Gold nanorods induced nanoplasmonic effect on structural changes during high intensity laser irradiation of UDMA polymer

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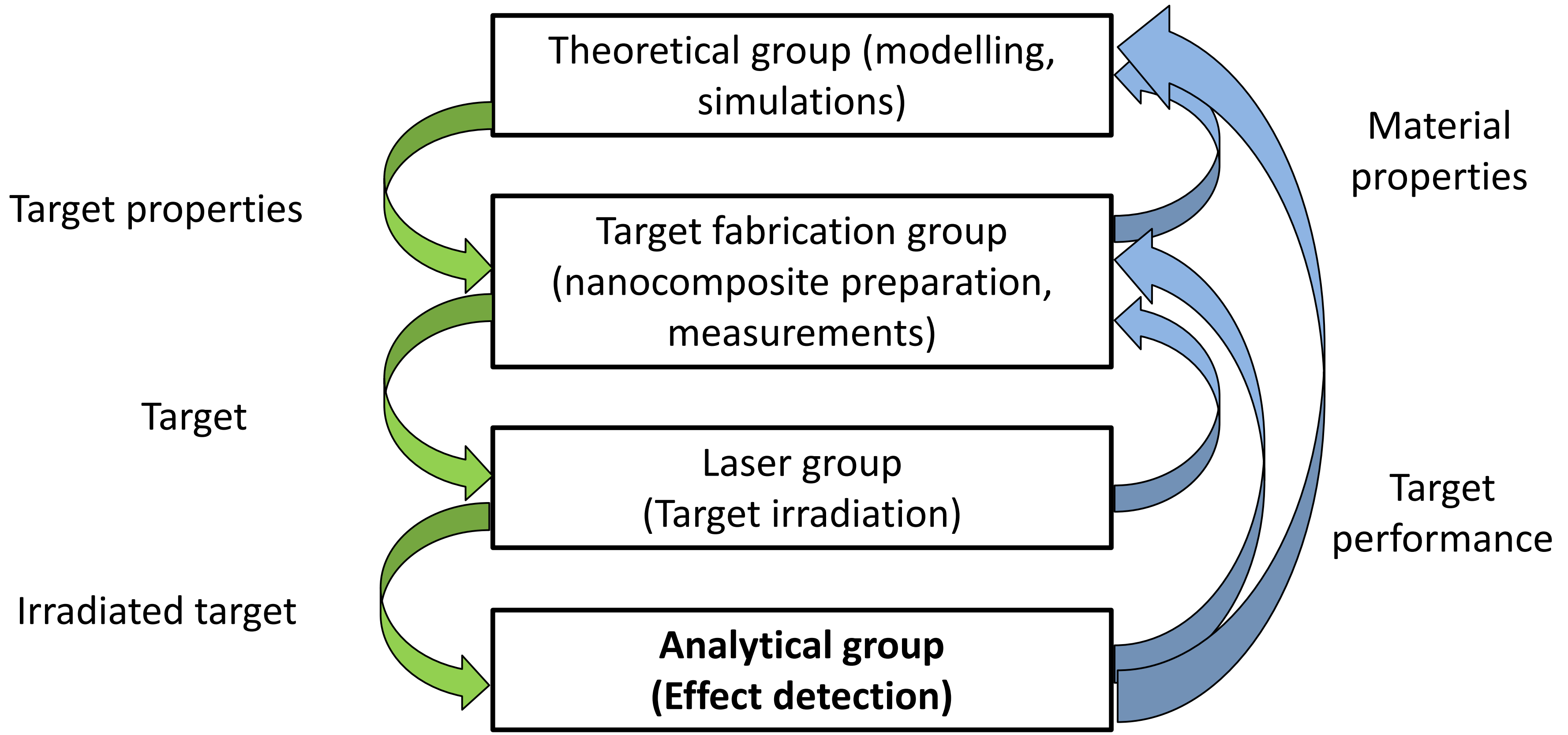
NAPLIFE project

Nano-Plasmonic 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. Raman-spectroscopy on irradiated targets
7. White light interferometry on irradiated targets

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 nano rods. Calculations via solving the Maxwell equations, and evaluating the Ohmic heating were performed.

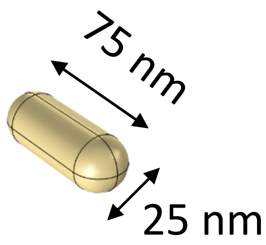
Simulations were performed to:

Optimize the particle geometry considering the RI of the target.

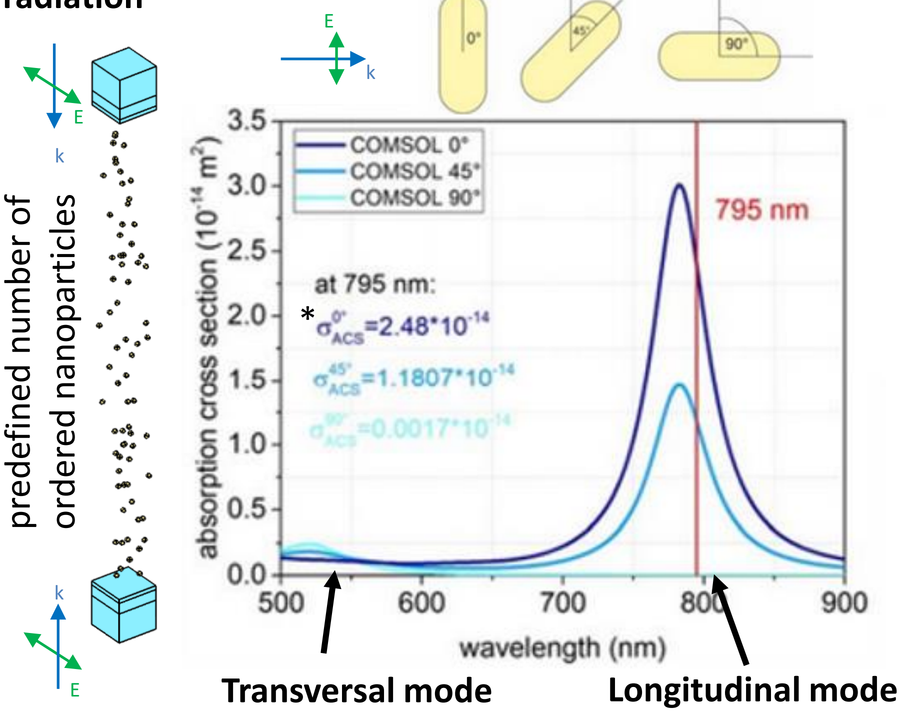
Investigate the effect of random orientation and distribution.

