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Short communication

A simple mild hydrothermal route for the synthesis of nickel phosphide powders

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Abstract

Nickel phosphide was synthesized via a hydrothermal reaction between nickel chloride ($NiCl_2 \cdot 6H_2O$) and red phosphor (P) in water at 200 °C. Phase constitution, morphology and composition were determined by XRD, SEM and EDS, respectively. The effect on the final products of experimental conditions such as the molar ratio of red phosphor to nickel chloride and reaction time were discussed, as well as the formation mechanism of nickel phosphides.

Keywords: Hydrothermal; Nickel phosphides; Red phosphorous

1. Introduction

The preparation of transition-metal phosphides has been extensively investigated, owing to their special properties and potential applications in many fields, including hydroprocessing catalysis [1,2]. Especially, dinickel phosphide (Ni_2P) is an excellently hydroprocessing catalyst, corrosion-proof, oxidation-resistant, and wear-proof material [3]. Many techniques have been applied to the preparation of transition-metal phosphides, including combination of the elements [4], disproportionation of phosphides [5], metathesis [6], fused salt electrolysis [7], hydrogen reduction of phosphates [8], chemical vapor deposition of organometallic precursors [9], reactions with phosphine [10] and so on. All the reported methods to transition-metal phosphides usually need high temperature and/or high pressure, and/or inert atmosphere protection, and/or toxic phosphides used as raw materials. Furthermore it is difficult to obtain nanocrystals under such conditions. So these method are very dangerous and expensive. On the other hand, nanocrystalline Co_2P, Ni_2P, and Cu_3P have been prepared [11] through a solvothermal process based on the direct reactions of metal halides ($CoCl_2 \cdot 6H_2O$ and $NiCl_2 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$) with yellow phosphorus and ethylenediamine used as the solvent. Cu_3P and Ni_2P hexagonal phases have also been obtained under solvothermal conditions based on the reactions of $CuCl_2 \cdot 2H_2O$ and $NiCl_2 \cdot 6H_2O$ with yellow phosphorus in ammonia liquor systems [12]. The two methods above make use of toxic and tangy substances, and the treatment process of yellow phosphorus is dangerous. So we need a more simple and safe route and cheaper raw materials to obtain useful fine materials under mild and non-toxic conditions. In this work, we report a convenient, simple, mild and non-toxic hydrothermal route to synthesize nickel phosphides, based on the direct reactions of $NiCl_2 \cdot 6HO$ with non-toxic red phosphor in water systems.

2. Experimental

2.1. Synthesis

Red phosphor powder (P) and nickel chloride ($NiCl_2 \cdot 6H_2O$) were weighed in appropriate amounts and loaded into a 77 mL Teflon cup. No more than 60 mL mixture of solvents was added to the cup. The Teflon cup was capped and then placed inside a stainless steel autoclave. The autoclave was inserted into an oven already at the reaction temperature (200 °C), allowed to stay there for 24–48 h and subsequently removed and allowed to cool to room temperature. The resulting product was filtered by vacuum suction and washed with distilled H_2O and absolute ethanol several times to remove the impurities. In one example of an ideal synthesis, 6.5037 g red phosphorus (0.21 mol) was combined with 4.991 g $NiCl_2 \cdot 6H_2O$ (0.021 mol) in 60 mL of distilled H_2O and heated at 200 °C for 24 h.

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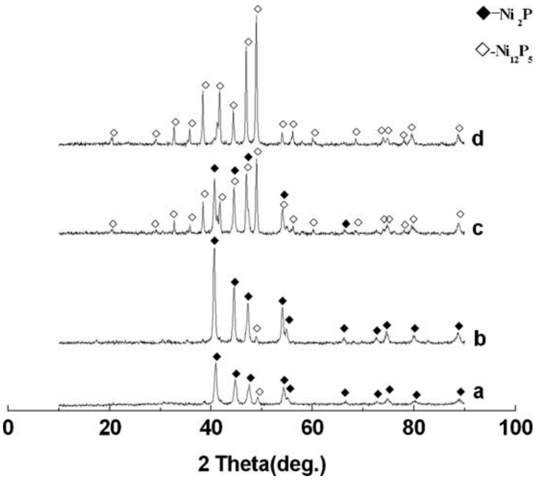

Fig. 1. Powder X-ray diffraction pattern of the as-prepared products (a–d).

