Polymer Composites with Plasmonic Metal Nanoparticles

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Summary: A two-phase method has been adapted for the preparation of polymer composites consisting of regioregular poly(3-octylthiophene-2,5-diyl) and Au or Ag nanoparticles. This work compares optical and morphological properties of nanocomposites formed by mixing metal organosols and polymer solution (type I composites) with nanocomposites formed by in-situ reduction in polymer solutions (type II composites). Both types contained very small metal nanoparticles (1–10 nm). Interestingly, more than ten-fold enhancement of Raman scattering of the polymer by the electromagnetic (EM) mechanism of SERS (surface-enhanced Raman scattering) resulted from the coupling of the polymer with plasmonic Au nanoparticles into a nanocomposite system.

Keywords: metal nanoparticles; nanocomposites; plasmonics; π-conjugated polymers

Introduction

Nanocomposite materials consisting of metal nanoparticles (NPs) and π-conjugated polymers, such as polythiophene or polyaniline, have received much attention in recent few years.[1–3] These hybrid nanomaterials have unique physical properties and wide potential applications in catalysis[4], sensors[5], luminescent devices[6] and others. With the development of nanotechnology, various composites of π-conjugated polymers and metal NPs have been synthesized. Metal NPs/π-conjugated polymers nanocomposites have been prepared by several methods: blending[7], use of templates for arranging nanoscopic metal and semiconductor clusters into spatially well-defined structures[8], spontaneous reduction of metal salts by electroactive polymers[9] or electrochemical deposition[10].

In this paper we describe the synthesis of nanocomposites consisting of Ag or Au NPs and poly(3-octylthiophene-2,5-diyl), and compare their properties using various techniques such as UV-vis absorption spectroscopy, transmission electron microscopy (TEM) and Raman micro-spectroscopy.

Experimental Part

Chemicals

All the chemicals used for NP preparation as well as poly(3-octylthiophene-2,5-diyl) (P3OT) were purchased from Sigma-Aldrich and used as received.

For the preparation of NPs/P3OT composites, two procedures were adopted:

(i) *Composites type I.* First, Au or Ag organosols were prepared according to the procedure originally developed by Brust et al. for Au NP preparation[11] and later adapted for Ag NP preparation[12]. Typically, 6 mL of 30 mM

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aqueous solution of $AgNO_3$ or $HAuCl_4$ was added to 16 mL of 50 mM toluene solution containing tetraoctylammonium bromide (phase-transfer agent) to form a two-phase system. The system was stirred vigorously for 20 min to transfer metal ions into the organic phase. The aqueous phase was then separated from the organic phase and removed. Then 5 mL of 0.4 M $NaBH_4$ aqueous solution (reducing agent) were slowly added to the organic phase. The system was maintained under stirring for 3 h. After 3-h stirring, the organic phase was separated and washed three times with redistilled deionized water. The resulting Au organosol was dark purple and its surface plasmon extinction (SPE) band showed a maximum at 514 nm. The Au organosol showed sufficient stability since no sedimentation was observed within one month after its preparation. The Ag organosol was yellow and optically transparent with a narrow SPE band centered at 414 nm. In comparison with Au, the Ag organosol was stable only for several days. After 8 days, a shift of the SPE maximum to 418 nm and a marked broadening of the extinction band were observed. The composites I were prepared by addition of 6 mL of polymer solution (concentration 0.66 wt %) to 16 mL of the respective metal organosols and by subsequent vigorous stirring of the mixture for 3 h.

(ii) *Composites type II.* The procedure described above for composites type I has been carried out up to the phase-separation step. To the organic phase containing Au or Ag ions, 6 mL of the polymer solution (0.66 wt %) was added.[1] Then, the reduction of the metal ions was performed in situ by addition of 5 mL of 0.4 M $NaBH_4$ aqueous solution. The systems were maintained under stirring for 3 h.

After the preparation, both types of composites were purified by addition of an excess of methanol and subsequent isolation by centrifugation, and finally dried in vacuum oven at 75 °C for 8 h. Dry products were redissolved in toluene.

