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Construction of high electrical conductive nickel phosphide alloys with controllable crystalline phase for advanced energy storage

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ABSTRACT

Nickel–based compounds are promising energy storage materials due to their high specific capacitance and energy density, but their practical applications are severely prevented by the poor rate capability which ascribed to the low conductivity. Herein controllable synthesis of high electrical conductive nickel phosphide alloys is achieved by conversion of Ni_3C into Ni_2P, Ni_7P_3 and $Ni_{12}P_5$ using trioctylphosphine as phosphorus source. The current-voltage curves indicating that the conductivity of these nickel phosphide alloys is higher than commercial graphite. They deliver excellent electrochemical characteristics including high specific capacitance and excellent rate capability. Simultaneously, the asymmetric supercapacitors with high energy density and long cycle life are also assembled based on nickel phosphide alloys as positive electrode and activated carbon as negative electrode. The AC//Ni_2P asymmetric supercapacitor delivers the highest specific capacity of 239.5C g^{-1} at a current density of 0.5 A g^{-1} and a maximum energy density of 53.2 Wh kg^{-1} (at a power density of 0.3998 kW kg^{-1}). The study will provide a new strategy for the construction of high performance energy storage materials by enhancing their intrinsic electrical conductivity and controlling their microstructure.

1. Introduction

Electrochemical energy storage devices (EESDs, i.e., batteries and electrochemical capacitors) have been hailed as promising candidates to exploitation of renewable but intermittent energy sources and powering the now-ubiquitous portable electronics as well as electric vehicles [1,2]. Due to the high power density, fast charging/discharging rate, and excellent cycle performance, electrochemical capacitors (ECs) have been considered as a kind of efficient EESDs [3,4]. Unfortunately, the energy density of carbon based electric double layer capacitors is still lower than batteries and prevents their practical applications [5,6]. Therefore, most of studies are focused on improving the energy density of ECs while maintaining their high power density and long cycle life [7]. One of the effective approaches is to developing transitional metal oxides and sulphides based pseudocapacitive materials [8].

Typical transitional metal oxides/sulphides include nickel, cobalt, manganese, molybdenum, and vanadium based oxides/sulphides as well as their binary systems [9–13]. Among them, nickel based oxides/sulphides is one of the most promising candidates due to its high specific capacitance and large energy density [14–18]. However, these nickel-based energy storage materials are severely prevented by their poor electrical conductivity which limits rate capability of ECs. It is because that the O and Ni atoms in these nickel oxides are completely combined by covalent bonds due to the high electronegativity of the O element. According to the theory of chemical bonds, all the electrons in the covalent bonds are shared by both of the bonding atoms and there are no free electrons exist. Therefore, the materials combined by covalent bonds show very poor electrical conductivity. Unfortunately, the low electrical conductivity will resulted incompetent rate capability and power density. On the 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

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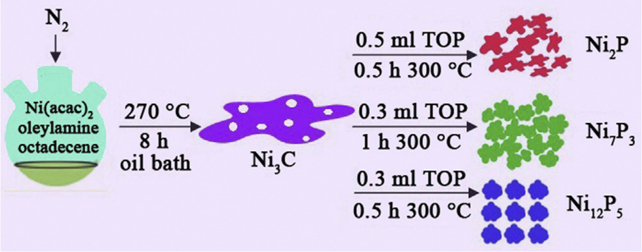
high rate charge-discharge condition, and introducing severe electrochemical polarization which could reduce the utilization efficiency of active materials. Therefore, improving the electrical conductivity is regarded as an urgent research task for electrode materials.

Generally, the strategy of improving conductivity is adding high electrical conductive porous carbons, carbon nanotubes, carbon fibers, or graphene which can provide high electrical conductivity, such as three-dimensional carbon nanotube networks supported nickel oxide [19], poly(aniline-co-m aminophenol)/graphene/NiO nanocomposite [20], carbon nanotubes/NiO nanocomposites [21], and microtubular carbonized kapok fiber/NiO composites [22] are fabricated to improve the electrical conductivity and showed better capacitive performance than NiO. However, the rate capability of these composites is still poor due to the limited improvement of the conductivity. This because that the intrinsic electrical conductivity of nickel oxides would not be improved by only adding the high conductive materials. Therefore, it is a challenge to exploit new nickel based materials with high electrical conductivity.

Interestingly, nickel phosphide possesses the metalloid characteristics and superior electrical conductivity [23], is a novel high electrical conductive electrode material of ECs. It is because phosphorus (P) atoms shows lower electronegativity than O atoms, thus both of the metal bonds and covalent bonds are existence in the nickel phosphides, rather than only covalent bonds in the NiO. This is important for nickel phosphides to serve as high performance electrode materials. On the one hand, the Ni(II) combined by covalent bonds in nickel phosphides could store charges and provide high capacitance through Faradaic reactions. On the other hand, the Ni combined by metallic bonds could provide free electrons and greatly improving electrical conductivity. This means that nickel phosphides will not only possess high capacitance, but also provide high electrical conductivity, is a kind of ideal electrode materials. Presently, Ni_2P nanoflakes [24], Au/$Ni_{12}P_5$ core/shell nanocrystals [25], Ni_2P/rGO nanoparticles [26], and Ni-coated Ni_2P [27] are fabricated as pseudocapacitive materials and exhibited excellent performance. However, the controllable construction of the nickel phosphides with different crystalline phases as well as unique particles structure has not been achieved and still remains a challenge.



