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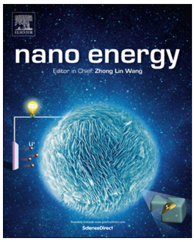

RAPID COMMUNICATION

Porous MnO/Mn_3O_4 nanocomposites for electrochemical energy storage

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Abstract

Controlling the morphology of nanostructured manganese oxide materials can be an effective way to improve capacitance for supercapacitor applications. Herein we demonstrated for the first time the synthesis of MnO/Mn_3O_4 nanocomposite tetrahedrons with a porous structure, and a new method to synthesize porous urchin-shaped MnO/Mn_3O_4 nanocomposite. Compared with the non-porous MnO nanocrystalline octahedrons and the mixture of non-porous MnO and Mn_3O_4, the porous MnO/Mn_3O_4 nanocomposite 'urchins' exhibited superior capacitance in supercapacitor application, while the porous MnO/Mn_3O_4 nanocomposite tetrahedrons displayed superior stability. The excellent capacitance and stability of these nanocomposites could be explained in terms of the much higher surface area associated with their porous structure. These porous nanostructures offered a good model to investigate the effects of morphology and surface area on the capacitance of nanocomposites.

Introduction

Energy storage systems such as rechargeable batteries and electrochemical supercapacitors are of great interest in recent years due to the emergence of applications such as electrical vehicles, personal multimedia systems, wearable medical devices and portable electronic devices [1-5]. Supercapacitors, with the advantages of high power density, fast charging, long cycling life over lithium ion batteries, are considered to be one of the most promising energy storage systems for future needs [6-10]. Supercapacitors store energy using either ion adsorption at the electron/electrolyte interface (electrical double-layer capacitors) or fast and reversible redox reactions in the electrode materials (pseudocapacitors). As supercapacitor electrode materials, pseudocapacitive transition metal oxides have attracted significant attention because of their higher energy density than the electrochemical double-layer capacitive carbon materials [11-16]. Among the various transition metal oxides, manganese oxides (MnO, MnO_2, M_3O_4 and Mn_2O_3) possess the unique advantages of high specific capacitance (1233 F g^{-1} for MnO_2), various oxidation states and crystal structures, low cost, and high abundance, which make it a promising candidate as an electrode material for supercapacitors [17-22]. In addition, MnO_x-based electrodes can

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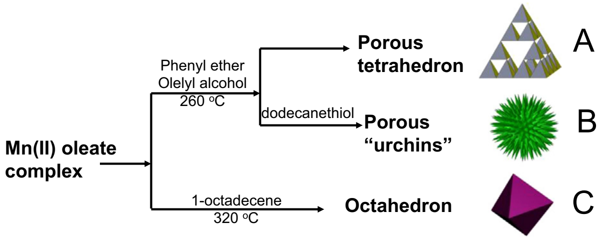
work in neutral aqueous electrolytes, which is ideal for large-scale systems [23,24]. The capacitance of MnO_x is dependent on many factors, such as porosity, morphology, cation distributions, oxidation state(s) and crystal structure [25-29]. Brousse et al. studied different MnO_2 polymorphs and found that the capacitance of the crystallized materials is dependent on the crystalline structure [27]. Chen et al. and Devaraj et al. studied different crystallographic MnO_2 forms, and found that the α and δ structures offer high capacitance [28,29]. However, due to the low conductivity of MnO_x, the charge storage all occur within a thin layer of the surface, resulting in a much lower capacitance than the theoretical value. It has been shown that ultrathin films of MnO_2 can achieve a high capacitance, suggesting that nanostructured materials may allow for access to the storage sites in the entire MnO_x [30,31]. In particular, nanostructured MnO_x with precisely controlled morphology may be of great interest for supercapacitor applications.

