Effect of the embedded plasmonic gold nanorods on the interaction of high intensity laser irradiation with UDMA polymer – morphological and structural changes during crater formation

Judit Kámán[1)], Miklós Veres[1)], Ágnes Nagyné Szokol[1)], István Rigó[1)], Péter Rácz[1)], Márk Aladi[1)], Miklós Kedves[1)], Archana Kumari [1)], Attila Bonyár[2)], Melinda Szalóki[3)], Alexandra Borók[2)], Zsolt Fogarassy[4)], Mária Csete[5)] , László Csernai[6)], Norbert Kroó[1)], Tamás Biró[1)]

1) ELKH, Wigner Research Centre for Physics
2) Department of Electronics Technology, Budapest University of Technology and Economics, Budapest, Hungary
3) Department of Prosthetic Dentistry, University of Debrecen
4) ELKH, Centre for Energy Research, Institute for Technical Physics and Materials Science
5) Institute of Phyics, University of Szeged
6) University of Bergen, Norway
kaman.judit@wigner.hu

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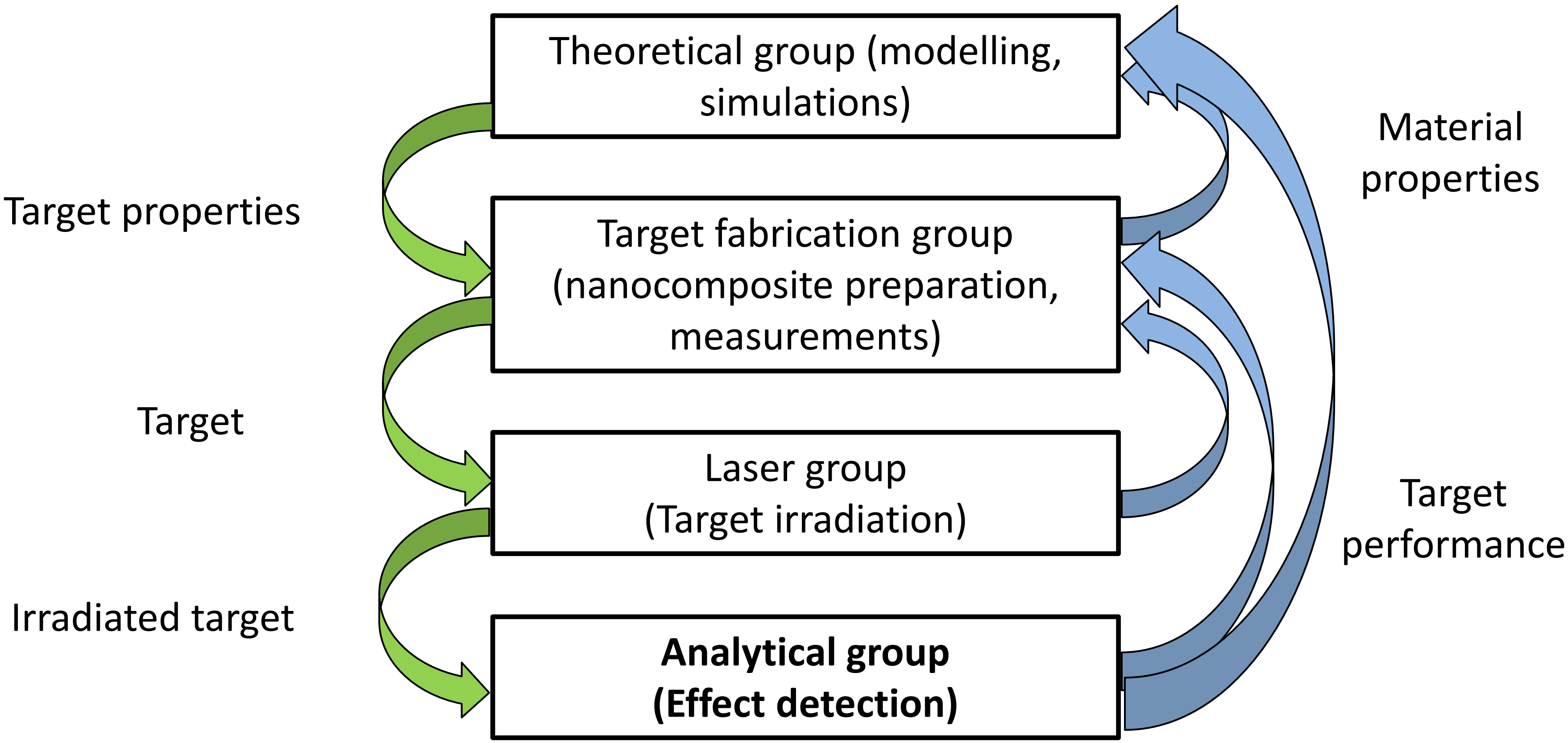
NAPLIFE project

Nanoplasmonic Laser Inertial Fusion Experiment Collaboration



Outline

1. Laser fusion target considerations
2. Nanocomposite preparation
3. Fabrication methods
4. Nanorod characterization with TEM
5. Laser irradiation experiments
6. Surface investigation techniques after the irradiation
7. Surface structure of the laser ablated area
8. Surface roughness

1. Target fabrication considerations

Our general idea is to increase the absorptivity of the target by using different types of nanomaterials, such as core-shell structures and nanorods. Calculations via solving the Maxwell equations, and evaluating the Ohmic heating were performed.

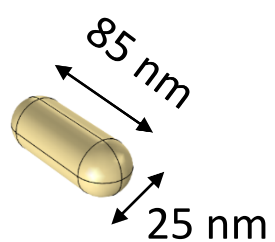
Simulations were performed to:

Optimize the particle geometry considering the RI of the target.

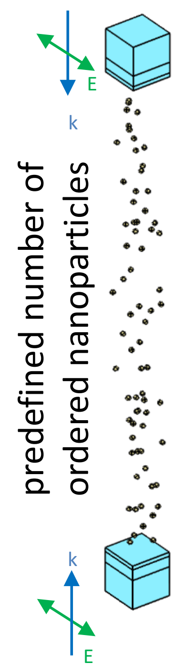
Investigate the effect of random orientation and distribution.

