Geometry-dependent electrochemistry of graphene oxide family

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ABSTRACT

The influence of graphene oxide geometry on electrochemical performance is of great interest, but there are few reports on this subject. Three different members of the graphene oxide family, graphene oxide nanosheets, graphene oxide nanoribbons, and graphene oxide quantum dots were comparatively investigated as electrode materials to systematically study the effect of geometric structure. The results showed that, as the geometric structure varies, the three graphene oxide materials possess different electrical conductivities, various defect densities and oxygen contents, as well as diverse electrode surface chemistry and microstructures, which combine together to result in the distinct electrochemical responses for the modified electrodes, depending on the redox system involved. This work broadens the method of studying the electrochemical performance of many other materials from the perspective of geometry.

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1. Introduction

Graphene is a novel material that has emerged as a rapidly rising star in the field of material science [1–4]. One specific branch of graphene research deals with graphene oxide (GO). GO is usually produced by the chemical treatment of graphite through oxidation [5,6]. These treatments assume the presence of various oxygen-containing functional groups in the GO [7–9], which can strongly affect the electronic, mechanical, and electrochemical properties of GO. Thus, solution processability, high dispersibility in a range of solvents, capability of coupling electroactive species onto the surface, and versatile properties make GO attractive for fundamental research as well as in applications, especially in electrochemical applications [10–18].

Recently, several studies have reported that the different geometric structures of graphene endow them with different electronic, magnetic, thermoelectric properties, and bonding configurations [19–25]; the band gap openings in graphene can be affected by the dimension, geometric structure, and edge saturation [26,27]; in addition, the graphene nanopore geometries can influence DNA sequencing [28]. These theoretical and experimental studies indicate that geometric structure will be an interesting hotspot in the future studies of graphene. Based on the different geometric structures, the GO family can be subdivided into graphene oxide nanosheets (GONSs), graphene oxide nanoribbons (GONRs), and graphene oxide quantum dots (GOQDs). The difference in geometric structure from the GONSs to GONRs and GOQDs plays an important role in dictating the electronic properties and electrochemical performance of the three GO members. First, the varied band gap can influence the electrical conductivity of the three [29–31]. Second, the chemical oxidation process used to prepare GO can introduce diverse structure defects and oxygen functional groups into all three members. The structure defects can impact the density of electronic states (DoS) and electron transfer during the electrochemical process, while the oxygen functional groups on the edges of graphene can reduce the graphene in-plane conductivity, but may accelerate the electron transfer. Last, the different geometric structures of the GO materials may also lead to variable surface chemistry and microstructures on an electrode, including morphology, surface coverage, and stack, and electrostatic interaction with the analyte. Therefore, the electrochemical behavior of a GO electrode material is controlled by its electrical conductivity, defect density, oxygen functional groups, and the electrode surface state, all of which account for the influence of geometry on the electrochemistry of GO.

To date, the systematic, comparative study of the electrochemical performances of GONSs, GONRs, and GOQDs electrode materials has not been given much attention, particularly the effect of geometry of different GOs on their electrochemistry. Here, we investigated the electrochemistry of GONS-, GONR-, and GOQD-modified glassy carbon electrodes (GCEs) to determine the underlying geometry effect using three well-known outer- and inner-sphere redox probes [32]. Our work provides further insights into the electrochemistry of graphene materials and shows promise for electrochemical investigations of other potential electrode materials, such as titanate or molybdenum disulfide.

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2. Experimental

2.1. Reagents and material synthesis

Graphite powder (purity > 99.99%, <45 μm) and Ru(NH$_3$)$_6$Cl$_3$ (stored at 2–8 °C) were purchased from Sigma-Aldrich. Multiwalled carbon nanotubes (purity > 97%, ca. Φ 20–40 nm) were used as received from Shenzhen Nanotech Port. K$_2$IrCl$_6$ was purchased from Alfa Aesar. HCl, HNO$_3$, H$_2$SO$_4$, H$_3$PO$_4$, KMnO$_4$, H$_2$O$_2$ (30 wt% in H$_2$O), K$_3$Fe(CN)$_6$, K$_4$Fe(CN)$_6$, and KCl were obtained from Sinopharm Chemical Reagent Co., Ltd., China, and of analytical grade. All solutions were prepared with ultrapure water (<18.25 MΩ/cm). GONSs, GONRs, and GOQDs were prepared according to the method proposed by Hummers and Offeman [33], Tour et al. [34], and Pan et al. [35].

2.2. Apparatus

Transmission electron microscopy (TEM) was obtained with a Tecnai G2F20 S-TWIN field emission transmission electron microscope. Raman spectroscopy (Renishaw, UK) and X-ray photoelectron spectroscopy (XPS, Thermo Scientific, USA) were used to analyze the composition of the as-prepared graphene oxide materials. Electrochemical experiments were performed with a CHI 660E electrochemical workstation (Shanghai Chenhua Instrument, China). All the experiments were carried out with a three-electrode system with a GCE as the working electrode, a platinum wire as the auxiliary electrode, and a saturated calomel electrode (SCE) as the reference electrode.

2.3. Electrode preparation

The GCEs were polished with alumina slurries. Afterward, they were modified by drop coating with the 1 mg/mL GONS, GONR or GOQD dispersions, and dried in the air. We used bare GCE for control experiment to verify the effects we obtained on GONS-, GONR-, or GOQD-modified electrodes are not due to the underlying GCE.

