

Polymer-assisted synthesis of Co₂P nanocrystals

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Abstract

Co₂P nanocrystals were successfully synthesized by a polymer-assisted hydrothermal method. The reaction was carried out at 190 °C–220 °C using cobalt chloride hexahydrate (CoCl₂·6H₂O) as Co-source and yellow phosphorous as P-source. Polyacrylamide (PAM) was used as surfactant. By controlling the experiment parameters such as the reaction temperature and the amount of polyacrylamide (PAM), Co₂P nanocrystals with the rod-like or flower-like morphology could be prepared successfully. The phase and the morphology of the samples were characterized by X-ray diffraction (XRD), transmission electron microscopes (TEM), electron diffraction pattern (ED) and high resolution transmission electron microscope (HRTEM). Furthermore, based on the results of the TEM observation, the possible formation processes of the Co₂P nanorods or nanoflowers were also discussed.

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1. Introduction

Nanoscale one-dimensional (1D) materials have attracted great research interest owing to their importance in fundamental research and technological applications [1]. Therefore, much effort has been devoted to their synthesis and characterization. Recently, a solution-phase synthesis route with the help of a polymer including long-chain amines, polyvinylpyrrolidone (PVP) [2], polyethylene glycol (PEG) [3] and poly (diallyldimethylammoniumchloride) (PDAC) [4] has been developed for synthesizing binary nanomaterials. Here, a polymer may be a good choice as a stabilizer or a structural director and can be designed with certain physical properties [2].

Transition-metal phosphides form a large family. Many of them play a key role due to their potential applications in many fields, such as electricity, luminescent devices and electronic components [5] and as superior catalysts [6]. Among them, Co₂P has been extensively investigated as potential components for magnetic applications. Traditionally, Co₂P nanocrystals have been prepared by different methods. For example, Co₂P

was prepared by directly reacting phosphine (e.g. PH₃) or phosphorus pentachloride with cobalt or cobalt salts, or by metal-organic chemical vapor deposition or self-propagation high temperature synthesis routes [7]. These procedures require either high reaction temperature (1000 °C) or long annealing periods. Recently, solution-phase synthesis [8], sol–gel methods [9] and solvothermal method [10, 11] have also been reported. Some of them gave some interesting results [11], which attract us to explore the simpler methods.

In this paper, we present a facial polymer-assisted hydrothermal method, in which Co₂P nanocrystals can be successfully prepared. Here, PAM acts as the stabilizer and the shape controller. As an available stabilizer and controller (soft template), PAM has been used to synthesize calcium carbonate [12], CdSe [13] etc. But few researches have been focused on the synthesis of the Co₂P nanocrystals.

2. Experimental

All of the reactants are of analytical grade and used without any further purification.

In a typical procedure, the appropriate amount of CoCl₂·6H₂O (2 mmol), polyacrylamide (PAM, 0.2 g) and 45 mL water were mixed into a Teflon liner autoclave of 50-mL capacity.

