the atoms contributing to different cluster sizes are tracked back to the initial film prior to laser irradiation. To facilitate experimental validation of the computational predictions, the variation of scattering and reflectivity of the ablation plume is calculated for atomic configurations predicted in the simulations and related to the results of pump-probe optical imaging [1] of the ablation plume.

[1] M. Park M. Park, J. Jeun, G. Han, and C. P. Grigoropoulos, *Appl. Phys. Lett.* **116**, 234105 (2020).

Light-matter Interactions inside a Transmission Electron Microscope: A New Paradigm for Studying Laser Ablation at the Atomic Scale

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The advent of the transmission electron microscop~~e~~ (TEM) has revolutionized the way we determine the structure-property relationship of crystalline solids for decades, remaining essential in the toolbox of a materials scientist. In the ongoing upgrades to our FEI Titan TEM, we aim to broaden our spectroscopic capabilities with the installation of a large bore, free-space optical probe with the added capability to perform Raman and cathodoluminescence spectroscopy. This photon source is equipped with tunable wavelengths and a nanomanipulator, providing a wide array of parameters for laser patterning. Next, the addition of a Newport half-waveplate allows for one to rotate the plane of linearly polarized light prior to interaction with the sample, yielding information on the orientation of molecular vibrations. In this contribution, we showcase a photo-exfoliation reaction occurring in few layer MoS_2 sheets. An Nd:YAG laser (operating at 1064 nm) is aligned collinear with the electron beam to ensure the viewing area of the sample is being irradiated. Since the energy of the laser is below the bandgap of MoS_2, the target does not absorb the energy coming from the laser. By increasing the optical output of the laser beyond first-order perturbation theory, the energy between two or more photons combine to overcome the bandgap of MoS_2, giving MoS_2 the ability to absorb the impinging photons. The solid-state multiphoton absorption leads to a photo-exfoliation of the MoS_2 nanosheets to quantum dots, followed by the spectroscopic characterization in the TEM. Ultimately, combining these spectroscopic techniques inside the TEM allows us to revolutionize the structure-processing-property relationship in materials science.

Fundamental Studies of Femtosecond Laser Ablation by Single and GHz Train of Pulses

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The mode of vaporization that occurs through a massive homogeneous nucleation of vapor bubbles in a volume of the strongly superheated liquid, called “explosive boiling” or “phase explosion,” is a phenomenon that plays a key role in numerous practical applications ranging from generation of nanoparticles and nanomaterials to surface cleaning and nano/microfabrication. Despite decades of extensive experimental and theoretical studies, a clear understanding of the conditions and microscopic mechanisms of the phase explosion is still lacking. The objective of this work is to gain an understanding of the mechanisms and kinetics of the explosive phase decomposition in a metastable liquid superheated up to the limit of its thermodynamic stability by short pulse laser irradiation. Time-resolved probing of the transient dynamics of the phase explosion is applied to track all stages of the process, from the emergence of the density fluctuations to the formation and coarsening of distinct liquid regions, and to disintegration of the continuous liquid foamy structure into individual liquid droplets. Spectral scattering and transmission pump-diagnostics in conjunction with direct imaging are applied to probe the decomposition of the irradiated melt layer in the ultrafast to nanosecond time scales.[1] The dependence of the dynamics of the phase explosion on the environment, geometry of the target, and the heating rate is investigated to gain further insights into the fundamental mechanisms and to enable control over the process for practical applications. Implications on the production of nanoparticles are discussed. The ablation dynamics of copper (Cu) by GHz fs bursts are studied using *in situ* multimodal diagnostics.[2] It is shown that GHz fs bursts rapidly remove molten liquid Cu from the irradiated spot due to the recoil pressure exerted by following fs pulses. Material ejection stops after burst irradiation due to the limited amount of remnant matter, combined with the suppressed heat conduction into the target material.

1. Park M, Jeun J, Han G, Grigoropoulos CP, 2020, “Time-resolved emission and scattering imaging of plume dynamics and nanoparticle ejection in femtosecond laser ablation of silver thin films,” *Applied Physics Letters*, **116**, 234105, DOI: 10.1063/5.0009227
2. Park M, Gu Y, Mao XL, Grigoropoulos CP, Zorba V, 2023, “Mechanisms of ultrafast GHz burst fs laser ablation,” *Science Advances*, **9**, eadf639, https://www.science.org/doi/10.1126/sciadv.adf6397

Tuning Wettability of Graphene Oxide by Laser Induced Reduction in Liquids

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The ability to control the wettability of surfaces as well as their patterning is at the centre of technology development efforts due to the broad applicability of such type of surfaces in fields like self-cleaning surfaces, oil-water separation, microfluidics, to name a few. To achieve this, combinations of methods have been used, including lithography, plasma surface modifications, spray coating, and self assembly [1,2]. In this study, we report a method to both pattern and tune the wettability of a graphene oxide (GO) surface, from hydrophilic to hydrophobic. In this method, a GO film deposited onto a substrate is immersed into an organic solvent and patterned by laser scribing while in the liquid environment. The GO film, initially fully wetted by any solvent, is now reduced by the laser and can be characterized by contact angle measurements. In Figure 1 we can observe that by changing solvent we are able to continuously tune the contact angle of such surface, and thus its wettability. Further surface characterization includes Electron Microscopy, optical profilometry, Raman and FTIR spectroscopies and X-Ray Photoelectron Spectroscopy (XPS). We hypothesize that a combination of multiple factors determines the surface roughness of the surfaces, which in turn determines their wettability. Such factors may include solvent properties like boiling point, dipole moment, surface tension etc. and will be further investigated.

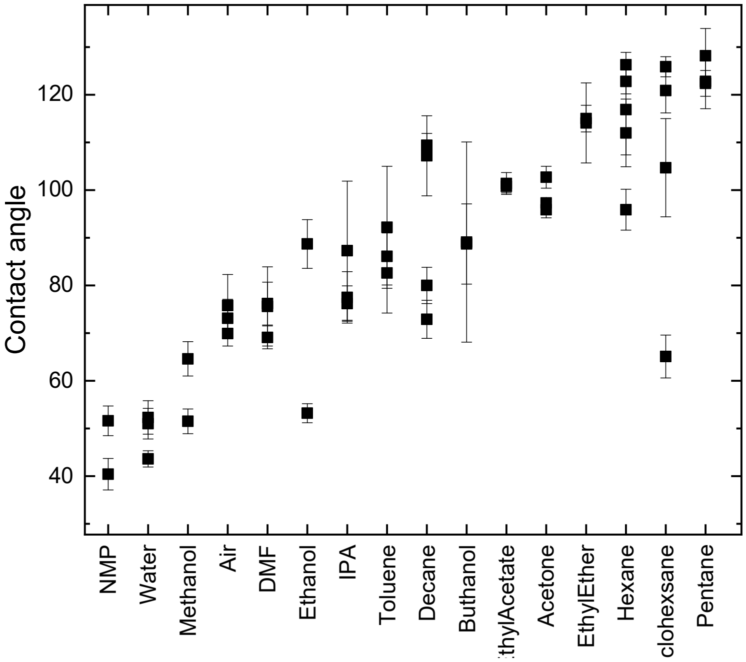

Figure 1**.** Contact angles for GO films reduced in different solvents

[1] S Y. Wang, et al., Small, 17, 2103322 (2021)
[2] X. Gao, et al., Adv. Mater., 28, 168-173 (2016)

