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Short communication

A one-pot 'green' synthesis of Pd-decorated PEDOT nanospheres for nonenzymatic hydrogen peroxide sensing

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ABSTRACT

We developed a novel nonenzymatic biosensor based on palladium/poly(3,4-ethylenedioxythiophene) (Pd/PEDOT) nanocomposite modified glassy carbon electrode (GCE) for the detection of hydrogen peroxide (H_2O_2). Pd/PEDOT has been successfully fabricated by a facile one-pot 'green' method using H_2PdCl_4 as an oxidant and a source of metal nanoparticles without any surfactants and templates. The as-synthesized PEDOT nanospheres are quite uniform in size (~60 nm) without aggregation and provide a good platform for anchoring the Pd nanoparticles (NPs). Pd NPs (~4.5 nm) are homogenously dispersed on surface of PEDOT nanospheres. The Pd/PEDOT nanospheres on GCE exhibit a good electrocatalytic activity towards the H_2O_2 reduction. The electrochemical response of Pd/PEDOT to H_2O_2 exhibits a low detection limit of 2.84 μM in the range of 2.5×10^{-3}–1.0 mM with a high sensitivity, good repeatability, acceptable reproducibility and good long-term stability. The good recoveries achieved in spiked human urine samples demonstrated the potential application of Pd/PEDOT for H_2O_2 detection.

1. Introduction

Hydrogen peroxide (H_2O_2) is one of the most important analytical objects in food, pharmaceutical, clinical, environmental, and industrial analysis (Bian et al., 2010; Chen et al., 2012a; Lin et al., 2010; Tsiafoulis et al., 2005). The precise and rapid detection of H_2O_2 is of practical significance for both food safety and industrial manufacture. In comparison with the conventional techniques for H_2O_2 determination, electrochemistry based on a biosensor show the advantages of low cost, easy preparation, rapid detection, low consumption, high selectivity and sensitivity (Chen et al., 2012b; Karyakin, 2001). In recent years, an increasing effort has been devoted to the development of efficient electrochemical biosensors due to the significance in biological systems and practical applications (Krishnamoorthy et al., 2004; Kros et al., 2001). In particular, the nonenzymatic biosensors can potentially overcome the drawbacks of high cost and poor stability compared to enzymatic ones (Liu et al., 2012).

Conducting polymers have been considered to be good materials for the construction of H_2O_2 sensing, since they provide an excellent platform with porous structure and large surface area (Dhand et al., 2007; Lu et al., 2011). To further enhance their sensing properties, nanocomposites have been developed by combining metal nanoparticles (NPs) and conducting polymers (Guo et al., 2009; Santhosh et al., 2009). The composite can not only enhance the charge transport ability, but also effectively improve the electrochemical and catalytic properties of conducting polymers (Park et al., 2012; Sih and Wolf, 2005). Among many of noble metals, palladium (Pd) is one of the best candidates for nanocomposite due to its low cost and excellent catalytic activity (Bo et al., 2010; Chen et al., 2012a; Huang et al., 2008; You et al., 2011). On the other hand, poly(3,4-ethylenedioxythiophene) (PEDOT) has been developed to be various sensors with excellent reversibility and reproducibility in response (Jang et al., 2005; Krishnamoorthy et al., 2004; Kros et al., 2001). Especially, the nanostructured PEDOT offers a higher surface-to-volume ratio and exhibits desirable chemical, physical and electronic properties that are different from those of bulk polymers (Han and Foulger, 2005; Zhang et al., 2006). Although the Pd/PEDOT composite has demonstrated to be a good combination for the applications of sensors (Santhosh et al., 2009; Yin and Zhu, 2010), there is almost no studies in the nonenzymatic H_2O_2 sensing. Recently, a one-step fabrication of metal/PEDOT has been reported using metal salts as an oxidant and a source of metal atoms (Chang et al., 2012; Kumar et al., 2007; Park et al., 2012; Yin and Zhu, 2010). However, such one-step synthetic strategy usually leads to aggregation of nanocomposites and performance degradation of metal/conducting polymer composites, or involves using solid templates and massive additional surfactants.

