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Preparation and characterization of Pt-polypyrrole nanocomposite for electrochemical reduction of oxygen

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Abstract An easy and simple method of one-step reaction was employed to synthesize the platinum-adsorbed polypyrrole nanocomposite (Pt-PPy). The prepared nanocomposite materials were characterized using UV–vis absorption spectroscopy, scanning electron microscopy, Fourier transform infrared spectroscopy, thermogravimetric analysis, and cyclic voltammetry. Polypyrrole within nanocomposite could crosslink to improve its stability on the Au substrates. O_2 reduction was performed at Au electrodes modified Pt-PPy in O_2-saturated 0.5 M H_2SO_4 solution. The results clearly show that modification of Pt-PPy nanocomposite results in the enhancement of the electrocatalytic reduction of oxygen. The nanocomposite may provide a novel electrode material for application in fuel cells and oxygen sensors.

Introduction

The electrocatalytic oxygen reduction reaction is of basic and practical interest in fuel cells and various oxygen-based electrochemical sensors, which has made it one of the most thoroughly studied reactions of modern electrochemistry [1, 2]. It is believed that platinum and platinum-based systems are so far the most active and practical catalysts for the electroreduction of oxygen in acid media [3], and that the nanostructured materials can produce electrocatalyst more effectively due to their large surface-to-volume ratio and the increased surface activity. In the recent years, the preparation of platinum and platinum-based nanoparticles as electrocatalytical materials has aroused a strong interest [4]. Hamers et al. fabricated the nanoscale hybrid electrodes using platinum nanoparticles onto vertically aligned carbon nanofibers electrode by electrostatic interaction [5]. The results show that this nanocomposite still retains high electrocatalytic activity. Cui et al. assembled platinum nanoparticles via electrodeposition onto loosely multi-walled carbon nanotubes (MWCNTs) grown on a Ta substrate [6]. The electrocatalytic reduction of oxygen was observed in Pt nanoparticles electrodeposited onto MWCNTs-modified electrode, which made it possible to develop a novel electrode material for applications in fuel cells and oxygen sensors.

Conducting Polymers are also actually developing as candidate materials for synthesis of nanostructured materials and devices [7–9]. Because of being mechanically and chemically stable and easy to prepare, polypyrrole (PPy) has been long recognized as one of the most promising member for application in electrocatalytic as well as for other purposes [10, 11]. PPy has been successfully applied as the conducting matrixes of composite materials incorporating Fe_3O_4, V_2O_5, and noble metals such as Au, Ag, Pd, or Pt [12–17]. Although synthesis of Pt-PPy nanocomposites and study of its electrochemistry properties have been explored, the chemical synthesis of Pt-PPy nanocomposite and the study of their application in electrocatalytic reduction of oxygen have received less attention.

In this paper, we adopted the chemical methods to synthesize Pt-PPy nanocomposite and extend it for electrocatalytic applications. The present results demonstrate that the Pt-PPy nanocomposite exhibits extraordinary electrocatalytic activity towards oxygen reduction. A facile and versatile route to immobilize the nanoparticles onto Au electrode is also obtained because of the existence of PPy.

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Experiment

Chemicals and reagents

Cation-ionic surfactant hexadecyl trimethyl ammonium Bromide (CTAB) was the product of Shanghai Sanpu Chemical Co. Ltd. Dipotassium hexachloroplatinate (IV) (K_2PtCl_6) and pyrrole were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai). All chemicals were commercial materials of analytical grade purity and were used as received without further purification. All solutions were prepared by ultra-pure water from Milli-Q water.

Synthesis of composite

The Pt-PPy nanocomposite was prepared using the following synthetic route. Briefly, CTAB (10 mM) was dissolved in 2 mL of H_2SO_4 solution (0.5 M), and then, 0.1 μL pyrrole, a reducing agent, was added dropwise with stirring. Finally, 40 μL K_2PtCl_6 solution (20 mM) was added to the mixed solution under vigorous stirring. In order to make the reaction complete, the vigorous stirring was continued overnight. The obtained colloid solution was stable.

