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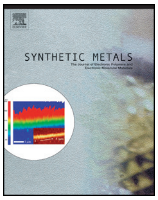

Water-soluble gold/polyaniline core/shell nanocomposite: Synthesis and characterization

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ABSTRACT

Two-step reaction has been developed to produce colloids of gold/polyaniline (Au/PANI) core/shell nanocomposites. A colloid of monodispersed gold nanoparticles was firstly prepared. Aniline monomer was used to form PANI shell with the aid of residual gold ions as an oxidizing agent. The *in situ* UV–vis spectra were studied to speculate the formation process of the nanocomposite. The obtained nanocomposites were characterized with transmission electron microscope (TEM), zeta-potential, dynamic light scattering (DLS), Fourier transform infrared (FTIR) spectrometer and spectrofluorometer. The synthetic procedure was detailed and the possible mechanism related to the formation of Au/PANI core/shell was proposed.

1. Introduction

Polymer nanocomposites have occupied a large portion of researchers think due to their wide potential applications including medical [1], catalytic [2], electronics [3], sensors [4], optical [5] magnetic [6], photodetector [7], battries [8], flat panel displays [9], solar cell [10]. The polymer/inorganic hybridization offers the opportunity to combine the properties of the individual constituents and/or generate novel and advanced properties of the composite materials. This opens the way to new and miscellaneous applications for those materials.

Among the various types of polymer nanocomposites gold (Au)/polyaniline (PANI) nancomposites have received a sophisticated concern owing to their unique optical and electrical characteristics [11]. These particular nanocomposites have recently attracted much concern due to their high surface area to volume ratio, size tunability and potential applications in chemical sensors, electronic devices and biomedicine [12,13].

Several synthetic pathways were proposed to fabricate Au/PANI nanocomposites. $HAuCl_4$ was used as an oxidizing agent for aniline polymerization in synthesis of polyaniline nanofiber and polyaniline-capped gold nanoparticles (Au NP) [14]. A thin film of Au/PANI nanocomposite was fabricated using the reduction effect of aniline to convert $AuCl_4^-$ to Au NP which in turn oxidized the aniline monomer to PANI [15]. Nanoscaled fibrous aggregates of gold/PANI nanocomposites were synthesized through the reaction of the chloroauric acid with ethanolic solution of aniline [16]. Nearly uniform polyaniline/Au nanocomposites, with a diameter of 450 ± 80 nm, were produced via direct chemical reaction between $AuCl_4^-$ ions and aniline in ionic liquid [17]. Hollow nanosphere composites of Au NP and PANI were prepared via oxidative polymerization reaction between aniline and $HAuCl_4$ in medium of p-toluenesulfonic acid [18]. Au/PANI core/shell nanocomposites with controlled size were deposited on the highly oriented pyrolytic graphite using the electrochemical method [19].

Herein, we report a new synthetic route to obtain water-soluble Au/PANI core/shell nanocomposite through the use of solution chemistry method. The Au NP was firstly prepared using the seed-growth method to get monodispersed nanoparticles. Thereafter, the aniline monomer was added to the gold nanoparticles solution where a redox reaction took place and the core/shell structure was formed. This method is considered as a striking approach to core/shell structure in three aspects. First, the preparation can be carried out at room temperature. Second, it is possible to fine tuning the growth rate and particle size of the nanocomposite by adjusting the amount of aniline used. Finally, there is no need for complicated experimental setup and/or expensive surfactant.

