

SEMICONDUCTIVE POLYMER NANOCOMPOSITES WITH PLASMONIC NANOPARTICLES: HOW TO ACHIEVE STRONG POLYMER ELECTRON SYSTEM – SURFACE PLASMON INTERACTION

Jiri Pflieger, Karolina Siskova, Klara Podhajecka, Ondrej Dammer
Institute of Macromolecular Chemistry, ASCR, v.v.i., Heyrovského nám. 2,
162 06 Prague 6, Czech Republic

Introduction

Polymer composites containing metal particles have been traditionally used in electronic industry as conductive varnishes for creating conductive patterns or for electromagnetic shielding, and as substitutes of soldering alloys for electrically or thermally conductive attachment of components. In such applications metallic conductivity of particles is combined with a good processibility and mechanical properties of polymers that play only a role of a passive matrix.

New properties and functionality appear in the composites when decreasing the size of metal nanoparticles (NPs) to a nanometer scale. Such metal NPs were found to induce spatially strongly localized optical phenomena due to a resonance interaction of surface plasmons with incident light or with excited states of molecules located in a close vicinity of a NP surface. These plasmonic phenomena are applicable in various optoelectronic devices where local enhancement of optical fields or photoinduced transitions is desirable, like optical memories based on photochromic transitions, local enhancement or quenching of light emission. It showed to be promising to combine plasmonic NPs with semiconductive π -conjugated polymers that bring their own optoelectronic functionality.

Since the effect of surface plasmons decays rapidly with increasing distance from the metal surface¹ the functional polymer molecules must be in a close contact with the nanoparticle. A facile method of preparing effective plasmonic systems with semiconductive polymer will be shown, based on the preparation of metal nanoparticles with laser ablation combined with electrophoretic deposition for the thin film preparation on conductive substrates.

Experimental

Preparation procedures: For Au nanoparticles preparation a laser ablation of Au target in ethanol, butanol or solution of poly(3-octylthiophene) in chloroform, all electrically nonconductive environments, were performed using the experimental setup depicted in Fig. 1. An Au target immersed in a solvent was impacted by high power nanosecond laser pulses (active Q-switched NdYAG laser system Continuum Surelite I equipped with a KDP crystal frequency doubler, 3 – 6 ns pulse duration (FWHM), repetition rate 10 Hz and

yielding a maximum energy 260 mJ/pulse at 1064 nm and 170 mJ/pulse at 532 nm). The beam was focused to limit high laser fluence only to the close vicinity of the Au target surface and to avoid chemical changes of the organic medium. The system was flushed by argon during the operation. Prior to ablation, all glassware was cleaned by the mixture of sulphuric acid and hydrogen peroxide (“piranha” solution) and aqua regia in order to remove residual organics and Au from previous experiments, respectively, and finally rinsed with distilled water. For the electrophoretic deposition two conductive ITO/glass substrates connected to a power supply were placed in the ablation medium.

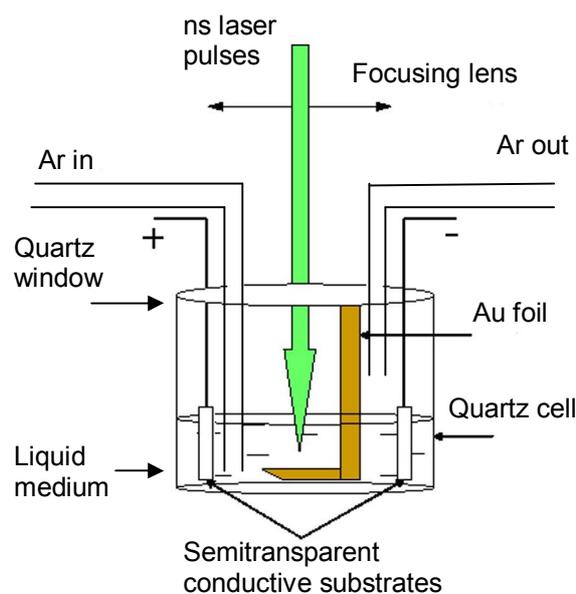


Fig. 1 Experimental setup for laser ablation/electrophoretic deposition experiment.

Instrumentation: UV-Vis optical absorption spectra were acquired using spectrophotometer Lambda 950 (Perkin Elmer); liquid samples measured in 1 cm quartz cuvette and for solid samples a holder with 2 mm aperture was used. Raman spectra were measured on thin films using confocal Raman microscope LabRam HR800 (Horiba Jobin-Yvon) equipped with nitrogen cooled CCD detector and a 600 grooves/mm grating monochromator. SEM images were obtained on films cast on ITO glass using a microscope Quanta 200 FEG (FEI, Czech Republic) with field emission gun and a secondary electron detector. Nanoparticle size distribution and zeta potential were measured by

dynamic light scattering using a Nano-ZS, Model ZEN3600 (Malvern, UK) zetasizer.

