



Synthesis of polypyrrole nanocomposites decorated with silver nanoparticles with electrocatalysis and antibacterial property



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ABSTRACT

Polypyrrole nanowire/silver nanoparticle composites (PPy/Ag) are obtained in aqueous media through a one-pot method without any external stimulus. PPy nanowires were assembled on the reactive self-degraded template of the complex of AgNO₃ and methyl orange (MO). During the synthesis process in the dark surrounding, Ag nanoparticles could be uniformly decorated onto the surface of PPy nanowires *in situ* by the redox reaction of pyrrole and AgNO₃. Neither additional reducing agents for the growth of silver nanoparticles nor oxidizing agents for the polymerization of pyrrole are utilized. The formation mechanism, morphologies, structural characteristics, and conductivity of the obtained PPy/Ag nanocomposites are reported. The as-prepared PPy/Ag nanocomposites exhibit well-defined response to the electrochemical reduction of hydrogen peroxide. Moreover, the preliminary antibacterial assays indicate that the PPy/Ag nanocomposites also possess antibacterial abilities against *Escherichia coli*.

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1. Introduction

Organic/inorganic nanocomposites have received significant attention from academic and industrial fields. Various approaches have been employed to design and fabricate organic/inorganic nanocomposites to combine the features of different materials and achieve the controlled properties and promising applications [1–3]. Among these nanocomposites, great efforts have been put on the incorporation or the decoration of metal nanoparticles in the matrix or on the surface of conducting polymer because of the potential applications in chemical sensors, catalysis, optical and electrical devices [4–8].

Of particular interest is polypyrrole (PPy) in the family of conducting polymers, as it shows good environmental stability, high conductivity and biocompatibility. PPy with different nanostructures, such as nanowire, nanotube, and nanoparticle, has been utilized as a matrix to embed or disperse various metal nanoparticles for use in sensors and electrocatalysts [9–15]. However, the aggregation of inorganic nanoparticles, due to minimizing their surface

energy, will lead to a loss of surface area and decrease the expected properties. Recently, several synthetic methods have been developed to overcome this shortcoming. For example, PPy-coated gold nanoparticles have been synthesized with the aid of hydrophilic polymer [16]. Ag-PPy core-shell nanocomposites have been prepared in the process of interfacial polymerization and then further functionalized with gold nanoparticles for biosensor application [17]. Ag nanoparticles have been produced on the surface and inside the cavity of PPy nanotubes prepared by vanadium oxide nanowires as the reactive template [18]. PPy nanotubes functionalized with imidazolium-type ionic liquids have been used to anchor and grow PtAu alloy nanoparticles via NaBH₄ as the reductant [19].

Although dramatic efforts have been dedicated to develop new methods for the fabrication of the composites of conducting polymers and metal nanoparticles, most of these methods involve a sophisticated process and usually require multi-step reactions. The preparation for the composites with controlled nanostructure in a simple and cost-effective way is still a novel challenge. In our previous work, the one-dimensional PPy nanostructures have been synthesized by using methyl orange (MO) as the template and Fe[III] salt as the oxidant [20]. In this paper, we inherit this facile method and extend it to decorate Ag nanoparticles onto the surface of PPy nanowires by using MO as the template in the presence of silver nitrate (AgNO₃) as the oxidants without any external

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stimulus. In this work, the novel design of PPy/Ag nanocomposites has the following advantages. Firstly, there are no additional oxidant and reductant in the reaction system. It is a simple and green approach. Accompanied with the assembly of PPy nanowires on the reactive self-degraded template of the complex of AgNO₃ and MO, Ag nanoparticles could be uniformly decorated onto the surface of PPy nanowires *in situ* by the redox reaction of pyrrole and AgNO₃ in the dark surrounding during the synthesis process. Secondly, MO serves as the template, dopant and stabilizer in the reaction. Thirdly, there are no complicated reaction steps and instruments. The approach is straightforward and convenient to fabricate an important kind of conducting polymer/metal nanocomposites. The morphology and structure of PPy/Ag nanocomposites were investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), UV–vis, and X-ray diffraction (XRD). Moreover, the resulting PPy/Ag nanocomposites not only showed significant electrocatalytic activity for the reduction of hydrogen peroxide, but also displayed effective antibacterial activity against *Escherichia coli*.

2. Experiment

2.1. Reagents

Pyrrole monomer was purchased from Aldrich and distilled under reduced pressure. Methyl orange (MO) and AgNO₃ were purchased from Shanghai Chem. Co. in China and used as received.

2.2. Preparation of PPy/Ag nanocomposites

In a typical experiment, 5 mL of AgNO₃ (1.5 mmol) aqueous solution was added into 20 mL of 5 mmol/L MO (sodium 4-[4'-(dimethylamino) phenyldiazo] phenylsulfonate (CH₃)₂NC₆H₄N=NC₆H₄SO₃Na) deionized water solution. A flocculent precipitate appeared immediately. Then 1.5 mmol of pyrrole monomer was added to the above solution. The resulting system was stirred for 2 min to ensure complete mixing and the reaction was allowed to proceed in darkness for 10 days at room temperature. Finally, the product was washed with copious deionized water and ethanol and dried under a vacuum atmosphere at 45 °C for 24 h.