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Herein, we report a facile one-pot green synthesis of Pd-decorated PEDOT nanospheres (Pd/PEDOT) without any surfactants and templates. The as-synthesized Pd/PEDOT modified glassy carbon electrode (GCE) as a nonenzymatic H_2O_2 sensor exhibits high sensitivity and low detection limit.

2. Experimental

2.1. Chemicals

3,4-ethylenedioxythiophene (EDOT) was purchased from Bayer. $PdCl_2$ and $FeCl_3 \cdot 6H_2O$, were obtained from Sinopharm Chemical Reagent Co., Ltd. All other chemicals were analytical grade and all aqueous solutions were prepared with double distilled water. A 5.0 mM H_2PdCl_4 aqueous solution was prepared by dissolving 17.7 mg of $PdCl_2$ in 20 mL of 10 mM HCl solution with sonication. Phosphate buffer solution (PBS, 0.1 M, pH=7.0) was prepared by mixing stock standard solutions of K_2HPO_4 and KH_2PO_4. All experiments were carried out at room temperature.

2.2. Apparatus

S-4700 scanning electron microscope (SEM), energy dispersive X-ray spectrometry (EDX), and TecnaiG220 transmission electron microscopy (TEM) were used to obtain the morphologic information and Pd loading of sample. Fourier transform infrared (FT-IR) spectra were recorded using a Bruker Vertex 70 FT-IR spectrometer with KBr pellets. The powder X-ray diffraction (XRD) pattern was obtained using a PANalytical X'Pert Pro MPD system with Cu K_α radiation operated at 40 kV and 30 mA.

2.3. Preparation of Pd/PEDOT nanospheres

The entire synthesis of Pd/PEDOT nanospheres were carried out in a 50 mL round-bottom flask equipped with a magnetic stirrer. Briefly, a 5.0 mL of 14.2 wt% 3,4-ethylenedioxythiophene (EDOT) alcoholic solution was rapidly added into a 5.0 mM H_2PdCl_4 solution (20 mL) under vigorous stirring for 3 h. The resulting mixture was filtered, washed, and dried at 60 °C for 12 h. The reaction route is shown in Fig. 1A. For electrochemical measurements, 5.0 mg Pd/PEDOT powders were dispersed by ultrasonically in 1.0 mL deionized water with 50 μL Nafion solution (5 wt%) for 30 min, and then a 5.0 μL homogeneous Pd/PEDOT ink was spread on the GCE surface. For comparison, the pure PEDOT polymer was prepared by mixing a 5.0 mL of 14.2 wt% EDOT alcoholic solution and 20 mL $FeCl_3 \cdot 6H_2O$ (1.0 M) aqueous solution for 24 h.