Preparation of electrode

Prior to modification, the basal Au electrodes were polished with alumina slurry of 0.1 and 0.05 μm particle sizes, respectively. After polishing, the electrodes were sonicated in Mini-Q water for 1 min. Then, the electrodes were soaked in a 3:1 mixture of sulfuric acid and 30% hydrogen peroxide (piranha solution) for 10 min, followed by a thorough rinse with ethanol and Mini-Q water.

A total of 3 μL Pt-PPy nanocomposite colloid solution was dripped down the surface of Au electrodes. Then a centrifuge microtube was capped on the electrode to prevent Pt-PPy colloid solution from drying. The process lasted overnight at room temperature (20 °C). The formed Pt-PPy Au electrodes were rinsed with ultra-pure water.

Apparatus and methods

A Model CHI 660C electrochemical workstation was used for electrochemical measurements. Electrochemical experiments were carried out using a conventional three-electrode system. The gold electrodes (2 mm in diameter) coated with Pt-PPy nanocomposite served as the working electrodes. A Pt wire and an Ag/AgCl/3.0 M KCl were used as the auxiliary electrode and reference electrode, respectively.

Field emission scanning electron microscopy (SEM, S-4800 UHR FE-SEM) images was used for the physical characteristics of the Pt-PPy nanocomposite. The samples were prepared by dropping the nanocomposite aqueous solution on the platinum substance followed by drying with vacuum overnight.

The thermal stability of Pt-PPy nanocomposite was analyzed using Thermogravimetric analysis (TGA) (STA 449 C Jupiter, Germany). About 7.0 mg of the sample was heated from 30 °C to 600 °C at a rate of 10 °C min^{-1} under an argon atmosphere to burn off the organic fraction.

Fourier transform infrared (FT-IR) spectra were collected on a Nicolet-Nexus Infrared Spectrometer (Thermo Nicolet Corporation).

Results and discussion

The surface morphology of the Pt-PPy composite film was investigated by SEM. Figure 1 shows the light particles and gray features corresponding to Pt nanoparticles and the PPy matrix, respectively. We can see that the PPy matrix in the Pt-PPy contains same small spherical nanoparticles. It also indicates that the PPy matrix is not only amorphous, but also has a disordered structure. Meanwhile, it is believed that the PPy is an ideal matrix for electrocatalysis because of supplying large-surface-area conducting support. The Pt particles in the Pt-PPy are less than 50 nm in size and highly dispersed in the PPy film.

TGA is commonly employed to determine the thermal stability and the relative compositions of the organic monolayer. Figure 2 shows the TGA curves of Pt-PPy composites. The thermal decomposition of the nanocomposite begins at ~180 °C and completes at 500 °C. There is a slope before the temperature of 120 °C, which is believed to be due to the loss of water. The TGA data also determine the organic fractions on the nanocomposite to be 29.46 wt% of the nanocomposite except the water. From this data, a useful conclusion that PPy is about 30% of the composite in mass is obtained. That is to say, impureness may save the mass of the platinum effectively.

FT-IR spectrometry can be employed to identify the types of functionality of ligands attached to the nanoparticles. Figure 3 displays the FTIR spectra of Pt-PPy. All have characteristic absorption bands of PPy. The peak at 3,425 cm^{-1} is attributed to N–H stretch vibration. The bands at 1,563 and 1,464 cm^{-1} may be assigned to typical PPy ring vibrations. The band at 1,300 cm^{-1} corresponds to =C–H band in plane vibration.

