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ORIGINAL ARTICLE

Hydrothermal synthesis of cobalt–nickel bimetallic phosphides

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Abstract Ultrafine cobalt–nickel bimetallic phosphides were prepared by mild hydrothermal method and characterized by techniques, such as XRD, EDS, and TEM. The results showed that the as-prepared products were well crystallized and particle sizes ranged from 10 to 20 nm. With the increasing amount of Ni^{2+} in the suspensions, the crystallinity of obtained products was improved gradually and the crystallite sizes increased accordingly.

Keywords Cobalt–nickel bimetallic phosphide · Hydrothermal · Nanoparticles

Introduction

Transition metal phosphide compounds have great application prospects in the catalytic agent (Brock and Senevirathne 2008; Rodriguez et al. 2003) due to their excellent antisulfur-poisoning property and superior catalytic activity. They are the promising candidates in industrial application and have attracted the attention of many researchers. Considering this, many scientists have done plentiful research work in this field. They have investigated a series of synthesis methods, such as chemical combination by elementary substances directly (Rundqvist 1966), replacement reaction by solidity (Fjellvag et al. 1984) chemical reaction between metal halide lamp and phosphate (Rowley and Parkin 1993), and decomposition of organic compound of metal (Gingerich 1964). However, these procedures typically suffer from relatively high reaction temperature and long annealing periods.

Aitken et al. (2005) have firstly reported solvothermal syntheses of Cu_3P. Thereafter, our group has synthesized Ni_2P, $Ni_{12}P_5$, and Co_2P with hydrothermal method using red phosphorus as raw material (Liu et al. 2010; Huang et al. 2010, 2011). Until now, few related studies have paid any attention to the above-mentioned synthesis process. In this study, we synthesized ultrafine cobalt–nickel bimetallic phosphide powders with red phosphor, which was a benign and substantial phosphor source to synthesize transition metal phosphide. In addition to the advantageous raw material, the hydrothermal experiments were conducted under a relative low temperature (200°C) for only 10 h.

Experiment

Preparation of the starting suspension

Starting materials were analytical reagents: $NiCl_2 \cdot 6H_2O$ ($\geq$99.0%), $CoSO_4 \cdot 7H_2O$ ($\geq$99.5%), and red phosphor (Fig. 1). The hydrothermal synthesis process was carried out as follows. Firstly, a desired amount of $NiCl_2 \cdot 6H_2O$ and $CoSO_4 \cdot 7H_2O$ were added to distilled water to get a mixed aqueous solution of Ni^{2+} and Co^{2+}. Then red phosphor was added to the solution under vigorous stirring to get the starting suspension. Concentrations of the suspensions and hydrothermal conditions of the experiments are presented in Table 1. In this work, the molar ratio of Co^{2+} and P remained 1:5, and the amount of Ni^{2+} was adjusted according to Table 1.

Preparation of the samples

The prepared suspension was poured into a Teflon-lined autoclave with 0.8 filling factor, sealed, and

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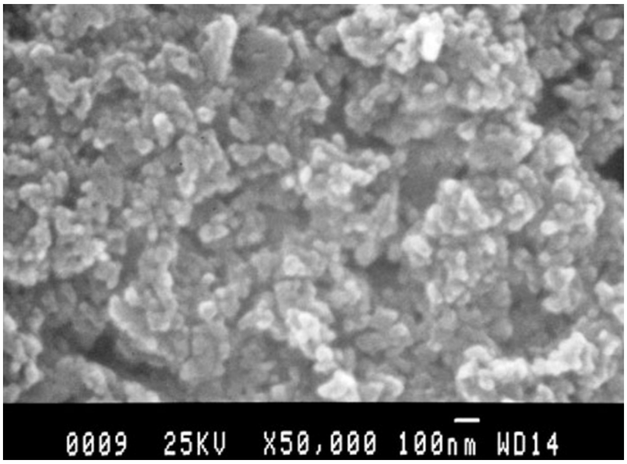

Fig. 1 SEM image of red phosphor raw material

hydrothermally treated at 200°C for 10 h. After the autoclave cooled to room temperature, the black products were collected and washed with plenty of distilled water. They were then dried at 50°C for 5 h in the air.

