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Electrical Conductivity of Poly(3-octylthiophene)/Au Nanocomposites

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Summary: The stabilizing effect of Au nanoparticles on electrical conductivity of poly(3-octylthiophene-2,5-diyl) based composite films was investigated. For the content of Au nanoparticles 1 vol %, the turning point where the conductivity starts to decrease, shifts to 110 °C, compared with 50 °C for the neat polymer. At low temperatures, the composites show the common activation energy of conductivity $E_a = 0.3$ eV independent of the Au nanoparticle concentration. It corresponds to the activation energy of neat polymer and suggests that the conductivity of the composite is controlled by the same mechanism.

Keywords: metal nanoparticles; nanocomposites; π-conjugated polymers

Introduction

Embedding metal nanoparticles into π-conjugated polymer matrices provides a means for tuning of properties of hybrid materials. For example, the presence of Ag and Au nanoparticles was recently demonstrated to enhance the efficiency of photovoltaic cells based on poly(3-octylthiophene-2,5-diyl), P3OT, and a fullerene derivative.[1] The authors suggest that the dominant mechanism of the efficiency increase is an improved electrical conductivity of P3OT. As far as the conductivity of the composite systems containing semiconductive polymer is concerned, the presence of a conductive metal component leading to a percolation behavior[2] contributes to its increase. The conductivity can be also modified by changes in the morphology of the host polymer.[3]

In this work we study the temperature dependence of conductivity of nanocomposite thin films based on P3OT and Au nanoparticles. We show that the electrical properties of the composite are influenced by both the conductivity of metal nanoparticles and the morphological changes in the polymer matrix.

Experimental Part

Chemicals

Poly(3-octylthiophene-2,5-diyl), P3OT, regioregularity >98.5%, was purchased from Sigma-Aldrich and used as received. According to liquid chromatography on HP 1100 apparatus, using polystyrene calibration standards, molar weight was determined as $M_n = 18\,700$ g/mol, polydispersity $I_p = 1.4$.

Synthesis

First, Au organosol was prepared according to the procedure originally developed by Brust et al.[4] Nanoparticle preparation comprise the reduction of an Au (III) salt in a two phase water/toluene system using tetraoctylammonium bromide, TOAB, as a phase transfer agent. After that, a P3OT solution (concentration 0.66 wt %) was added to aliquots of a TOAB-stabilized Au organosol to obtain P3OT/Au composites of the desired Au content. Finally, TOAB was removed by precipitation of the composites in an excess of methanol, the composites were isolated by centrifugation and dried in vacuum at 75 °C. The

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elemental analysis showed the content of the residual TOAB to be below the determination limit (0.3 wt %).

Transmission Electron Microscopy, TEM

A small drop of a composite sample dissolved in toluene (polymer concentration 2 wt %) was transferred onto a carbon-foil-covered copper grid. After 15 s, the residual liquid was removed with a filtration paper. The TEM imaging on these samples was performed with a JEOL JEM200CX transmission electron microscope.

Scanning Electron Microscopy, SEM

Thin films for SEM measurements were prepared by spin coating (4100 rpm) from toluene solutions (polymer concentration 2 wt %) on a quartz substrate. The micrographs were obtained with a secondary-electron detector at the accelerating voltage 30 kV in a SEM microscope Quanta 200 FEG, equipped with a field emission gun.

Electrical Measurements

Neat P3OT and P3OT/Au nanocomposites were deposited by spin coating from toluene solution (2 wt % of polymer) on glazed ceramic substrates with gold interdigital electrodes (the gap between adjacent electrode bars, $g = 30$ μm; total length $l = 30$ cm). The thickness of all layers was $t = 100$–150 nm unless otherwise stated. The electrical conductivity, σ, was determined from the sample geometry using the equation: $\sigma = I \times g/(U \times l \times t)$, where U denotes the applied voltage and I stands for the measured current. For the electrical measurements, samples were placed in a thermostatted sample holder in an oil-free dynamic vacuum (turbomolecular pump, 5×10^{-5} Pa) and the DC current was measured in a serial connection of the sample to a stabilized power supply Keithley 230 and an electrometer Keithley 617.

Results and Discussion

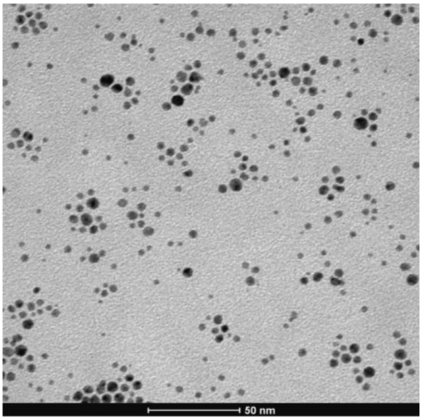

Figure 1.
TEM image of P3OT/Au composite (5 vol % Au).

