Co_2P nanostructures constructed by nanorods: hydrothermal synthesis and applications in the removal of heavy metal ions

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In this paper, we report the successful synthesis of cobalt phosphide (Co_2P) nanostructures built up of nanorods *via* a simple hydrothermal route using white phosphorus (WP), sodium hypophosphite and cobalt dichloride as starting reactants in the presence of polyvinylpyrrolidone (PVP, 30 K). The as-obtained product was characterized by means of X-ray powder diffraction (XRD), energy dispersive spectrometry (EDS), (high resolution) transmission electron microscopy (TEM/HRTEM), selected area electron diffraction (SAED) and field emission scanning electron microscopy (FESEM). It was found that sodium hypophosphite played an important role in the formation of the Co_2P nanostructures. Some factors influencing the morphology of the product, including the reaction temperature, amount of sodium hypophosphite, surfactant, and so on, were investigated. The capacity of the product to remove heavy metal ions was also studied.

Introduction

Waste water from industry often contains various toxic and non-biodegradable heavy metal ions, such as Cr(VI), As(V), Cd(II), Pd(II) and Hg(II), that can seriously threaten the health of human beings, and so must be strictly treated before drainage. At present, the most widely used methods for removing heavy metal ions are chemical or electrochemical precipitation[1] and ion exchange. Moreover, some aquatic plants,[2] agricultural by-products,[3,4] microorganisms,[5] humic acid[6] and zeolites[7] have been found to possess the capacity to adsorb and accumulate heavy metal ions. Unquestionably, adsorption is one of the most convenient methods for removing heavy metal ions.

Recently, as a group of stable, sulfur-resistant metallic compounds, transition metal phosphides have attracted much research interest because they are considered to be a new class of highly active hydroprocessing and degradation catalysts that have substantial promise as next generation catalysts.[8,9] Transition metal phosphides also have extensive potential applications in magnetic, photonic, electronic and data storage devices due to their novel magnetic and semiconducting properties.[10–16] In 2006, our group successfully prepared hollow $Ni_{12}P_5$ nanospheres *via* a hydrothermal microemulsion route, and we found that the as-obtained hollow $Ni_{12}P_5$ nanospheres possessed an excellent ability to photocatalytically degrade organic dyes.[17] This fact implies that the as-prepared transition metal phosphides may have potential applications in waste water treatment.

The traditional approach to prepare metal phosphides is based on the direct reaction between highly toxic phosphines (*e.g.*, PH_3) or phosphorus pentachloride and metals or metal salts.[14,15] Later, the above approach was developed. $P(SiMe_3)_3$ was employed as the P^{3-} ion source, which reacted with metal ions or metal carbonyl complexes at elevated temperatures.[18–19] Transition metal phosphides can also be synthesized by the hydrogen reduction of metal phosphates at high temperature.[20] Recently, magnetic phosphides with anisotropic nanostructures have been obtained in solution phases *via* the multiple or continuous injection of a metal trioctylphosphine (TOP) precursor solution.[21–22] Herein, TOPs were used as phosphorus sources. Furthermore, a solvothermal synthesis route to metal phosphide nanoparticles was also reported by Xie and Qian.[23–26] However, it is still a challenge to prepare morphology- and size-controlled metal phosphide nanocrystals in a simple aqueous solution.

In this paper, we report the preparation of Co_2P nanostructures built up of nanorods *via* a simple hydrothermal route employing sodium hypophosphite (NaH_2PO_2), white phosphorus (WP) and $CoCl_2$ as starting reactants, and polyvinylpyrrolidone (PVP) as a surfactant. It was found that NaH_2PO_2 played an important role in the formation of the Co_2P nanostructures. Some influencing factors, including the reaction temperature, and the amounts of NaH_2PO_2 and surfactant, were also investigated. The as-prepared Co_2P nanostructures built up of nanorods show excellent capacities to remove heavy metal Pb^{2+} and Cd^{2+} ions, which implies that the product has potential applications in waste water treatment and environment protection.

