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Full Length Article

Monodisperse MnO_2@$NiCo_2O_4$ core/shell nanospheres with highly opened structures as electrode materials for good-performance supercapacitors

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ABSTRACT

The monodisperse MnO_2@$NiCo_2O_4$ core/shell nanospheres for good-performance supercapacitors are designed and synthesized by a two-step solution-based method and a simple post annealing process. In the composite, both MnO_2 (the "core") and $NiCo_2O_4$ (the "shell") are formed by the accumulation of nanoflakes. Thus, nearly all the core/shell nanoflakes are highly opened and accessible to electrolyte, making them give full play to the Faradaic reaction. Our results demonstrate that the composite electrode exhibits desirable pseudocapacitive behaviors with higher specific capacitance (1127.27 F g^{-1} at a current density of 1 A g^{-1}), better rate capability (81.0% from 1 to 16 A g^{-1}) and superior cycling stability (actually 126.8% capacitance retention after 1000 cycles and only 3.7% loss after 10,000 cycles at 10 A g^{-1}) in 3 M KOH aqueous solution. Moreover, it offers the excellent specific energy density of 26.6 Wh kg^{-1} at specific power density of 800 W kg^{-1}. The present MnO_2@$NiCo_2O_4$ core/shell nanospheres with remarkable electrochemical properties are considered as potential electrode materials for the next generation supercapacitors.

1. Introduction

With the rapid consumption of nonrenewable energy resources and worrying global environmental pollution, there is an expanded demand for exploring sustainable and clean resources and energy storage devices [1–4]. Recently, supercapacitors (SCs) have received considerate interest as the versatile energy storage systems for portable communication equipment, hybrid electric vehicles and memory backup devices due to their admirable characteristics including high power/energy density, rapid charge/discharge rates, and long cycle lifetime [2,5–7]. In fact, scientists have been making great efforts to develop different electrode materials of supercapacitors such as various forms of carbon [8–10], conducting polymers [11–13], and transition metal oxides [14–16].

Among them, the transition metal oxide $NiCo_2O_4$ is usually regarded as the most promising one for the electrode materials because of its high natural abundance, low cost, good conductivity, and ideal charge storage capability [6,17,18]. To date, nanostructured $NiCo_2O_4$ with various structures and morphologies has been fabricated, for example, nanowires [19,20], nanorods [21,22], nanotubes [23,24] and nanosheets [25,26]. However, bare $NiCo_2O_4$ suffers from some disadvantages like agglomeration, volume expansion and instability during the redox reactions, leading to the inadequate utilization for supercapacitors to a certain extent [27–29]. Therefore, how to overcome the above problems, ongoing explorations are still needed.

Lately, there have been many reports of $NiCo_2O_4$-based materials, for instance, Fe_2O_3@$NiCo_2O_4$ [30,31], $NiCo_2O_4$@$NiCo_2O_4$ [27,32], Co_3O_4/$NiCo_2O_4$ [33,34], $NiCo_2O_4$@graphene [35,36] etc. Facts have proved that multi-element combination can not only overcome the shortcomings of their materials, but there may be synergies, and it can achieve unexpected results just using the right way [15]. Take a look at a specific example. Xu et al. [37–39] sent a stream of reports on the process of $NiCo_2O_4$. They announced hollow $NiCo_2O_4$ nanospheres with large specific surface area, which displayed a high specific capacitance, remarkable rate performance and good cycling performance. Furthermore, they voiced hierarchical Co_3O_4@$NiCo_2O_4$ core-shell nanosheets with the areal capacitance of 1.33F cm^{-2}, the specific capacitance of 1330 F g^{-1} at 3 mA cm^{-2} and hierarchical $NiCo_2O_4$@MnO_2 composites with high rate capability. As well as having the previous performance, both composites have superior cycling stability (>100%). Getting this idea, we choose a substance to compound with $NiCo_2O_4$ as well, that is, a honeycomb-like MnO_2. As we all know, honeycomb-like MnO_2 has large surface area, "opened"

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structures, and good monodispersity [40,41]. Obviously, when the two substances hang together, $MnO_2@NiCo_2O_4$ composite can develop their respective advantages. On one hand, MnO_2 acts as a monodisperse nucleus for the deposition of $NiCo_2O_4$, avoiding the accumulation of materials. On the other hand, $NiCo_2O_4$ as a shell, tightly attached to MnO_2, overcoming the poor conductivity and capacitive performance of MnO_2 as an individual electrode material.

In this context, here, we fabricate monodisperse and highly opened $MnO_2@NiCo_2O_4$ core/shell nanospheres via a facile two-step solution method at room temperature coupled with a subsequent thermal treatment. In the composite, the MnO_2 nanospheres (the "core") with a honeycomb-like structure are coated with $NiCo_2O_4$ nanoflakes (the "shell"), in which nearly all the core/shell possess a high degree of porosity. This monodisperse and porous structure has a higher specific surface area and more active sites, so that increase electrode/electrolyte contact area, thereby enhancing the utilization of materials. The structure, morphology and electrochemical properties of the $MnO_2@NiCo_2O_4$ core/shell nanospheres were studied in detail, and obtained results revealed that the hybrid materials were very promising for electrochemical applications as the advanced supercapacitive electrodes.

2. Experimental

2.1. Materials

Potassium permanganate ($KMnO_4$), oleic acid, ammonia solution ($NH_3 \cdot H_2O$, 25–28%) were purchased from Chuandong Chemical Reagent Company (Chengdu, China). Nickel sulfate hexahydrate ($NiSO_4 \cdot 6H_2O$), cobalt (II) sulfate heptahydrate ($CoSO_4 \cdot 7H_2O$), potassium peroxydisulfate ($K_2S_2O_8$), potassium hydroxide (KOH) were received from Kelong Chemical Reagent Factory (Chengdu, China). All the reagents were of analytical-reagent grade and directly available.

