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Rapid one-step synthesis of conductive and porous MnO_2/graphene nanocomposite for high performance supercapacitors

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ABSTRACT

Herein, we report a rapid and simultaneous synthesis of manganese oxide (MnO_2) nanoparticles deposited on porous graphene foam by microwave-assisted method. The microwave irradiation enables simultaneously reduction and porous structure of graphene oxide and deposition of MnO_2. As-synthesized MnO_2/graphene nanocomposites are characterized by scanning electron microscopy, transmission electron microscopy, X-ray diffraction, and X-ray photoelectron spectroscopy. The resultant MnO_2/graphene nanocomposite electrodes exhibit as high as specific capacitance of 372 F g^{-1} at 0.5 A g^{-1}, high rate capability (82% retention at 5 A g^{-1}), and good long-term stability (98.5% retention during 3000 cycles). This synthetic method could be applicable to the mass production of porous nanocomposites as energy storage materials for supercapacitors and lithium-ion batteries.

1. Introduction

The attractive features of short charging time, long lifespan, and high power density have made supercapacitors (SCs) as the important intermediate system between the batteries and conventional electrostatic capacitors in terms of energy and power densities [1]. In order to meet the increasing demands for sustainable and renewable energy sources in modern electronic industry, tremendous research efforts have been made in hopes to improve the limitation of SCs; energy density, which is an order of magnitude lower than that of batteries [2–7]. In general, two types of SCs have been explored; carbon-based electric double layer capacitors (EDLCs) and analogous metal-based pseudocapacitors [8]. The former accumulates electrical charges from the electrostatically reversible adsorption of ions onto high surface area, while the latter uses redox-based Faradaic reactions for electrical charge storage. However, since EDLCs generally deliver specific capacitances of around 100–200 F g^{-1}, their values limit to increase energy densities [9]. Pseudocapacitors can provide higher specific capacitance (200–1000 F g^{-1}) than EDLCs, but suffer from inferior rate capability and cycling performance because of intrinsically poor electrical conductivity of the electrode materials [10].

In order to find a breakthrough for SCs, considerable research efforts have been devoted to the synthesis of hybrid composite structures where pseudocapacitive materials are combined with carbon materials [11–15]. Owing to the extraordinary electrical, thermal, and mechanical properties, graphene sheets have been regarded as attractive building blocks for preparing new heterostructured materials [16]. On the other hand, MnO_2 is one of the most promising transition metal oxides for pseudocapacitors because of its high theoretical specific capacitance (1370 F g^{-1}), environmental friendliness, and relatively low cost [17]. Several reports of graphene/MnO_2 hybrid electrodes have been investigated [18–20]. For instance, Zhao et al. described that composite materials composed of functionalized reduced graphene oxide with MnO_2 nanosheets exhibited comparatively high specific capacitance as an electrode material for supercapacitors [21]. Wu and co-workers synthesized chemically modified graphene/MnO_2 composites through chemical reduction of graphene oxide and precipitation method of MnO_2 [22]. These approaches, however, require hazardous reducing agent, long reaction time, and complicated experimental condition. In this regard, there is an urgent need for the development of a simple and efficient synthetic method for preparation of graphene/MnO_2 nanocomposites.

Herein, we developed a rapid and scalable approach to directly produce high conductive, porous, and exfoliated MnO_2/graphene composites through microwave-assisted solid-state reaction. Microwave irradiation allows graphene oxide powders to reduction conversion into exfoliated reduced graphene oxide (RGO) within ~10 s without any reducing agents, while MnO_2 nanoparticles were successfully grown onto the surface of RGO sheets. The resulting nanocomposites demonstrated their great potential as electrode materials for application

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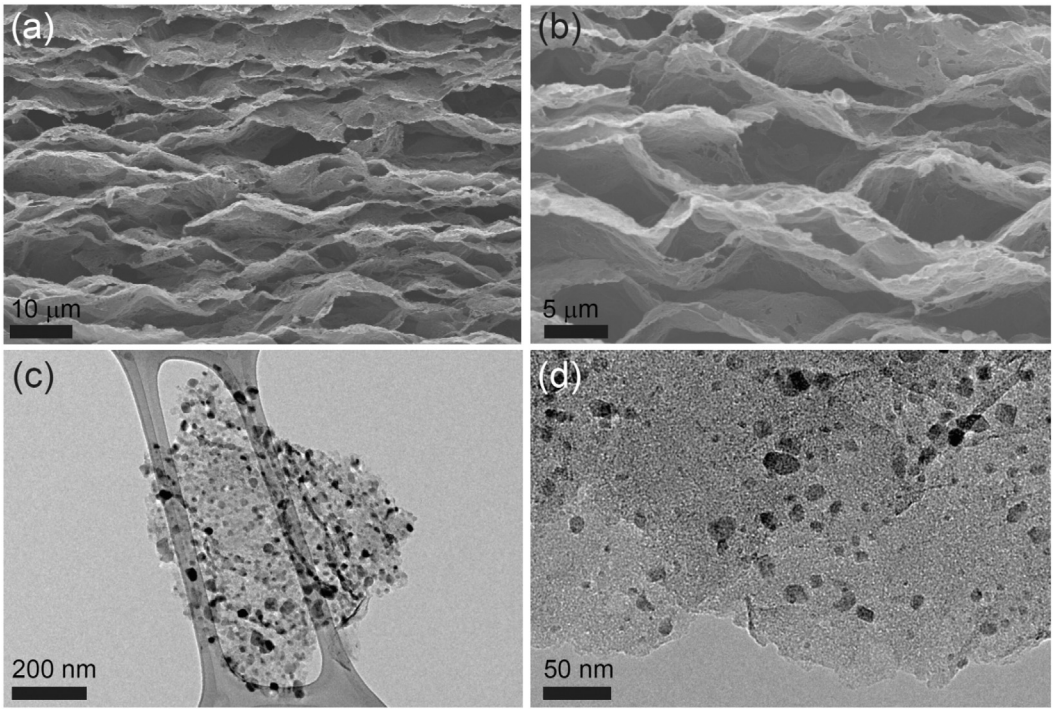