Characterization

Phase constitution, chemical composition, 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 transmission electron microscopy (TEM; Model JEM-1200EX, JEOL Co, Japan), respectively.

Results and discussion

Figure 2 presents the XRD patterns of samples from different ratios of Ni/Co/P prepared at 200°C for 10 h. It showed that products of Groups 1–5 (especially for Groups 2 and 3) were well crystallized. All the reflection peaks had a good agreement with the reported results so far (Burns et al. 2008; Aal et al. 2008). Along with the decreasing amount of initial Ni^{2+}, peaks of Groups 4 and 5 became relatively wider and smaller than those of Groups 1–3. When the ratio of Ni/Co/P was 1:25:125 (Group 6), the main peaks were hardly observed which should be attributed to small crystallite sizes. Based on XRD results, the mean crystal size of the obtained products was about 10–20 nm estimated by Scherrer equation through half width of the main peak in the 40° region. It was obvious that with the increasing amount of Ni^{2+} in the suspensions, the crystallinity of obtained products was improved gradually and the crystallite sizes increased accordingly.

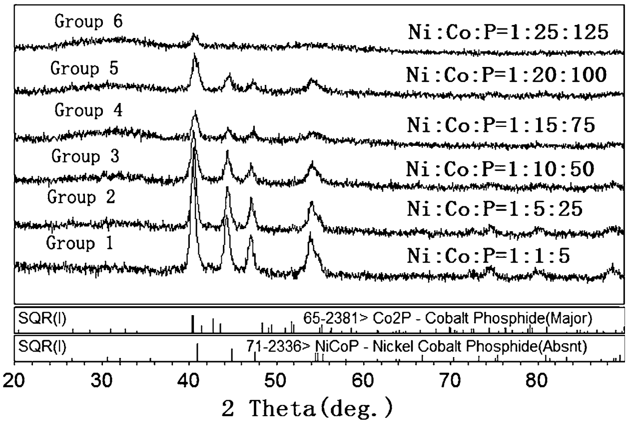

Fig. 2 XRD patterns of products synthesized by hydrothermal method

The EDS spectra of Groups 2 and 3 in Fig. 3 show the presence in the products of Ni, Co and P, and there are no other impurity peaks in the spectra. The Ni/Co/P ratios were 50:4:20 and 44:4:19, respectively. The EDS results confirmed the chemical composition of the as-prepared products and agreed well with the XRD results in Fig. 2.

Table 1 Hydrothermal conditions of Groups 1–6

	Starting Ni^{2+} (mol/L)	Starting Co^{2+} (mol/L)	Starting P (mol/L)	Ni^{2+}:Co^{2+}:P (molar ratio)	Soaking temperature (°C)	Holding time (h)
Group 1	0.156	0.156	0.75	1:1:5	200	10
Group 2	0.031	0.156	0.75	1:5:25	200	10
Group 3	0.016	0.156	0.75	1:10:50	200	10
Group 4	0.010	0.156	0.75	1:15:75	200	10
Group 5	0.008	0.156	0.75	1:20:100	200	10
Group 6	0.006	0.156	0.75	1:25:125	200	10

