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Electron beam irradiation dose dependent physico-chemical and electrochemical properties of reduced graphene oxide for supercapacitor

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ABSTRACT

Reduced graphene oxides (rGOs) with micropores were successfully obtained from a graphite oxide (GO) suspension in 2-propanol/water by electron beam irradiation at room temperature under ambient air conditions. During the radiolysis reaction, hydrated electrons (e^-_{aq}) were generated and acted as a reducing agent for the reduction of GO. The physico-chemical properties, such as disorder degree, oxygen content, specific surface area, pore structure, and sheet resistance of the rGOs were systematically controlled by adjusting the electron beam irradiation dose (50~360 kGy). Especially, higher irradiation dose reduced the oxygen content, increased the specific surface area, and increased the number of micropores of rGO, which are important factors for supercapacitor performance. In order to investigate the electrochemical performance of the rGOs, electrochemical measurements were performed with a three-electrode system in 6.0 M KOH aqueous media. The highest capacitance of 206.8 F g^{-1} was achieved at a charge/discharge current density of 0.2 A g^{-1} in 6.0 M KOH aqueous solution for a sample reduced by electron beam irradiation of 200 kGy.

1. Introduction

Graphene, a two-dimensional nanosheet of sp^2-hybridized carbon, has attracted tremendous interest as a key material in various fields such as electronic devices [1], sensors [2], Li-ion batteries [3], polymer nanocomposites [4], and supercapacitors [5], because of its unique physical, chemical, and mechanical properties [6–8]. In particular, graphene possesses high specific surface area, excellent electrical conductivity, low production cost, long cycle life, outstanding chemical tolerance, and good mechanical properties, which render it as an ideal electrode material for lithium ion batteries or supercapacitors [9–11]. However, the realization of these applications is still not practical because of the limitations for large-scale and safe production of graphene nanosheets. Until now, to fabricate graphene, various preparation routes have been developed including mechanical cleavage [12], chemical vapor deposition [13], epitaxial growth [14], the reduction of graphite oxide (GO) by reducing agents [15] and thermal treatment [16]. Among these various methods, the reduction of GO is one of the most promising processes for the mass production of graphene. Nevertheless, these reduction processes need strong chemical reducing agents such as hydrazine, elevated temperatures (over 80 °C) for long periods of 12~24 h or heat treatment at high temperature (over 900 °C) in an inert atmosphere. The use of highly toxic and dangerously unstable reducing agents for chemical reduction of GO must be avoided for large-scale and safe production of graphene.

Recently, the reduction of GO has been achieved through the radiolysis method. In comparison with the conventional approach, this strategy has many advantages such as being chemical reductant free, cost-effective, eco-friendly, and easily scalable [17–20]. These reduction processes of GO are dominated by the radiation-chemical reaction in water/alcohol solution systems. Water, when exposed to high energy irradiation, can decompose into both oxidative (hydroxyl radical, $^{\bullet}OH$) and reductive (hydrogen radical and hydrated electron, $^{\bullet}H$ and e^-_{aq}) species [21]. Meanwhile, alcohols can eliminate the oxidative $^{\bullet}OH$, a radical scavenger, and stabilize reductive radicals, which can be used as a reducing medium for the chemical reaction [22]. Gamma-ray irradiation-induced reduction of GO in the absence of oxygen has been recently reported [17–19]. Although gamma-ray irradiation has various advantages for radiolysis, it must be carried out under oxygen-free conditions because the relatively lower energy of

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gamma-ray is significantly suppressed by oxygen quenching process in air. However, an electron beam can supply sufficient hydrated electrons in air due to its high energy density [20]. In this regard, electron beam irradiation can reduce GO even at room temperature under ambient air conditions. However, little research has been conducted to systematically investigate the effect of electron beam irradiation dose on the physico-chemical properties such as disorder degree, oxygen content, pore structure, specific surface area, sheet resistance and electrochemical performance of supercapacitors. Especially, tailoring the pore structure of graphene is quite important in terms of both power delivery rate and energy storage capacity for various applications. In this regard, the electron beam can simultaneously reduce GO and generate micropores on the surface of reduced graphene oxides (rGO) even at room temperature under ambient air conditions along with fine tuning porous parameters of rGO.

In this work, we present a simple approach to obtain rGOs with high porosity by using electron beam irradiation at room temperature under ambient air conditions. The degree of oxygen and porosity of rGO were controlled by the electron beam irradiation dose (50∼360 kGy). Both the oxygen content and pore characteristics of the rGOs were found to be critical factors influencing the other physico-chemical properties such as disorder degree, specific surface area, and sheet resistance. Furthermore, the supercapacitor performance of the rGOs was investigated by using aqueous electrolyte in a three-electrode system. The effects of the physico-chemical properties on the electrochemical performances for supercapacitor are discussed in detail. As a result, we could control the physico-chemical properties and its supercapacitor performance as a function of irradiation time. The highest specific capacitance (206.8 F g^{-1}) in aqueous media was achieved at 0.2 A g^{-1} for the sample reduced by the electron beam irradiation of 200 kGy.