2.2. Characterization

Phase constitution, chemistry and morphology were characterized by X-ray powder diffraction (XRD; Model D/max, Rigaku Co., Japan) with Cu Kα radiation (40 kV, 150 mA), energy dispersive X-ray spectroscopy (Oxford Instruments' INCA EDS system), and scanning electron microscopy (SEM; Model JSM-840, JEOL Co, Japan), respectively.

Table 1
Summary of hydrothermal reactions performed at 200 °C.

Name	Ni/P (molar ratio)	Reaction time	pH value		Phase constitution
			Initial pH	Final pH	
a	1/5	24 h	5.76	2.66	Ni_2P ($Ni_{12}P_5$)
b	1/10	24 h	5.85	2.14	Ni_2P ($Ni_{12}P_5$)
c	1/5	48 h	5.76	2.98	$Ni_{12}P_5$ (Ni_2P)
d	1/10	48 h	5.85	2.93	$Ni_{12}P_5$

3. Results and discussions

Fig. 1 shows the XRD patterns of the as-prepared products. Table 1 shows the hydrothermal experiment conditions and results of X-ray diffraction.

We can see from Table 1 and Fig. 1 that reaction of nickel chloride ($NiCl_2{\cdot}6H_2O$) with red phosphor in 1/10 molar ratio

