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Short communication

Hydrothermal synthesis of cobalt phosphide nanoparticles

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Abstract

Cobalt phosphide (Co_2P) nanoparticles were prepared under mild hydrothermal conditions. The influence of the molar ratio of Co/P, temperature and duration were studied. The product was characterized by X-ray powder diffraction, transmission electron microscopy and energy dispersive spectroscopy tests, which indicated that the obtained products were pure and well crystallized Co_2P with an average particle size of about 30 nm.

Keywords: Hydrothermal synthesis; Co_2P; Nanoparticle

1. Introduction

Nowadays, substantial research interest has been focused on transition metal phosphides for a wide range of properties including superconductivity, catalytic activity, ferromagnetism, and magnetocaloric effects [1]. Among various options, cobalt phosphides are of great interests because of their magnetic, catalytic, and anode-material for lithium iron battery properties [2,3].

Conventionally, Co–P compounds are prepared by a solid-state route, which requires high calcining temperature and prolonged calcining time [4,5]. Alternate routes have been explored to overcome these shortcomings, such as acid dissolution method, sol–gel method and co-precipitation method, etc. [6]. However, few of them have successfully reduced the calcination time less than 10 h with high performance. Futhermore, they contain multi-step and time-consuming processes to prepare precursors [7,8].

In this paper, we report an one-step route to synthesize Co_2P powders via the mild hydrothermal method which does not need troublesome processes such as preparation of precursors and heat treatments. Also in our experiments, we use the harmless red phosphorus instead of white phosphorus. Our group has successfully synthesized Ni–P compounds by using this methods [9].

2. Experimental

2.1. Preparation of the starting suspension

The starting materials were $Co(NO_3)_2{\cdot}6H_2O$(≥99.0%) and red phosphorus powder(≥99.0%). The process was carried out as follows. Firstly, a desired amount of $Co(NO_3)_2{\cdot}6H_2O$ was dissolved in distilled water to obtain an aqueous solution. Then the red phosphorus powder was added into the solution under vigorous electromagnetic stirring with the molar ratio of Co/P varied from 1/4 to 1/12 (Table 1).

2.2. Preparation of samples

The prepared suspension was rapidly poured into a Teflon-lined autoclave, the filling factor was 80%. Then the autoclave was seated in a stainless steel bomb hydrothermally treated at 180–220 °C for 10, 14 or 18 h. The product was collected by vacuum filtration, washed four times with 200 ml distilled water and then dried at 60 °C for 3 h in air.

2.3. Characterization

The crystalline phase, chemical composition and morphology were characterized by X-ray powder diffraction

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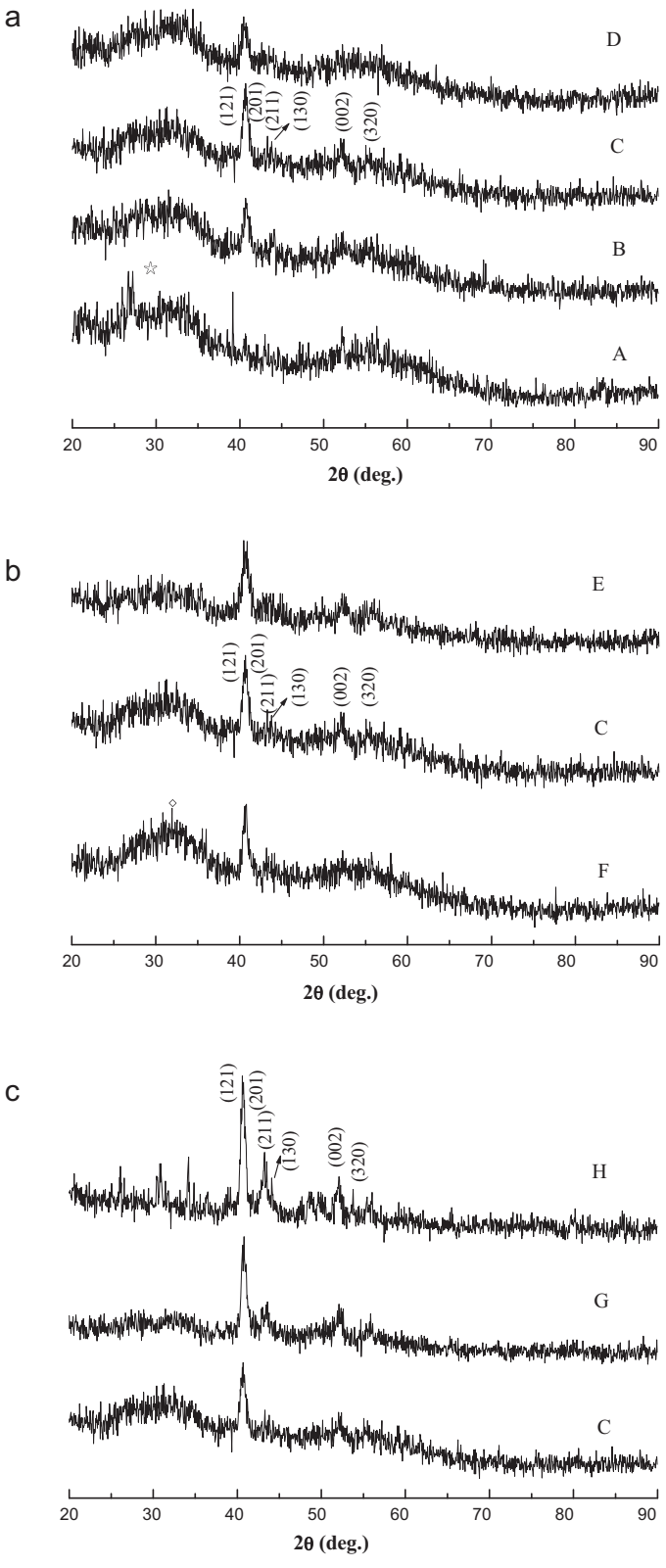

