Graphene-supported PtPd Bimetallic Gathered Nanocrystals for Non-enzymatic Sensing of Oxalic Acid

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A novel non-enzymatic oxalic acid (OA) sensor was developed using a nanocrystal PtPd loaded reduced graphene nanosheets (PtPdNCs/RGO)-modified electrode. PtPdNCs/RGO were successfully achieved by a facile, one-step and template-free method, in which PtPd nanoparticles with 100 nm-scale were assembled from polyhedral PtPd nanocrystals of various shapes and dispersed on the graphene nanosheets. Resulting PtPdNCs/RGO were characterized and used for PtPdNCs/RGO-modified electrodes. Electrochemical oxidation of OA on the modified electrode was investigated by cyclic voltammetry and differential pulse voltammetry (DPV). Well-defined peaks of OA oxidation could be obtained using an electrode that indicated its high electrochemical activity. The concentration of OA and the current responses could be obtained in the ranges of 0.5 – 10 and 10 – 35 mM with correlation coefficients of 0.9994 and 0.9952; the detection limit (S/N = 3) was found to be 0.05 mM. The modified electrode presented good characteristics in terms of both stability and reproducibility, promising its applicability in practical analysis.

Keywords Polyhedral PtPd nanocrystals, graphene, non-enzymatic, oxalic acid, DPV

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Experimental

Reagents and chemicals

Graphite powders were purchased from Lvyin Co. (Xiamen, China); potassium permanganate, concentrated sulfuric acid and sodium nitrate were obtained from the Chemical Reagent Company of Shanghai (China); K₂PtCl₄ and K₂PdCl₄ were purchased from Wake Pure Chemicals, Co., Ltd. (Osaka, Japan); a 5% Nafion ethanol solution from the Aldrich Chemical Co. (USA); Pt/C catalyst was purchased from Alfa Aesar (10 wt%, HiSPEC30000, Johnson Matthey). Rod-like glassy carbon electrodes (GCEs) were from BAS Co., Ltd. (Tokyo, Japan). All other reagents were of analytical grade and used without further purification. The pure water for solution preparation was from a Millipore Autopure WR600A system (Millipore, Ltd., USA).

Apparatus

The morphology of the nanocrystal PtPd loaded reduced graphene nanosheets (PtPdNCs/RGO) was examined using a high-resolution transmission electron microscope (HRTEM, FEI Tecnai-F30 FEG). HAADF-STEM images and EDX were also recorded with FEI Tecnai-F30 FEG. All TEM samples were prepared by depositing a drop of diluted suspension in ethanol on a copper grid coated with a carbon film. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were performed with a CHI 660B Electrochemical Analyzer (CHI Co., Ltd., Shanghai, China). A saturated calomel electrode (SCE) was used as the reference electrode in this study.

Procedure

Graphene oxide (GO) was prepared according to a modified Hummer’s method. In the reduction of GO, 50 mg of the as-synthesized GO was dispersed in 100 mL dimethylformamide to obtain a yellow-brown aqueous solution with the aid of ultrasonication. Reduced graphene (RGO) could be obtained by heating the GO solution in an oil bath at 120°C for 24 h. In a typical synthesis of the PtPdNCs/RGO, a mixture of the homogeneous RGO suspension (8 mL 0.5 mg mL⁻¹), K₂PtCl₄ (0.05 mL 10 mM), K₂PdCl₄ (0.05 mL 10 mM) solution and 2 mL oleyl amine was kept in a vial. The mixture was then ultrasonicated for about 30 min. The resulting homogeneous solution was transferred to a Teflon-lined stainless-steel autoclave. The sealed vessel was then heated at 160°C for 8 h before being cooled to room temperature. The black reaction mixture was separated using a centrifuge, and further purified by an ethanol/acetone mixture. As a comparison, PtNPs on graphene were produced according to a previous report. Before preparing of the modified electrode, a GCE was polished with 1, 0.3 and 0.05 μm α-Al₂O₃, sequentially. In the surface coating of the GCE with the PtPdNCs/RGO nano-composite, 10 μL of the PtPdNCs/RGO suspension was dispersed in 100 μL of a 0.5% Nafion ethanol solution; then, 4 μL of the mixture was deposited on the polished GCE and dried in the air for 2 h at room temperature. After ultrasonication, 4 μL of the mixture was deposited on the polished GCE and dried in the air for 2 h at room temperature.

