Materials Research Bulletin 61 (2015) 333–339

Contents lists available at ScienceDirect

Materials Research Bulletin

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

One-step synthesis and graphene-modification to achieve nickel phosphide nanoparticles with electrochemical properties suitable for supercapacitors

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ARTICLE INFO

Article history:
Received 11 June 2014
Received in revised form 6 October 2014
Accepted 10 October 2014
Available online 17 October 2014

Keywords:
Nanostructures
Composites
Chemical synthesis
Electrochemical properties
Energy storage

ABSTRACT

A facile one-step method has been developed to synthesize nickel phosphide (Ni_2P) nanoparticles which were further modified by graphene to form graphene-modified Ni_2P nanocomposites. All of the synthesized samples were characterized in detail and investigated the corresponding electrochemical properties. Results show that the supercapacitor electrodes based on graphene-modified Ni_2P nanocomposites exhibit better electrochemical properties compared to free Ni_2P nanoparticles. When the loaded amount of graphene is 5% (wt%), the nanocomposite electrodes show higher specific capacitance, obviously improved cycle stabilization, better rate capability and higher energy density. This enhanced electrochemical behavior results from the graphene-modified Ni_2P nanocomposite network structure which not only promotes efficient charge transport and electrolyte diffusion, but also prevents the volume expansion/contraction and corrosion of Ni_2P nanoparticles. These encouraging findings demonstrate the possibility of graphene-modified Ni_2P nanocomposites for applications in high-performance supercapacitors.

1. Introduction

Supercapacitors (SCs), also known as ultracapacitors, have been widely applied in hybrid electric vehicles, large industrial equipment, and renewable energy power plants due to their fast charge and discharge process, large lifespan, and high dynamic of charge propagation, etc. [1–3] However, the practical application of SCs are greatly hindered due to the lack of high-performance electrode materials available from a facile synthesis or at a lower cost of production. Hence, seeking ideal electrode material is always the research focus in the past decades. Among the present electrode materials of SCs, lower specific capacitance of carbon nanostructures (e.g.,: carbon particles, [4] graphene (GR) [5], carbon nanotubes (CNTs) [6], fullerene-like carbon doped with phosphorus or nitrogen [7,8], etc.), and the mechanical degradation of conducting polymers (e.g.,: polyaniline [9], polypyrro [10], etc.), largely restrict their application as electrode materials. As for transition metal compounds (e.g.,: oxides [11,12], hydroxides [13,14], sulfides [15], phosphates [16], etc.), they can not only store energy like electrostatic carbon nanomaterials but also exhibit electrochemical Faradaic reactions between electrode materials and ions although such materials also have some drawbacks (e.g.,: poor electrical conductivity). Therefore, transition metal compounds generally possess higher specific capacitance and have been devoted massive efforts in recent years. Early transition metal compound applied as electrode materials is ruthenium oxide [17]. However, its large-scale application is hindered by the very high cost and rareness of the ruthenium element. As a result, some cheaper compounds of cobalt, nickel, or manganese have become a preferred substitute and a research advances have been reviewed in a recent article [18].

As one of the important functional phosphides [19,20], nickel phosphide (Ni_2P) nanomaterials have been used in many technical field due to excellent physicochemical properties, e.g.,: catalysts for organic synthesis [21–23], anode materials for lithium-ion batteries [24,25], and electrocatalyst for the H_2 evolution [26], etc. Up to date, Ni_2P nanostructures have been synthesized by many different methods, e.g.,: pyrolysis of organometallic precursors [26–29], high-temperature reduction of phosphates and phosphinates [30,31], solid-state phase transformations [32], and low-temperature hydrothermal or solvothermal methods [33,34], etc. Especially in recent, a work about Ni_2P nanoparticles applied in SCs

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http://dx.doi.org/10.1016/j.materresbull.2014.10.038
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were just reported, i.e.,: Ni_2P nanoparticle synthesized via high-temperature reduction at 500 °C with NiS_2 as the precursor showing a high value of 1050 F/g at 2 A/g [35]. However, expensive organometallic precursors, highly toxic reagents or/and high-temperature treatment are often needed in the above methods which largely increased the cost of production and prevented Ni_2P nanomaterials from commercial applications. It follows that the great challenge still remains how to prepare Ni_2P nanostructures through a simple, inexpensive, and convenient synthetic process. The corresponding performance investigations might provide some novel approaches to the development of Ni_2P nanostructures for nano-device applications and can also enrich our understanding of the nano-world.

In this study, an inexpensive solvothermal method was successfully developed to construct Ni_2P nanoparticles and the corresponding electrochemical properties were investigated. A maximum specific capacitance of 600.1 F/g at a current density of 1 A/g was obtained for free Ni_2P nanoparticles. To further improve the electrochemical performances of Ni_2P nanoparticles, a simple physic approach was adopted for preparing the graphene-modified Ni_2P nanocomposites. Compared to free Ni_2P nanoparticles, hierarchical carbon materials [36], graphene paper [5] Co_3O_4 thin films[37] and NiO nanoparticles [38] (see Supporting information Table S1) the graphene-modified Ni_2P nanocomposites exhibited enhanced electrochemical behavior when the loaded amount of graphene is 5% (wt%), i.e.,: higher specific capacitance (672.4 F/g at 1 A/g), good cycling stability (maintained as 200 F/g after 2000 cycles), better rate capability (499.5 F/g at 3 A/g), and higher energy density (38.0 Wh/kg at a power density of 2401.3 W/kg), which make it a promising electrode candidate material for supercapacitors in the future.

