A Mild One-Step Solvothermal Route to Metal Phosphides (Metal = Co, Ni, Cu)

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Nanocrystalline Co_2P, Ni_2P, and Cu_3P were successfully prepared through a simple solvothermal process based on the direct reactions of metal halides with yellow phosphorus at rather mild temperatures (80–140°C) with ethylenediamine used as the solvent. XRD, XPS, and TEM were used to study the phases, compositions, and morphologies of the final products. A possible mechanism is proposed and the influential factors in the process are discussed in detail.   © 2000 Academic Press

Key Words: solvothermal process; metal phosphides; ethylenediamine; nanocrystals.

I. INTRODUCTION

The preparation of transition-metal phosphides has been received extensive attention, owing to their important properties and potential applications in many fields (1, 2), such as electricity, mechanics, corrosion-resistance, and so on. Especially, dinickel phosphide (Ni_2P) is an excellently corrosion-proof, oxidation-resistant, and wear-proof material; copper phosphide is a kind of fine solder and important alloying addition (3, 4). Many methods have been adopted to synthesize transition-metal phosphides, such as metal organic chemical vapor deposition and the high-temperature self-propagating route. These procedures typically require high reaction temperatures (even above 1000°C sometimes) and long annealing periods to produce the crystalline materials (5–8). I. P. Parkin and his coworkers reported an exothermic, self-propagating reaction which affords transition-metal phosphides by frictional or thermal initiation (25–550°C) of mixtures of sodium phosphide (Na_3P) and anhydrous transition-metal halides in an evacuated sealed Pyrex or quartz ampules. The reaction proceeded with a short thermal flash (1–2 s) and the reaction temperature was always more than 1000°C, so that the product often fused into a black mass (9).

We have been looking for convenient routes to metal nitride, chalcogenide, and phosphide materials at mild temperatures (10–12). Recently, there is a strong trend toward the application of solution chemical synthesis techniques for materials preparation (13, 14). Among them, the solvothermal technique is most promising, in which the phase and morphology can be well controlled under rather mild temperatures. In this work, we report our current progress in preparing pure nanocrystalline Co_2P, Ni_2P, and Cu_3P through a mild solvothermal route, based on the reactions of metal halides with yellow phosphorus at 80–140°C in ethylenediamine.

II. EXPERIMENTAL

Appropriate amounts of analytically pure metal halide, typically 0.594 g $NiCl_2 \cdot 6H_2O$ (2.50 mmol) or 0.595 g $CoCl_2 \cdot 6H_2O$ (2.50 mmol) or 0.312 g $CuCl_2 \cdot 2H_2O$ (1.83 mmol), and 1.24 g yellow phosphorus (10 mmol) were put into an 80-ml autoclave with Teflon liner, which was then filled with ethylenediamine up to 90% of its capacity. The autoclave was maintained at 80–140°C for 12 h and then cooled to room temperature naturally. The black precipitates were collected and washed with benzene, 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 2 h.

X-ray powder diffraction (XRD) analyses of the samples were carried out in the Japan Rigaku D/max γA X-ray diffractometer equipped with a graphite monochromatized Cu$K\alpha$ radiation ($\lambda = 1.54178$ Å). The purity and components are determined by X-ray Photoelectron Spectra (XPS), which were recorded on the ESCALab MKII X-ray photoelectron spectrometer. The morphology was determined by the transmission electron microscopy (TEM) images, which were taken by the Hitachi Model H-800 transmission electron microscope and the accelerating voltage was 200 kV.

III. RESULTS AND DISCUSSIONS

In the XRD patterns (Fig. 1), all peaks can be indexed to a single orthorhombic cell of Co_2P with $a = 5.64$ Å,
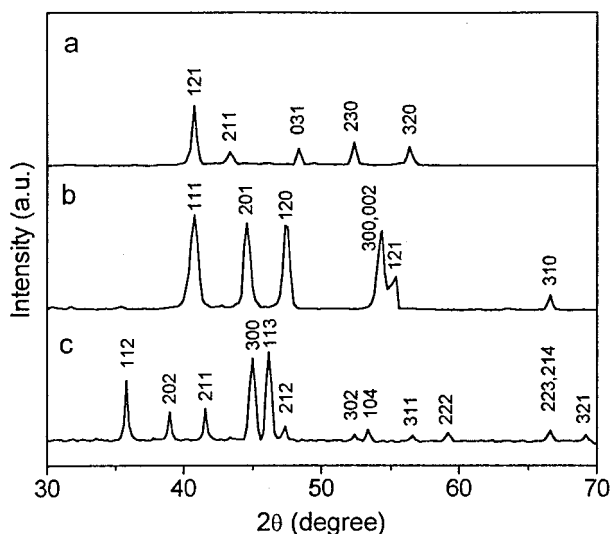
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FIG. 1. XRD patterns of as-prepared products: (a) Co_2P, (b) Ni_2P, and (c) Cu_3P.

