Effects of 3-dimensional porous graphene oxide network on solid-state sensors

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Abstract. The three-dimensional porous graphene networks (3DPGN) is recently developed graphene material. They possess both the highest mobility of graphene material and the increased surface areas possessed by the porous micro 3D structure. These powerful graphene materials have been exploited to be super-capacitors, batteries, biomedical sensors and other bioengineering applications. In this work, their foundational functions for solid-state sensors are examined with the use of 3D porous graphene oxide (GO) network (3DPGON) as proof-of-concept. Its effects on the classical glass-chemical-electrodes (GCEs) and the pH-sensing light addressable potentiometric sensor are examined, respectively. It is found that the peak currents of 3DPGON film coated GCEs are increased with the increased 3DPGON, while the LAPS' responding for pH are lowered. The increased currents of GCE are attributed to the enhanced electron transfer (ET) by GO and the enlarged surface area by micro-porous structure. While the lowered pH responding of LAPS is caused by the screen effect induced by 3DPGON coating. In conclusion, the decoration of 3DPGON on solid-state sensors should be considered seriously, it can enhance the total amount of charges exchanging at the liquid-solid interface which is propitious to forming solid-state sensor, but the drawback of 3DPGON modification does exist because the original surface sensing sites may be covered.

1. Introduction

Graphene is an excellent, single-atom-thick, sp2-hybridized carbon nanomaterial, with the highest carrier mobility, ambipolar field-effect characteristics, large surface area and low intrinsic electrical noises. The researches of graphene have covered almost all scientific fields and been exploited to be functional devices in electronics, biomedical engineering, environmental protection and remediations. Among tremendous graphene materials, the 3-dimensional porous graphene network (3DPGN) is a kind of recently developed graphene materials. It is in indifference with the 2-dimensional porous graphene (2DPG). In 2DPG, the pores are formed by the removal of carbon atoms in the lattice plane of 2D hexagonal crystal structure¹, ², as shown in Figure 1 (A). While in 3DPGNs, the pores are structured by the cross-linking of single- or few-layered graphene nano-sheets³, ⁴, as shown in Figure 1 (B)⁴, in which the graphene sheets include not only graphen oxide (GO) but also reduce graphene oxide (rGO). Besides, the pores in 2DPG are in atomic level, while in 3DPGNs they can be tailored from several or tens of nano-meters to hundreds of micro-meters depending on their synthesis methods.

From the view points of sensors, 3DPGNs are versatile to be functionalized as sensing materials. For examples, the ZnO nano-particles (NPs) decorated rGO based 3DPGNs (ZnO NPs-3DPrGONs) are developed as gas sensors, in which rGO acts as an electron acceptor to increase the depletion layer
of the decorated ZnO NPs, meanwhile the micro-porous structure serves as an ideal supporter with a larger surface area and space to hold and disperse the ZnO NPs [5]. In a very recent research, these synergy of the porous structure and the aptamer probe specific to thrombin are exploited to improve the photoelectrochemical responding. The reported experimental results give further demonstrations for the multidimensional electron transport possessed by the micro-3D architecture. Moreover, the micro-meter scaled pores in 3DPGNs are also an excellent single-cell culturing and proliferation scaffold for cells' monitoring [6, 7].

In general, 3DPGNs are believed to have great potential for biological or chemical applications. In this area, the 3DPGNs interfaced sensing surface on the solid-state sensor is the foundation for loading the subsequent biochemical reactions. However, in the published works about 3DPGNs which are mainly concentrated on their advanced applications, these foundational works for the preparations of 3DPGNs films on the surface of bioelectronic sensors are still missing. So, in this work, we would like to present an experimental works about the drop-coated 3DPGNs films on two kinds of solid-state sensors, which are the traditional glass-carbon electrode (GCE) and the light addressable potentiometric sensor (LAPS).

In this work, graphene oxide is prepared by modified Hummers method, firstly. Then, the hydrothermal method is utilized to form 3D porous network of GO (3DPGON). Thirdly, by scanning electron microscope (SEM) to characterize the as-prepared 3DPGON. At last step, the drop-coating method is applied to form a covalently-deposited 3DPGON on amino-modified LAPS and GCE surface. The electronic features of 3DPGON modified LAPS and GCE are measured and analyzed to have a better understanding for the function of 3DPGON to facilitate electron transfer (ET) at the interface of electrolyte solutions and solid-stated sensors, while LAPS and GCE are used as proof-of-concepts herein.

Figure 1. The sketch maps for 2DPG (A) and 3DPGNs (B) which are referred to Ref. [1] and [4].