Incorporating laser-synthesized $Fe_{50}Ni_{50}$ nanoparticles in photo-sensitive polymers for 4D printing of miniaturized magneto-responsive actuators

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Nanoparticle incorporation into polymer matrices represents an approach toward the optical, biomedical, or magnetic functionalization of the produced polymer parts. Magnetic nanoparticles (NPs) are additives to produce magneto-responsive polymeric actuators with fast, strong, and remote actuation controlled by external magnetic stimuli fields [1]. The composites hold great potential to develop soft, monolithic, and miniaturized robotics for various applications like microfluidics, artificial muscles, or tissue engineering [2]. Vat photopolymerization (VPP) 3D printing can be employed to generate functional custom polymer parts due to its precision and the liquid state of the educt photo-sensitive resin that facilitates the magnetic additive dispersion [3]. However, the printing is often accompanied by reduced processability and mechanical degradation originating from the large magnetic particle load required to achieve the desired actuation response.

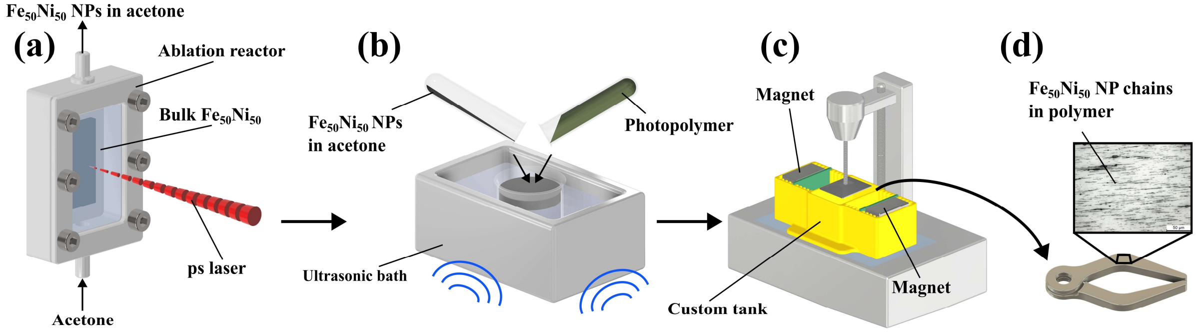

Figure 1. Process scheme for the generation of custom magneto-responsive polymer parts. (a) $Fe_{50}Ni_{50}$ NP synthesis by PLAL in acetone. (b) Composite formulation. (c) VPP printing with a custom printer. (d) Resulting magneto-responsive actuators with oriented $Fe_{50}Ni_{50}$ NP chains for magnetic anisotropy.

In this contribution, a novel technique is proposed to produce magneto-responsive polymer composites with reduced magnetic additive amounts via field-assisted VPP (Fig. 1) [4]. $Fe_{50}Ni_{50}$ NPs were synthesized by pulsed laser ablation in acetone (PLAL) with a 10 ps, 48 W, 1 MHz, 1064 nm laser source. After blending the photo-sensitive resin with the $Fe_{50}Ni_{50}$ NPs produced in acetone, a VPP printer equipped with permanent magnets to promote uniaxial $Fe_{50}Ni_{50}$ NP chain assembly was employed to print magneto-responsive structures. Indeed, high aspect-ratio $Fe_{50}Ni_{50}$ NP strands of up to 500 µm length formed, giving rise to a magnetic anisotropy of the printed parts as revealed by direction-dependent magnetization gradients in the low field. Different actuators were produced, exhibiting rotatory actuation upon exposure to fields of 40 mT. Remarkably, only 0.02 wt% of polydisperse $Fe_{50}Ni_{50}$ NPs (x_c = 16.8 nm) were required to achieve the actuation, and accordingly, the composites kept mechanical properties comparable to the ones of the blank photo-sensitive resin. This process presents a promising route to produce miniaturized polymer actuators by 3D printing.

[1] P. Martins, D. M. Correia, V. Correia, S. Lanceros-Mendez. *Phys Chem Chem Phys* **22,** 27 (2020).
[2] E. Yarali, M. Baniasadi, A. Zolfagharian, M. Chavoshi, F. Arefi, M. Hossain, A. Bastola, M. Ansari *et al. Appl Mater Today* **26** (2022).
[3] M. Shah, A. Ullah, K. Azher, A. U. Rehman, W. Juan, N. Aktürk, C. S. Tüfekci, M. U. Salamci. *RSC Adv* **13,** 2 (2023).
[4] J. L. Kricke, I. Y. Khairani, B. B. J. Beele, N. Shkodich, M. Farle, A. Slabon, C. Doñate-Buendía, B. Gökce. *Virtual Phys Prototyping* **18,** 1 (2023).

Formation of bismuth oxide nanostructures via laser ablation in water

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Bismuth oxide nanomaterials are increasingly recognized for their promising electronic and optical properties, especially in electrochemical and biomedical applications. In this study, we demonstrate that a variety of bismuth oxide nanostructures can be synthesized through pulsed laser ablation in liquids (PLAL) by adjusting the concentration of dissolved gases from ambient conditions. Structural and compositional analysis was performed using x-ray diffraction, Raman spectroscopy, and FTIR spectroscopy. Morphological studies were conducted using atomic force microscopy and transmission electron microscopy. Our findings reveal that factors such as pressure, dissolved gases, and laser fluence play critical roles in determining the final structure and composition of the resulting nanomaterial. The various phases observed ranged from spherical metallic bismuth nanoparticles to monoclinic bismuth oxide nanowire bundles, and orthorhombic bismuth carbonate oxide nanosheets, see Figure 1. This research highlights the importance of free radicals produced during the ablation event, alongside longer-term oxidation processes, in influencing the overall composition and morphology. [1]

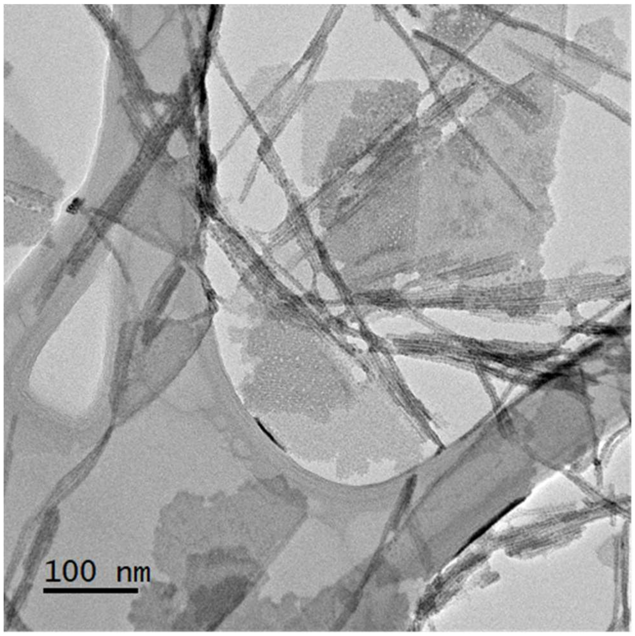

Figure 1. TEM image of bismuth oxide-based nanowire bundles and nanosheets.

