Nonenzymatic hydrogen peroxide electrochemical sensor based on carbon-coated SnO₂ supported Pt nanoparticles

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ABSTRACT

We describe a simple method for preparing the hybrid material of Pt nanoparticles (NPs) supported on carbon-coated SnO₂ nanospheres (Pt–SnO₂@C). The as-prepared Pt–SnO₂@C nanocomposite was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The presence of carbon-coated SnO₂ nanospheres (SnO₂@C) remarkably improves the electrocatalytic activity of Pt NPs towards hydrogen peroxide (H₂O₂) oxidation. The Pt–SnO₂@C nanocomposite modified glassy carbon (GC) electrode exhibited enhanced amperometric response to H₂O₂, with detection limit of 0.1 μM and sensitivity of 241.1 μA mM^{−1} cm^{−2}.

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1. Introduction

Platinum-based nanomaterials have shown attractive properties in applications of electrochemical sensors and biosensors [1–9]. Pt nanoparticles (NPs) usually possess large electrochemically active surface area which accounts for the number of available active sites towards electrochemical reaction and electron transfer [1]. Thus, the electrochemical reaction of detection molecules could be greatly promoted at the Pt NPs surfaces, leading to a more sensitive and rapid amperometric response. It is well-known that supported metal catalysts show improved stability and higher activity as compared to unsupported bulk metal catalysts, because the metal NPs dispersed on support matrix are less vulnerable to dissolution and aggregation under electrochemical environments. Owing to their large surface area and high electrical conductivity, carbon materials including carbon black, carbon nanotubes and graphene have been commonly used as catalyst support for Pt NPs [1,2,5,9–15]. Recently, carbon-coated metal oxide materials have emerged as a new kind of electrochemical enhanced materials in various applications [16–19]. The carbon-coated metal oxide could exhibit the advantages of carbon materials, and more importantly, also processes new physicochemical properties arising from metal oxide, such as high mechanical resistance and stability. For example, Pt NPs anchoring on carbon-coated CeO₂ exhibited enhanced

catalytic performance for methanol oxidation, due to the support effect of the CeO₂ and carbon mixture [19].

Hydrogen peroxide (H₂O₂) is a by-product of the reactions catalyzed by large number of oxidase enzymes [20]. Hence, the electrooxidation of H₂O₂ plays a major role in the development of electrochemical sensors and biosensors [21]. However, the direct oxidation of H₂O₂ at ordinary electrodes often requires high overpotential, which is disadvantageous to the sensitive and selective detection of H₂O₂. An efficient approach to overcome this problem is to modify the bare electrode with suitable electrocatalysts that can reduce the high overpotential for H₂O₂ oxidation [1,6–10,13]. In this work, we report on a new Pt-based hybrid material using carbon-coated SnO₂ nanospheres (SnO₂@C) as catalyst support. The as-prepared Pt–SnO₂@C nanocomposite was investigated for electrochemical sensing of hydrogen peroxide.

2. Experimental

2.1. Reagents and apparatus

K₂SnO₃·3H₂O (99.9%), glucose (99%), and H₂O₂ solution (30%) were purchased from Aladdin Chemistry Co., Ltd. H₂PtCl₆·6H₂O (Pt ≥ 37%) and NaBH₄ (98%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Water used throughout all experiments was purified with the Millipore system.

Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analyses were preformed using a Hitachi S-4800 field emission scanning electron microscope equipped with an energy-dispersive X-ray detector. Transmission electron microscopy (TEM)

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Fig. 1. XRD patterns of Pt-SnO₂@C.

images were obtained on a Hitachi H-7650 transmission electron microscope. X-ray diffraction (XRD) analyses were carried out with a Bruker D8/Advance X-ray diffractometer with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$). All electrochemical experiments were performed with a CHI 850C electrochemical analyzer (CH Instruments,

Shanghai, China). A conventional three-electrode system was used for all electrochemical experiments, which consisted of a platinum wire as counter electrode, an Ag/AgCl/3 M KCl as reference electrode, and a glassy carbon (GC) electrode (3 mm diameter) coated with the catalyst as working electrode.

2.2. Preparation of Pt-SnO₂@C

The SnO₂@C nanospheres were prepared by the literature method [16]. Briefly, 1.0 g of K₂SnO₃ was dissolved in 20 mL of 0.8 M aqueous glucose solution, and the mixture was hydrothermally heated in a Teflon-lined autoclave at 180 °C for 4 h. The resultant precipitate was carbonized by calcinations at 400 °C under high-purity N₂ in a tube furnace, resulting in the SnO₂@C nanospheres. The loading of Pt NPs on the SnO₂@C nanospheres was carried out through reduction of H₂PtCl₆ using NaBH₄ as reducing agent. In a typical procedure, 50 mg of SnO₂@C was dispersed in 50 mL of water by ultrasonic treatment. Then, 2 mL of H₂PdCl₆ solution (0.06 mM) was added and stirred for 1 h. A freshly prepared NaBH₄ solution (10 mL, 0.1 M) was added to the mixture at 0 °C, followed by stirring at room temperature overnight. Finally, the mixture was filtered, washed with water and ethanol, and vacuum-dried at 70 °C for 6 h. The as-prepared product was denoted as Pt-SnO₂@C. For comparison, Pt NPs were prepared under the same conditions without the addition of SnO₂@C nanospheres.

