Facile synthesis of three-dimensional graphene/nickel oxide nanoparticles composites for high performance supercapacitor electrodes
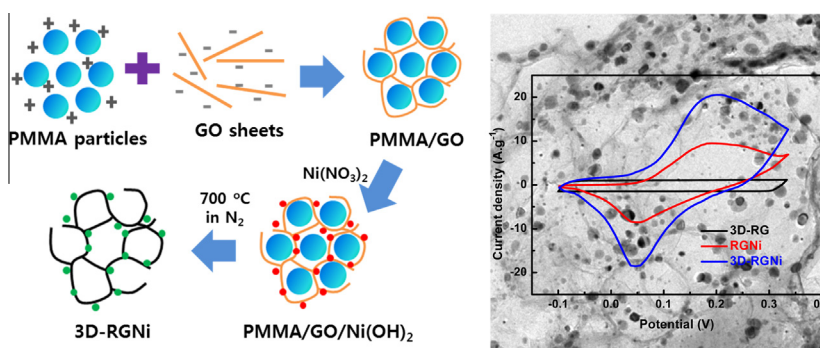
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HIGHLIGHTS

- The 3D porous graphene/NiO nanoparticle composites (3D-RGNi) are synthesized by a facile method.
- The porous reduced graphene decorated with NiO nanoparticles was fabricated from thermal treatment.
- The prepared 3D-RGNi possess the high electrochemically active surface area.
- The 3D-RGNi exhibits a high capacitance of 1328 F g^{-1} with an excellent cycling stability.

GRAPHICAL ABSTRACT

ABSTRACT

This study presents a simple and facile method for preparing three-dimensional (3D) porous reduced graphene oxide (rGO) and NiO nanoparticles composites (3D-RGNi) as high performance supercapacitor electrodes. The 3D porous graphene framework is first produced by the self-assembly of poly(methyl methacrylate) (PMMA) particles and graphene oxide (GO), followed the adsorption of Ni precursor on GO. High-temperature treatment is simultaneously carried out to fabricate the 3D porous structured rGO decorated with NiO nanoparticles. The as-synthesized 3D-RGNi electrode exhibits a high specific capacitance of 1328 F g^{-1} at a current density of 1 A g^{-1} and an excellent cycling stability with 87% retention of the capacitance after 2000 cycles of galvanostatic charge–discharge. These high capacitance performances are attributed to the synergistic effects from the incorporation of the rGO network and NiO nanoparticles, and the highly porous structure of 3D-RGNi. Hence, it is expected that 3D-RGNi might serve as a promising materials for electrochemical energy storage applications.

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1. Introduction

Electrochemical capacitors or supercapacitors are one of the most promising energy storage devices that have attracted consid- erable attention in recent years because of their higher power density than batteries and higher energy density than conventional capacitors [1,2]. Due to their excellent properties, they have been popularly used in electronic device where high power density and long cycle life are of extreme importance, and confirmed to be one of the most significant devices in new generation energy storage area [3,4]. The energy storage mechanism of

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supercapacitors can be divided into double-layer capacitors and pseudocapacitors [5]. Commonly, carbon materials such as activated carbon, carbon nanotubes, and graphene are used as double-layer capacitors electrodes due to their good electric conductivity and large surface area [6–8], and transition metal oxides, such as RuO_2 and MnO_2 are used for pseudocapacitors [9–12]. Among those oxides, RuO_2 exhibits high specific capacitance, wide potential windows, and high electrochemical stability. However, the high cost of raw materials limits its commercial applications. Hence, the inexpensive metal oxide such as CoO_x, NiO, $Co(OH)_2$, and $Ni(OH)_2$ have attracted great interest as the alternative electrode materials. Among them, NiO appears to be a promising alternative due to its low fabrication cost, environmental compatibility and well-defined redox behavior [13,14]. However, NiO usually delivers poor rate capability and reversibility during the charge/discharge process due to its relatively poor electrical conductivity and low accessible surface areas [15,16]. Various efforts have been made to enhance the electrochemical performance of NiO electrodes by preparing hybrids with carbonaceous materials, such as activated carbon [17], carbon nanotubes, and various mesoporous materials [18,19]. On the other hand, graphene, which is a monolayer of carbon atoms arranged in a two-dimensional (2D) honey comb network, has recently attracted considerable attention, because it is believed to be a potential electrode material due to its excellent electric conductivity, high surface area, and chemical stability. Thus, numerous efforts have been made to synthesize graphene-based hybrids with other functional materials to develop practical applications for energy storage. Therefore, many studies on the preparation of graphene/NiO hybrids using various approaches for electrochemical applications have been reported [20–23]. However, graphene based electrodes are limited due to the re-stacking problem caused by the strong π–π interaction and van der Waals forces between graphene sheets, resulting in a small surface area, low electric conductivity, and inferior ion accessibility. It is therefore crucial to fabricate a graphene structure with a high surface area and high conductivity, which is the key to high electrochemical performance using graphene/NiO hybrids [24–29].

