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Synthesis of microsphere silicon carbide/nanoneedle manganese oxide composites and their electrochemical properties as supercapacitors

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HIGHLIGHTS

- Oxygen-containing functional groups are introduced on the SiC surface.
- Nanoneedle MnO_2 is formed on the SiC surface using functional groups.
- SiC/nanoneedle MnO_2 composites are studied as cathode for capacitor in 1 M Na_2SO_4.
- The material has specific capacitance of 273.2 F g^{-1} with a scan rate of 10 mV s^{-1}.

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ABSTRACT

Synthesis of microsphere silicon carbide/nanoneedle MnO_2 (SiC/N–MnO_2) composites for use as high-performance materials in supercapacitors is reported herein. The synthesis procedure involves the initial treatment of silicon carbide (SiC) with hydrogen peroxide to obtain oxygen-containing functional groups to provide anchoring sites for connection of SiC and the MnO_2 nanoneedles (N–MnO_2). MnO_2 nanoneedles are subsequently formed on the SiC surface. The morphology and microstructure of the as-prepared composites are characterized via X-ray diffractometry, field-emission scanning electron microscopy, thermogravimetric analysis, and X-ray photoelectron spectroscopy. The characterizations indicate that MnO_2 nanoneedles are homogeneously formed on the SiC surface in the composite. The capacitive properties of the as-prepared SiC/N–MnO_2 electrodes are evaluated using cyclic voltammetry, galvanostatic charge/discharge testing, and electrochemical impedance spectroscopy in a three-electrode experimental setup using a 1-M Na_2SO_4 aqueous solution as the electrolyte. The SiC/N–MnO_2(5) electrode, for which the MnO_2/SiC feed ratio is 5:1, displays a specific capacitance as high as 273.2 F g^{-1} at 10 mV s^{-1}.

1. Introduction

Over the past few years, rapid development of methods for harnessing renewable energy (e.g., solar and wind energy) has increased the need for sustainable energy storage technologies to address the challenges of increasing energy demand and the cyclic nature of renewable energy sources [1–4]. The high power density, moderate energy density, good operational safety, and long cycling life of electrochemical double layer capacitors or supercapacitors have fueled extensive exploration of these promising technologies for various emerging energy applications such as in high-power electronic devices, electric vehicles, and hybrid electric vehicles [5–7].

Generally, supercapacitors can be classified into one of the two categories based on their energy storage mechanism: electric double layer capacitors (EDLCs) and pseudocapacitors [8,9]. High surface area carbon has typically been used as an electrode material for EDLC given that it is convenient for storing energy in a double layer formed on the electrode surface. Conversely, most of the electrode materials used in pseudocapacitors consist of conductive polymers and metal oxides, which transfer faradic charges between an electrolyte and electrode. Therefore, to enhance the energy density of supercapacitors, many researchers have utilized hybrid materials in which the electrode materials for EDLCs are combined with other redox

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pseudo-capacitive materials [10,11]; however, most of the research has focused on the application of the combination of graphene with metal oxides or a conductive polymer [12–15].

Recently, novel approaches have been proposed for application of semiconductor or cermet nanowires as EDLC electrode materials instead of traditional carbon materials such as activated carbons, aerogels, carbon nanotubes, and graphene. The application of silicon nanowires, silicon carbide nanowires, titanium nitride nanowires, and titanium dioxide nanotubes and nanowires as EDLC electrode materials has attracted much attention because these materials offer the merits of high specific surface area and electrical conductivity [16–21]. However, these materials are suitable for micro-supercapacitor electrodes because the working materials are grown directly on the current collector. In this regard, there is no literature on the application of semiconductor or cermet nanowires for use in macroscale supercapacitors as EDLC electrode materials. Furthermore, hybrid composites that combine semiconductor and redox pseudocapacitive materials have not been reported.

Metal oxide electrode materials are particularly attractive for redox pseudo-capacitive materials due to their high capacitance and fast redox kinetics. Manganese oxide (MnO_2) has been distinguished as the most promising transition metal oxide for next generation supercapacitors due to its high energy density, low cost, environmental friendliness, and natural abundance [22,23]. Some studies have attempted to achieve enhanced specific capacitance by preparation of MnO_2 with different morphologies in order to increase the specific area of MnO_2. Based on synthesis of MnO_2 with different crystallographic forms (α, γ) and morphologies (needles, rods, and spindles) and evaluation of their electrochemical performance, Chen et al. reported that needle-like MnO_2 samples exhibited greater specific capacitance than the other forms [24]. Similarly, Devaraj and Munichandraiah investigated the effect of the crystallographic structure of MnO_2 on its electrochemical capacitance properties and found that MnO_2 with α- and δ-crystallographic structures exhibited greater specific capacitance [25].

Chen et al. successfully created electrode materials by combining graphene oxide (GO) with nanoneedle MnO_2 for application of nanoneedle MnO_2 and electrode combination materials to EDLCs, and demonstrated that nanoneedle MnO_2 can be homogeneously dispersed on GO sheets using various functional groups [26]. Kim et al. suggested the use of activated carbon/nanoneedle MnO_2 composites obtained using oxygen-containing functional groups that were introduced by thermal treatment of activated carbon [27]. On the basis of their research, oxygen-containing functional groups appear to be essential for fabricating carbon-based EDLC materials/nanoneedle MnO_2 composites because the functional groups act as anchor sites enabling the homogeneous attachment of nanoneedle MnO_2 to the surface of the EDLC materials.