UV-vis Absorption Spectroscopy

Spectra were measured in an 0.2 cm quartz cuvette using a double-beam Perkin Elmer Lambda 950 UV-vis spectrometer.

Transmission Electron Microscopy (TEM)

A small drop of a composite sample was transferred onto copper grid covered with a carbon foil. After 15 s, the residual liquid was removed with a filtration paper. These samples were used for transmission electron microscopy (TEM) imaging performed with a JEOL JEM200CX transmission electron microscope.

Raman Micro-Spectroscopy

Thin films for Raman spectroscopy measurements were prepared by spin coating (2750 rpm) from an Au NPs/P3OT composite solution in toluene (polymer concentration 0.38 wt %) or from a solution of the neat polymer of the same concentration on a quartz substrate. The spectra were measured with a LABRAM HR-800 (Horiba Jobin-Yvon) Raman confocal microscope under the following experimental conditions: excitation wavelength 632.8 nm (He-Cd laser), laser power 0.02 mW, entrance slit 100 μm, confocal aperture 400 μm, accumulation time 60 s.

Results and Discussion

UV-vis Absorption Spectroscopy

UV/vis spectra of Au/P3OT composite solutions are shown in Figure 1 and compared with the optical absorption of a solution of regioregular P3OT and of an Au organosol. The main absorption band observed at 450 nm for both types (I and II) of Au/P3OT composite solutions is consistent with the known position of $\pi \rightarrow \pi^*$ transition of the polythiophene conjugated polymer chain. A distinct asymmetric broadening of the main absorption

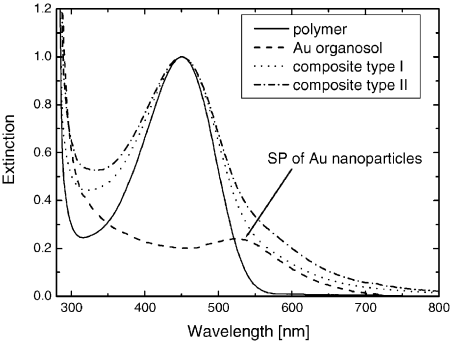

Figure 1.
UV-vis absorption spectra of Au/P3OT composites type I and II, neat P3OT and Au organosol. Toluene was used as a solvent in all cases. The spectra of Au/P3OT composites type I and II and neat P3OT were normalized at their absorption maxima.

band is observed in the spectra of Au/P3OT composites when compared with the spectrum of neat P3OT. Spectra of Au/P3OT composites show a substantially higher absorption in the regions 300–400 nm and 500–800 nm. Zhai et al.[1] explained the broad absorption in the range 500–600 nm by a combined effect of two factors: a long-range ordering of the polythiophene caused by self-assembling of polymers on metal NP surface, and by the SPE of Au NPs. Indeed, the increase in extinction in the red spectral region corresponds to the SPE of Au NPs (see Figure 1). On the other hand, neither spectral shift nor spectral structuring was observed, caused by increased intermolecular interaction during the self-assembling of the polymer. The higher absorption between 500 and 800 nm of the composite type II compared with composite type I could be explained by the presence of bigger NPs or NP aggregates.

Compared with Au NPs containing composites, UV-vis spectra of Ag/P3OT composites were almost identical to the spectrum of neat P3OT. This can be explained by a weak extinction of Ag organosol and by an overlap of the SPE band of Ag NPs with the absorption band of P3OT, both having absorption maxima in the same wavelength interval.

Transmission Electron Microscopy (TEM)

Representative TEM images of Au/P3OT composites are shown in Figure 2. The tendency of the Au NPs to two-dimensional assembling is clearly observable[13], manifesting itself as the formation of regions with nearly regular interparticle spacing and originating from stabilization of the Au NPs either by the residual alkylammonium bromide and/or by the polymer. The elemental analysis confirmed that the phase transfer agent was partly removed (a sample contained less than 0.25% nitrogen). Size distributions of metal NPs in Au and Ag/P3OT composites (Figure 3A and B) show that both procedures led to very small NPs (1–10 nm). The presence of small amount of bigger nanoparticles gives a relatively broader size distribution of composite type II compared to type I. Larger objects exceeding 10 nm, visible in Figure 2B, apparently consist of several NPs forming aggregates.