Fig. 1. (a) and (b) SEM images of porous MnO_2/RGO nanocomposites. (c) and (d) TEM images of porous MnO_2/RGO nanocomposites.

of supercapacitors, showing outstanding electrochemical performance of high specific capacitance, high rate capability, and good cycle life.

2. Experimental

2.1. Chemical and reagents

Aqueous solutions were prepared using Milli-Q water (18.2 M Ω cm^{-1} resistivity). Graphite powder (<20 μm), hydrazine monohydrate (64–65% in aqueous solution), manganese (II) acetate tetrahydrate ($Mn(CH_3COO)_2 \cdot 4H_2O$), and sodium sulfate ($Na_2SO_4$) were obtained from Sigma-Aldrich and used without further purification.

2.2. Preparation of MnO_2/RGO composites

Graphene oxide (GO) was synthesized by a modified Hummers method as described elsewhere [23]. As-prepared GO was dispersed in deionized (DI) water (pH 10) and added the hydrazine monohydrate as reducing agents. The resulting mixture was heated to 95 °C and kept for 2 h, yielding a homogeneous black suspension of RGO. The RGO was collected with filtration, washed with DI water several times, and dried at 90 °C. 20 mg of GO containing 5 wt% of RGO and 1.23 mg of $Mn(CH_3COO)_2 \cdot 4H_2O$ were manually mixed using a mortar and pestle. The RGO was used as a molecular heater to facilitate deoxygenation of GO and formation of MnO_2 nanoparticles under microwave irradiation due to weak microwave absorption ability of GO [24,25]. The resulting powder was transferred to 10 mL glass vial for the microwave irradiation. Subsequently, the glass vial was sealed and directly placed in domestic microwave oven (DAEWOO KR-G20MW, 2450 MHz, 700 W) and then run at highest power level for 10 s.

2.3. Material characterization

Scanning electron microscopy (SEM) images were obtained using a field emission scanning electron microscope (S-4800). High-resolution transmission electron microscopy (HRTEM) images were obtained using a field-emission TEM (JEM2100F, JEOL Ltd.) operated at 200 kV. X-ray diffraction (XRD) data were obtained on a Rigaku D/MAX-2500 (40 kW) with a q/q goniometer equipped with a Cu Kα radiation generator. X-ray photoelectron spectroscopy (XPS) data were obtained using a Thermo MultiLab 2000 system. Thermogravimetric analysis (TGA) was conducted using a TGA 92-18 (Setaram) with a heating rate of 10 °C min^{-1}.

2.4. Electrochemical measurement

All electrochemical measurements were carried out in a three-electrode system: MnO_2/RGO was used as working electrode materials. A platinum wire and Ag/AgCl were used as a counter and reference electrode, respectively. The fabrication of working electrodes was carried out as follows. Briefly, the as-prepared samples, carbon black, and poly(tetrafluoroethylene) were mixed in a mass ratio of 70:25:5 and dispersed in ethanol. The resulting dispersion was immediately coated on the titanium foil (1 × 1 cm^2) current collector, which was followed by drying at 100 °C for 12 h in a vacuum oven. The total mass of each

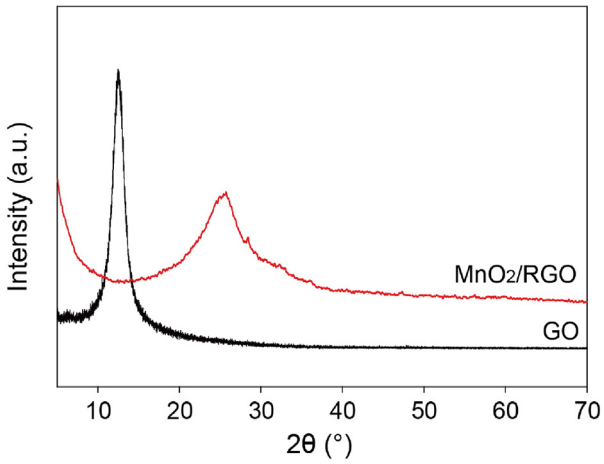

Fig. 2. XRD patterns of MnO_2/RGO and GO samples.