Synthesis, characterization and electrical properties of highly conductive polyaniline/gold and/or platinum nanocomposites

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ABSTRACT

Novel polyaniline/gold (PANI/Au) and polyaniline/platinum (PANI/Pt) core–shell nanocomposites were successfully synthesized via miniemulsion polymerization of aniline monomer in presence of chloroauric acid and chloroplatinic acid respectively. The morphology and structure of the prepared composites were characterized by scanning electron microscopy (SEM), light microscope (LM), transmission electron microscopy (TEM), dynamic light scattering (DLS), gel permeation chromatography (GPC), Fourier transform infrared spectroscopy (FTIR) and thermo gravimetric analysis (TGA). A possible formation mechanism of the PANI/Au and PANI/Pt core–shell nanocomposites was also proposed. The DC conductivity measurements at room temperature for the prepared nanocomposites showed very high conductivities due to presence of Au and Pt nanoparticles.

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1. Introduction

Polyaniline (PANI) is one of the most widely used conductive polymers and has distinctive electrical, optical, photoelectric properties and good environmental stability [1].

Incorporation of metal [2] or semiconductor nanoparticles [3,4] into PANI has been proposed as a way of enhancing its electrochemical, electrocatalytic activities as well as sensing properties.

Polyaniline/gold (PANI/AuNPs) nanocomposites are considered to be particularly unique materials because gold nanoparticles AuNPs have attractive electrical and optical properties as well as extensive applications in diverse areas [5].

Therefore intensive research work on the preparation of nanometric metals dispersed into conducting polymer matrices has been carried out in recent years. Polythiophene–Au [6], Pd [7], polypyrrole–Au [8], Ag [9], polyaniline–Pd [10,11], and Au [12,13] nanocomposites have been obtained and their optical [8], sensing [11,13] and catalytic [7,10] properties have been also investigated.

Formation of the PANI/metal composites has been mostly restricted to the mixing of these materials after previous separate growth [14] or sorption of metal anions by the previously formed polymer [15–17]. However, the dispersion of the metal in the polymer is limited because the anion typically reduces at the point of contact rather than dispersing into the polymer matrix and accumulation of metal nanoparticles in the sorption process has been reported to be as high as five times the original polymer weight [18]. The lack of chemical control of the metal-polymer sorption process at the imino nitrogen remains a strategic limitation of such processes. Electrochemical methods offer precise control of the polymer oxidation state, thus prompting the degree of interaction between the polymer and the metal anion. For example, Pt [19], Au [20], Ag [21] and Pd [22] have all been reduced into polyaniline using electrochemical methods. However, the quantity of material obtained from electrochemical methods is limited by the electrode size and the polymer/metal interface. In addition, the formation of oxidized units in the polymer happens as the metal anion is reduced and the polymer oxidized. The end result is a greater number of oxidized units in the polymer and reduced conductivity of the material.

In this context, it is important to produce the PANI/metal composite while maintaining the doping and oxidation state of the polymer, in order to preserve high conductance furthermore, the process should be conducted in the conditions which limit the growth of the crystals upon their formation and prevent them from subsequent agglomeration. To overcome all these drawbacks; we represent here a novel synthesis type route for the preparation of highly conductive PANI/Au and PANI/Pt composites using chloroauric acid and chloroplatinic acids, as both an oxidant and a post polymerization dopant via miniemulsion polymerization

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technique using a homogenizer at 10,000 rpm. The crushing and degradation effects of the homogenizer enable the production of uniform nobel metal nanoparticles encapsulated into PANI matrix and thus preventing the agglomeration of metal nanoparticles and eliminating the over-oxidation of the polymer with the formation of the polymer building block tied to the reduction of $AuCl^{-4}$ or $PtCl^{-6}$ by aniline rather than the pre-formed polymer.

No literature is available on the synthesis of PANI/Pt composite via simple chemical oxidative technique. Hence an attempt has been made to synthesize it.

2. Experimental

2.1. Materials

Chloroplatinic acid solution (8%wt in H_2O), tetrachloroauric acid aniline monomer and dodecyl benzene sulfonic acid (DBSA) are products of Sigma–Aldrich, USA.

2.2. Preparation of PANI/Au composite

Aniline and DBSA of ratio (1:1) have been mixed in water and isopropanol (IPA) mixture of ratio (3:1) respectively under continuous vigorous stirring using homogenizer at 10,000 rpm for 5 min to form the miniemulsion. A 20 ml of 1.5×10^{-2} M tetrachloroauric(III) acid solution has been added dropwisely to the former miniemulsion under continuous vigorous stirring at 10,000 rpm for further 10 min at room temperature. A color change from white to bluish green then to green has been observed. At the final stage of polymerization, a stable green colloidal dispersion has been obtained. The green dispersion was further centrifuged, washed several times with water/methanol mixture of ratio (1:3), filtered and then dried and kept for further use.