[1] Cory J. Trout, Robert Albertson, Julianne C. Griepenburg, Sean M. O'Malley, *Influence of environmental conditions on the morphological evolution of bismuth oxide nanostructures via pulsed laser ablation in liquids*, Colloids and Surfaces A: Physicochemical and Engineering Aspects **690,** 133768 (2024).

Fabrication of Organic Nanoparticle Colloids toward Bio and Medical Applications

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Fabrication of organic nanoparticle colloids has attracted increasing interest in the research fields of drag derivative system (DDS), photodynamic therapy (PDT). Among of organic nanoparticle preparation methods, laser fragmentation in water has some advantages because sample microcrystalline powder suspended in water can be converted directly to nanocolloids without using any organic solvent. [1] In bio-applications, moreover, the nanoparticles are required to have high dispersion stability in a culture medium and in vivo. Herein, we will report nanoparticle colloids preparations of metal porphyrins, flavonoids, and cancer drags by nanosecond laser fragmentation in aqueous solutions of Pluronics, which are amphiphilic triblock copolymers of polyethylene oxide and polypropylene oxide and have been widely used in DDS researches.[2, 3]

As an example, fabrication of metal porphyrins nanoparticle colloids is described here. The suspensions of metal (Pt, Zn) octaethylporphyrin (OEP) microcrystalline powders (20 mwt%) in Pluronic® F127 aqueous solutions (0.1 wt%) were exposed to nanosecond laser pulses (532-nm wavelength, 6-ns FWHM, 10-Hz repetition rate). We obtained the nanoparticle colloids (a mean diameter of about 100 nm) which dispersed stably in a phosphate buffered saline (PBS) solution and a cell culture medium for longer than 1 month. Figure represents the phototoxicity of the PtOEP nanoparticles to rat PC12 cells. Although the cell viability did not change after 1 day incubation under a dark condition, it decreased drastically by visible light irradiation. The results demonstrate clearly that the PtOEP nanoparticles work as an excellent reagent for PDT, i.e. a photosensitizer of reactive oxygen spices (ROS) generation. We examined the mechanism of the photosensitized ROS generation in comparison with a water soluble porphyrin and found that singlet oxygen (${}^1O_2$) through the energy transfer from the triplet excited state of the porphyrin was not generated and hydroxy radical ($\cdot$ OH) and super oxygen anion (O_2^-) generation through electron transfer processes was dominant in the case of the porphyrin nanoparticles.

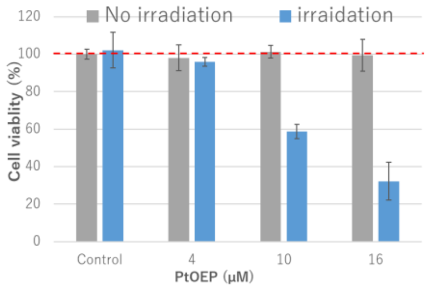

Figure: Phototoxicity of PtOEP nanoaprticles to rat PC12 cells, which were incubated in a culture medium containing the nanoparticles for 1 day, before(gray bars) and after (blue bars) visible light (500-650 nm) irradiation.

In the presentation, we also show some results of the laser fabrication of flavonoids and cancer drags nanoparticle colloids, and will demonstrate the cytotoxicity of the prepared nanoparticles.

[1] T. Asahi, T. Sugiyama, and H. Masuhara, Acc. Chem. Res, 2008, 41, 1790-1798.
[2] C.C Castro, et al. J. Control. Release 2023, 353, 802–822.
[3] Akash, M.S.H.; Rehman, K. J. Control. Release 2015, 209, 120–138.

The therapy enhancing effect of laser-fabricated metal and alloy nanoparticles in proton therapy is driven by surface chemistry

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Proton therapy (PT) is a modern form of radiation therapy, particularly useful when treating cancer in sensitive areas like brain, eyes, or in developing organs of children. In vitro and in vivo studies already demonstrated that metal nanoparticles (NP) can function as radiosensitizers in PT. Here, first evidence indicates that reactive oxygen species (ROS) generated in the presence of the NP are a main contributor [1]. However, the mechanism of ROS generation during PT in the presence of NP is still underexplored. In this work, we studied the effect of colloidal ligand-free Pt and Au nanoparticles derived from laser processing in liquids on ROS generation in water phantoms after irradiation with protons. ROS formation was monitored directly using fluorescent dyes and indirectly by the detection of model DNA breakage by gel electrophoresis. Here double strand breaks were identified as the main damage mechanism in the DNA, observable even at low, clinically relevant irradiation doses of 2-5 Gy. Utilization of initially ligand-free sterilizable [2] NP from laser synthesis proved particularly efficient in this context as we could observe disappearance of all enhancement effect when citrate ligands, commonly used in chemically generated gold colloids, were added [3]. We found a linear dependence of the ROS generation on irradiation dose and particle surface concentration [3][4]. However, we were also able to deduce a higher efficiency of smaller 5 nm AuNP in contrast to their 30 nm counterparts even at the same total surface area, which points at additional effects driven by surface chemistry e.g. the density of structural defects [3]. This was verified by comparing ligand free AuNP from LAL and LFL, which are also believed to possess different structural defect densities. Here, the AuNP from the fragmentation process had a significantly higher surface charge density and displayed more pronounced ROS formation in comparison to those from ablation, even at identical particle size and surface area [3]. These findings were complemented by the fact that PtNP were significantly more active than AuNP, which could be explained by the higher catalytic activity of Pt surfaces in generation of ROS [4]. We also performed initial irradiation experiments in the presence of PtIr and PtFe alloy NPs to further explore material effects. Finally, we also examined the impact of common biological stabilizers like serum albumin on PT efficiency to better emulate conditions in the body as another step towards in-vivo applicability.