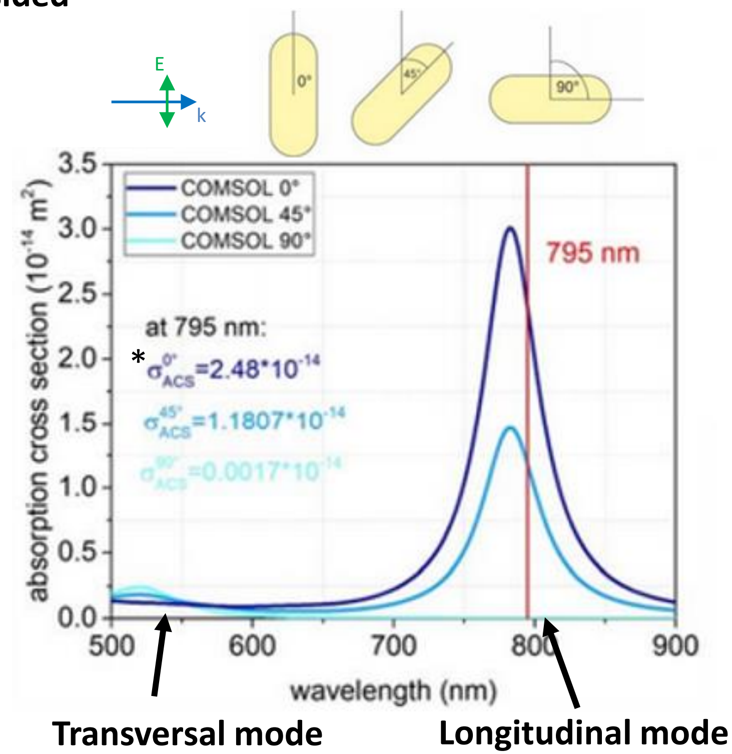
Maximize the absorption (and heating) in the target.

Nanorod:



one-/ two-sided irradiation





*ACS: Absoption Cross-Section

[M. Csete, et al., University of Szeged, HU]

2. Nanocomposite preparation

The fusion target will be a nanocomposite, where the nanoparticles are doped into the bulk of a polymer. The type of the polymer and the polymerization itself needs to be selected according to our requirements:

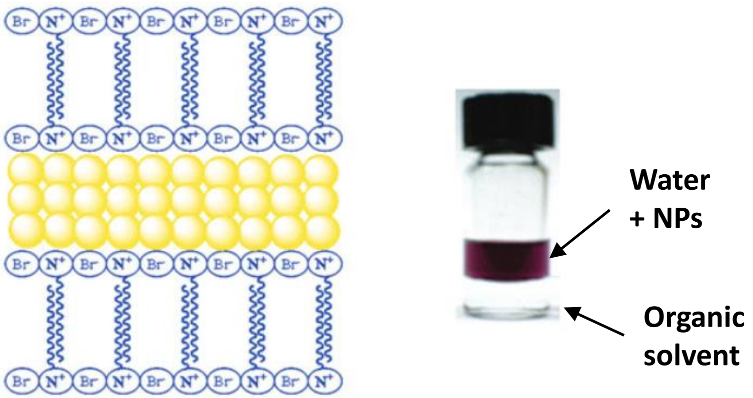
- **Uniform particle distribution,**
- **Avoid particle aggregation,**
- **Long-time particle stability,**
- **Possibility to build layers on each other.**

- Polymerization type:
  - Solution polymerization,
  - Bulk polymerization,
  - Photopolymerization.

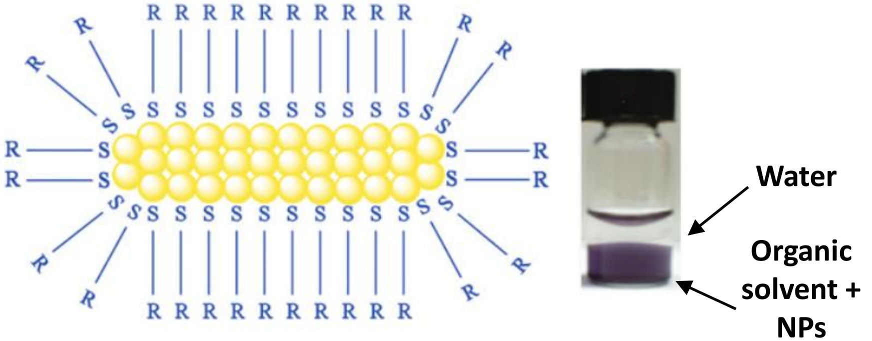
- Particle capping should be controlled.
  - Hydrophilic (synthesis),
  - Hydrophobic (for doping).

- Nanoparticle phase transfer

Au- CTAB (cetrimonium bromide)



Au-DDT (dodecanethiol)



El Khoury, 2009, 10.1039/b901826c

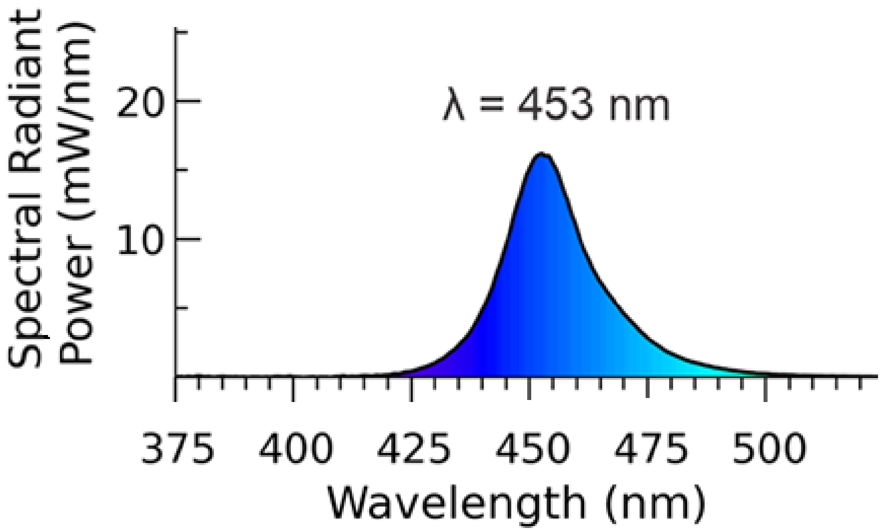
2. Nanocomposite preparation

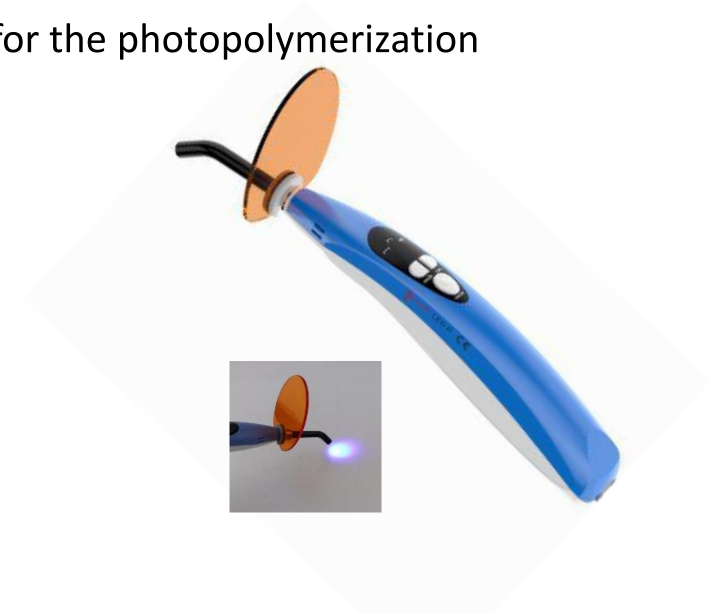
The selected polymerization method is **photopolymerization**:

- Works with thin layers (see microtechnology resists e.g. SU-8).
- Fast polymerization (a couple of minutes).
- Polymerized layers are stable in organic solvents.
- Layers can be built on each other.