We report herein, the synthesis of microsphere silicon carbide and nanoneedle MnO_2 composites based on the anticipation that the nanoneedle MnO_2 should promote reversible pseudocapacitance of electrodes constructed from the composite, whereas silicon carbide should act as the support for the formation of MnO_2 nanoneedles and the electronic conductive channels, thereby impacting the electrical double layer properties. The strategy involves creating oxygen-containing functional groups as anchorage sites for connecting the silicon carbide and MnO_2 nanoneedles to obtain a homogeneous dispersion of MnO_2 by treating silicon carbide with hydrogen peroxide. The morphology and microstructural characteristics of the silicon carbide/MnO_2 nanoneedle composites are investigated in detail, and the electrochemical performance of each composite is also investigated on the basis of cyclic voltammetry (CV), galvanostatic charge/discharge experiments, and electrochemical impedance spectroscopy (EIS). The specific capacitance and capacitance retention are also analyzed.

2. Experimental

2.1. Raw materials

The microsphere silicon carbide (the average particle diameter, 30 μm; >99% purity) used in this study were supplied by LG Innotek (Ansan, Korea). Hydrofluoric acid (HF, HPLC grade, Samchun Chemical, Pyungteak, Korea), Hydrogen peroxide (H_2O_2, HPLC grade, Samchun Chemical, Pyungteak, Korea), Isopropyl alcohol (IPA, HPLC grade, Samchun Chemical, Pyungteak, Korea) and *N*-methylpyrrolidone (NMP, HPLC grade, Samchun Chemical, Pyungteak, Korea) were used as received. Manganese(II) chloride tetrahydrate ($MnCl_2 \cdot 4H_2O$, Aldrich, Seoul), Potassium permanganate ($KMnO_4$, Aldrich, Seoul), Poly(vinylidenefluoride) (PVDF, Aldrich, Seoul) and deionized water (DI water, HPLC grade, Aldrich, Seoul) were purchased from Sigma Chemical. All of the chemicals were used without further purification.

2.2. Synthesis of silicon carbide/MnO_2 composites

The residual SiO_2 layer adsorbed on the surface of the microsphere SiC particles was removed by treatment with hydrofluoric acid (HF). In a typical synthesis, 120 g of SiC powder (hereafter, Raw SiC) was placed in 300 mL of 10% HF solution and stirred for 24 h. Subsequently, the sample was leached with distilled water until the pH of the leaching water reached 7–8. These samples were denoted as HF–SiC. In order to introduce the oxygen-containing functional groups on the SiC surface, HF-treated SiC powder was dispersed in a 34% hydrogen peroxide (H_2O_2) solution and heated to 85 °C for 24 h with vigorous stirring. The resulting mixture was filtered, washed several times, and dried in a vacuum oven at 60 °C for 24 h. The resulting products were denoted as H_2O_2–SiC. The H_2O_2-treated microsphere silicon carbide/nanoneedle MnO_2 (SiC/N–MnO_2) composite produced using a MnO_2/SiC feed ratio of 1:1 (SiC/N–MnO_2(1)) was synthesized as follows: SiC (0.05 g) and $MnCl_2 \cdot 4H_2O$ (0.068 g) were dispersed in isopropyl alcohol (50 mL) with ultrasonication for 0.5 h. Subsequently, the mixture was heated to approximately 85 °C in a water-cooled condenser with vigorous stirring; $KMnO_4$ (0.036 g) dissolved in 5 mL of DI water was then added to the boiling solution. The resulting mixture was filtered, washed several times, and dried in a vacuum oven at 60 °C for 24 h. The products were denoted as SiC/N–MnO_2(1) and SiC/N–MnO_2(5) corresponding to MnO_2/SiC feed ratios of 1:1 and 5:1, respectively.

2.3. Characterization methods

X-ray diffraction (XRD) patterns were collected (New D8-Advance/Bruker-AXS) at a scan rate of $1^\circ\ s^{-1}$ within the 2θ range 10°–80° using $CuK_{\alpha1}$ radiation (0.154056 nm). Field-emission scanning electron microscopy (FE-SEM, SIGMA, Carl Zeiss) was used to examine the morphology of the prepared samples. X-ray photoelectron spectroscopy (XPS) analysis was performed on a VGMicrotech ESCA2000 system using a spectrometer with a Mg Kα X-ray source (1253.6 eV) and a hemispherical analyzer. During the curve fitting, the Gaussian peak widths were constant in each spectrum. Thermogravimetric analysis (TGA) was performed on a TA Instruments TGA-2050 apparatus at a heating rate of $10\ ^\circ C\ min^{-1}$ in air.

2.4. Preparation and characterization of supercapacitors

Working electrodes were fabricated as follows. First, the as-prepared materials and poly(vinylidenefluoride) (PVDF) were mixed in a mass ratio of 95:5 and dispersed in *N*-methylpyrrolidone (NMP). The resulting mixture was then coated onto a nickel foam