Maximize the absorption (and heating) along 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:

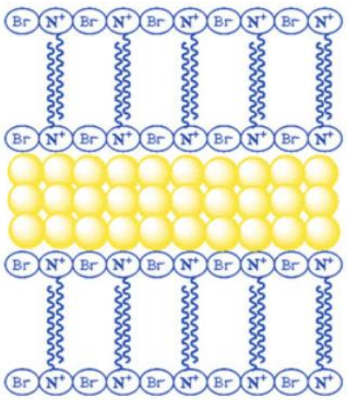
- **Uniform particle distribution,**
- **Avoid particle aggregation,**
- **Long-time particle stability,**
- **Possibility to build layers on each other.**

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

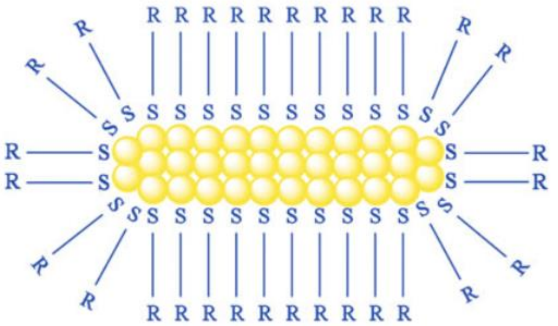
- Particle capping should be controlled.
  - Hydrophilic (synthesis),
  - Hydrophobic (for doping).

- Nanoparticle phase transfer

Au- CTAB (cetrimonium bromide)



Au-DDT (dodecanethiol)



[El Khoury, 2009, 10.1039/b901826c]

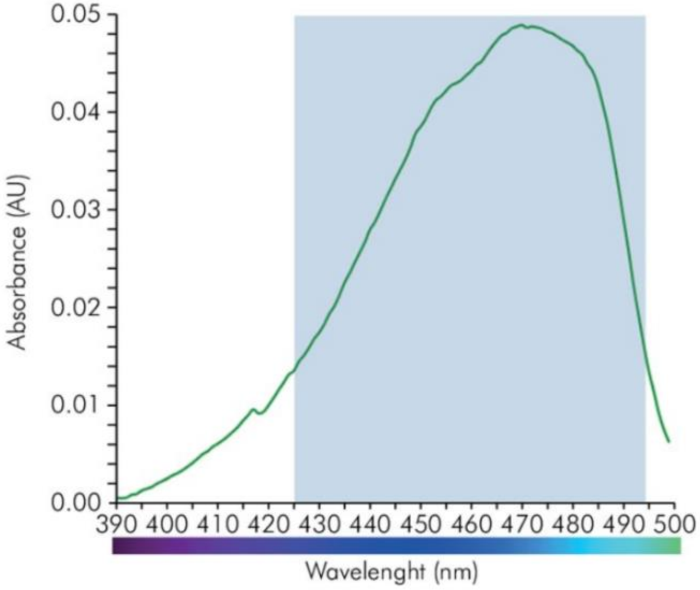
2. Nanocomposite preparation

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.

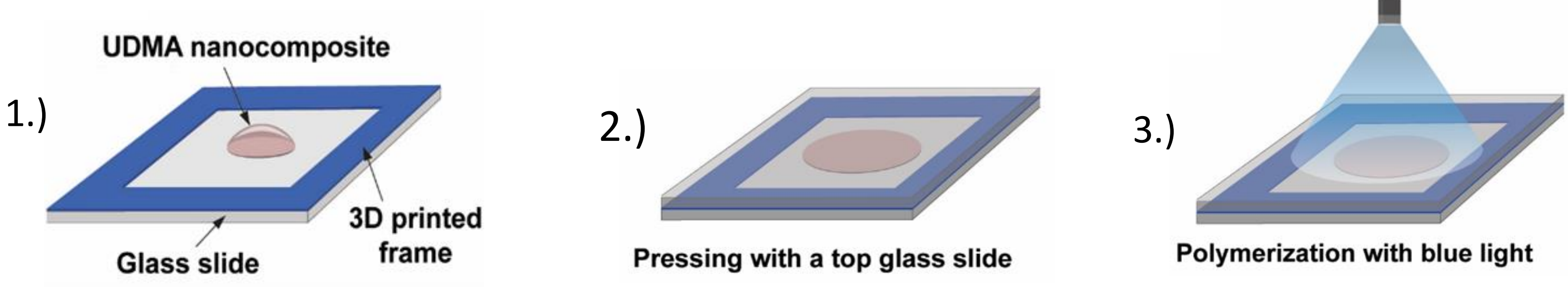
The selected polymer is **UDMA** (urethane dimethacrylate) with **TEGDMA** (Triethylene Glycol Dimethacrylate) dilution monomer, **CQ** (Camphorquinone) photoinitiator and **EDAB** (ethyl 4-dimethylaminobenzoate) co-initiator, which is a well-known mixture in dentistry.

Emission spectrum and equipment used for the photopolymerization

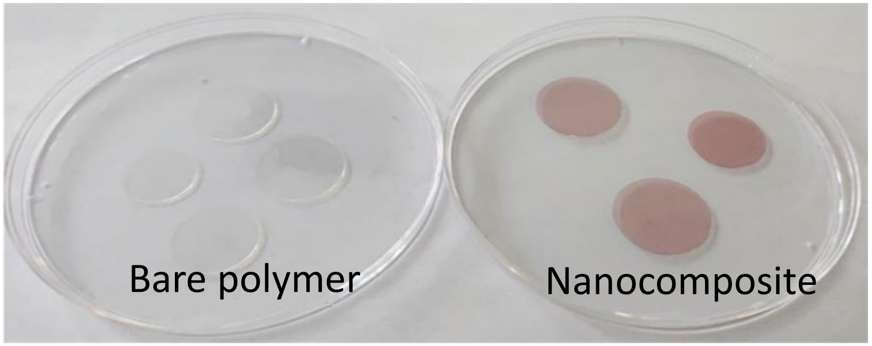


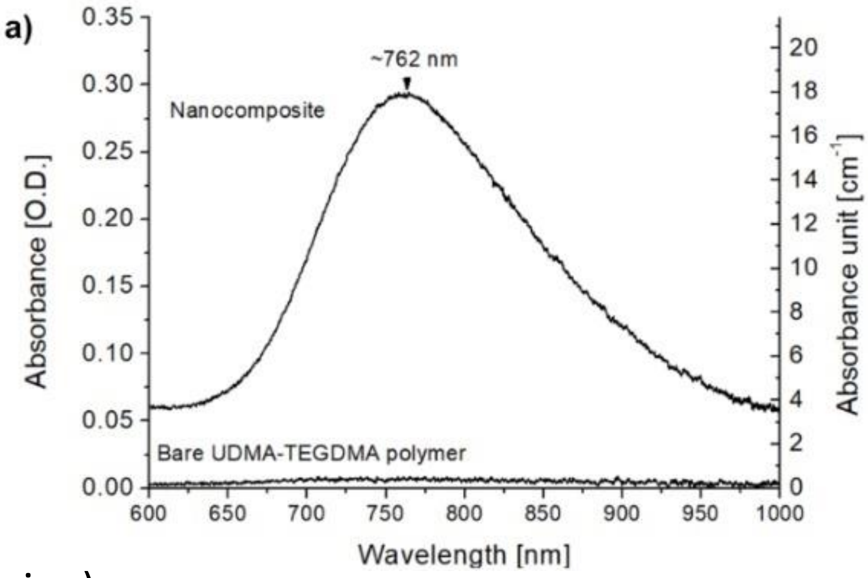
3. Fabrication methods – Sandwich Pressing