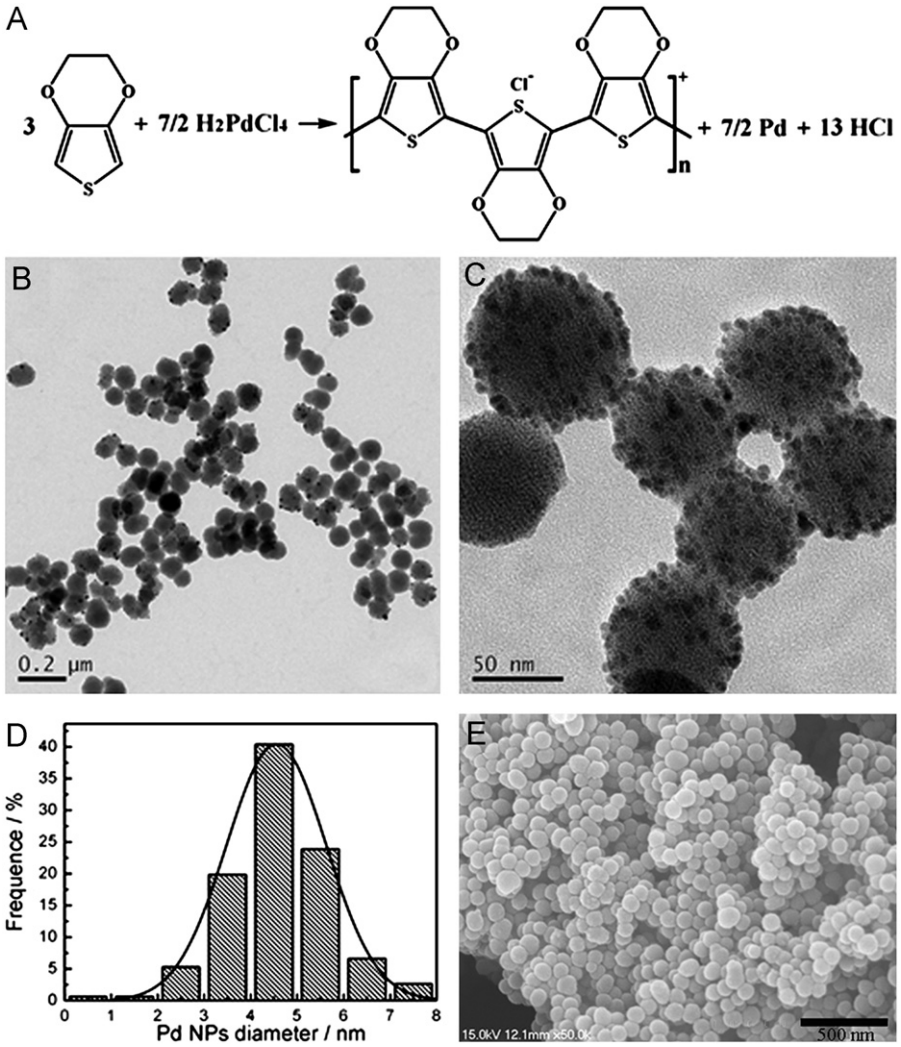

Fig. 1. Reaction route of synthesis (A) and TEM images (B) and (C) of Pd/PEDOT nanospheres. (D) Diameter size distribution of Pd NPs on PEDOT. (E) SEM image of Pd/PEDOT nanospheres.

2.4. Electrochemical measurements

The electrochemical measurements were carried out using CHI 660B electrochemical workstation (CH Instruments, China) in a classical three-electrodes-cell equipped with a GCE (3.0 mm in diameter), platinum plate and a saturated calomel electrode (SCE) as the working, counter and reference electrode, respectively. The electrolyte was in a nitrogen-saturated 0.1 M PBS (pH=7.0) in the presence and absence of H_2O_2. All the cyclic voltammetry (CV) curves were obtained at the scan rate of 50 mV s^{-1} from −0.5 to 1.0 V. The amperometric response to H_2O_2 was performed at −0.2 V υs. SCE.

3. Results and discussion

3.1. Characterization of Pd/PEDOT nanosphere

The morphology and microstructure of as-prepared Pd/PEDOT nanocomposites were characterized by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). As shown in Fig. 1B, the PEDOT particles are pseudo-spherical particles in shape and are quite uniform in size (~60 nm). Fig. 1C shows a closer view of Pd/PEDOT nanospheres at the high-magnification TEM image. It could be distinctly seen that Pd NPs were well dispersed and anchored on the surface of spherical PEDOT. Moreover, the Pd NPs show a narrow size distribution with an average diameter of 4.5 nm in Fig. 1D which is smaller compared with the previous reports (Chang et al., 2012; Kumar et al., 2007; Yin and Zhu, 2010). Additionally, it is interesting to see that SEM images of Pd/PEDOT nanocomposites exhibit a 3D porous structure on a large scale in Fig. 1E. The 3D porous structure of Pd/PEDOT nanospheres can provide a large surface area and enhance the accessibility of solution. For comparison, the PEDOT synthesized using $FeCl_3 \cdot 6H_2O$ as the oxidant shows an irregular morphology (the SEM image was not displayed here).

