



# Electrochemical investigation of a metalloporphyrin–graphene composite modified electrode and its electrocatalysis on Ascorbic Acid



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## ABSTRACT

In this paper, 5-(4-Aminophenyl)-10,15-20-triphenylporphyrin (ATP) and 5-(4-Aminophenyl)-10,15-20-triphenylporphyrin[Mn(III)](ATPMn) were successfully synthesized. ATP-graphene (ATPG) and ATPMn-graphene (ATPMnG) composite materials have also been prepared and characterized by using UV–vis, FT-IR, SEM, AFM and TEM. GO, ATPM and ATPMnG were used to modify glassy carbon electrode (GC) and investigate the electrocatalytic oxidation features of Ascorbic Acid (AA) by Cyclic voltammetry (CV) and differential pulse voltammetry (DPV), respectively. These results show the oxidation peak current of AA at the ATPMnG/GC electrode have a large shift negatively and the intensity of the oxidation peak current increased significantly compared with that at the other electrodes, which illustrate a quite good catalytic activity for the oxidation of AA at the ATPMnG/GC electrode. The linear relationship between the oxidation peak current and the AA concentration has been built.

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## 1. Introduction

Various carbon-based materials including highly ordered pyrolytic graphite (HOPG), glassy carbon, fullerenes, and carbon nanotubes have been used in both electroanalysis and electrocatalysis [1–5]. Especially, HOPG and vertically oriented CNT arrays can act as outstanding electrode materials owing to the highly reactive edge planes in contrast to the inert basal planes. However, these HOPG and vertically oriented CNT arrays were treated in strong acids for long times still contain residual metals encapsulating into multilayer graphene layers, which not only lead to potential misinterpretations of electrochemical measure but also impact on the electrochemical repeatability and stability [6,7]. Theoretically, 1D CNT arrays could be rolled up the different layers graphene and 0D fullerenes could be wrapped up by using single layer graphene. Graphene serves as a basic building unit for the other carbon materials and graphene has also been extensively used to describe the properties of various other carbon-based materials [8–10]. The graphene possesses a lot of open graphitic edge planes compared with the other various carbon-based materials [11–13], so the graphene as an electrode material can effectively avoid the defects that other various carbon-based materials unavoidably encapsulating the residual metals lead to misinterpretations and greatly improve the electrochemical repeatability and stability of electrochemical experiments. On the other hand, graphene with high huge specific surface area could be

one of best choices for electrode materials in all kinds of electrochemical experiments [14,15]. The graphene covalently or noncovalently modified with various molecules and nanomaterials has been used to tune electronic properties of graphene [16]. Porphyrins are very important biomolecule in biological system [17,18], which have been extensively used in mimic enzymatic systems. Their electrocatalytic capabilities on various analysts have been put forward, porphyrin derivatives have been used to modify graphene by the covalent or noncovalent bond and photochemical properties have also been investigated.

Ascorbic Acid (AA) as a kind of antioxidant existing in many biological species participates in many important biological processes. AA has been widely applied in food and pharmaceutical industries [19]. In addition, AA as an important component in human diet takes a vital role in neurochemistry, bioelectrochemistry and clinical diagnostics applications. Also, AA has been used to prevent and treat scurvy, mental illness and cancer. In order to effectively detect AA, the development of a simple and rapid method for the determination of AA with high selectivity and sensitivity is desirable for diagnostic and food safety applications. All kind of methods have been developed [20–23]. The electrochemical techniques have received considerable interest for the detection of AA because of their high sensitivity, rapid response, simple operation, and low expense. The sensitivity of the oxidation potentials of AA is dependent on the electrode materials. At present, the electrochemical detection of AA by various modified electrodes has been fabricated to overcome the electrode poor reproducibility of bare electrode substrates, including multi-walled carbon nanotubes hybrid composite, nitrogen doped graphene [24,25], electrochemical polymerized film

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[26], graphene [27], and so on. Especially, the electrode modified with porphyrin has also been used for detection of AA and obtained good experimental results.