3 steps of the sample preparation



Photographs of the bare and the doped samples





<u>Challenges:</u>

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

4. Nanorod characterization- STEM

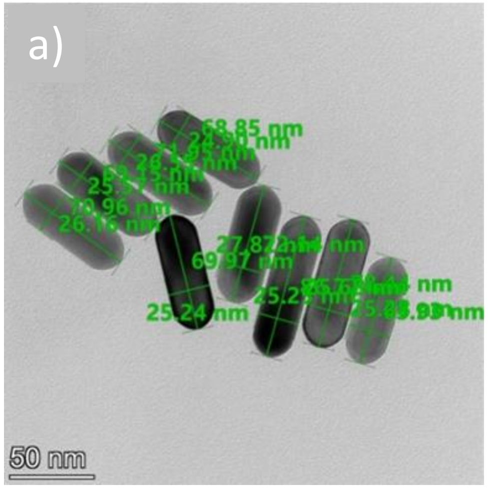
a) STEM image of the gold nanorods on a carbon filter

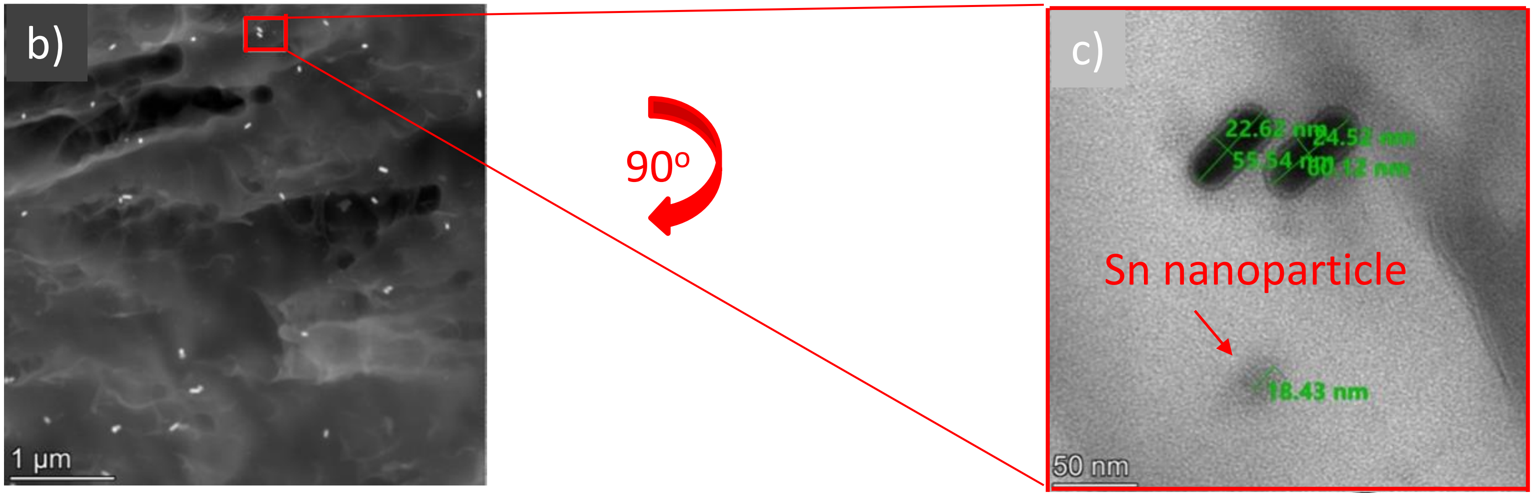
➡ Size of the nanorods: 76 ± 8 nm and 26 ± 2 nm

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

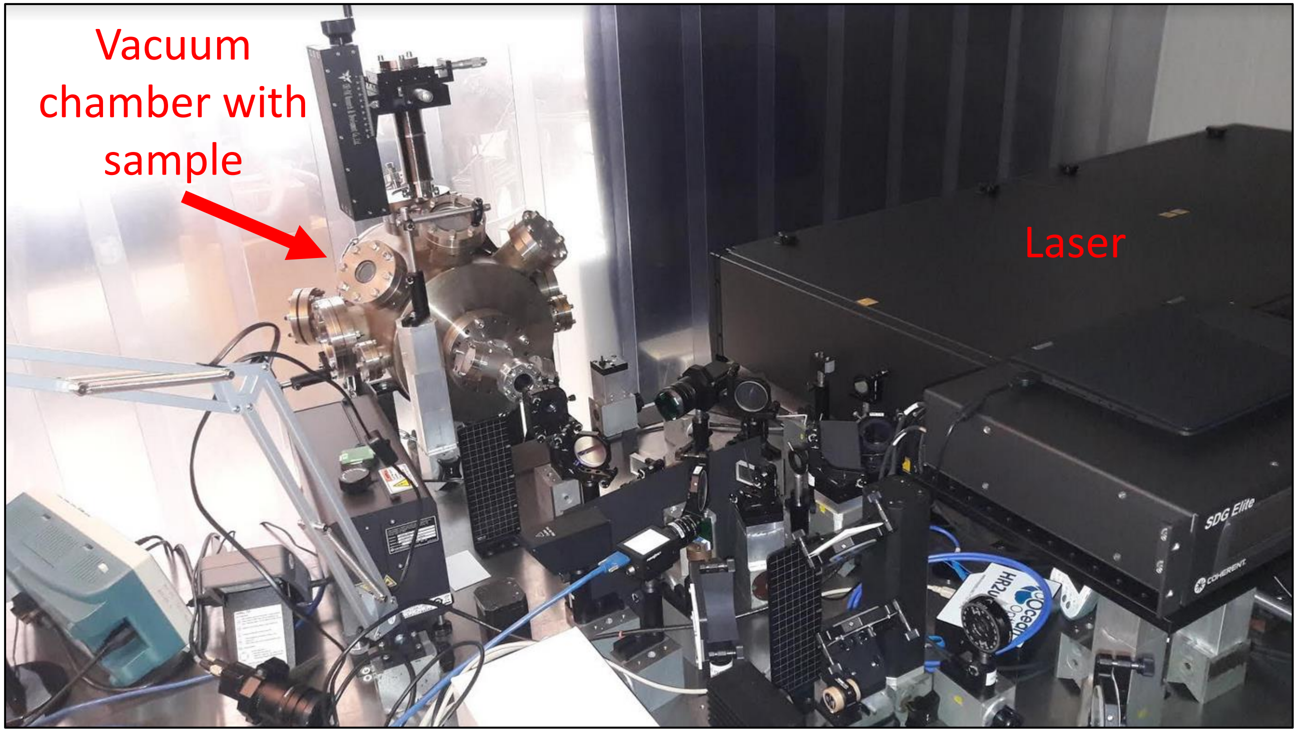




5. Laser irradiation experiments

Main laser parameters:

The setup at Wigner Research Centre for Physics



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

Smallest impulse 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

Laser beam parameters

(one-sided single shot):

