



Insight the effect of crystallinity of natural graphite on the electrochemical performance of reduced graphene oxide



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ABSTRACT

The effects of the crystallinity of natural graphites on the electrochemical performance of the resulting reduced graphene oxides (RGOs) were systematically researched. Electrochemical measurements were first carried out to characterize the electrochemical performances of the RGOs. The results showed that the RGO prepared from flaky graphite (FG) hold the best electrochemical performance with the greatest specific capacitance, the smallest charge transfer resistance (R_{ct}), the best capacitive behavior, and the lowest ions diffusion resistance in comparison with the other RGOs synthesized from natural lumpy graphite (LG) and amorphous graphite (AG) under the same conditions. Furthermore, XPS and Raman analysis were conducted to scientifically explain the phenomena. The results illustrated that RGO prepared from FG (FRGO) hold the highest reduction degree, the greatest size of the in-plane sp^2 domains, and the fewest defects, leading FRGO to hold the best electrochemical performance. The crystallinity of natural graphite affected the microstructure of the resulting RGO by influencing its oxidation, exfoliation and chemical reduction process, and then indirectly controlled the electrochemical properties of the RGO.

Introduction

Graphene, with the thickness of a single layer of carbon atom, has attracted a lot of well-deserved attention [1]. Due to its excellent properties, numerous methods including mechanical exfoliation [2], electrostatic deposition [3], chemical vapor deposition (CVD) [4], exfoliation in liquid phase [5], solvothermal method [6], and reduction of graphene oxide [7] have been extensively studied for preparing graphene. Among them, reduction of graphene oxide has been widely used for large-scale preparing graphene in the industrial application, which is the fieriest area in the preparation of graphene and carbon-based composites [8].

Increasingly serious energy shortage and environmental pollution issues drive the need of renewable energy to become extremely urgent [9]. Electrode materials are regarded as a promising replacement for fossil fuels attributed to their high redox reactivity, low-budget and environmentally friendly [10,11]. Graphene is becoming a fervent electrode material ascribed to its great specific surface area, outstanding electrical conductivity, stable chemical property, remarkable mechanical property, and relative low-cost [12,13]. Graphene and graphene-based materials have been widely used as the electrode

materials in energy storage [14–19]. It has been reported that the residual oxygenous functional groups (OFGs), defects and the size of the in-plane sp^2 domains in reduced graphene oxide (RGO) obviously affected its electrical conductivity and electrochemical performance [20–22]. And numerous variables that controlled the microstructure and defect degree of the as-prepared RGO in the overall process have been reported previously [23–26].

Natural graphites are widely used as the ingredient for preparing RGO due to their abundant reserves and good crystallinity. Based on the difference of crystalline morphology, natural graphite can be categorized as flaky graphite (FG), lumpy graphite (LG), and amorphous graphite (AG) [27]. Natural FG, LG, and AG varied in the crystalline morphology, crystallinity, defect degree, and specific surface area, etc. [25,28]. It has been confirmed that the crystallinity of the natural graphites reduced in the sequence of $LG > FG > LG$ [28]. Specifically, the lateral size, crystal size, and crystallinity of the parent graphites all signally affected the oxidation process, functionality and sheet size of GO, and microstructure of the resulting RGO [29,30]. The characteristics of natural graphites and their resulting products are listed in Table 1. In our previous work, the characterization of RGO synthesized from natural FG, LG, and AG had been detailedly

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Table 1
Characteristics of natural graphites and their resulting products [25,28]

Properties and products	Flaky graphite (FG)	Lump graphite (LG)	Amorphous graphite (AG)
Crystallinity	LG > FG > AG		
Grain size	LG > FG > AG		
Defect degree	LG < FG < AG		
Specific surface area	LG < FG < AG		
Graphite oxide (GrO)	FGrO	LGrO	AGrO
Graphene oxide (GO)	FGO	LGO	AGO
Reduced grapheme oxide (RGO)	FRGO	LRGO	ARGO

investigated. The resulting RGOs had obvious differences in layers, defects, content of residual OFGs, etc., and then the oxidation, exfoliation and chemical reduction process were further interpreted [25]. However, the effects of natural graphites' crystallinity on the electrochemical performance of the resulting RGOs are scarcely reported.

In the work, RGOs were first prepared from natural FG, LG and AG under the same conditions. Then, the electrochemical performances of the resulting RGOs were systematically researched via the tests of cyclic voltammetry, galvanostatic charge-discharge and electrochemical impedance spectroscopy. Finally, XPS and Raman analysis were adopted to interpret the reasons for the electrochemical performance differences of the resulting RGOs in microstructure level. It is of great significant to provide an effective approach to choose the appropriate pristine natural graphite according to the requirements of RGO's application.

Experimental

Materials and chemicals

The FG, LG, and AG were sampled from Sanchaya (Yichang, China), Kalutara (Sri Lanka), and Panshi (Jilin, China), respectively, and the purities of them were all more than 99.5%. Besides, the size fraction of the sample was 45–38 μm .

