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One-pot hydrothermal synthesis of porous nickel cobalt phosphides with high conductivity for advanced energy conversion and storage

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ABSTRACT

High electrical conductivity is a vital factor to improve electrochemical performance of energy storage materials. In this work, bimetallic nickel cobalt phosphides with high electrical conductivity and different Ni/Co molar ratios are directly fabricated via a simple hydrothermal method. The samples show uniform teeny nanoparticles morphology and excellent electrochemical performance. The NiCoP sample exhibits the most prominent specific capacity (571 C g^{-1} at 1 A g^{-1}) and out-bound rate characteristic (72.8% capacity retention with a 20-fold increase in current densities), which can be attributed to the good crystallinity, larger specific surface area, and noteworthy intrinsic conductivity that convenient for fast electron transfer in active material and fleet reversible faradic reaction characteristics. Simultaneously, an optimal asymmetric supercapacitor based on NiCoP as positive and activated carbon as negative is assembled. It can achieve a high energy density of 32 Wh kg^{-1} (at a power density of 0.351 kW kg^{-1}) and prominent cycling stability with 91.8% initial capacity retention after 3000 cycles. It demonstrates that nickel cobalt phosphides are promising as energy storage materials. The study could also pave the way to explore a new class of bimetallic phosphides materials high electrical conductivity for electrochemical energy storage.

1. Introduction

With the rise of energy requirement on account of the rapid consumption of energy and demand exceeds supply of electronic devices, stimulating researchers to develop high performance energy storage devices [1–4]. Supercapacitors as a sort of energy storage system are the most promising reserve force compared to Li ion battery and NI-MH batteries on the basis of their high power density, fleet kinetics of charge propagation and longevity [5–9]. The properties of supercapacitors usually depend on electrode materials. Many researchers try hard to exploit new electrode material which could contribute the optimal electrochemical performance. In consideration of the customary non-ideal energy density of supercapacitors, an anticipant strategy is to seek an electrode material that satisfies high energy density without sacrificing the power density.

Ni-Co based battery-type materials have been widely studied recently in terms of providing abundant redox reaction lead to greater charge storage than double electrode layer [10–14]. For battery-type materials, cyclic voltammetry curves have distinct redox peaks and charge-discharge curves appear corresponding voltage platform. In spite of these battery-type materials are distinguishing to the true pseudocapacitance according to perfect rectangle (carbon material or MnO_2) [15], as positive electrode materials can combine the advantage of both supercapacitors (power density) and batteries (energy density) [16,17]. Therefore, this kind of materials is studied widely.

Compared with single metallic Ni or Co compounds, bimetallic Ni-Co compounds possess ameliorative properties. For instance, Wu *et al.* [18] synthesized $NiCo_2O_4$ possesses at least two magnitudes higher electrical conductivity than that of NiO and Co_3O_4. Chen et al. [19] synthesized the $Ni_xCo_{3-x}O_4$ samples exhibited higher capacitance than NiO and Co_3O_4 under the same conditions. Chen *et al.* [20] fabricated bimetallic nickel cobalt selenides show more outstanding capacity characteristic than NiSe and CoSe. Zhang *et al.* [21] studied hollow $Ni_xCo_{9-x}S_8$ urchins which displays higher electrical conductivities than cobalt sulfides (CoS_x),

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nickel sulfides (NiS_x). The nickel-cobalt hydroxide has more excellent performance than monometallic hydroxides of $Co(OH)_2$ and $Ni(OH)_2$ [22–24]. Although these bimetallic Ni-Co compounds provide remarkable electrochemical performance, they suffered from poor electrical conductivity which is adverse for electrochemical energy storage. On one hand, low electrical conductivity could increase the IR potential drop of electrode in the large current charge-discharge possess, and seriously weaken the practical potential window of materials. On the other hand, low electrical conductivity prevents the rapid migration of electrons in great rate charge-discharge condition, and introducing severe electrochemical polarization, which could reduce the utilization efficiency of active materials. Thus, the electrical conductivity is a significant factor which determines property of super-capacitive materials. Enhancing electrical conductivity or exploiting new-style electrode materials with high electrical conductivity play an important role for improving the electrochemical property.

Ni-Co phosphides as a sort of submetallic alloy possess much higher intrinsic conductivity than oxide semiconductors, and have abundant natural resources as well as environmentally genial nature [25]. They were applied to some other fields in published papers. For example, Hemeda et al. [26] synthesized semi-crystalline NiCoP film and investigate its magnetic properties. Liu *et al.* [27] fabricated NiCoP hollow spheres applied to lithium ion batteries. Ni-Co phosphides as electrode material for supercapacitors have not been studies by researchers despite in fact that they have high electrical conductivity [28]. So Ni-Co phosphides just can be used as a new kind of electrode materials with high electrical conductivity.

