

Morphology-controlled graphene nanosheets as anode material for lithium-ion batteries



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ABSTRACT

Morphology-controlled graphene nanosheets can be easily synthesized as anode material for application in high-capacity lithium-ion batteries. A modified version of an improved method for higher degree of oxidation of graphite oxide (GO) has been developed and characterized. X-ray diffraction analysis shows that GO prepared using this method has a higher degree of oxidation than that of using the improved method. The interlayer *d*-spacing increases from 0.87 nm (using the improved method) to 0.92 nm (using the modified-improved method). Also, it is confirmed by XPS analysis that the O/C ratio in GO increases from 2.51 (improved method) to 8.27 (modified-improved method). It is hypothesized that GO, which has a higher degree of oxidation, is more reducible to graphene. The more reduced graphene has a larger amount of free π -bonds and fewer layers, and it can be easily altered to morphology-controlled graphene. Graphene nanosheets prepared using the modified-improved method exhibits discharge capacities of 1079 mAh g⁻¹ (at a constant current of 40 mA g⁻¹) and 1002 mAh g⁻¹ after 50 cycles. The capacity retention of the synthesized graphene nanosheets is 1070 mAh g⁻¹ at a current of 40 mA g⁻¹ after the rate capability test, and their rate capability is 463 mAh g⁻¹ at a current of 400 mA g⁻¹. The morphology-controlled graphene nanosheets prepared by the modified-improved method shows better discharge performance compared to graphene prepared by the improved method.

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1. Introduction

Lithium rechargeable batteries require increasingly high power and energy density owing to the development of high-performance portable electric devices, electric vehicles, and energy-storage systems. To meet these challenges, an innovative material is needed. Graphite is widely used as an anode material for lithium-ion batteries because of its high columbic efficiency and acceptable specific capacity by forming intercalation compounds (LiC₆) [1–3]. However, graphite has theoretically a Li storage capacity of ~370 mAh g⁻¹ by the limited Li-ion storage sites within the sp² carbon structure [4–7]. In order to enhance its energy and power density, another anode material has been desired. One of the candidates is Si- and Sn-based materials. Silicon and its alloys have been studied

as alternative high-capacity anode materials to graphite but these materials have severe problems such as volume expansion during charging–discharging [8–13]. Another potential candidate is graphene. Graphene is considered a potential alternative material of graphite as an anode in lithium-ion batteries [14–17]. It has been receiving intense attention recently because it has a single two-dimensional (2D) atomic layer (sp² carbon configuration and π – π complexation) in a honeycomb lattice. Graphene also has many advantages, such as high electronic conductivity, large surface area, and high mechanical strength [18–26]. In addition, graphene with high reversible capacities ranging from 500–1200 mAh g⁻¹ for Li storage capacities has been reported [27–30]. The graphene nanosheets obtained from various fabrication routes have already been utilized as the anode materials for lithium ion batteries [14–17,27,28]. The representative methods for graphene synthesis are microcleavage, chemical vapor deposition, and wet chemistry [31–33]. Microcleavage and chemical vapor deposition can produce high-quality graphene, but the yield is very low. The wet chemistry methods are inexpensive and advantageous for electrochemical

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Table 1
Preparation of graphite oxide by improved-method and modified improved method. Wook Ahn et al.

Sample name	Precursor	Oxidant			Post-treatment (ultra-sonication)	Microwave susceptor	Microwave condition for RGO
		H ₂ SO ₄	H ₃ PO ₄	H ₂ O ₂			
GOI	Commercial graphite	360 mL	40 mL	3 mL	None	None	None
GOK	Commercial graphite	350 mL	50 mL	20 mL	None	None	None
RGOI	GOI	None	None	None	30 min	Acetylene black	90 sec
RGOK	GOK	None	None	None	30 min	Acetylene black	90 sec

device applications which require mass production because the final product can be in the form of a powder [34]. This synthesis method has critical drawbacks, however, such as low quality of the graphene produced [35]. The Hummers method is generally considered a typical wet chemistry method for producing graphite oxide, using a mixture of sulfuric acid (H₂SO₄), sodium nitrate (NaNO₃), and potassium permanganate (KMnO₄). This method is still widely used, often with a modified version of it [33–36]. However, the graphene prepared by Hummers method or modified Hummers method have exhibited multi-layered graphene of low quality by lots of stacks. Generally, these low quality graphene nanosheets can result from low oxidation degree of the graphite oxide in conventional Hummers method. In our previous report, the “modified-improved method” for graphite oxide synthesis showed the enlarged interlayer spacing (*d*-spacing) using phosphoric acid as a second acid with first sulfuric acid [37,38]. The addition of phosphoric acid to this reaction produced RGO (reduced graphite oxide) with more intact graphitic basal planes indicating graphite oxide with fewer defects in the basal plane, as compared to graphite oxide prepared by the Hummers method. Also, the protocol for running the reaction does not involve a large exotherm and produces no toxic gas. Moreover, the improved method yields a higher fraction of well-oxidized hydrophilic carbon material [39].

