One-pot Solution-phase Synthesis of Paramagnetic Co_2P Nanorods

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A solution-phase route has been developed for the synthesis of cobalt phosphide nanorods, which have been characterized by techniques of X-ray diffraction (XRD), electron microscope (SEM), and X-ray photoelectron spectroscope (XPS). The microscope analysis reveals that the nanorods have width of about 10 nm and length of 200–300 nm, which exhibit paramagnetic behavior down to 2 K, determined by a commercial superconducting quantum interference device (SQUID) magnetometer.

Metal phosphides are currently of great scientific interest in materials science and chemistry because of their important magnetic, electronic, and chemical properties.[1] Up to now, the studies on nanostructures of metal phosphides were rarely advanced in comparison to other semiconductor materials because of their difficult synthetic chemistry.[2]

Recently, MnP nanoparticles have been produced by a reaction of $Mn_2(CO)_{10}$ with $P(SiMe_3)_3$ in trioctylphosphine oxide (TOPO) and myristic acid.[3] FeP nanorods and nanowires have been synthesized in the TOPO and trioctylphosphate (TOP) solvent system via solution-phase injection route.[4] Fe_2P nanorods from thermal decomposition of delivered precursors using a syringe pump have been reported.[5] Meanwhile, Fe_2P nanocrystalline have also been prepared through an ethylenediamine solvothermal route.[6] To the best of our knowledge, high-quality and uniform Co_2P nanorods have never been reported up to now. Here, we report a novel one-pot solution-based synthesis to large-scale Co_2P nanorods from metal halides with yellow phosphorus at mild temperature. This low-cost and easily controllable method is much expected for fundamental and practical applications.

In a typical procedure, 0.475 g of $CoCl_2{\cdot}6H_2O$ (2 mmol) and 1.24 g of yellow phosphorus (10 mmol) were put into a 40-mL Teleon-lined autoclave, which were then filled with aqueous ammonia (28%) up to 80% of its capacity. The autoclave was maintained at 220 °C for 24 h and then cooled to room temperature. After reaction, black precipitates were collected and washed with absolute ethanol and distilled water in sequence to remove the by-products and possible impurities. The final products were dried in vacuum at 60 °C for 3–4 h for further characterized.

From the X-ray diffraction (XRD; Phillips X'Pert using Cu Kα radiation) patterns (Figure 1a), no impurities, such as P, CoP_3, could be found. All of the diffraction peaks could be indexed to the orthorhombic Co_2P (JCPDS file No.74-287). The X-ray photoelectron spectra (XPS; ESCALab MKII) of the Co_2P nanorods were shown in Figure 1b. The binding energy is 778.2 eV for Co $2p_{3/2}$, which is in good agreement with that in the literature.[7] The P 2p binding energy of our product, 129.8 eV, is consistent with the previous results (129.1 eV) for P.[8] From the integral peak areas of Co and P in the XPS spectra, the Co_2P nanorods have the appropriate molar ratio of Co:P = 1.95:1, which is close to the stoichiometry of Co_2P. No obvious impurities such as chloride or phosphate could be detected in the samples.

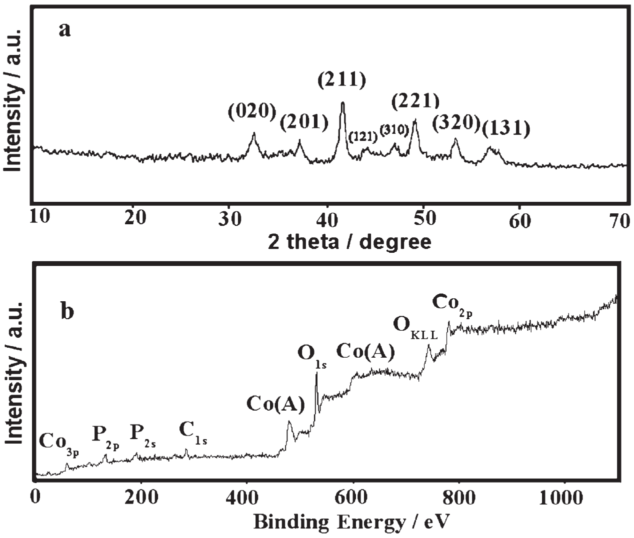

Figure 1. XRD patterns (a) and XPS analysis (b) of the as-prepared Co_2P nanorods.

Figure 2 shows representative field emission electron microscopic (FESEM; JEOL JSM-6700F) images of the products. The low magnification image (Figure 2a) reveals that the as-prepared product consisted of a large scale of group rod-shaped structures. From a high magnification image (Figure 2b), it is found that these nanorods are straight and uniform.

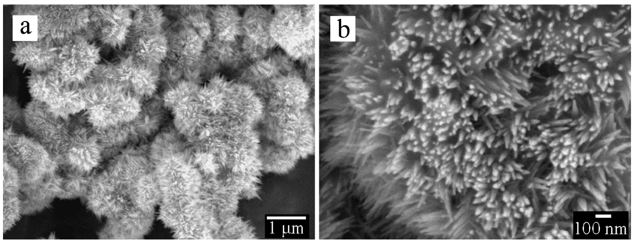

Figure 2. FESEM images of Co_2P nanorods: (a) at a low magnification, (b) at a high magnification.