Results and Discussion

Characterization of the PtPdNCs/RGO composite

The morphology and nanostructure of PtPdNCs/RGO composites were examined by TEM, HRTEM, HAADF-STEM and EDX. Figures 1(a) - 1(d) show representative TEM images of the product at different magnifications. A low-magnification TEM image (Fig. 1(a)) shows that PtPdNCs nanoparticles were uniformly dispersed on the graphene surface. The absence of isolated PtPdNCs nanoparticles in the product indicates strong interactions between the PtPdNC and graphene. The magnified image (Fig. 1(b)) shows that the average size of these PtPdNC particles was about 100 nm. Zooming-in further, Fig. 1(c) shows that the particle was formed through the aggregation of some smaller polyhedral nanocrystals. The HRTEM image (Fig. 1(d)) indicates that the polyhedral nanocrystals presented a single-crystalline structure. The interplanar spacing is 0.223 nm, which agrees well with the (111) lattice spacing of face-centered-cubic (fcc) Pt (0.223 nm). In addition, it can be observed in Fig. 1(a) that smaller particles were scattered on graphene, except for a large one. Figure 1(e) lists some of the polyhedral nanocrystals, such as hexagonal, pentangular plate and cube, which possess plentiful facets, corners, edges and planes.

As shown in Fig. 2(a), we further characterized an individual hexagonal by HAADF-STEM and EDX line scanning analyses. The compositional line profiles of Pd and Pt that cross the individual hexagonal suggested that it was an essential PtPd alloy with homogeneous distributions of Pt, Pd elements. As shown in Fig. 2(b), obvious Pt and Pd peaks could be found from a typical EDX analysis of the prepared PtPdNCs/RGO composite. This result suggested that the PtPdNCs were successfully attached to the graphene surface.

Electrochemical oxidation of OA

In the study, CV and DPV were applied to test the characteristic of the PtPdNCs/RGO for the sensing of OA. Generally, CV allows discrimination against other oxidizable interferents in the potential domain, and DPV gives higher sensitivity for the analytes. Figure 3(a) presents the CV responses using a PtPdNCs/RGO-modified electrode in both the presence and absence of 5 mM OA in a 0.1 M HClO₄ solution at a scan rate of 50 mV/s. In the absence of OA, no cathodic and anodic peaks for OA could be observed. When OA was introduced in the electrolyte solution, the CV profile was completely different, and there was a new and well-defined oxidation peak at 1.0 V. The observed oxidation peak with a high current response could be attributed to the electro-oxidation of OA on the electrode. The result indicates that the metal nanocrystals reveal catalysis to the electrochemical oxidation of OA. Previous studies have pointed out that the oxidation of OA at higher potentials involves a direct chemical reaction between HC₂O₄⁻ and metal ions generated on the electrode surface. In this experiment, the electro-oxidation of H₂C₂O₄ involves the step of the preliminary adsorption of H₂C₂O₄ on the metal nanoparticles:

\[ \text{M}^n + \text{H}_2\text{C}_2\text{O}_4 \rightarrow \text{M(H}_2\text{C}_2\text{O}_4)_{\text{ads}} \]

In addition, the adsorbed complex undergoes a subsequent probable fast hydrogen abstraction mechanism where the reactive Pt(II) species catalyst are involved,

\[ \text{H}_2\text{C}_2\text{O}_4 + \text{M} \rightarrow \text{M} + 2\text{CO}_2 + 2\text{H}^+ \]
We further compared the effect of different electrode materials toward OA oxidation. Figure 2(b) shows the comparison results of the OA voltammograms using an RGO-GCE, a Pt/C-GCE, a PtNPs/RGO-GCE and a PtPdNCs/RGO-GCE. It has been reported that the electrochemical reaction of OA is highly dependent on the electrode material. In the experiments, the RGO-GC electrode did not show any characteristic responses in the potential window used, suggesting that the metal nanoparticles efficiently catalyze the oxidation of OA. As can be seen from the onset potential of OA oxidation in the CV curves, the reaction rate determined on these electrodes decreased as follows: PtNP/RGO > Pt/C > PtPdNCs/RGO. The PtPdNCs/RGO-GCE showed more positive potential of OA oxidation since the slower electron-transfer kinetics caused by the larger size of PtPdNCs presumably. Although the onset potential of OA oxidation on Pt/C-GCE or PtNPs/RGO-GCE was more negative than that on PtPdNCs/RGO-GCE, it could be readily found that an improved voltammetric response was obtained for the oxidation of OA on PtPdNCs/RGO-GCE. The current response of the OA oxidation peak on PtPdNCs/RGO-GCE was 2-fold higher than that of PtNPs/RGO-GCE, and 3.8-fold higher than that of Pt/C-GCE. Although our previous work had shown that PtNPs/RGO possesses superior electrocatalytic oxidative activity towards OA, the PtPdNCs/RGO-GCE showed more excellent performance. The greater current response suggests that the abundant corners, edges and planes of PtPdNCs present numerous active sites of reaction. Moreover, the synergetic effect between Pt and Pd also enhanced the electrocatalytic activity. Herein, graphene possessed a large active surface area, which allows the biomolecules to readily accessible to the surface of the catalyst. When the interaction of OA molecules with the electrode surface is particularly strong, the oxidation reaction is fast. Generally, a higher electrooxidation current response indicates a superior...
electrocatalytic activity of the electrode. These results illustrate that the PtPdNCs/RGO-GCE presented a better catalytic performance among the tested electrodes.