[1] Sicard-Roselli, C.; Brun, E.; Gilles, M.; Baldacchino, G.; Kelsey, C.; McQuaid, H.; Polin, C.; Wardlow, N.; Currell, F., Small 10, 3338-3346 (2014)

[2] Johny, J.; van Halteren, C.; Zwiehoff, S.; Behrends, C.; Bäumer, C.; Timmermann, B.; Rehbock, C.; Barcikowski, S., Langmuir 38, 43, 13030-13047, (2022)

[3] Johny, J.; van Halteren, C. E. R.; Cakir, F. C.; Zwiehoff, S.; Behrends, C.; Bäumer, C.; Timmermann, B.; Rauschenbach, L.; Tippelt, S.; Scheffler, B.; Schramm, A.; Rehbock, C.; Barcikowski, S., Chem.-Eur. J., 29, 13, (2023)

[4] Zwiehoff, S.; Johny, J.; Behrends, C.; Landmann, A.; Mentzel, F.; Bäumer, C.; Kröninger, K.; Rehbock, C.; Timmermann, B.; Barcikowski, S., Small 18, (2022)

Laser ablation synthesis of biodegradable and multifunctional nanoalloys for nanomedicine

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Alloy nanoparticles containing noble and transition metals are appealing for a series of applications and fundamental studies in catalysis, optics and nanomedicine. However, the thermodynamics is unfavorable to the largest part of these alloys, which can be obtained only by non-equilibrium routes. To this end, laser ablation in liquid (LAL) is a powerful technique for the synthesis of metal alloys, also with thermodynamically forbidden composition. By mastering the LAL synthesis, a whole catalogue of alloys is accessible for fundamental studies about the structural motifs adopted by elements frozen at the nanoscale and the consequent set of physical-chemical properties. The insights on the structure-properties relation provided the basis for further optimization of the nanoalloys for specific applications. The cases of Fe alloys acting as 4-D multimodal contrast agents with enhanced clearance from the body or theranostic agents will be discussed or radiosensitizers for x-ray and boron neutron capture therapy.[1-4] These nanosystems provided clear directions for further development of the intended functionalities, which are the subject of ongoing efforts.

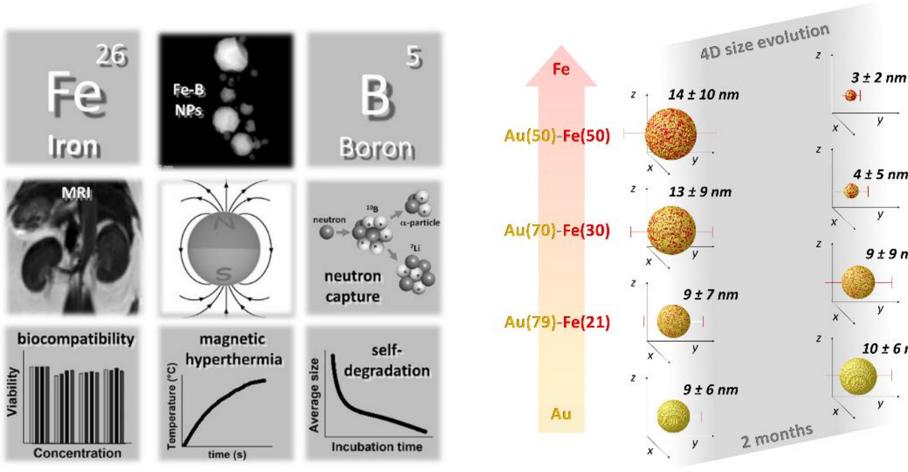

Figure 1. Sketch of Fe-B alloy NPs with theranostic abilities (left) and composition-biodegradability relationships in Au-Fe multimodal contrast agents (right).

[1] V. Torresan, D. Forrer, A. Guadagnini, D. Badocco, P. Pastore, M. Casarin, A. Selloni, D. Coral, M. Ceolin, M. B. Fernández van Raap, A. Busato, P. Marzola, A. E. Spinelli, V. Amendola, 4D Multimodal Nanomedicines Made of Nonequilibrium Au−Fe Alloy Nanoparticles, *ACS Nano*, **14**, 12840−12853 (2020).

[2] V. Torresan, A. Guadagnini, D. Badocco, P. Pastore, G. A. Muñoz Medina, M. B. Fernàndez van Raap, I. Postuma, S. Bortolussi, M. Bekić, M. Čolić, M. Gerosa, A. Busato, P. Marzola, V. Amendola, Biocompatible Iron–Boron Nanoparticles Designed for Neutron Capture Therapy Guided by Magnetic Resonance Imaging, *Adv. Health. Mater.*, **10**, 2001632 (2021).

[3] V. Amendola, A. Guadagnini, S. Agnoli, D. Badocco, P. Pastore, G. Fracasso, M. Gerosa, F. Vurro, A. Busato, P. Marzola, Polymer-coated silver-iron nanoparticles as efficient and biodegradable MRI contrast agents, *J. Coll. Interf. Sci.*, **596**, 332-341 (2021).

[4] S. Scaramuzza, C. M. G. de Faria, V. Coviello, D. Forrer, L. Artiglia, D. Badocco, P. Pastore, P. Ghigna, I. Postuma, L. Cansolino, C. Ferrari, S. Bortolussi, R. Vago, A. E. Spinelli, M. Bekić, M. Čolić, V. Amendola, A Laser Synthesis Route to Boron-Doped Gold Nanoparticles Designed for X-Ray Radiotherapy and Boron Neutron Capture Therapy Assisted by CT Imaging, *Adv. Funct. Mater.* **33**, 2303366 (2023).

Plasmonic nanoparticles synthesized by laser ablation in liquid for SERS sensors with high enhancement in sensitivity and stability

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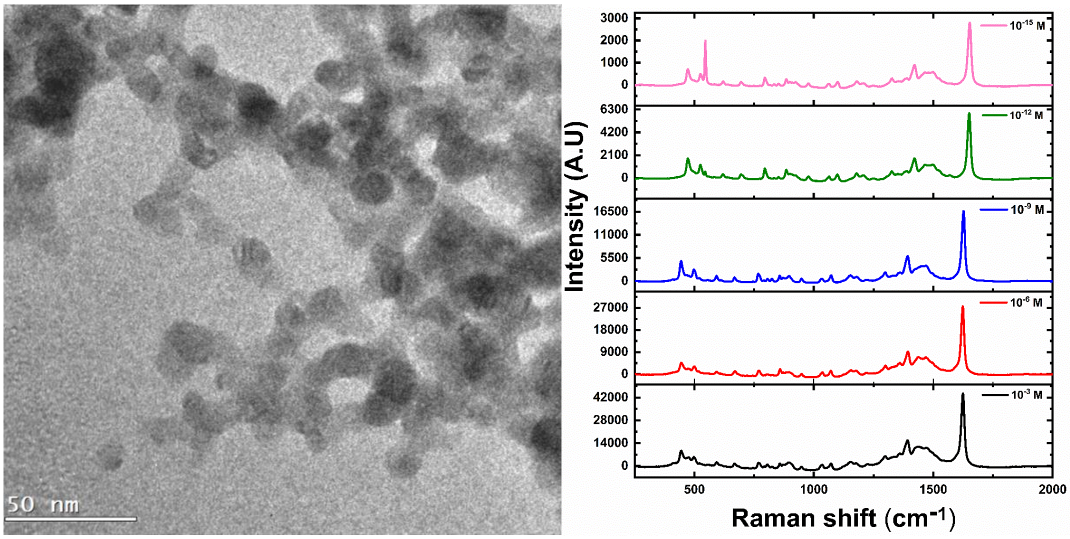
Surface Enhanced Raman Spectroscopy (SERS) is a powerful technology for fast, label free detection of broadband class of molecules. Here we present novel, ultrasensitive, reproducible, and chemically stable SERS sensors fabrication using plasmonic nanoparticles generated by pulsed laser ablation in liquid. The nanoparticles and SERS substrates formed are characterized for their structure, morphology, composition and SERS activities. Incorporation of metal/bimetallic nanoparticles (Ag, Au and Ag:Au) on silver deposited Si wafer substrates formed first, second and third generation hotspots and the synergistic effect between Au and Ag contributed to the ultra-sensitivity (pico and femto molar concentrations) of SERS sensors. The sensors are found to be chemically stable for more than a month, still maintaining their sensitivity. They showed Raman signal enhancement (analytical enhancement factor ~10^8 to 10^9) for 532 and 780 nm excitation wavelengths for different organic dyes. The SERS samples showed excellent reusability after a quick thermal treatment to remove the analyte molecules. It is also found that the SERS enhancement improved significantly after thermal treatment and the substrates are reusable. SERS spectra for semiconductor nanoparticles are also evaluated at different concentrations. These SERS sensors can be created in a matter of hours, and the experimental methodologies can be scaled up to large-scale manufacturing.



