Self-Assembled Ionic Liquid-Phosphomolybdic Acid/Reduced Graphene Oxide Composite Modified Electrode for Sensitive Determination of Dopamine

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A novel reduced graphene oxide (RGO) coated glassy carbon electrode (IL-PMo12/RGO/GCE) modified with ionic liquid (IL, [BMIM][BF4]) and phosphomolybdic acid (PMo12, H3PMo12O48) was fabricated via electrostatic self-assembling. The phosphomolybdic acid anionic monolayer could electrostatically adsorbed ionic liquid cations to form an organic and inorganic hybrid film on graphene sheets. The modified electrode was used for the determination of dopamine (DA) in the presence of uric acid (UA). This electrode anticipated the good electron mobility and large surface area of graphene, high ionic conductivity of ionic liquid besides the electron transfer property of phosphomolybdic acid. Optimization of the sensor’s performance is presented and resulted in a better current signal. The linear range of the modified electrode was from 0.1–100 μM for determination of DA with an R-Square 0.9924 and with a detection limit of 3.3 × 10^{-8} M (S/N = 3). The IL-PMo12/RGO/GCE also presented good stability and reproducibility.

Reagents and apparatus.—Phosphomolybdic acid (H3PMo12O48, PMo12), sodium dihydrogen phosphate and disodium hydrogen phosphate (H3PO4, Na2HPO4) was purchased from Aldrich. All these chemicals were of analytical reagent grade and used without further purification. The supporting electrolyte was a 0.2 M phosphate buffer saline (PBS) (pH 7.0, 25 °C).

Experimental

Reagents and apparatus.—Phosphomolybdic acid (H3PMo12O48, PMo12), sodium dihydrogen phosphate and disodium hydrogen phosphate (H3PO4, Na2HPO4) was purchased from Sinopharm Chemicals Reagent Co., Ltd., China. Graphite powder was provided by Qingdao Fujin graphite Co., Ltd., China. Ionic liquid (IL, 1-butyl-3 methylimidazolium tetrafluoroborate ([BMIM] [BF4]), dopamine (DA) and uric acid (UA) were purchased from Aldrich. All these chemicals were of analytical reagent grade and used without further purification. The supporting electrolyte was a 0.2 M phosphate buffer saline (PBS) (pH 7.0, 25 °C). Doubly distilled water was employed throughout the experiment.

Preparation of modified electrodes.—Before modification, glassy carbon electrode substrates were activated by polishing with successively finer grade aqueous alumina slurries (0.05 μm after 0.3 μm) on a polishing cloth. Preparation of the ionic liquid-PMo12/modified graphene oxide hybrid film modified glassy carbon electrode (IL-PMo12/RGO/GCE) was achieved via the following immersion scheme. Graphene oxide (GO) was prepared based on the modified Hummers method. A 250 mL three-necked flask was
charged with a stirring bar, graphite (0.6 g), NaNO₃ (1.0 g) and 35 mL of concentrated H₂SO₄. The flask was placed into an ice bath, allowed remain here to reactor for 60 min. 3.0 g KMnO₄ was added into the flask with vigorous stirring, keeping the temperature lower than 20 °C. Then, 150 mL of water was slowly poured into the flask with vigorous agitation for 45 min. After the temperature of the suspension was raised to 98 °C by heating, it was poured into a beaker containing 60 °C water. Finally, 10 mL of 30% H₂O₂ was added to the suspension. The product was washed by 5% HCl and water for several times. Graphene oxide powder was obtained by vacuum drying the filter mass for 12 h. Chemical reduction of graphene oxide was carried out according to the method mentioned in our previous work.²⁶ Graphene oxide powder (50 mg) was dispersed in a flask containing 20 mL water by ultrasonication for 60 min to obtain a uniform dispersion. After 0.5 mL of hydrazine monohydrate was added, the flask was heated with constant vigorous magnetic stirring to 90 °C and reacted for 24 h. The product was filtration washed by water for several times and vacuum dried for 12 h to obtain the reduced graphene oxide (RGO). As shown in Scheme 1, the first step was the preparation of graphene modified glassy carbon electrode (RGO/GCE). 1 mg of RGO was ultrasonically dispersed in 1 mL of ethanol to generate a homogeneous black suspension. 5 μL of the suspension was dropped onto a GCE and dried at room temperature to form RGO/GCE. Then RGO/GCE surface was modified with a self-assembled PMo₁₂ monolayer (PMo₁₂/GCE) by dipping the RGO/GCE substrate for 10 min in an aqueous solution of 0.2 M H₃PMo₁₂O₄₀. Introduction of BMIM cations onto PMo₁₂ monolayer was achieved by immersing the PMo₁₂/RGO/GCE in a 0.5 M solution of [BMIM] [BF₄] in H₂O for 5 min. And, the IL-PMo₁₂ modified electrode (IL-PMo₁₂/GCE) was prepared by the same process without the modification of RGO on GCE substrate.