The selected polymer is **UDMA** (urethane dimethacrylate) with **TEGDMA** (Triethylene Glycol Dimethacrylate) dilution monomer, **CQ** (Camphorquinone) photoinitiator and **EDAB** (ethyl 4-dimethylaminobenzoate) co-initiator, which is a well-known mixture in dentistry.

Emission spectrum and equipment used for the photopolymerization



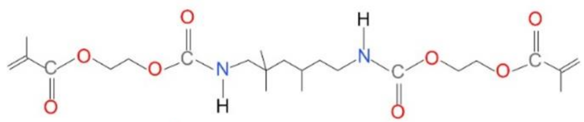


Maucoski et al.; https://doi.org/10.1371/journal.pone.0267359

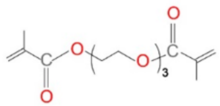
2. Nanocomposite preparation

Structure of the components:

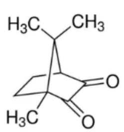
UDMA



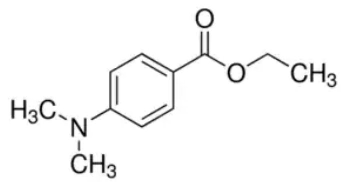
TEGDMA



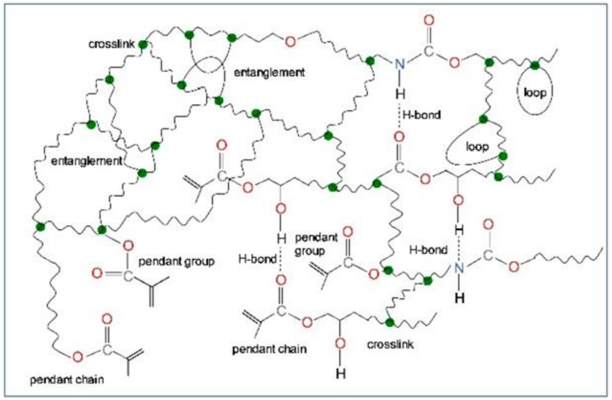
CQ



EDAB



Network and network defects of a polymer:



Materials **2019**, *12*(24), 4057

Sample types:

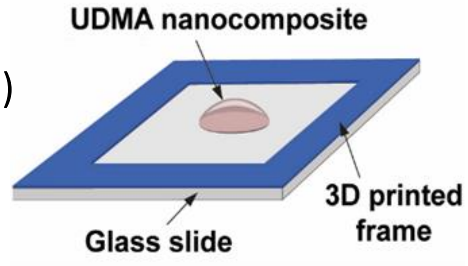
Sample ID | *concnetration of the nanorods*

- UDMA_X — 0 - bare polymer
- UDMA_AU1 — 0.1236 m/m%
- UDMA_AU2 — 0.182 m/m%

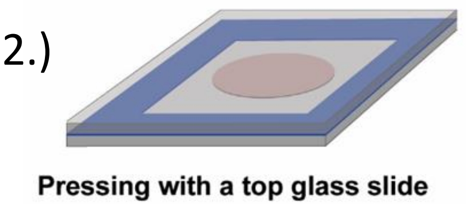
3. Fabrication methods – Sandwich Pressing

3 steps of the sample preparation

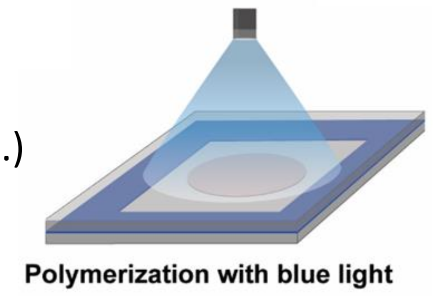
1.)



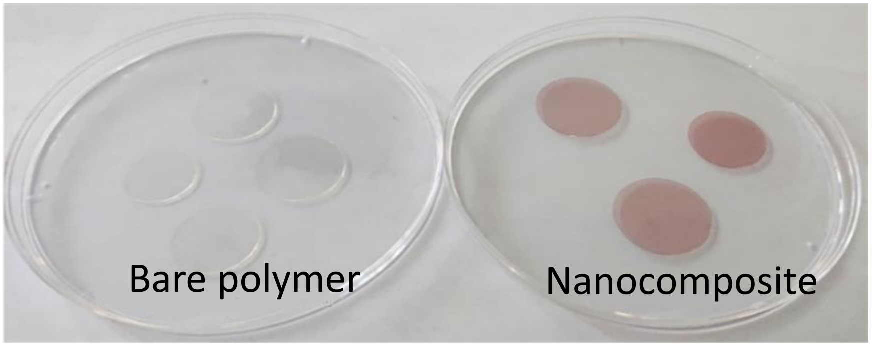
2.)

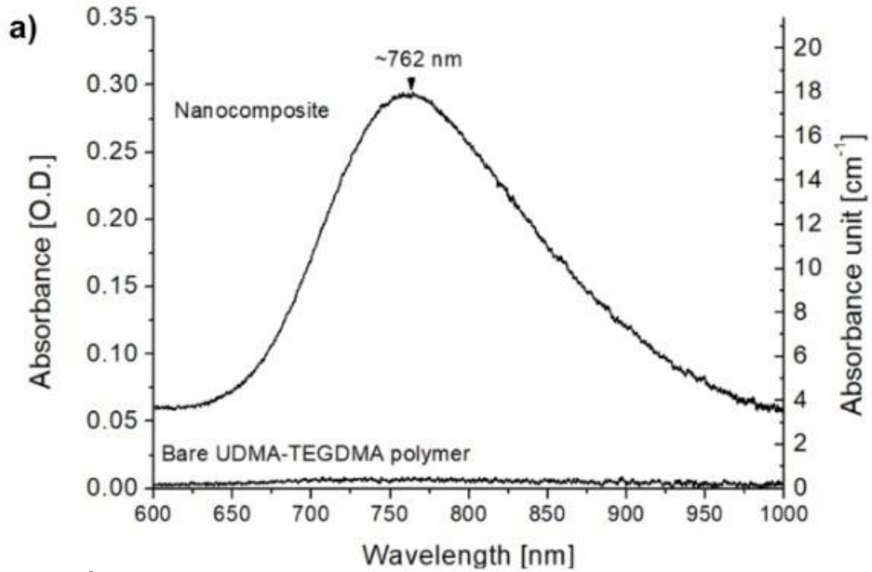


3.)



Images of the bare and the doped samples





Challenges:

- ➢ the viscosity needs to be controlled,
- ➢ layer uniformity needs to be controlled (pressing).

