



# Zinc porphyrin–fullerene derivative noncovalently functionalized graphene hybrid as interfacial material for electrocatalytic application



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## ABSTRACT

In this paper, a *p*-methoxy zinc porphyrin–fullerene derivative (ZnP<sub>p</sub>-C<sub>60</sub>) noncovalently functionalized electrochemically reduced graphene oxide (ERGO) hybrid (ERGO@ZnP<sub>p</sub>-C<sub>60</sub>) was facily obtained by  $\pi$ - $\pi$  stacking interaction between zinc porphyrin ring and ERGO. The hybrid was characterized by scanning electron microscope (SEM), electrochemistry, UV–vis spectra, and density functional theory (DFT), which demonstrated that the presence of ERGO caused more redox reversibility and higher electrocatalytic activity of ZnP<sub>p</sub>-C<sub>60</sub>. By using their synergistic effects of the remarkable mechanical, electrical, catalytic, and structural properties, ERGO@ZnP<sub>p</sub>-C<sub>60</sub> incorporated in tetraoctylammonium bromide (TOAB) film was modified on the glassy carbon electrode (GCE) to construct a novel non-enzymatic electrochemical sensor. The sensor exhibited enhancing response sensitivity for the electrocatalytic reduction of hydrogen peroxide with a high sensitivity of 451.3  $\mu\text{A mM}^{-1}$  and a limit of detection (LOD) as low as 0.27  $\mu\text{M}$ . The sensitivity is 2-fold larger than that of TOAB/ZnP<sub>p</sub>-C<sub>60</sub>/GCE in the absence of ERGO. Although a high detecting sensitivity of 162.5  $\mu\text{A mM}^{-1}$  for electrocatalytic oxidation of nitrite could be also obtained on the presented sensor, the sensitivity is lower than that of TOAB/ZnP<sub>p</sub>-C<sub>60</sub>/GCE (233.9  $\mu\text{A mM}^{-1}$ ) due to the change in the structure of ZnP<sub>p</sub>-C<sub>60</sub> and the electronic interactions between GO and ZnP<sub>p</sub>-C<sub>60</sub>. Even though, the smart hybrid (ERGO@ZnP<sub>p</sub>-C<sub>60</sub>) possesses obvious advantage for the fabrication of non-enzymatic electrochemical sensor and paves a new avenue for constructing C<sub>60</sub> derivative and graphene based materials.

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## 1. Introduction

Non-enzymatic electrochemical sensors with high sensitivity and extreme stability are always being focused and have been constructed by using various modified materials such as nano-materials, carbon materials, porphyrin and its derivatives, and some organic dyes [1–7]. Among them, carbon allotropes including fullerene, carbon nanotubes (CNTs), and graphene (G) have been extensively used due to their remarkable mechanical, electrical, catalytic, optical, and thermal properties [8–10]. Graphene, two-dimensional sp<sup>2</sup> carbon network, possesses the above properties and is considered as an ideal candidate for the applications in nanoelectronics, supercapacitors, solar cells, and hydrogen storage [8,11]. Fullerene also has unique biological activities of toxicity, antioxidant capacity, and possible HIV inhibition and has been

extensively used in physics, chemistry, life and material sciences [12]. Similarly, One-dimensional CNT with the advantages including the excellent electrochemical properties, mechanical strength and tunable functionality in conjugation with biomolecules is also a promising candidate for fabrication electrochemical sensor [13]. In order to improve the biocompatibility and direct electron transfer of biomolecules, combining with metal or metal oxides nanoparticles such as gold, silver, platinum, nickel oxide, titanium dioxide, or manganese oxide, these carbon allotropes of graphene, CNTs and fullerene based composite materials hold a domain position in constructing high sensitive electrochemical sensors [14–16], which show the synergistic effects to induce interesting properties that are different from those of each component [17]. However, the hybrid materials consisting of only carbon nanomaterials, such as CNTs/fullerene, graphene/fullerene, and graphene/CNTs, was rarely used in the field of electrochemical analysis due to their insoluble physical properties and inhibited inner redox activity in aqueous media [18].

