

Homogeneous, surfactant-free gold nanoparticles encapsulated by polythiophene analogues†

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The synthesis of nanocrystal–polymer nanocomposites is reported, in which 2-(2-ethoxyethoxy)ethoxy modified polythiophene serves as the protecting group for dispersion and homogeneous size distribution of the nanoparticles, showing potential of this polymer-based material in optoelectronics and microelectronics.

The photophysical properties and electrical conductivity of conjugated polymers have drawn much attention since Shirakawa *et al.*¹ revealed the electrically conducting phenomenon of polyacetylene in 1977. Unlike other types of polymers, conjugated polymers exhibit conducting and/or semiconducting behaviors and thus serve as promising candidates for development of light emitting diodes, photovoltaic, field effect transistor, and thermoelectric materials.^{2–7} However, the devices composed of conjugated polymers are still lower in efficiency compared to those prepared from traditional inorganic materials. One current approach to expand the feasibility of polymer-based devices lies in the design and synthesis of nanocomposites incorporating a polymer matrix and nanocrystals.^{8,9} For example, in 2005, Carroll's group reported a new class of P3HT-based, organic–inorganic hybrid heterojunction photovoltaic solar cells.¹⁰ It was expected that the high electron mobility of the additive nanocrystals could partially overcome the charge-transport limitations. Unfortunately, addition of surfactant to stabilize the nanocrystals might lead to unexpected damage on film morphology of the conjugated polymer and consequently the hindrance of electrons during the transportation process.

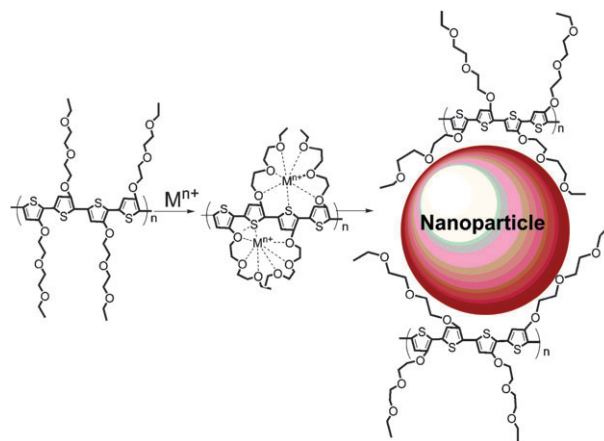
It is thus of interest to consider the preparation of nanocrystals free from surfactants/ligand. Unfortunately, the absence of surfactant is severe for dispersion of nanoparticles, and aggregation is unavoidable. One route to circumvent this obstacle is *via* chemical modification, in which both polymers and nanoparticles are first modified with complementary functional groups.^{11–14} Subsequently, they are allowed to react with each other under mild conditions. However, experimental steps embarking on this method are rather complicated, and aggregation of nanoparticles is still a problem *en route* to

polymer bound nanocomposites. In order to improve *e.g.* the electrical properties of polymers for device applications, the search of new synthetic routes that ensures the dispersion of nanoparticles in the polymer matrix is an emergent issue.

We report herein a facile process to prepare homogeneous, surfactant-free metal nanoparticles encapsulated by polythiophene analogues. In contrast to previous attempts that ubiquitously utilized blending process between the as-prepared polymers and nanoparticles, we use poly(alkoxythiophene) to chelate the designated metal ions. These polymer bound metal ions are then applied as precursors and metal ions are reduced *in situ* to obtain the corresponding poly(alkoxythiophene)-bound well dispersed nanoparticles with homogenous size distribution. Detailed syntheses, characterization and applications are described as follows.

A qualitative illustration of the synthetic route is depicted in Scheme 1. In brief, 2-(2-ethoxyethoxy)ethoxy-modified polythiophene (P3EEET, M_n : 8890, PDI: 1.29) was synthesized *via* polymerization of dibromo[2-(2-ethoxyethoxy)ethoxy]thiophene monomer (see ESI†). Subsequently, while stirring, various amounts of HAuCl₄ solution (0.05 M in H₂O) were added to the solution containing P3EEET (4 mg P3EEET in 5 ml acetonitrile) to allow chelation. The Au(III) ion chelation process was allowed to proceed for ~2 h before the characterization.

Fig. 1(b)–(d) show the absorption spectra of P3EEET with 20, 40 and 80 μ L added HAuCl₄ (0.05 M) solution, respectively. Fig. 1(a) also shows the absorption spectrum of



Scheme 1 A qualitative illustration of the polymer backbone conformation with metal ion complexation and the polymer-nanoparticle nanocomposite.