The main objective of this work is to examine the electrocatalytic effect of the nanosized Pt-PPy composite towards the reduction of oxygen. Figure 4a shows a typical set of CV curves for O_2 reduction at the Au and Pt-PPy/Au

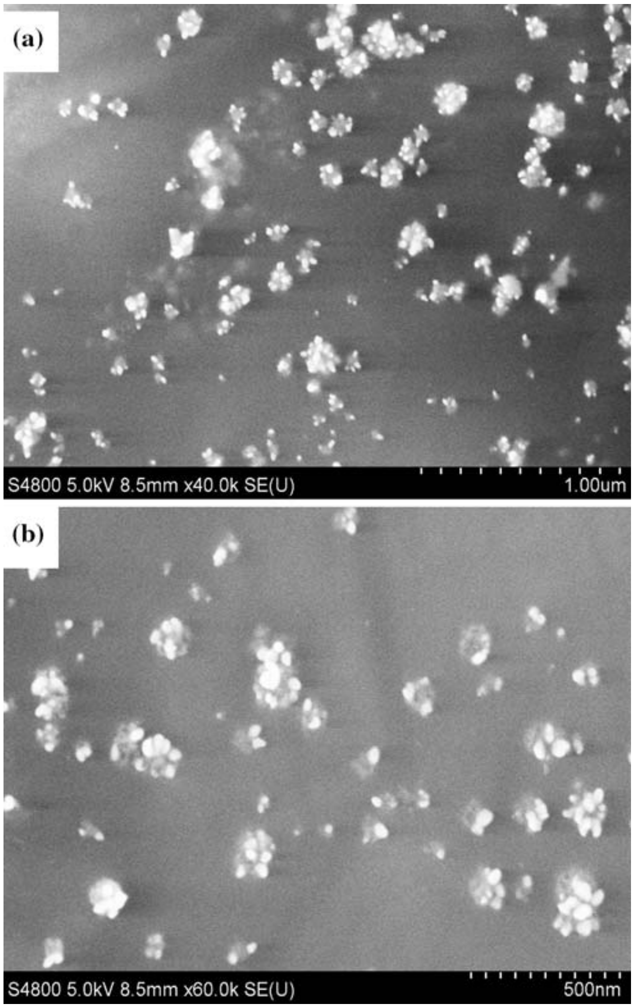

Fig. 1 SEM of Pt-PPy in different magnifications (**a**) low, (**b**) high

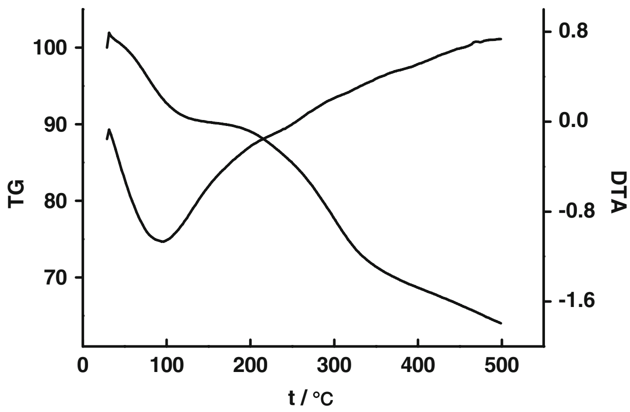

Fig. 2 Thermogravimetric curves of Pt-PPy composites

in 0.5 M H_2SO_4 solution at a scan rate of 100 mV s^{-1}. This figure reflects two important catalytic features of the Au electrode modified with the Pt-PPy. First, there is important evidence supporting the presence of Pt-PPy on