2.2. Material synthesis

Synthesis of honeycomb-like MnO_2 nanospheres: MnO_2 nanospheres were produced by a microemulsion method [40,42]. Specific procedure, 1 g $KMnO_4$ and 500 mL of deionized (DI) water were put into a suitable erlenmeyer flask, keeping constant magnetic stirring until the mixture completely dissolved. Then, 10 mL of oleic acid was added to the above dark purple solution, and followed by continue whisking considerably for 24 h at room temperature. After cleanout several times with DI water and ethanol, the products were collected by centrifugation and obtained after dried at 60 °C for 12 h.

Synthesis of $MnO_2@NiCo_2O_4$ core/shell nanospheres: Before the deposition, the obtained MnO_2 nanospheres were re-dispersed into DI water and refluxed at 100 °C for 2 h under stirring in order to couple with the hydroxyl groups, forming precursor MnO_2. The detailed steps are as follows: Firstly, 60 mL of 1 M $NiSO_4$ and 60 mL of 2 M $CoSO_4$ mixed together to form a heavy pink solution. Then, 27 mg MnO_2 was uniformly dispersed to the mixture solution with the aid of ultrasonication and mechanical agitation for half an hour, while 80 mL of 2.5 M $K_2S_2O_8$ was precisely configured and added to the above dispersion. Hereafter, 0.2 mL of $NH_3 \cdot H_2O$ was dropwised into the mixture and stirred violently at room temperature for 8 h. After deposition, the products were amassed by filtration, washed with lots of DI water, and dried at 60 °C for 12 h. To get well crystallized $MnO_2@NiCo_2O_4$ nanostructures, the samples were annealed at 300 °C with a slow heating rate of 3 °C min^{-1} in argon for 2 h. By variation of the amount of MnO_2 during deposition process, $MnO_2@NiCo_2O_4$ core/shell nanospheres with various amount of MnO_2 were fabricated at the same condition and named as $MnO_2@NiCo_2O_4$-x with x representing the mass ratio of $NiCo_2O_4$ to MnO_2 in the reaction systems (x = 1, 3 and 4). In this article, $MnO_2@NiCo_2O_4$ refers to $MnO_2@NiCo_2O_4$-2. For comparison, bare $NiCo_2O_4$ was synthesized in the same way without adding MnO_2.

2.3. Material characterization

The crystallographic information of the materials was established by powder X-ray diffraction patterns (XRD) with Cu (Kα) radiation at 40 kV and 30 mA. X-ray photoelectron spectroscopy (XPS) measurements were performed using an ESCALAB250 system, equipped with a monochromatic Al Kα X-ray source. The morphologies being honeycomb and flakes of the materials were tested by a field-emission scanning electron microscope (FE-SEM, JEOLJSM-6335F). The core-shell structures of $MnO_2@NiCo_2O_4$ composite were further determined by the high-resolution TEM (HRTEM, 200 kV). Nitrogen adsorption-desorption isotherms and porosity analyzer were investigated with a Micromeritics ASAP 2020.

2.4. Electrochemical measurements

Electrochemical experiments were measured on an Autolab (PG302 N) using a three-electrode system at room temperature. 3 M KOH was used as the electrolyte. For making a working electrode, mixing the $MnO_2@NiCo_2O_4$, acetylene black and polyvinylidene fluoride (PVDF) according to 8:1:1 in N-methylpyrrolidone (NMP) and the slurry was spread onto a nickel foam, whose coverage area was 1 cm^2. Then, the electrode was dried in a vacuum oven at 30 °C for 24 h. Must be mentioned that prior to painting, nickel foam substrates as current collector, were cut into uniform size of 1 cm × 3.5 cm, and carefully rinsed with acetone, distilled water, ethanol solution in order in an ultrasonic bath for 30 min to remove the possible NiO layer from their surfaces. A platinum plate and Hg/HgO were used as the counter and reference electrodes, respectively. As a comparison, the bare MnO_2 and $NiCo_2O_4$ electrodes were also examined under the same conditions. The positive electrodes were evaluated by cyclic voltammetry (CV) techniques with varying scan rates of 5, 10, 20 and 50 mV s^{-1} in a potential range of 0–0.65 V and galvanostatic charge-discharge (GCD) experiments with current densities of 1, 2, 4, 8, 10, 16 A g^{-1} in 0–0.55 V. The electrochemical impedance spectroscopy (EIS) was conducted in the frequency range of 0.01 Hz to 100 kHz at open-circuit potential.

3. Results and discussion

Scheme 1 states a growth process of $MnO_2@NiCo_2O_4$ composite. Firstly, the honeycomb-like MnO_2 nanospheres are generated through the reaction between $KMnO_4$ and oleic acid in water. Secondly, MnO_2 is modified with abundant hydroxyl groups, making it have higher hydrophilicity and adsorbability. The better adsorption ability should be attributed to the strong electrostatic attraction between the surface hydroxyl groups and the cationic groups (Ni, Co-ions) [43]. Thirdly, $NiCo_2O_4$ thoroughly and evenly covers the surface of MnO_2 by chemical bath deposition and post annealing process. In this step, MnO_2 acts as primary nuclear for the growth of Ni, Co-hydroxide, then completely dispersing and growing up with the progress of reaction, afterward a calcination, $MnO_2@NiCo_2O_4$ hybrid materials are gained.