Results and discussion

Fig. 1(a) is the XRD pattern of the product prepared under the present experimental conditions. All peaks can be indexed as an orthorhombic Co_2P phase by comparison with the JCPDS card file no. 32-0306. Among the diffraction peaks, the three strong ones centered at 40.8, 52.3 and 55.9° are ascribed to the overlapping of neighboring peaks (40.7 and 40.9, 52.0 and

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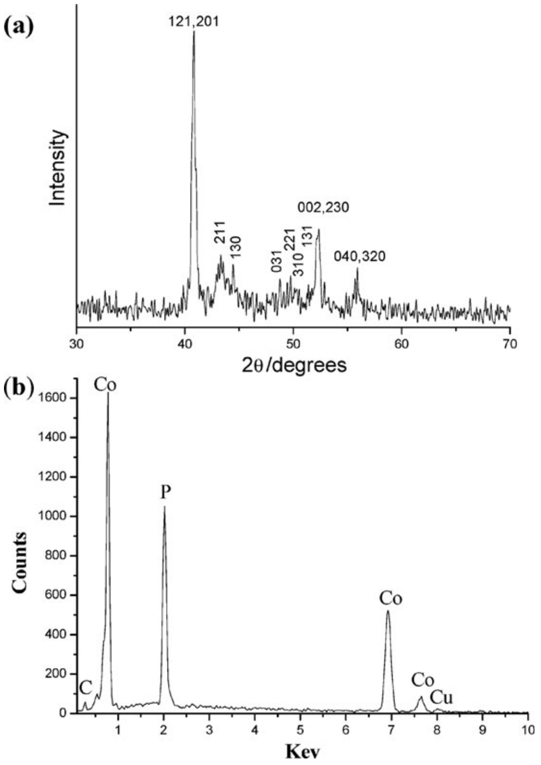

Fig. 1 (a) The XRD pattern and (b) the EDS analysis of the product prepared with PVP as a surfactant at 180 °C for 15 h.

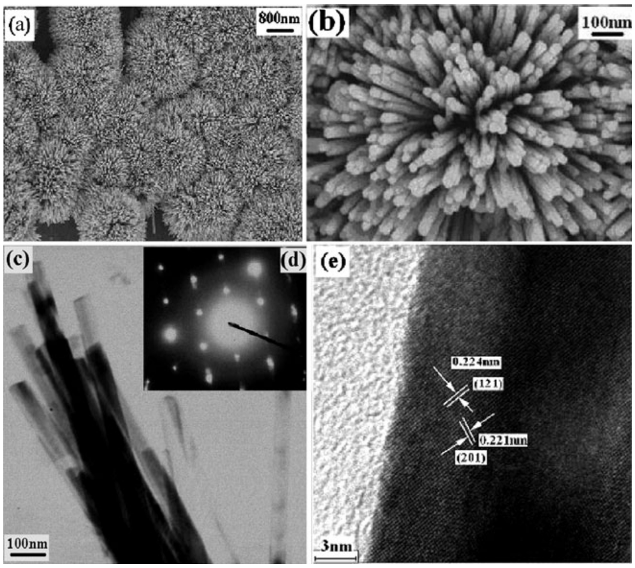

Fig. 2 (a,b) SEM images, (c) TEM image, (d) SAED pattern and (e) HRTEM image of the as-prepared Co_2P with PVP as a surfactant at 180 °C for 15 h.

52.6, and 55.6 and 56.2°). No impurity peaks are detected, indicating that the product is rather pure. An energy dispersive spectrometry (EDS) analysis of the as-prepared product confirmed the formation of Co_2P (see Fig. 1(b)). The peaks of Co and P can be easily seen, and the atomic ratio of Co/P in the nanocrystallines is 1.92 : 1 based on a calculation of peak areas. This result is close to the stoichiometry of Co_2P. The weak C and Cu peaks are attributed to the Cu support coated by a carbon film.