2.3. Preparation of PANI/Pt composite

The same as previously mentioned except that we have used 20 ml of 1.5×10^{-2} M H_2PtCl_6 solution instead of auric acid solution. The stable dispersion was then centrifuged, washed, filtered, dried and finally kept for further use.

2.4. Characterization of the prepared composites

2.4.1. Gel permeation chromatography (GPC)
The molecular weight and the polydispersity index were investigated using Agilent 1100 series, Germany, Detector: Refractive Index, Styrogel HR-DMF, (3 μm), 7.8 × 300 mm, Water Company Ireland. (5000–600000) one column.

2.4.2. Dynamic light scattering (DLS)
The particle size distribution as well as average size diameter were determined using a Zetasizer from Malvern Instruments, England (model 3000-HS) using a He–Ne laser at a wavelength of 632 nm. The samples were dispersed in water and sonicated for 20 min before the measurement.

2.4.3. Light microscope (LM)
The obtained composites were examined by Mitutoyo Microscope, MRL fabrication facility, University of Illinois at Urbana Champaign (UIUC), USA.

2.4.4. Fourier transform infrared (FT-IR) spectra
FT-IR analysis of the prepared composites has been carried out at Infra-Red Unit, Central Service Labs, National Research Center (NRC) using FT-IR-6100, Japan.

2.4.5. Thermal analysis (TGA)
Thermal analysis for the prepared materials has been carried out at Thermal Analysis Unit, Central Service Labs, (NRC) under constant rate of nitrogen using PerkinElmer (TAC 7DX) and Shimadzu-TGA 50H thermal analysis system, Germany. The heating rate was 10 °C/min.

2.4.6. Scanning electron microscope (SEM)
Samples have been measured using SEM JOEL 6060 LV, Japan at the MRL Lab, University of Illinois – Urbana Champaign (UIUC).

2.4.7. Transmission electron microscope (TEM)
Samples have been measured using transmission electron microscope HTEM (JOEL) 2010F, Japan at MRL Lab, University of Illinois – Urbana Champaign (UIUC).

2.5. Electrical conductivity measurements

For the conductivity measurements, the samples were compacted using direct uniaxial pressing into cylindrical pellets under a pressure of 12.5 MPa. Electrical conductivity measurements were carried out using Kethly (6451A) bridge at Electron Microscope Laboratory, Physics Department, National Research Center (NRC).

3. Results and discussion

The molecular weight determination and polydispersity of the prepared PANI/Au and PANI/Pt composites have been investigated using GPC technique. The purified composite samples were dissolved in DMF for testing. It was found that the formed composites are polydisperse and have low molecular weights. The molecular weights of PANI/Au and PANI/Pt composites are 7.518×10^3 and 6.528×10^3 g/mol respectively.

Gold and platinum nanoparticles and their arrays are some of the most studied nanomaterials, with promising applications in many fields such as electronics, optoelectronics, catalysis and biology. In order to protect bare gold and platinum nanoparticles from aggregation, to manipulate the optical, electronic and catalytic properties of the gold and platinum core, as well as to control interfacial properties, the gold and platinum nanoparticles are generally capped by an organic layer. Here we represent a novel type synthesis route for uniform encapsulation of gold and platinum nanocrystals into conducting polyaniline shell. The formation of the nanocrystals depends on the crushing and degradation effects of the homogenizer which enables the gold and platinum ions in their solvated state of high free energy to transform to one of low free energy in the crystal lattice.

The mechanism of the formation of PANI encapsulated gold and platinum nanocrystal is as follows:

First: functionalized protonic acids have been used to transform PANI into the metallic form and, consecutively, render the resulting PANI complex soluble in common organic solvents Cao et al. [23] in 1992. The functionalized counter ion acts like a 'surfactant' in that the charged head group is ionically bound to the oppositely charged protonated PANI chain, and the 'tail' is chosen to be compatible with nonpolar or weakly polar organic liquids [24–27]. This method is also known as 'counter-ion-induced processability'.

A mechanism for the stepwise formation of nanoclusters [28,29] based on nucleation, growth, and agglomeration has been proposed. The model is as follows: in the developing stage of nucleation, the metal salt is reduced to give zerovalent metal atoms. These can collide in solution with other metal ions, metal atoms, or clusters to form irreversible "seed" nuclei, which can be below 1 nm depending on the strength of the metal–metal bonds and the difference between the redox potentials of the metal salt and the reducing agent (anilinium salt) applied. We believe that