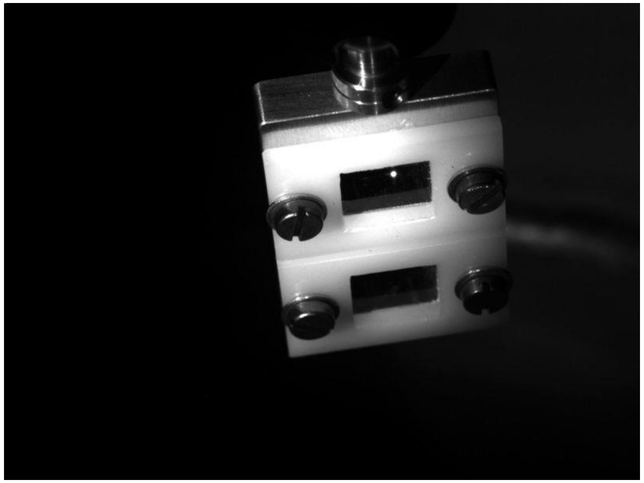
Impulse length: ~50fs

Beam diameter in the focus: ~44μm

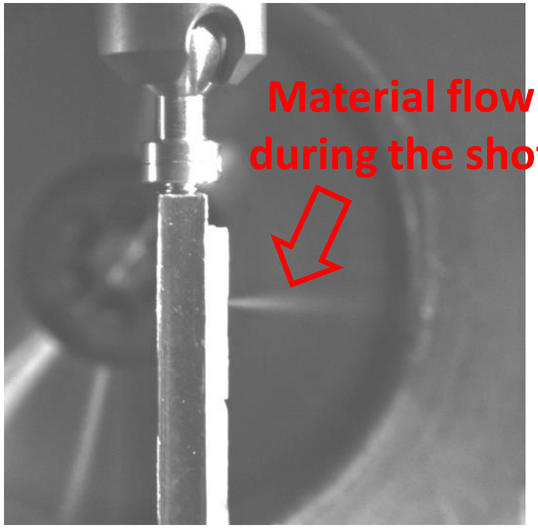
Irradiation energies vary between:

0,6 mJ – 30 mJ

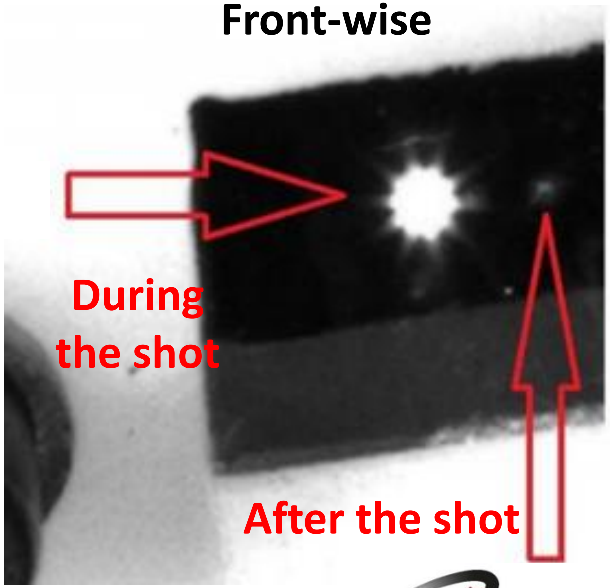
Estimated peak intensity at 1mJ: 2.66 x 10^{15} W/cm^2



Side-view



Front-wise



6. Raman spectroscopy

Renishaw inVia micro-Raman spectrometer and a LeicaDM2700 optical microscope

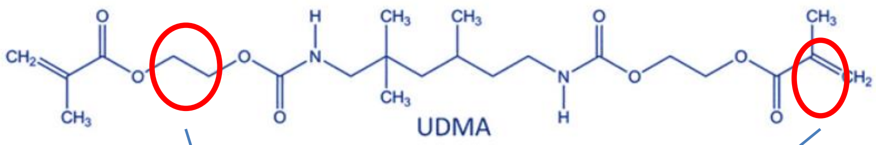
Experimental conditions

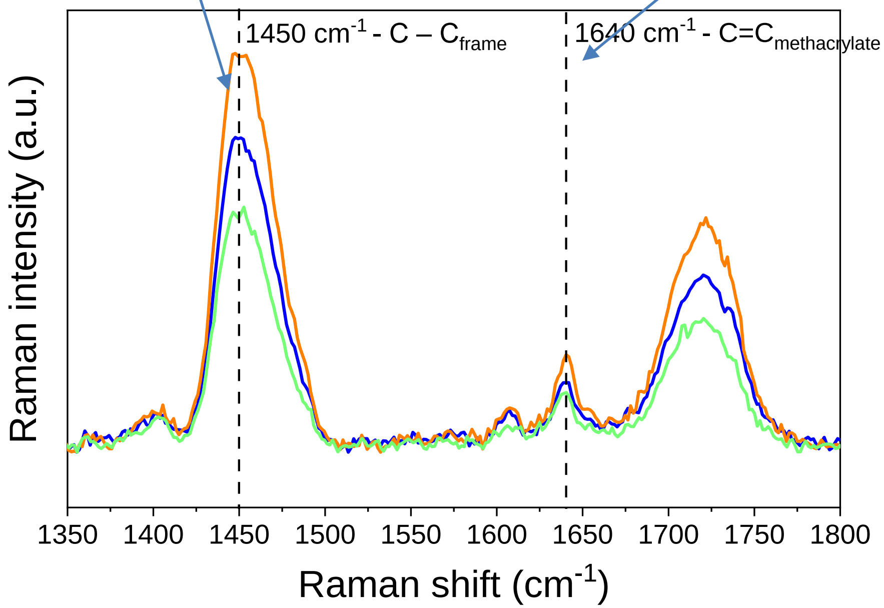
Excitation wavelength: 532 nm
Focus diameter: 1.3 μm
Laser power in focus: 6 mW
Exposition time: 10 s
Accumulation number: 20