4. Nanorod characterization- STEM

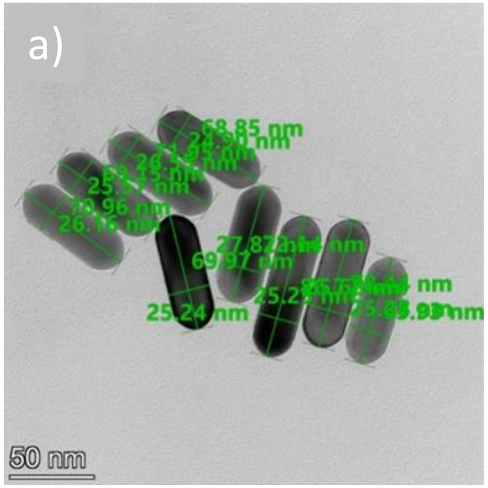
a) STEM image of the gold nanorods on a carbon filter

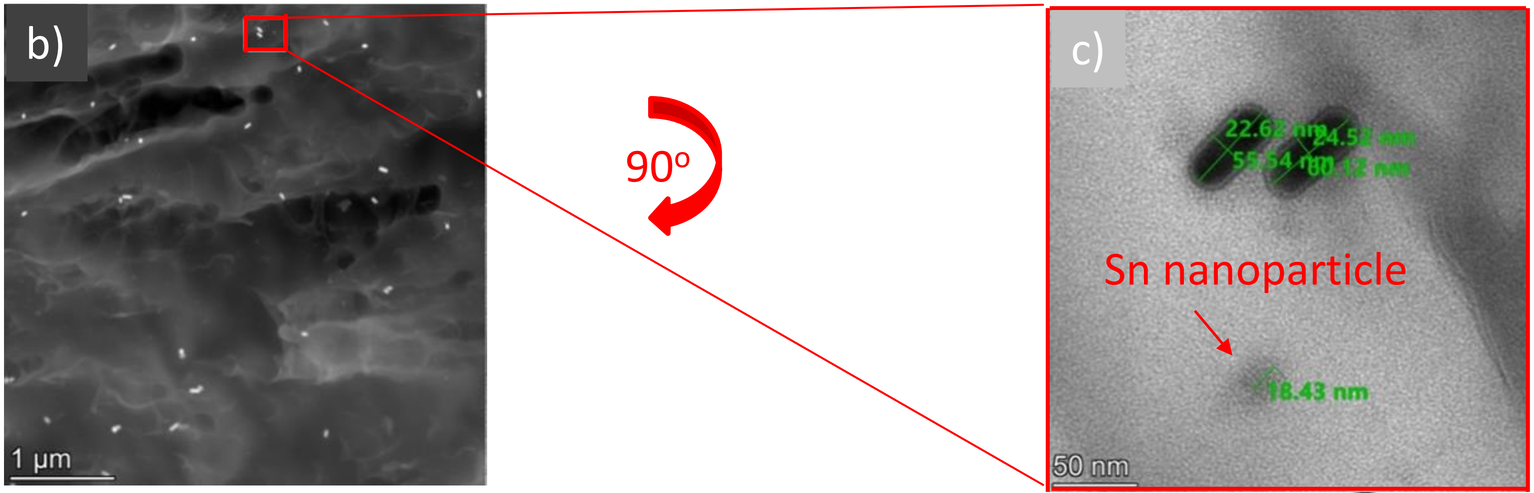
➡ Size of the nanorods: 76 ± 8 nm and 26 ± 2 nm

b) HAADF STEM image of the implanted nanorods inside the polymer matrix

➡ Distribution of the nanorods: 9 - 20 μm^{-3}

c) HRTEM image of nanoparticles inside the polymer matrix

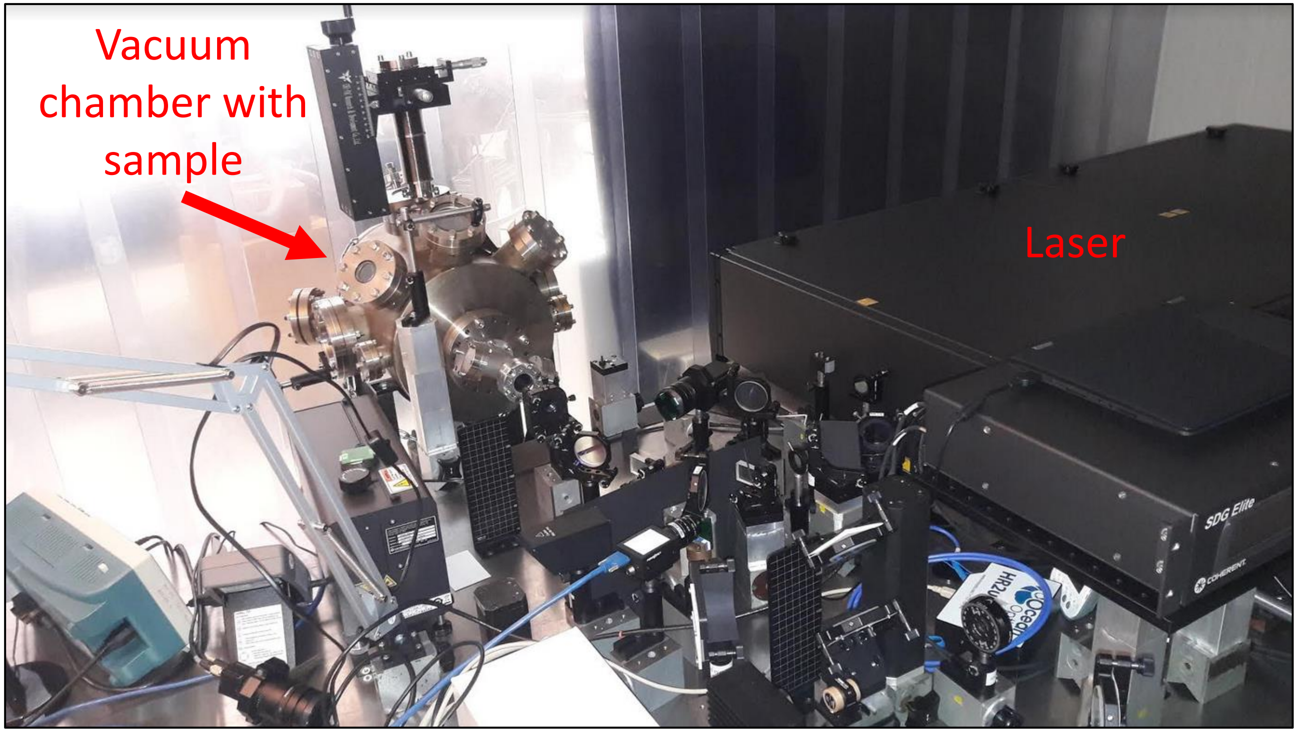




5. Laser irradiation experiments

Main laser parameters:

The setup at Wigner Research Centre for Physics



Ti:Sa based chirped-pulse two-stage amplifier-laser system (Coherent Hydra)