$b = 6.60$ Å, $c = 3.50$ Å; a hexagonal cell of Ni_2P with $a = 5.86$ Å, $c = 3.37$ Å; a hexagonal cell of Cu_3P with $a = 7.08$ Å, $c = 7.13$ Å, respectively. The cell parameters are in good agreement with the reported data (15). XPS (Fig. 2) also indicates that the products are rather pure with the molar ratios as Co:P = 1.921:1, Ni:P = 1.953:1 and Cu:P = 2.872:1, which are close to the forms Co_2P, Ni_2P, and Cu_3P, respectively. No obvious impurities, e.g., chloride ion or elemental phosphorus, could be detected in the sampels, indicating that the level of impurities is lower than the resolution limit of XPS (1 at.%)

From the TEM images shown in Fig. 3, one can see that the products Co_2P and Ni_2P are uniform plate-like particles with a size of ca. 50 nm and for Cu_3P, the grains are spherical with the size ranging from 30 to 90 nm. The wider size distribution reveals that some small particles easily aggregate into secondary particles, owing to their small dimensions and high surface energy. So it is difficult for nanoparticles to determine the precise sizes of nanocrystals only from the TEM images.

In this approach, we have done a lot of experiments to explore the possible mechanism in the formation of metal phosphides and the results indicate that the formation of nanocrystalline metal phosphides probably is through an intermediate step. Being an intermediate, the formed elemental metals caused by the reduction of yellow phosphorus are much more active and can react with yellow phosphorus as soon as they are formed. This process can be described in terms of Eqs. [1]–[4].
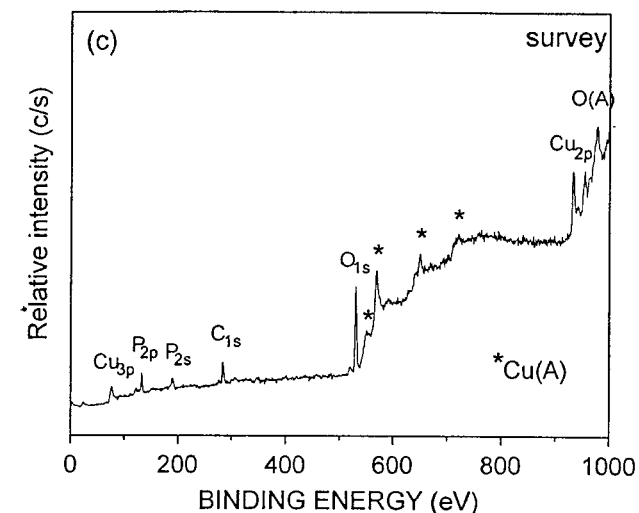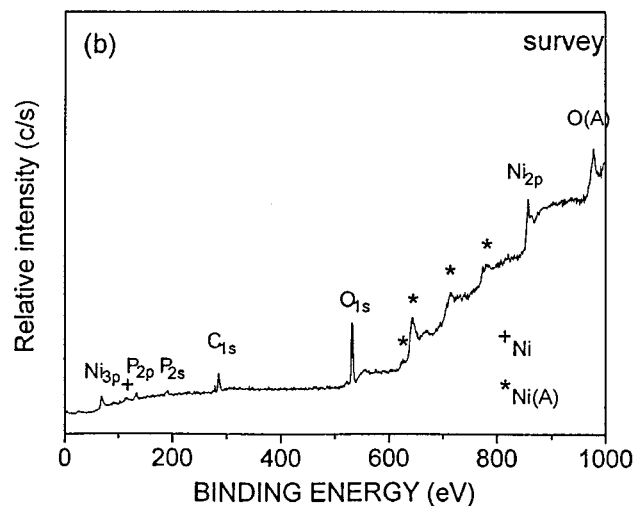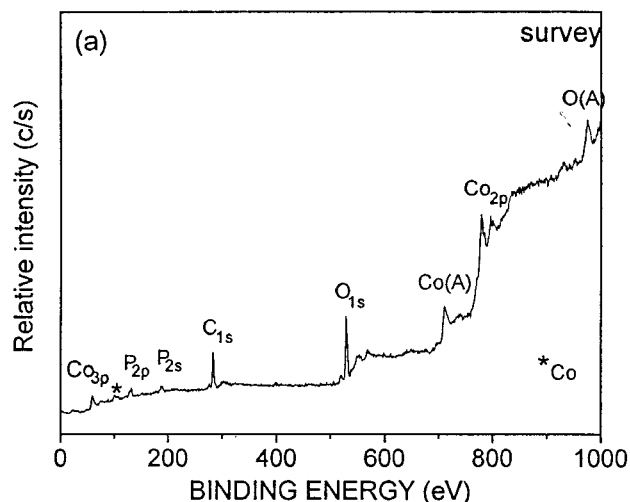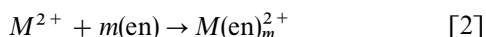
$$P_4 + 28OH^- \rightarrow 4HPO_4^{2-} + 12H_2O + 20e \qquad [1]$$