When MnO_x is used as electrode for supercapacitor applications, it undergoes redox reactions through either intercalation of a charge carrier cation into the van der Waals gaps of the materials, or chemisorption at the surface. The latter is kinetically more facile because there is no need for long-range diffusion of ions through the van der Waals gaps [31,32]. Therefore, the surface is actively involved in the charge storage process for MnO_x electrode in supercapacitors. A rational design to maximize the electrochemically active sites for redox reactions would be to increase surface area via the creation of porosity in these materials. Herein we reported for the first time the synthesis of porous MnO/Mn_3O_4 nanocomposite tetrahedrons (Scheme 1A), and investigated their application as supercapacitor using neutral aqueous electrolytes (1 M Na_2SO_4). We have also developed a new method to synthesize porous MnO/Mn_3O_4 nanocomposite with an urchin-like morphology, and evaluated its properties as a supercapacitor. For comparison, conventional non-porous MnO nanocrystalline octahedrons and non-porous Mn_3O_4 nanocrystals were prepared and examined. The capacitance and stability of MnO_x materials were strongly dependent on their morphologies and surface areas. Porous MnO/Mn_3O_4 nanocomposite 'urchins' exhibited superior capacitance, while the porous MnO/Mn_3O_4 nanocomposite tetrahedrons displayed excellent stability.

Experimental

Chemicals

Manganese(II) chloride tetrahydrate ($MnCl_2 \cdot 4H_2O$, 98%), sodium oleate [$CH_3(CH_2)_7CH{=}(CH_2)_7COONa$, 95%], oleyl alcohol (technical grade, 60%), phenyl ether (90%), dodecanethiol (90%), 1-octadecene (90%), methanol (98%) and hexane (99%) were purchased from Sigma-Aldrich. All glassware and Teflon-coated magnetic stir bars were cleaned with aqua regia, followed by copious rinsing with deionized water before drying in an oven.



Scheme 1 Synthesis of manganese oxide nanomaterials as (A) porous tetrahedrons, (B) porous 'urchins', and (C) non-porous octahedrons.

Materials characterization

The products were characterized by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) (FEI Tecnai G^2 F20 electron microscope). Samples for TEM studies were prepared by placing a drop of the solution on a copper grid coated with a thin carbon film, and then evaporating it in air at room temperature. X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max-3B diffractometer using Cu K_α radiation (λ=1.54056 Å). X-ray photoelectron spectroscopy (XPS) spectra were obtained with an ESCALAB MKII spectrometer (VG Scientific) using Al-K_α radiation (1486.71 eV).

Synthesis of porous MnO/Mn_3O_4 nanocomposite tetrahedrons

MnO/Mn_3O_4 nanocomposites were synthesized by thermal decomposition of Mn(II) oleate complex following a published procedure [33]. In a typical synthesis of Mn(II) oleate complex, manganese chloride ($MnCl_2 \cdot 4H_2O$, 3.96 g, 20 mmol) and sodium oleate (12.08 g, 40 mmol) were added to a solvent mixture of ethanol (40 mL), deionized water (30 mL), and hexane (70 mL). The mixture was refluxed at 70 °C for 4 h; the upper hexane layer containing the Mn (II) oleate complex was separated, and washed several times with deionized water. Hexane was evaporated in a rotary evaporator, yielding the Mn(II) oleate complex. For the synthesis of porous MnO/Mn_3O_4 tetrahedrons, Mn(II) oleate (1.24 g) was dissolved in phenyl ether (10 mL) and oleyl alcohol (4 mL). The mixture was heated up to 260 °C for 1 h under argon. The resulting solution was cooled to room temperature. The nanoparticles in the solution were precipitated by methanol, and washed twice with methanol to remove the free ligands, followed by re-dispersion in hexane. The nanoparticles were collected *via* centrifugation, and dried at room temperature in vacuum.

Synthesis of porous MnO/Mn_3O_4 nanocomposite 'urchins'

For the synthesis of porous MnO/Mn_3O_4 nanocomposite 'urchins', Mn(II) oleate (1.24 g) was dissolved in phenyl ether (10 mL), 1-dodecanethiol (1 mL) and oleyl alcohol (4 mL). The mixture was heated to 260 °C for 1 h under argon, and the solution was cooled to room temperature.

Synthesis of non-porous MnO nanocrystalline octahedrons

For the synthesis of MnO nanocrystalline octahedrons, Mn(II) oleate (1.24 g) was dissolved in octadecene (10 mL) [33]. The mixture was heated to 320 °C for 1 h under argon. The resulting solution was cooled to room temperature. The nanoparticles in the solution were precipitated by methanol, washed twice with methanol to remove the free ligands, and