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Influence of graphite size on the synthesis and reduction of graphite oxides

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ABSTRACT

We investigated the influence of the precursor, graphite, size on the synthesis and reduction of graphite oxide. Three precursors of graphite with different size were used to synthesize the graphite oxide which was consecutively reduced by hydrazine of different concentration ratios. Size dependent effect on the reduction of the graphite oxide was found, and the graphite oxide of the smallest size provided the best reduction result. Electrochemical properties of the reduced graphene oxide were investigated in both of the base and acid electrolytes, finding the reduced graphene oxide of the smallest size gives the best electrochemical performance due to the high reduction. Therefore, the precursor size is a very important factor in the synthesis and reduction of graphite oxide, affecting the electrochemical performance considerably for the energy storage applications.

1. Introduction

Graphite is low-cost material and has enormous potential for many kinds of applications, making graphene as “black-gold” material in 21st century with lots of precious properties [1,2]. Two general types of graphite are natural and synthetic. Natural graphite is mined using standard hard or soft rock-mining techniques [3]. Synthetic graphite is obtained from the graphitization of selected carbon precursors such as petroleum and coal tar-based coke in very high temperature [4]. Individual layer of graphite is so-called graphene, forming a giant covalent structure between six carbons and having high electric conductivity due to the vast electron delocalization within the carbon layer – the phenomenon called aromaticity [5].

Four techniques currently used for the production of graphene are mechanical exfoliation [6], chemical exfoliation or graphitization [7], epitaxial growth [8], and chemical wet method through graphite oxide (GO). The chemical wet method gives advantages of straightforward up-scaling, versatile handling of the suspension, and rapid process. GO could be reduced to graphene restored considerable electronic conjugation. The chemical method, therefore, has been considered as a popular and low-cost way to make graphene [9].

Properties of the graphene reduced from GO depend on the atomic structure [10] and metallic impurities [11] of the precursor graphite, demonstrating direct effect of the precursor graphite on the reduced graphene oxide. It is, therefore, important to consider the influence of size of the precursor on the reduction and corresponding electrochemical properties for the energy storage applications. In this paper we used three kinds of precursor graphite of different grain size for the synthesis and reduction of GO and investigated the corresponding physical, chemical, and electrochemical properties. We found that the graphene oxide of the smallest size was the best in the reduction as well as in the electrochemical performance.

2. Experimental

2.1. Synthesis

Three kinds of the precursor natural graphite which have different grain size of 20, 74, and 149 μm, respectively, were purchased from Sigma Aldrich and used as it was. GO was first synthesized from the precursor graphite by the modified Brodie method as described elsewhere [12]. The precursor graphite with

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the grain size of 20, 74, and 149 μm were named by PG20, PG74 and PG149, respectively, and the corresponding graphite oxides are GO20, GO74, and GO149 made from the precursor graphite with the grain size of 20, 74 and 149 μm, respectively.

Reduction of GO was carried out using hydrazine. We chose two concentration of the hydrazine: low and high concentrated hydrazine followed by Park et al. [13] and Stankovich et al. [14], respectively. First, graphene oxide solution was made from 3 mg of GO in 1 ml of deionized (DI) water, and then 0.6 (low concentration) or 15 μl (high concentration) of hydrazine hydrate (80%, Aldrich) was added into the graphene oxide solution. The mixed solution was heated in an oil bath at 90 °C for 24 h. The solution was cooled to room temperature followed by vacuum filtration with a lot of DI water several times and dried in an oven at 60 °C for overnight. The reduced graphene oxide samples followed the hydrazine treatment were referred as A149, A74 and A20 for the low concentration and B149, B74, and B20 for the high concentration of the hydrazine and the following numbers represent the size of the original precursor graphite.

2.2. Characterization

The interlayer distance of the samples was analyzed by powder x-ray diffraction system (XRD, D/MAX-2500/PC, Rigaku, Japan). Metallic impurities of precursor graphite were measured by inductively coupled plasma mass spectroscopy (ICP, Optima 7300DV, USA). The surface morphology was examined by field emission scanning electron microscope system (FE-SEM, S-4300, Hitachi, Japan). Fourier transformed infrared spectroscopy (FT-IR, Nicolet 380, Thermo Scientific) was used to investigate functional groups. The content of carbon, nitrogen, oxygen, and hydrogen of the samples was confirmed by element analyzer system (EA, Vario EL, US). X-ray photoelectron spectroscopy (XPS, Thermo scientific K-alpha, Al anode, 20 eV of pass energy) with contact with the gold subtract was performed to know the reduction level and the chemical bonding around carbon atoms.