The morphology and structure of the nanorods were further characterized by (high-resolution) transmission electron microscopy ((HR)TEM, JEOL-2010). The TEM image as shown in

Figure 3a demonstrates that the nanorods have width of about 10 nm and length of 200–300 nm. The inset selected area electron diffraction (SAED) pattern, recorded with the incident electron beam perpendicular to the surface of an individual nanorod, demonstrates that the as-produced nanorods are single crystals. This result can be supported by the HRTEM observation (Figure 3b), which clearly shows that the d value of 2.22 Å is corresponding to the interplanar spacing of (211) plane.

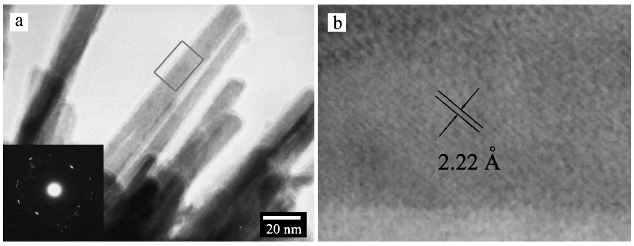

Figure 3. (a) A representative TEM image of Co_2P nanorods (inset: the corresponding SAED pattern), (b) An HRTEM image of an individual nanorod.

The magnetic properties of the Co_2P nanorods were measured using a commercial superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS). The magnetific-field dependence of magnetization (M vs H) at 2 K for Co_2P nanorods, as shown in Figure 4a, reveals no ferromagnetic characteristics and the results can be well described by paramagnetic moments.[3,6] The temperature dependence of the magnetization for Co_2P nanorods measured in an applied magnetic field of 500 Oe between 2 and 300 K is shown in Figure 4b. The results can be well described by the Curie–Weiss law, which agree well with those obtained from the M–H data. It is concluded that Co_2P nanorods is paramagnetic with no evidence of ferromagnetic ordering, which accord well with the magnetic properties of epitaxial Mn-doped ZnO thin films.[9] Further, the early reported paramagnetic $CoSi_3P_3$ validated the magnetic properties of the Co_2P nanorods, in which the transition metal is determinant.[10]

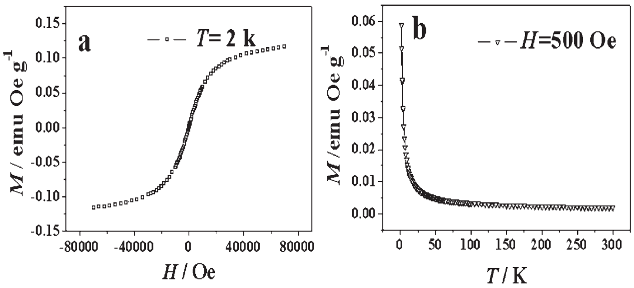

Figure 4. Magnetic properties of the Co_2P nanorods. (a) magnetific-field dependence of magnetization at 2 K. (b) temperature dependence of magnetization under an applied magnetic field of 500 Oe.

In the present route, the synthesis of Co_2P is based on the reaction of amino compounds with PH_3 which was produced from yellow phosphorus dismutation.[11] During the whole process, ammonia not only acted as a ligand to form complexes of $Co(NH_3)_4^{2+}$ with cobalt ions, but also as an alkaline solution, which activates the dismutation of yellow phosphorus. Once generated, the active PH_3 will immediately react with the cobalt-containing complex to form Co_2P.[12] The by-product H_3PO_3 induced circular reactions in the route,[11] which also increased the production of PH_3 and consequently accelerated the reaction of PH_3 with the cobalt complex to produce Co_2P at the same time. The possible reactions can be described as follows:

$$NH_3 \cdot H_2O \rightleftharpoons NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O \qquad (1)$$

$$Co^{2+} + 4\ NH_3 \rightarrow Co(NH_3)_4^{2+} \qquad (2)$$

$$P_4 + 3\ OH^- + 3\ H_2O \rightarrow PH_3 + 3\ H_2PO_2^- \qquad (3)$$

$$12\ [Co(NH_3)_4]Cl_2 + 7\ PH_3 + 3\ H_2O \rightarrow 6\ Co_2P + 24\ NH_3 + 24\ NH_4Cl + H_3PO_3 \qquad (4)$$

$$4\ H_3PO_3 \rightarrow PH_3 + 3\ H_3PO_4 \qquad (5)$$

$$P_4 + 6\ H_3PO_4 + 6\ H_2O \rightarrow 10\ H_3PO_3 \qquad (6)$$

In the detailed procedure, yellow phosphorus (melting point, 44.1 °C and boiling point, 280 °C) could form droplets dispersed in the aqueous solution to form heterogeneous liquid–liquid two phases with temperature elevated in the system. Obviously, the reactions easily occurred on the two-phase interfaces, from which Co_2P could grow epitaxially to form rod-like structures because of the capping effect of ammonia and the intrinsically anisotropic growth properties of orthorhombic Co_2P.[4–6,13,14] With the prolongation of reaction time, it is found that the length of the nanorods are elongated in the route. When ammonia was replaced by H_2O, ethanol, or benzene, there are not any nanorods only some particles were obtained.

In summary, we have developed a one-pot solution-phase route to Co_2P nanorods. XRD, XPS, and microscope analyses indicate that the orthorhombic Co_2P nanorods have width of about 10 nm and length of 200–300 nm. Additionally, the produced Co_2P nanorods exhibit paramagnetism down to 2 K. It is expected that the Co_2P nanorods may offer exciting opportunities for potential applications in areas of photoelectronic devices in the near future. The application of the solution-phase method has given us an edification to synthesize other one-dimensional metal phosphides.

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