Journal of Solid State Chemistry 184 (2011) 1421–1427

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

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

Green synthesis of graphene nanosheets/ZnO composites and electrochemical properties

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ARTICLE INFO

Article history:
Received 19 November 2010
Received in revised form
27 January 2011
Accepted 3 March 2011
Available online 12 April 2011

Keywords:
Graphene nanosheet
ZnO
Composite electrode
Supercapacitor

ABSTRACT

A green and facile approach was demonstrated to prepare graphene nanosheets/ZnO (GNS/ZnO) composites for supercapacitor materials. Glucose, as a reducing agent, and exfoliated graphite oxide (GO), as precursor, were used to synthesize GNS, then ZnO directly grew onto conducting graphene nanosheets as electrode materials. The small ZnO particles successfully anchored onto graphene sheets as spacers to keep the neighboring sheets separate. The electrochemical performances of these electrodes were analyzed by cyclic voltammetry, electrochemical impedance spectrometry and chronopotentiometry. Results showed that the GNS/ZnO composites displayed superior capacitive performance with large capacitance (62.2 F/g), excellent cyclic performance, and maximum power density (8.1 kW/kg) as compared with pure graphene electrodes. Our investigation highlight the importance of anchoring of small ZnO particles on graphene sheets for maximum utilization of electrochemically active ZnO and graphene for energy storage application in supercapacitors.

1. Introduction

The increasing demand for energy and growing concerns about air pollution, global warming and the development of renewable energy production, hybrid electric vehicles with low CO_2 emission have stimulated intense research on energy storage and conversion from alternative energy sources [1]. Supercapacitors (SCs), also called electrochemical supercapacitors (ESCs) or ultracapacitors, are considered as promising candidates for energy storage due to high power performance, long cycle life, and low maintenance cost [2,3]. Compared with secondary batteries, supercapacitors can provide high power in short-term pulses, and can be used as peak-power sources in hybrid electric vehicles, memory backup devices, or back-up supplies to protect against power disruption [4].

Supercapacitors can be categorized into two main types based on their charge-storage mechanisms: (i) electrical double-layer capacitors (EDLCs), where the electrical charge is stored at the interface between the electrode and the electrolyte; (ii) redox electrochemical capacitors, where capacitance arises from reversible Faradaic reactions taking place at the electrode/electrolyte interface [2]. To date, carbon materials [5], transition metal oxides [6–11] and conducting polymers [12–15] have been identified as most promising materials for SCs. However, each material has its unique advantage and disadvantage for SCs application. For example, carbon material has high power density and long life cycle, but the small double layer capacitance limits its application. Transition metal oxides, hydroxides and conducting polymers have relative higher capacitance and fast redox kinetics, while the relative low mechanical stability and cycle life are major limitations for SCs. If different kinds of materials are integrated into the electrodes of SCs, their capacitive performance will be enhanced largely because most of the redox electrochemical (pseudo-capacitive) materials can contribute higher capacitance to the total capacitance, apart from the double-layer capacitance of carbon materials.

As a rising star in carbon family, two-dimensional graphene has attracted a great deal of attention due to its high surface area, electrical conductivity, high flexibility and mechanical strength since its discovery in 2004 [16,17]. Recently, one new perspective is to utilize ideal single-atom-thick GNS as a support to anchor functional nanomaterials to form new nanocomposites with potential application in catalysis, light energy conversion, fuel cells [18]. This perspective opens up new opportunities for designing next-generation electronic and energy conversion

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0022-4596/$ - see front matter
doi:10.1016/j.jssc.2011.03.006

devices [19], since GNS has been shown excellent electrochemical behavior as electrodes of SCs [20–22]. Williams et al. [23] used a UV-assisted photocatalytic method to obtain photoactive graphene-semiconductor composites, opening up a new way to synthesize graphene-based nanocomposite materials. Wang et al. [7] made $Ni(OH)_2$ nanoplates grown on graphene, as advanced electrochemical pseudocapacitor materials, which exhibit a high specific capacitance and excellent cycling ability. Li et al. [24] fabricated SnO_2/graphene composite electrode materials by reducing graphene oxide with $SnCl_2$ and studied their application in SCs. GNS composites have shown its superior property as supercapacitor materials. However, research on the potential of graphene/metal oxide composite materials for supercapacitors has so far been limited.

ZnO, as a potential semiconductor with large band gap (3.37 eV), has received enormous scientific attention because of its promising applications [25–27]. And, ZnO is a well-known battery active material having high energy density of 650 A/g [28,29]. Recently, it has been used as a potential candidate for supercapacitor application. Selvakumar et al. [30] have fabricated nano ZnO/activated carbon composite electrodes for the first time which showed a specific capacitance of 84 F/g and good electrochemical reversibility. Lu et al. [31] successfully synthesized graphene/ZnO electrode materials by ultrasonic spray pyrolysis, which exhibited a specific capacitance of 61.7 F/g and maximum power density of 4.8 kw/kg. ZnO, therefore, is a promising electrode material for supercapacitors due to its electrochemical activity and eco-friendly nature.