5 points were averaged for each datapoint

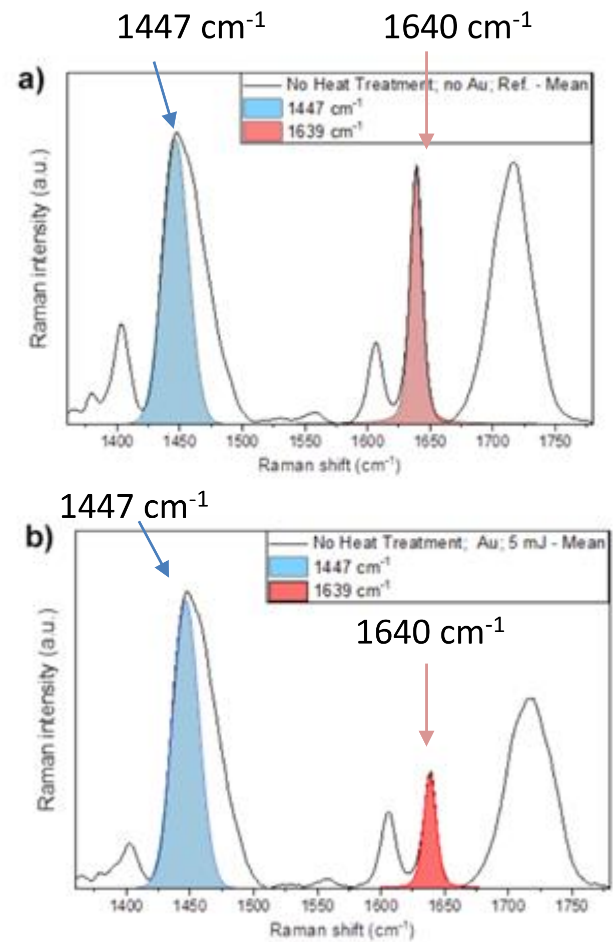
6. Raman spectroscopy

Structure of the urethane dimethacrylate (UDMA) monomer



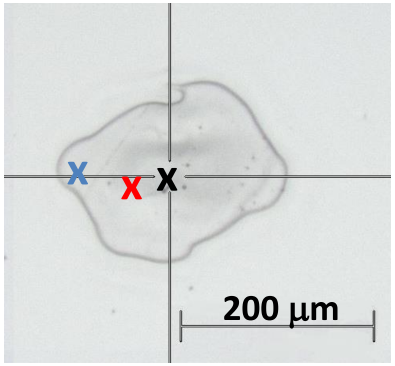


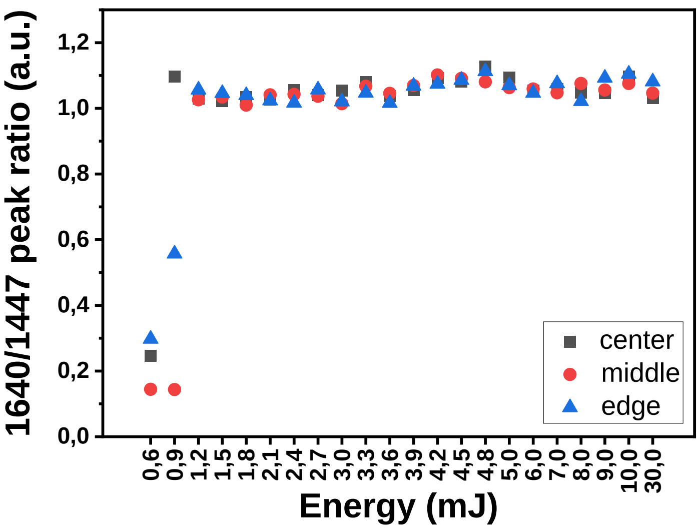
Typical Raman spectra of UDMA polymer



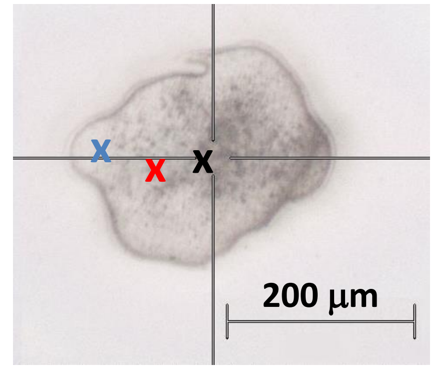
6. Raman spectroscopy on irradiated targets

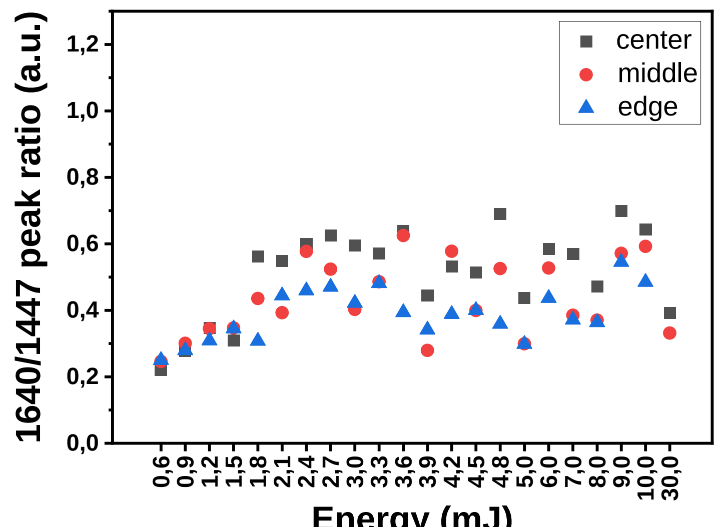
Bare polymer





Nanocomposite



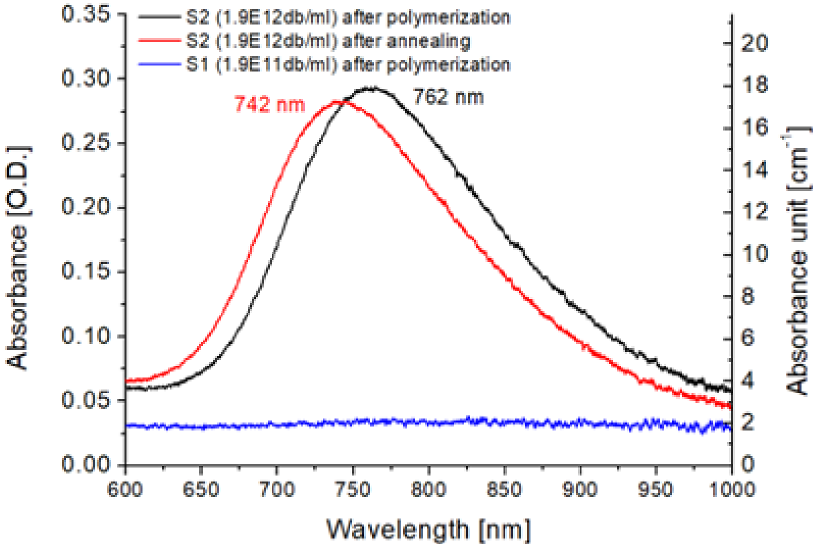


The doped and the undoped, laser irradiated targets show different tendencies!

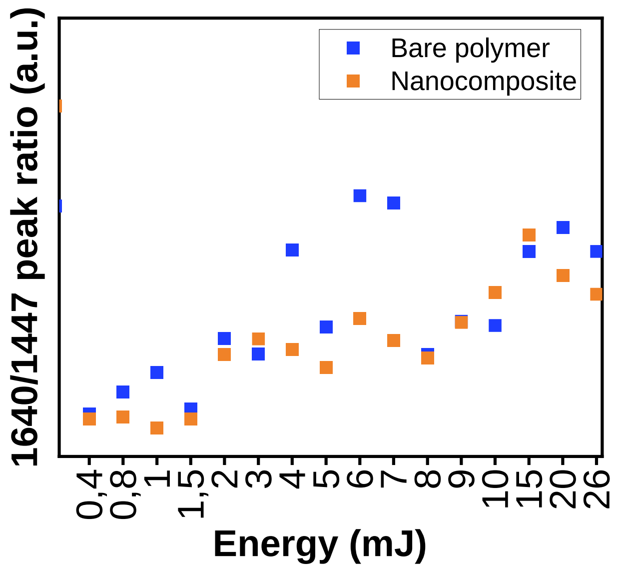
6. Targets with different nanoparticle concentrations

- Normal/ effective concentration: 1.9 x 10^{12} nps/ml
- Too high concentration: 1.9 x 10^{13} nps/ml -> aggregation of the nanorods
- Low concentration: 1.9 x 10^{11} nps/ml -> there is no effect

