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A quick electrochemical approach for synthesizing the metal nanostructures stabilized with conducting polymers

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ABSTRACT

We demonstrate a simple technique to produce gold nanoparticles (GNPs) stabilized with polyaniline (PANI) in the aqueous solution. The method is extremely efficient yet an uncomplicated process, which involves the in situ electrochemical-*cum*-chemical polymerization of aniline to yield the metal nanoparticles. The nanosize particles were examined with the help of UV–vis and HRTEM. The proposed method although combines electrochemical and chemical synthesis events, however it is essentially a single step process. The method can also be extended for various other combinations of metals and conducting polymers.

1. Introduction

Conducting polymers have been used to obtain different kinds of nanostructures such as nanotubes, nanofibers, nanorods and nanoparticles with metals [1–11]. Polyaniline (PANI) is studied extensively but it can still act as a model system for analyzing the behavior of conducting polymers. PANI is arguably the most studied conducting polymers for preparing polymeric nanostructures. In the literature two main methods are described for the preparation of the PANI, chemical and electrochemical methods. The common examples of the oxidizing agents for aniline oxidation during the chemical synthesis of PANI are ammonium peroxydisulfate, hydrogen peroxide, etc. Whereas acids such as sulfuric acid, hydrochloric acid and other strong acids are commonly used electrolytes during the electrochemical synthesis of PANI. Reports are also available on the use of chloroaurate ($AuCl_4^-$) as an oxidizing agent for the aniline oxidation [9–11]. For example, Wang et al. have in their work prepared polyaniline nanofibers and gold nanoparticles simultaneously by using chloroaurate as the oxidizing agent for aniline. The observed size of the gold nanoparticles from X-ray diffraction studies was found to be 26 nm [10]. Recently researchers have also shown different structures from gold and PANI ranging from needles, wires, core shells, flowers and plates and majority of the synthetic methods available in the literature are solution based. There is however lack of literature on electrochemical preparation of the Au-PANI nanocomposite. In the present paper we discuss about a simple electrochemical-cum-chemical method to produce Au nanoparticles stabilized with PANI. The nanoparticles were formed in situ during the galvanostatic dissolution process in the presence of aniline in dil. HCl with Au wire working as anode and another large area gold electrode as cathode. The electrochemical process consists of the in situ polymerization of aniline and subsequently the formation of gold nanoparticles in the solution. The present method is of significance owing to the fact that it is a single step method without the extra steps of the preparation of the individual components separately and their subsequent mixing.

2. Experimental methods

All the chemical reagents used in this study were analytical grade reagents. Aniline AR grade and hydrochloric acid (high purity grade) were used in our study. Millipore water with a resistivity of 18.2 MΩ cm was used throughout the study to prepare the aqueous solutions. We have carried out the galvanostatic dissolution experiments with a large area gold substrate as working electrode, which was prepared by depositing the gold with the help of vacuum deposition method on glass substrate with chromium underlayer. The electrode has a geometric area of 0.1 cm^2. A high purity Au wire was used as anode having length 5.0 mm and 0.5 mm diameter. The cell was thoroughly cleaned before each experiment and kept in a hot air oven at 100 °C for at

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least an hour before the start of the experiment. Prior to use, the gold substrate and wire were thoroughly cleaned in "piranha" solution (a mixture of 30% H_2O_2 and conc. H_2SO_4 in 1:3 ratio; *Caution! Piranha solution is highly reactive with organic compounds, storing in a closed container and exposure to direct contact should always be avoided*). Finally, the electrodes were cleaned by rinsing in millipore water before the electrochemical experiment. Galvanostatic dissolution method was carried out using an EG&G potentiostat (model 63A) interfaced to a computer through a GPIB card (National Instruments). The UV–vis spectra were obtained using a spectrometer from SHIMADZU. TEM studies were carried out with Model FEI (Tecnai G2 20 S-Twin 200 kV) TEM.

3. Results and discussion

There are some reports in the literature on the electrochemical preparation of metal nanoparticles, for example; Reetz et al. have used a sacrificial anode technique in order to produce Pd nanoparticles in the electrolyte solution, which were stabilized with the help of tetraalkylammonium cation. Pd ions migrate towards the cathode and subsequently the reduction takes place on cathode [12,13]. Our approach is unique because for the first time we have simultaneously carried out the in situ electropolymerization and gold nanoparticles formation. The nanoparticles preparation method can be summarized as following. A 10 ml electrochemical cell was used for the galvanostatic dissolution, 5 mg aniline solution was prepared in 5 ml 0.1 M HCl, a current of 50 mA was used during the process. This current was optimized after several attempts at different currents. At lower currents than 50 mA the dissolution was sluggish and could not result in nanoparticles formation. On the other hand, a current higher than 50 mA was resulted in rapid dissolution followed by agglomerated mass formation in the solution. The electrolyte solution was continuously stirred during deposition process. In the beginning of the experiment the solution was colorless, which turned to light blue initially and at the end of experiment turned to wine red. This is the indication of the formation of gold nanoparticles in the solution. After 30 min the reaction was stopped and the colored aqueous solution was collected in a conical flask. We then added toluene into the aqueous solution and a phase transfer method was used to separate the nanoparticles from the electrolyte impurities. As we stirred the solution the toluene phase slowly turned to wine red color and aqueous phase to light colored. This is an indication that gold nanoparticles transfers from the aqueous phase to the organic (toluene) phase. The nanoparticles present in toluene phase were used for the further characterization.