The mean diameter of Au nanoparticles, 3.3 ± 1.2 nm, in the P3OT/Au composites was determined using statistical analysis of TEM images. The TEM image of the composite containing 5 vol % of Au nanoparticles (Figure 1) shows the tendency of nanoparticles to aggregate, keeping the minimum distance between adjacent nanoparticles in the range 1–2 nm. A similar minimum gap between nanoparticles in aggregates was found also for composites with a ten-times lower Au nanoparticle concentration. To determine the nanoparticle organization in films used for electrical measurements, SEM imaging of films of similar thickness (100 nm), cast on fused silica substrate, was used (Figure 2). It was found that the Au nanoparticles are not homogeneously distributed in the polymer matrix. Instead, we observed a tendency of Au particles to aggregate and to form larger structures with dimensions of tens of nanometers.

The TEM images do not show real morphology in thicker films prepared for electrical measurements. Nevertheless, we assume that the minimum distance between the nanoparticles is given by the polymer shell formed around the nanoparticles, which is not influenced by the casting conditions. The interfacial layers separating the nanoparticles in these aggregates could be composed of P3OT but the presence of TOAB, persisting in the composite after purification due to the affinity of Br^- ions to the Au nanoparticle surface, cannot be

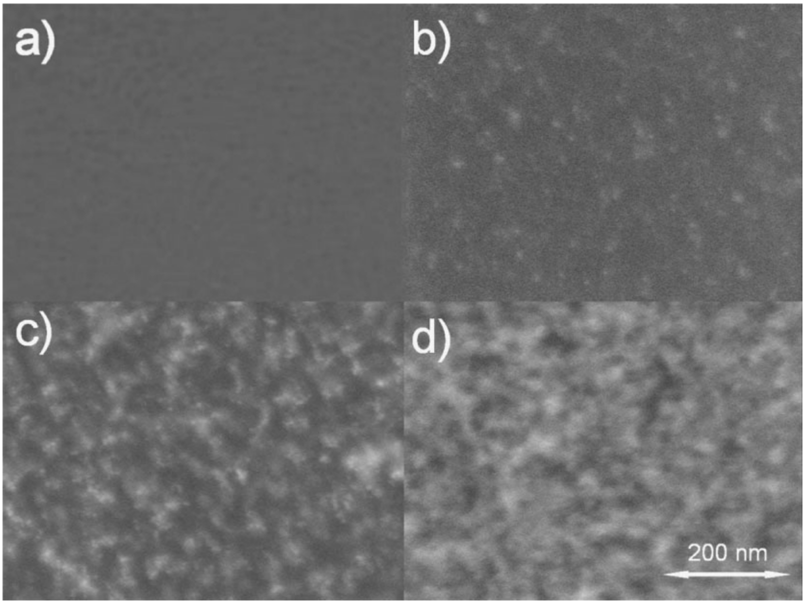

Figure 2.
SEM image of P3OT/Au nanocomposites of different Au content: a) neat P3OT, b) 1 vol % Au, c) 5 vol % Au, d) 13 vol % Au.

excluded. The minimum gap between nanoparticles corresponds roughly to the thickness of 1–2 monomolecular layers of TOAB. If we assume that a full coverage of one NP surface requires about 20 molecules of TOAB, the maximum concentration of Br necessary for the coverage would be 0.1 wt %, the concentration below the detection limit of the employed analytical methods.

Since the electrical properties of the composites showed a strong dependence on the history of the sample, caused by progressive oxygen removal and/or some morphological changes, the measurements were made in relaxed conditions achieved by evacuating for at least 5 days and annealing at 120 °C for 1 h. The *U-I* characteristics of the composites cast on substrates with interdigital gold electrodes showed in all cases Ohmic behavior with a linear dependence on the applied voltage. For nanoparticles with diameters above 1 nm, the electron work function does not markedly differ from that of the bulk metal,[5] which is close to the HOMO level of the polymer, and no barrier between the gold surface of the electrodes and P3OT is formed. This shows that P3OT is in direct contact with the surface of nanoparticles and if any residual TOAB adsorbs on the surface it is penetrated with P3OT.