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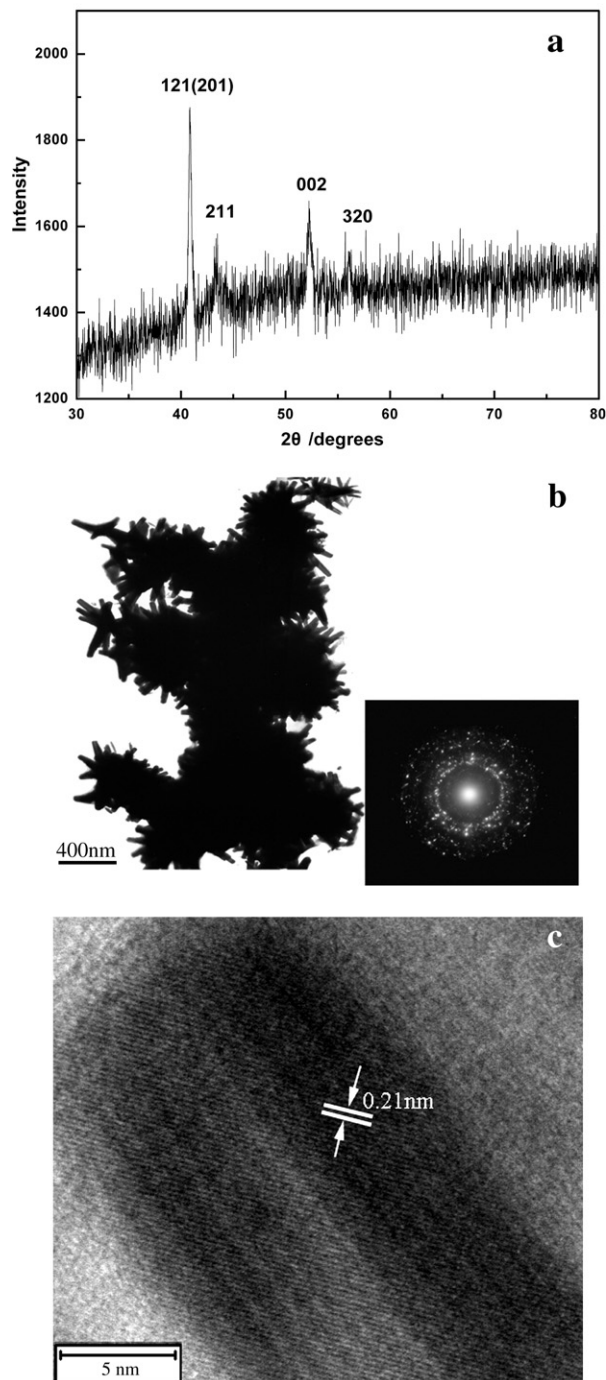


Fig. 1. The typical XRD pattern (a), TEM image (b), ED (the inset) and HRTEM image (c) of the Co_2P sample prepared at 190 °C.

When the solution was transparent, yellow phosphorus (0.62 g) was added. The autoclave was sealed and was maintained at 190 °C for 48 h, then air cooled to room temperature. The resulting black precipitates were washed successively with benzene, absolute ethanol and water and dried in vacuum at 50 °C for 4 h.

The samples were characterized by X-ray powder diffraction (XRD, Bruker D8). The morphologies and the electron diffraction pattern (ED) of the samples were investigated

using an H-600 transmission electron microscope and a JEM-2100 high resolution transmission electron microscope respectively.

3. Results and discussion

A typical XRD pattern of the as-prepared sample is shown in Fig. 1a. All peaks of the sample prepared at 190 °C for 48 h in this pattern can be indexed to orthorhombic Co_2P phase with lattice constants $a=5.6407 \text{ \AA}$, $b=6.5751 \text{ \AA}$, which are close to those of the reported values (the Joint Committee on Powder Diffraction Standards (JCPDS) Card. No. 32-0306). No other peaks that belong to the impurities such as P, Co could be detected.

Fig. 1b shows the TEM image of the as-prepared Co_2P sample. From this figure, some beautiful Co_2P nanoflowers can be seen clearly and each nanoflower is composed of a large number of nanorods extending radially from the center. We believe that these nanoflowers are formed by crossing of bundles of nanorods, where many such nanorods aggregate and form nanoflowers. The inset shows the corresponding electron diffraction (ED) pattern of the sample, where ED rings from inner to outer can be indexed as the diffraction of the planes of (201), (121), (130), (131) and (320) of orthorhombic Co_2P , respectively. Fig. 1c depicts the HRTEM image of the as-prepared sample. The lattice spacing between the adjacent planes is about 0.21 nm, which is close to the (211) lattice spacing of Co_2P nanocrystals.

As the experimental system we designed here was rather complex, a series of experiments were also carried out. And the results indicate that reaction temperature and polymer surfactant play important roles in the experiments.