Optical spectra



Ratio of the Raman peaks of the doped and the undoped samples

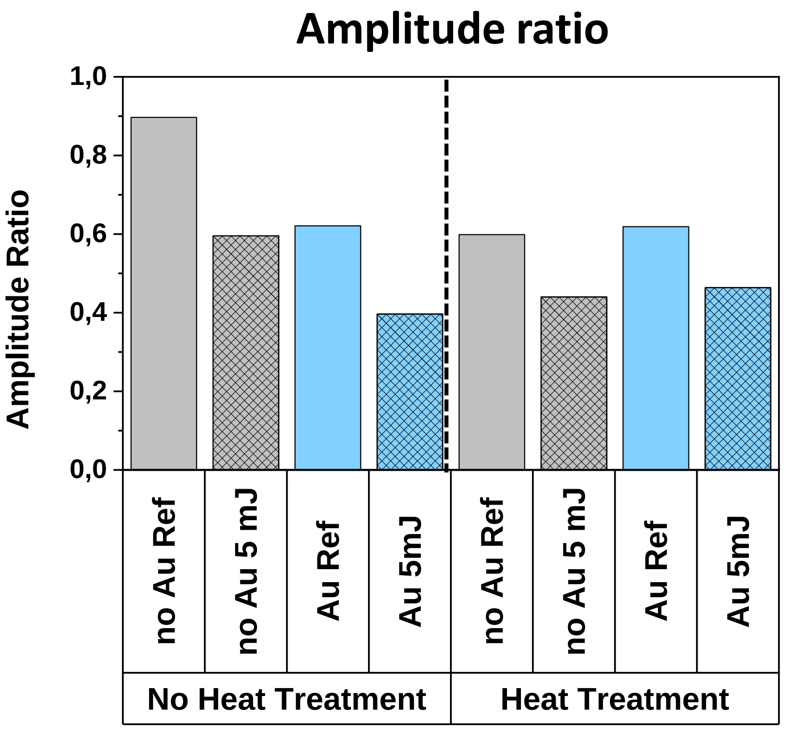


6. Raman spectroscopy: the effect of the thermal treatment

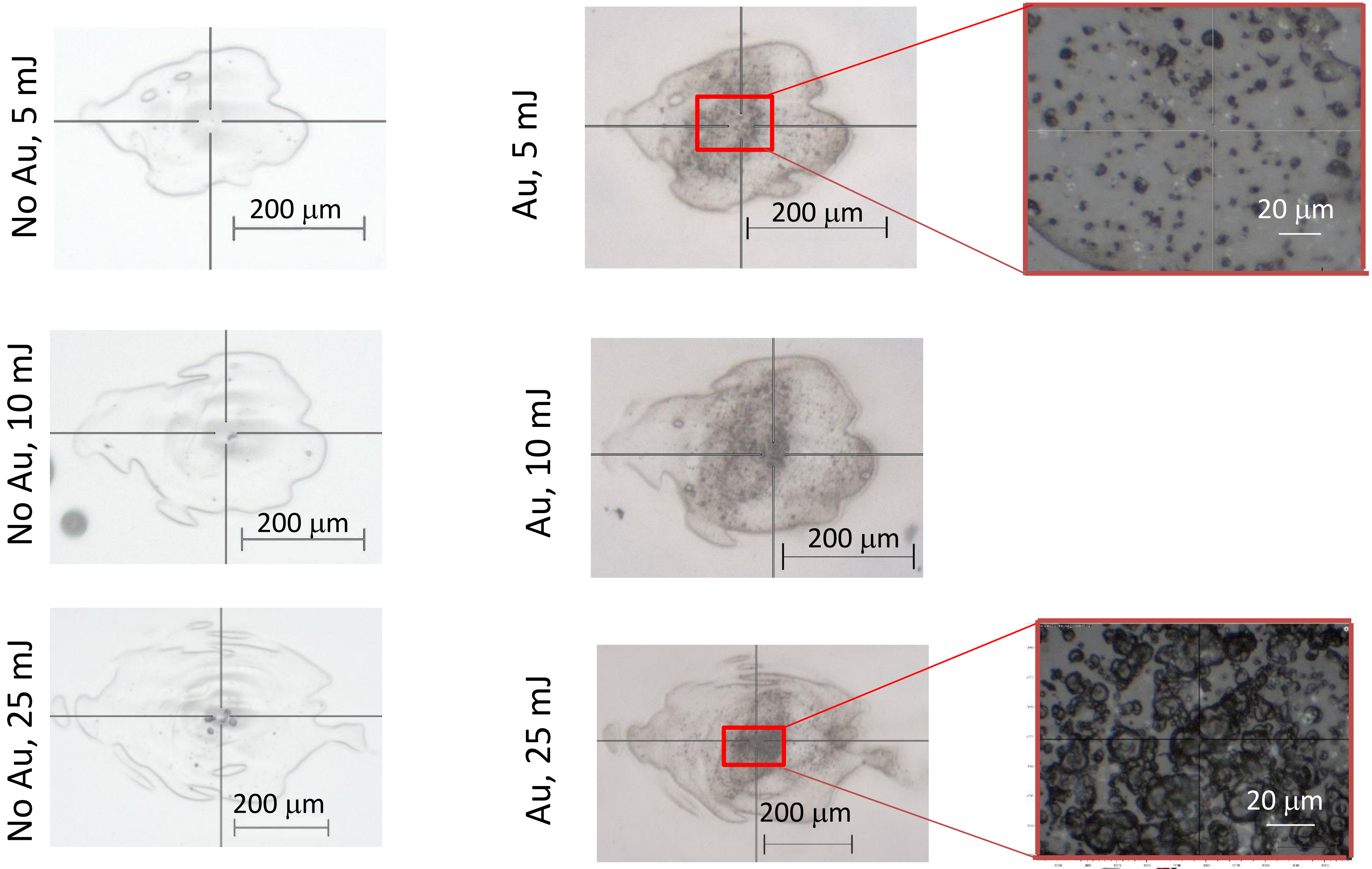
Heat treatment: 30 min at 180°C after the blue-light curing.

Observations:

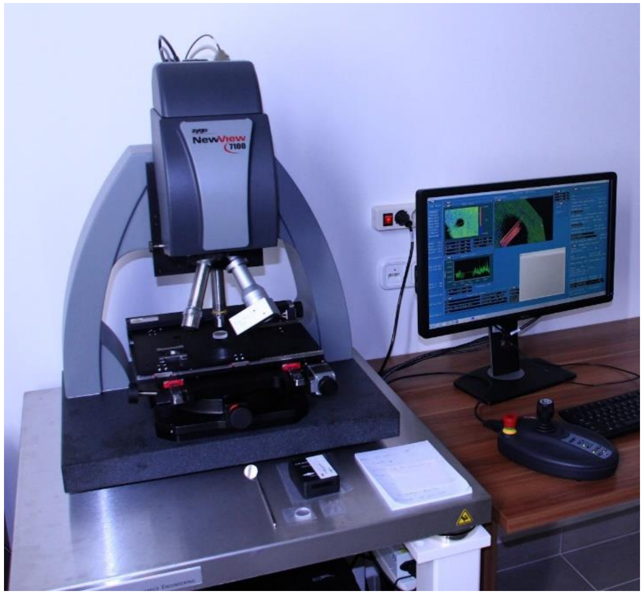
- Irradiation facilitates the polymerization process in every cases
- If heat treatment was applied, there is no significant difference between the nanorod doped and undoped samples
- The presence of the gold nanorod alone can cause the same effect in the polymerization than the heat treatment
- The best polymerization was achieved in case of „No Heat Treatment”, nanorod doped, and laser irradiated sample.