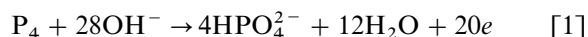$$M^{2+} + m(en) \rightarrow M(en)_m^{2+} \qquad [2]$$

FIG. 2. XPS analyses of as-prepared products: (a) Co_2P, (b) Ni_2P, and (c) Cu_3P.
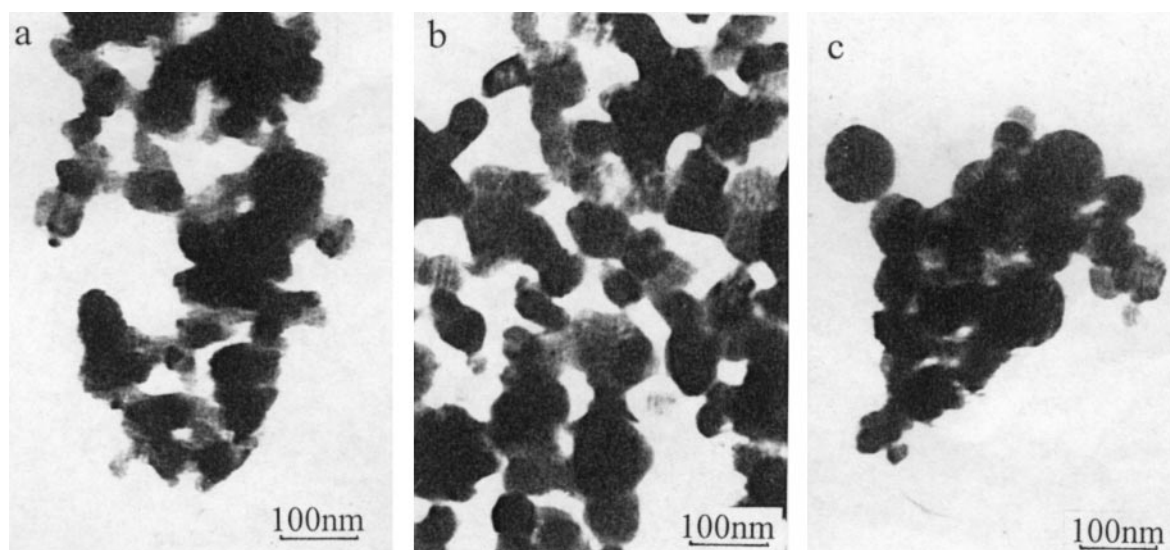
FIG. 3. TEM images of as-prepared products: (a) Co_2P, (b) Ni_2P, and (c) Cu_3P.

$$M(\text{en})_m^{2+} + 2e \rightarrow M + m(\text{en}) \quad (M = \text{Ni, Co, Cu}) \quad [3]$$