The hybrids of carbon allotropes or their derivatives have been reported that they exhibited efficient electron transfer, high

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photocatalytic activity, improved capacity and cyclic stability and have been applied in energy conversion [17,19]. Yang et al. used reduced graphene oxide (RGO) and fullerene ( $C_{60}$ ) to form the hybrid through the  $\pi$ - $\pi$  stacking interaction, which was applied in photovoltaic devices [17]. Yu et al. covalently bonded mono-substituted  $C_{60}$  onto graphene nanosheets and it significantly improved electron transport and enhanced the overall device performance [19]. In addition, carbon nanotube peapods, fullerenes inside CNTs and nanobuds, fullerenes attached on the surface of CNTs or graphene, have been suggested as building blocks of nanoelectronic devices and have promise in the field of spintronics [20]. Obviously, the hybridization of these carbon allotropes or derivatives can form novel hybrid nanostructures and obtain improved physical and chemical properties with synergetic effects. However, only a limited few reports referred to their applications in non-enzymatic electrochemical sensors [21,22]. Firstly, it may be attributed to the hydrophobic property of the carbon nanomaterials causing difficulty for the construction of the stable modified interfaces. Secondly, CNTs and graphene do not possess inner redox activity and they have to be combined with other mediators. Thirdly,  $C_{60}$  or its derivatives owned its inner redox activity except for the advantages of CNT and graphene, however, it's difficult to arouse its inner redox activity in aqueous solution [23]. Compared with CNTs, the 2D structure and excellent electronic property of graphene provide a large donor/acceptor interface for efficient charge separation and facilitate charge transfer [19]. Therefore, if graphene and  $C_{60}$  or  $C_{60}$  derivatives are combined to construct electrochemical sensors and it may be significant for broadening their applications.

Our group has reported a non-enzymatic electrochemical sensor based on a  $C_{60}$  derivatives (*p*-methoxy zinc porphyrin- $C_{60}$  derivative,  $ZnP_p-C_{60}$ ) [1]. Two typical  $ZnP-C_{60}$  derivatives of *para*- $ZnP-C_{60}$  ( $ZnP_p-C_{60}$ ) and *ortho*- $ZnP-C_{60}$  ( $ZnP_o-C_{60}$ ) were designed and synthesized by the combination of *p* (*o*)-methoxy porphyrin and  $C_{60}$  moieties using a flexible methylene chain (Scheme S1). Their conformations and redox mechanism have been investigated and compared by density functional theory (DFT) and electrochemical methods, which suggested that  $ZnP_p-C_{60}$  possessed excellent electrochemical properties. Thus,  $ZnP_p-C_{60}$  was also chosen as a mediator in this research. Because noncovalently modified graphene is mainly through molecular interactions such as hydrogen bonding, van der Waals force, hydrophobic force, electrostatic interaction, and  $\pi$ - $\pi$  stacking,  $ZnP_p-C_{60}$  with zinc porphyrin moiety can easily hybridize with graphene through strong  $\pi$ - $\pi$  interaction to obtain  $G@ZnP_p-C_{60}$  composite [24]. Therefore, in this study, soluble graphene oxide (GO) was selected to prepare  $GO@ZnP_p-C_{60}$  hybrid and it was then electrochemically reduced to  $ERGO@ZnP_p-C_{60}$ , which was used to fabricate a novel non-enzymatic electrochemical sensor. The electrochemical behavior, electrocatalytic activity, and the redox mechanism were investigated and compared with our previous report. The results showed that the changes in the conformation of  $ZnP_p-C_{60}$  on ERGO altered the catalytic sensitivity of the sensor towards  $H_2O_2$  and nitrite. The present work achieves the combination of ERGO and  $ZnP_p-C_{60}$  and their analytical application, which supplied a novel electrode interfacial material and pave a new strategy for the construction of non-enzymatic electrochemical sensor.