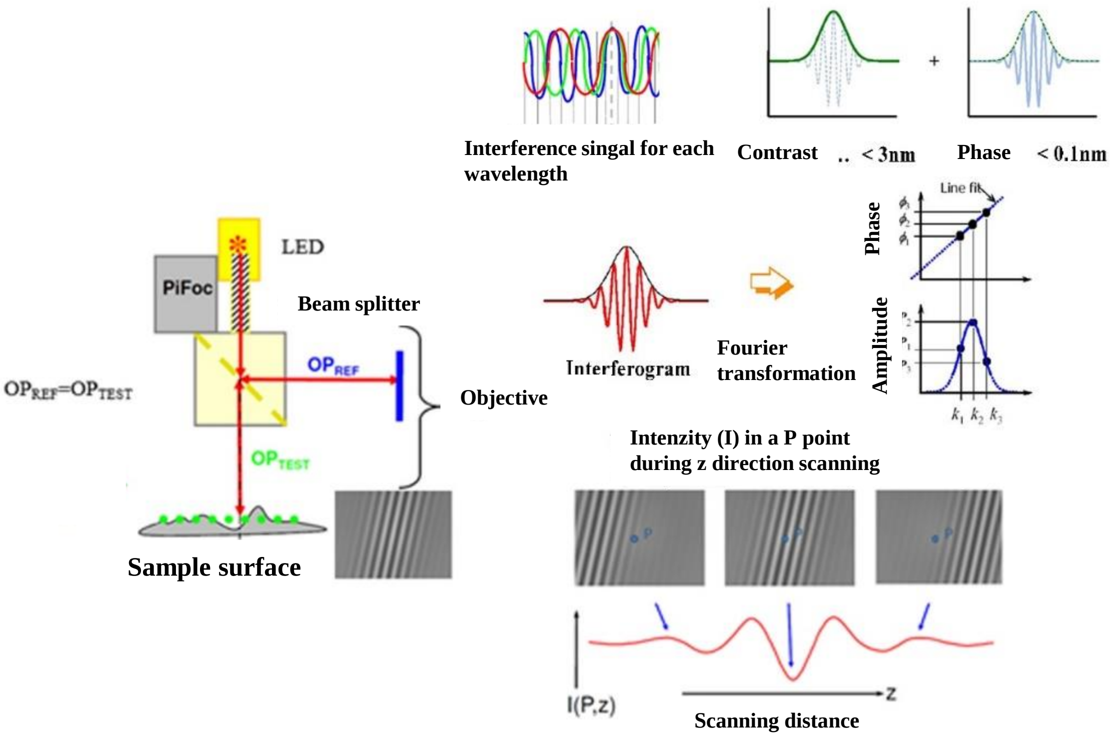
7. Surface structure of the illuminated area



7. White light interferometry measurements

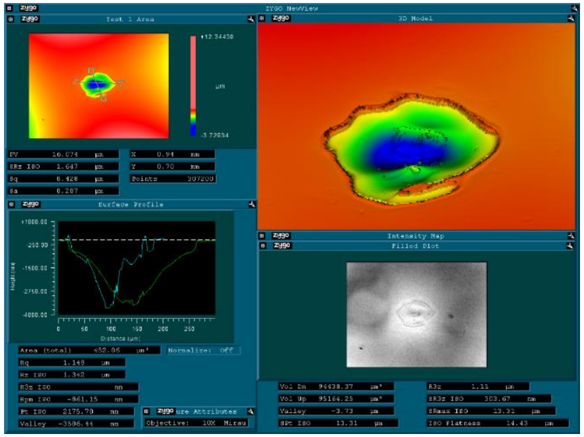


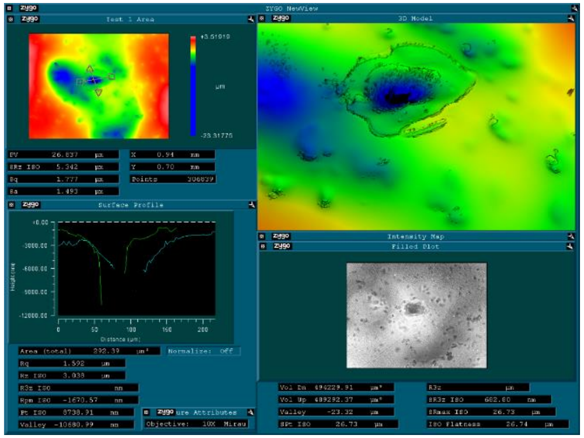
Zygo NewView™ 7100



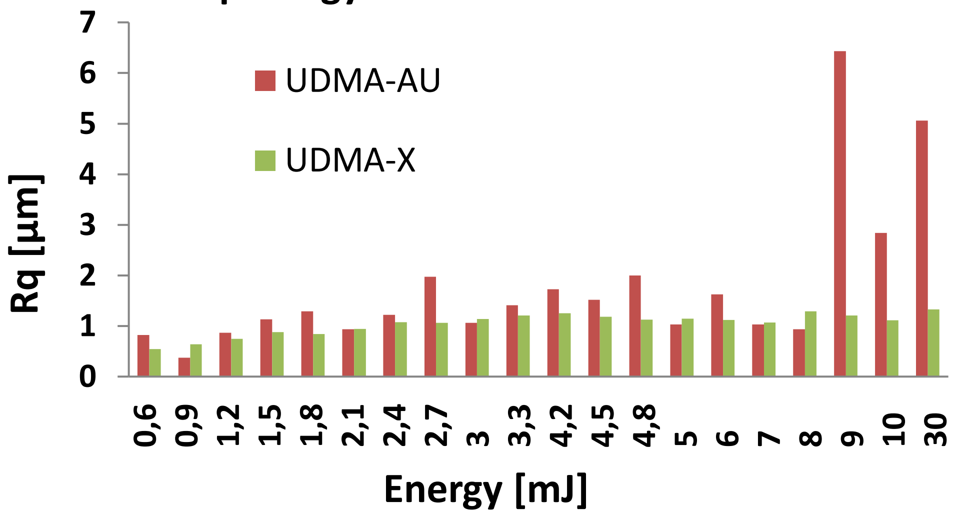
Light source: white LED (central wavelength: 580 nm, spectral width: 140 nm) , vertical resolution: 0,1 nm

7. White light interferometry measurements





Surface morphology :

