Ionic Liquid-assisted Synthesis of Polyaniline/Gold Nanocomposite and Its Biocatalytic Application

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Abstract In this report, a novel chemical synthesis of polyaniline/gold nanocomposite is explored using ionic liquid (IL) 1-Butyl-3-methylimidazolium hexafluorophosphate. The direct chemical synthesis of polyaniline/gold nanocomposite was initiated via the spontaneous oxidation of aniline by AuCl4− in IL. A nearly uniform dispersion of polyaniline/Au particles with a diameter of 450 ± 80 nm was produced by this method, which indicates that this method is more suitable for controlling particle dimensions. It was also found that the electrical conductivity of the polyaniline/gold nanocomposite was more than 100 times higher than that of the pure polyaniline nanoparticles. The polyaniline/gold nanocomposite displays superior function in the biocatalytic activation of microperoxidase-11 because of the high surface area of the assembly and the enhanced charge transport properties of the composite material. We also report the possible application of polyaniline/gold nanocomposite as a H2O2 biosensor.

Keywords Ionic liquid · Nanocomposite · Biocatalytic application

Introduction

Electrically conducting polymers have attracted attention for applications in various electrochemical devices including batteries [1], capacitors [2], electrochromic windows [3], displays [3], actuators [4, 5], photovoltaic cells [6], electrochemical biofuel cells [7], and biosensors [8]. Polyaniline is one of the most useful conducting polymers due to its facile synthesis, environmental stability, and simple acid/base doping/dedoping chemistry [9]. Room-temperature ionic liquids (ILs) [10] are organic salts with melting points near room temperature, which are regarded as environmentally friendly benign solvents because of their nonvolatility and high stability. The advantages of ILs in synthetic processes of functional materials have been gradually realized and have received more and more attention. ILs have widely been used in organic synthesis, electrochemistry, catalysis, and separation, but synthesis of nanostructured materials in ILs is relatively new and has been attracting growing interest in recent years. By using ILs as a reaction media, some nanostructured materials, such as gold nanoparticles [11, 12], mesoporous materials [13], hollow microspheres [14–17], CuCl nanosheetlets [18, 19], CoPt nanorods [20], and polymer nanoparticles [21, 22] have been successfully synthesized. The potential benefits of using ILs as reaction media for conducting polymers are...
drawing increasing attention [23]. Hybrid systems consisting of metallic or semiconducting nanoparticles and organic compounds became an interesting research topic in recent years [24] and have stimulated substantial research efforts directed to the development of hybrid materials of new catalytic, electronic, and optoelectronic functionalities [25, 26]. In particular, the incorporation of metallic or semiconducting nanoparticles in conductive redox polymers, such as polypyrrole and polyaniline, is of interest because of strong electronic interactions between the nanoparticles and the polymer matrices. The ability to control the shape and size of nanocomposites is an important factor for defining their properties, such as the electronic band gap, conductivity, and light-emission efficiency [27].

Recently, it was found that chloroauroate ions (AuCl₄⁻) could also be applied as an oxidant in the oxidative polymerization of pyrrole, leading to gold nanostructures capped with polypyrrole [28, 29]. Sastry and co-authors [30, 31] demonstrated that AuCl₄⁻ could be reduced by amine-containing molecules including hexadecylaniline and diamine-containing oxyethylene linkage, resulting in metallic gold particles accompanied with the formation of corresponding polymers. In this present work, we studied the oxidative polymerization of aniline using HAuCl₄ as the oxidant and 1-Butyl-3-methylimidazolium hexafluorophosphate as the growth media that resulted in the formation of the polyaniline/gold nanocomposite. It was found that the polyaniline/gold nanocomposite possesses enhanced electrochemical activity and superior conductivity compared to the conducting polymers prepared by the conventional approach. In addition, the polyaniline/gold nanocomposite was used to immobilize microperoxidase-11 (MP-11) and its biocatalytic properties were also investigated. It was found that MP-11 could be easily immobilized with high loading and activity because of the large specific surface area, excellent conductivity, and strong interaction between the polyaniline/gold nanocomposite and MP-11. Furthermore, the small dimensions and the high surface-to-volume ratio of the nanocomposite allow the electrons transmit rapidly and hence enhance current response. Thus, the polyaniline/gold nanocomposite can be used as an excellent matrix for electrocatalysis and enzyme immobilization. The aim of the present study is to develop a novel type of electrode material for using in hydrogen peroxide biosensor [32, 33] and biofuel cell [34].