The dependence of electrical conductivity on the Au content at room temperature is shown in Figure 3. The conductivity of neat P3OT (10^{-10} S cm^{-1}) corresponds well to values obtained by other authors for undoped P3OT. The conductivity gradually increases on increasing concentration of

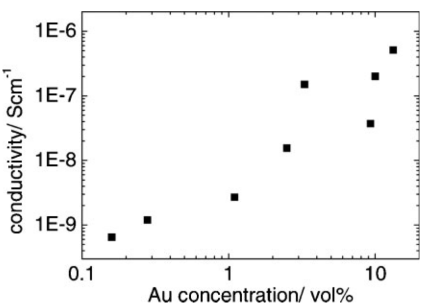

Figure 3.
Dependence of electrical conductivity at room temperature on Au content in P3OT/Au nanocomposites.

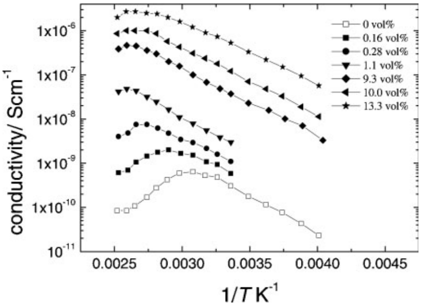

Figure 4.
Dependence of conductivity on reciprocal temperature for P3OT/Au nanocomposites for different Au nanoparticles content.

aggregates of electrically conductive[5] Au particles. Addition of 13 vol % (75 wt %) of Au nanoparticles to P3OT causes an increase in conductivity of four orders of magnitude. The temperature dependences of conductivity for films of neat P3OT and for composite films containing various amounts of Au nanoparticles are shown in Figure 4. At low temperatures, all the samples show linear dependence of logarithm of conductivity on reciprocal temperature. At high temperatures the conductivity passes through a maximum and then drops to lower values. The occurrence of conductivity maxima observed for poly(3-alkylthiophenes) was rationalized on the basis of different thermodynamic transitions in the polymer. Show-An et al.[6] explained this phenomenon by distortion of main chains above the glass transition temperature. In the glass transition region, as temperature increases, the number of defects in coplanarity of neighboring thiophene rings increases, leading to lower delocalization of π electrons and lower mobility of charge carriers. Liu et al. ascribed the decline of conductivity to a decrease in in-plane π–electron orbital stacking caused by the melting of crystallized side chains and consequent thermal disturbance of stacks with increasing temperature.[7]

In our systems the temperature of the conductivity maximum, T_m, depends on the film composition. In neat P3OT, T_m appears at about 50 °C, it increases in the concentration interval from 0 to 1 vol % of Au, reaching its saturation value $T_m = 110$ °C at ca 1 vol %. On the other hand, the slope of the logσ vs. $1/T$ dependences remains independent of the Au content, leading to the same activation energy $E_a = 0.3$ eV. This value is close to the activation energy obtained for regioregular P3OT 0.24–0.26 eV.[8] For highly regioregular P3HT, it was shown that the charge carrier mobility and electrical conductivity depend on the connectivity between highly ordered microcrystalline domains.[9,10] In the present case of P3OT/Au nanocomposite, the independence of activation energy of the Au content suggests that a similar mechanism governs the conductivity behavior in neat polymer and in the composite, the critical parameter being the charge transport between zones of higher mobility - either crystalline domains or electrically conductive nanoparticles. This picture is supported by the TEM observation that the individual Au nanoparticles are separated (Figure 1). The increased concentration of nanoparticles shifts the thermodynamic transition responsible for the charge carrier mobility deterioration to higher temperatures. The origin of this transition as well as the reason for its shift remain unclear. The main chain distortion above the glass transition is probably not responsible for this effect as only a weakly pronounced glass transition is observed in both P3OT and P3OT/Au at 20 °C. It is interesting to note that a similar stabilization effect was observed in thin films of neat P3OT, where T_m increases while the sample thickness decreases (Table 1). If we consider the melting of side chains as the cause of the conductivity decrease, we could explain the shift of the turning point towards higher temperatures

Table 1.
Dependence of the maximum electrical conductivity on film thickness for neat P3OT.

t (nm)	T_m (°C)
40	68
70	59
130	52

by the structure stabilization due to the interaction of the polymer with substrate or metal surface.

Conclusions

The conductivity of nanocomposites comprising aggregates of well separated Au nanoparticles embedded in the P3OT matrix increases with increasing Au content. The activation energy of conductivity 0.3 eV common for all the investigated Au/P3OT ratios suggests a common mechanism of charge transport in the neat P3OT and P3OT/Au composites based on restricted conduction between zones of high conductivity - crystalline domains and/or Au nanoparticles. The stability of electrical conductivity of P3OT, which is known to deteriorate at high temperatures, was improved by shifting the transition temperature with increasing the Au nanoparticles content from 50 °C for neat P3OT to 110 °C for composites with the Au nanoparticles content above 1 vol %.

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