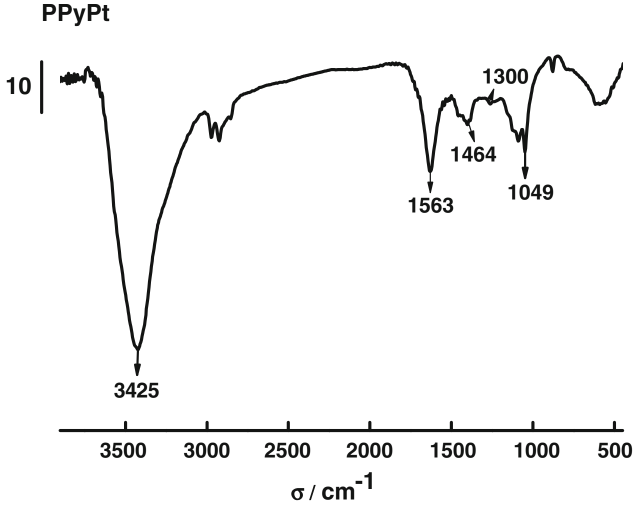

Fig. 3 FT-IR spectrum of Pt-PPy composites

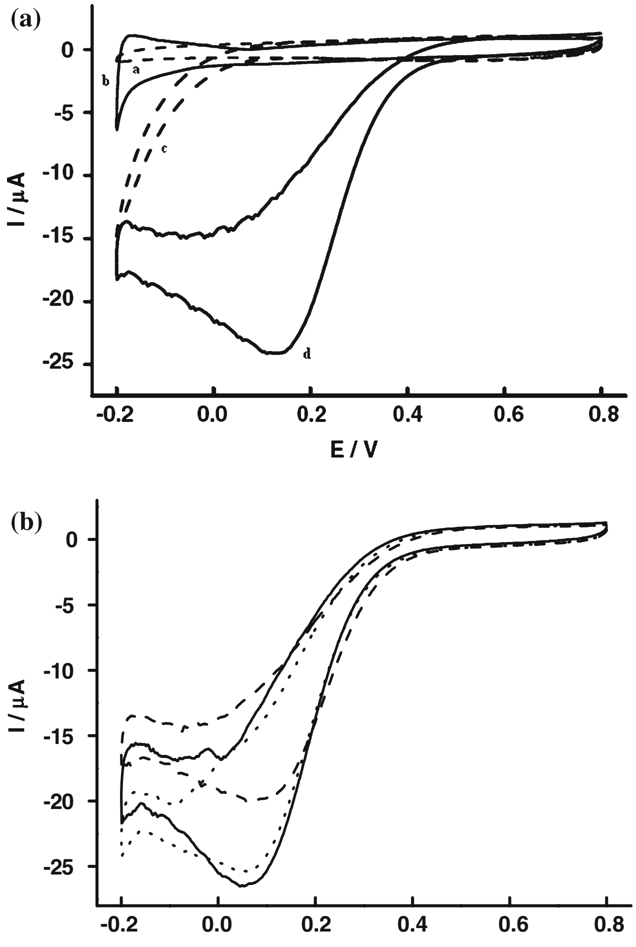

Fig. 4 (**a**) CVs obtained for the O_2 reduction at Au (*dash curves*) and Pt-PPy/Au (*solid curves*) electrodes in 0.5 M H_2SO_4 saturated with N_2 (*dash line* a, *solid line* b) and O_2 (*dash line* c, *solid line* d); (**b**) CV curves for Pt-PPy/Au electrodes using infrared lamp irradiation for 1 h (*dot line*), 2 h (*solid line*), and 12 h (*dash line*) in O_2-staurated H_2SO_4 solution (0.1 V s^{-1} potential scan rate)

the surface of the catalyst. Second, the Pt-PPy modified electrodes have shown excellent electrocatalytic properties for O_2 reduction in 0.5 M H_2SO_4, that is to say, the oxygen reduction wave at Pt-PPy/Au electrodes showed a positive shift compared to that for bare Au. The increase in O_2 reduction activity has been observed for Pt-PPy/Au electrodes using irradiation with infrared lamp (Fig. 4b). The current of O_2 reduction increases over the time of irradiation at first, but the current decreases when the time of the infrared illumination exceeded 12 h (Fig. 4b dash line). This is a novel method to immobilize the materials onto the electrodes. We believe the infrared illumination may induce the polymerization of pyrrole oligomer and react more strongly with electrodes [18, 19]. Therefore, the electrocatalytic effect of this method to O_2 reduction shows a positive shift.

Conclusion

In summary, a facile method for preparing catalytically active polypyrrole-supported Pt catalysts is demonstrated. Because of strong absorptive properties, polypyrrole can be immobilized onto Au electrodes for the convenient studying of electrocatalytic. The obtained Pt-PPy nanocomposite modified Au electrodes exhibit a strong elctrocatalytic activity toward O_2 reduction in acid solution. It can be concluded that the Pt-PPy composite maybe developed for its application in fuel cells and oxygen sensors.

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