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In situ spectroscopic and electrochemical impedance study of gold/poly (anthranilic acid) core/shell nanoparticles

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ABSTRACT

The present study reports a facile and simple method to prepare (Gold/Poly Anthranilic acid) (Au/PANA) core/shell nanostructures with uniform size and morphology in an aqueous solution through oxidation of the monomer (3-aminobenzoic acid) and reduction of the Au(III) ions simultaneously. In this work, gold nanoparticles were highly dispersed and stabilized by the oxidation of 3-aminobenzoic acid in order to form a uniform metal–polymer core/shell nanocomposite. Fabricated nanocomposites have been characterized by UV–Visible spectroscopy, attenuated total reflection–Fourier transform infrared (ATR–FTIR) and X-ray diffraction. Morphology of nanocomposites was analyzed by atomic force microscopy (AFM), scanning electron microscopy (SEM). Electroactivity of Au/PANA core/shells were investigated by electrochemical impedance spectroscopy (EIS) and equivalent circuit modeling was performed.

In situ spectroscopic characterization of polymerization reaction indicated the reaction between gold ions and 3-aminobenzoic acid and formation of Au/PANA core/shell nanoparticles during reaction period. FTIR–ATR and UV–Vis spectroscopy results evidenced the incorporation of Au nanoparticles into PANA. XRD analyses indicated the high degree of crystallinity of Au. SEM images showed homogeneous distribution of Au/PANA core/shell nanocomposites with the size of ~20 nm. EIS data suggested that as the initial concentrations of Au and PANA increased, the core/shell nanocomposites started to act like as an ideal capacitor.

1. Introduction

Nowadays, there is a growing interest in the research areas dealing with heterogeneous materials. Core–shell nanostructures are one of the heterogeneous materials with desirable properties Due to the combination of two different components i.e. matrix and filler in core–shell structures, the processability of the material will be enhanced, depending on the dimensions and properties of the core or the shell, the thermal and electrical properties of the composites will be balanced for various applications. Core–shell studies have flourished over the past years for applications in a wide range of fields such as drug delivery [1], catalysis [2], batteries [3], cell imaging [4], nanoscale electronics [5], photonics [6], sensors [7], and energy storage [8].

For many of these applications, the core–shell structures with core of metal nanoparticles based on Au [9], Cu [10], Pt [11], and Pd [12] and shell of conducting polymers (CPs), have attracted great interest.

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Among the various conducting polymers, Polyaniline (PANI) has been considered as the potentially one of the most useful semiconducting polymer because of its high conductivity, environmental stability, low-cost of its synthesis and controllable electrical conductivity with interesting redox properties [13]. However, some undesirable properties of PANI such as low solubility and poor processability, limit its usage [14]. In this study, Poly(anthranilic acid) (PANA) which is a PANI derivative was used, since PANA is more processable due to its solubility in aqueous, non-aqueous solvents and other polar solvents [15].

Some methods have been reported to synthesize core/shell nanostructures such as, one-step hydrothermal reaction using the colloidal stabilizer [16], UV radiation [17], interfacial polymerization in the presence of PVP [18], one-step synthesis of core–shell morphologies using PVA as a colloidal stabilizer [19], synthesis of nanoparticle, followed by polymerization around the particles or dispersion of the nanoparticle in a polymer matrix [20]. However, in these methods it is difficult and time-consuming to control the size of core/shell nanoparticles.

Here, we report an in situ, feasible, fast and low-cost oxidative polymerization route for the preparation of Au/PANA core/shell nanostructures with size distribution control. In this method, oxidation of monomer and reduction of metal ions take place simultaneously for forming composite structures (metal–polymer) [21,22]. Use of gold(III) chloride as an oxidant for polymer synthesis provides a new route for chemical synthesis of core/shell nanocomposites.