Also, the peak centered at 40.8° is far stronger than the other peaks in the XRD pattern, which implies the possible oriented growth of the product. This was confirmed by SEM observations; Fig. 2(a) shows a representative SEM image of the product. A large number of Co_2P nanostructures built up of nanorods can clearly be seen. Further magnification shows that these nanorods are homogeneous and their mean diameter is ~40 nm (see Fig. 2(b)). TEM observations further confirmed the SEM result (see Fig. 2(c)); some nanorods overlapping each other can easily be seen. The mean diameter of the rods is ~40 nm and their average length is above 1 μm. The SAED pattern of the product is shown in Fig. 2(d). The clear diffraction dots imply the single-crystal nature of the as-prepared Co_2P nanocrystals. The slight elongation of the ED spots can be attributed to disturbance by neighboring nanorods. Fig. 2(e) is a HRTEM image of the nanorods. The clear stripes further confirm their single-crystal nature. According to our measurements, the distances between the neighboring planes are 0.224 and 0.221 nm, corresponding to the (121) and (201) planes of Co_2P, respectively.

It was found that NaH_2PO_2 plays a crucial role in the preparation of the Co_2P nanostructures but that changing the amount of NaH_2PO_2 did not change the phase of the product (see Fig. 3(a) and 3(b)). If no NaH_2PO_2 was present in the system, the reaction could not be initiated at the present temperature (180 °C). When 0.318 g of NaH_2PO_2 was used, small amounts of Co_2P were produced. A typical SEM image of the as-prepared product is given in Fig. 4(a), in which many prickly nanostructures built up of abundant irregular nanorods can be seen. After increasing the amount of NaH_2PO_2 to 0.845 g, a greater amount of upstanding Co_2P nanostructures built up of nanorods was produced in high yield (Fig. 2). However, upon further increasing the amount of NaH_2PO_2 to 1.053 g, the Co_2P nanostructures built up of nanorods disappeared and some nanorods and nanoflakes co-existed in the product (see Fig. 4(b)). The above experiments indicate that an appropriate amount of NaH_2PO_2 is necessary for the formation of Co_2P nanostructures built up of nanorods.

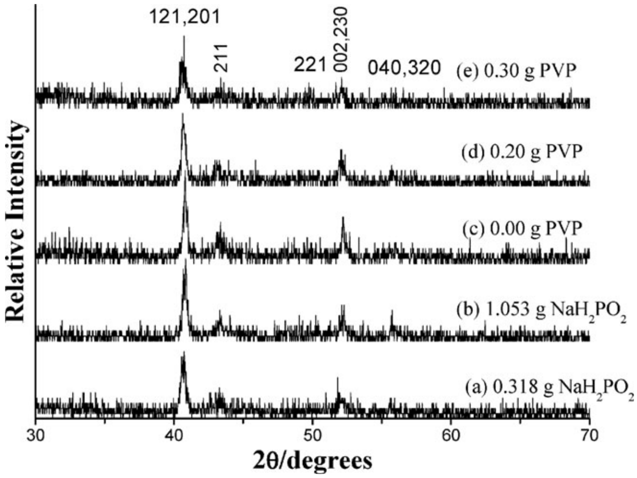

Fig. 3 XRD patterns of the products prepared under various experimental conditions: (a,b) only changing the amount of NaH_2PO_2 and (c,d and e) only changing the amount of PVP.

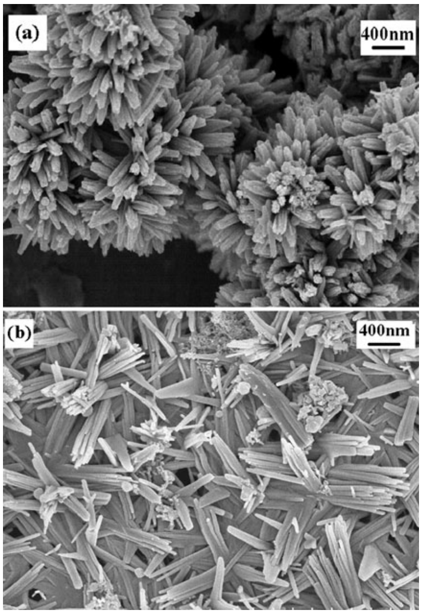

Fig. 4 FESEM image of the as-prepared cobalt phosphides with different amounts of NaH_2PO_2: (a) 0.318 g and (b) 1.053 g.