Analytical purity of KMnO_4 and NaNO_3 , 30% H_2O_2 aqueous solution, and 85% $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ were bought from the Sinopharm Chemical Reagent Co., Ltd (China). 98% H_2SO_4 and 36% HCl were purchased from the Xinyang Chemical Reagent Co. (China). The deionised water used in all the experiments holds the resistivity of 18.25 $\text{M}\Omega\cdot\text{cm}$.

Preparation of reduced graphene oxide (RGO)

Graphite oxide (GrO) was prepared according to the modified Hummers method as reported previously [25,31,32]. The GrOs prepared from FG, LG and AG were marked as FGrO, LGrO and AGrO, respectively. Furthermore, the preparation of graphene oxide (GO) and chemical reduction of the concentrated GO were as the same to our previous reports [15,25,26]. The RGOs prepared from FGrO, LGrO and AGrO were signed as FRGO, LRGO and ARGO, respectively.

Measurements

A Renishaw INVIA Raman microscope purchased from England was used to test the resulting FRGO, LRGO and ARGO with the shift range of 500–3000 cm^{-1} .

The X-ray photoelectron spectroscopy (XPS) spectra of the RGOs were obtained from the PHI 3056 XPS brought from PERKIN ELMZR of USA. A Mg anode source of the XPS operated at 15 kV was used in the characterization.

Electrochemical measurements

A VersaSTAT-450 potentiostat analyser purchased from PAR of USA

was used to the electrochemical tests in a typical three-electrode system at room temperature. Platinum foil ($1.5 \times 1.5 \text{ cm}$) and saturated calomel electrode were served as counter and reference electrodes, respectively, and the electrolyte was 1 M of KOH aqueous solution. Moreover, the working electrodes were made as our previous reports [15,33].

Cyclic voltammetry (CV) was conducted over a sweep potential scope of -0.90 to 0.10 V at various scan rates. The average capacitance of the resulting rGO can be calculated by the following equation

$$C = \frac{\int IdV}{2m \cdot \Delta V \cdot v} \quad (1)$$

where C is the average capacitance (F/g), I is the oxidation or reduction current (A), ΔV is the potential scope (V), v is the scan rate (mV/s), and m is the mass of active materials (g).

Galvanostatic charge-discharge curves were achieved in a potential scope of -0.80 to 0 V at different current densities. The specific capacitance, C_{sc} (F/g), of the resulting rGO was calculated by

$$C_{sc} = (I\Delta t)/(m\Delta V) \quad (2)$$

where I , Δt , ΔV , and m are the constant current of discharging (A), discharging time (s), potential deviation after a full discharge (V), and mass of the RGOs (g), respectively.

Electrochemical impedance spectroscopy (EIS) was measured in the frequency scope of 10^{-2} to 10^5 Hz with an ac perturbation voltage of 5.0 mV .

Results and discussion

Electrochemical performance of the RGOs

Fig. 1a shows the CV curves of the three kinds of RGO at a scan rate of 10 mV/s . It can be seen from Fig. 1a that all the CV curves appear to be an approximately symmetric and rectangular shape, which indicates that the three kinds of RGO are typical double capacitor. In addition, no obvious faradaic redox peaks were observed in the three curves at the range of the scanning voltage, indicating that the electrical double-layer capacitor plays a dominate role in the charge-discharge process. Furthermore, as well known that the average capacitance is proportional to the area surrounded by the CV curve [10], the integral areas of the CV curves at the scan rate of 10 mV/s increased in the order of $\text{ARGO} < \text{LRGO} < \text{FRGO}$, which suggested that FRGO had the greatest average capacitance.

The CV curves of the RGOs at various scan rates are illustrated in Fig. 1b–d. The CV curves of the three kinds of RGO were increasingly deviating from the rectangular shape with the increase of the scan rates. It may be due to that as the increase of the scan rates, the polarization of concentration difference and electrochemical became serious, the electrolyte ion could not completely spread over the surface of the electrode material, leading to the reduce of its utilization [34].

Furthermore, the average capacitances of ARGO, LRGO and FRGO at various scan rates calculated by the Eq. (1) are shown in Fig. 2. It can be gotten from Fig. 2 that the average capacitances of FRGO were greater than those of ARGO and LRGO at any scan rates. Furthermore, the average capacitances of the three types of RGO were decreased with the increasing scan rates. Conclusively, the differences of the microstructure of the three RGOs may be responsible for the diversities of the average capacitances [35].

Fig. 3a–c illustrates the galvanostatic charge-discharge curves of the resulting RGOs at different current densities. The charge-discharge curves of the RGOs were similar to be symmetrical linear, indicating that FRGO, LRGO and ARGO all had a good double-layer capacitive performance with well charge-discharge property. In addition, the redox reaction of the residual OFGs in the charge-discharge processes led to the curves did not present well form of symmetric linear.

Fig. 3d. shows the specific capacitances of the RGOs as a function of

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