

Polymer communication

Conjugated polymer mediated synthesis of nanoparticle clusters and core/shell nanoparticles

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ABSTRACT

Two water soluble conjugated polymers, poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) and ammonium ion stabilized poly(phenylene vinylene) (P2), are found to be able to reduce noble metal ions to zero-valent metals via a direct chemical deposition technique. Au nanoparticle clusters can be obtained through reduction of Au³⁺ ions by PEDOT:PSS and the electronic coupling between them can be controlled by HAuCl₄ concentration. Core/shell Ag/polymer nanostructures are prepared from reduction of Ag⁺ ions by P2, which have a ppb detection limit for 4-MBA using surface-enhanced Raman spectroscopy (SERS). This conjugated polymer mediated synthesis of metal nanoparticles may open a new avenue for fabricating nanomaterials and nanocomposites with tunable optical properties that are dominated by their structure and electronic coupling between nanoparticles.

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1. Introduction

Metal nanostructures have revealed potentials toward optical, electronic, sensing and biomedical applications due to their size-dependent and quantum confined photophysical properties [1]. Various synthetic platforms, including chemical, physical and even biological approaches, have been developed to achieve size and morphology control of the metal nanoparticles [2,3]. Among them, solution chemistry processes are commonly used for synthesizing noble metal nanocrystals with well-defined shapes and structures wherein polyol [4], sodium citrate [5], borohydride [6,7], ascorbic acid [8], aldehyde and hydrazine [9] have been used as reducing agents. However, solution chemistry methods typically consume a large amount of organic solvents and hazardous chemicals that are considered environmentally unfriendly.

In the past few years, we have demonstrated that a conjugated polymer with a lower reduction potential than a metal ion can reduce the metal ion into zero-valent metal. Polyaniline (PANI),

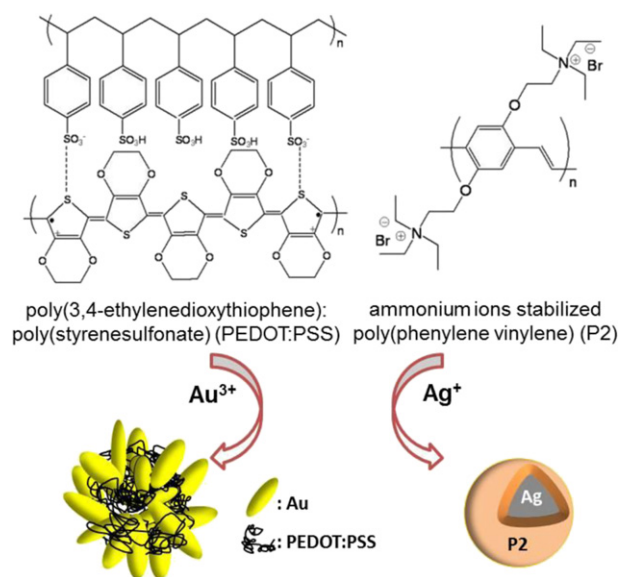
polypyrrole (PPy), and PANI-PPy copolymers have been used as reducing agents to prepare Ag, Au, Pt and Pd nanostructures [10–15]. Our recent work shows that even Ag–Au alloys can be formed by sequential deposition at PANI surfaces [16]. Of particular interest is that monomers of some conjugated polymers, e.g. 3,4-ethylene dioxythiophene and aniline, can also react with noble metal salts (HAuCl₄) to produce metal-polymer nanocomposites through a one-step process [17–20]. Those metal-polymer nanocomposites produced by the conjugated polymer mediated technique can be promising as catalysts in organic synthesis [13–15] and sensitive platforms in surface-enhanced Raman spectroscopy (SERS) [21–26].

Here, we demonstrate two kinds of water soluble conjugated polymers (Scheme 1), poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) and ammonium ion stabilized poly(phenylene vinylene) (P2), that can be used as reducing agents to synthesize metal nanoparticles. The advantage of this technique lies in the ease of obtaining water soluble metal/polymer nanocomposites via a direct chemical reduction route, which is not accessible by using other conducting polymers like PANI and PPy. Morphology and size of the Au nanostructures produced through chemical reduction by PEDOT:PSS can be easily tuned by the HAuCl₄ concentration. Reduction of AgNO₃ by P2 can lead to metal/polymer core/shell structures. We believe the conjugated polymer mediated synthesis of metal nanoparticles can open a new avenue

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Scheme 1. Schematic illustration of the conjugated polymer mediated synthesis of Au nanoparticle clusters by PEDOT:PSS and Ag/polymer core/shell nanoparticles by P2.

for fabricating nanomaterials and nanocomposites with tunable optical properties that are dominated by their structure and electronic coupling between nanoparticles.

2. Experimental

2.1. Materials

Poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) in water (1 wt%, Baytron P), HAuCl_4 (99% Aldrich) and AgNO_3 (99.9999% Aldrich) are used as received. Ammonium ion stabilized poly(phenylene vinylene) (P2) is prepared according to a previous work [28].