Smallest pulse length: 40 fs

Central wavelength: 795 nm

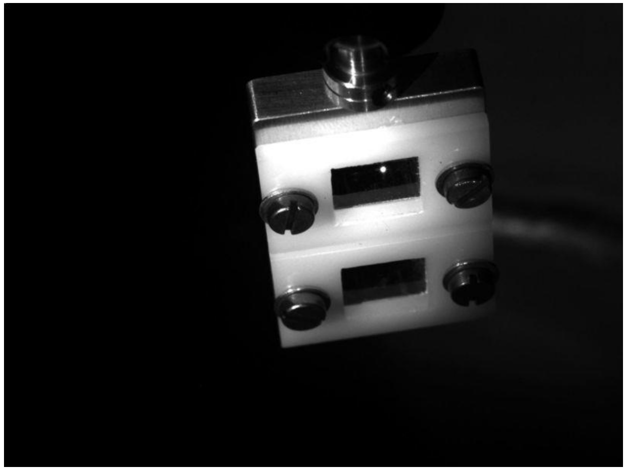
Repetition rate: 10 Hz

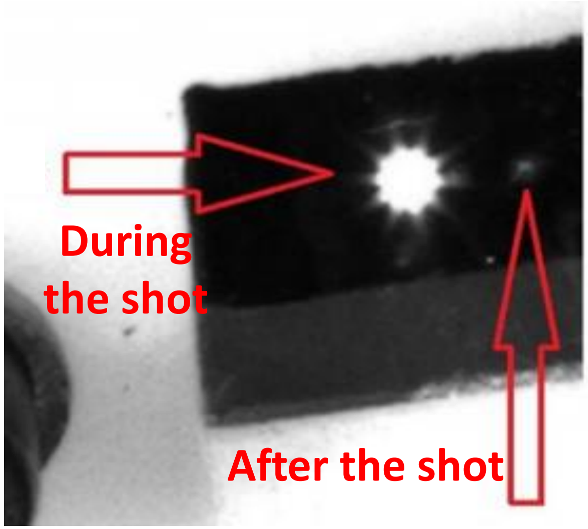
Max. pulse energy: 30mJ

The pressure in the vacuum chamber: ~10^{-5} mbar

5. Laser irradiation experiments

Front-view





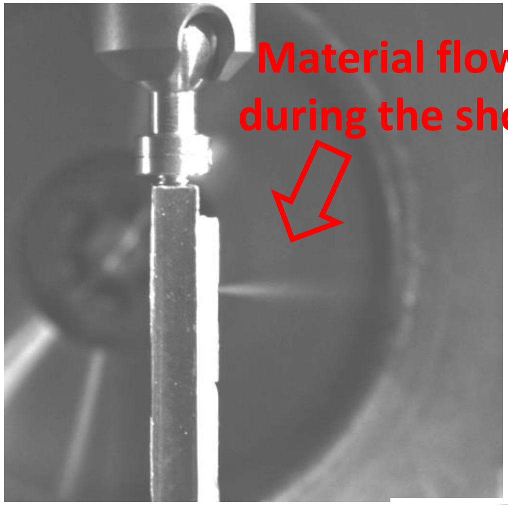
Laser beam parameters (one-sided single shot):

- Pulse length: ~50fs
- Beam diameter in the focus: ~44μm
- Irradiation energies:

  1 - 5 – 10 – 15 - 20 - 25 mJ
- Estimated peak intensity at 1mJ:

  2.66×10^{15} W/cm^2

Side-view



6. Surface investigation techniques after the irradiation

	What can we investigate?	Resolution	Presenter
Scanning electron microscopy (SEM)	2D Surface (topography) Material contrast	Vertically: material dependent, few nm	J. Kámán
White light interferometry	3D topography -> crater volume	Vertically: ~0,1 nm Horizontally: less than few 100 nm	Á. Nagyné-Szokol
Raman spectroscopy	Molecular bonds	Spot size of the laser: ~ 1,3 um	M. Veres

7. Scanning electron microscopy (SEM)

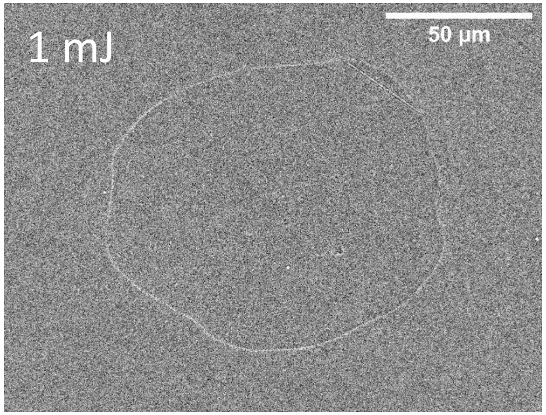
TESCAN MIRA3 SEM at Wigner Research Centre for Physics

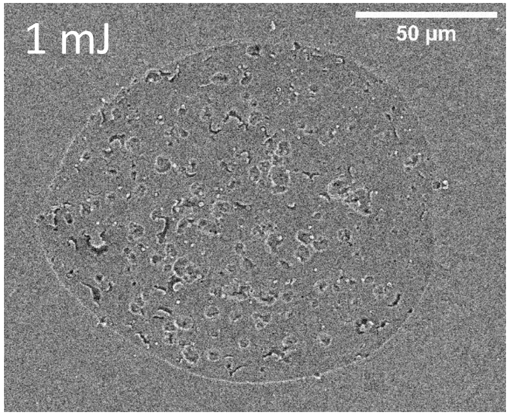
Measurement parameters for the non-conductive samples:

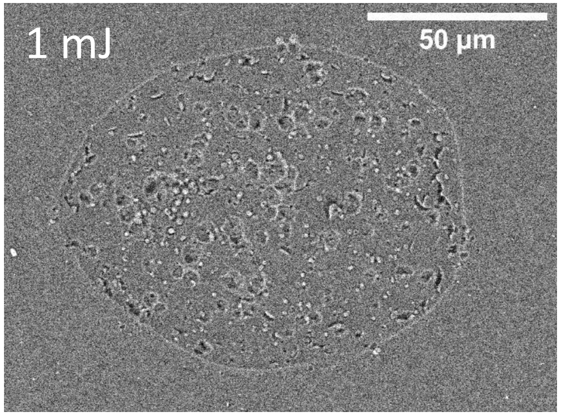
- Detectation mode: Back-scattered electrons (BSE)
- Low vacuum mode: 50 Pa
- SEM HV: 8.0 kV
- Stage tilt: 0°
- Magnifications:
  - 4.00 kx
  - 6.40 kx

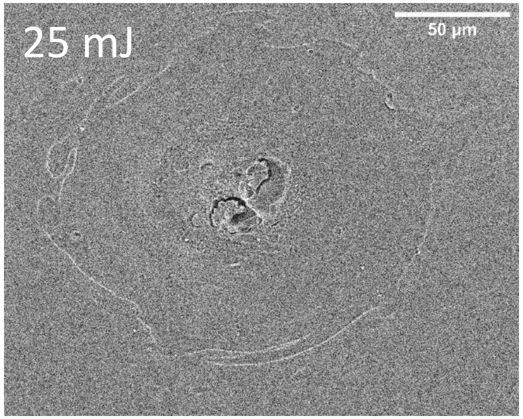
7. Surface structure of the laser ablated area, investigated by SEM