Herein, we report a simple and versatile method to produce the three-dimensional porous reduced graphene and NiO nanoparticle hybrids (3D-RGNi) for the supercapacitor electrode. The proposed method involves the formation of poly(methyl methacrylate) (PMMA) particle/graphene oxide (GO) composites and subsequent adsorption of $Ni(OH)_2$ on PMMA/GO composites. Finally a high-temperature treatment is performed to yield the removal of PMMA particles for a 3D porous structure, the reduction of GO for high electric conductivity, and the transformation of $Ni(OH)_2$ into NiO crystal. The as-synthesized 3D-RGNi represented a high specific capacitance of up to 1328 F g^{-1} at a current density of 1 A g^{-1} with excellent cycle stability. This enhanced electrochemical capacitance is obtained from a high surface area and electric conductivity of 3D-RGNi, providing a better ion adsorption and electron transport between the electrode and electrolyte.

2. Experimental

2.1. Preparation of 3D-RGNi

GO was prepared by chemical exfoliation of the expanded graphite powder (grade 1721, Asbury Carbon) through a modified Hummers method by applying the microwave-assisted thermal expansion of graphite powder using the procedure described elsewhere [30]. The obtained GO powder was dispersed in deionized (DI) water for the GO aqueous solution with a concentration of 1.0 mg/ml. PMMA particles were synthesized by surfactant-free emulsion polymerization, and the detailed polymerization proce-

dure is described elsewhere [31]. The synthesized PMMA particles were diluted with deionized water to prepare the PMMA particle aqueous solution with a concentration of 1.0 wt%. Typically, the prepared GO sheets are negatively charged in aqueous solutions, and the synthesized PMMA particles are positively charged in aqueous solutions. To fabricate the GO encapsulated PMMA particles (PMMA/GO) via electrostatic interaction, 50 ml of GO solution was gradually added to 45 ml of PMMA solution with vigorous stirring for 2 h. For the synthesis of NiO nanoparticles on the PMMA/GO particle, 50 ml of $Ni(NO_3)_2$ solution with a concentration of 0.1 M was introduced slowly to 50 ml of PMMA/GO solution, followed by slowly adding a NH_4OH solution with stirring at room temperature for 12 h to anchor the $Ni(OH)_2$ on the graphene layer. The resulting black material of PMMA/GO/$Ni(OH)_2$ was then collected by filtration and thoroughly washed with HCl and DI water to remove unreacted NH_4OH. High-temperature treatment of the as-prepared PMMA/GO/$Ni(OH)_2$ hybrid was conducted to obtain the 3D-RGNi. For the high-temperature treatment, the sample was placed into a quartz tube and heated at the rate of 10 °C/min to 700 °C with N_2 flow for 4 h. As a control, the 3D porous rGO sample (3D-RG) and the simple rGO/NiO composites (RGNi) were also prepared to compare the electrochemical performance with the 3D-RGNi. The 3D-RG was obtained by following the same procedure as that of 3D-RGNi, though without adding $Ni(NO_3)_2$. The RGNi was prepared using the same synthesis procedure, though using only GO sheets instead of PMMA/GO composites.

2.2. Characterizations

The morphology of the samples was characterized using a field-emission scanning electron microscope (FE-SEM, JEOL, JSM-600F) and a high resolution transmission electron microscopy (HR-TEM, JEOL, JEM-2100F). X-ray diffraction (XRD) measurements were conducted at room temperature using a high-power X-ray diffractometer (D/MAZX 2500V/PC, Rigaku) at 40 kV and 30 mA with a scan rate of 2°/min. The chemical composition analysis for the hybrid sample was performed using X-ray photoelectron spectroscopy (XPS, Thermal Scientific) with monochromatic Al Kα radiation with $h\nu$ = 1486.6 eV. Raman spectra (Thermo Scientific) were measured using 532 nm wavelength incident laser light. Fourier transform infrared (FT-IR) spectra were obtained using a Nicolet IR 200 FT-IR spectrometer (Thermo Scientific). Thermal gravimetric analysis (TGA, TA instruments, Q50) was performed under N_2 atmosphere with a heating rate of 10 °C/min. N_2 adsorption measurements (Micromeritics, ASAP 2020) were conducted and the specific surface area was obtained using Brunauer–Emmett–Teller (BET) analysis.

2.3. Electrochemical measurements

Electrochemical measurements were carried out by a three-electrode system, in which a Pt wire was used as a counter electrode and a saturated calomel electrode (SCE) as a reference electrode (in 2 M KOH) and at room temperature. The working electrode was prepared by mixing the electroactive materials, carbon black, and polytetrafluoroethylene (PTFE, Sigma Aldrich) binder in ethanol in a mass ratio of 85:10:5 to obtain a slurry. Then the slurry was casted into thin sheet and dried overnight, and cut into pieces of 3 mm diameter disc. Following, the electrode disc was pressed onto a glassy carbon electrode (GCE) surface under 10 MPa pressure. The mass loading of active material was estimated to be 0.3 mg. Cyclic voltammetry (CV), galvanostatic charge–discharge, and electrochemical impedance spectroscopy (EIS) were performed using a multi-channel potentiostat–galvanostat analyzer (VSP, Bio-logic). The CV measurements were taken between −0.1 and 0.35 V at different scan rates and galvanostatic