For the electrochemical analysis, each sample was diluted in isopropyl alcohol solution with ratio of 1:1 and the mixture was sonicated for 3 h. Then, 10 μl of the mixture was drop casted onto the glassy carbon electrode (OD: 6 mm ID: 3 mm) for the working electrode. Silver—Silver chloride and nickel electrodes were used as the reference and counter electrodes, respectively, for the three-electrode cell. Two kinds, 6 M KOH and 1 M H_2SO_4, of aqueous electrolytes were used and compared for investigation of the nitrogen doping effect in the base and acid electrolytes. Potentiostat/Galvanostat with impedance spectroscopy (Bio-Logic SAS, SP-150) was performed for cyclic voltammetry at the scan rate of 50 mV s^{-1}.

3. Results and discussion

Fig. 1(a) shows the XRD results of the precursor graphite (PG20, PG74, PG149), representing the (002) peaks along the c-axis near 26.5°. Interlayer distances of about 3.4 Å were obtained, and the precursor graphite of the biggest size, PG149, presented the most prominent (002) peak compared to the others because of better crystallinity along the c-axis from the big size. Metallic impurities of the precursors were investigated by ICP, and all samples had pretty low metallic impurities less than 104 ppm so that we could rule out the impurity concern. The interlayer distance increased to around 6.4 Å in GO after the chemical oxidation as shown in Fig. 1(b). GO20, made from the smallest graphite, had the biggest peak among the samples, demonstrating easy oxidation due to the small size and consistent with the previous studies [15,16]. The (002) peak came back to 25° after the low and high concentrated hydrazine treatment shown in Fig. 1(c) and (d), respectively, informing the considerable reduction of the graphene oxide. However, the less hydrazine treated samples (A20, A74, A149) showed an additional small bump around 19° making two phases

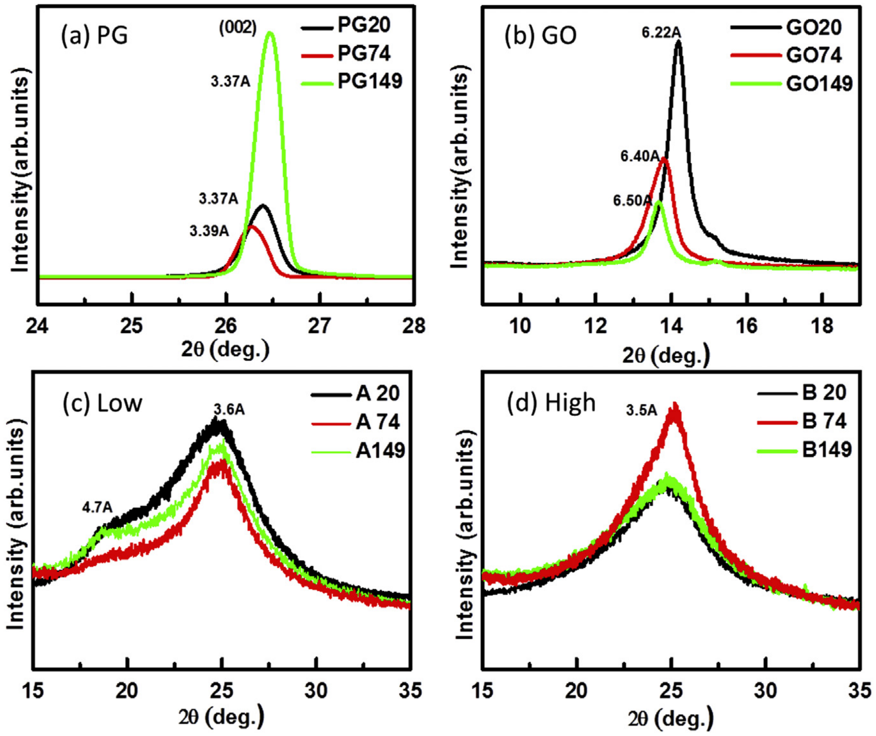

Fig. 1. XRD of (a) pristine graphite samples (PG20, PG74, PG149), (b) graphite oxide samples (GO20, GO74, GO149), (c) low hydrazine treated samples (A20, A74, A149), and (d) high hydrazine treated samples (B20, B74, B149).