Experimental Section

All chemicals were of analytical grade and used as received. 1-Butyl-3-methylimidazolium hexafluorophosphate was purchased from Sigma-Aldrich. MP-11 was obtained from Sigma and used as received. Aniline was distilled twice under atmospheric pressure and stored in dark at low temperature prior to use. Hydrochloric acid and other reagents were used without further purification. All aqueous solutions were prepared using Mill-Q water.

In a typical synthesis, 0.2 g of aniline was dissolved in 10 mL of IL, and 0.1 g of HAuCl₄ · 3H₂O was dissolved in 10 mL water with 0.5 mL hydrochloric acid (1 M HCl). The two solutions were then carefully transferred to a glass tube, and an interface was formed between the aqueous phase and the 1-Butyl-3-methylimidazolium hexafluorophosphate. After 5 min, green polyaniline formed at the interface and then gradually diffused into the aqueous phase. After 24 h, the entire water phase was filled homogeneously with dark-green polyaniline/gold nanocomposite. The aqueous phase was then collected, and washed with ethanol and water to remove the unreacted chemicals and aniline oligomers. The obtained polyaniline/gold nanocomposite was dried in a vacuum oven at 40 °C for 24 h.

Transmission electron microscopy (TEM) characterization was performed with a Philips CM12. All the electrochemical experiments were carried out with a BAS 100B electrochemical workstation (USA). A conventional three-electrode system comprising a bare or modified glassy carbon electrode (GCE) as the working electrode, a platinum foil as the auxiliary, and an Ag/AgCl/3.0 M NaCl electrode (from BAS) as the reference. The GCE (3 mm in diameter) was polished with 1.0, 0.3, and 0.05 μm alumina slurry followed by rinsing with doubly distilled water and drying at room temperature. XP spectra were obtained using an EscaLab 220-IXL spectrometer with a monochromated Al Kα source (1486.6 eV), a hemispherical analyzer and a multichannel detector. The spectra were accumulated at a take-off angle of 90° with a 0.79 mm² spot size at a pressure of less than 10⁻⁶ mbar.

The polyaniline/gold nanocomposite was dispersed in Mill-Q water and an amount of 10 μL of the solution was coated on the surface of GCE. The surface coverage of the nanocomposite was about 2.8 × 10⁻⁶ g/cm². Subsequently, the electrode was thoroughly rinsed with water and immersed in a 1 mg mL⁻¹ MP-11 in 0.1 M phosphate buffer solution (PBS, pH 7.0) at 4 °C for 10 h to obtain MP-11/polyaniline/gold nanocomposite electrodes. The electrode was thoroughly rinsed with Mill-Q water before each experiment. The enzyme electrodes were kept in PBS at 4 °C when not in use. The PBS buffers were purged with purified nitrogen for 20 min prior to a series of electrochemical experiments. A nitrogen environment was kept over solutions in the cell to keep them oxygen free. A 10 mM H₂O₂ solution was prepared by adding 0.12 mL of the 30% H₂O₂ solution to 4.8 mL of PBS Buffer. Once diluted, the H₂O₂ should be used promptly, as it degrades rapidly.
Results and Discussion

In this report, a polyaniline/gold nanocomposite was produced by polymerization of aniline using chloroaurate acid (HAuCl₄) as the oxidant in water/ILs interface. Both water and ILs are environmental benign solvents. The reduction of AuCl₄⁻ was accompanied by oxidative polymerization of aniline, leading to the formation of uniform submicron sized composite particles (450 ± 80 nm in diameter, Fig. 1) of polyaniline and gold. The mechanism of the formation of the polyaniline/gold nanocomposite is not clear so far. It is known that aniline is protonated in acidic solution. Therefore, in the experiment, when aniline acidic solution was mixed with chloroaurate acid, the protonated aniline was first electrostatically complexed with AuCl₄⁻, and then reduction of HAuCl₄ and oxidation of aniline occurred simultaneously, leading to the formation of the polyaniline/gold nanocomposite.

