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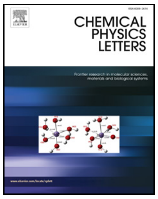

Research paper

# Free-standing palladium modified reduced graphene oxide paper based on one-pot co-reduction and its sensing application

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## HIGHLIGHTS

- A facile palladium functionalized reduced graphene oxide paper was prepared via one-pot co-reduction method.
- Evenly-distributed Pd particles show to decorate graphene paper surface and interpose between graphene sheets.
- As-prepared freestanding Pd/rGOP can potentially be used as a glucose sensor.

## ARTICLE INFO

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## ABSTRACT

A free-standing palladium/reduced graphene oxide paper (Pd/rGOP) based on one-pot co-reduction was prepared. The as-prepared Pd/rGOPs contain evenly distributed Pd particles interposing between the rGOP layers. The structure and composition of Pd/rGOP were characterized by SEM, EDX, XRD and Raman spectra. We investigated the glucose sensing performance of Pd/rGOP by chronoamperometry, the sensitivity reach as high as 6.70 $\mu A\,mM^{-1}\,cm^{-2}$ with the linear range between 0.5 mM and 8 mM. The sensor also exhibits a good anti-interference ability and detection selectivity toward the interference. The proposed sensor has great potential to become a reliable tool in point-of-care medical devices.

## 1. Introduction

In recent years, portable and wearable devices have attracted great interest because of their great convenience. However, the development of an ideal functionalized, low-cost, and lightweight material for such devices is still challenging. Paper-like conductive materials may be an alternative because of their applications in sensors [1], Li-ion batteries [2], supercapacitors [3], fuel cells [4], hydrogen storage [5] and so on.

Graphene is a two-dimensional (2D) atom-thin sheet with $sp^2$-hybridized carbons that has been intensively studied because of its unique thermal, mechanical, chemical and electric properties [6]. Graphene oxide (GO) contains oxygen functional groups on its basal planes and edges, resulting in its easy dispersibility in water. On the other hand, graphene oxide has poor electrical conductivity due to the disruption of its $sp^2$ bonding networks by oxygen functional groups. Thus, the poor electrical conductivity may limit the use of GO in electrical or electrochemical applications such as supercapacitors [7,8], fuel cells [9–11], Li-ion batteries [12,13] and sensors [14,15]. To recover the electrical conductivity of GO, most of the oxygen functional groups must be removed, thus obtaining fully reduced GO. However, the reduced graphene oxide (rGO) is difficult to disperse in water due to its tendency to aggregate. Recently, GO or rGO was selected to assemble into well-ordered and free-standing paper-like materials [16,17]. Compared to other paper-like materials (carbon nanotubes or graphite), GO or rGO paper is superior due to its mechanical strength [18]. The preparation of GO paper (GOP) involves vacuum filtration [16,19–23], evaporation [24–26], mechanical compression [27,28], speed vacuum centrifugation [29], mold-casting [30] and other techniques. Vacuum filtration is a rapid, simple, low-cost procedure that is most commonly used to obtain GOP. To prepare rGO paper (rGOP) or its functionalized materials, normally, a three-step method has been selected based on vacuum filtration [19,21–23]. To facilitate the preparation of metal-functionalized rGOP, the metal salt and GO could be co-reduced by reductant, and then, the vacuum filtration is conducted to obtain the metal particle-functionalized rGOP. Correspondingly, the functionalized rGOP made by metal particles interposing between graphene

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sheets can be prepared.

As one of the transition metals, palladium is widely used as an electrocatalytic active center. In this work, a free-standing palladium/reduced graphene oxide paper (Pd/rGOP) based on one-pot co-reduction was prepared using vacuum filtration. We co-reduced $PdCl_2$ and GO by hydrazine in the presence of polyvinyl pyrrolidone (PVP) in a one-pot reaction followed by vacuum filtration, thus obtaining a free-standing Pd/rGOP. The one-pot co-reduction facilitates the preparation of functionalized rGOP. Hydrazine acts as the reductant and promoting the dispersion of rGO; PVP plays an important role in effectively reducing the aggregation of rGO during the process. The as-prepared Pd/rGOP showed its potential application in glucose sensing.

## 2. Materials and methods

### 2.1. Reagents and chemicals

Graphite powder, $PdCl_2$, and glucose were purchased from Sigma-Aldrich and used as received. PVP (K30) and hydrazine hydrate (85%) were purchased from Sinopharm Chemical Reagent Beijing Co. Ltd. and used without further purification. Deionized water from a Milli-Q system (18.2 MΩ cm at 25 °C) was used throughout the experiments.

### 2.2. Apparatus and electrochemical measurements

The electrochemical experiments were carried out using an electrochemical workstation (760e, CHI, China). A three-electrode system was applied, using rGOP or Pd/rGOP (punched into 3 mm in diameter) as the working electrode, a Pt net (1 × 1 cm) as the auxiliary electrode and a saturated calomel electrode (SCE) as the reference electrode. The morphology and microstructure were characterized by scanning electron microscopy (SEM, S-4800, Hitachi, Japan) carried out at the acceleration voltage of 10.0 kV. The elemental composition data were obtained using an energy dispersive X-ray spectrometer (EDX) attached to the SEM instrument. The phase and crystallinity of the samples were analyzed by X-ray diffraction using a monochromatized Cu target radiation source ($\lambda = 1.5418$ Å) at the $2\theta$ in the 20–80° range at a scanning rate of 8°/min, (XRD, D8-Advance, Bruker, Germany). The intrinsic structures of GOP, rGOP and Pd/rGOP were characterized by Raman spectroscopy (Senterra, Germany). To make the solution disperse evenly, the sample was ultrasonicated by an ultrasonic cleaning machine (360 W, 15L, Jiemeng, China).