TEM image of bimetallic Au:Ag nanoparticles by PLAL and SERS detection of Methylene Blue (milli molar to femto molar) .

Laser Generation of Silver Nanoparticles from Recycled Solar Cells

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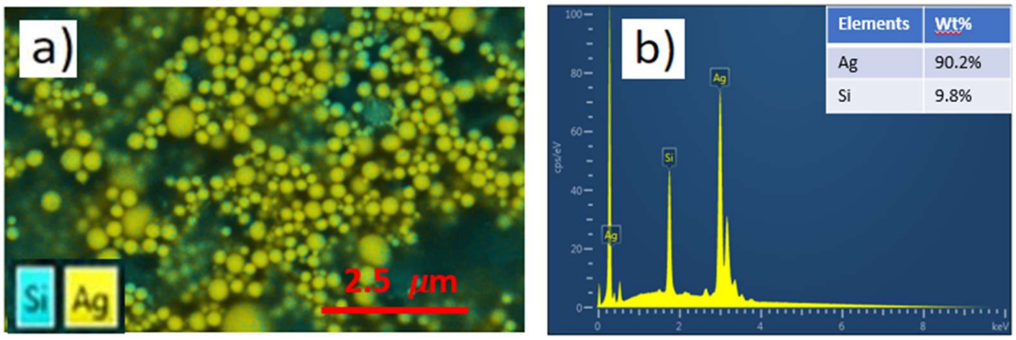
In the realm of sustainable metal recovery from end-of-life (EOL) and discarded solar cells, this study represents a significant stride forward, particularly in the eco-friendly extraction of silver from electrical contact lines using a precise laser ablation technique. Our investigation delves into the efficacy of silver recovery in nanoparticle form by employing UV picosecond pulse laser. The optimization of laser parameters, like power, laser scanning speed, number of laser passes has yielded a tailored eco-friendly silver removal process by producing the high value silver nanoparticles.

Through precise alignment of the laser beam with Ag lines and utilizing a UV picosecond laser with a 355 nm wavelength, we successfully demonstrated the generation of silver nanoparticles. Profilometry measurements offered valuable insights into the dimensions and variations of silver contact lines on solar cells, guiding the positioning of the laser beam on silver lines. Confirmation of silver nanoparticle formation, characterized by a spherical morphology, was obtained through both UV-visible spectral measurements (not shown here) and SEM-EDS analysis (Figure 1a). Optimization of experimental parameters, such as the thickness of the liquid layer on the solar cell sample, focal position of the sample, and laser power, was crucial for producing silver and silicon nanoparticles with distinct morphologies and sizes based on their composition. Adjusting the water level from 0.6 mm to 0.8 mm and increasing the power from 15 W to 20 W led to transformations in silicon particle size and structure (submicron spherical to micron sized plate like structures) while preserving the size and shape (around 150 nm spherical particles) of the silver nanoparticles. Maintaining a sample at a focal position with a 0.8 mm water layer and 20 W laser power resulted in larger plate-like silicon nanoparticles compared to silver nanoparticles, facilitating easy separation through size-based filtration and centrifugation. This facilitated easy separation of silicon impurities from silver nanoparticles through size separation (filtering) and gravity separation (centrifugation). To significantly enhance the purity of the recovered silver nanoparticles, a combination of filtration and centrifugation techniques was employed, achieving an approximate 90% purity by weight (Figure 1b). This method, producing up to 4 mg/minute of silver nanoparticles while operating the laser at 70 W (including all electronic appliances), showcases its energy efficiency and cost-effectiveness for recycling solar cells, while also minimizing hazardous chemical usage and reducing operational costs, offering a sustainable solution to the challenge of photovoltaic waste.



Elements	Wt%
Ag	90.2%
Si	9.8%

Figure 1. (a)) EDS mapping of silver nanoparticles after filtering and centrifugation for improving purity. (b) Composition of silver and silicon nanoparticles in the area mapped in (a).

Laser-generated Metal Oxide Nanodots for Magnetic Resonance Imaging

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As an important link between discrete atoms and nanoparticles, nanodots have been drawing extensive attentions because they can serve as unique platforms to explore interfical features for nanomaterials at an extremely small size scale. Metal oxide nanodots, especially for polyvalent metal oxides, are widely used in the areas of healthcare (for example fluorescence imaging, magnetic resonance imaging (MRI), catalytic therapy, photothermal therapy) due to their tunable compositon, crystal structure, and interfical features. In this presentation, the progress of polyvalent iron oxide and manganese oxide nanodots as contrast agents for MRI will be discussed. These nanodots used in the present study were physically prepared via an approach of laser irradiation of the corresponding nanoparticles in ultrapure water, allowing the fabrication of particles with ultrasmall size and very active surface properties[1,2]. By modulation the laser synthesis processes in this presentation, the accordingly changed surface structures enhanced the interaction between metal ions on particle surface and surrounding water molecules. Thus, laser-generated metal oxide nanodots displayed strong vitality to exchange with water molecules under magnetic field, and this allowed the potential application as MRI contrast agents.