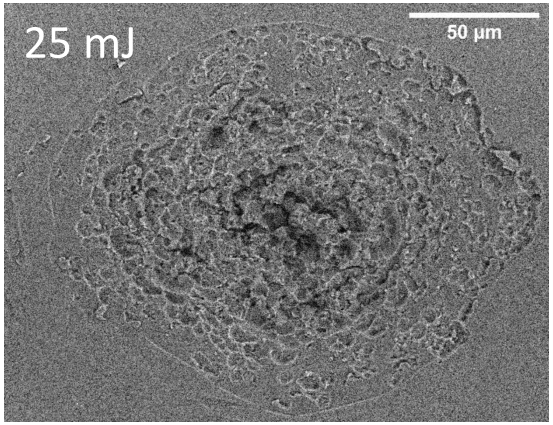
UDMA_X | **UDMA_AU1** | **UDMA_AU2**

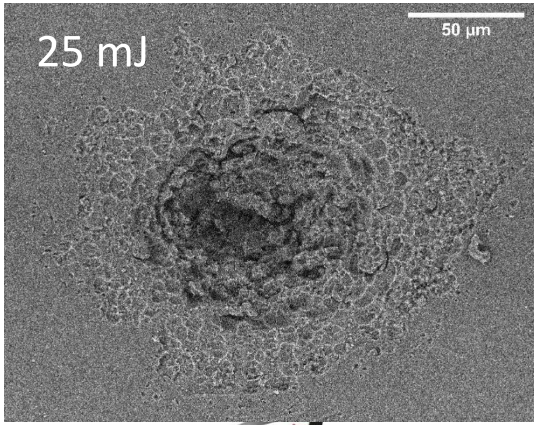




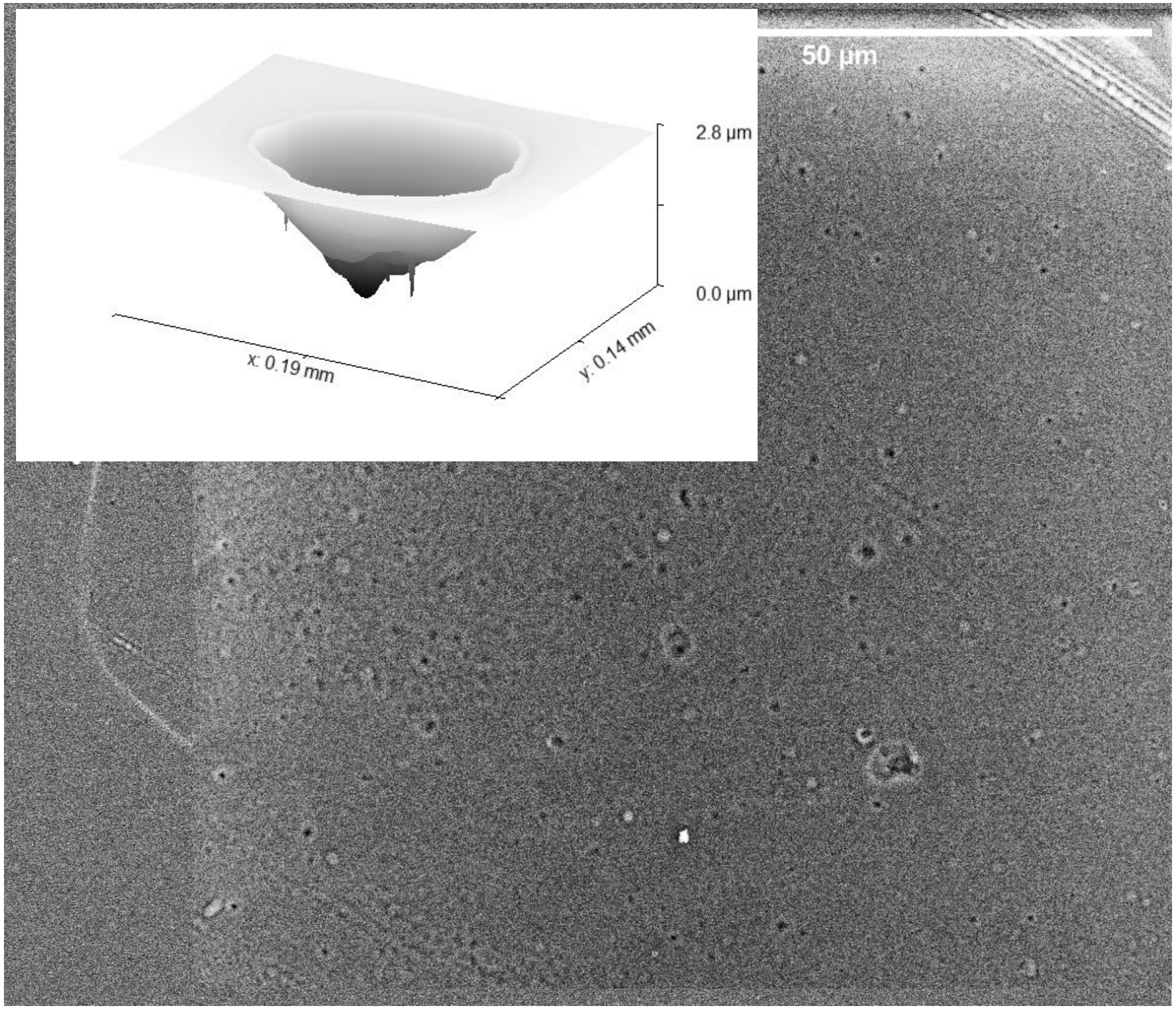








7. Surface structure of the laser ablated area

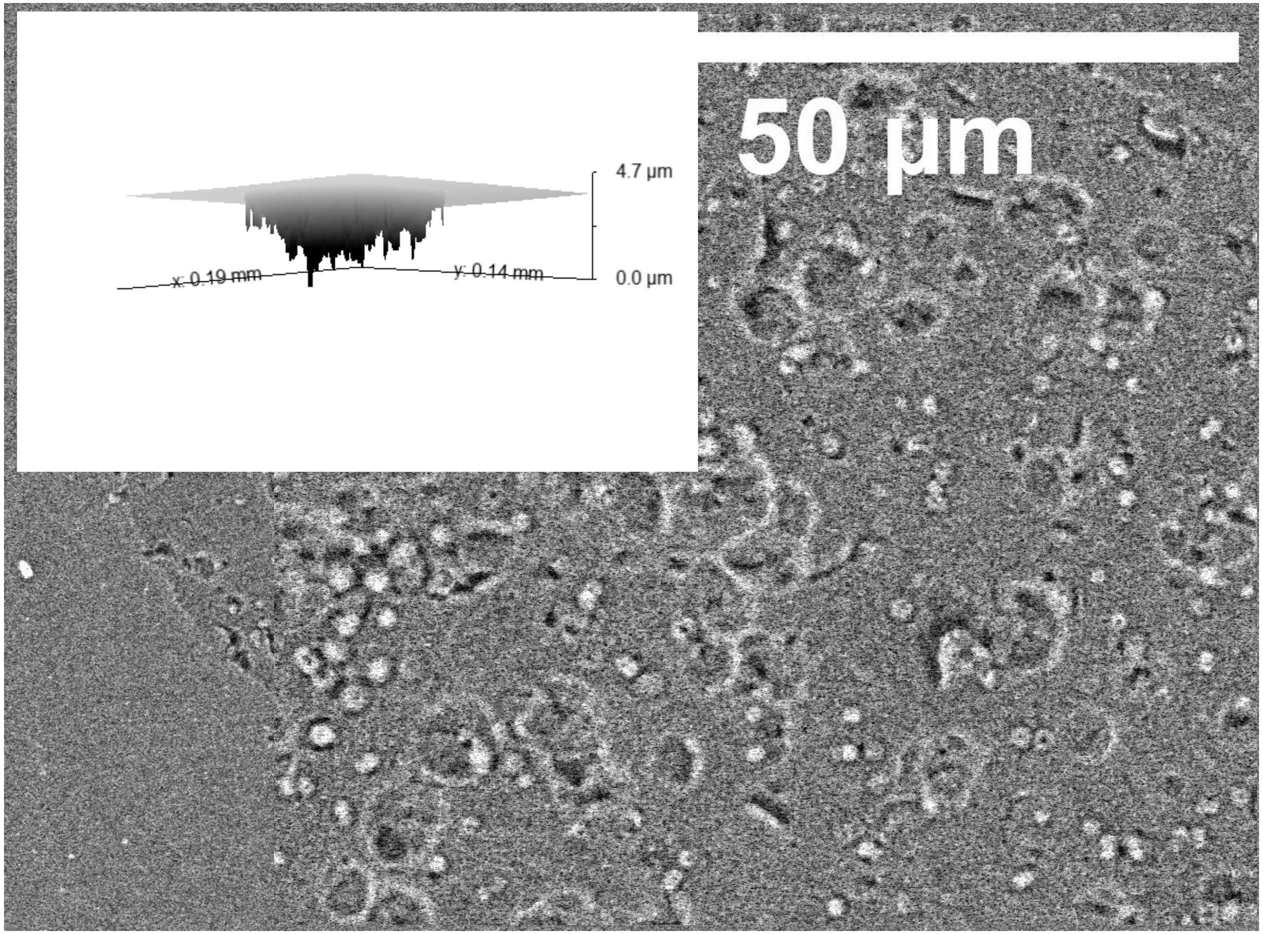


Undoped sample, 1 mJ

Diameter of the small depressions on the surface of the crater: 505 nm ± 180 nm

