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Characterisation of reduced graphene oxides prepared from natural flaky, lump and amorphous graphites

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ABSTRACT

The characterisation of reduced graphene oxides (rGOs) prepared from natural flaky, lumpy, and amorphous graphites using Hummers method was investigated. The prepared graphite oxides (GrOs) and rGOs were characterised by X-ray diffraction, Fourier transform infrared spectroscopy, Raman spectroscopy, UV–vis spectroscopy, atomic force microscopy and electrochemical performance. The results showed that amorphous graphite was much easier to oxidise than lumpy and flaky graphites and was preferable for preparing single or double layer graphene because low graphitisation degree, high defect degree, high specific surface area and small crystal size were beneficial for (1) the oxidants to attack the exposed carbon atoms, (2) the intercalation of oxidants, and (3) the diffusion of oxidants between graphitic layers. In addition, rGO synthesised from amorphous graphite had the most defects and the smallest size of the in-plane sp^2 domains compared to those obtained from the other two nature graphites.

1. Introduction

Graphene is a graphitic material involving two-dimensional hexagonal networks of carbon atoms [1]. Graphene is widely applied in electronics, biological engineering, filtration, light-weight/strong composite materials, photovoltaic devices and energy storage due to its outstanding properties [2]. Mechanical exfoliation [3], heat treatment of silicon carbide wafers [4], epitaxial growth by chemical vapour deposition (CVD) of hydrocarbons on substrates [5], bottom-up assembly [6], electrostatic deposition [7], liquid phase exfoliation [8], arc-discharging [9], solvothermal method [10], and reduction of graphite oxide [11] have been reported for the synthesis of high-quality graphene. It has been well-demonstrated that GrO is an excellent precursor to prepare graphene via thermal [12], annealing [13], electrochemical [14], and chemical reduction methods [15]. Furthermore, using the GrO route to prepare graphene offers the possibility of controlling its quality while producing it on a large scale. Graphene oxide (GO) and partially rGO are graphene derivatives that have a structure marked by defects produced during the oxidation and/or reduction processes. It has been reported that numerous variables could influence the structure and defect degree of graphene in the overall process, including oxidation, exfoliation and reduction. In particular, different types of natural graphite should be considered when graphite is used as the raw material for graphene synthesis because the structure of crystal lattice varies with the type of natural graphite.

In general, graphene is prepared from the natural graphite, which has a high amount of reserves [16]. Natural graphite could be classified as flaky, lumpy, and amorphous graphite based on the crystalline morphology [17]. Flaky and lumpy graphites are crystallised clearly. In particular, the crystal in the flaky graphite aligns directionally, whereas that in the lumpy graphite aligns desultorily. In addition, the particle size of crystal in the lumpy graphite is larger than 0.1 mm, while that in the flaky graphite is larger than 1 μm (the mean value ranges from 0.05 mm to 0.5 mm). In contrast, amorphous graphite is poorly crystallised with a smaller crystal size less than 1 μm [18].

Numerous variables during the overall procedure for rGO synthesis that may affect the properties of rGO have been reported in many literature studies [19,20]. Peng et al. [21] confirmed that the silicate minerals in the pristine graphite did not influence the characteristics of the prepared rGO. Wu et al. [22] observed that both the lateral size and crystallinity of the starting graphites notably influenced the number of graphene layers, and Botas et al. [23,24] confirmed that the size of graphite crystal affected the oxidation process and the functionality and sheet size of the resulting GO. It can be inferred that the crystal morphology of the

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natural graphites may have an influence on the characteristics and properties of synthesised rGO. However, few reports have investigated this influence.

Therefore, natural flaky, lumpy, and amorphous graphites were used to synthesise GrOs and rGOs. The study focused on (1) characterisation and comparison of the GrOs and rGOs prepared from the three types of natural graphite and (2) investigation of the effect of the crystal morphology (such as graphitisation degree and crystal size) on the oxidation process of GrO and the characteristics of the prepared rGO.

2. Experimental

2.1. Materials and chemicals

The samples of flaky graphite (FG), lumpy graphite (LG), and amorphous graphite (AG) were obtained from Sanchaya (Yichang, China), Kalutara (Sri Lanka), and Panshi (Jilin, China), respectively. In particular, the FG sample was flotation concentrate, and the LG and AG samples were obtained from natural deposits. The three types of sample were classified with screening to obtain the size fraction of 45–38 μm. Next, the samples were leached in the mixture of HF and HCl solution to eliminate the impurity minerals. The final samples were assayed with purities of 99.36% for FG, 99.27% for LG and 99.34% for AG.