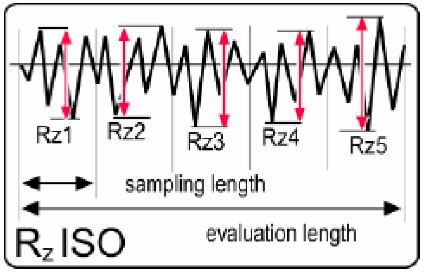


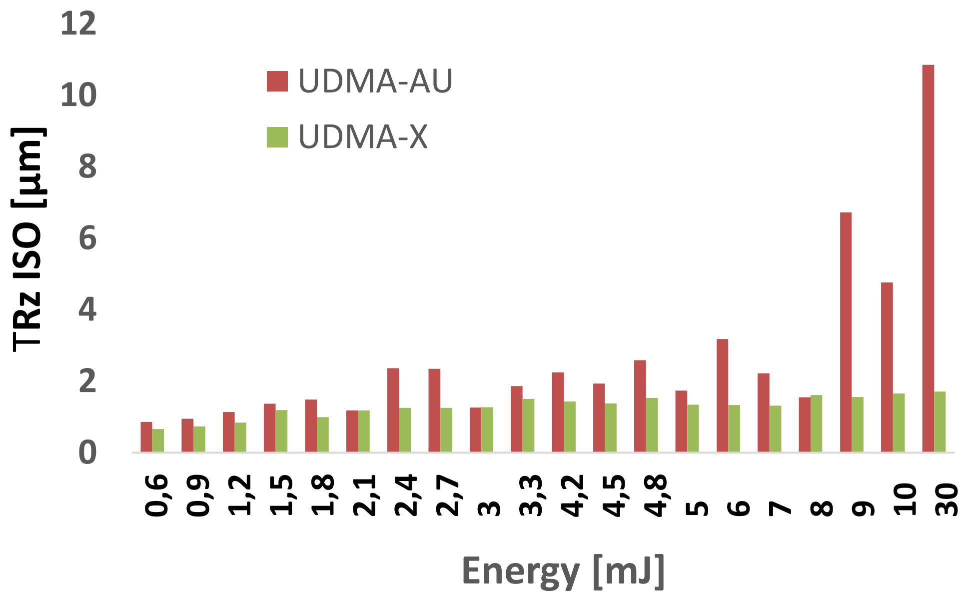
Rq - *Root-mean-square* (rms=Rq) roughness. The average of the measured height deviations taken within the evaluation length or area and measured from the mean linear surface. Available for profile and areal data. Rq is the rms parameter corresponding to Ra.

7. White light interferometry measurements

R_z ISO

Average peak-to-valley profile roughness. The average peak-to-valley roughness based on one peak and one valley per sampling length. The single largest deviation is found in five sampling lengths and then averaged.





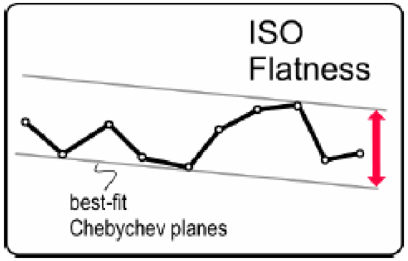
7. White light interferometry measurements

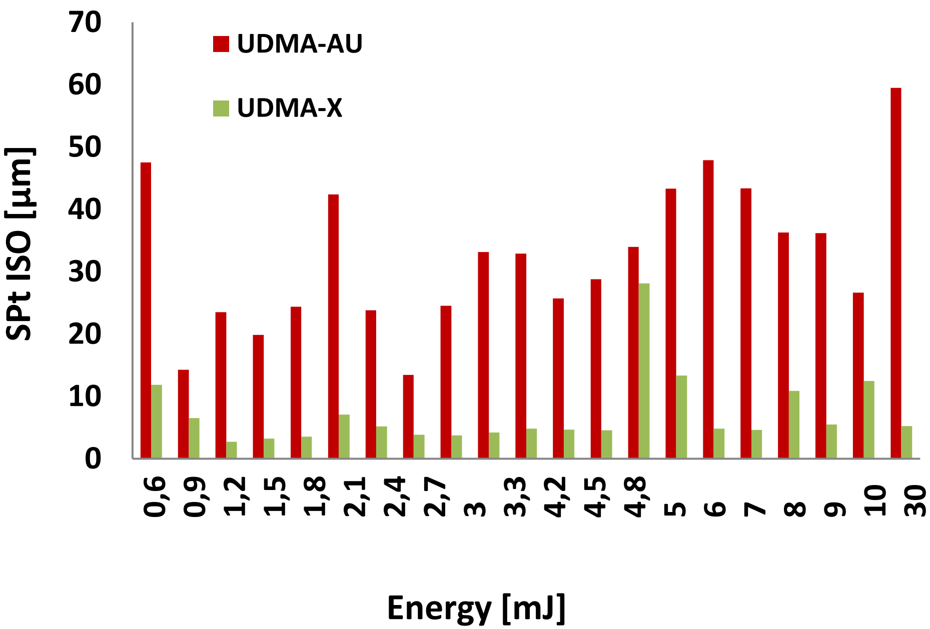
General surface parameters

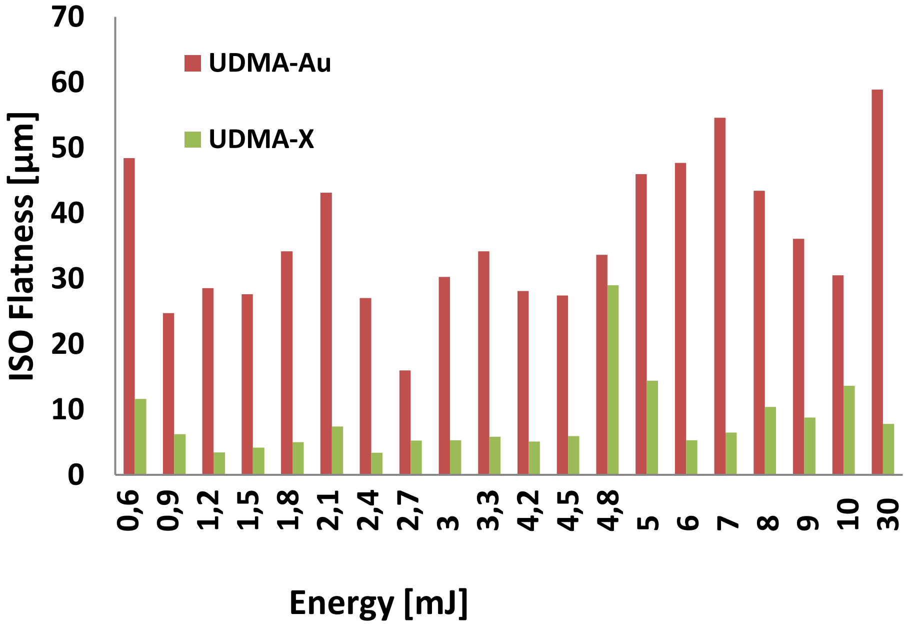
SPt ISO
Total peak-to-valley areal height. The distance between the highest peak and the deepest valley over the entire evaluation area.

ISO Flatness

Areal flatness deviation. The measure of surface deviation from perfectly flat.







Conclusion

In case of 1.9 x 10^{12} nps/ml nanorod concentration of the target polymer:

- Based on the Raman spectroscopy measurements, it seems that plasmonically excited nanorods can facilitate the breakage of methacrylate C=C double bonds and the formation of crosslinks, independently from the primary photopolymerization process.

- According to the Rq and the Rz values, the variation of the surface structure in the spot is highly sensitives to the larger laser energies,

- while the values of SPt ISO and ISO Flatness can help to distinguish the doped and the undoped samples.

THANK YOU FOR YOUR ATTENTION!