In this study, we focus on the strategic synthesis of morphology-controlled graphene nanosheets by using simple post-process treatment (ultra-sonication), and the morphology of graphene nanosheets from graphite oxide having high degree of oxidation prepared optimized reaction process could be easily controlled. Also, we demonstrate significantly improved electrochemical capacity of the prepared graphene as an anode electrode for Li ion battery application.

2. Experimental

2.1. Preparation of graphite oxide

We refer to the prepared graphite materials as GOI, GOK, RGOI, and RGOK, as shown in Table 1. In order to prepare graphene nanosheets, graphite oxide is first produced by a technique developed in our previous research called the “modified-improved method” [37,38]. The resulting graphite oxide is called “GOK.” This procedure is modified to optimize the reaction condition from the “improved method” (Marcano et al. [39]), which produces graphite oxide we refer to as “GOI.” The fabrication process for GOK is as follows: 3 g of graphite (<45 μm, ≥99.99%, Sigma-Aldrich) powder was mixed in a round-bottomed flask with 350 mL of sulfuric acid (95.0–98.0%, ACS reagent, Sigma-Aldrich) and 50 mL of phosphoric acid (≥85 wt% in H₂O, ACS reagent, Sigma-Aldrich), as a solvent, in an ice bath. When the temperature dropped below 10 °C, 18 g of potassium permanganate (99.3%, Samchun Chemical) was gradually added to the mixture. Then, the mixture was transferred to a heating mantle to provide an oxidation process with isothermal conditions at 45 °C and maintained for 12 h before it was cooled to room temperature. When the oxidation procedure was over, the

mixture was transferred to the ice bath, and the flask was slowly filled with 400 mL of de-ionized (DI) water to accommodate the highly exothermic nature of the reaction. Next, 20 mL of H₂O₂ was added and the color of the mixture turned to bright yellow and generated many bubbles. After the reaction began, the mixture was stirred for 48 h to complete the reaction. The resulting paste was centrifuged at 8000 rpm for 5 min. The remaining solid paste was washed five times with a mixture containing 100 mL of H₂O, 100 mL of hydrochloric acid (37%, ACS reagent, Sigma-Aldrich), and 100 mL of ethanol solution. It was then washed with DI water until the pH reached 5. Centrifugation at 8000 rpm was conducted for each washing cycle. After the final washing step, the product was first frozen and then dried overnight in a vacuum freeze dryer at -55 °C. Details of the fabrication process for GOI are the same as that for GOK except for the amount of oxidant (H₂O₂: 3 mL, H₂SO₄: 360 mL, H₃PO₄: 40 mL) and the reaction time (24 h after adding of H₂O₂).

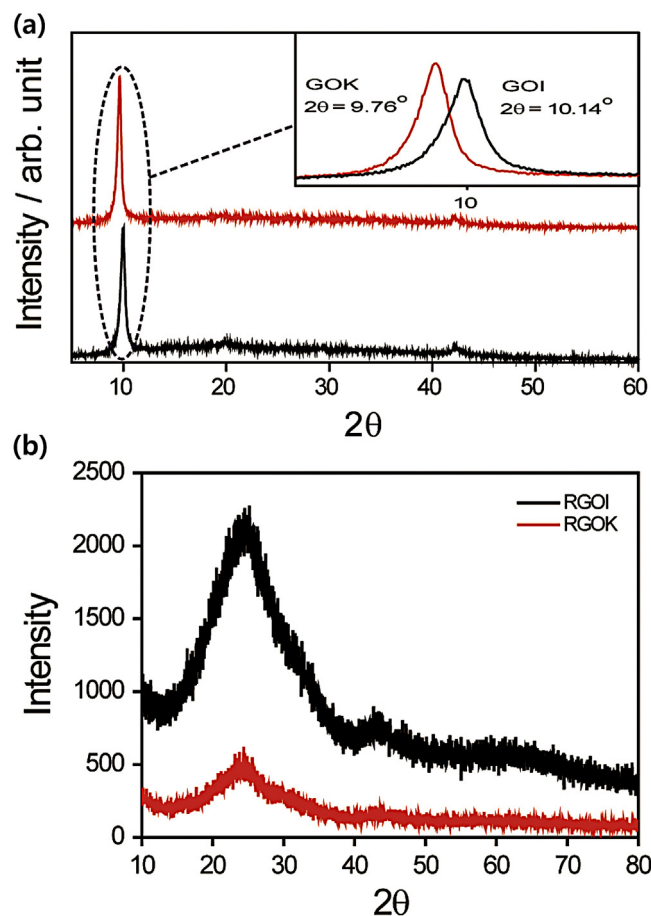


Fig. 1. XRD patterns of (a) graphite oxide (GOI and GOK) and (b) reduced graphite oxide (RGOI and RGOK) using microwave-induced thermal reaction.

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