Results and Discussion

Morphology and characterization.— The morphologies of RGO and IL-PMo₁₂/RGO composite were characterized by scanning electron microscopy (SEM). As shown in Fig. 1A, RGO has a typically curved, layer-like structure. Fig. 1B shows that IL-PMo₁₂ film uniformly coat on the surface of RGO, which attributes to the electrostatically self-assembling between PMo₁₂ anions and ionic liquid cations.

![Scheme 1. The structure of ionic liquid-phosphomolybdic acid/graphene modified electrode.](image)

**Figure 1.** SEM images of RGO (A) and IL-PMo₁₂/RGO (B).

Electrochemical behavior of IL-PMo₁₂/RGO/GCE toward dopamine and uric acid.— The electrochemical behavior of IL-PMo₁₂/RGO/GCE is shown in Fig. 2 and Fig. 3, compare with the bare GCE, RGO/GCE and IL-PMo₁₂/GCE which act as the blank under exactly the same conditions. Fig. 2 gives the cyclic voltammetry (CV) curves of a mixture of DA (1 × 10⁻⁴ M) and UA (1 × 10⁻⁴ M) in 0.2 M PBS (pH 7.0) at bare GCE, RGO/GCE, IL-PMo₁₂/GCE and IL-PMo₁₂/RGO/GCE electrodes. As can be seen, the oxidation peaks of DA and UA can hardly observed on the bare GCE and IL-PMo₁₂/GCE (Figs. 2D and 2C). The RGO/GCE shows an increase for the oxidation of DA and UA (Fig. 2B), which is contributes to the outstanding electron transport capabilities of graphene. The obvious enhancement of the peak current and good separation for DA and UA oxidation are obtained at the IL-PMo₁₂/RGO/GCE (Fig. 2A). These improved performances are mainly due to the self-assembled organic and inorganic hybrid structure and synergistic effects of RGO with well-defined layered structure, biocompatible PMO₁₂ and conductive ILs. Fig. 3 shows the CV curves of 1.0 × 10⁻⁴ M DA (a), 1.0 × 10⁻⁴ M UA (b) and their mixture (c) on IL-PMo₁₂/RGO/GCE in 0.2 M PBS (pH 7.0). The oxidation peaks of DA and UA appear at 0.15 V and 0.65 V respectively.

**Figure 2.** CV curves of the mixture of DA and UA in 0.2 M PBS (pH 7.0) on the IL-PMo₁₂/RGO/GCE (A), RGO/GCE (B), IL-PMo₁₂/GCE (C) and bare GCE (D). Scan rate: 50 mV s⁻¹.

**Figure 3.** CV curves of 1.0 × 10⁻⁴ M DA (a), 1.0 × 10⁻⁴ M UA (b) and their mixture (c) on IL-PMo₁₂/RGO/GCE in 0.2 M PBS (pH 7.0). Scan rate: 50 mV s⁻¹.
0.30 V, corresponding to a peak current of 11.4 μA and 14.9 μA. The potential difference between the two peaks is 0.15 V, which is enough to well distinguish DA from UA.

**Effect of pH on the oxidation of DA and UA.**—In order to fabricate an efficient sensor, different factors including pH value of the solution were investigated. The effect of pH value on the electrochemical response of the IL-PMo12/RGO/GCE toward the oxidation of DA was studied. As shown in Fig. 4, the anodic peak current of DA increased with an increase in the solution pH until it reaches 7.0 and then the anodic peak current decreased with the increase of pH value. In this work, a 0.2 M PBS solution with pH 7.0 was chosen as the optimal pH value.

**Effect of scan rate.**—The CV curves of IL-PMo12/RGO/GCE in the 0.2 M PBS solution at pH 7.0 in the presence of DA recorded at various scans from 50 mV/s to 300 mV/s was shown in Fig. 5a, which shows an increasing peak current along with the scan rate. As we can see in Fig. 5b, there is a liner correlation between the cathodic current and scanning rates (v), suggesting that the kinetics of the oxidation process of DA surface-controlled process. This result is well indirectly indicated that IL-PMo12/RGO/GCE exhibited a positive charge in aqueous solution due to BMIM cations existed on the surface of the self-assembled film. It is noteworthy that the anodic oxidation peak potential shifts slightly to more positive potentials with increasing of the scan rate. These results indicate that at higher scan rates a kinetic limitation exists in the course of the reaction between the IL-PMo12/RGO hybrid film and DA.