In this work, we employed a green and facile approach to prepare GNS/ZnO composites. First, graphene nanosheets were synthesized via using glucose as a reducing agent [32], then ZnO was directly grown onto conducting graphene nanosheets to obtain GNS/ZnO composites. With this method the reductant and the oxidized product are environmentally friendly. And, the small ZnO particles homogeneously anchor onto graphene sheets, performing as spacers to keep neighboring sheets separate. The graphene sheets overlap with each other so that this factor not only affords a three-dimensional conducting network for fast electron transfer between the active materials and the charge collector, but also improves the contact between the electrode materials and the electrolyte. Electrochemical tests showed that these composites have a good reversible capacity, high coulombic efficiency, and excellent cyclic performance.

2. Experimental

2.1. Synthesis of GNS/ZnO composites

All the chemicals were of analytical grade and were used without further purification. The GNS/ZnO composites were synthesized via an in situ crystallization technique. GO was prepared from natural graphite by a modified Hummers method as described previously [33]. Exfoliation of GO was achieved by ultrasonication of the dispersion using an ultrasonic bath (KQ-500DB, 250 W). Compared with the traditional procedure using highly toxic hydrazine as reductant for chemical conversion of GO to GNS, we used glucose as a reducing agent to prepare GNS. Typically, 2 g glucose was added into 250 mL of homogeneous GO dispersion (0.5 mg/mL), followed by stirring for 30 min. Then 1 mL ammonia solution (25% w/w) was added to the resulting dispersion. After vigorously shaking for a few minutes, the mixture was stirred for 60 min at 95 °C. The resulting black dispersion was then filtered and washed with water for several times and the obtained GNS was redispersed in water for further use.

To synthesize GNS/ZnO composites, 250 mL of the as-obtained GNS suspension (0.5 mg/L) was transferred into a round bottom flask, then a certain amount of $Zn(NO_3)_2$ and NaOH solution (mole ratio was 1:10) was added into the above GNS suspension. The mixture was then heated to 95 °C with stirring for 5 h. We obtained GNS/ZnO composites with different mass ratios (GNS:ZnO was, respectively, 1:1, 1:2 and 1:3) by changing the amounts of GNS and ZnO. Finally, the composites were filtered, and washed several times with distilled water and alcohol, and dried at 80 °C for 12 h in a vacuum oven.

2.2. Characterization methods

The crystallographic structures of the materials were characterized by a powder X-ray diffraction system (XRD, TTR-III) equipped with Cu $K\alpha$ radiation ($\lambda=0.15406$ nm). Raman measurements were performed with a Jobin Yvon HR800 micro-Raman spectrometer at 457.9 nm. The microstructure of the samples was investigated by an atomic force microscopy (AFM, Nanoscope IIIa), scanning electron microscopy (SEM, JEOL JSM-6480A microscope) and a transmission electron microscopy (TEM, PHILIPS CM 200 FEG, 160 kV).

2.3. Preparation of electrodes and electrochemical characterization

The working electrodes were fabricated by mixing the prepared powders with 15 wt% acetylene black and 5 wt% polytetrafluorene–ethylene (PTFE) binder. A small amount of ethanol was added to the mixture to produce a homogeneous paste. Then the resulting mixture was coated onto the nickel foam substrate (1 cm × 1 cm) with a spatula. The amount of composites onto the electrode including the electroactive material, conducting agent and binder was approximately 10 mg. The electrochemical properties of as-obtained products were investigated under a three-electrode cell configuration: The Ni foam coated with GNS/ZnO composites was used as working electrode, platinum foil (1 cm × 1 cm) and a saturated calomel electrode (SCE) as the counter and reference electrodes, respectively. The measurements were carried out in a 1 M KOH aqueous electrolyte at room temperature. Cyclic voltammograms (CV), galvanostatic charge/discharge and electrochemical impedance spectroscopy (EIS) were measured by a CHI 760b electrochemical work station. CV tests were done between -0.6 and 0.3 V (vs. SCE) at different scan rates of 5, 10, 20, and 40 mV s^{-1}. Galvanostatic charge/discharge curves were measured in the potential range of -0.6 to 0.2 V (vs. SCE) at different current densities of 5, 10, and 20 mA cm^{-2}, and EIS measurements were also carried out in the frequency range from 100 kHz to 0.05 Hz at open circuit potential with an ac perturbation of 5 mV.

3. Results and discussion

3.1. Formation mechanism and microstructure characterizations

Fig. 1 illustrates the fabrication process and formation mechanism for ZnO/GNS composites. As shown by previous studies, GO sheets have their basal planes covered mostly with epoxy and hydroxyl groups, while carbonyl and carboxyl groups are located at the edges [23]. These functional groups, acting as anchor sites, enable the subsequent in situ formation of nanostructures to attach to the surfaces and edges of GO sheets. However, these oxygen-containing functional groups impair the conductivity of GO sheets to such an extent that the GO sheets are not suitable for electrode materials. On the other hand, GNS have an excellent conductivity, with ideal single-atom thick