In the present work, the pH of the system changed from 6.8 before the reaction to 2.4 after the reaction. Namely, the reaction producing Co_2P nanostructures should be carried out in an acidic environment. Since the standard redox potentials of H_3PO_3/NaH_2PO_2, Co^{2+}/Co and P/PH_3 are −0.499, −0.277 and −0.063 V in acid systems, respectively, WP can be reduced more easily by NaH_2PO_2 (to PH_3) compared to Co^{2+} ions at our elevated temperature. The generated PH_3 rapidly reacts with Co^{2+} ions in solution to form Co_2P. In order to prove the above hypothesis, we prepared Co_2P using cobalt acetate as the Co^{2+} ion source instead of $CoCl_2$ to eliminate disturbance by Cl^- ions. Then, 0.5 ml of a 0.1 M $AgNO_3$ solution was dropped into the mother solution after the reaction. A white precipitate of silver phosphite appeared, implying that the above hypothesis is reasonable. The influence of the amount of NaH_2PO_2 on the formation of Co_2P nanostructures can be successfully explained by the above hypothesis. No PH_3 was produced in the system without NaH_2PO_2 under the current conditions, so the reaction could not be initiated. After the amount of NaH_2PO_2 was increased to 0.318 g, the reductive reaction of WP partly occurred, which led to the production of a small quantity of Co_2P nanostructures, while when 0.845 g of WP was used, enough PH_3 was produced. This resulted in the preparation of Co_2P nanostructures built up of nanorods. However, upon further increasing the amount of NaH_2PO_2 to 1.053 g, much PH_3 was produced within a short time due to the higher concentration of NaH_2PO_2. As a result, more Co_2P nuclei were formed, which led to the regression of Co_2P nanostructures built up of nanorods.

Usually, the presence of surfactants in a system efficiently controls the morphology and size of a product during the synthesis of nanomaterials. PVP is a common surfactant and is often used for the synthesis of materials. In our work, a suitable amount of PVP also played an important role in the high yield formation of our Co_2P nanostructures built up of nanorods. Fig. 5 shows SEM images of the products prepared in the presence of different amounts of PVP. XRD analyses also showed that the as-obtained products were still orthorhombic Co_2P (see Fig. 3c, 3d and 3e). When no PVP was used, the low yield product was composed of stubby nanorods (see Fig. 5(a)). This implies the intrinsically anisotropic growth properties of orthorhombic Co_2P. After 0.10 g PVP had been added to the system, Co_2P nanostructures built up of uniform nanorods were obtained (Fig. 2), which indicates that the capping effect of PVP leads to the formation of rod-like nanostructures. However, upon further increasing the amount of PVP to 0.20 g, many retrograded Co_2P nanostructures built up of shorter nanorods appeared (Fig. 5(b)). After the amount of PVP had been increased to 0.30 g, some flowers composed of irregular short rods were prepared (Fig. 5(c)). The above phenomena show that a suitable amount of PVP acts mainly as the structure-directing reagent during the reaction, while superfluous PVP acts mainly as a surfactant.

Additionally, our investigations showed that no reaction could be initiated in the present system when the temperature was below 180 °C. Upon further increasing the temperature to 200 °C, only Co_2P particles with mixed morphologies were obtained. The above facts imply that 180 °C is the optimum temperature to prepare Co_2P nanostructures built up abundantly of nanorods.

