One pot synthesis of $Ni_{12}P_5$ hollow nanocapsules as efficient electrode materials for oxygen evolution reactions and supercapacitor applications

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ABSTRACT

The $Ni_{12}P_5$ hollow nanocapsule structure is synthesized adopting a facile one-pot hydrothermal method without any templates. The size of the obtained $Ni_{12}P_5$ nanocapsules is about 20 nm, and the wall thickness is about 3 nm. The XPS spectra of $Ni_{12}P_5$ samples were measured to identify the surface chemical composition and valence states. Oxygen evolution reaction results show that the onset overpotential of $Ni_{12}P_5$ is 290 mV and clearly demonstrates the Tafel slope of 49.8 mV dec^{-1}. Meanwhile, the $Ni_{12}P_5$ nanocapsules show excellent electrochemical properties with specific capacitance of 949 F g^{-1} at 1 A g^{-1} and 81% of the initial value after cycles. Excellent electrochemical performances demonstrate that the nickel phosphide from a facile synthesis strategy could be a candidate for high performance energy storage and conversion.

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1. Introduction

The increasing demand for clean energy and the growing global environmental concerns have stimulated research activities in the development of effective conversion and storage systems for sustainable alternative energy sources [1], such as water splitting [2,3], metal-air batteries [4,5], fuel cells [6,7] and supercapacitors [8,9]. The oxygen electrode catalysts for oxygen evolution reaction (OER) as key roles for those systems have attracted particular interests [10–12]. Similarly, it is urgently needed to develop efficient noble-metal-free catalysts with high catalytic activity for the OER to substitute high cost and low abundance RuO_2 and IrO_2 [13]. Alternatively, supercapacitors have received much research attentions for their high efficiency energy storage because of their prominent properties such as high power density and long lifespan [14–16]. Pseudocapacitors can engender high specific capacitance based on the fast and reversible redox reactions [17–19]. The phase composition and structural parameters of the efficient pseudoca-pacitance active material as research emphasis are the key to determine performance for supercapacitors [20,21]. Therefore, one key point of the two energy storage and conversion systems has been heavily focused on a kind of highly efficient, inexpensive and environmentally friendly electrode active materials.

Nickel phosphides have received increasing attention owing to their excellent physicochemical properties and widespread applications in many fields [22], such as electrocatalysts [23,24], supercapcitors [25,26], and lithium-ion batteries [27]. In recent years, among them, nickel phosphides (especially nickel-metal phases, such as Ni_2P) are potent catalysts for HER and OER due to their species diversity, efficient and low-overpotential [23,28,29]. For example, the porous nickel phosphides foam exhibits high catalytic current density of 191.0 mA cm^{-2} at an overpotential of 0.35 V) and outstanding long-term stability and durability [30]. Ni_2P nanoparticles show an overpotential of only 290 mV at 10 mA cm^{-2} in 1 M KOH [31]. In addition, nickel phosphides have begun to attract attention as electrode materials for super-capacitors [32]. For instance, $Au/Ni_{12}P_5$ core/shell nanocrystals [33] show 806.1 F g^{-1} with a retention of 91.1% after 500 cycles. The Ni_2P and Ni_5P_4 nanoparticles [34] Exhibit 843.25 F g^{-1} and 801.5 F g^{-1} at 1 A g^{-1}, respectively. The Ni-coated Ni_2P [35] achieves 1115 F g^{-1} at 2 A g^{-1}, which can still maintain 92.3% after 3000 cycles. The amorphous Ni—P [18] Exhibits 1597 F g^{-1} at 0.5 A g^{-1} and good cycling stability. However, a large number of work for metal phosphides focused on the preparation of more complex and high energy consumption, such as solution-phase (using

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trioctylphosphine, TOP at about 300 °C), gas–solid reaction (calcined over 300 °C under Ar or N$_2$). For instance, Ni$_{12}$P$_5$, Ni$_2$P and Ni$_5$P$_4$ nanocrystals were synthesized via the thermal decomposition approach in TOP at 320 °C for 2 h [36]. Ni$_2$P nanoparticles were synthesized in TOP at 320 °C [24]. Ni-P porous nanoplates were obtained at 300 °C for 2 h by thermal decomposition of NaH$_2$PO$_2$ under Ar flow [37]. However, the preparation method and formation mechanism of metal phosphides with special microstructures have not been worked out well.

Hollow nanostructures are composed of compact walls with a larger surface area than bulk for more abundant active sites, so that hollow structures is an effective activity to achieve high performance electrochemical process [38–40]. However, there are few reports on hollow nanostructures by a one-step without using template, especially for transition metal phosphide. In this work, we report facile one-pot synthesis of Ni$_{12}$P$_5$ hollow nanocapsules without any templates using hydrothermal method. The size of the obtained Ni$_{12}$P$_5$ nanocapsules is about 20 nm, and the wall thickness is about 3 nm. The onset overpotential of Ni$_{12}$P$_5$ is 290 mV and clearly demonstrates the Tafel slope of 49.8 mV dec^{-1}. Meanwhile, the Ni$_{12}$P$_5$ nanocapsules show excellent electrochemical properties with specific capacitance of 949 F g^{-1} at 1 A g^{-1}.

2. Experimental Section

2.1. Preparation of samples

2.1.1. Preparation of Ni$_{12}$P$_5$ nanocapsules
In a typical experiment, 2 mmol Ni(CH$_3$COO)$_2$·4H$_2$O, 8 mmol red phosphorus, and 1 mmol hexadecyl trimethyl ammonium Bromide (CTAB) were dissolved in mixed solution of 20 mL deionized water and 40 mL ethanol. Then, the above solution was transferred into a 100-mL teflon-lined stainless autoclave, and kept at 180 °C for 30 h. Then, the product was filtered washed several times with deionized water and ethanol. The final product was obtained after drying in vacuum at 60 °C for 12 h.