To achieve the simultaneous detection, IL-PMo12/RGO/GCE was used to detect DA and UA with different concentrations. Fig. 6a presents differential pulse voltammetry (DPV) response of IL-
Table I. Comparison of IL-PMo12/RGO/GCE with other reported modified electrodes for the determination of dopamine.

| Modified electrodes | Linear range (μM) of DA | Detection limit (μM) of DA | ΔEp (DA, UA) (mV) | References |
|---------------------|--------------------------|----------------------------|-------------------|------------|
| Poly (4-(2-pyridyl-azo)-resorcinol)/GCE | 5–30 | 0.2 | 199 | 29 |
| Graphene/SnO2/GCE | 1–20 | 1 | 180 | 30 |
| MgO/Graphene/Ta | 0.1–7.0 | 0.15 | 147 | 31 |
| PIL/MWCNT/GCE | 10–600 | 2.01 | 120 | 32 |
| IL-PMo12/RGO/GCE | 0.1–100 | 0.03 | 150 | This work |

(Ta), tantalum wire; (PIL), polymeric ionic liquid; (MWCNT), multi-walled carbon nanotube; (IL), ionic liquid; (PMo12), phosphomolybdate; (RGO), reduced graphene oxide

Figure 7. (a) DPV curves of IL-PMo12/RGO/GCE in 0.2 M PBS (pH 7.0) with 1.0 × 10^{-4} M DA and different [UA]: I–VII: 1.0 × 10^{-6} to 1.0 × 10^{-4} M; (b) plot of the peak current vs. [UA]. PMo12/RGO/GCE in PBS with 1.0 × 10^{-4} M UA and different concentrations of DA. Two well defined oxidation peaks appeared obvious at 0.12 and 0.27 V, which is corresponding to the oxidation potential of DA and UA. Along with the increasing of the concentrations of DA, the oxidation peak current of DA gradually increased, but the oxidation peak current of UA mostly kept constant. Fig. 6b displays that the oxidation peak current of DA presented a good linear relationship to [DA] from 1.0 × 10^{-7} to 1.0 × 10^{-4} M (y = 0.1526 + 45.08x, R^2 = 0.9924), with a detection limit of 3.3 × 10^{-8} M (S/N = 3). The above results reveal the excellent anti-interference ability of our method.

Reproducibility, stability of the IL-PMo12/RGO/GCE.—Under the optimum conditions, eight electrodes were independently fabricated through the same procedures as mentioned above. The fabrication reproducibility was investigated by comparing the oxidation peak currents of DA and UA in a mixed solution. From the results, the RSDs were 2.76% and 2.58% for DA and UA, respectively. The repeatability of one electrode was also examined by successive measurements. The RSD of 1.40% showed a good reproducibility of the fabricated IL-PMo12/RGO/GCE. Additionally, the stability of the modified electrode was investigated by storing it at 4°C and measuring once a day over a period of 3 weeks. Only a small decrease of the oxidation peak current was observed (the signal changes were 4.90% for DA and 4.31% for UA), which could be attributed to the excellent long-term stability of IL-PMo12/RGO/GCE.

Interference of coexisting substances.—The possible interferences of some common inorganic ions and other organic compounds on the determination of DA and UA were also investigated. The results in Table II shown that 1000- fold concentration of Na^+, K^+, NH4^+, Ca^{2+}, Mg^{2+}, Cu^{2+}, Zn^{2+}, NO3^− and 100- fold concentration of Fe^{3+}, phenol or resorcinol had no effects on the detection signals of DA and UA (signal change ≤5%). The above results reveal the excellent anti-interference ability of our method.

Application of the modified electrode.—In order to evaluate the applicability of IL-PMo12/RGO/GCE for real sample, this electrode was employed in the detection of DA in human serum samples. All samples were diluted 20 times with 0.2 M PBS (pH 7.0), and the
analytical results were shown in Table III. The recoveries were between 99.46% and 100.50%, which revealed that the proposed modified electrode could be effectively applied to the detection of DA in real samples.

Conclusions

It has been demonstrated that the ionic liquid- phosphomolybdic acid, organic-inorganic hybrid film was fabricated on the surface of a reduced graphene oxide modified glassy carbon electrode based on electrostatically self-assembly process. The as-prepared modified electrode could be effectively applied to the detection of DA in the existence of UA. The self-assembling on the surface of graphene sheets changed the surface property and improved uniformity of the hybrid film, resulted in good electro catalytic performance toward the oxidation of DA and UA. The application in serum samples revealed that the proposed modified electrode could be effectively applied to the detection of DA in real samples.

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