Potassium permanganate and sodium nitrate in analytical purity, 30% hydrogen peroxide aqueous solution, and 85% hydrazine hydrate were purchased from the Sinopharm Chemical Reagent Co., Ltd (China). Sulphuric acid with concentration of 98% and hydrochloric acid with concentration of 36% were obtained from the Xinyang Chemical Reagent Co. (China). Deionised water with the resistivity of 18.25 MΩ cm was used in this study.

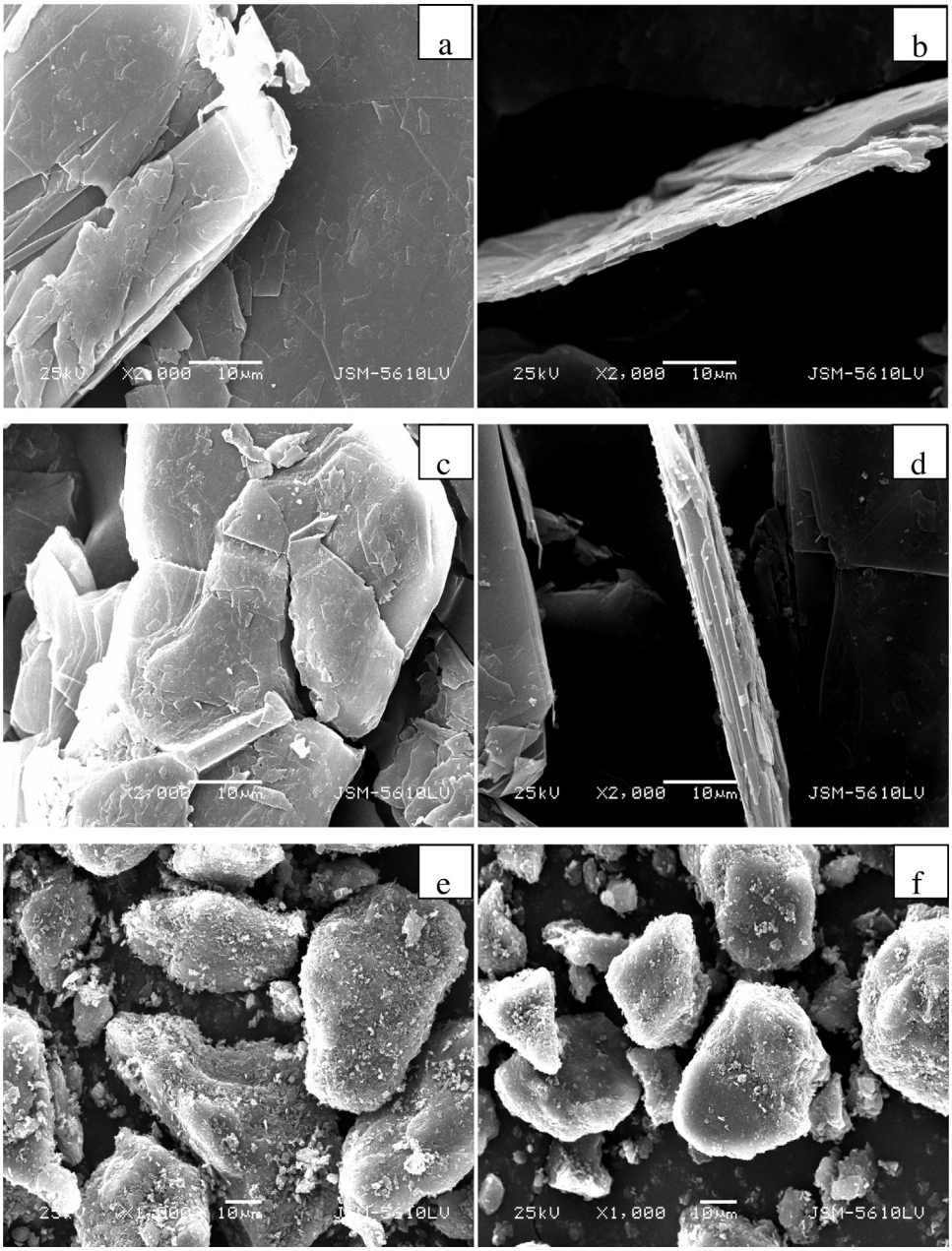

Fig. 1. SEM images of natural graphites: (a, b) FG; (c, d) LG; (e, f) AG.