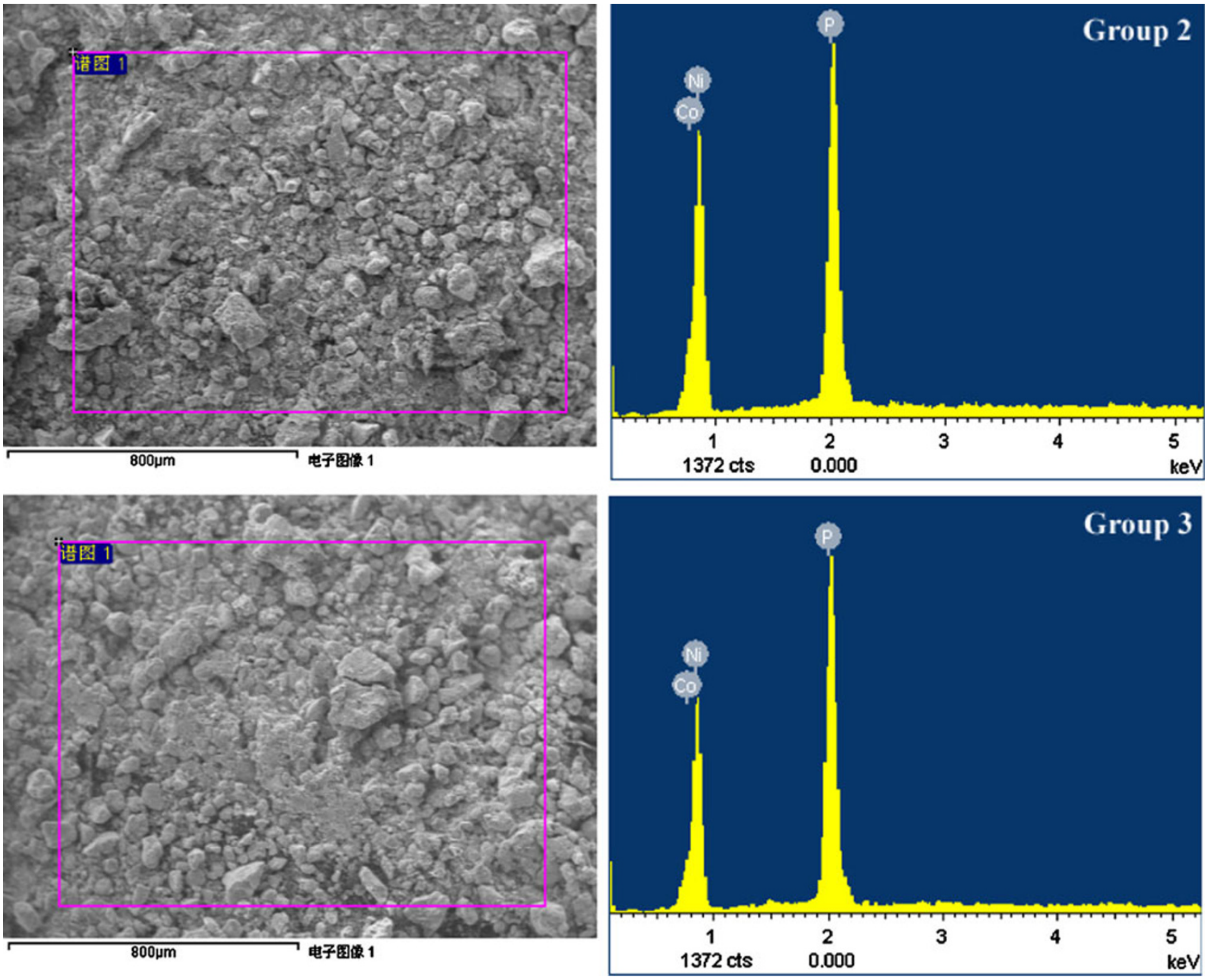

Fig. 3 EDS of Groups 2 and 3

Transmission electron microscopy and selected area electron diffraction (SAED) images of the obtained products from Groups 2 and 3 are shown in Fig. 4. The powders were composed of irregular aggregates forming from nanosize crystallites (10–20 nm estimated by Scherrer equation). SAED patterns recorded on particle in the TEM image confirmed that our products were made up of nanocrystalline compounds that showed characteristic diffuse and faint electron diffraction rings. And it also indicated that the as-prepared aggregates were polycrystal particles (Revaprasadu et al. 1999; Yang et al. 1998).

