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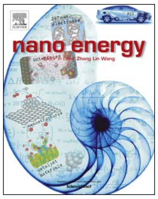

Communication

Low temperature synthesis of ternary metal phosphides using plasma for asymmetric supercapacitors

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ABSTRACT

We report a versatile route for the preparation of metal phosphides using PH_3 plasma for supercapacitor applications. The high reactivity of plasma allows rapid and low temperature conversion of hydroxides into monometallic, bimetallic, or even more complex nanostructured phosphides. These same phosphides are much more difficult to synthesize by conventional methods. Further, we present a general strategy for significantly enhancing the electrochemical performance of monometallic phosphides by substituting extrinsic metal atoms. Using NiCoP as a demonstration, we show that the Co substitution into Ni_2P not only effectively alters the electronic structure and improves the intrinsic reactivity and electrical conductivity, but also stabilizes Ni species when used as supercapacitor electrode materials. As a result, the NiCoP nanosheet electrodes achieve high electrochemical activity and good stability in 1 M KOH electrolyte. More importantly, our assembled NiCoP nanoplates//graphene films asymmetric supercapacitor devices can deliver a high energy density of 32.9 Wh kg^{-1} at a power density of 1301 W kg^{-1}, along with outstanding cycling performance (83% capacity retention after 5000 cycles at 20 A g^{-1}). This activity outperforms most of the NiCo-based materials and renders the NiCoP nanoplates a promising candidate for capacitive storage devices.

1. Introduction

The utilization of sustainable energies such as sunlight and wind holds the promise to fulfil the ever-growing global energy demands of future societies [1,2]. Harvesting energy from these renewable sources requires efficient and affordable energy storage technologies. Supercapacitors, which store energy in terms of charges on electrode surfaces, are now considered as one of the most promising energy storage devices [3–9]. One of the most attractive characteristics of supercapacitors is that they can provide higher energy density than that of traditional capacitors, and greater power density than that of rechargeable batteries, bridging the gap between traditional capacitors and batteries [3–9]. Based on the charge storage mechanism, supercapacitors can be divided into two categories, the electrical double layer capacitors (EDLCs) which accumulate charges by ion adsorption at the electrode/electrolyte interface and pesudocapacitors which chemically store charges via faradaic redox reactions at the surface [3–9]. The latter has attracted intense attention due to their much higher (typically 10–100 times) specific capacitance and energy density compared to that of EDLCs [10,11]. Transition metal-based compounds are popular pesudocapacitors electrode materials because of their multiple valence states that enable fast surface faradaic redox reactions [10,12–18].

Among them, hydroxides and oxides are of particular interest owing to their high theoretical capacitances, earth abundance, and environmental friendliness [10,12–16,19–22]. However, they suffer from poor electrical conductivity. One effective approach to overcome this drawback is to hybridize with highly conductive materials such as graphene [19,21–26]. Another strategy is to improve the conductivity by elemental doping or, searching for new electrode materials that are intrinsically more conductive. From this perspective, metallic transition metal sulfides, selenides, and phosphides should be promising candidates [27,28]. Indeed, several sulfides and selenides have been explored as new electroactive materials for supercapacitors and often show superior performance than oxides and hydroxides [29–31]. Besides, metal phosphides also exhibit promising electrochemical properties and have been widely employed as electrocatalysts and lithium-ion battery electrodes [28,32–34]. Unexpectedly, however, the use of metal phosphides for supercapacitors is still quite limited. We noticed that there are only a few reports on Ni-P for supercapacitors [35–38], which show that the Ni-P can deliver high specific capacity (we use capacity here because Ni and Co based compounds are

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recognized as battery-type materials [39]) but with poor rate capability and cycling performance. This phenomenon is commonly seen for Ni-based materials [20,40–43], possibly due to the poor structural stability during the fast charge-discharge process. On the other hand, Co-based compounds possess excellent stability even though their specific capacity is relatively low [44–46]. Further, bimetallic NiCo compounds show richer faradaic redox reactions, higher electrical conductivity and stability, thus often result in enhanced electrochemical performance than their corresponding single metal counterparts, as already demonstrated for NiCo oxides and chalcogenides [29–31,47]. Encouraged by these findings, we predicted that the electrochemical activity and stability of nickel phosphides could be dramatically improved through Co substitution.

Herein we report a promising approach toward enhancing the electrochemical performance of monometallic phosphides as supercapacitor electrodes through extrinsic metal substitution. Using NiCoP as a demonstration, we showed that Co incorporation into Ni_2P doesn't change the crystal structure (both the Ni_2P and NiCoP adopt the hexagonal Fe_2P structure, see Fig. S1 in the Supporting Information), but effectively tunes the electronic structure and the intrinsic reactivity and electrical conductivity. Compared to Ni_2P and CoP, the bimetallic NiCoP exhibits superior electrochemical performance in terms of high specific capacity and good cycling performance. Furthermore, the asymmetric supercapacitor devices based on NiCoP nanoplates and graphene films can deliver a high energy density of 32.9 Wh kg^{-1} at a power density of 1301 W kg^{-1}, along with outstanding cycling performance (83% capacity retention after 5000 cycles at 20 A g^{-1}). This result outperforms most of the NiCo-based materials, indicating that NiCoP nanoplates are promising candidates for energy storage devices.