Results and discussion

Laser ablation of Au target by laser pulses at 532 nm wavelength yielded NPs with a mean size 4-7 nm, NPs prepared in ethanol were slightly smaller compared to those in butanol (ref. Fig. 2a). Zeta potential for NPs in ethanol was about 40 mV, NPs prepared in butanol possessed zeta potential only 11 mV. Surprisingly, NPs ablated in ethanol had higher tendency to aggregation (see Figs. 2a, b) showing that the stabilization depends on the alkyl chain of the respective alcohol. As can be seen from the UV-Vis spectra measured on NPs electrophoretically deposited on ITO/glass substrate the system shows a typical plasmon extinction for interacting Au NPs. The extended extinction in NIR region for NPs prepared in ethanol confirms their aggregation. The in-situ electrophoretic deposition of NPs during the laser ablation works well also on the surface covered by P3OT film prepared previously by other methods.

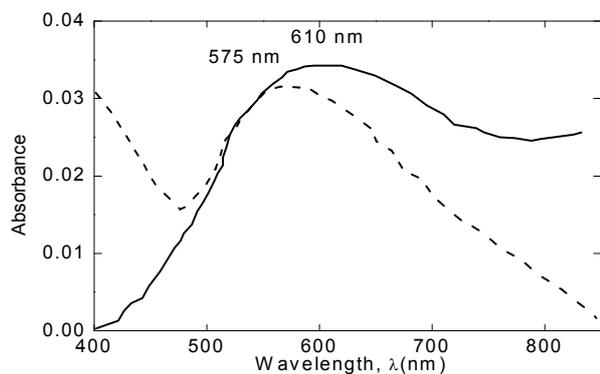
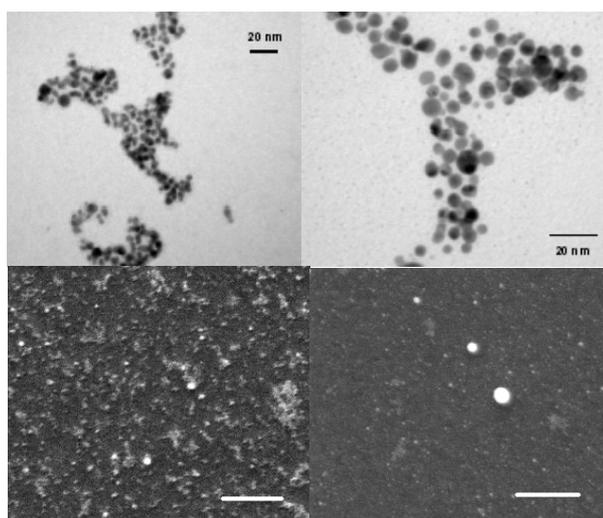


Fig. 2 a) TEM images of as prepared Au nanoparticles prepared by laser ablation at 532 nm, b) SEM images and c) UV-Vis differential optical absorption spectra of Au nanoparticles after electrophoretic deposition on conductive substrate. Left and full line: ablation in ethanol, right and dashed line: ablation in butanol. Deposition current $10 \mu\text{m}^2$

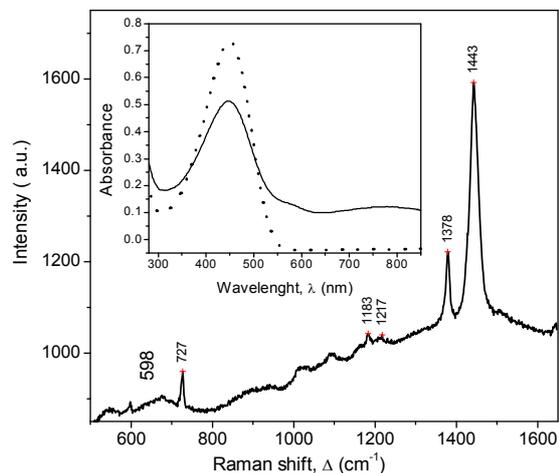


Fig. 3 SERS spectra of the composite of Au NPs laser ablated in P3OT dissolved in chloroform (0.01 % w.t.) deposited on carbon coated Cu-grid. Excitation 632.8 nm, acquisition time 60x 1s. Inset: UV-Vis optical absorption of organosol of Au NPs prepared by laser ablation in 0.01 % w.t. chloroform solution of P3OT (full line), and spectrum of pure P3OT solution (dashed line).

A variation of the method was tested with the laser ablation in chloroform containing dissolved P3OT. In order to limit the destructive interaction of high energy laser pulses with organic environment the wavelength 1064 nm was selected and the laser beam was divergent and focused on the Au target. Although some traces of pyrolytic graphite was detected after the ablation in the Raman spectrum of the resulting organosol, polythiophene still maintains its characteristic optical properties. Two shoulders in the optical spectrum of organosol in Fig. 3 observed at 580 and 780 nm can be explained by the presence of larger NPs and their aggregates. Raman scattering observed from these aggregates deposited on the substrate showed strong surface enhancement originated in plasmonic effects in these aggregates. Simultaneously, fluorescence, that usually hinders the observation of Raman signal in π -conjugated polymers, has been quenched.

Conclusion: Laser ablation in organic medium in combination with electrophoretic deposition was proved to provide an efficient way of preparing layers of plasmonic nanoparticles with π -conjugated polymers.

References

1. Quinten, M. Local fields close to the surface of nanoparticles and aggregates of nanoparticles. *Appl. Phys. B* 73(2001)245-255.

Acknowledgements: Financial support No. KAN100500652 of the Grant Agency of the ASCR, Program Nanotechnology for Society, and No. 203/07/0717 of the Grant Agency of the Czech Republic are greatly acknowledged