The present method of synthesis is similar to other routes with the exception of using chloroaurate acid as an oxidant in ILs, and the products possess similar chemical structure but different morphology and improved conductivity. Previously, Wang et al. [35] demonstrated a facile route to the synthesis of polyaniline nanofibers by polymerization of aniline using chloroaurate acid (HAuCl₄) as the oxidant. Clearly the morphology of the polyaniline/gold nanocomposite based on the present method is quite different from that of the previous work. Also the conductivity of the polyaniline/gold nanocomposite was found to be 0.12 S/cm, whereas that of polyaniline was found to be $2.4 \times 10^{-3}$ S/cm [36]. Thus, there was an increase of about three orders of magnitude in conductivity upon incorporation of gold in the conductive form of polyaniline prepared using the present method. Because gold is a conductor, it is beneficial for improving the conductivity of polyaniline when it is combined with gold. Therefore, with increasing gold content, the conductivity of the polyaniline/gold nanocomposite should be enhanced.

The polyaniline/gold nanocomposite was further characterized by XPS and the core level spectrum of N 1s is shown in Fig. 2. The peak A at binding energy of 399.4 eV corresponds to the benzenoid amine (–NH–). A higher binding energy peak (Peak B) centered at 401.2 eV is also found in Au–Polyaniline.

As reported before, MP-11 immobilized on gold electrodes can catalyze the reduction of H₂O₂ [34, 37, 38]. In the present work, the reduction of H₂O₂ was also investigated using the modified polyaniline/gold nanocomposite electrode. Figure 3 shows cyclic voltammograms of the polyaniline/gold nanocomposite electrode in 0.1 M PBS (pH 7.0) in the absence and presence of H₂O₂ at a scan rate of 20 mV/s. In the absence of H₂O₂, a pair of the redox peaks of MP-11 was observed, which is similar to that observed by Gorton et al. [38]. In the presence of H₂O₂, however, the voltammetric behavior changed drastically. A large cathodic current for the reduction of H₂O₂ appeared while the anodic peak decreased till it disappeared completely. A current–time plot of the enzyme electrode on successive step changes of H₂O₂ concentration is displayed in Fig. 4. When an aliquot of H₂O₂ was added into the buffer solution, the reduction current rose steeply to reach a
stable value and the response time was less than 10 s, which indicated a fast biocatalytic and diffusion process and a high activity of the MP-11 in this enzyme/nanostructured hybrid system (Fig. 4). The linear range of H2O2 concentration is between 2.0 mM and 20 μM with a correlation coefficient of 0.99 (Fig. 4). The modified polyaniline/gold nanocomposite electrode has a detection limit of 0.8 μM at a signal-to-noise ratio of 3. In addition, the long-term stability of the polyaniline/gold nanocomposite electrode was investigated over a 10-day period. When the modified electrode was stored at 4°C and measured intermittently, no apparent change in the response to 0.1 mM H2O2 was found over this period. The observed stability could be attributed to the strong interactions between the polyaniline/gold nanocomposite and MP-11, which obviously indicates that MP-11 was firmly immobilized on the surface of the polyaniline/gold nanocomposite films.

Conclusions

In summary, the polyaniline/gold nanocomposite has been successfully prepared by employing chloroaurate ions as the oxidant in ILs. The direct electrochemistry of MP-11, modified on microelectrode, and its catalytic activity for the reduction of H2O2 were studied by CV. A pair of well-defined redox waves corresponding to the conversion of MP-Fe(III) and MP-Fe(II) was obtained, which demonstrates that the polyaniline/gold nanocomposite has a good promotion toward the reduction/oxidation of MP-11. The high conductivity, large specific surface area, and excellent electroactivity of the polyaniline/gold nanocomposite make it an excellent matrix for enzyme immobilization and electrocatalysis. When combined with MP-11, the nanocomposite electrode displays a potential application for the detection of H2O2 with a low detection limit and rapid response time. Moreover, the nanocomposite-modified electrode exhibits high stability.

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