3. Results and discussion

3.1. Physicochemical characterizations

The geometric structural features of the prepared GONSs, GONRs, and GOQDs were characterized using TEM (Fig. 1A–C). The GONSs had a lateral size of several hundred nanometers, with thicknesses of a few layers. The sheets formed wrinkles on the surface and crimps at the edges, resulting from the unstable state of the two-dimensional nanostructure. The GONRs exhibited a strip-like structure with a high aspect ratio and an average width of ca. 100 nm. The ribbons are entangled and stacked with each other because of the strong molecular interaction. The GOQDs were uniformly dispersed discs with diameter mostly in the range of 3–5 nm.

Raman spectroscopy (Fig. 1D) was used to probe the structural characteristics of the samples [36]. The contribution of the disorder-induced D bands is ascribed to graphene edges, stacking disorders between layers, and atomic defects within the layer [37]. From GONSs to GOQDs, the ratio of the D to G band intensities (I_D/I_G) increases (Table 1), reflecting the increase in their defect densities, which is caused by the reduction in size of the sp^2 domains as a result of the reduced sizes and varied geometric structures. Additionally, the 2D band becomes sharper and stronger, suggesting the transition from the multilayers of GONSs to the monolayer of GOQDs [36].

XPS was used to verify the existence of oxygen functional groups linked to the samples. The deconvoluted C1s XPS spectra are shown in Fig. 1E. Detailed data are listed in Table 1. The O/C ratios for GONSs, GONRs, and GOQDs are 0.6, 0.37, and 1.8, respectively. These results demonstrate that the chemical oxidation process used to prepare GO materials has successfully introduced oxygen functional groups into the edges and basal planes of the samples. Taking the geometric structures into account, the GONSs exhibit a large specific surface area with sufficient edges to link oxygen groups; the GOQDs possess quantum confinement and edge effects as well as the most exposed edges to attach oxygen groups, and the GONRs have few basal plane and edges for the oxygen groups to anchor, leading to the lowest oxygen content.

The electronic band structures of the GONSs, GONRs, and GOQDs were also studied using UV–vis (Fig. 1F). Graphene is known to behave as direct-gap semiconductors, so the optical band gap could be determined from the UV–vis spectra via the Eq. (1):

$$E_g = \frac{1239.86}{\lambda} \tag{1}$$

where λ is the intercept of the extrapolation of the absorption edges to x axis. The band gaps are shown in Table 1, which agreed well with the previous reports [38–40] and varied with the geometric structures of the three GO members.

Besides, the electrical resistivity (ρ) and electrical conductivity (σ) were calculated by the Eq. (2):

$$\rho = \frac{V}{I} \times F(D/S) \times F(W/S) \times W \times F_{sp} = 1/\sigma \tag{2}$$

where $F(D/S)$, $F(W/S)$, and F_{sp} are the correction coefficients for the diameter (D) and width (W) of the samples, and the space (S) between the probes, which are determined as 4.322, 0.9215, and 1 by using the table look-up method based on the trim sizes of the samples. As discussed above, the varied geometric structures from GONSs to GONRs and GOQDs result in an increase of band gap for the three, which would lead to a decreased density of electronic states with energies near the Fermi level, therefore generating a continuously decreased electrical conductivity.

3.2. Fundamental electrochemical characterizations

Afterward, the GONSs, GONRs, and GOQDs were coated on the GCE surfaces to construct the modified GCEs. The morphologies of the three GO-modified GCEs were represented with a schematic diagram (Fig. 2A). This provides information about the surface microstructure, such as the surface coverage and the manner in which the GO materials are stacked. The GONSs exhibited a large specific surface area and formed uniform, smooth, and complete coverage on the GCE surface. The GONRs were entangled and stacked with each other, presenting a rugged configuration with porous coverage on the GCE surface. Because of the rather small sizes of the GOQDs, there was uneven and incomplete coverage on the GCE surface. Besides, as was shown in the XPS data, for GONSs, there were many amounts of hydroxyl on the basal plane and few carbonyls, carboxyls at the edges; for GONRs, the amounts of the three were relatively less; for GOQDs, a great many of carboxyls linked at the edges were observed.

Returning to the electrochemical study, electrochemical impedance spectroscopy (EIS) is an effective reflection technique used to probe the ability of the electrode materials to transfer and exchange charges within the electrolyte solution [41]. In our case (Fig. 2B), the difference in the electron-exchange ability, i.e., the charge transfer resistance (R_{ct}), is strongly influenced by the surface chemistry and microstructure of the three-electrode materials. For GONRs, the ribbons formed a rugged configuration with a porous coverage; meanwhile, the oxygen groups are negatively charged at the working pH, which would repel the [Fe(CN)$_6$]$^{3-/4-}$ electrostatically. Therefore, the given electrode surface coverage and the lowest oxygen content in GONRs lead to the minimum R_{ct}. For GONSs, the uniform and complete electrode surface coverage with the moderate oxygen content results in the middle R_{ct}. For GOQDs, the uneven and incomplete electrode surface coverage, as well as the highest oxygen content, give rise to the maximum R_{ct}.