The Pd loading on PEDOT nanospheres was estimated about 36.5 wt% based on the EDX data in Fig. S1 (supplementary). Pd NPs were also confirmed by XRD patterns in Fig. S2 (supplementary). The peaks at 40.1°, 46.7°, 68.1° and 81.1° are assigned to the diffraction of Pd [1 1 1], [2 0 0], [2 2 0] and [3 1 1] planes, respectively, which represents a typical face-centered-cubic crystalline Pd. Fig. S3 (supplementary) shows the FT-IR result of Pd/PEDOT. The absorbance peaks at 1064 and 2926 cm^{-1} is assigned to the C–H bending and stretching vibrations, respectively. The bands at approximately 1213 and 1093 cm^{-1} are attributable to the stretching modes of the ethylenedioxy group. Vibrations at 976, 835, and 688 cm^{-1} correspond to the C–S bond in the thiophene ring. The C–C and C=C vibrations can be seen at 1353 and 1432–1520 cm^{-1}, respectively. The characteristic absorptions indicates a typical PEDOT polymer structure.

3.2. Electrocatalytic activity studies

The electrocatalytic activity of as-prepared Pd/PEDOT nanospheres modified GCE towards the reduction of H_2O_2 was investigated by CV in 0.1 M PBS containing 1.0 mM H_2O_2. As shown in Fig. 2A and B, the CV curves obtained in 0.1 M PBS without and with H_2O_2 presented the similar current response for the bare GCE and pure PEDOT, indicating that the H_2O_2 reduction can be hardly achieved on them. Contrastingly, a significant difference in shape can be observed at the CV curves of Pd/PEDOT from −0.5 to 1.0 V in the absence and presence of H_2O_2 in Fig. 2C. The CV curve of Pd/PEDOT in 0.1 M PBS+1.0 mM H_2O_2 solution exhibits an intense cathodic peak at −0.2 V and the reduced peak current is up to 39.9 μA. These results suggest that Pd/PEDOT has a good electrocatalytic activity towards the H_2O_2 reduction and the Pd NPs anchored on the surface of PEDOT nanospheres play an important role as the main electroactive materials. The PEDOT nanospheres mainly served as the platform for anchoring the Pd NPs. For the mechanism for H_2O_2 reduction, it could be proposed according to previous literature (Liu et al., 2012), as described by:

$$H_2O_2 + e^- \rightarrow OH_{ad} + OH^- \quad (1)$$

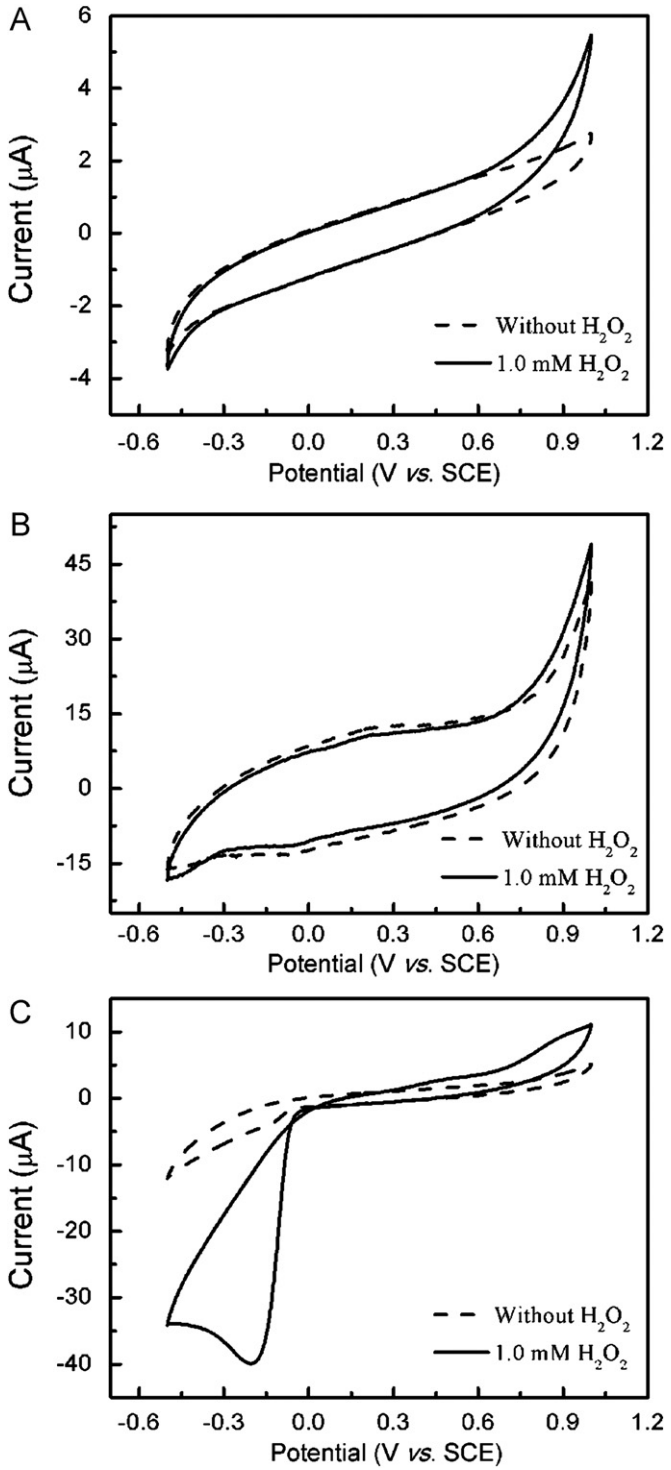

Fig. 2. CVs of bare GCE (A), pure PEDOT (B), and Pd/PEDOT (C) modified GCE in 0.1 M PBS (pH=7.0) in the absence (dashed line) and presence (solid line) of 1.0 mM H_2O_2 at the scan rate of 50 mV s^{-1}, respectively.

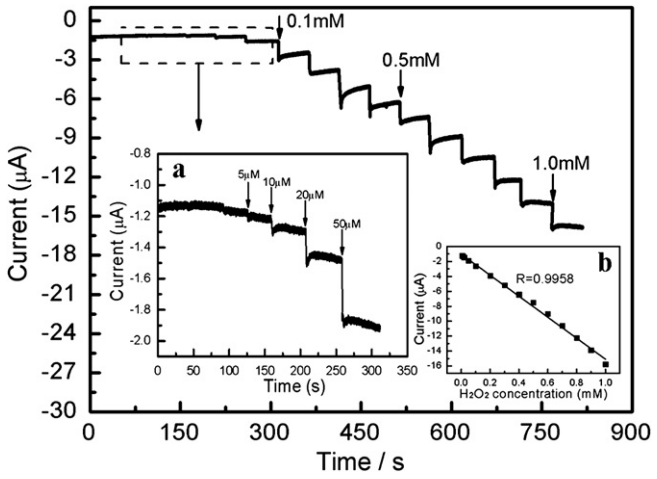

Fig. 3. Successive amperometric response of the Pd/PEDOT nanospheres modified GCE to H_2O_2 in 0.1 M PBS at −0.2 V *vs.* SCE. Inset: (a) the magnification and (b) the corresponding calibration plot of steady-state currents against concentrations of H_2O_2.