2.2. Synthesis

For the preparation of metal nanoparticles by PEDOT:PSS, 1 ml of as-obtained PEDOT:PSS solution was firstly diluted in 2 ml of H_2O . Then, 1 ml of HAuCl_4 solution or AgNO_3 solution was added. The solutions were manually mixed and then kept undisturbed. Here, HAuCl_4 solutions of different concentrations were used. For the preparation of metal nanoparticles by P2, an aqueous P2 solution with a concentration of 0.5 mg/ml was made as a stock solution. 1 ml of P2 solution and 1 ml 10 mM AgNO_3 solution or HAuCl_4 solution were mixed together and kept undisturbed for 6 h.

2.3. Characterization

The morphology of the prepared metal nanoparticles was imaged on a JEOL 3000F transmission electron microscope (TEM) by dropping the metal nanoparticle solution onto a carbon coated TEM grid. UV–vis spectra were recorded on a UV–visible transmission absorption spectroscopy (Varian Cary 300). The Ag/polymer core/shell nanoparticles were dispersed in MBA ethanol solution of different concentrations for 30 min before the surface-enhanced Raman scattering (SERS) response was determined. The SERS spectra were recorded on a Kaiser Raman spectrometer through a $20\times$ (0.50 NA) microscope objective, coupled with a liquid-nitrogen-cooled charge-coupled device (CCD) detector (wavelength: 785 nm). The incident laser power was kept at 2 mW and total accumulation times of 5 s were employed.

3. Results and discussion

In a typical procedure, 1 ml of PEDOT:PSS solution (Baytron P) was diluted in 2 ml of H_2O , and then 1 ml HAuCl_4 solution was added. The solutions were manually mixed and then kept undisturbed. The reaction solution was then kept undisturbed. PEDOT:PSS under TEM is micron sized sheet-like structures (See Fig. S1). The as-synthesized Au nanoparticles can be separated from the reaction system by centrifugation. At a medium speed (3000 rpm), the PEDOT:PSS will sink to the bottom, and the Au nanoparticles can be collected from the supernatant. Fig. 1 shows the TEM images of the Au nanoparticles produced by mixing PEDOT:PSS solution with HAuCl_4 solution of various concentrations at a reaction period of 2 h. With a HAuCl_4 concentration ≤ 10 mM, only scattered Au nanoparticles are produced (See Fig. S2). Here, one can see Au nanoparticles with an average diameter of 20 nm and very narrow size distribution with a HAuCl_4 concentration of 10 mM (Fig. 1a). Increasing the HAuCl_4 concentration to 20 mM has resulted in Au nanoparticle clusters (Fig. 1b), resembling the Pt–Pd structures produced through a chemical route with ascorbic acid as reducing agent [27]. The high resolution TEM image inset in Fig. 1b shows that these cluster structures are actually ensembles of Au nanorods with ~ 2 nm in width, and they are well crystallized along the (111) plane. An increase in the concentration of HAuCl_4 to 30 mM leads to Au nanospheres (~ 100 nm in size) consisting of close packed Au nanorods (Fig. 1c). However, a HAuCl_4 concentration ≥ 50 mM will produce bigger Au nanospheres, with a very broad size distribution. Moreover, Au nanoparticles that form the nanospheres are even more aggregated and it is not easy to distinguish the individual nanoparticles (Fig. 1d).

Actually, HAuCl_4 can react immediately with PEDOT:PSS upon mixing, and the reaction between PEDOT and HAuCl_4 was tracked by time-dependent UV–vis spectra. It can be seen that PEDOT:PSS solution only displays a very broad absorption band in the region of 400–800 nm, with no distinct absorption peak (Fig. 2). As we mix the PEDOT:PSS with 20 mM HAuCl_4 solution, an absorption peak corresponding to Au nanoparticles can be found at 540 nm in just 1 min, indicating that reduction of Au^{3+} ions by PEDOT follows a very fast reaction pathway. As the reaction proceeds, the Au absorption peak intensifies coupling with a slightly red-shifted λ_{max} , presumably due to the increase in nanoparticle concentration and size. After 100 min, the absorption peak stabilized at 552 nm, and thus the reaction is then terminated at a time period of 2 h. Inset in Fig. 2 shows the normalized UV–vis spectra of the Au nanoparticles prepared by using HAuCl_4 solution of different concentrations at a reaction time of 2 h. It is apparent that with increase in the HAuCl_4 solution, the size of the obtained Au nanoparticles becomes larger, as manifested by the red shifts in the UV–vis spectra, which is also consistent with the TEM results. It is important to note that the Au nanoparticle clusters obtained at 20 mM exhibit a relatively narrow and slightly red-shifted UV–vis spectrum, suggesting that these Au nanoparticles have a relatively weak electronic coupling between them. The strong coupling between Au nanoparticles emerges when the concentration reaches >30 mM, as manifested by fairly broad and heavily red-shifted absorption spectra. We believe such difference is due to Au nanoparticle clusters that are loosely bounded by polymer (Fig. 1b) as compared to some nanoparticles that are almost fused together with minimum insulation by PEDOT (Fig. 1c, d). The time-dependent UV–vis spectra of samples obtained at various concentrations can be found in Fig. S3–S5. PEDOT:PSS can also be used to reduce Ag^+ ions to Ag nanoparticles, which is found to process slower due to a lower reduction potential of Ag^+/Ag (0.799 V), as compared to that of Au growth (reduction potential of $\text{Au}^{3+}/\text{Au} = 1.50$ V). Unfortunately, shape and size control of the Ag

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