### 2.3. Fabrication of palladium/reduced graphene oxide paper

GO was synthesized on the basis of our previous report [31], and then, a 1 mg/mL GO aqueous solution was prepared by dissolving GO in deionized water with the aid of ultrasonication. To obtain Pd/rGOP, $PdCl_2$ and GO were co-reduced in one pot: 50 mg $PdCl_2$, 50 mg PVP and 5 mL 1 mg/mL GO were mixed together, and the mixture was then diluted to 70 mL by deionized water. The mixture was heated to 90 °C under magnetic stirring. Then, 10 mL of 85% hydrazine hydrate was added dropwise. The resulting solution was kept at 90 °C for 1 h. Prior to vacuum filtration, the solution was ultrasonicated for 1 h to make the resulting solution disperse evenly. The obtained aqueous dispersion was then filtered with a membrane (mixed cellulose ester, 5 cm in diameter and 0.22 μm in pore size). The as-prepared Pd/rGOP was washed several times with deionized water to remove the excess reagent. For comparison, rGOP was also fabricated without $PdCl_2$ added in the aforementioned preparation process, and GOP was fabricated by vacuum filtering of 5 mL of 1 mg/mL GO. After filtration, the prepared papers were kept in room temperature conditions overnight, and the as-prepared papers were peeled off from the membrane. A schematic illustration of the preparation process for the Pd/rGOP is shown in Fig. 1.

## 3. Results and discussion

Using simple vacuum filtration, GO can be easily assembled into well-ordered and free-standing GOP due to its easy dispersibility in water. For rGO, its loss of oxygen functional groups will reduce its dispersibility, and it will tend to aggregate in water, which will hamper the assembly of rGO into a high-quality paper-like material. In other words, good dispersibility in water is critical for the assembly of rGO into a well-ordered paper-like material. The reducibility of hydrazine will remove oxygen functional groups from GO to form rGO. At the same time, the excess hydrazine will lead to the rGO, which carries a negative charge to be surrounded by the $N_2H_4^+$ counter ions, and the charge stabilization will lead to a good dispersion of rGO in water [32]. Overall, in this work, we used the excess hydrazine not only to reduce GO to form rGO but also to provide a good dispersibility for rGO.

Fig. 2 shows images of the different solutions prepared by various recipes. As shown in Fig. 2A, the uniformly dispersed solution was obtained by the reduction of excess GO by hydrazine ($GO + N_2H_4$), and it can be stable for several months. As discussed above, the good dispersion of rGO benefits from the charge stabilization of the counter ions. Fig. 2B shows that after the addition of $PdCl_2$, the reduction of GO by excess hydrazine ($GO + N_2H_4 + PdCl_2$) will lead to aggregation. This is because the addition of $PdCl_2$ will destroy the charge balance established in the early stage, leading to rGO aggregation. PVP is a water-soluble polymer, according to our experimental experience, the addition of PVP can effectively reduce the aggregation of rGO. As shown in Fig. 2C, with participation of PVP ($GO + N_2H_4 + PdCl_2 + PVP$), the resultant solution becomes uniformly dispersed again. Since PVP is a poor conductor, the amount of PVP must be carefully controlled. The more PVP added, the better rGO dispersion produced with poorer electrical conductivity of the as-prepared Pd/rGOP obtained.

The surface morphologies of the as-prepared GOP, rGOP and Pd/rGOP were characterized using SEM, as shown in Fig. 3. As illustrated from Fig. 3A, the wrinkle and folds of GOP can be clearly observed. After the addition of PVP, rGOP assembled from the $N_2H_4$-reduced GO also shows similar wrinkles and folds to GOP (Fig. 3B). Compared to GOP, rGOP shows improved electron transfer ability and metallic gloss on both sides. Fig. 3C indicates that the as-prepared Pd/rGOP with Pd particles anchored on both sides of the graphene sheet has fewer wrinkles and folds compared to GOP and rGOP, which is due to the introduction of the Pd particles reducing the restacking or agglomeration of the rGO sheets [33]. Additionally, Pd particles are well-distributed on the rGOP surface. The inset of Fig. 3C shows the image of the as-prepared Pd/rGOP. Fig. 3D shows the cross-section of the as-prepared Pd/rGOP, where the well-packed layered structure of the rGO sheets can be clearly observed, and the thickness of the Pd/rGOP can be easily controlled by the amount of the solution during filtration. At the same time, image of Pd particle found in the cross-section of Pd/rGOP is shown in the inset of Fig. 3D.

Fig. 4A shows the enlarged view of Fig. 3C, and it can be seen that the Pd particles have irregular shapes, which may be due to the aggregation of smaller Pd nanoparticles during the synthesis. At the same time, we observe that Pd particles are distributed in different layers of the rGO sheet. For example, examination of the framed area (1) shows that the Pd particle is located right on the surface of Pd/rGOP, whereas for the framed area (2), the Pd particle is located on the surface several layers below. Fig. 4B–D are EDX characterizations of the corresponding areas marked in Fig. 4A with carbon and palladium as the constituent elements. The amounts of the Pd and C elements are similar. The C element is mainly from rGOP, and the Pd element is from the reduced $PdCl_2$. The only found element C and Pd but no O or Cl may indicate the successful co-reduction of GO and $PdCl_2$ in one pot.

XRD was used to characterize the crystallinity, as shown in Fig. 5A. The XRD patterns of rGOP show a main diffraction peak at 22.6° which is indexed to the C(2 0 0) of the short range order in graphene sheet,