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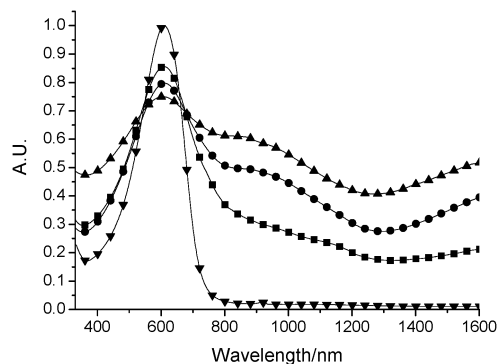


Fig. 1 Absorption spectra of P3EEET reacted with different concentrations of HAuCl₄ in acetonitrile: (a) 0 uL (▼); (b) 20 uL HAuCl₄ (■); (c) 40 uL HAuCl₄ (●); (d) 80 uL HAuCl₄ (▲). Note that the P3EEET samples containing Au(III) ion were allowed to react for 2 h before measuring the absorption spectra.

Au(III)-free P3EEET in a control experiment. For the Au(III)-free P3EEET, the lowest-lying absorption band, showing a maximum at 610 nm, can be reasonably ascribed to the backbone $\pi \rightarrow \pi^*$ transition of the polythiophene units. Upon addition of HAuCl₄ followed by aging for 2 h, a new absorption band gradually appeared at 950 nm, accompanied by a decrease of the 610 nm band. This phenomenon is reminiscent of the ionochromic effect documented in previous literature,^{15–19} and the variation of absorption is mainly due to the conformational perturbations of polythiophene molecules.

The roles of metal ions in the reaction system incorporating polythiophene analogues have been reported.^{16,18} We accordingly propose there exists a non-covalent, electrostatic (ion–dipole) interaction among Au(III) ions, oxygen atoms on ether side chains and sulfur atoms of P3EEET (see Scheme 1), which restricts the free rotation around the thiophene–thiophene bond. As a result, the backbone of P3EEET is driven from a non-planar conformation to a planar one. As for conjugated polymers, there is a correlation between the electronic structure and backbone conformation, such that the variation of absorption shown in Fig. 1 is mainly due to the conformational perturbations of polythiophene molecules. The increase of the 950 nm band implies that Au(III) ions induce an evolution which transforms disordered P3EEET molecules to the ordered, planar conformation, compared with the Au-free P3EEET samples.

To provide another spectral evidence for the interaction between P3EEET and Au(III) ion, X-ray absorption near-edge structure (XANES) data was performed at the Au L_{III} edge as shown in Fig. S1 (ESI[†]). After adding HAuCl₄ into the P3EEET solution, the resulting data of the prepared sample is consistent with the presence of cationic gold formally represented as Au(III) ion, as evidenced by the position of the absorption edge at 11919 ± 0.5 eV, characteristic of Au(III) ion. The result supports the viewpoint that the 950 nm band in the absorption spectrum is caused by the conformational change of P3EEET but not the *e.g.* redox reaction between Au(III) ion and the polymer backbone. The rise of the absorption at >1300 nm in Fig. 1 could be rationalized by taking the polaron–bipolaron mechanism into consideration.^{20,21} The polaron–bipolaron model predicts a metallic-like optical transition with a band gap down to the near infrared region.

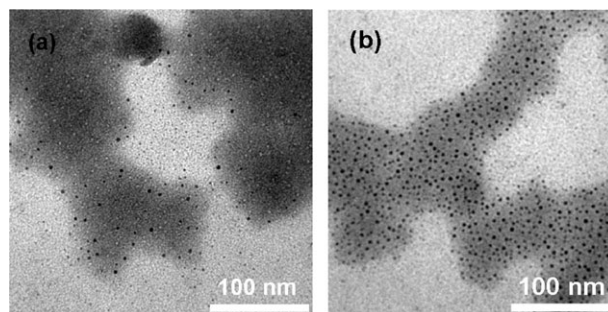


Fig. 2 TEM image of P3EEET–Au nanocomposites with different amounts of HAuCl₄ (0.05 M): (a) 20 uL; (b) 80 uL.

We then made further attempts to synthesize the P3EEET–Au nanocomposite using Au(III) doped P3EEET as a precursor. In this approach, ascorbic acid was added as a reducing agent to the Au ion–P3EEET system and the solution was aged for 24 h. The progress of reaction can be visualized *via* the color changes from dark green to deep blue. The resulting product was dried and then washed with deionized water. Unreacted gold ions and uncapped gold nanoparticles would be washed out because of poor solubility of P3EEET in H₂O. TEM images of nanocomposite with 20 uL and 80 uL HAuCl₄ (0.05 M) solution are shown in Fig. 2(a) and (b), respectively. The Au nanoparticles are well dispersed in the polymer matrix, and the size distribution is quite homogeneous, indicating excellent capping ability of P3EEET. The corresponding histogram of size distribution and EDS analysis for the Au nanocomposite are depicted in Fig. S2 and S3 of ESI.[†] TEM analysis of the diameters of 200 relatively uniform nanoparticles in Fig. 2(b) yielded an average diameter of 4.0 ± 0.5 nm.