In this work, an ATPMnG composite material has been synthesized and utilized to modify GC electrode. The ATPMnG/GC composite electrode can effectively improve the electrochemical repeatability and stability compared with GC modified with the non-covalent porphyrin functionalized graphene. The ATPMnG/GC electrode was used to detect the electrocatalytic features of AA by CV and DPV. The results show that the ATPMnG/GC electrode has a better electrochemical response for AA species. The oxidation peak current of AA at the ATPMnG/GC electrode has greatly negative shift and the intensity was significantly enhanced compared with that at the bare GCE, which exhibited a quite well electrocatalytic activity for the oxidation of AA. The oxidation peak current has a good linear relationship with the AA concentration ranges from 0.2 to 2.0 mM. The corresponding linear equations were  $I(\mu\text{A}) = 10.033C(\text{mM}) + 2.812$  with a correlation coefficient of  $R^2 = 0.997$ . In order to obtain the lower detection limitation of AA, DPV was used to detect AA. The experimental results showed that the good linear relationship between the oxidation peak current and the lower AA concentration ranges from 40  $\mu\text{M}$  to 280  $\mu\text{M}$ . The corresponding linear equations were  $I(\mu\text{A}) = 31.656C(\text{mM}) - 0.0991$  with a correlation coefficient of  $R^2 = 0.999$ . The lowest detection limit at the ATPMnG/GC electrode for AA is 8.5  $\mu\text{mol/L}$  which has been determined by the traditional method when the signal-to-noise ratio is 3.

## 2. Experimental

### 2.1. Materials and methods

All chemical reagents were analytical grade and used without any further purification. AA was purchased from Sinopharm Chemical Reagent Co., Ltd. in Shanghai, China. Phosphate buffer solutions (0.1 M pH 7.4) served as the supporting electrolyte and were prepared using 0.1 M  $\text{Na}_2\text{HPO}_4$  and 0.1 M  $\text{NaH}_2\text{PO}_4$ . (PBS) the deionized water was used throughout the experiment. In a typical synthesis, graphene oxide (GO) powders were initially prepared according to the previous literature by Hummers from graphite powder (Aldrich, powder,  $<20 \mu\text{m}$ , synthetic) [28,29].

### 2.2. Synthesis of ATP

ATP was synthesized according to the literature [30]. The spectra of ATP were as followed: (Supporting information Figs. 5 and 6) Mass [FAB],  $m/z$ : calc. 629.7, found 630.3 [M + 1];  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$ (ppm): -2.75 (s, N-H), 3.72 (s, 2 H), 7.07 (d, 2 H, J = 8.1 Hz), 7.73–7.78 (m, 9 H), 8.00 (d, 2 H, J = 8.1 Hz), 8.22 (d, 6 H, J = 5.7 Hz), 8.83 (s, 6 H), 8.94 (d, 2 H, J = 4.8 Hz) UV-vis [DMF,  $\lambda_{\text{max/nm}}$ ( $\epsilon \cdot 10^5$ ): 419 (8.2), 515 (0.21), 552 (0.06), 589 (0.03), 649 (0.07).

### 2.3. Synthesis of ATPMn

A mixture of 0.44 mg TPP-NH<sub>2</sub> (0.07 mmol) and 0.5 g  $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$  in 30 mL DMF was reacted for 1.5 h at 80 °C with Magnetic stirring under nitrogen atmosphere. After cooling to room temperature, 100 mL dichloromethane was added to the reacted solution. The solution was washed three times with the deionized water, after the excess  $\text{MnCl}_2$  and DMF was removed, the solution was dried with anhydrous sodium sulfate overnight, concentrated and placed on a silica gel column using dichloromethane as the eluant and collect the main chromatographic band, Yield: 0.42 g (61.5%).