Fig. 1. (a) XRD patterns of as-prepared products with differert Co/P ratios at 200 °C, 10 h (A = 1/4, B = 1/8, C = 1/10, D = 1/12). (b). XRD pattern of as-prepared products with differert holding temperatures at the ratio of 1/10, 10 h (E = 180 °C, C = 200 °C, F = 220 °C). (c) XRD pattern of as-prepared products with differert reaction times at the ratio of 1/10, 200 °C (C = 10 h, G = 14 h, H = 18 h).

Table 1
Summary of the selected hydrothermal reactions.

Reference	Ratio Co/P	Soaking time (h)	Hold temperature (°C)
A	1/4	10	200
B	1/8	10	200
C	1/10	10	200
D	1/12	10	200
E	1/10	10	180
F	1/10	10	220
G	1/10	14	200
H	1/10	18	200

(XRD; Model D/max, Rigaku Co., Japan) with Cu Kα radiation (40 kV, 150 mA), energy dispersive X-ray spectroscopy (EDS; Oxford Instruments' INCA EDS system), and transmission electron microscopy (TEM; Model JEM-1200EX, JEOL Co, Japan), respectively.

3. Results and discussions

The summary of the selected hydrothermal reactions in 80 ml of Teflon-lined starting from 10 mmol of $Co(NO_3)_2{\cdot}6H_2O$ powder and appropriate amounts of red phosphorus is shown in Table 1. Analysis of the obtained data reveals that important parameters for the synthesis of Co_2P by hydrothermal method are the initial components ratio, duration and temperature. Fig. 1(a)–(c) shows the XRD patterns of the as-prepared products. The powder XRD analysis of sample A shows that the reaction between cobalt and red phosphorus does not result in the formation of significant amount of Co_2P at low Co/P ratio of 1/4. The sample mainly consisted of cobaltous nitrate (☆) with a minor admixture of the title compound.

Fig. 1(a) indicates that with the decreasing Co/P ratio from 1/4 to 1/10, the peak intensity of Co_2P increased. The reflection peaks of as-prepared products can be readily indexed to a crystalline phase of Co_2P. When the ratio was low, like sample A, there was not sufficient red phosphorus to reduce cobalt from its nitrate and it was mostly cobaltous nitrate (☆) with a minor