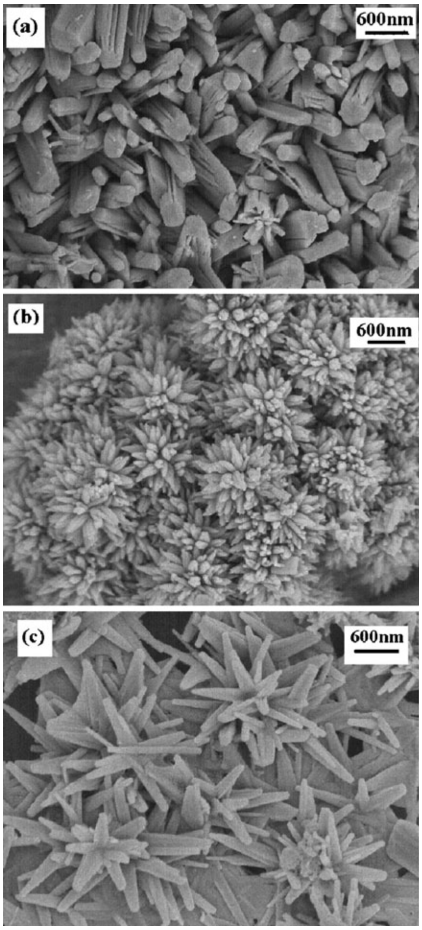

Fig. 5 FESEM images of the as-prepared Co_2P with different amounts of PVP: (a) 0 g, (b) 0.20 g and (c) 0.30 g.

As for various other materials, one of the challenging and intriguing problems is to find and study their potential properties, and thus achieve applications in life-related fields. The presence of heavy metal ions and dyes in waste water pose a major environmental health risk to local residents in our current world. Applications of nanomaterials in these fields may thus provide a direction for materials research.

In our previous work, we found that transition metal phosphides could photocatalytically degrade organic dyes in aqueous solution, which indicates that transition metal phosphides have a potential application in environmental treatment.[17] Pb^{2+} and Cd^{2+} ions are highly toxic pollutants in water courses, so their efficient removal is of great importance. Herein, we investigate the possible applications of our as-obtained Co_2P nanostructures built up of nanorods in water treatment, though metal phosphides are not traditional adsorbents. To evaluate the capacities of our as-prepared Co_2P nanostructures to remove heavy metal ions, we studied the absorbency changes of solutions containing Pb^{2+} and Cd^{2+} ions before and after introducing Co_2P nanostructures (see Fig. 6). When 10 mg of Co_2P nanostructures was added into 50 ml of Pb^{2+} solution with an initial concentration of 6.0 mg L^{-1} at room temperature under stirring for 30 min, the absorbency of the solution containing Pb^{2+} ions changed from initially 0.083 to 0.033 (Fig. 6(a)); the adsorption capacity was calculated to be 17.0 mg g^{-1}. Under the same experimental conditions, the as-obtained Co_2P nanostructures could also remove Cd^{2+} ions from a solution containing Cd^{2+} ions with an initial concentration of 4.5 mg L^{-1} (Fig. 6(b)); the removal capacity was calculated to be 8.8 mg g^{-1}. Experiments also showed that the spent materials could easily be regenerated by washing with distilled water several times and drying in a vacuum at 60 °C for 1 h. Heavy metal ions could still be removed by using the regenerated Co_2P nanostructures as absorbents; although their removal capacity for Pb^{2+} or Cd^{2+} ions slightly decreased, it was still 13.5 and 5.8 mg g^{-1}, respectively, in the second removal. Compared to other traditional absorbents (*e.g.*, activated carbon),[27] the removal capacity of the product is low. This is possibly ascribed to the influence of PVP. As a capping agent, the PVP molecules probably block a number of active surface sites on the nanostructures that are potentially available for adsorption. Nevertheless, the above results show that the present product can remove a certain quantity of Pb^{2+} and Cd^{2+} ions from water resources, which should mean that it has potential applications in the treatment of waste water and the protection of the environment. Furthermore, experiments also proved that the amount of heavy metal ions removed from water could be affected by the morphology of the Co_2P nanostructures. When Co_2P with different morphologies (as shown in Fig. 4) were employed as absorbents, the amount of Pb^{2+} removed from water was 15.2 and 13.4 mg g^{-1}, respectively. The above results show that the Co_2P nanostructures built up of nanorods have the best capacity for the removal of heavy metal ions from water resources in the current work.