In this study, gold(III) chloride was used as an oxidant for 3-aminobenzoic acid (PANA monomer), to fabricate Au/PANA core/shell nanocomposites. Detailed in situ spectroscopic characterization which provides a precise control over proceeding of the polymerization in each step of reaction between gold ions and monomer has been performed. The structural properties and crystallinity of the Au/PANA core/shells were determined by FTIR–ATR and XRD. Morphologies of AU/PANA nanocomposites were investigated by SEM and AFM. The effect of initial oxidant and monomer amounts on the electrochemical impedance (EIS) properties of resulting Au/PANA core/shell nanocomposites were studied. The incorporation of Au nanoparticles into PANA was evidenced by FTIR–ATR and UV–Vis spectroscopy. XRD analyses indicated the high degree of crystallinity of Au with face-centered cubic (FCC) crystal structure. SEM and AFM images showed the formation of gold nanoparticles with the size of ~20 nm. EIS and equivalent circuit modeling of Au/PANA core/shell nanocomposites indicate that as the initial concentrations of Au and monomer increased, the core/shell nanocomposites started to act like as ideal capacitors and capacitance values of nanocomposites were increased with the increase of Au and PANA.

2. Materials and methods

2.1. Materials and instruments

3-Aminobenzoic acid ($C_7H_7NO_2$), and Hydrogen aurichloride ($HAuCl_4$) were obtained from Sigma Aldrich. Ammonium persulfate (APS) was obtained from AKSA Chemicals. All the chemicals used were as analytical grade. Double-distilled deionized water was used in all of the experiments.

2.2. Synthesis of Au/PANA core/shell nanocomposites

Polymerization process was carried out at an average room temperature of 25 ± 1 °C. 3-Aminobenzoic acid was dissolved in double distilled water with the final concentration of 123 μM and the solution was sonicated for 15 min. $HAuCl_4$ as an oxidant was added drop wise to the monomer solution and polymerization was carried out for 24 h. The molar ratio of oxidant ($HAuCl_4$) to 3-aminobenzoic acid (anthranilic acid) in the final solution was 1:1. After 1 h, the color of yellow 3-aminobenzoic acid/gold solution changed to purple. Then this solution was stored at 25 ± 1 °C.

To investigate the effect of gold and polyanthranilic acid on the electrochemical properties of fabricated nanocomposites, two groups of samples were prepared. First group was prepared in increasing concentrations of $HAuCl_4$ (oxidant) and 3-amino benzoic acid (monomer) (123 μM) with a constant molar ratio between them. These samples were labeled as (Au/PANA), 2(Au/PANA), 3(Au/PANA) and 4(Au/PANA) for increasing concentrations. Second group was prepared with increasing concentration of $HAuCl_4$ (oxidant) and a constant concentration of 3-amino benzoic acid. Samples of second group were labeled as (Au/PANA), (Au/PANA) (1/1), (Au/PANA) (2/1), (Au/PANA) (3/1) and (Au/PANA) (4/1). A tentative reaction mechanism of polymerization is given in Fig. 1.

2.3. Characterization of Au/PANA core/shell nanocomposites

Au/PANA core–shell nanocomposites were analyzed and characterized using the following techniques: In order to study the reaction kinetics in detail, in situ polymerization reaction was followed in equal time intervals (4 min) by UV–visible spectroscopy (Perkin Elmer, Lambda 45). The structural properties of the synthesized Au/PANA core/shell structures were characterized by Fourier transform infrared–attenuated total reflectance (FTIR–ATR) spectrophotometer (Perkin Elmer, Spectrum One, with a universal ATR attachment with a diamond and ZnSe crystal, USA). Crystalline structure of Au/PANA core/shell nanocomposites were analyzed by XRD (Shimadzu XRD-6000). Surface morphologies of nanocomposites, were investigated by atomic force microscope (Nanosurf EasyScan2) in non-contact mode using Al coated high resonance frequency silicon tips Nanosensors NCRL tips (40 μm width, 225 μm length) and (SEM) (scanning electron microscopy) (QUANTA 400 F) with 10 kV accelerating voltage. Electrochemical impedance spectroscopy (EIS) measurements of solutions of Au/PANA core/shell nanocomposites were performed using potentiostat 2263 Electrochemical Analyser (Princeton Applied Research, USA) with frequency range between 0.01 Hz and 100 kHz and AC voltage of 10 mV. EIS measurements were performed on both solutions of Au/PANA core/shell nanocomposites which were synthesized in two groups and the dilutions of 4(Au/PANA) and (Au/PANA) (4/1). The synthesized Au/PANA core–shell