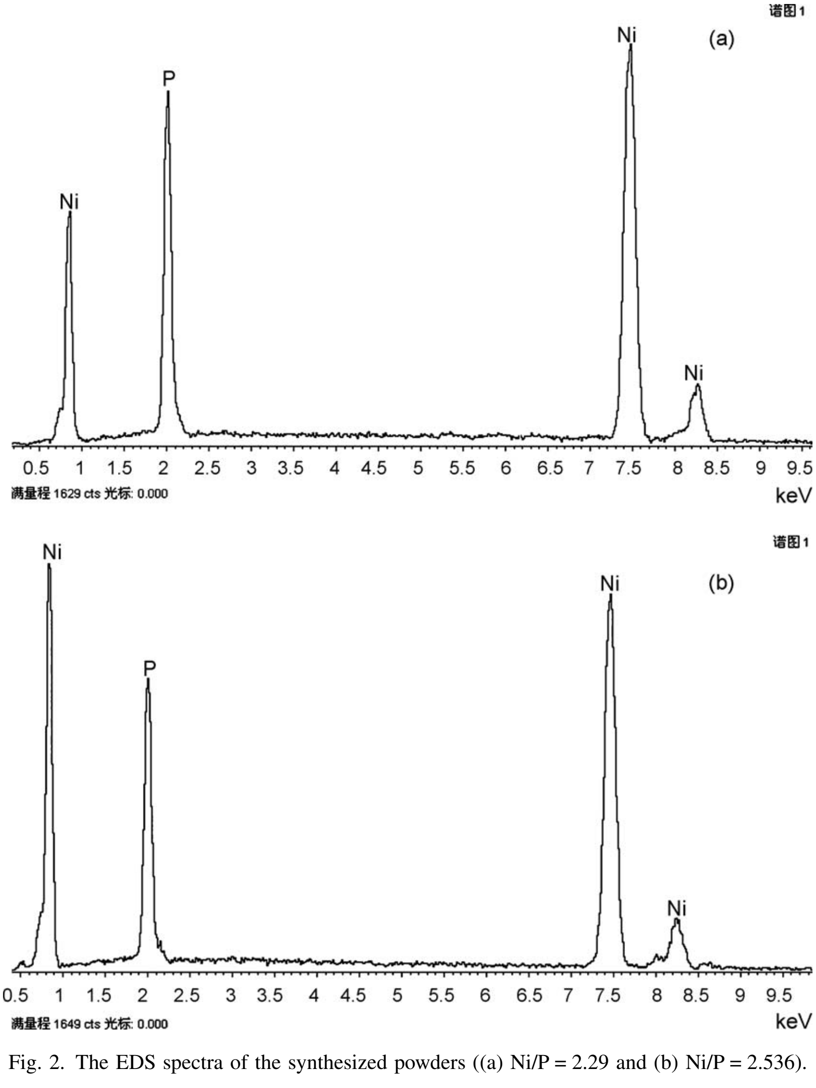

Fig. 2. The EDS spectra of the synthesized powders ((a) Ni/P = 2.29 and (b) Ni/P = 2.536).

heated at 200 °C for 24 h in H_2O produced almost pure Ni_2P with minimum amounts of $Ni_{12}P_5$ (Fig. 1b). When the reaction time was increased to 48 h, the final product was only $Ni_{12}P_5$ with almost identical XRD patterns (Fig. 1d) and no other impurity phases. If the ratio of Ni/P is changed to 1:5 at the same temperature (200 °C) for 24 h, the X-ray diffraction pattern shows Ni_2P plus a small amount of $Ni_{12}P_5$ (Fig. 1a). Increasing reaction time to 48 h, $Ni_{12}P_5$ will be the main phase with minimum Ni_2P (Fig. 1c). So it can be concluded that: (a) a noticeable amount of excess phosphor is needed to ensure a complete reaction and generate a pure phase product and (b) increasing reaction time goes against obtaining pure Ni_2P, but it is beneficial to $Ni_{12}P_5$ formation.

The EDS spectra of the synthesized powders (Fig. 2) show presence in the final products of Ni and P, the molar ratio of Ni/P being 2.293 (a) and 2.536 (b). There were no other impurity peaks in the spectra. The EDS results agree with the XRD results, further demonstrating that the final products of the reaction systems (Fig. 1b and d) were Ni_2P with minimum amounts of $Ni_{12}P_5$ and $Ni_{12}P_5$, respectively.

The SEM images of the ground red phosphor and the powders are shown in Figs. 3 and 4a–d, respectively. Fig. 3 shows the ground red phosphor to consist of relatively big aggregates with irregular shape with the particles size ranging from several hundred nanometers to a few micrometers. The SEM images of the nickel phosphide powders (Fig. 4a–d) are similar to the ground red phosphor. The morphology and particle size of the products are determined by the morphology and particle size of the red phosphor. The concentration of Ni^{2+} in the solution is higher than that at the surface of red phosphor, so Ni^{2+} diffuses from the solution to red phosphor, where it reacts to produce Ni_2P and $Ni_{12}P_5$.

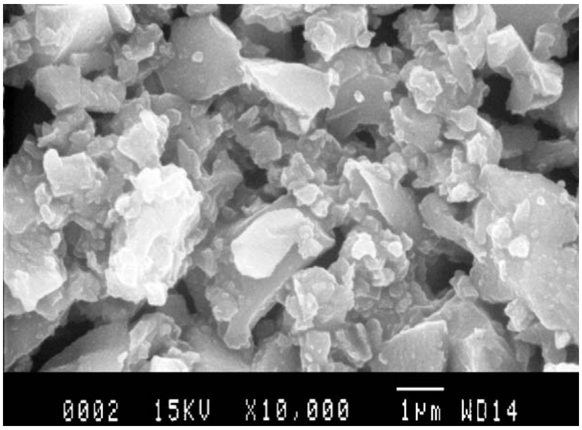

Fig. 3. The SEM image of the ground red phosphorus.