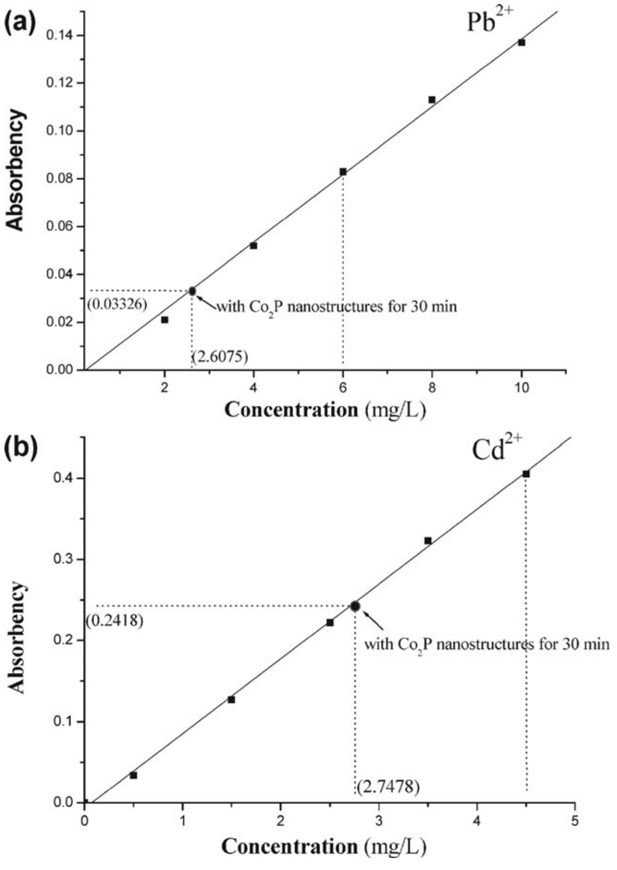

Fig. 6 The absorbency of a solution containing heavy metal ions: before (●) and after (· · ·) introducing our Co_2P nanostructures.

Conclusions

Co_2P nanostructures built up of nanorods have been successfully prepared by a simple and reliable hydrothermal route in the presence of PVP by employing white phosphorus, sodium hypophosphite and cobalt dichloride as starting materials. Our experimental results indicate that many parameters must be strictly controlled for the formation of Co_2P nanostructures built up of nanorods, including the amounts of sodium hypophosphite and PVP, and the reaction temperature. Our research also revealed that the as-synthesized Co_2P nanostructures possessed good capacities to remove heavy metal ions, such as Pb^{2+} and Cd^{2+}, from water resources. The above facts indicate that the present product has potential applications in the treatment of waste water and in the protection of the environment.

Experimental

All reagents were purchased from the Shanghai Chemical Company and used without further purification. In a typical experiment, the appropriate amount of $CoCl_2{\cdot}6H_2O$ (0.475 g), PVP (0.100 g) and NaH_2PO_2 (0.843 g) were dissolved in distilled water by vigorously stirring them with a magnetic stirrer at room temperature for 20 min to form a 20 ml solution. The as-prepared solution was poured into a Teflon-lined stainless steel autoclave with a capacity of 25 ml and WP (0.200 g) then added. Based on safety considerations, all operations relating to WP were carried out in water.

The autoclave was sealed and maintained at 180 °C for 15 h, then allowed to cool down to room temperature naturally. The black precipitates were collected, washed with carbon disulfide, distilled water and absolute ethanol several times in turn to remove impurities. Finally, the as-prepared sample was dried in a vacuum at 60 °C for 6 h.

X-Ray powder diffraction patterns of the products were recorded on a Japan Shimadzu XRD-6000 X-ray diffractometer equipped with graphite-monochromatized Cu-K_α radiation (λ = 0.15406 nm) using a scanning rate of 0.02° s^{-1} in the 2θ range from 30 to 70°. TEM, HRTEM and SAED measurements were carried out using a JEOL-2010 high resolution transmission microscope employing an accelerating voltage of 200 kV. FESEM and EDS images of the products were obtained using a Hitachi S-4800 field emission scanning electron microananlyser employing an accelerating voltage of 5 kV (15 kV for EDS measurements). A copper grid covered by a holey carbon film was used as the support.

Absorbency changes of solutions containing Pb^{2+} or Cd^{2+} ions before and after adsorption for 30 min were measured on an atomic absorption spectrometer (Thermo SOLAAR M6) by dispersing 10 mg of Co_2P nanostructures built up of abundant nanorods into 50 ml Pb^{2+} (6.0 mg L^{-1}) or Cd^{2+} (4.5 mg L^{-1}) solutions with stirring for 30 min, respectively.

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