### 2.4. Synthesis of covalently attached porphyrin graphene oxide hybrids

50 mg graphene oxide which has been previously prepared by using modified Hummers method was refluxed in 30.0 mL  $\text{SOCl}_2$  and 2.0 mL

DMF at 70 °C for 24 h under nitrogen atmosphere. The excess  $\text{SOCl}_2$  was removed by the distillation. Then 3 mL triethylamine and 70 mL DMF were added and reacted at 80 °C for 72 h under a nitrogen atmosphere, and then the reacted solution was treated 8 h with the intermittent sonication. A homogeneous black dispersion was obtained. Then 100 mg TPP-NH<sub>2</sub> was added into the solution and continuously reacted for 24 h at 80 °C under a nitrogen atmosphere. 300 mL ether was poured into the solution after the solution was cooled to room temperature. The solution was filtered with 0.45  $\mu\text{m}$  millipore filter. The precipitate was thoroughly washed with  $\text{CH}_2\text{Cl}_2$  and a small quantity of  $\text{H}_2\text{O}$ , respectively. The precipitate was dispersed into 50 mL DMF and sonicated for 30 min, and then centrifuged at 10,000 rpm for 25 min to collect ATPG, discarding the supernatant. UV-vis spectra and thin layer chromatography (TLC) were used to check the supernatant layer to ensure no TPP-NH<sub>2</sub> existed in the final washing. This same methodology was implemented for ATPMnG by replacing ATP with ATPMn. The synthesis scheme of covalently linked porphyrin graphene oxide hybrids is shown in Scheme 1.

### 2.5. Apparatus

UV-vis spectra and Fluorescence spectra were performed on a Varian 4000 UV-Vis-NIR spectrometer and Cary Eclips (Varian Company, U. S. A). The scanning electron microscopy (SEM) was performed with a Quanta 200 scanning electron microscope (FEI Company, Holland) and a Hitachi H-7650 transmission electron microscope (TEM) (Hitachi, Pleasanton, CA). Raman studies were carried on a HORIBA Jobin Yvon LabRAM Xplo Raman spectrometer using 532.0 nm excitation and the optical power delivered on to the sample was 50 mW/cm<sup>2</sup>. IR spectra were recorded on a Perkin-Elmer 1730 FT-IR spectrometer equipped with DTGS/KBr detector and windows with a spectral resolution of 4 cm<sup>-1</sup>. The FTIR spectra were collected in a transmission mode. Electrochemical measurements were conducted by using a Bio-Logic VSP-300-6 electrochemical working station. A conventional three-electrode system was used for all electrochemical experiments, which consisted of a high purity platinum rod ( $\varphi = 3.0 \text{ mm}$ ) as auxiliary electrode, a saturated calomel electrode (SCE) as reference electrode, and a bare Glassy Carbon Electrode ( $\varphi = 3.0 \text{ mm}$ ) (GCE) or a GCE ( $\varphi = 3.0 \text{ mm}$ ) modified by ATPMn, GO, and ATPMnG was used as the working electrode. All potentials were referenced to SCE, and all the values of pH were in 7.0 PBS.

### 2.6. Preparation of the modified electrode

For the working electrode preparation, the GCE was polished to a mirror finish with 0.03 and 0.05 mm alumina slurry. Then, it was ultrasonically washed with doubly distilled water and ethanol to remove the physically absorbed substance. Then the GCE was dried at room temperature. The pre-treated GCE electrode was monitored in 10.0 mM  $\text{K}_3[\text{Fe}(\text{CN})_6]$  aqueous solution by CVs. When the potential difference ( $\Delta E$ ) between the oxidation potential and the reduction potential is less than or equal to 80 mV, the pre-treated GCE electrode meets our experimental requirements. In our all electrochemical performances, the  $\Delta E$  of the pre-treated GCE electrode is 72 mV. 15.0  $\mu\text{L}$  of the ATPMnG suspension (0.5 mg/mL) was dropped on to the surface of the pre-treated GCE to fabricate ATPMnG/GCE and dried at room temperature. The other modified electrode was prepared by same experimental procedures, we will only replace ATPMnG with GO and ATPMn, respectively.

## 3. Results and discussion

### 3.1. Characterization of graphene structure

The surface morphologies of GO are characterized by SEM (Fig. 1A), the graphene nanosheets on the top of the flat copper sheet base were observed. The typical wrinkled sheet texture of graphene that was

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