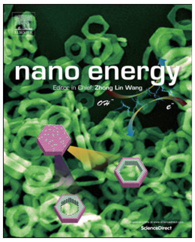
Nano Energy (2014) **5**, 28-35

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/nanoenergy



RAPID COMMUNICATION

Facile structural tuning and compositing of iron oxide-graphene anode towards enhanced supacapacitive performance

Q.X. Low[a], G.W. Ho[a,b,*]

[a]Engineering Science Programme, National University of Singapore, Singapore
[b]Department of Electrical and Computer Engineering, National University of Singapore, 4 Engineering Drive 3, 117576 Singapore, Singapore

Received 26 November 2013; received in revised form 8 January 2014; accepted 21 January 2014
Available online 31 January 2014

KEYWORDS
Fe_2O_3;
Nanoparticles;
Nanorods;
Graphene;
Supercapacitor;
Hydrothermal

Abstract

Hydrothermal has been demonstrated to effectively tune the various morphologies of nanostructured Fe_2O_3 materials from 0D nanoparticles, 1D nanorods to self-assembled nanorods which form 3D ovoid architecture. Subsequently, compositing and reduction of graphene oxide (GO) were carried out simultaneously via facile base reduction. The as-synthesized nanocomposite was fabricated into an electrode material of hybrid supercapacitor and characterized by cyclic voltammetry (CV), and galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS). The synergistic effects of highly uniform 1D Fe_2O_3 nanorods of low internal resistance, enhanced ion diffusion as well reduced graphene sheets incorporation lead to superior electrochemical performances. The nanocomposite exhibits pseudocapacitive properties of high specific capacitance $\sim$504 F g^{-1} at 2 mA/cm^2. Although many metal oxide and reduced GO hybrid systems have been investigated as electrode materials, this study demonstrates simple and effective tuning of Fe_2O_3 nanostructures morphologies to significantly impact the pseudocapacitive performances.

Introduction

Hybrid capacitor utilizes both Faradaic and non-Faradaic processes to store charges hence exploit the advantages of electrochemical double-layer (EDL) capacitors and pseudocapacitors characteristics to achieve enhance energy and power densities. To fabricate an effective composite supercapacitor, carbon-based materials are commonly integrated with either conducting polymer or metal oxide materials. The carbon-based materials provide capacitive double-layer charge and high surface area matrix to increase contact between the deposited pseudocapacitive materials and electrolyte. On the other hand, the conducting polymer or metal oxide materials aim to improve the pseudocapacitance through Faradaic reactions. However, metal oxide is

---

[*] Corresponding author. Tel.: +65 65168121.
E-mail address: elehgw@nus.edu.sg (G.W. Ho).

2211-2855/$ - see front matter © 2014 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.nanoen.2014.01.002

commonly used over conducting polymer for pseudocapacitive properties since there is a lack of efficient, n-doped conducting polymer. Furthermore, the charge-discharge cycle instability of conducting polymer hampers its development as pseudocapacitive material. There have been many studies on transition metal oxides as electrode material in pseudocapacitors. One of the most promising electrode materials is hydrous ruthenium dioxide (RuO_2), which exhibits pseudocapacitance as high as $720\,F\,g^{-1}$. However, its toxic nature and high cost limit its commercial applications [1]. Other transition metal oxides such as manganese oxide (MnO_2), nickel oxide (NiO) and cobalt oxide (Co_3O_4) have also been intensively investigated as potential materials for electrochemical capacitors [2-7]. Even though these classes of metal oxides have been well-established for its electrochemical energy storage applications, there is still a high demand to explore alternative electrode materials that is cost-effective, non-toxic and yet exhibit superior capacitive behavior.

Iron oxide is one of the most studied transition metal oxides for various technological applications [8]. Two commonly examined iron oxide phases are hematite, α-Fe_2O_3 and magnetite, Fe_3O_4. Hematite has its Fe ions in a trivalent state (ferric Fe), where each of its oxygen atoms is bonded to two Fe ions, and therefore, only two out of three available oxygen octahedrons are occupied. This arrangement makes the structure neutral with no charge excess or deficit, making it a chemically stable compound. It has n-type conductivity (E_g=2.1 eV) with highly chemical and thermodynamical stable structure [9] hence allow it to be a promising pseudocapacitor electrode material with respect to both its high specific capacitance and cost effectiveness [10-12].