Estimated depth of the small depressions on the surface of the crater based on white light intermerometry image: 380-600 nm

7. Surface structure of the illuminated area

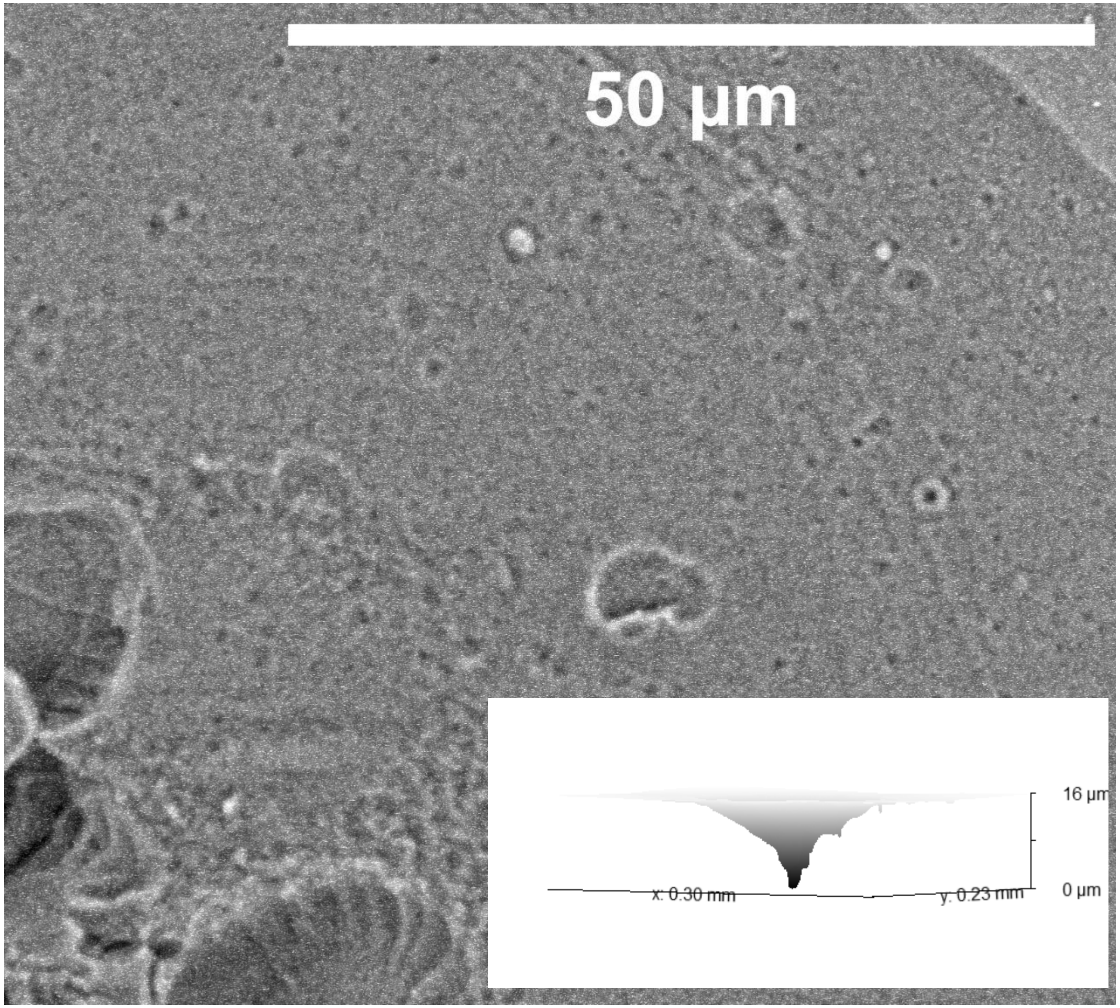


Au2 sample, 1 mJ

Diameter of the small depressions on the surface of the crater: 658 nm ± 217 nm

Estimated depth of the small depressions on the surface of the crater based on white light intermerometry image: 900 nm ± 280 nm