2.1.2. Preparation of flower-like Ni(OH)$_2$ and flower-like NiO
For the synthesis of flower-like Ni(OH)$_2$, 10 mmol Nickel nitrate hexahydrate (Ni(NO$_3$)$_2$·6H$_2$O) and 10 mmol hexamethylenetetramine (HMTA) were dissolved in 60 mL deionized (DI) water. The mixture was stirred for 30 minutes, following which it was transferred into a 100 mL Teflon-lined stainless autoclave and kept at 100 °C for 10 h. The green Ni(OH)$_2$ was obtained after washed and dried. For the synthesis of flower-like NiO, the above green Ni(OH)$_2$ was put into the sequencing tube furnace and heated to 400 °C with air drummed into at the rate of 5 °C per minute, and kept at 400 °C for 2 h. Then black NiO was collected after gradually cooled to room temperature.

2.2. Materials Characterization

X-ray diffraction (XRD, Philips X'Pert PRO; Cu Kα, λ = 0.1542 nm) was used to analyze the phase of the sample, the micro-structure of sample was examined by FEI Quanta 200 scanning electron microscope (SEM). Energy dispersive X-ray spectroscopy (EDS) analyzes the component of the samples during SEM measurements. The hollow nanostructure was investigated by means of transmission electron microscopy (TEM, Philips, TecnaiG2 20). The X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra DLD-600W XPS system) spectra was measured the electronic structure and surface composition with a monochromatic Al Kα (1486.6 eV) as X-ray source.

2.3. Electrochemical measurement

For oxygen evolution reaction, the sample as active material and Ketjen black as conductive additives were mixed in a weight of 5 mg and 1 mg with 32 μL of 5 wt.% Nafion solution in 0.968 mL of 4:1 V/V water/ethanol. And then, 7 μL of the mixed slurry was loaded onto a glassy carbon electrode of 5 mm in diameter after sonication for at least 30 min. The OER tests were carried out in a conventional three electrode electrochemical cell by using CHI660E electrochemical workstation and Pine Modulated Speed Rotator with a Pt foil electrode as a counter electrode and an Ag/AgCl electrode as the reference electrode. The reversible hydrogen electrode (RHE) was used as scale for all potentials measured according to the Nernst equation [41]: $E_{RHE} = E_{Ag/AgCl} + 0.197 + 0.059*pH$ ($= E_{Ag/AgCl} + 1.0006$, 1 M KOH PH ≈ 13.62). Polarization curve measurements for OER were carried out in N$_2$-saturated 1 M KOH solution at different scan rates at 1600 rpm to eliminate the side effects of oxygen bubble adsorbed on the electrode surface. Overpotential was calculated as follows: $\eta(V) = E_{vs. RHE} - 1.23$.

For supercapacitor, the sample as active material, poly (tetrafluoroethylene) (PTFE) suspension (60 wt%) as binder and acetylene black as conductive additives were mixed in a weight ratio of 8:1:1. The part of mixture were coated on the 1.13 cm^2 of foam nickel, and dried in vacuum at 60 °C for 12 h. Then, the electrodes were pressed by 15 MPa. The mass of the active materials is about 4–6 mg cm^{-2} on 1.13 cm^2 electrodes. Electrochemical properties of as-obtained electrodes were measured by cyclic voltamogram (CV) and chronopotentiometry via a CHI660E in a conventional three-electrode system at 6 M KOH solution, in which Pt and Hg/HgO served as the counter electrode and the reference electrode, respectively.

3. Results and discussion

The Ni$_{12}$P$_5$ hollow nanocapsule was obtained with red phosphorus as the phosphorus source and nickel acetate as the nickel ion precursor by hydrothermal reaction. Formation mechanism diagram of the Ni$_{12}$P$_5$ hollow nanocapsule was shown in Fig. 1a. At first, the surface of red phosphorus is smooth without any signs of rough before the reaction (Fig. 1b), which reveal that red phosphorus is difficult to dissolve in deionized water and anhydrous ethanol. With increasing reaction time, red phosphorus gradually decomposed into phosphorus ions [42] (Fig. 1c). In the following, nickel phosphides formed by the reaction of phosphorus ion and nickel ion were assembled into a hollow nanostructure, the diameter of hollow nanospheres is about 20∼50 nm as shown in Fig. 1d.

The morphology of Ni$_{12}$P$_5$ hollow nanocapsule product was investigated by FE-SEM and TEM images, as presented in Fig. 2. From the SEM image from Fig. 2a and b, the nano-size of the obtained product is about 20∼50 nm. In order to accurately determine the composition and distribution of nanostructures, the composition analysis of the product was conducted. The EDS element mapping confirms that Ni and P homogenously distribute among the nanostructures (Fig. 2d–f). Moreover, the quantitative analysis of EDS data reveals the average Ni/P ratio to be approximately 12:5 (Fig. 2g). The TEM images in Fig. 2h and i show that the edges of the Ni$_{12}$P$_5$ spheres are significantly thicker than the center, which further confirms that the as-prepared nanospheres are hollow structures, and the wall thickness is about 4 nm. The HRTEM images (Fig. 2j and Fig. S1) reveal that the fringe spacings are about 3.07, 1.93, 1.86 Å, corresponding to the (211), (240) and (312) lattice planes of tetragonal Ni$_{12}$P$_5$.

The crystal of the prepared Ni$_{12}$P$_5$ was examined by XRD analysis (Fig. 3a). The diffraction peaks are observed at 29.2, 32.7,