Scheme 1. The synthetic process of Ni_3C, Ni_2P, Ni_7P_3 and $Ni_{12}P_5$ samples.

In this work, the Ni_3C is fabricated through the thermolysis of nickel acetylacetonate using oleylamine as a reducing agent and 1-octadecene as the solvent. Then high electrical conductive nickel phosphides (Ni-P) alloys with different crystalline phases (Ni_2P, Ni_7P_3 and $Ni_{12}P_5$) are controllable synthesized using Ni_3C and trioctylphosphine as precursor. When used as supercapacitor electrodes, the obtained Ni-P alloys exhibit higher electrical conductivity, high specific capacitance and excellent rate capability. It manifested that Ni-P alloys are ideal electrochemical materials and have great capacity for high-performance electrochemical energy storage systems.

2. Experimental section

2.1. Synthesis of the Ni_3C particles

Ni_3C particles were synthesized through liquid phase reaction [28]. As shown in the following process: 0.5 g acetylacetonate hydrate ($Ni(acac)_2 \cdot xH_2O$, 98%, TCI America), 5 ml of oleylamine (97% primary amine, Acros) and 5 ml of 1-octadecene (ODE, 90%, Sigma-Aldrich) were mixed in a three-necked round-bottomed flask. The mixture was degassed before backfilling with nitrogen and then heated to 270 °C for 8 h. After cooling to room

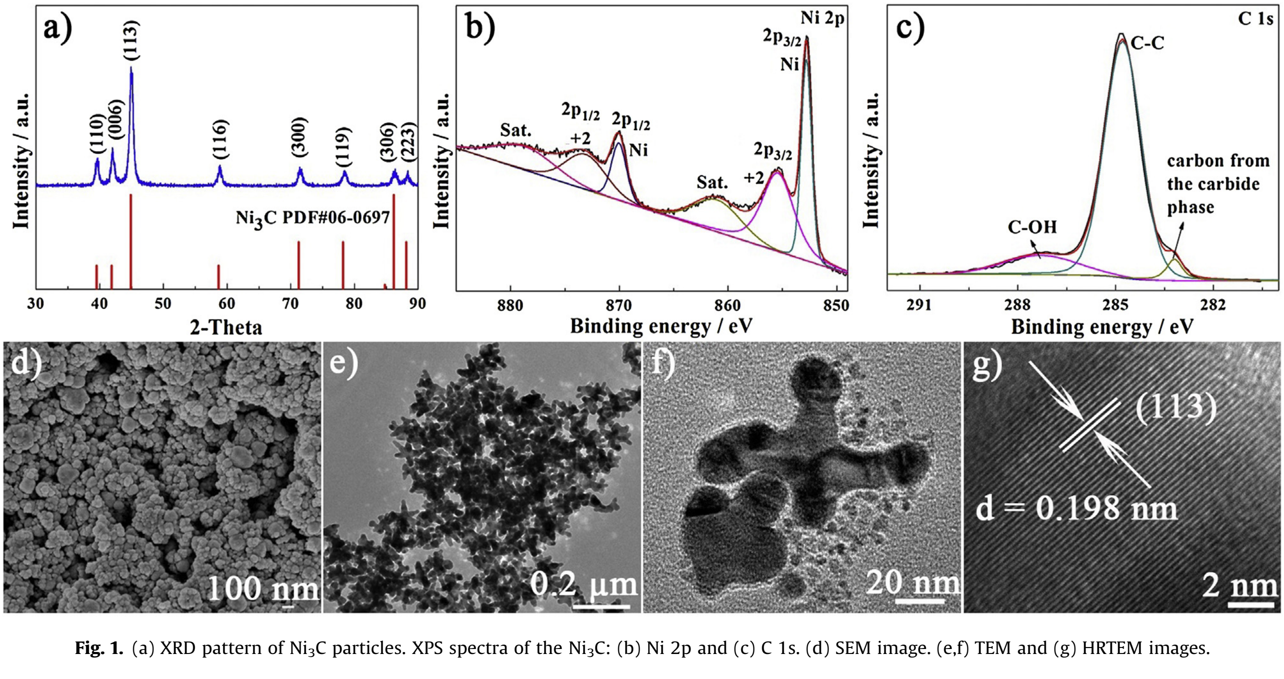


Fig. 1. (a) XRD pattern of Ni_3C particles. XPS spectra of the Ni_3C: (b) Ni 2p and (c) C 1s. (d) SEM image. (e,f) TEM and (g) HRTEM images.