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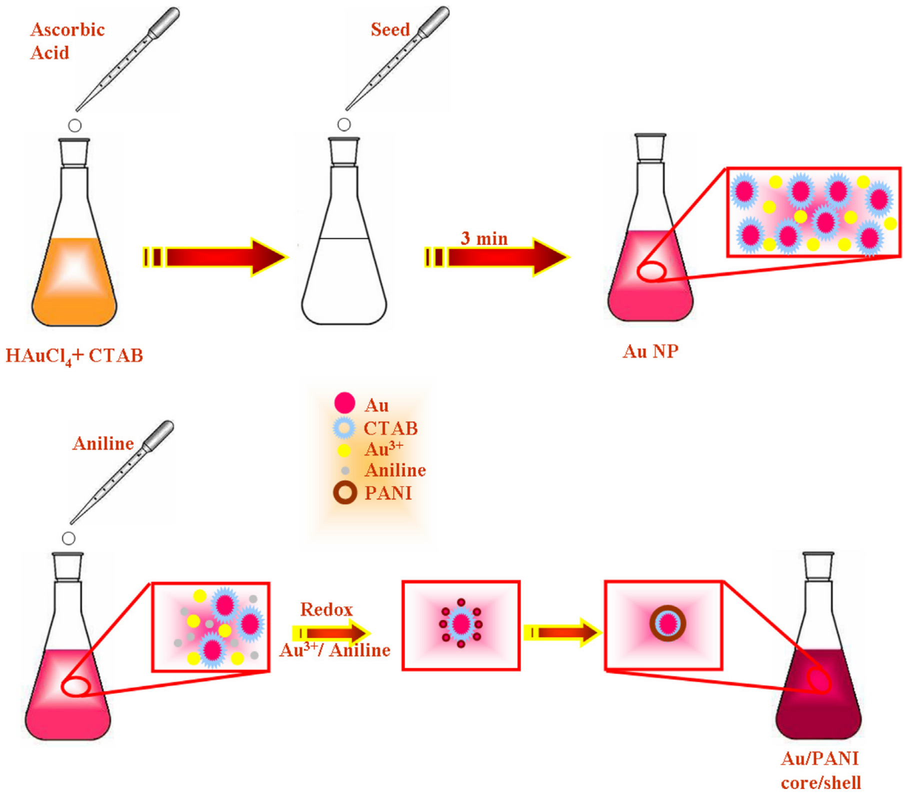

Scheme 1. The preparation steps of Au/PANI core/shell nanocomposites.

2. Materials and experimental

2.1. Materials

Gold chloride, hydrate ($HAuCl_4 \cdot H_2O$) was purchased from Electron Microscopy Sciences Co. Aniline ($C_6H_5NH_2$), Cetyltrimethylammonium bromide (CTAB), ascorbic acid and sodium borohydride ($NaBH_4$) were obtained from Sigma–Aldrich Co. All solutions were prepared using deionized water.

2.2. Sample synthesis

The whole process and the successive steps of the experiment were summarized in Scheme 1.

2.2.1. Synthesis of Au NPs

Au NPs were prepared using seed mediated growth method described elsewhere [20] with little variation. Typically, Au seeds were prepared by adding 5 mL (5×10^{-4} M) of $HAuCl_4$ to 5 mL (0.2 M) of CTAB solution with vigorous stirring. Thereafter, 0.6 mL (10^{-2} M) of ice-cold $NaBH_4$ was injected at once to obtain a brownish yellow solution.

The growth solution was prepared by mixing 5 mL (10^{-3} M) of $HAuCl_4$ to 5 mL (0.2 M) of CTAB solution under gentle shaking to obtain orange solution. To this solution, 70 μL (7.88×10^{-2} M) of ascorbic acid was added with gentle shaking. The mixture color changed from orange to colorless immediately. Herein, we eliminate the use of silver nitrate solution to obtain Au NPs instead of gold nanorods.

Finally, 12 μL of seed solution were injected at once to the growth solution and left without disturbing. The color of the solution gradually changed to red within 3 min.

2.2.2. Synthesis of Au/PANI core/shell nanocomposites

Different volumes (10, 50 and 100 μL) of aniline solution (10 M) were added to 10 mL of the Au NP solution. The mixture was stirred for 5 min to insure complete miscibility of its components. Thereafter, 3 mL of the above mixture were transferred to the quartz cuvette to follow the time course of the reaction progress. After reaction compilation, the prepared samples were centrifuged at 13,500 rpm for 15 min to get rid of unreacted species. The flocculates were collected, redispersed in deionized water and used for further characterizations.

2.2.3. Characterization

The absorption spectra of Au NP and Au/PANI colloids were recorded using V-630 UV–VIS Spectrophotometer (Jasco, Japan). Transmission electron microscopy (TEM) images were obtained using JEOL JEM 2010 TEM operated at 100 kV accelerating voltage. Additionally, zeta potential and the size of the working particles were measured using a NICOMP 380 ZLS (Particle Sizing Systems, Santa Barbara, CA) that determines particle size by dynamic light scattering (DLS). The chemical structure of the prepared samples were confirmed by recording infrared spectra using FT/IR 6100 (Jasco, Japan) in the range of 400–4000 cm^{-1}. The fluorescence spectra were collected for Au NP and Au/PANI colloids, using FP-6500 spectroflurometer (Jasco, Japan).

3. Results and discussions

3.1. Formation of Au/PANI core/shell nanocomposite in aqueous solution

In order to get further insight into the formation process of Au/PANI core/shell nanocomposite, we recorded in situ UV–vis absorption spectra as a function of time (every 2 min) to track the process (see Fig. 1). At the beginning of the reaction, only one