## 2. Experimental

### 2.1. Chemicals and reagents

$ZnP_p-C_{60}$  was synthesized using our previous method [25]. Tetraoctylammonium bromide (TOAB, 98%) was obtained from Sigma. Graphene oxide (GO) was obtained from Chengdu Organic

Chemicals Co. Ltd. (China). Toluene, potassium chlorate (KCl), sodium nitrite ( $NaNO_2$ ), and  $H_2O_2$  (30%) were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai). All other chemicals were of analytical reagent grade and used as received. Aqueous solutions were prepared with high purity water at ambient temperature.

### 2.2. Preparation of modified electrodes

$ZnP_p-C_{60}$  (1.3 mg) and TOAB (5.7 mg) were sonicated in 0.50 mL toluene for 30 min 2.6 mg GO was dissolved in 5.00 mL high purity water and sonicated for 30 min 0.50 mL GO aqueous solution mixed with 0.50 mL TOAB/ $ZnP_p-C_{60}$  toluene solution and sonicated for 4 h. After that, 10.0  $\mu$ L of the TOAB/ $GO@ZnP_p-C_{60}$  suspension was spread on the surface of cleaned GCE and dried at ambient temperature. Then, the TOAB/ $GO@ZnP_p-C_{60}$ /GCE was electrochemically reduced by 12 successive cyclic voltammograms in 0.5 M KCl solution over a potential range of 1.0 V to  $-1.30$  V at a scan rate of  $0.10$  V  $s^{-1}$  to prepared TOAB/ERGO/ $ZnP_p-C_{60}$ /GCE. The resulting TOAB/ERGO/ $ZnP_p-C_{60}$ /GCE served as working electrode for experiments. For comparison, TOAB/ $ZnP_p-C_{60}$ /GCE, TOAB/GO/GCE, and  $GO@ZnP_p-C_{60}$ /GCE were prepared under the same conditions.

### 2.3. Apparatus and measurements

The electrochemical measurements were carried out with CHI660C electrochemical workstation (Chenhua, Shanghai, China). A conventional three-electrode system was used and it consists of a platinum wire (auxiliary electrode), Ag/AgCl electrode (3 M KCl, reference electrode), and modified electrode (working electrode). The electrochemical experiments was performed in 0.5 M KCl solution in the potential range from 1.0 V to  $-1.30$  V. Prior to all electrochemical experiments, the solution was purged by high purity nitrogen for 15 min to remove dissolved oxygen and nitrogen atmosphere was maintained throughout the measurements. All experiments were carried out at room temperature.

The morphology of modified electrode was characterized by scanning electron microscope (SEM) measurements (Sirion 200, Netherlands). GCEs with detachable surfaces were used to be modified and characterized by SEM before and after electrochemical experiments. UV-vis spectroscopic measurements were performed on an indium tin oxide (ITO)-coated glass plate. The ITO-coated glass plate was modified using the same procedures as those for the GC substrate.

To understand the interactions of  $ZnP_p-C_{60}$  with the ERGO, the molecular geometries were optimized by B3LYP hybrid functional of DFT calculations (Gaussian 09) [26]. A LanL2DZ basis set was used for Zn, while the 6-31 G(d) basis set was used for C, O, H, and N atoms [1].

## 3. Results and discussion

### 3.1. Characterization of modified electrode

The morphologies of different modified GCE were examined by SEM with different magnification. As shown in Fig. 1A, GO on the surface of GCE exhibits a typical wrinkled layered structure.  $ZnP_p-C_{60}$  incorporated in TOAB film shows well-dispersed and uniform morphology with particle sizes of 100–200 nm (Fig. 1B). As can be seen from the SEM image of the TOAB entrapped  $GO@ZnP_p-C_{60}$  hybrid on GCE (TOAB/ $GO@ZnP_p-C_{60}$ /GCE, Fig. 1C), the GO sheets are decorated with  $ZnP_p-C_{60}$  nanoparticles and the wrinkled layered structures are not changed by the presence of TOAB. Moreover, obvious difference between TOAB/ $GO@ZnP_p-C_{60}$  and

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