Synthesis of functional iron oxide nanostructures in different dimensional and morphologies has always fascinated researchers because of their versatile range of scientific and technological applications. Though many aqueous chemical methods are widely known to synthesize iron oxides nanomaterials, tailoring morphologies in nano dimension still remains a challenging task. Here, we demonstrated a facile synthetic route towards tunable Fe_2O_3 nanostructures from 0D nanoparticles, 1D nanorods to 3D self-assembled nanorods composited with rGO and investigated their morphology dependent electrochemical properties. An added advantage of this method is its non-templated synthesis avenue towards large scale and economical production. Although many metal oxide and rGO hybrid systems have been investigated as electrode materials, this study demonstrates simple and effective tuning of Fe_2O_3 nanostructures morphologies as one of the predominant factors to significantly enhance pseudocapacitive performances.

Material and methods

In a typical procedure, 0.32 g of H_3BO_3 was added to 10 ml of DI water followed by 2.3 ml of the 2.0 M aqueous $FeCl_3$ and 1.75 ml of the 4 M aqueous NaOH solution. The molar ratio of $FeCl_3/H_3BO_3/NaOH$ was 2:3:4. The mixture was stirred and transferred to a teflon-lined autoclave and heated at 90 °C for 12 h. The resultant nanorods (NR) product was washed and dried overnight to form powder. To obtain Fe_2O_3 nanoparticles (NP) and assembled nanorods (ANR) which forms ovoid architecture, the molar ratio of $FeCl_3/H_3BO_3/NaOH$ was tuned to 2:3:6 and 2:1:6 respectively. The growth temperature was set at 120 °C for 12 h. Finally, reduction and compositing of GO were carried out simultaneously. 10 ml of 2 mg/ml GO solution (produced by modified Hummers method) was added to 10 ml of methanol and DI water for photo and base reduction methods respectively. Then, 20 mg of the as prepared Fe_2O_3 sample was added to the solution. The photo reduction was carried out by a 300 W Xe lamp (Excelitas, PE300BFM) illumination for 3 h under constant stirring. The base reduction method was carried out by addition of 1 ml NaOH (4 M) solution under 1 h reflux at 90 °C. Finally, the nanocomposite was washed and dried for further characterizations.

Scanning electron microscopy (SEM) characterization was carried out using a JEOL FEG JSM 6700F field-emission operating at 15 kV. X-ray photoelectron spectroscopy (XPS), VG ESCALAB 220I-XL system equipped with an Mg Kα x-ray source was employed chemical composition studies. X-ray diffraction (XRD) was carried out on a Philips X-ray diffractometer with Cu Kα radiation (λ=1.541 Å). The crystalline structures were analyzed using transmission electron microscopy (TEM, Phillips FEG CM300) operated at 200 kV.

A three-electrode system, a Pt foil and a Ag/AgCl were used as the counter and reference electrodes, respectively. The working electrode consists of the nanocomposite slurry coated on a stainless steel mesh. All 3 electrodes were immersed in an aqueous 1 M Na_2SO_4 electrolyte to evaluate the capacitive performances of the electrode materials. Cyclic Voltammetry (CV), Galvanostatic Charge Discharge (GCD) and Electrochemical Impedance Spectroscopy (EIS) measurements were conducted using the Versastat 4000 Potentiostat/Galvanostat (Metek) to test the capacitance and internal resistance of the electrochemical cell. In CV test, scan rates of 0.02, 0.05 and 0.1 V/s were carried out within a fixed potential window of −1.0 to 0 V for all the CV measurements. In GCD measurement, charge and discharge of the electrochemical cell were conducted at a constant current. Multiple loops of chronopotentiometry measurements using both forward and reverse current in each loop were conducted. The specific capacitance was calculated from galvanostatic discharge according to the formula:

$$C = \frac{I}{(\Delta V/\Delta t)m} \qquad (1)$$

where I is the discharge current (A), $\Delta V/\Delta t$ is the best fit slope of the discharge curve after the IR drop, Δt is the discharge time (s) and m is mass of the electroactive material (g). In potentiostatic EIS mode, a DC voltage superimposed by a sinusoidal AC excitation signal was applied to the electrochemical cell. During testing, the frequency of the input signal was varied and the AC response was measured to calculate the impedance Z of the system. The data, in the form of Nyquist plot was plotted, where Z_{im} and Z_{re} refer to the imaginary and the real parts of the complex impedance. The EIS measurements were recorded under AC voltage amplitude of 5 mV, frequency range of 100 kHz to 0.01 Hz at 0 V reference.