

Preparation of novel core-shell nanoparticles by electrochemical synthesis

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Abstract: Nanostructural gold/polyaniline core/shell composite particles on conducting electrode ITO were successfully prepared via electrochemical polymerization of aniline based on 4-aminothiophenol (4-ATP) capped Au nanoparticles. The new approach to the fabrication included three steps: preparation of gold nanoparticles as core by pulse electrodeposition; formation of ATP monolayer on the gold particle surface, which served as a binder and an initiator; polymerization of aniline monomer initiated by ATP molecules under controlled voltage lower than the voltammetric threshold of aniline polymerization, which assured the formation of polyaniline shell film occurred on gold particles selectively. Topographic images were also studied by AFM, which indicated the diameter of gold nanoparticles were around 250 nm. Coulometry characterization confirmed the shell thickness of polyaniline film was about 30 nm. A possible formation mechanism of the Au/polyaniline core-shell nanocomposites was also proposed. The novel as-prepared core-shell nanoparticles have potential application in constructing biosensor when bioactive enzymes are absorbed or embedded in polyaniline shell film.

Key words: core-shell nanocomposites; polyaniline; gold nanoparticles; electrodeposition; 4-aminothiophenol

1 Introduction

In recent years, the development of inorganic particles and polymer composites has attracted intensive interest due to a wide range of the potential use of these materials[1–5]. Particularly, the preparation of composites of metal particles and conducting polymers with core-shell structure is of interest and becomes a novel challenge because of their interesting properties and potential applications in technological fields. LU et al[6] and ZHAO et al[7] have reported the synthesis of Ag/polyaniline core-shell nanocomposites based on silver nanoparticles colloid, respectively. KHANNA et al[8] have reported the synthesis of Ag/polyaniline nanocomposite via an in situ photo-redox mechanism. Moreover, one-pot synthesis of Ag/polyaniline composite has also been reported[9–10]. All these composites are synthesized from aqueous media containing the monomer and a dispersion of Ag particles. LIU and CHUANG[11] have reported gold/polypyrrole core-shell nanocomposites prepared by electrochemical methods in aqueous solutions. More recently, SMYTH et al[12] has reported in situ electropolymerised silica-polyaniline

with core-shell structures. Encouragingly, herein, the fabrication and characterization of gold/polyaniline core-shell nanocomposites via electrochemical polymerization of aniline based on 4-aminothiophenol capped Au nanoparticles on ITO surface were reported.

2 Experimental

2.1 Au nanoparticles on ITO substrate

Gold particles were deposited using a double pulse potential on a CHI-660 electrochemical workstation. The clean ITO glass electrode was put in a 1 mmol/L $\text{HAuCl}_4 + 3$ mmol/L LiCl solution, and a 1 ms nucleation pulse with amplitude of -200 mV vs SCE was first applied. A second growth pulse having amplitude of 350 mV was then applied for 30–50 ms. Following deposition, the ITO electrode was removed from the plating solution, rinsed with pure water.

2.2 Polyaniline-covered gold nanoparticles on ITO substrate

The Au/ITO electrode was immersed in 1 mmol/L 4-ATP+ethanol solution overnight. After rinsing with ethanol solution, the ATP monolayer modified Au/ITO

electrode was transferred in 5 mmol/L aniline+0.5 mol/L H_2SO_4 solution and deposition of aniline was carried out by cycling from -200 mV to 780 mV for 30 scans at a scan rate of 20 mV/s. After cycling, thus obtained polyaniline-covered gold shell-core nanoparticles on ITO substrate was removed from the solution and rinsed with ultrapure water and subsequently dried in a stream of N_2 before AFM experiments were performed.

3 Results and discussion

3.1 Micrograph of Au and Au/polyaniline particles

The morphology and structure of the Au and Au/polyaniline particles were characterized by AFM. Typical topographic non-contact AFM images of the Au nanoparticles are shown in Fig.1, where the Au particles exhibit spherical structure with diameter ranging from 250 to 300 nm. As can be seen, the spacing and size of Au nanoparticles can be regulated by changing step potential and pulse intervals. Fig.2 shows the AFM image of the Au/polyaniline core-shell nanocomposites, where the Au nanoparticle with a mean diameter of ca. 250 nm is the core of the nanocomposite and the polyaniline as the shell wrap of the Au nanoparticle. The polyaniline film thickness is estimated to be around 30 nm based on the AFM image.

