

π -Conjugated Polymer Composites with Plasmonic Nanoparticles - Preparation and Properties

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Noble metal nanoparticles are a new class of components for a design of polymer composites which can play an important role in advanced applications utilizing the excitation of surface plasmons with the resonance frequency in the visible spectral region [1]. Their unique electronic and optical properties were considered also for the design of photovoltaic devices exploiting (i) modification of the photoinduced charge transfer from donor to acceptor, (ii) modification of deactivation processes in excited molecules, (iii) optical absorption enhancement due to the surface plasmon extinction, and (iv) decrease of the serial resistance of the active system by improvement of its electrical conductivity. Incorporation of silver clusters (prepared by thermal evaporation in high vacuum) in an organic solar cell was found to induce an enhancement of the photovoltaic conversion efficiency [2]. The observed photocurrent enhancement was discussed in terms of resonant light absorption in the metal clusters. The insertion of an interfacial layer of gold nanoparticles between the indium tin oxide (ITO) and the photoelectrically active semiconducting polymer has shown a marked improvement of photovoltaic conversion efficiency recently [3].

This contribution deals with the preparation of π -conjugated polymer nanocomposites consisting of poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene], MeH-PPV, or poly(3-alkylthiophene)s with hexyl-, P3HT, resp. octyl-, P3OT, substituents, and Au nanoparticles or their aggregates. The composites were prepared by two different pathways: (i) by simple mixing of Au organosol with a polymer solution, and (ii) by reduction of metal ions in the presence of the polymer. The morphological, optical and electrical properties of both types of the hybrid materials were examined with regards to the advantages/disadvantages of the preparative methods.

Mixing of Au nanoparticles with a solution of MeH-PPV gives nanocomposites, in which the parent polymer remains almost intact as to its molecular weight as well as chemical structure, and forms a matrix with uniformly distributed isolated Au nanoparticles. However, at a very low concentration MeH-PPV was found to induce aggregation and changes in nanoparticle size distribution. The in-situ formation of Au nanoparticles in MeH-PPV matrix gives nanocomposites with chain-like aggregated nanoparticles. Contrary to poly(3-alkylthiophene)s, the molecular structure of MeH-PPV was partly damaged due to its reaction with tetraoctylammonium bromide/AuCl₄⁻ complex. This side reaction can be partially limited by an early addition of a reducing agent such as NaBH₄. The preparation route based on a simple mixing, however, seems to be generally more suitable from the point of view of the polymer stability.

Compared to the pure polymers all nanocomposites showed significantly broadened optical absorption due to the Au nanoparticles plasmon extinction centered at 530 nm. The electrical conductivity of Au/poly(3-alkylthiophene) nanocomposites showed a continuous increase with increasing nanoparticles volume concentration – no clear percolation threshold was observed. Thermal stabilizing effect of Au nanoparticles on the electrical conductivity of Au/P3OT films was found - with Au nanoparticles content above 1 vol%: the turning point where the conductivity starts to decrease shifts to 110 °C, compared to 50 °C for the pure polymer. In Schottky barrier cells the open circuit voltage decreased markedly with increasing nanoparticles content.

To prepare systems with enhanced surface effects of metal nanoparticles an application of combined laser ablation and electrophoretic deposition was tested. Laser ablation of a metal target in liquid environment provides a possibility to prepare noble metal nanoparticles with nearly bare surfaces and tunable properties. Utilizing the negative surface potential of nanoparticles, the electrophoresis was applied for the deposition of Au nanoparticles onto a conductive substrate. The effect of Au nanoparticles on a layered system based on P3HT sandwiched between ITO/glass substrate and Al electrode is discussed.

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[2] O. Stenzel et al., Sol. Energy Mater. Sol. Cells 37, 337 (1995).
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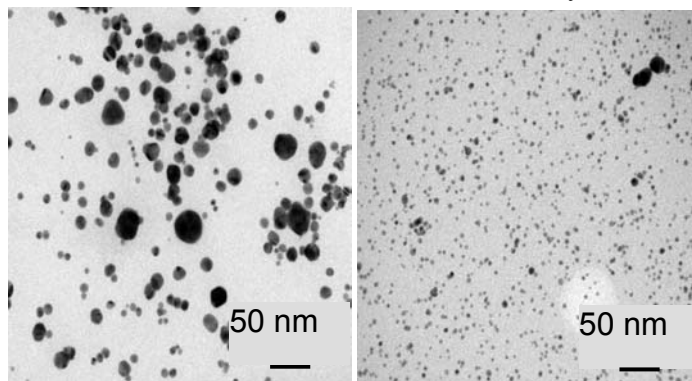


Figure 1. TEM images of Au nanoparticles for composites with the Au/MEH-PPV ratio 7/1 (a) and 1/1 (b), respectively.