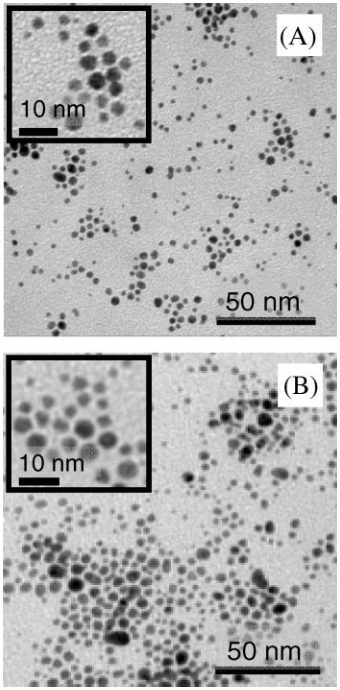

Figure 2.
TEM images of Au/P3OT composites type I (A) and type II (B).

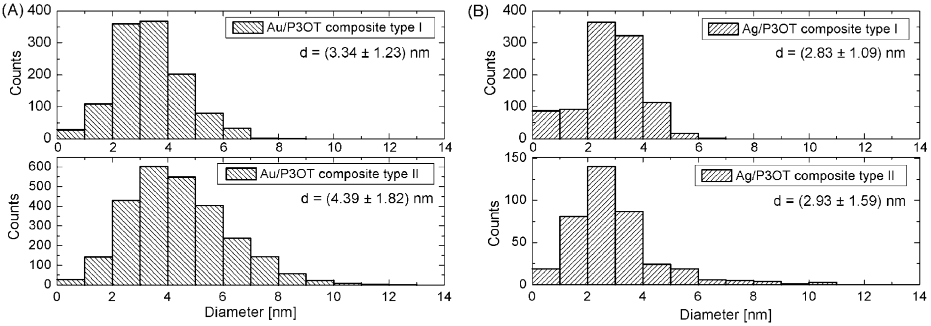

Figure 3.
Nanoparticle size distributions of composites type I and II containing Au (A) and Ag nanoparticles (B).

The slightly smaller mean particle size in Ag/P3OT composites (TEM images not shown here) compared with composites containing Au NPs can be explained by a higher affinity of bromide ions, originating from the quaternary ammonium salt used as the phase transfer agent in the preparations, to Ag NPs. In the case of Ag, adsorption of bromide ions causes the formation of large intergrown NPs, which further aggregate into macroscopic objects with fast sedimentation.[14] As a result, only very small NPs remain in the organosol. On the other hand, the lower adsorption affinity of Br^- to gold surfaces limits the formation of macroscopic aggregates in the case of Au NPs. The long-term stability of these composites is supported by dispersion interactions involving the alkyls of the quaternary alkylammonium cation and alkyl substituents of polymer.[13]

Raman Micro-Spectroscopy

Raman spectra of Au/P3OT composites (Figure 4) yielded enhanced Raman signal with clearly observable bands typical of polythiophene. The positions of the most characteristic bands were assigned on the basis of the earlier published results of polyalkylthiophenes cast on roughened gold electrodes.[15,16] The most intensive bands at 1444 cm^{-1} and 1380 cm^{-1} were assigned to the $C_\alpha = C_\beta$ symmetric stretching mode and to the C_β - $C_{\beta'}$ single-bond stretching mode of the thiophene ring, respectively. The ratio of the integral intensities of these two bands, known to be sensitive to the polymer oxidation[15], remained the same as in neat P3OT. The band at 727 cm^{-1} (C-S-C ring bending) as well as the positions of Raman bands at 1509, 1208, 1198, 1182, 1090, 1013 and 598 cm^{-1} are the same as those reported for P3OT in the literature.[16] The integrated relative intensities of the most intense Raman bands at 1444 cm^{-1} are more than ten times higher for the composites compared with the neat polymer (as follows from the results of the band decomposition and integration procedure). This enhancement can be explained by the electromagnetic amplification mechanism in the presence of the plasmonic Au NPs in the composites. The absence of any shifts of the polymer Raman bands in the composites compared with the