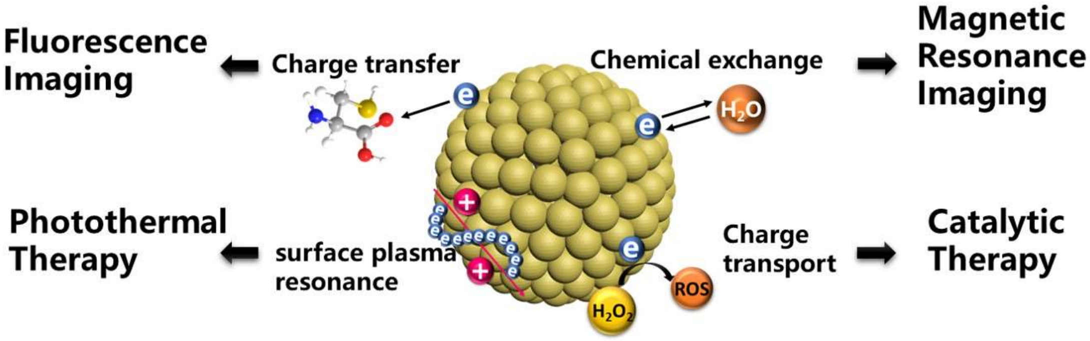

Figure 1. Schematic illustration of healthcare application for nanodots

[1] S. Ji, P. Li, X. Zhao, S. Wei, X. Cheng, L. Wu, Y. Ye, K. Ma, Y. Cai, C. Liang, Laser-generated defect-rich MnO_x nanobelts with high oxidase mimic activity for glutathione detection, Sensors and Actuators B: Chemical, 383, 2023, 133595.

[2] L. Wu, Y. Ye, Y. Cai, Y. Ma, T. Fan, C. Liang, Environmental Effects of Surfactant-Free Silver Nanoparticles on Enzyme Activities, Bacterial Diversity, and Soil Function, Environmental Toxicology and Chemistry, 2023, 42, 1685–1695.

Application of pulsed laser ablation in liquids in photovoltaic devices

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The unique characteristics of ultrashort pulsed lasers, emitting light pulses shorter than a few tens of picoseconds, have paved the way for new avenues in photonic applications. This paper provides an overview of the irradiation schemes and the physical mechanisms we have been proposed to investigate the generation of metallic nanoparticles in liquids. A series of parameters and conditions are demostrated to influence the shape and composition of the induced nanoparticles. The exploitation of metallic nanoparticles generated in liquids in photovoltaic devices is presented and discussed. In particular, the impact of NPs' incorporation into various building blocks within the solar cell architecture on the photovoltaic performance and stability is presented and analyzed for the current state of the art photovoltaic technologies.

Electric field assisted laser ablation in liquids: main features and application for the controlled synthesis of nanocomposites

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Laser ablation in liquids has been recently recognized as a "green", efficient and controllable method of nanoparticles (NPs) production. As a result of recent developments in this field, a range of novel approaches and setups was suggested and implemented: apart from the traditional basic setups based on laser ablation in a steady or stirred liquid, several works introduced laser ablation in a continuous liquid flow or liquid jet through a capillary tube [1]. Further control of the NPs formation process was reached by laser ablation utilizing the effects induced by the application of external magnetic, temperature and electric fields [2]. The novel approaches provided the routes for overcoming the typical drawbacks of the laser ablation method, e.g. enhancement of NPs production efficiency, as well as served as an additional tool for the control over NPs parameters thus allowing to significantly broaden the range of nanomaterials produced as well as their potential application fields. As an example, many of the practical applications, such as catalysis, energy generation and storage require nanostructures with composite structure and developed surface that allows creation of more active sites for efficient performance. However, generation of non-spherical nanostructures by laser ablation in liquids is still challenging as thermodynamic conditions created in plasma favour the spherical shape of the growing NPs. To overcome this issue, in this work application of an external electric field was suggested that allowed forming non-spherical nanomaterials, such as nanoflowers, nanosponges or nanoneedles depending on the ablated target material. The distinctive feature of the developed approach is application of an electric field directly to the ablated target that allows simultaneously assembly forming nanomaterials on the counter electrode (Figure 1). The control of nanomaterials morphology was provided by the selection of the strength and polarity of an electric field along with a liquid composition. As an example, laser ablation of a Zn cathode and Zn anode in water result in nanodisc or nanoflower morphology that was sufficiently different from the spherical NPs produced without an applied voltage. As shown by the time-resolved imaging of the plasma formed, the applied voltage reduced plasma lifetime that can explain the observed differences in morphology and structure.

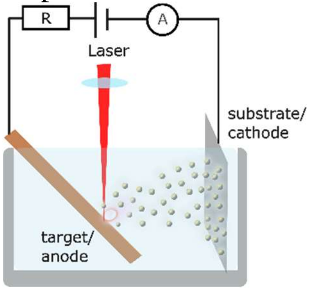

Figure 1. Sketch of the developed scheme of laser ablation in the external electric field.

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[1] N.G. Semaltianos, G. Karczewski, *ACS Appl. Nano Mater.* **4**, 6407 (2021).

[2] N.N. Tarasenka et al, *ACS Appl. Nano Mater.* **6**, 5918 (2023).

Spatial and temporal beam control for laser ablation in liquids productivity increase and nanoparticle size modification

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Nanoparticles (NPs) generated by pulsed laser ablation in liquids (PLAL) have benefited key applications such as catalysis, energy harvesting, or additive manufacturing. However, nanoparticle size control and further productivity increase remain a challenge. The spatial and temporal modification of the laser beam appears as an ideal approach to modify the cavitation bubble dynamics, influence NP size distribution, and to increase productivity by reducing cavitation bubble pulse shielding. Here we describe the recent advances in PLAL size control and productivity increase by double pulse PLAL, and multi-beam PLAL.

Synchronous-double-pulse PLAL is proposed to understand bubble interaction effects on the nanoparticle size [1]. The cavitation bubble pair interaction is recorded using a unique coaxial diffuse shadowgraphy system, Fig. 1a. This system allows to record the bubble pair interaction from top and side, enabling the identification of the bubble's morphology, lifetime, and displacement velocity. A dimensionless parameter, H*, is introduced to quantify the ratio between double bubble spatial separation and their maximum height. Notably, a four-fold increase in nanoparticle size is observed for Au and YAG at H* = 2, Fig. 1a.

To reduce the characteristic NP bimodality in ps-PLAL, a double pulse configuration with inter-pulse delays between 300 ps and 1200 ps is proposed [2]. In this temporal delay window, the initial bubble is still flat so that shielding of the second laser pulse by the cavitation bubble is avoided, Fig. 1b; minimizing pulse shielding that could reduce NP productivity. At a pulse delay of 600 ps, a (9 ± 1) wt% reduction of the large NP fraction is demonstrated, Fig. 1b.