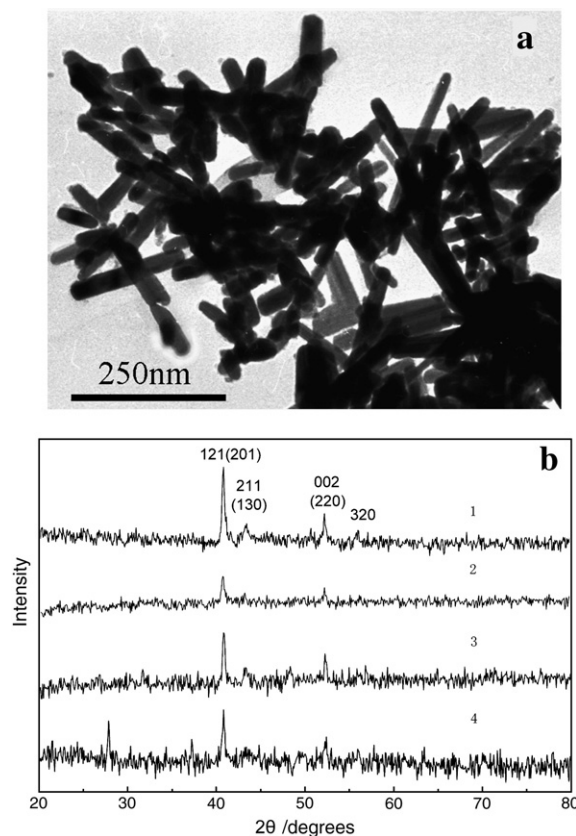


Fig. 2. TEM image of the Co_2P sample prepared at 220 °C, 24 h (a) and XRD patterns (b) of the Co_2P samples (1.220 °C; 2.190 °C; 3.180 °C; 4.170 °C).

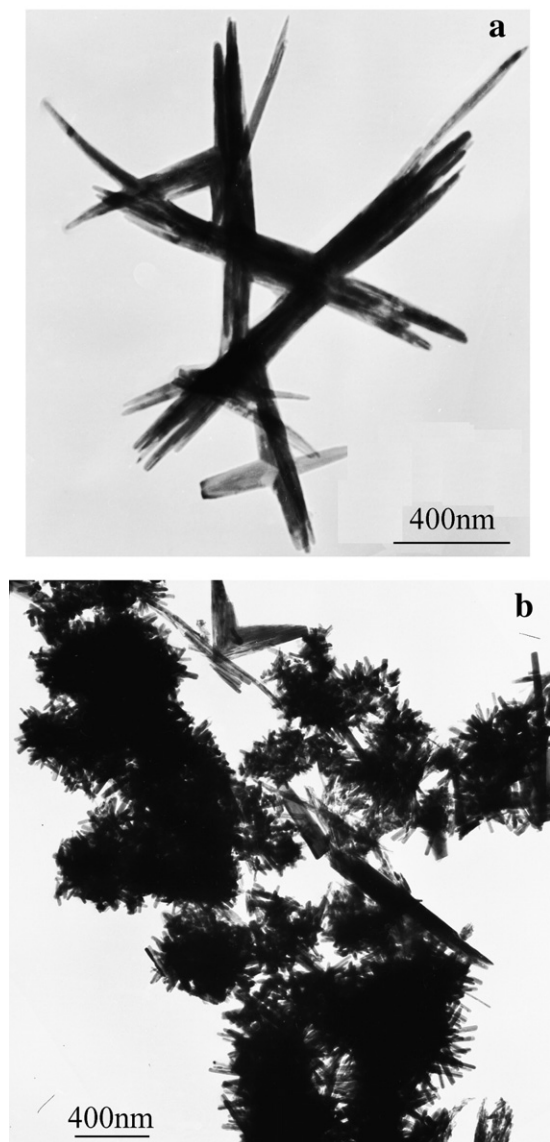


Fig. 3. The effects of PAM on the Co_2P samples prepared at a. 220 °C; b. 190 °C.

When the temperature was increased from 190 °C to 220 °C, nanoflowers disappeared and nanorods appeared (Fig. 2a). Further observation found that these nanorods were short but some of them crossed each other, which indicates that higher temperature is favored for dispersing of nanorods or nanoflowers. The length and the average diameter of these nanorods are 100 to 200 nm and 18 nm, respectively. But when temperature was below 190 °C, from the XRD results of Fig. 2b, poor purity or crystallization would appear.

The polymer surfactant PAM is another key factor which affects the final Co_2P sample. When PAM was used, Co_2P nanorods or nanoflowers could be obtained with a high yield. Moreover, increasing the amount of PAM from 0.2 g to 0.4 g only resulted in the increasing length of nanorods (Fig. 3a), but had little effect on their diameter. Additionally, when the amount of PAM exceeded a certain value, it might retard the reaction because of the large viscosity of the system. Therefore, the surfactant PAM used here may not only act as a structure directing agent, which can be adsorbed selectively on some specific facets of crystals and consequently control crystal growth direction, but

also provides an alkaline surrounding, in which yellow phosphorus can much easier initiate the reaction and form as-prepared product. However, when the amount of PAM was about 0.15 g, some special morphology with wider diameter coexisted with nanoflowers (Fig. 3b); further reducing the amount of PAM, the yield of the Co_2P sample decreased and the sample with the irregular morphology appeared.