Served as energy storage materials, monometallic nickel phosphides have been widely applied to supercapacitors [29,30], whereas cobalt phosphides are relatively few for supercapacitors [31]. Studies have shown that nickel phosphides have high specific capacity, while cobalt phosphides possess outstanding rate capability and cycle performance. The most important thing is that both of them have high intrinsic conductivity contribute to fleet charge storage. In order to combine high electrical conductivity, upper specific capacity, remarkable rate capability and cycle performance, it enlightens us designing and studying the electrochemical performance of Ni-Co phosphides. In this work, relied on one-step hydrothermal synthetic approach, a train of Ni-Co phosphides with high electrical conductivity and different Ni/Co molar ratios were synthesized and their electrochemical performance as positive materials for supercapacitors was investigated. It is found that Ni/Co molar ratios have a great influence on electrochemical properties of Ni-Co phosphides. The results showed that the Ni-Co phosphides, especially NiCoP possessed the highest specific capacity, high electrical conductivity, noteworthy rate capability and prominent cycle life, which indicated that NiCoP is an ideal electrochemical material and has great capacity for high-performance electrochemical energy storage systems. Besides, the AC//NiCoP asymmetrical supercapacitor attained both upper energy and power density, indicating superior performance of asymmetrical supercapacitor and active material in practical application.

2. Experimental section

Typical Ni-Co phosphides were synthesized via a hydrothermal process: a set number of $NiCl_2{\cdot}6H_2O$, $CoCl_2{\cdot}6H_2O$ and red phosphorus (200 °C 10 h hydrothermal pretreatment for the sake of thining grain size) were dissolved into 40 ml DI water along with continuous stirring. After ultra-sonication for 15 min, the hybrid suspension liquid decanted a 50 ml Teflon-lined stainless steel

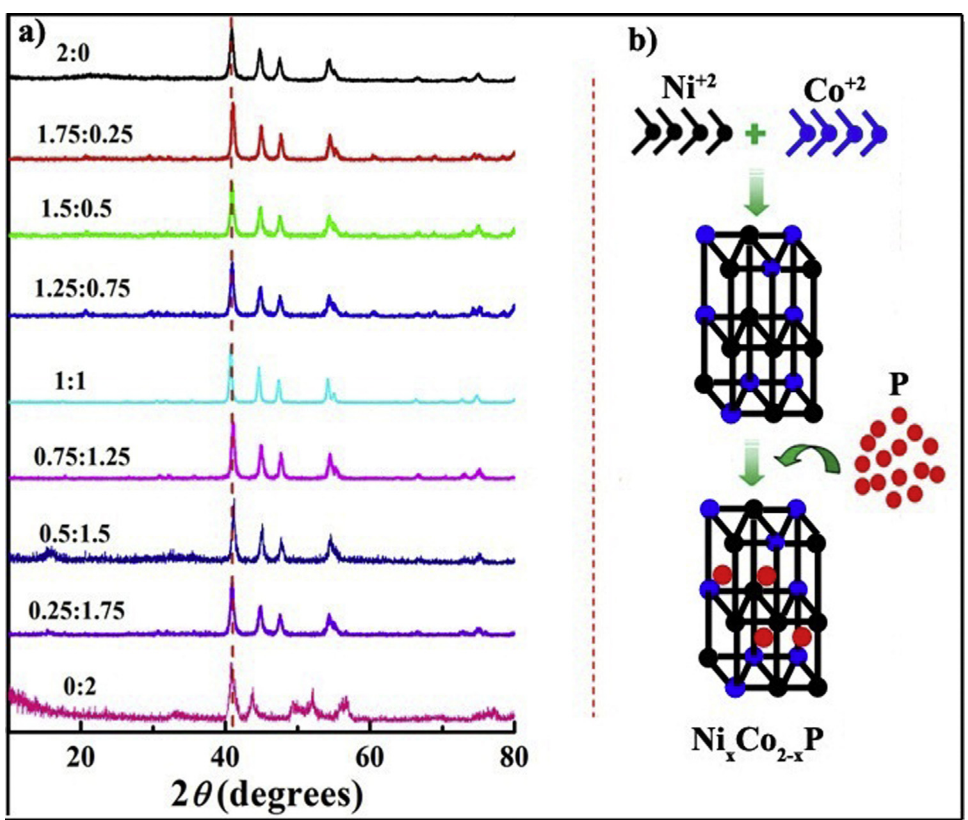

Fig. 1. (a) Typical XRD patterns of $Ni_xCo_{2-x}P$ with different Ni/Co molar ratios. (b) Schematic illustration of the formation mechanism of $Ni_xCo_{2-x}P$.