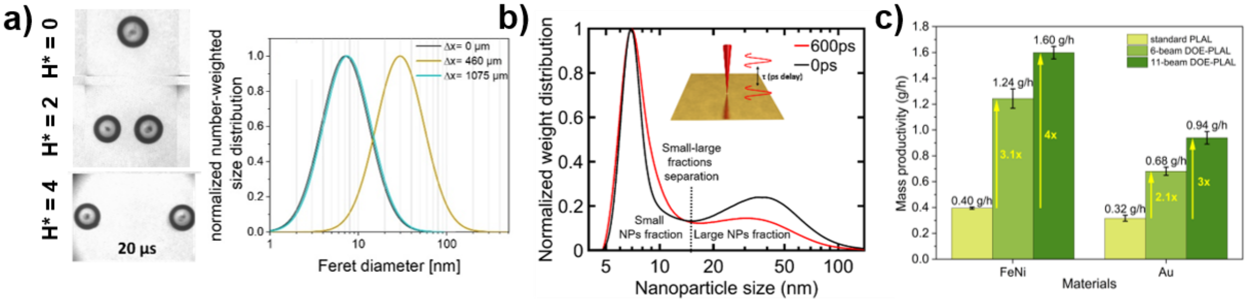

Figure 1. a) Left. Two simultaneously generated cavitation bubbles at different distances. Right. Number-weighted size distributions of YAG NPs. b) Nanoparticle distribution for double-pulse delay times of 0 ps (black line) and 600 ps (red line). c) Nanoparticle mass productivity comparison between FeNi and Au in water for PLAL and DOE-PLAL.

Finally, a cost-effective approach to upscale PLAL productivity is proposed, the addition of static diffractive optical elements (DOE) to the standard PLAL technique to achieve parallel processing (DOE-PLAL). DOE-PLAL with 11 beams is proved to reach a factor 4 productivity increase for iron-nickel alloy (Fe50Ni50) nanoparticles compared to the standard single beam setup (0.4 g/h to 1.6 g/h), and a factor 3 increase for gold (Au) nanoparticles (0.32 g/h to 0.94 g/h), Fig. 1c.

[1] F. Riahi, A. Bussmann, C. Doñate-Buendía, S. Adami, N. Adams, S. Barcikowski, B. Gökce, *Phot. Res.*, Accepted, doi: 10.1364/PRJ.498204 (2023).

[2] C. Doñate-Buendia, M. Spellauge, R. Streubel, F. Riahi, S. Barcikowski, H. P. Huber, B. Gökce, *J. Phys. D. Appl. Phys.*, **56**, 104001 (2023).

Beam splitting as a way to increase the nanoparticle production by laser ablation in liquids

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Pulsed laser ablation in liquids (PLAL) is a well-established versatile technique to produce high-purity colloidal nanoparticles (NPs) of a large variety of materials attractive for various applications. However, industrial applications of the PLAL-produced NPs are still very limited, mainly due to the low productivity of the method [1]. The main limiting factor for the PLAL efficiency is the cavitation bubble generated in the liquid which shields the subsequent laser pulses from the target [1,2]. A milestone in the PLAL synthesis of NPs was achieved when the bubble was spatially bypassed by using a high-speed polygon scanner increasing the NP productivity to the industrial-scale level up to several g/h [1]. However, the polygon scanner is an expensive and rather troublesome device that prevents its wide usage. Therefore, there is still a significant demand for a practical, cost-effective method for upscaling the PLAL synthesis. We propose here a novel upscaling approach by bypassing the cavitation bubble through splitting the laser beam into several beams.

In this work, we investigate the effect of laser beam splitting on NP productivity by PLAL using diffractive optical elements (DOEs). As a model material, we use a multimetallic high-entropy alloy (HEA) CrFeCoNiMn. HEA NPs show great potential for applications but their controllable and efficient synthesis is still a challenge [3,4]. We incorporate DOEs into the optical PLAL scheme and analyze the HEA NP productivity as a function of synthesis parameters (laser fluence, repetition rate, beam scanning speed). We demonstrate that the proposed multi-beam method helps to bypass the PLAL-generated bubble both temporally (the same ablation events can be achieved at lower repetition rates) and spatially (lower beam scanning speeds are needed). This allows to increase dramatically the PLAL productivity of colloidal NPs (Figure 1). Furthermore, we have performed time-resolved imaging of the cavitation bubble under the considered PLAL conditions to correlate the observed increase in NP productivity with the possibility of bypassing the bubble using the proposed multi-beam strategy.

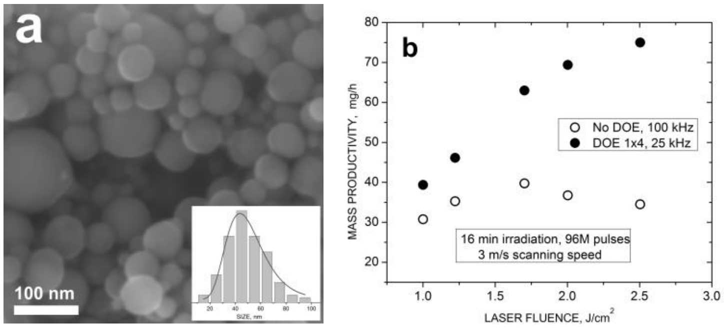

Figure 1. (a) SEM image of HEA NPs produced by multi-beam PLAL (1030 nm, 7 ps, 2.5 J/cm^2) using a 1×4 DOE. The inset shows the NP size distribution. (b) NP productivity as a function of laser fluence with and without DOE.

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[1] R. Streubel; S. Barcikowski; B. Gökce, *Opt. Lett*. **41**, 1486 (2016).

[2] S. V. Starinskiy, Y. G. Shukhov, A. V. Bulgakov, *Appl. Surf. Sci*. **396**, 1765 (2017).

[3] F. Waag, Y. Li, A. R. Ziefuß, E. Bertin, M. Kamp, V. Duppel, G. Marzun, L. Kienle, S. Barcikowski, B. Gökce, *RSC Adv*. **9**, 18547 (2019).

[4] B. Wang, C. Wang, X. Yu, Y. Cao, L. Gao, et al. *Nat. Synt.* **1**, 138 (2022).

Improving the production efficiency of gold nanoparticles in the laser-induced reduction method by optical system modulation

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We describe the improvement of nanoparticle (NP) production yields by laser-induced reduction method using optical system modulation. In this technique, pure metal or alloy NPs are produced by reducing metal ions by irradiating single or multiple metallic salt solutions with intense ultrashort laser pulses, as typified by femtosecond pulsed lasers[1, 2]. Unpaired electrons are instantaneously generated by electron transfer or emission through excitation of solvent molecules by photons, and these unpaired electrons reduce the metal ions to metal NPs. Therefore, it is supposed that the production yield of NPs can be improved by generating a large amount of these unpaired electrons per unit time. In this presentation, we demonstrate the verification whether the yield can be improved by modification of an optical system in the laser-induced nucleation method.

A laser beam emitted from a femtosecond pulsed laser with a center wavelength of 800 nm, pulse width of 100 fs, pulse intensity of 7 mJ, and repetition rate of 1 kHz was modulated by an optical system, and introduced into a synthetic quartz container containing a metal salt solution. A spectroscopic system capable of detecting absorption spectra from 200 nm to 900 nm was installed in a separated optical path. The sample for verification of NP yield was an aqueous gold chloride solution, with a concentration of 5.0×10^{-4} mol/L and a volume of 100 mL. Figure 1 shows the spectral changes in the gold NPs formation with movement of the light-focusing position due to continuous prism rotation. The absorbance of surface-plasmon resonance (SPR) depends on the number, and the absorption peak wavelength of SPR depends on the size of gold NPs, respectively. The time variation of absorbance and wavelength of the absorption peak (closed circle) become constant after 8 minutes irradiation indicating formation of uniform particle by light modulation. Accordingly, the modulation of the focus position shortens the production of the NPs.