$$OH_{ad} + e^- \rightarrow OH^- \quad (2)$$

$$2OH^- + 2H^+ \rightarrow 2H_2O \quad (3)$$

3.3. Electrochemical response studies

In order to further evaluate the sensing ability as a nonenzymatic sensor towards the detection of H_2O_2, the amperometric response to H_2O_2 on the as-prepared Pd/PEDOT nanospheres was recorded at −0.2 V in Fig. 3. It can be seen that the amperometric reduction current exhibits a stepped increase with the successive addition of H_2O_2. As H_2O_2 was added into the PBS, the reduced current increased stepwise, and a well-defined amperometric response was obtained during 800 s until the H_2O_2 concentration was up to 1.0 mM. It is noted that an obvious steady-state current response can be observed when H_2O_2 concentration reaches 10 μM in Fig. 3a (inset). This is attributed to the rapid diffusion of H_2O_2 molecules from the solution to the modified electrode (Liu et al., 2012). The sensitivity of the Pd/PEDOT nanospheres was calculated to be 215.3 μA mM^{-1} cm^{-2} which is higher than the reported value on PEDOT/CNTs (174 μA mM^{-1} cm^{-2}) (Lin et al., 2010), dendritic Pd (78.3 μA mM^{-1} cm^{-2}) (Zhou et al., 2007), Pt/polypyrrole (80.4 μA mM^{-1} cm^{-2}) (Bian et al., 2010) and PEDOT-PtNPs/SPC (19.29 μA mM^{-1} cm^{-2}) (Chang et al., 2012). Moreover, the corresponding calibration curve in Fig. 3b (inset) shows a linear response to H_2O_2 concentration in the range of 2.5×10^{-3}–1.0 mM with a linear regression equation of I (μA) = −14.05 c (mM) − 1.03 (R = 0.9958) and a detection limit of 2.84 μM based on a signal-to-noise ratio (S/N) of 3. The detection limit of Pd/PEDOT modified GCE was much lower than that of peroxidase-based Au/ITO (8 μM) and nonenzymatic Pd/poly(acrylic acid) (5 μM), slightly higher than 1.2 μM on Pt/polypyrrole (Bian et al., 2010; Tang et al., 2009; Wang and Wang, 2004). The as-prepared Pd/PEDOT modified GCE shows good repeatability with a relative standard deviation (RSD) of 3.9% for five successive detections at 1.0 mM H_2O_2. Also, it exhibits an acceptable reproducibility with a RSD of 5.2% for five individual electrodes. Additionally, the current response retained 92% of its initial value after a storage period of 3 weeks, indicating the good long-term stability of Pd/PEDOT.

Furthermore, the sensing property of Pd/PEDOT in real sample analysis was evaluated by using the proposed method to determine H_2O_2 in spiked human urine samples. The healthy human urine was collected and diluted 100 times with 0.1 M PBS (pH = 7.0) to reduce the matrix complexity (Chatterjee and Chen, 2012). The comparison of analytical values was recorded in Table S1 (supplementary). The recovery for spiked urine samples at three different levels are in the range from 96.1 to 105.8%, indicating the appreciable practicality of the nonenzymatic biosensor for the detection of H_2O_2 in real samples.

4. Conclusion

This work shows a one-pot green synthesis of Pd-decorated PEDOT nanospheres without any surfactants and templates. PEDOT nanospheres are quite uniform in size (~60 nm) without aggregation and Pd NPs with an average diameter of 4.5 nm are well dispersed on the surface of PEDOT nanospheres. It is also found that Pd/PEDOT nanospheres exhibit good electrocatalytic activity towards the H_2O_2 reduction. Moreover, the as-prepared Pd/PEDOT nanospheres have a good sensing ability with high sensitivity and low detection limit serving as a nonenzymatic H_2O_2 sensor. Furthermore, the synthetic approach can be developed to fabricate other noble metal (e.g., Au, Pt, etc.) and conducting polymers nanocomposites for the application of electrochemical sensors.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.bios.2013.01.003.

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