Analytical performance of the electrochemical sensor for OA detection

Sensitive DPV was used to detect the trace quantity of OA at different concentrations. To improve the performance of the non-enzymatic OA sensor, the acidic medium was optimized. When the PtPdNCs/RGO-GCE was used in 0.1 M HCl, the OA reaction was rather inhibited by Cl–. When the experiment was carried out in 0.1 M H2SO4, a fast voltammetric response to OA oxidation could be obtained, but the current peak was lower than that in HClO4, which is in accordance with the Pt electrocatalytic activity being higher in perchloric than in sulfuric acid.2,31,32 As a result, 0.1 M HClO4 was selected as the supporting electrolyte.

Figure 4 displayed the DPV response of the PtPdNCs/RGO-GCE towards the increasing concentrations of OA under the experimental conditions. The peak currents increased linearly with an increase of the OA concentration in two ranges of 0.5 to 10 and 10 to 35 mM with correlation coefficients of 0.9994 and 0.9952 (the inset of Fig. 4). The detection limit was determined based on the 3 sigma method, and the limit of detection was calculated to be 50 μM (S/N = 3). It is obvious that the slope of the OA concentration in the 0.5 to 10 mM range was larger than that in 10 to 35 mM. Moreover, the potential peaks shifted positively with the increase of the OA concentration. These results indicated that the detection performance became lower with the increase of OA concentration. Although the PtPdNCs show high electrocatalytic...
activity in OA electro-oxidation and oxygen-containing groups of the graphene could improve the tolerance of the PtPdNCs to some extent, during the detection, PtPdNCs could also be gradually poisoned by the adsorption of molecules, which affected the detection sensitivity. By taking advantage of the well-dispersed, plentiful active sites of PtPdNCs as well as the large surface area and high conductivity of the RGO, the PtPdNCs/RGO-GCE revealed an excellent performance for the OA determination. Although PtPdNCs/RGO exhibit an enhanced current response in contrast to that of PtNPs/RGO, PtPdNCs/RGO possess a smaller linear range and a higher detection limit. That may be caused by the slower electron-transfer kinetics of the larger size of PtPdNC and the incompletely clean surface. It is still worth comparing the analytical performance of the presented PtPdNCs/RGO-GCE with those of available recent OA sensor. Liu et al. observed a detection limit of 0.2 mM for OA with palladium nanoparticle-loaded carbon nanofiber (Pd/CNF). Ahmar et al. reported a linear response in the range of 0.03 – 5.0 mM by palladium nanoparticles encapsulated on polyamidoamine dendrimer-grafted multi-walled carbon nanotubes (PdNPs/PAMAM-MWCNTs). Subsequently, Araújo et al. reported a linear response between 1.5 – 30 mM with a detection limit of 0.6 mM using the GCE modified cysteic acid layer film. The long-term storage stability of the modified electrode toward OA sensing was studied over a week by monitoring its DPV responses to 5 mM OA in 0.1 M HClO4 with an intermittent usage (at 1 day intervals), and storage in air at room temperature when not in use. It was found that the response of the modified electrode gradually decreased to approximately 90% of its initial value within a week. In the preparation of the modified electrode, different 5 GCEs were selected and their surfaces were modified by PtPdNCs/RGO under the same conditions and process. The reproducibility within a mean value of ±5% could be achieved in the DPV determination of 5 mM OA.

Conclusions

In summary, this study proposed a novel non-enzymatic OA sensing approach based on a PtPdNCs/RGO modified electrode. This PtPdNCs/RGO-GCE exhibited a higher catalytic oxidation current towards OA oxidation than other electrodes as PtNPs/RGO and Pt/C. Moreover, the oxidation current of OA was linear to its concentration in a wide range by DPV. The PtPdNCs/RGO also showed excellent sensitivity in the OA detection with a detection limit of 0.05 mM (S/N = 3) and excellent reproducibility. This approach provides a new facile route to construct effective OA sensing, and may provide a promising way to detect other biologically important compounds.

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