2. Materials and methods

2.1. GO preparation
Modified Hummers’ method is used to prepare GO, which is outlined at here. Firstly, the graphite powder (Beijing HWRK Chem Co., LTD) is oxidized by H$_2$SO$_4$, KMnO$_4$ and H$_2$O$_2$ (Tianjin Chemical Reagent wholesale company), in sequence, in order to intersect oxygen atoms into the stacked graphene layers. After thoroughly rinsing and drying, the oxidized graphite powder can be obtained.

Thirdly, the water bath sonication is carried out to obtain GO in few-layer state. At last, the centrifugation is performed to obtain GO.

2.2. Preparation of 3DPGON
The dried GO powder is dissolved in deionized water (DIW) to form GO solution. Then 0.1g thiocarbamide (Tianjin wind boat chemical reagents Technology Co., Ltd.) is added into the prepared GO solution (50ml, 2mg/ml ) to make GO layers being functionalized by thiol groups which are possessed by thiocarbamide. After reaction in autoclave at 180°C for 4.5 h, and removing the residue thiocarbamide, the desired 3DPGON can be obtained by freeze-drying method. At last, the solution of 3DPGON is prepared by dissolving 3DPGON’ powder in DIW with concentration of 0.5 mg/ml.
2.3. Deposition of 3DPGON on GCE and LAPS
The polished and cleaned GCEs are covered by different volumes of the as-prepared 3DPGON and dried at ambient conditions, then they are undergone the test of Cyclic voltammetry (CV). LAPS chips are the same as what we have used in our previous works [8]. The desired 3DPGON film is drop-coated on LAPS which is pretreated by 2.5% GA-DIW solution, then drop-coated by the as-prepared 3DPGON.

2.4. Apparatus
The SEM images are obtained by SEM S-3500N (Hitachi, Japan). CV is carried out by the chemistry work station (LK2006A, Lanlike chemical electronic high-tech Co. Ltd., Tianjin). LAPS experiments are executed by our home-made measuring system.

3. Results and discussions

3.1. SEM identification
The micro 3D-structure in the as-prepared 3DPGON film is evidenced by the measured SEM image as shown in Figure 2. It could be identified obviously that a porous microstructure is achieved. The size of pores in the 3DPGON film is varied from several to several hundred micro-meters.

![Figure 2. SEM image of drop-coated 3DPGON on glass substrate.](image)

3.2. CV tests of 3DPGON modified GCE

![Figure 3. CV features of GCEs after incubated in different volumes of 3DPGON solutions from 0 to 30 μL. (A) CV curves measured when the scanning voltage is form 0.6 to -0.1V with the scanning rate of 50 mv/s. (B) is the extracted currents of the oxidize-peak and reduce-peak verse the volumes of 3DPGON solutions.](image)
The function of 3DPGON on the classical GCEs are examined by CV method, the measured data are plotted in Figure 3 (A). When the voltages of RE with the reference to WE are scanned from 0.6 V to -0.1 V, the typical oxidize- and reduce- peaks of K₃[Fe(CN)₆] are measured when GCEs are not modified and modified with different volumes of 3DPGON. Though the voltages of the oxide-peaks are concentrated at about 0.14 V and the voltages of the reduce-peaks are in the region of 0.22-0.25 V, their deviations are small, the peak currents are increased obviously as shown in Figure 3 (B). The explanations for them could be derived as the increased ET and surface area which are induced by 3DPGON. The general effect of 3DPGON on GCE is to boost the amount of exchanging electrons in the Redox reaction of K₃[Fe(CN)₆], which is expressed as the increased peak currents, as shown Figure 2 (B).

3.3. pH responding of 3DPGON modified LAPS

The outmost surface of LAPS used in this work is silicon nitride (Si₃N₄) which is sensitive to pH. The pH responding of unmodified LAPS (named as Blank) is measured and compared with 3DPGON modified one, as shown in Figure 4. In this experiment, it is found that the original pH sensing ability is inhibited. The reason for this phenomena may be the pH sensing sites on the original Si₃N₄ surface is covered by the coated 3DPGON film. This screen effect is very similar to the reported protein modification induced pH-screening effect in Ref. [9].

4. Conclusion

The effects of 3DPGON on two different solid-state sensors, GCE and LAPS, are examined in this work. For the former one, the increased peak currents are measured, it is closely related to the promoted ET effect of GO and the enlarged surface area in micro-porous structure. While, for the latter one, the pH responding sites on blank LAPS are hidden which cause the lowered pH responding on 3DPGON modified LAPS. So, there are double-side effects in 3DPGON modified solid-state sensors, the beneficial effect is that the decoration of 3DPGON can boost the total quantum of exchanged electrons, while the disadvantage of screening the effect is also coexisted.

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