In the present route, the synthesis of Co_2P nanocrystals is based on the reaction between Co^{2+} and PH_3 . PH_3 is produced by the reactions of yellow phosphorus with solvent (in Eq. (1)) [14–16]. Once PH_3 gases were generated, cobalt ions will immediately combine with them to form Co_2P nuclei. While the as-produced H_3PO_3 and H_3PO_4 undergo successive reactions in Eqs. (2) and (3), which increase the amount of PH_3 and accelerate the reaction of PH_3 with cobalt ions until one of the raw materials runs out [17,18].



After the initial nucleation, newly formed Co_2P nuclei grew into nanoparticles. When the reaction time was carried out at 190 °C for 24 h, small Co_2P nanoparticles were observed to coexist with some crossing nanorods (Fig. 4a); when time was prolonged to 48 h, nanoparticles disappeared and a large amount of beautiful flowers formed (Fig. 4b). However, when temperature was increased to 220 °C for 24 h, only a small quantity of nanoparticles with short nanorods could be picked out due to the fast velocity of the system (Fig. 4c), these nanoparticles or short nanorods grew and further formed longer nanorods when time was extended to 48 h (Fig. 4d). Based on the observation of TEM, it is plausible that the newly formed Co_2P nanoparticles aggregated and self-assembled preferentially into rod-like nanocrystals with the help of PAM. Driven by the minimization of interfacial energy or magnetic forces, these nanorods may aggregate and form bundles of nanorods or nanoflowers.

4. Conclusion

In conclusion, Co_2P were synthesized by a simple polymer-assisted solvothermal method. In the present route, Co_2P nanorods or nanoflowers could be obtained in water by selecting the appropriate polymer surfactant. The nature of one-dimensional (1D) nanostructure of Co_2P nanocrystals may be expected to play an important role in fabricating nanoscale devices and magnetic properties applications.

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References

- [1] J. Hu, T.W. Odom, L.C.M. Ieber, Acc. Chem. Res. 32 (1999) 435.
- [2] R. Maity, U.N. Maiti, M.K. Mitra, K.K. Chattopadhyay, Physica, E, Low-Dimens. Syst. Nanostruct. 33 (2006) 104.