Previously, a number of groups have synthesized Au or Ag nanoparticles by using polypyrrole, polyaniline and poly(3-octylthiophene)s (P3OT) as protecting groups.^{22–24} The reported procedures, unfortunately, involved complicated experimental protocols. Some convenient procedures have been reported to synthesize polythiophene–Au nanoparticle composites^{25,26} by reducing Au(III) ions with thiophene, followed by forming polymer *in situ*. However, due to the lack of molecular weight controlling process, it was difficult to manipulate the molecular weight of the as-prepared polythiophene. In comparison, in this study, because of the confined molecular weight distribution of polythiophene, regioregular polythiophene with PDI < 1.3 could be obtained.²⁷ Note that PDI is critical while considering the conductivity of polymers.

Fig. 3 shows the absorption spectra of Au–P3EEET nanocomposites with different amount of Au(III) ion added. In comparison to the absorption spectrum of Au(III) ion capped P3EEET, a new absorption band obviously appears at around 575 nm for the as prepared Au–P3EEET nanocomposite. It is reasonable to assign this peak to the surface plasma resonance (SPR) band of Au nanoparticles, the origin of which is well documented in the literature.²⁸ Slight deviation from the typical SPR of ~ 525 nm for the similar size (3.0–4.5 nm) Au nanoparticles in solution may indicate that the SPR band is highly sensitive to the local environment such as interparticle spacing and ligands, *etc.* in addition to size and shape.^{29,30}

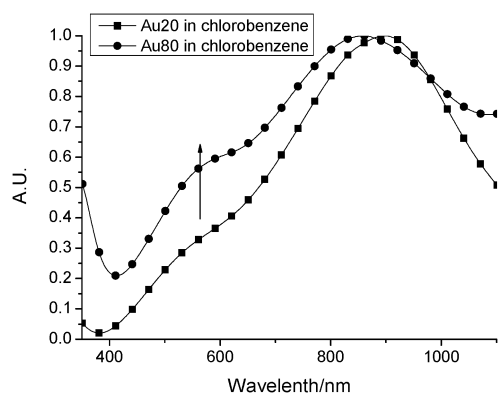


Fig. 3 Absorption spectra of Au-P3EEET nanocomposites with different amount of Au in acetonitrile: (a) 20 μL HAuCl_4 (■); (b) 80 μL HAuCl_4 (●).

We then performed a comparative experiment by first synthesizing Au nanoparticles *via* reduction of Au(III) using citric acid. Interestingly, upon mixing the as-prepared Au nanoparticles with P3EEET, no evidence of the 575 nm band was observed and the Au nanoparticles were found to precipitate and aggregate at the bottom of the reaction vial. This finding further supports the indispensability of *in situ* synthesis for obtaining P3EEET capped Au nanoparticles. To examine the role of P3EEET, a set of experiment has been performed, in which 80 μL of HAuCl_4 (0.05 M) was added into 5 mL acetonitrile. Subsequently, ascorbic acid was quickly injected into the solution. During the reaction, a brown precipitate at the bottom of vial appeared, which is believed to be due to the aggregation of gold nanoparticles. Hence, the presence of P3EEET is indispensable for obtaining monodispersed gold nanoparticles.

From the viewpoint of applications, the as-synthesized Au-free P3EEET and Au-P3EEET samples were spin coated on indium tin oxide conductive glass (ITO), and the electrical properties measured and plotted as I - V curves. As shown in Fig. 4, comparing to that of the Au-free P3EEET, the increase of Au(III) concentration in the precursor leads to a decrease of the inflection voltage of conductivity. This result may be rationalized by the facilitation of electrons hopping through metal islands in the Au nanocomposite. Raising the density of the nanoparticles could reduce the Schottky barrier formed between the nanocomposite film and electrode. Hence, the ability of electron injection from electrode to nanocomposite is significantly improved.

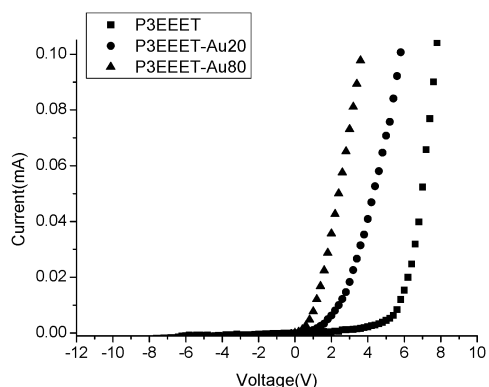


Fig. 4 I - V characteristic curves of different thin films.

In conclusion, a new approach to synthesize Au nanocrystal bound polymer nanocomposites is reported, in which P3EEET serves as the encapsulation agent. The results reveal, for the first time, the good dispersion and homogeneous size distribution of the nanoparticles in the polymer matrix. In a preliminary examination, the electrical properties of the as-synthesized nanocomposite revealed a substantial improvement of charge injection compared with that of neat P3EEET. Since the length of alkoxy side chains can be fine-tuned, this protocol, in theory, can be expanded to prepare size dependent metal NP-polymer or even semiconductor NP-polymer nanocomposites, in which the nanomaterials are derived from the corresponding metal (semiconducting metal) cation precursor. The results presented herein thus demonstrate the potential of alkyloxy modified polythiophene-based nanocomposites in the field of optoelectronics and microelectronics devices.

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