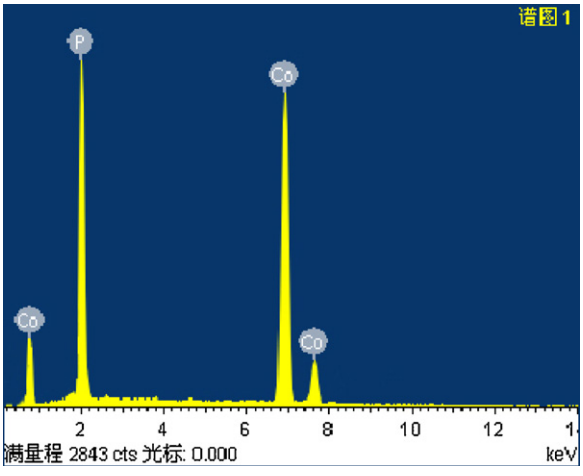

Fig. 2. EDS of Co_2P powders prepared at 200 °C for 18 h with starting Co/P = 1/10 (Co:P = 18.46:10.09 ≈ 2:1).

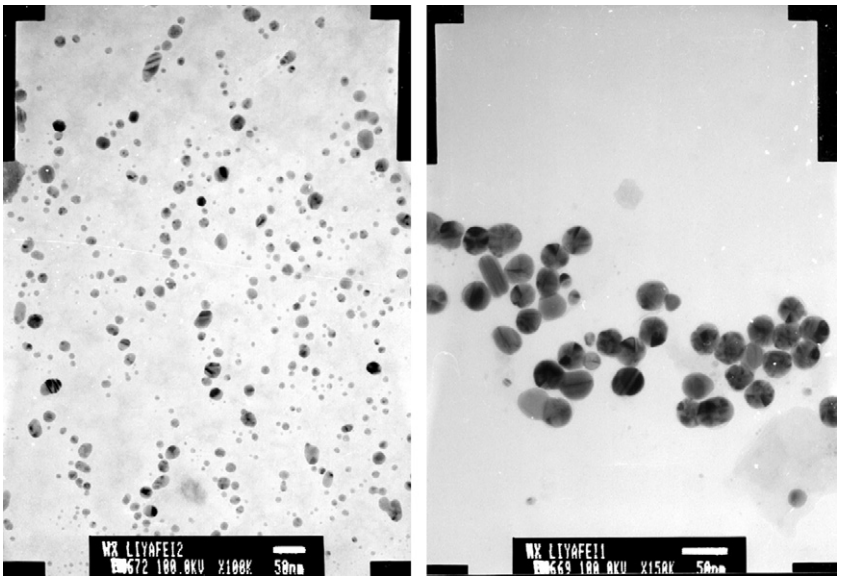

Fig. 3. TEM images of Co_2P powders prepared at 200 °C for 18 h with starting Co/P = 1/10.

admixture of Co_2P. Sample C presents a relatively narrow and sharp diffraction peaks. The mean crystal size of the products was about 30 nm estimated by Scherrer equation [10]. But when the ratio was 1/12, for example sample D, the peak intensity of Co_2P declined and peaks widened obviously.

Fig. 1(b) presents the influence of temperature on the formation of Co_2P. When temperature varied from 180 °C to 200 °C, the peak intensity increased and peaks became more narrow, indicating a higher crystallinity of obtained products. But when the temperature was 220 °C, a relatively high amount of impurity phase (◇) was formed.

As shown in Fig. 1(c), increasing the duration of the synthesis leads to significant formation of Co_2P. When the duration was 18 h as sample H, an ultrafine crystallized compound was formed.

The EDS spectra of the synthesized powders (sample H) in Fig. 2 shows presence in the final products of Co and P, and there were no other impurity peaks in the spectra. The Co/P ratio was about equal to 1:2, which was corresponding to the XRD results.

Fig. 3 shows the transmission electron microscopy (TEM) images of the Co_2P powders prepared at 200 °C for 18 h. The powders were composed of nanoparticles with spherical shape. These results were in good agreement with the characteristic of sharp peaks in XRD pattern in Fig. 1 (corresponding to the mean crystal size of 30 nm estimated by Scherrer equation).

4. Conclusions

Co_2P nano-particles were successfully synthesized by the hydrothermal method using $Co(NO_3)_2{\cdot}6H_2O$ and red phosphorus. The Co/P ratio, holding temperature and duration influenced the phase composition and the crystallinity of the final products. An ultrafine Co_2P powder was synthesized at 200 °C for 18 h with starting Co/P ratio of 1/10. Starting Co/P ratio and holding temperature both could affect the formation and crystallinity of Co_2P. Lengthen in duration could benefit the crystallinity of the particles.

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