2. Experimental

2.1. Chemical synthesis of Ni_2P nanoparticles

All the reagents were of analytical grade (purchased from Aladdin Chemical Reagent Company) and used without further purification. Typical Ni_2P nanoparticles were synthesized by an improved solvothermal process similar to that of nickel diselenide in our previous work [39]. In a typical procedure, 0.24 g Ni $(AC)_2\cdot4H_2O$, 2 mL oleylamine and 1 mL oleic acid were added to 21 mL anisole at room temperature. A homogeneous solution was obtained after the resulting mixture was heated to 60 °C and maintained for 30 min. The resulting mixture was transferred to a Teflon-lined stainless steel autoclave with a capacity of 30 mL. Then, 0.15 g white phosphorus was added in the above solution after washed successively with absolute ethanol, toluene, and anisole. After the autoclave was sealed and maintained at 200 °C for 24 h in a preheated oven, it was taken out and cooled to 50–60 °C naturally. Ni_2P nanoparticles were collected after being repeatedly washed with absolute ethanol and dried in a vacuum oven.

2.2. Preparation of graphene-modified Ni_2P nanocomposites

Graphene (GR) was prepared from commercial graphite by a modified Hummers method [40]. Detailed synthetic process and characterizations of graphene was provided in Supplementary information. Graphene-modified Ni_2P nanocomposites were obtained by a simple physic process. According to a certain weight ratio (wt%) of synthesized GR ($GR{:}Ni_2P = 5{:}100$), Ni_2P nanoparticles and GR nanosheets were mixed in 20 mL absolute ethanol at room temperature. The mixture was ultrasonic for 30 min until there is not obvious particulate matter. After magnetically stirred for 24 h, the turbid liquid was centrifuged and dried in a vacuum oven. Finally, graphene-modified Ni_2P nanocomposites with 5% loaded amount of GR were obtained and labeled as Ni_2P@5%GR. As a contrast, graphene-modified Ni_2P nanocomposites with different loaded amount of GR (e.g.,: 1%, 10%) were also synthesized by the similar process and labeled as Ni_2P@1%GR and Ni_2P@10%GR.

2.3. Fabrication and tests of working electrodes

Working electrodes of SCs were prepared by mixing as-synthesized active material (85 wt%) with acetylene black (10 wt %) and poly(tetrafluoroethylene) (5 wt%), coating on a piece of foamed nickel of about 1 cm^2 and pressing to be a thin foil at a pressure of 10 MPa. The weight of active material is about 5 mg. All electrochemical properties of self-made electrodes, including cyclic voltammogram (CV), and galvanostatic charge–discharge (CD), were carried out at room temperature in a three-electrode system equipped with platinum electrode and a saturated calomel electrode (SCE) as counter and reference electrodes, respectively. The electrolyte was 3.0 M KOH solution.

2.4. Characterizations

Crystal structures of the products were characterized on a Rigaku Ultima III X-ray diffractometer (XRD) equipped with a Cu Kα radiation source ($\lambda = 0.15418$ nm). The chemical state was analyzed using X-ray Photoelectron Spectroscopy (XPS, PHI 5000 VersaProbe). Transmission electron microscopy (TEM) image and high-resolution transmission electron microscopy (HRTEM) image were captured on the JEM-2100 instrument microscopy at an acceleration voltage of 200 kV. Three-dimensional morphologies of samples were studied by scanning electron microscope (SEM, JSM 6701). The surface area of the product was calculated from N_2 adsorption/desorption isotherms at 77 K that were conducted on a Gemini VII 2390 Analyzer. Cyclic voltammogram (CV), and galvanostatic charge–discharge (CD) tests were measured by an electrochemical working station (CHI660E, Chenghua, Shanghai, China) with the potential window from 0 V to 0.5 V (vs. SCE). Cycle stability tests were carried out with an Arbin electrochemical instrument.

3. Results and discussion

3.1. Structural, morphological, and chemical state characterizations of typical Ni_2P samples

X-ray diffraction (XRD) patterns of the standard data and typical sample are shown in Fig. 1a. All of the diffraction peaks of typical sample can be indexed to the hexagonal phase of Ni_2P (JCPDS No.: 74-1385) with the *P-62m* space group and a hexagonal unit cell $a = 0.5859$ nm and $c = 0.3382$ nm. No peaks from other phases were detected, e.g.,: Ni, NiO, phosphate, phosphite, or organic compounds related to the reactants indicating that the product is of high purity. It can be found from the crystal structure in Fig. 1b that Ni_2P adopts the hexagonal Fe_2P structure and this structure of the metal-rich phosphides is based on trigonal prisms, which can well accommodate the relatively large phosphorus atoms. These prisms are similar to those in sulfides, but phosphides do not take on layered structures. In addition, the average length of Ni—P bond is 0.227 nm and the Ni—Ni bond length is 0.261 nm which is similar to that of metal Ni ($d_{Ni-Ni} = 0.250$ nm). The short Ni—Ni metal distance in Ni_2P indicates a strong metal bonding and this material does exhibit metallic character [41]. Contrast experiments indicate that the volume ratio between oleylamine and oleic acid has an important role on the phases of products. Too high or too low would lead to the generation of impure phase or amorphous samples (see Supplementary information Fig. S3). The morphology