Fig. 2. SEM image (a), TEM images (b and c) and EDX spectrum (d) of Pt-SnO₂@C.

2.3. Preparation of modified electrode

The as-prepared Pt–SnO₂@C nanocomposite was dispersed in ethanol with ultrasonication for 1 h to get a homogenous suspension (1 mg mL^{−1}). Then, 5 μ L of the suspension was dropped onto the surface of freshly polished glassy carbon (GC) electrode and dried at room temperature, resulting in the Pt–SnO₂@C modified GC electrode. For comparison, 5 μ L homogenous suspension of Pt NPs dispersed in ethanol (1 mg mL^{−1}) was coated on a bare GC electrode to obtain the Pt NPs modified GC electrode.

3. Results and discussion

3.1. Characterization of Pt–SnO₂@C

The crystallographic structure of the Pt–SnO₂@C nanocomposite was characterized by powder X-ray diffraction (XRD). The XRD pattern (Fig. 1) shows the coexistence of SnO₂ and Pt crystalline. The diffraction peaks at $2\theta = 39.4^\circ$, 45.6° and 81.0° are indexed as the (1 1 1), (2 0 0) and (3 1 1) planes of Pt, respectively, indicating that Pt forms the typical face-centered cubic (fcc) crystal structure. The average crystalline size of Pt is estimated to be about 2 nm from the Pt (1 1 1) peak broadening using the Scherrer equation. The other diffraction peaks with 2θ values of 26.5° , 34.0° , 51.5° and 66.1° can be well indexed to the tetragonal rutile structure of SnO₂ (JCPDS card no. 41-1445) [16]. No diffraction peaks corresponding to graphitic carbon were observed in the XRD pattern, meaning that the carbon coating is amorphous. The morphology of Pt–SnO₂@C was investigated by SEM and TEM. As shown in Fig. 2, a number of the uniform sphere-like NPs with diameter of ca. 60–80 nm were interconnected by the thick carbon coating. There was a distinct contrast difference in the image, confirming the existence of amorphous carbon phase. The composition of Pt–SnO₂@C was investigated using energy dispersive X-ray (EDX) spectroscopy which confirms the elemental presence of Pt, Sn, O and C.

3.2. Electrooxidation of H₂O₂ and its detection

Fig. 3A shows the cyclic voltammograms (CVs) for hydrogen peroxide oxidation at different catalyst-coated GC electrodes. Smooth curves were obtained at Pt–SnO₂@C and Pt NPs modified electrodes in the absence of H₂O₂. With addition of H₂O₂, broad oxidation peaks were observed with peak potentials at 0.45 and 0.50 V on the Pt–SnO₂@C and Pt NPs modified electrodes, respectively. Compared to that of Pt NPs, the anodic peak current was remarkably improved at the Pt–SnO₂@C. These results indicate that the Pt NPs supported on SnO₂@C nanospheres have enhanced electrocatalytic activity towards H₂O₂ oxidation. Cyclic voltammograms of H₂O₂ at various scan rates on the Pt–SnO₂@C modified electrode was also investigated. As shown in Fig. 3B, at scan rates in the range of 60–500 mV s^{−1}, the oxidation peak currents increase linearly with scan rates, suggesting that the electrocatalytic oxidation of H₂O₂ on Pt–SnO₂@C is a surface-controlled process. The linear regression equation is expressed as: $I_{pa}/\mu A = 12.94 + 0.01849v/mV s^{-1}$ ($R^2 = 0.9986$).

Fig. 4 shows the amperometric response of Pt–SnO₂@C modified electrode to successive additions of H₂O₂ at a working potential of 0.5 V. Upon addition of H₂O₂, the electrode responded rapidly to the substrates and could achieve 97% of the steady-state current within 2 s. The fast amperometric response to H₂O₂ can be attributed to the good catalytic activity and conductivity of Pt–SnO₂@C, which facilitate the electrochemical reaction and electron transfer at electrode surface. The Pt–SnO₂@C modified electrode has linear amperometric responses to H₂O₂ with concentrations between 1 and 100 μ M. The linear regression equation obtained is

Fig. 3. (A) CVs of Pt–SnO₂@C (a and c) and Pt NPs (b and d) modified electrodes in the absence (a and b) and presence (c and d) of 5 mM H₂O₂ in 0.1 M PBS (pH 7.4). Scan rate: 50 mV s^{−1}. (B) CVs of 1 mM H₂O₂ on Pt–SnO₂@C modified electrode in 0.1 M PBS (pH 7.4) at different scan rates from 50 to 600 mV s^{−1}. Insert, the plot of the oxidation peak current vs. scan rate.