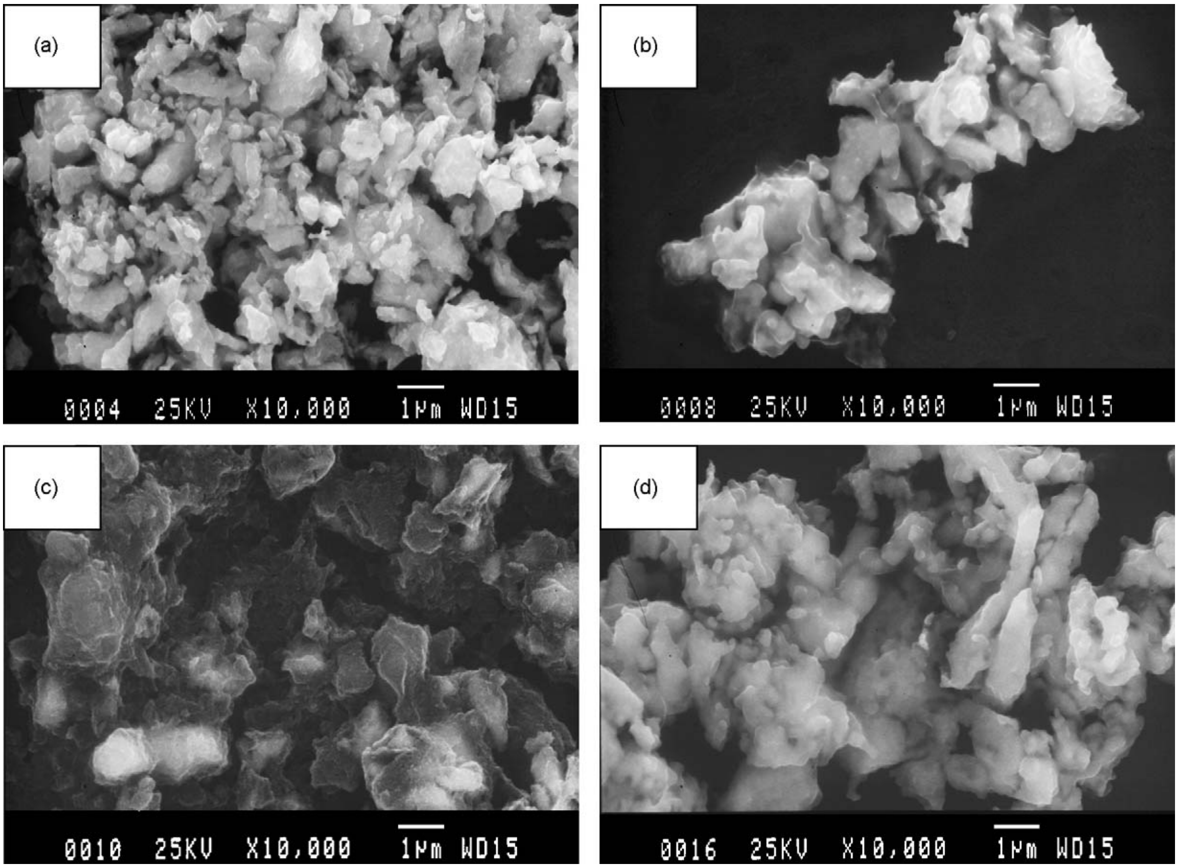

Fig. 4. The SEM images of the obtained powders (a–d).

4. Conclusions

Pure and well-crystallized Ni_2P and $Ni_{12}P_5$ powders were successfully synthesized by the hydrothermal method through a solid–liquid reaction between nickel chloride ($NiCl_2 \cdot 6H_2O$) and red phosphor (P) at 200 °C for 24 h and 48 h, respectively. The increase in the Ni/P ratio causes better crystallization of Ni_2P, while increasing the reaction time goes against obtaining pure Ni_2P, but it is beneficial to $Ni_{12}P_5$ formation.

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