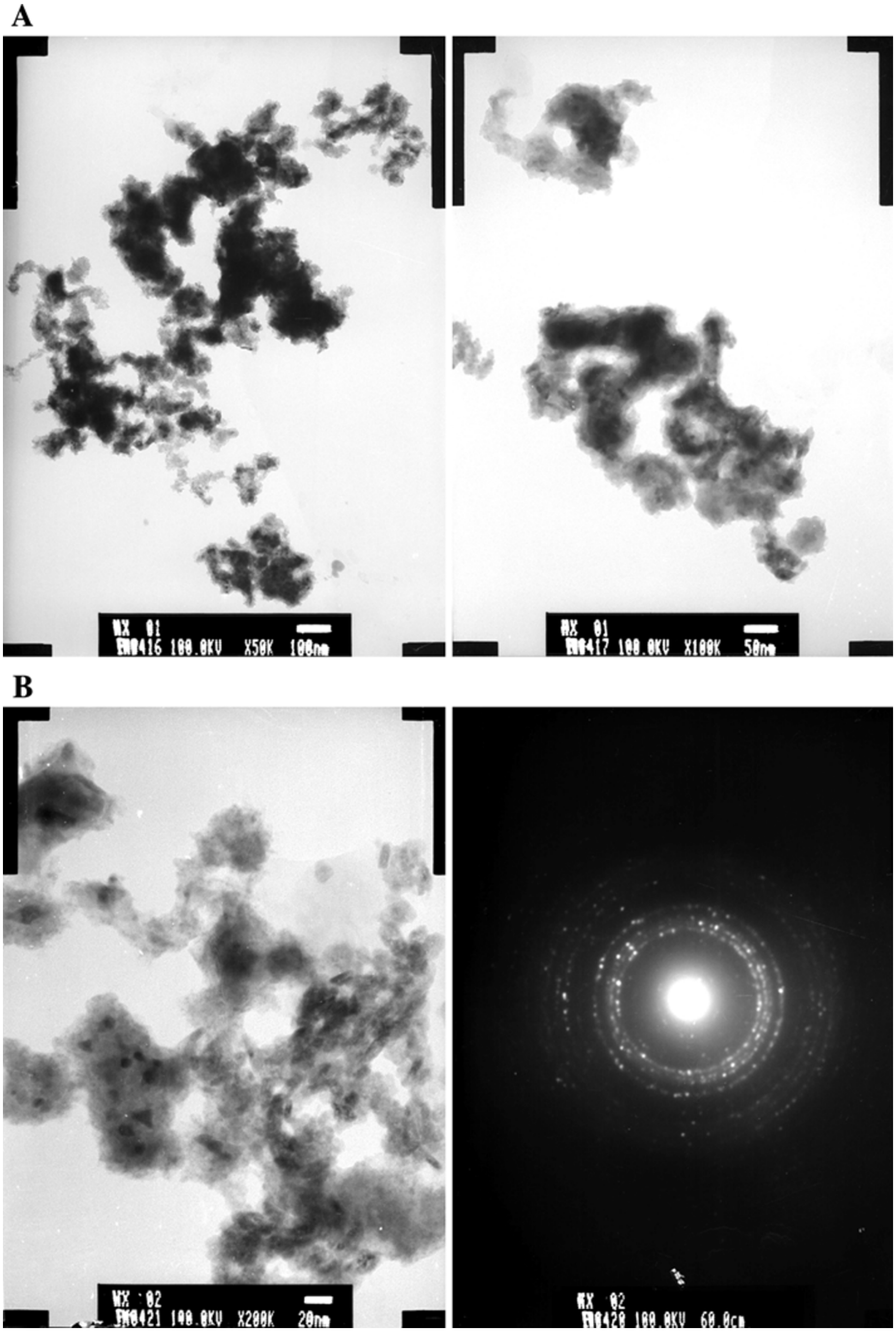

Fig. 4 **a** TEM images of Group 2; **b** TEM and SAED images of Group 3

Conclusion

Cobalt–nickel bimetallic phosphide nanoparticles were successfully synthesized by the hydrothermal method at 200°C for 10 h. The sizes of as-prepared products were 10–20 nm. With the increasing amount of Ni^{2+} in the suspensions, the crystallinity of obtained products was improved gradually.

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