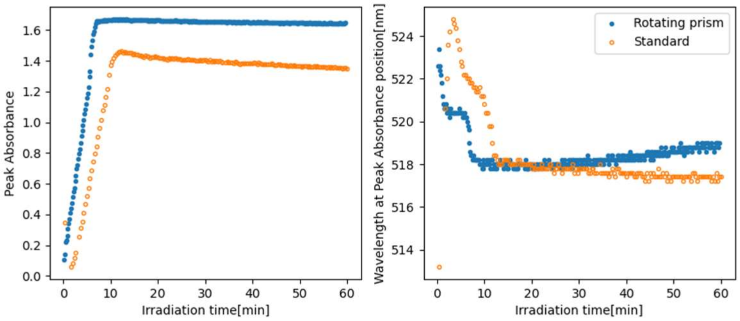

Figure 1. Time variation of the (a) absorbance and (b) absorption peak wavelength of the SPR of gold NPs obtained by the spectroscopy with (closed circle, rotating system) and without (open circle, standard) prism rotating system.

In this report, we demonstrated that the production efficiency differed depending on the laser irradiation method. Therefore, optimization of laser specifications such as threshold energy, pulse width, repetition rate, and wavelength, as well as optimization of Rayleigh length, volume, multi-point irradiation, and movement speed of the focusing position, may lead to a significant improvement in production yield of NPs in laser-induced reduction method.

[1] T. Nakamura et al., *Appl. Phys*. A, **104,** 1021–1024, (2011).

[2] T. Nakamura et al., *AIP Adv*, **3**, 082101, (2013).

Laser-generated FeRh nanoparticles inks for laser-assisted direct writing of custom magnetocaloric microstructures

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Magnetocaloric refrigeration has the potential to replace compress gas-based refrigeration systems due to its higher energy efficiency and lower environmental impact. However, a large magnetocaloric effect is typically observed in materials containing rare earth or expensive elements. To reduce the required amount, these materials can be used in miniaturized applications such as magnetic microcoolers. To that end, the generation of nanometric magnetocaloric materials suitable as building blocks to fabricate magnetocaloric microstructures represent a challenge due to oxidation during synthesis, elemental and size control.

The near-equatomic FeRh alloy is recognized for showcasing a significant magnetocaloric effect during the first-order antiferromagnetic-ferromagnetic phase transition. This contribution demonstrates a procedural approach to produce ink formulations containing equiatomic magnetocaloric FeRh nanoparticles, minimizing oxidation and making them suitable for writing personalized magnetocaloric microstructures through a sintering process. The paramagnetic near-to-equimolar FeRh nanoparticles, Fig. 1a, are generated by laser ablation in ethanol in an argon environment [1]. The colloids are concentrated by solvent evaporation to a 1. wt% ink dispersed on PVP-coated glass substrates, Fig. 1b, and patterned using a continuous wave laser, Fig. 1c.

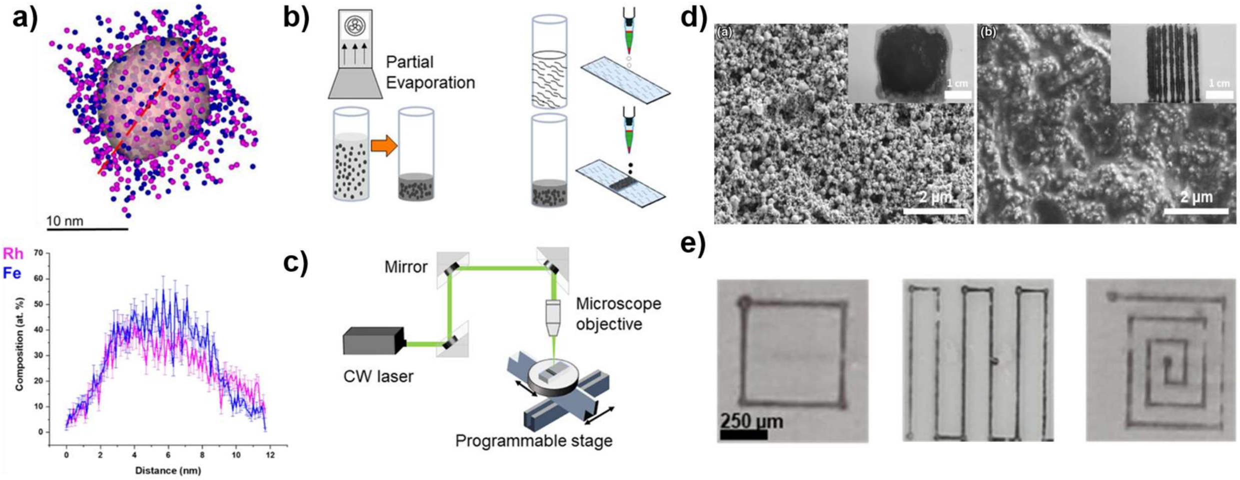

Figure 1: (a) FeRh nanoparticle (25 at% of FeRh iso-composition surface) and line scan of selected FeRh nanoparticle. **(b)** Partial evaporation of ethanol from the FeRh NP colloid and deposition on a glass substrate. **(c)** Sintering by continuous wave laser. **d)** SEM image and light optical microscopy image of the drop-casted FeRh ethanol-based ink before and after sintering. **e)** Custom structures produced through laser sintering.

Continuous wave direct writing leads to the sintering of the deposited nanoparticles into micrometric structures, Fig. 1d, [2]. Finally, 2D magnetocaloric custom structures were created [3], confirming this route as a promising approach to fabricate micrometric cooling structures for miniaturized applications, Fig. 1e.

[1] R. Nadarajah, S. Tahir, J. Landers, D. Koch, A.S. Semisalova, J. Wiemeler, A. El-Zoka, S.-H. Kim, D. Utzat, R. Möller, B. Gault, H. Wende, M. Farle, B. Gökce, *Nanomat.*, **10**, 2362 (2020)

[2] R. Nadarajah, J. Landers, S. Salamon, D. Koch, S. Tahir, C. Doñate-Buendía, B. Zingsem, R.E. Dunin-Borkowski, W. Donner, M. Farle, H. Wende, B. Gökce, B. *Scient. Rep.*, **11**, 13719 (2021)

[3] S. Tahir, J. Landers, S. Salamon, D. Koch, C. Doñate-Buendia, A. Ziefuß, H. Wende, B. Gökce, *Adv. Eng. Mat.*, **25**, 2300245 (2023)

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