$I/\mu A = 0.02065 + 0.01714C_{H_2O_2}/\mu M$ ($R^2 = 0.9992$) and the sensitivity is calculated as 241.1 $\mu A mM^{-1} cm^{-2}$. The Pt–SnO₂@C nanocomposite film provided a low-detection limit of 0.1 μ M, estimated at a signal-to-noise ratio of 3 ($S/N = 3$).

A comparison of detection limit, linear range, sensitivity, and applied potential for the Pt–SnO₂@C modified GC electrode with other nonenzymatic H₂O₂ electrochemical sensors is presented in Table 1. It can be seen that the Pt–SnO₂@C modified electrode has favorable analytical performance.

3.3. Interference study and real sample analysis

The selectivity and anti-interference ability of the Pt–SnO₂@C modified electrode was investigated by chronoamperometry. Fig. 5 shows the amperometric response to the consecutive injection of 0.1 mM H₂O₂ and 0.1 mM interfering species including ascorbic acid (AA) and uric acid (UA). A well-defined H₂O₂ response was observed after its injection. However, the subsequent injections of AA and UA did not show any obvious additional response. It is obvious that the low overpotential for H₂O₂ detection at this electrode excludes the effects from interference, indicating good selectivity of the Pt–SnO₂@C composite film.

Table 1Performance of nonenzymatic H_2O_2 electrochemical sensors.

Electrode material	Detection limit (μM)	Linear range (μM)	Sensitivity ($\mu\text{A mM}^{-1} \text{cm}^{-2}$)	Potential (V)	Reference
PNEGHNs ^a	0.08	1–500	–	0	[1]
Graphene–Pt	0.5	2–710	–	0	[13]
Pt/OMCs ^b	1.2	2–4212	173.4	–0.10	[10]
Pt/PPy ^c	1.2	1000–8000	80.4	–0.1	[7]
PDDA ^d /Pt	0.042	0.042–160	500	0.6	[8]
Se/Pt	3.1	10–15,000	–	0	[4]
Pd/Au/CNTs/chit ^e	0.1	0.1–6000	–	–0.2	[22]
LNT–CFO ^f	0.023	0.1–8200	321	0.6	[23]
Pt–SnO ₂ @C	0.1	1–170	241.1	0.5	This work

^a Pt nanoparticle ensemble-on-graphene hybrid nanosheet.^b Ordered mesoporous carbons.^c Polypyrrole.^d Poly(diallyldimethylammonium chloride).^e Chitosan.^f $\text{LaNi}_{0.5}\text{Ti}_{0.5}\text{O}_3/\text{CoFe}_2\text{O}_4$. **Fig. 4.** Current–time curves for Pt–SnO₂@C modified electrode with successive additions of different amounts of H_2O_2 at a working potential of 0.5 V. Electrolyte: magnetically stirred 0.1 M PBS (pH 7.4). Insert: calibration curves for H_2O_2 at Pt–SnO₂@C modified electrode (RSD = 3.8%, $n = 5$). Error bars are the standard deviation of five repetitive experiments. **Fig. 5.** Amperometric responses of Pt–SnO₂@C modified electrode to 0.1 mM H_2O_2 , UA and AA in stirred 0.1 M PBS (pH 7.4) at a working potential of 0.5 V.

The determination of H_2O_2 in ultra-high-temperature (UHT) processed milk was carried to verify the practical application of the present electrochemical sensor. 200 μL of milk sample was added to 10.0 mL 0.1 M PBS solution (pH 7.4), and the current response was recorded at +0.5 V. The H_2O_2 concentrations of two milk samples were determined to be 2.1 and 3.0 mg L^{-1} , respectively. The recoveries of H_2O_2 determined by standard addition method were 94.3% and 96.0%, respectively. The agreeable recovery of the Pt–SnO₂@C modified GC electrode confirms that the proposed sensor is suitable for real sample analysis.

The electrochemical sensor retained more than 95% of its original response to H_2O_2 after 15 days during storage in a refrigerator at 4 °C. To establish the reproducibility, ten Pt–SnO₂@C modified GC electrodes were fabricated and their amperometric responses towards 10 μM H_2O_2 were examined, respectively. The relative standard deviation (RSD, $n = 10$) was 3.5%. These results indicate that this electrochemical sensor has good stability and repeatability, as required for the determination of H_2O_2 .

4. Conclusions

In this work, the Pt–SnO₂@C hybrid material was prepared and applied for electrochemical sensor fabrication. The crystallographic structure and morphology were characterized. The as-prepared Pt–SnO₂@C exhibited enhanced electrocatalytic activity and amperometric response towards H_2O_2 oxidation. This Pt–SnO₂@C based electrochemical sensor has excellent analytical performance for H_2O_2 detection with low detection limit, high sensitivity and long-term stability.

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