2.3. Instrumentation

The morphologies of the products were characterized by scanning electron microscope (SEM, JSM-5510LV) and transmission electron microscope (TEM, JSM-9300). XRD patterns were obtained on PHILIPS PW 3710 diffractometer in the reflection mode using Cu K α radiation. The electrical conductivity was measured by a standard four-probe method. FTIR spectra were recorded on a PerkinElmer spectrum 100 FT-IR spectrometer using KBr pressed pellets with accumulating 64 scans at a resolution of 4 cm⁻¹. Optical absorption spectra were acquired with a Lambda UV–vis spectrophotometer.

2.4. Electrochemical measurements

Electrocatalytic measurements were performed on a CHI660C with conventional three-electrode system. A PPy/Ag modified glassy carbon electrode (GCE) was used as the working electrode. PPy/Ag nanocomposites were dispersed in distilled water to form a 1.0 mg/mL solution and then the colloidal solution (5 μ L, 10 μ L and 20 μ L) was dropped onto the GCE surface and allowed to dry under ambient conditions (denoted as PPy/Ag5, PPy/Ag10 and PPy/Ag20, respectively). A platinum wire and saturated calomel

electrode (SCE) were used as the counter electrode and reference electrode, respectively. A solution containing 0.2 M PBS and 1.0 mM H₂O₂ was used as an electrolyte solution and degassed by high purity nitrogen gas prior to the measurement.

2.5. Antibacterial evaluation

In the antibacterial test, *Escherichia coli* (*E. coli*) were used as the experimental strains. Nutrient agar plates were prepared by dissolving agar, beef broth, protein, and NaCl in water. The pH of the solution was then adjusted to 7.0. The contents were then sterilized by autoclaving at a pressure of 0.1 MPa for 30 min. The suspensions of bacterial cultures with 10⁸ CFU/mL were made and streaked over the surface of agar plates to obtain uniform growth. The samples were then applied onto the surface of inoculated agar plates. The zones of inhibition were measured after incubating the plates at 37 °C overnight.

3. Results and discussion

3.1. Synthesis and characterization of the nanocomposites

In the present work, when AgNO₃ was added to MO solution, a red flocculent precipitate appeared immediately. After the addition of pyrrole monomers, the color of the mixture was changed gradually from red to black. Finally, a black powder could be obtained after the whole reaction. In our previous studies, the same precipitate can be observed when Fe³⁺ ions were added into MO solution, and then the one-dimensional nanostructures of polypyrrole can be obtained by the reactive self-degraded MO–Fe³⁺ templates with or without stirring during the reaction [20,21]. It indicated that the complexation occurred between MO and Ag⁺, which is similar with other complexation between organic dyes and flocculent such as Al³⁺ and Fe³⁺ [22]. During the process of the fabrication of PPy/Ag nanocomposites, pyrrole monomers were polymerized along the complex MO–Ag⁺ template, and at the same time Ag nucleus was formed on the surface of complex MO–Ag⁺ template. In contrast to the conventional template, MO–Ag⁺ template need no subsequent removal treatment because MO–Ag⁺ template itself degraded automatically due to the reduction of Ag⁺ oxidant and the obtained PPy can be doped by anionic MO. In general, the stabilizers such as cetyltrimethyl ammonium bromide (CTAB), sodium dodecyl sulfonate (SDS), or polyvinylpyrrolidone (PVP) were introduced into the reaction system to suppress the agglomeration of nanoparticles and favor the dispersion of nanoparticles [13,23]. In our case, MO with a planar hydrophobic section and hydrophilic edge group (–SO₃⁻) can act as an effective stabilizer to promote the strong interaction between the Ag nanoparticles and PPy nanowires. And MO promoted the nucleation of inorganic species and prevented the aggregation of Ag nanoparticles efficiently, which will be confirmed in the following TEM image.

The feed ratio of reactants and the reaction time were further studied. The feed ratio of pyrrole monomer to AgNO₃ had less influence on the morphology of the products. On the other hand, because no external oxidants or stimulus were applied to the reaction system, the reaction time was more important to the reaction. Although the standard reductive potential of Ag⁺ is similar with that of Fe³⁺ [24], PPy/Ag nanocomposites cannot be prepared within 12 h. Then the reaction time was extended to 10 days to promote the complete polymerization of pyrrole. Moreover, the darkness was necessary during the reaction because the silver salts are unstable and will decompose in the light. On the basis of the above results, the schematic of the formation of PPy/Ag nanocomposite is described in Fig. 1. The formation of Ag nanoparticles decorated polypyrrole nanowires could be ascribed to the

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