In a similar approach Pd wire was used in place of Au, in 5 mg aniline, 5 ml 0.1 M HCl and a current of 50 mA was used during the process. The solution turned to light red colored after 30 min of dissolution. After the Pd dissolution, we also observed black colored deposit floating on the solution surface, which was characterized under an optical microscope and TEM.

The mechanism of nanoparticles formation in the case of Au dissolution can be summarized as following. During the process of electrochemical dissolution, gold dissolves as Au^{3+} ions from the Au wire. The Au^{3+} ions react with the chloride ions present in the solution and forms chloroaurate salt [10,11]. The chloroaurate salt electrostatically couples with the aniline present in the solution and forms a complex. Then the oxidation of aniline and the reduction of the chloroaurate salt take place. The aniline polymerization reaction was evident as the blue color of the solution in the beginning of the experiment. The polymerized aniline can bind the Au clusters, formed after the reduction of Au ions, within its matrix and thus the Au-PANI nanocomposite forms in the solution. This is similar to the bulk polymerization reaction with only difference that during the electrochemical synthesis gold ions originate from the Au wire anode (Fig. 1).

We performed UV–vis measurements to verify the surface plasmon band of gold nanoparticles. In order to do this, the nanoparticles solution in toluene was used for UV–vis experiment. Fig. 2 shows the UV–vis spectra of the nanoparticles in toluene, we can see that a surface plasmon band appears at a wavelength of around 500 nm. This band is attributed to the presence of nanosize clusters of gold in the solution. The band is present at 500 nm, which is an indication that the nanoparticles are very small of about 2–10 nm in dimension [14].

To further verify the size and shape of nanoparticles we have carried out TEM measurements on the nanoparticles solution. Fig. 3 shows the TEM images of the nanoparticles. In Fig. 3a we can see that the average size of the nanoparticles is around 5–10 nm and they are fairly uniform in size. Fig. 3b is the high resolution image of the nanoparticle, which reveals the lattice fringes. Fig. 3c shows the selected area diffraction pattern of nanoparticles and it reveals a polycrystalline structure of the nanoparticles. The most prominent ones are at distance 0.235 and 0.2 nm and they can be indexed to (1 1 1) and (2 0 0) fcc structure of gold respectively. All the indices are shown in Table 1.

We have also prepared a thin film of nanoparticles on a substrate and performed XPS experiment, which provides valuable information on the density of occupied electronic states in a surface. In a typical XPS experiment the X-ray beam penetrates the material and ejects electrons from the valence or core levels

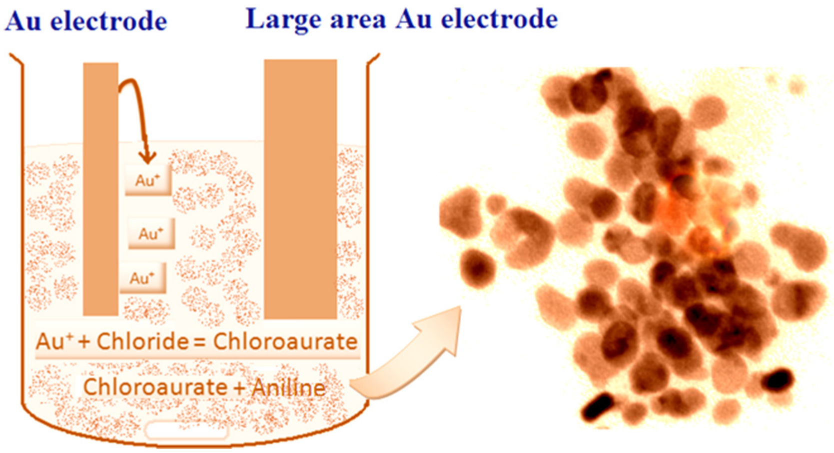

Fig. 1. Schematic representation of the metal–polymer nanostructures preparation method. We performed UV–vis measurements to verify the surface plasmon band of gold nanoparticles. In order to do this, the nanoparticles solution in toluene was used for UV–vis experiment.