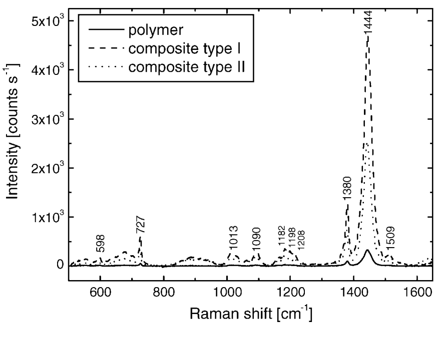

Figure 4.
SERS spectra of thin films of Au/P3OT composites type I, II and neat polymer on quartz substrate. Baseline was subtracted in program Origin.

neat polymer indicates that the polymer is not chemisorbed on Au NPs. Therefore, the observed enhancement can be attributed only to the electromagnetic (EM) mechanisms of SERS, in particular to parts of the polymer chains localized in the vicinity of Au NPs surfaces or, even more probably, in the strong optical fields localized in interstices between rather closely spaced Au NPs.

Conclusions

The Raman spectra of composites indicated the Raman enhancement, which was assigned to the EM mechanism of SERS. The mean particle sizes and stability of composites were influenced by the adsorption of bromide anion on NP surface. Whereas the Au NPs containing composites show sufficient stability, Ag NPs would require an additional stabilizing agent such as alkylamine to obtain an applicable polymer composite. Surprisingly, no oxidation of the polymer during the in-situ composite preparation was observed.

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[1] L. Zhai, R. D. McCullough, *J. Mater. Chem.* **2004**, *14*, 141.

[2] M. M. Oliveira, E. G. Castro, C. D. Canestraro, D. Zanchet, D. Ugarte, L. S. Roman, A. J. G. Zarbin, *J. Phys. Chem. B* **2006**, *110*, 17063.

[3] Z. Zhang, F. Wang, F. Chen, G. Shi, *Mater. Lett* **2006**, *60*, 1039.

[4] C. Coutanceau, M. J. Croissant, T. Napporn, C. Lamy, *Electrochim. Acta* **2000**, *46*, 579.

[5] J. Matsui, K. Akamatsu, S. Nishiguchi, D. Miyoshi, H. Nawafune, K. Tamaki, N. Sugimoto, *Anal. Chem.* **2004**, *76*, 1310.

[6] P. G. Nicholson, V. Ruiz, J. V. Macpherson, P. R. Unwin, *Chem. Commun.* **2005**, *8*, 1052.

[7] K. V. Sarathy, K. S. Narayan, J. Kim, J. O. White, *Chem. Phys. Lett.* **2000**, *318*, 543.

[8] S. M. Marinakos, M. F. Anderson, J. A. Ryan, L. D. Martin, D. L. Feldheim, *J. Phys. Chem. B.* **2001**, *105*, 8872.

[9] Y. Zhou, H. Itoh, T. Uemura, K. Naka, Y. Chujo, *Langmuir* **2002**, *18*, 277.

[10] B. C. Sih, M. O. Wolf, *J. Phys. Chem. B* **2006**, *110*, 22298.

[11] M. Brust, M. Walker, D. Bethell, D. J. Schiffrin, R. J. Whyman, *J. Chem. Soc., Chem. Commun.* **1994**, 801.

[12] M. M. Oliveira, D. Ugarte, D. Zanchet, A. J. G. Zarbin, *J. Colloid Interface Sci.* **2005**, *292*, 429.

[13] J. Fink, C. J. Kiely, D. Bethell, D. J. Schiffrin, *Chem. Mater.* **1998**, *10*, 922.

[14] M. Husein, E. Rodil, J. H. Vera, *J. Colloid Interface Sci.* **2004**, *273*, 426.

[15] E. A. Bazzaoui, M. Bazzaoui, J. Aubard, J. S. Lomas, N. Félidj, G. Lévi, *Synth. Met.* **2001**, *123*, 299.

[16] M. Baibarac, M. Lapkowski, A. Pron, S. Lefrant, I. Baltog, *J. Raman Spectrosc.* **1998**, *29*, 825.