3.2 Electrochemical response of gold/polyaniline core-shell structural particles

Electrochemical confirmation of gold particle formation was carried out in 0.1 mol/L KCl by cyclic voltammetry as shown in Fig.3. It displays a broad anodic peak at 0.8 V and a relatively small cathodic peak at 0.4 V on the negative scan, corresponding to oxidation and reduction between Au(0) and Au(III), while the small reduction peak is due to the flux of a significant portion of Au^{3+} cation from oxidation of Au(0) at the electrode to solution and less diffusion to electrode surface and thus less Au^{3+} is re-reduced.

The electrochemical response of polyaniline covered gold ITO electrode was investigated by cyclic voltammetry in the potential range between -0.2 V and $+0.8$ V in 0.5 mol/L H_2SO_4 solution, and the result is shown in Fig.4, in which, two pairs of redox peaks center at around 0.20 V and 0.55 V corresponding to the transformation of leucoemeraldine base to emeraldine salt and emeraldine salt to pernigraniline salt, respectively, which is in good agreement with typical polyaniline redox features in Refs.[13–14]. It is worthy to note that no gold features are visible any more in the cyclic voltammogram, indicating a full coverage of

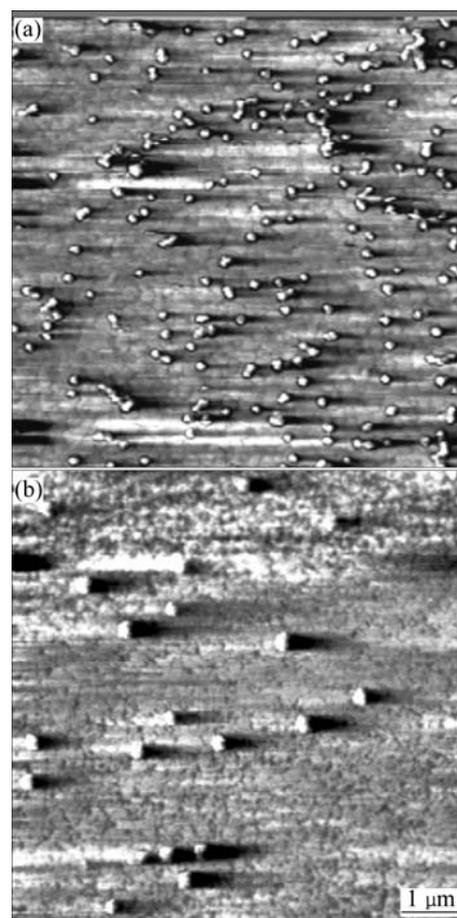


Fig.1 AFM images of Au/ITO with different diameters and densities: (a) High density; (b) Low density

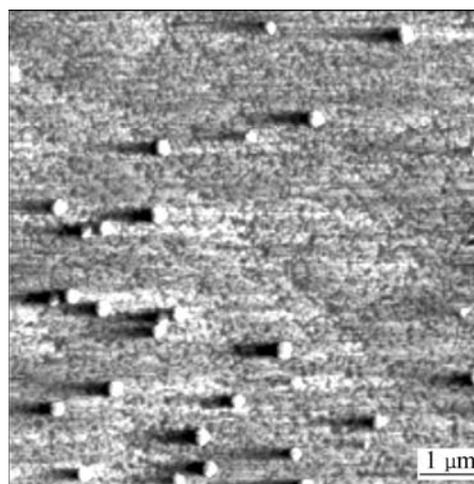


Fig.2 AFM image of gold/polyaniline particles on ITO polyaniline thickness estimated to be 30 nm

polyaniline film on gold surface. It could also be observed that little polymerization appears to take place on the underlying ITO electrode surface.