$$4xM + P_4 \rightarrow 4M_xP \quad (x = 2, 3; \; M = \text{Ni, Co, Cu}). \quad [4]$$
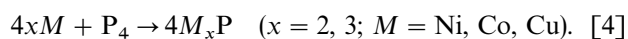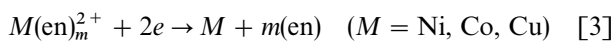
In the whole reaction process, ethylenediamine plays an important role in the formation of pure nanocrystalline phosphides. Being not only the solvent, but also a basic ligand, ethylenediamine directly takes part in the whole solvothermal processes. As an N-chelating ligand, ethylenediamine can chelate these metallic ions to form stable complexes; thus metallic ions are homogeneously dispersed in whole system. In such a basic solvothermal system, yellow phosphorus has enough strong reducing ability, so that metallic ions are easily reduced to active atoms. Meanwhile, yellow phosphorus also homogeneously disperses in ethylenediamine and is rather active under the solvothermal condition. So once generated, metallic atoms will immediately combine with elemental phosphorus to form corresponding metal phosphides. In addition, the liquid medium is beneficial to the formation of nanocrystalline particles since it may act as an absorbent of heat. This role is similar to that of LiCl as an inert heat sink used in Ref. (16). Thus the whole process can proceed under mild conditions, which differs greatly, from the pathway in the solid state reactions at high temperatures.

Here, no extreme conditions such as absolutely anhydrous and nonoxygen systems are required. Within the reducing environment caused by yellow phosphorus in basic system, the oxygen in the reaction system can be reduced to a negligible amount. In fact, small amount of water in the system is essential to the electron-generate and charge-transfer process in the reaction. Metal phosphides can also be obtained from the similar solvothermal processes, which are also carried out using anhydrous metal halides as starting materials in nonpolar solvents, such as benzene and toluene. However, the reactions are not complete and some unknown materials coexist in the desired phosphides. On the other hand, no metal phosphides can be obtained at all if anhyudrous salts are used in such solvents as benzene and toluene. Meanwhile, in the polar solvents such as methanol or ethanol, the desired phosphides can also be obtained, but the synthetic temperature needs to a little higher than that in ethylenediamine.

The preparation of nanocrystalline metal phosphides through the solvothermal processes is also dependent on several other factors such as temperature, reaction time, and the amount of yellow phosphorus. It is observed that at least 100% excess yellow phosphorus is essential for ensuring, the complete conversion of metal halides to metal phosphides. If a substantial excess of yellow phosphorus is not used, elemental metals exist in the products, which can be clearly detected by XRD. If the temperature is not high enough, elemental metals also remain in the final products due to the incomplete phosphatization of the produced newborn metals. The optimum condition for pure metal phosphides is 80–140°C for 12 h. For temperatures lower than 70°C, the reactions cannot initiate even when maintained for over 2 days in the case of Co_2P and Ni_2P. It is easiest to obtain Cu_3P and the reaction seems to initiate at about 40°C. A higher temperature than 150°C or a longer time than 12 h has no significant effect on the formation and quality of the metal phosphides, but results in an increase in the particle sizes. The by-products, small amount of excess P or possible unreacted MCl_2 can be removed by washing with benzene,

absolute ethanol, and water in sequence. Experiments show that the kinds and valence state of metal halides seems to have little influence on the purity of products, especially in the formation of Cu_3P. For example, nanocrystalline Cu_3P can also be obtained under similar conditions, while CuI substitutes for $CuCl_2 \cdot 2H_2O$. All the above results confirm the possible proposed mechanism.

Equation [4] has been confirmed by solvothermal reactions between metallic powders and yellow phosphorus. Experiments show that metallic copper and nickel can be reacted with yellow phosphorus at above 170°C, while the temperature for metallic cobalt is higher than 200°C. TEM images show that the sizes of as-obtained metal phosphides are much larger (even up to 1 μm), with irregular shapes and a wider size distribution. XRD examinations also show that there is still an amount of metal remaining in the products due to the incomplete reaction between the metal and the yellow phosphorus, since the formed metal phosphides may cover the surface of metal powders and prevent the further reactions. In the solvothermal reactions between metal halides and yellow phosphorus, the newly formed atomic metal is much more active and can easily react with yellow phosphorus at rather low temperature.

IV. CONCLUSIONS

In summary, nanocrystalline Co_2P, Ni_2P, and Cu_3P were successfully synthesized through a mild solvothermal process, based on the reaction of metal halides with yellow phosphorous at 80–140°C with ethylenediamine as solvent. XRD and XPS identified the phase of Co_2P, Ni_2P, and Cu_3P, respectively, and TEM showed the morphology of products. Being a basic ligand, ethylenediamine played an important role in the formation of nanocrystalline metal phosphides. Bound water in the raw materials was also helpful in generating a reducing system; thus, metallic ions could be reduced to active atoms and phosphatizing reactions could easily proceed under mild temperatures.

Other nanocrystalline metal phosphides are also expected to obtain through similar solvothermal routes. Further studies are in progress to determine the scope of this route.

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