2. Experimental section

2.1. Synthesis of hydroxides precursor

Carbon paper substrate was treated by annealing in air at 700 °C for 10 min to improve the surface hydrophilicity before use. Then NiCo hydroxide nanoplates were synthesized by a hydrothermal method. In a typical synthesis, 2.5 mmol of $Ni(NO_3)_2 \cdot 6H_2O$, 2.5 mmol of $Co(NO_3)_2 \cdot 6H_2O$, and 10 mmol of hexamethylenetetramine (HMT) were dissolved in 30 mL of distilled water, which was then transferred to a 50 mL autoclave containing the carbon paper substrate (typically 2×5 cm). The autoclave was sealed and heated at 100 °C for 10 h. After cooling, the substrate was removed, rinsed with ethanol and water, and dried under a flow of nitrogen gas. The Ni and Co hydroxides were synthesized using the same procedure as that of NiCo hydroxide, except 5 mmol $Ni(NO_3)_2 \cdot 6H_2O$ or $Co(NO_3)_2 \cdot 6H_2O$ instead of 2.5 mmol of $Ni(NO_3)_2 \cdot 6H_2O$ and 2.5 mmol of $Co(NO_3)_2 \cdot 6H_2O$ was used.

2.2. Conversion of hydroxides to phosphides

The carbon paper substrate (typically 0.5×2 cm) covered with hydroxides was placed in the chamber of a plasma-enhanced chemical vapor deposition (PECVD) system, followed by thermal phosphorization at 250 °C for 15 min using PH_3 plasma. The conditions for the plasma treatment were PH_3/He (5:95 volumetric ratio) flux of 50 sccm, a base pressure of 980 mTorr, and a power of 100 W.

2.3. Structural characterization

The as-synthesized samples on carbon paper were characterized using a Bruker D8 ADVANCE X-ray diffractometer (XRD) using Cu Kα radiation (λ=1.5406 Å), a FEI Nova Nano 630 scanning electron microscope (SEM), and a FEI Titan 80–300 ST (300 kV) transmission electron microscope (TEM) with energy dispersive X-ray spectroscopy (EDS) capabilities. Note that the XRD patterns were taken on the powder scraped off the carbon paper substrate. The electron energy-loss spectroscopy (EELS) analyses were performed under the aberration corrected scanning TEM (STEM) mode. The Ni-L23 (855 eV), Fe-L23 (710 eV), and P-L23 (132 eV) energy loss edges were selected to generate the Ni, Fe, and P maps, respectively. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Kratos Axis Ultra DLD spectrometer with Al Kα radiation ($h\nu$ =1486.6 eV). All XPS spectra were calibrated by shifting the detected adventitious carbon C 1 s peak to 284.4 eV.

2.4. Electrical conductivity measurements of individual phosphide nanoplates

The phosphide nanoplates grown on carbon paper were immersed into ethanol and sonicated for 30 min. Then a few drops of the suspension were casted onto Si/SiO_2 (280 nm) wafers. Afterwards, the Ti (10 nm)/Au (100 nm) electrodes for transport tests were fabricated on the high-quality samples (flat and large nanoplates) using standard e-beam lithography (EBL) and e-beam evaporation. The transport properties of as-made nanodevices were analyzed by Keithley 4200 semiconductor characterization system.

2.5. Electrochemical measurements

The electrochemical measurements were carried out at room temperature in both three-electrode (half-cell) and two-electrode (full cell) configurations. In the half-cell measurements, the NiCoP on carbon paper was directly used as the working electrode without adding any extra binders or conductive additives, a Pt wire and a Ag/AgCl electrode were used as the counter and reference electrodes, respectively. Whereas in the full cell measurements, a carbon paper with NiCoP nanoplates grown on it and a graphene film were used as the positive and negative electrodes respectively with a porous polymer membrane (Celgrad 3501) as the separator to assemble a coin cell. Prior to the fabrication of the asymmetric supercapacitors, the mass of the positive and negative electrodes was balanced according to the following equation:

$$\frac{m_+}{m_-} = \frac{C_{s-} \cdot \Delta V_-}{C_{s+} \cdot \Delta V_+} \tag{1}$$

where m is the mass, C_s is the specific capacitance and ΔV is the voltage range for positive (+) and negative (-) electrodes, respectively. For a typical device, the total mass loading is ~3.4 mg cm^{-2} with a stack thickness of ~0.8 mm. For all measurements, 1 M KOH aqueous solution was used as electrolyte. Cyclic voltammetry, galvanostatic charge-discharge tests, and electrochemical impedance spectroscopy (EIS) measurements were conducted on a Bio-Logic VMP3 potentiostat. EIS tests were performed at open circuit voltage in the frequency range of 100 kHz–0.01 Hz at an amplitude of 5 mV.

2.6. Calculations

The capacities were calculated from the galvanostatic charge-discharge curves. For the half cell, the specific capacity (C_s, mAh g^{-1}) was calculated according to

$$C_s = \frac{2i\int \mathrm{V}dt}{m\mathrm{V}} \tag{2}$$

whereas for the full cell, the cell capacity (C_c, mAh g^{-1}) was calculated according to

$$C_{cell} = \frac{2i\int \mathrm{V}dt}{M\mathrm{V}} \tag{3}$$

where i (A) is the current density, t (s) the discharge time, V (V) the potential window, m (g) the mass of the active materials on the single electrodes, and M (g) the total mass of the active materials on both the