7. Surface structure of the illuminated area

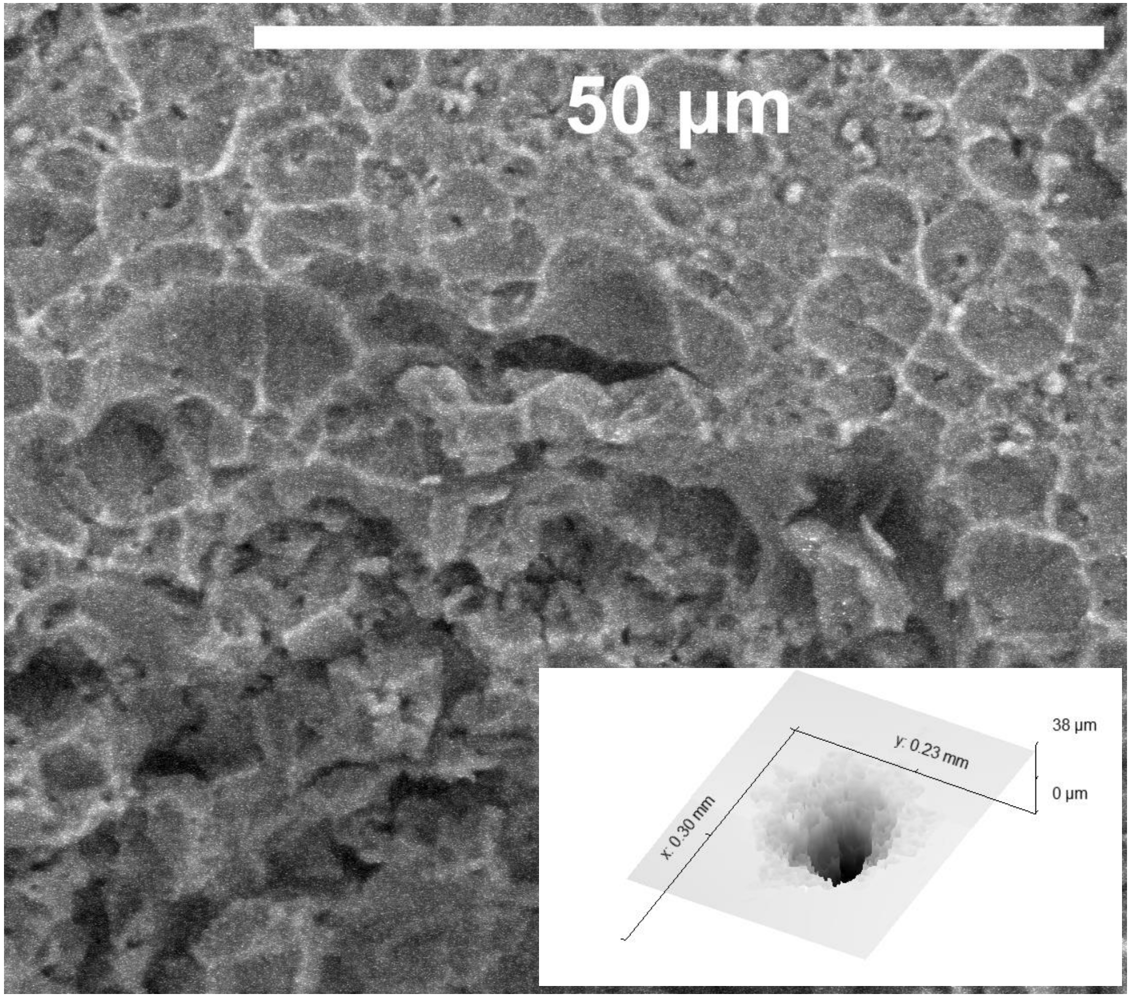


Undoped sample, 25 mJ

Diameter of the small depressions on the surface of the crater:
517 nm ± 128 nm

Estimated depth of the small depressions on the surface of the crater based on white light intermerometry image:
500 nm – 1200 nm

7. Surface structure of the illuminated area



Au2 sample, 25 mJ

Diameter of the small depressions on the surface of the crater:
770nm ± 360 nm

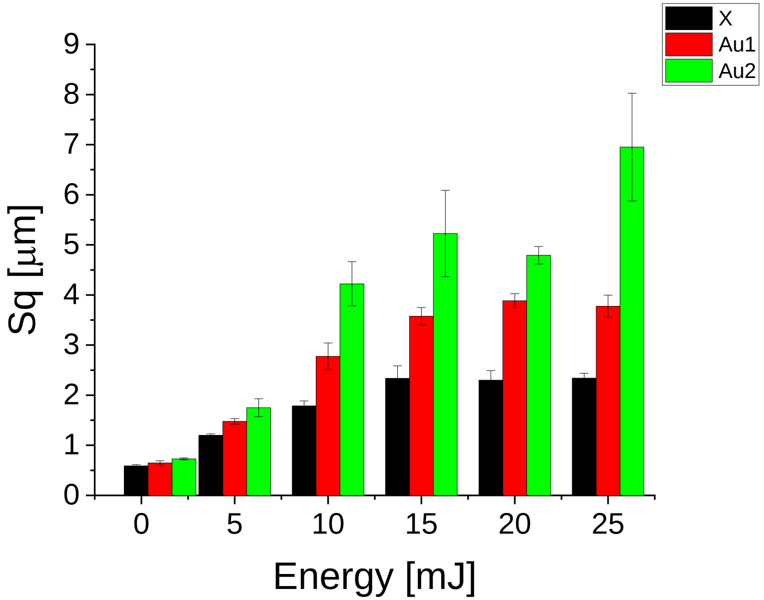
Estimated depth of the small depressions on the surface of the crater based on white light intermerometry image:
3000 nm – 5000 nm

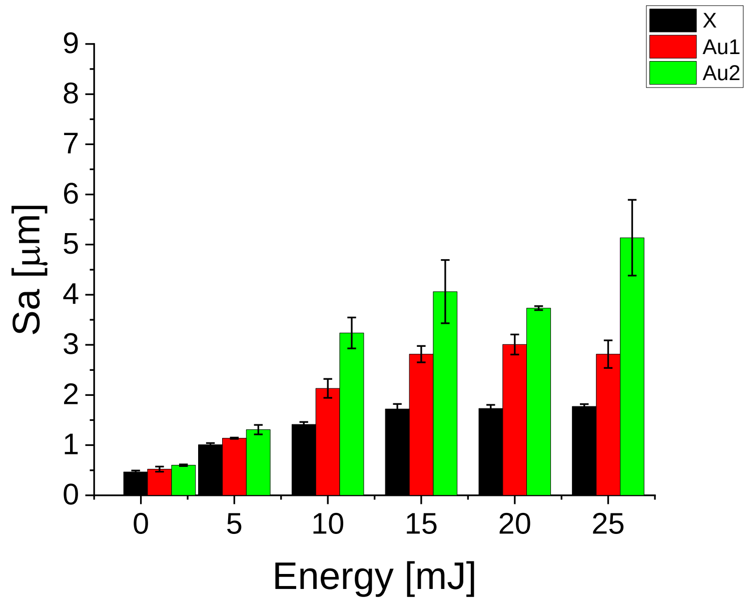
8. Surface roughness based on White light interferometry measurements

The built-in functions of Gwyddion software were used for the evaluation.

Sq: mean square roughness (RMS) of height irregularities, computed from 2nd central moment of the surface data values

Sa: mean roughness of height irregularities. It is calculated from the sum of absolute values of data differences from the mean.





X: undoped sample

Conclusion

Gold nanorod doping highly modified the surface morphology during femtosecond laser irradiation

During the laser irradiation, additional small depressions are formed in the crater, and their number and depth increase with the laser intensity and the doping concentration

Sq and Sa values are significantly different according to the doping concentration and they are suitable for distinguishing the samples after irradiation.

Thank you for your attention!