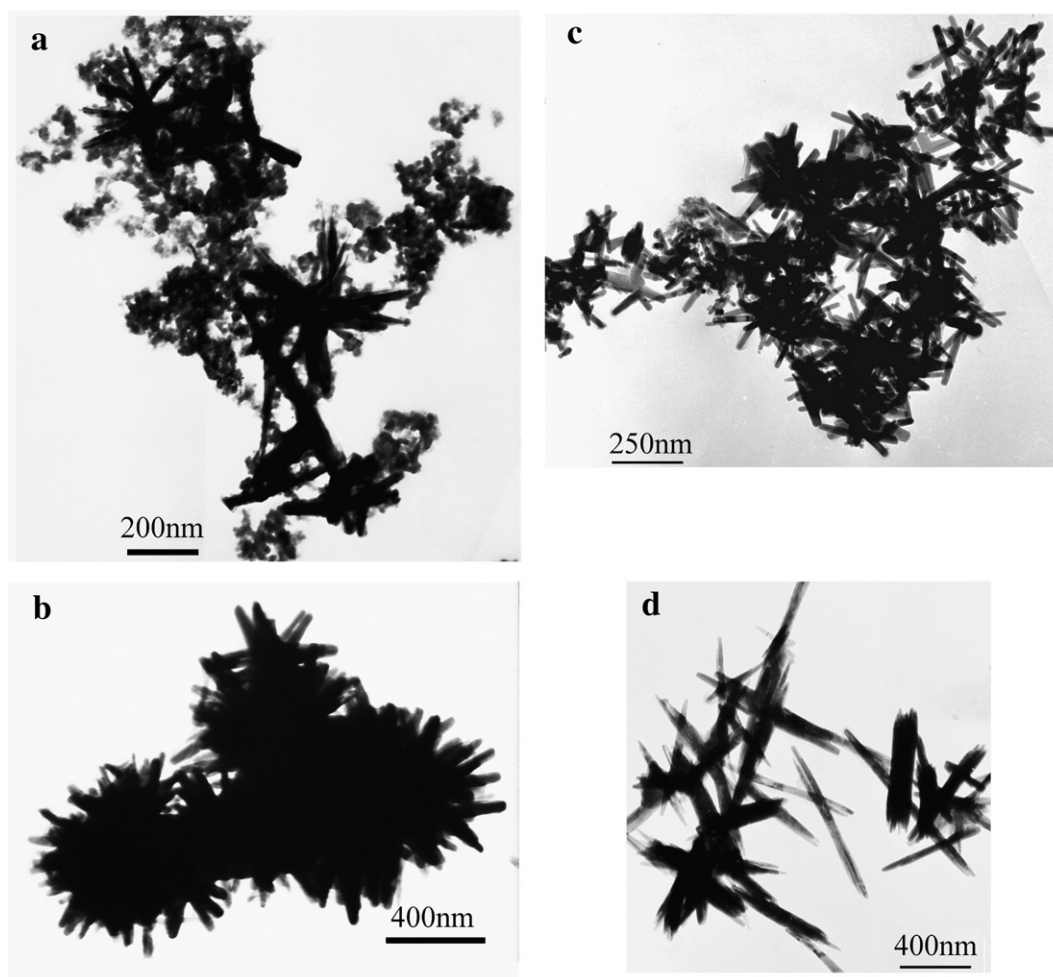


Fig. 4. TEM images of the Co_2P samples prepared at a. 190 °C, 24 h; b. 190 °C, 48 h; c. 220 °C, 24 h; d. 220 °C, 48 h.

- [3] X.F. Zhou, S.Y. Chen, D.Y. Zhang, X.F. Guo, W.P. Ding, Y. Chen, *Langmuir* 22 (2006) 1383.
- [4] G. Nizri, S. Magdassi, J. Schmidt, Y. Cohen, Y. Talmon, *Langmuir* 20 (2004) 4380.
- [5] B. Aronsson, T. Landstrom, S. Rurdquist, *Borides, Silicides and Phosphides*, Wiley, New York, 1965.
- [6] S.T. Oyama, P. Clark, X. Wang, T. Shido, Y. Iwasawa, S. Hayashi, J.M. Ramallo-Lopez, F.G. Requejo, *J. Phys. Chem. B* 106 (2002) 1913.
- [7] P.R. Bonneau, P.F. Jarris, R.B. Kaner, *Nature* 349 (1991) 510.
- [8] J. Park, B. Koo, K.Y. Yoon, Y. Hwang, M. Kang, J.G. Park, T. Hyeon, *J. Am. Chem. Soc.* 127 (2005) 8433.
- [9] C.M. Lukehart, S.B. Milne, S.R. Stock, *Chem. Mater.* 10 (1998) 903.
- [10] F. Luo, H.L. Su, W. Song, Z.M. Wang, Z.G. Yan, Ch.H. Yan, *J. Mater. Chem.* 14 (2004) 111.
- [11] H.W. Hou, Q. Peng, Sh.Y. Zhang, Q.X. Guo, Y. Xie, *Eur. J. Inorg. Chem.* (2005) 2625.
- [12] Q. Yu, H.D. Ou, R.Q. Song, A.W. Xu, *J. Cryst. Growth* 286 (2006) 178.
- [13] Y. Hu, J.F. Chen, W.M. Chen, J.Q. Ning, *Mater. Lett.* 58 (2004) 22.
- [14] J.R.V. Wazer (Ed.), *Phosphorus and its Compounds*, vol. I, Interscience Publishers, Inc., New York, 1958, p. 99, (“Chemistry”).
- [15] S. Brunauer, J.F. Schultz, *Ind. Eng. Chem.* 33 (1941) 828.
- [16] S.C. Chen (Ed.), *Important Inorganic Reactions*, 3rd ed., Shanghai Science and Technology Press, China, 1994, p. 1765.
- [17] S.M. Gao, J. Lu, N. Chen, Y. Zhao, Y. Xie, *Chem. Commun.* 24 (2002) 3064.
- [18] M. Lukehart, S.B. Milne, S.R. Stock, *Chem. Mater.* 10 (1998) 903.