A scheme was proposed to explain the formation mechanism of Au/polyaniline core-shell nanocomposite (Fig.5). When the gold particle-modified ITO glass

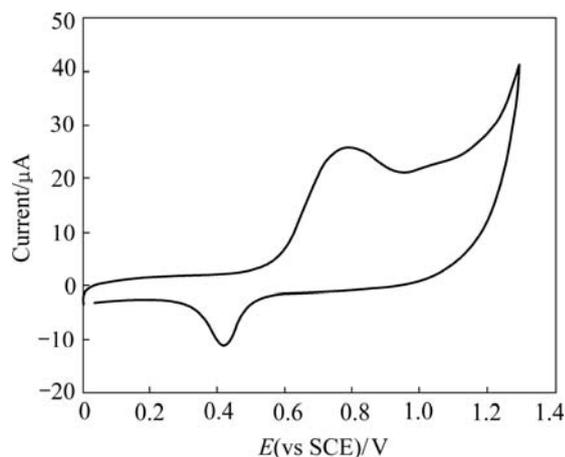


Fig.3 Cyclic voltammetry of Au/ITO in 0.1 mol/L KCl solution

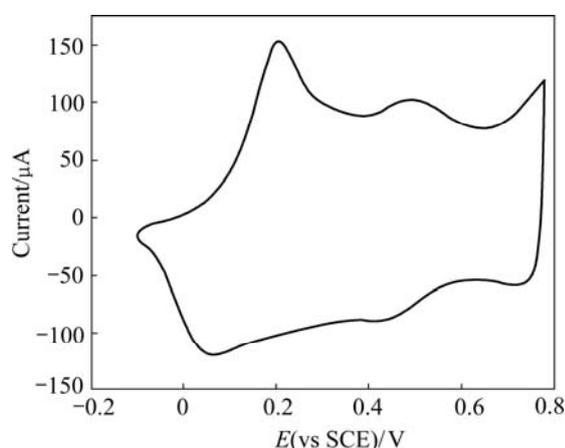


Fig.4 Cyclic voltammetry of gold/polyaniline on ITO from -100 mV to 800 mV at scan rate of 100 mV/s

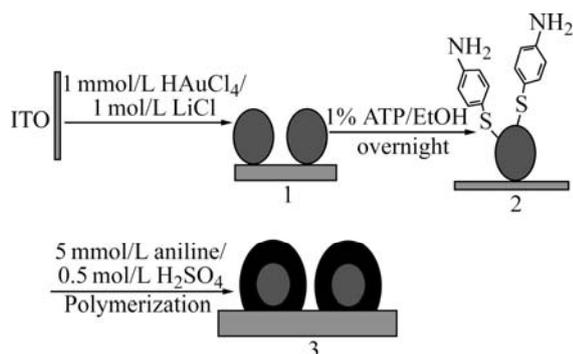


Fig.5 Formation mechanism of Au/polyaniline core-shell nanocomposite

electrode was immersed in ethanolic solution of 4-aminothiophenol (4-ATP) for 24 h, a self assembly monolayer (SAM) of 4-ATP formed on the surface of gold particles. The application of 4-ATP to form capped gold particles on ITO electrode surface played an important role. It is reported that oxidation of 4-ATP occurred at 730 mV vs SCE, about 260 mV earlier to oxidize than aniline in solution phase, which was

approximately at 1.05 V[15–17]. Thus, with the application of onset oxidation potential of 4-ATP, 4-ATP radical cations were electrogenerated on the particle surface in aqueous media, which acted as a point of nucleation to initiate the polymerization reaction of aniline monomer. During the electropolymerisation, polyaniline (PANI) was initially formed within the 4-ATP sites, and then it preferentially grew around the gold particles rather than on the underlying electrode surface because the electrode was held at the 4-ATP oxidation potential and no radical cations were present in solution. The formed PANI was conductive and it could continue the in situ electropolymerisation. As a result, a localized electropolymerization of aniline on ATP molecular sites, which are covalently attached on gold, results in the formation of shell-core composites.

The as-prepared core-shell Au/polyaniline nanocomposites could be a good candidate for the construction of electrochemical biosensors when bioactive enzymes are embedded into the nano-PANI film, which will be discussed elsewhere.

4 Conclusions

1) Au/polyaniline nanocomposites with core-shell structure were successfully prepared on ITO conducting electrode based on 4-aminothiophenol capped Au nanoparticles via electrochemical synthesis.

2) The novel as-prepared core-shell nanoparticles were characterized by AFM and cyclic voltammetry, indicating the core size of gold particles ranging from 250 to 300 nm and a full coverage of 30 nm polyaniline shell film on gold surface.

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