2. Experimental

2.1. Sample preparation

2.1.1. Synthesis of exfoliated graphite oxide (GO) aqueous dispersion

Exfoliated GO aqueous dispersion was prepared from commercial graphite (Sigma Aldrich, 20 μm) by a modified Hummers' method [23]. Briefly, 5.0 g of graphite and 2.5 g of $NaNO_3$ (Sigma Aldrich) were added to 250 ml of concentrated H_2SO_4 (purity 95%) and stirred in an ice bath. Then, 30.0 g of $KMnO_4$ (Daejung, purity 99%) was gradually added with vigorous stirring and the temperature of the mixture was kept at below 20 °C. After the ice-bath was removed, the mixture was reacted at 35 °C for 3 h and then 460 ml of distilled water was slowly added until the temperature reached 98 °C. The dark brown suspension was maintained at this temperature for 30 min and then further diluted by adding 1.4 L of distilled water. Finally, the reaction was terminated by the addition of 30 ml of H_2O_2 (Daejung, purity 30%). The color of the solution changed from dark brown to bright brown. The reaction product was then separated by centrifugation at 9000 rpm for 10 min and washed with 1.0 M HCl solution (approximately 2 times) and distilled water (approximately 2 times). After the final sediment was redispersed in distilled water by an ultrasonicator (160 W for 30 min), the undispersed component was separated by centrifugation at 4000 rpm for 10 min to obtain the aqueous dispersion containing well-exfoliated GO nanosheets with a concentration of about 6.0 mg ml^{-1}.

2.1.2. Synthesis of reduced graphene oxides (rGOs) through electron beam irradiation

The rGOs were synthesized through facile radiolysis using electron beam irradiation. In a typical procedure, a GO aqueous dispersion was diluted by adding a solution of 2-propanol and distilled water. The final GO concentration was about 2.0 mg ml^{-1} and the fraction of 2-propanol was about 25% (v/v) in the mixture. The mixed solutions were then put into an uncovered petri dish and irradiated with an electron beam with 50∼360 kGy doses at room temperature, under ambient air conditions. The electron beam irradiation was performed at a dose rate of 0.1 kGy s^{-1} in a linear electron beam accelerator (UELV-10-10S) provided by the Advanced Radiation Technology Institute of the Korea Atomic Energy Research Institute (KAERI). Upon electron beam irradiation, the color of the solution turned black because of the reduction of the GO suspension. As a result, the rGOs were aggregated and precipitated owing to the removal of the oxygen-containing functional group in the GO, followed by the gradual decrease of their hydrophilicity, as a function of the irradiation dose. Finally, the dispersed rGOs were centrifuged and washed several times with ethanol. Black powders were obtained by drying in a vacuum oven at 120 °C. Hereafter, the resulting samples were denoted as rGO-dose.

2.2. Sample characterization

The structural characteristics of GO and the rGOs were obtained by powder X-ray diffractometer (XRD, Rigaku, Ultima IV) using Ni-filtered Cu K_α radiation (λ = 1.5418 Å) with a graphite diffracted beam monochromator at a scan rate of 1° min^{-1} from 5° to 50°. The patterns were recorded at an operating voltage of 40 kV and a current of 30 mA. The chemical compositions were determined by performing elemental analysis (Thermo Scientific, Flash 2000) with combustion of GO and rGO powders at 950 °C. The morphology of rGO-360 was characterized by field emission scanning electron microscopy (FE-SEM, JEOL, JSM-7100F), high-resolution transmission electron microscopy (HR-TEM, JEOL, JEM-3010) and atomic force microscopy (AFM, Bruker, N8 NEOS). For FE-SEM measurements, the powder sample was attached to an Al mount with carbon tape. HR-TEM images and selected area electron diffraction (SAED) patterns were obtained by using carbon-coated Cu grid (Carbon Type-B, 200 mesh) at an accelerating voltage of 300 kV. The AFM was operated in tapping mode using a Tap 190AI-G probe (Nanosensor). The sample was prepared by spin coating of a diluted colloidal dispersion in ethanol media on a freshly cleaved mica surface. X-ray photoelectron spectroscopy (XPS, Thermo Scientific, SIGMA probe) measurements of GO and the rGOs were obtained by using a monochromatized Al K_α X-ray source (1486.71 eV). Raman spectra were obtained by using a confocal Raman microscope (Nanobase, Xperam 200) at an excitation wavelength of 532 nm. The sheet resistances of the samples were measured by a four-probe method (Keithley, Model 2000 multimeter). Prior to XPS, Raman, and sheet resistance measurements, the samples were prepared by pressing the material into tablets with a 1 cm diameter under a pressure of 10000 psi. To determine the specific surface area and porous properties of the resulting samples, nitrogen adsorption-desorption isotherms were measured volumetrically at 77 K (Microtrac, BELsorp-mini II). The GO and rGOs were degassed at 80 °C for 12 h and at 120 °C for 5 h, respectively, under vacuum prior to the sorption measurements. The specific surface areas were calculated from the adsorption data using the Brunauer-Emmett-Teller (BET) method. The pore size distribution was calculated by the Barrett-Joyner-Halenda (BJH) method from the nitrogen desorption isotherm curves.

2.3. Electrochemical properties measurements

The electrochemical properties of the rGOs samples were investigated by cyclic voltammetry (CV), galvanostatic charge-