



# Fabrication of the gold-polymer nanocomposites using pulsed laser deposition:

## DEPENDENCE OF THE OPTICAL PROPERTIES ON THE TYPE OF POLYMER SUBSTRATES

M. Ivković<sup>1</sup>, D. K. Božanić<sup>2</sup>, N. Bibić<sup>2</sup>, J. Pionteck<sup>3</sup>, R. Žikić<sup>1</sup>, V. Djoković<sup>2</sup>

<sup>1</sup>Institute of Physics, Belgrade, Serbia

<sup>2</sup>Vinča Institute of Nuclear Sciences, Belgrade, Serbia

<sup>3</sup>Leibniz-Institut für Polymerforschung, Dresden, Germany

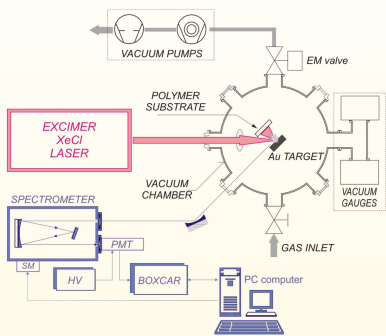
### Preparation of Au-polymer nanocomposites

Nanocomposite materials comprised of gold nanoparticles and various polymer matrices such as polystyrene (PS), NH<sub>2</sub>-terminated polystyrene (PS+NH<sub>2</sub>), polymethylmethacrylate (PMMA), NH<sub>2</sub> terminated polymethylmethacrylate (PMMA+NH<sub>2</sub>), COOH terminated polymethylmethacrylate (PMMA+COOH), and polymer blend of PS-NH<sub>2</sub> and PMMA-COOH, were prepared by pulsed laser deposition (PLD).

Detailed schematic of the experimental setup is given in the figure. Vacuum chamber (30 x 15 cm) is capable of maintaining the pressure of magnitude of 10<sup>-5</sup> mbar using two-step mechanical and turbo-molecular pumps. Au target was placed in the center of the chamber and the 50 μm thick polymer substrate was positioned 3.7 cm from the target at 45° relative to the axis of excimer XeCl (308 nm) laser beam.

The nanocomposite samples were obtained after ablation of the Au target (by focusing the 60 mJ laser beam using quartz lens) and subsequent deposition of the evaporated material on the polymer substrate. Deposition time for all the samples was 110 s and pulse repetition rate 9 Hz. In order to facilitate the diffusion of gold into the polymer, during deposition substrates were heated at 80° C.

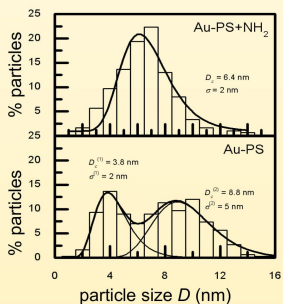
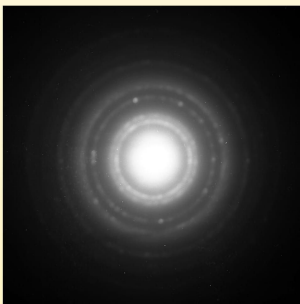
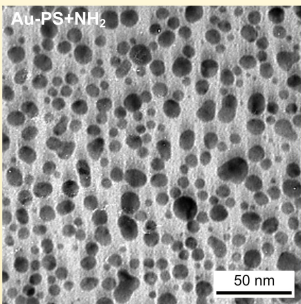
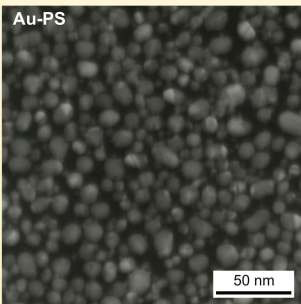
The obtained materials were light blue to purple in color indicating the formation of nano-sized gold structures.



### TEM analysis

The morphology, dispersion in polymer matrices and crystal structure of deposited gold was examined by transmission electron microscopy (TEM) using Philips EM 400 instrument at an operating voltage of 120 kV. For the TEM experiments, 100 nm thick polymer substrates were prepared on flat silicon wafers by spin coating and deposited simultaneously and under the same conditions as the nanocomposites used for other investigations. Deposited films were removed from the substrate by floating the polymer films in water containing few drops of 20% HF solution.

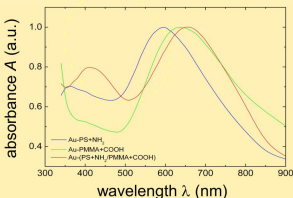
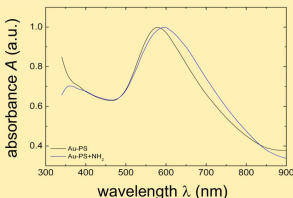
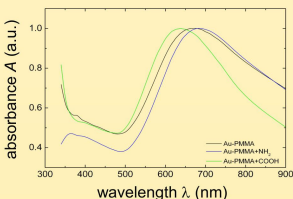
The results of the TEM analyses for Au-PS and Au-PS+NH<sub>2</sub> are given in the figures. The presented procedure for the preparation of TEM samples allows direct insight in the morphology of obtained surface nanocomposites. The micrographs depict large number of nano-sized spherical particles well dispersed in the polymer matrices. Typical electron diffraction pattern of the investigated samples corresponds to crystal structure of cubic Fm3m phase of gold. The difference in morphology and dispersion of gold nanoparticles in Au-PS and Au-PS+NH<sub>2</sub> samples is the consequence of the stabilizing effect that NH<sub>2</sub> groups have on metal nanoparticles. Namely, in the Au-PS case initially formed nanoparticles diffuse in direction parallel to the substrate and consequently grow by coalescence mechanism, whereas, the diffusion is prevented to a certain extent for the Au-PS+NH<sub>2</sub> nanocomposite.



### Optical properties

#### Absorbance spectra of Au-polymer nanocomposites

The UV-vis absorbance spectra of the nanocomposites are presented. In all of the samples a pronounced SPR band was observed and it's position varied with the type of matrix used. In comparison to Au-PS, the band of Au-PS+NH<sub>2</sub> is 20 nm blue shifted. Effects of termination on optical properties were also detected in the PMMA samples, but in the case of PMMA+COOH, SPR red-shifted by 30 nm. The absorbance spectrum of the polymer blend showed two spectral maxima possibly as a consequence of structural anisotropy of nanoparticles.



#### Maxwell-Garnett (M-G) effective medium theory

In order to investigate the differences in the SPR band positions, we used M-G theory. In the theory, polymer nanocomposite can be treated as an effective medium in which the occurrence of the metallic phase is described by the filling factor  $f$ . From the dependences (given in the figure) of the peak position  $\lambda_c$  on  $f$  for PS and PMMA, the absorption bands were calculated using M-G formula

$$A(\lambda) = \text{const.} \times \text{Im} \left\{ \frac{\epsilon_m (1 + 2f)\epsilon(\lambda) + (1 - f)2\epsilon_m}{(1 - f)\epsilon(\lambda) + (2 + f)\epsilon_m} \right\}$$

where  $\epsilon(\lambda)$  is the dielectric function of Au.

