JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

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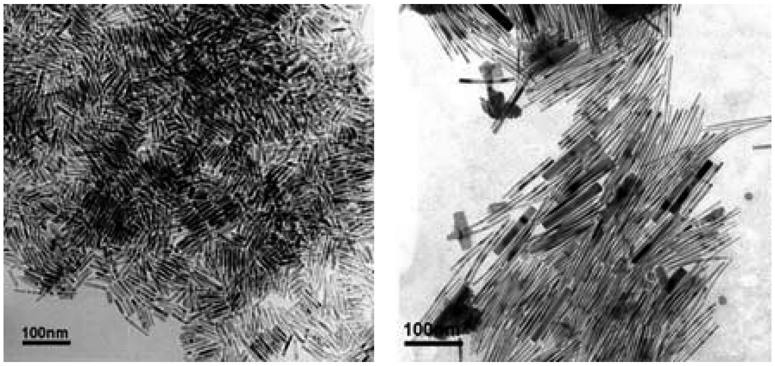
J. Am. Chem. Soc., **2005**, 127 (46), 16020-16021• DOI: 10.1021/ja055963i • Publication Date (Web): 27 October 2005



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Synthesis of Single-Crystalline CoP Nanowires by a One-Pot Metal−Organic Route

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One-dimensional (1D) magnetic nanocrystals have received attention due to their novel properties which result from having both anisotropic structures and critical dimensions on the order of nanometers.[1,2] Such materials have been investigated as potential components for magnetic, photonic, electronic, and data storage devices.[3] There is an increasing interest in metal phosphides for such applications because they exhibit novel magnetic and semiconducting properties.[4,5] The direct reaction between highly toxic phosphines (e.g., PH_3) or phosphorus pentachloride and metals or metal salts is one synthetic method often used; however, this approach does need good control of experimental conditions to obtain highly crystalline materials.[4,6] Recently, $P(SiMe_3)_3$ or trioctylphosphine (TOP) has been used as phosphide sources for the synthesis of transition metal phosphide nanocrystals by solution-phase syntheses[7,8] or sol−gel methods.[9] Liu[7] and Hyeon[10] reported the preparation of anisotropic nanostructures of magnetic phosphides via multiple or continuous injection of a metal−TOP precursor solution. In the present work, CoP nanowires with a high aspect ratio have been prepared by a simple one-pot method, which utilized long-chain alkylphosphonic acids as a phosphorus source.

CoP nanocrystals have potential applications in the development of magnetic field sensing devices and inductors due to its distinctive magnetic properties: low coercivity and high permeability.[11,12] CoP also can be used as an anode materials in lithium ion cells[13] or as a hydrotreatment catalyst.[14] $Co_{80}P_{20}$ nanowire arrays with polycrystalline structure have been prepared by employing an electrodeposition method.[15] However, the nature of the nanowires formed seriously limits the utility of the method. High-quality CoP nanowires with a single-crystalline structure have not been prepared yet.

The CoP nanowires we report were prepared by the thermal-decomposition of $[Co(acac)_2]$ (acac = acetylacetone) and tetradecylphosphonic acid (TDPA) in a mixture of trioctylphosphine oxide (TOPO) and hexadecylamine (HDA). Such mixtures have been widely used to prepare highly luminescent monodispersed nanocrystalline semiconductors.[16,17] Single-crystalline CoP nanowires with uniform diameters and large aspect ratio were obtained using this new method, which does not require the continuous injection of precursor to promote the growth of anisotropic nanocrystals. The procedure also allows easy control of the length of CoP nanowire by simply adjusting the ratio of TOPO and HDA.

In a typical reaction, a vigorously stirred mixture of HDA (15 g, 98%) and TOPO (15 g, 99%) under vacuum was kept at 140 °C for 1 h to remove water. The mixture was cooled to 100 °C, and $[Co(acac)_2]$ (0.128 g, 0.5 mmol) and TDPA (0.5 g, 98%) were added and stirred magnetically under a flow of nitrogen. The temperature was slowly increased to 340 °C over 1 h and kept at this temperature for 3 h. The color of the solution changed from an initial transparent violet to turbid dark brown. The solution was then allowed to cool to 60 °C. An excess of ethanol was added to the solution to give a black precipitate, which was separated by centrifugation and dried under vacuum. The black powder could easily be redispersed in organic solvents, such as chloroform, hexane, toluene, etc. Samples for transmission electron microscopy (TEM) were prepared by dropping a hexane suspension of samples onto a copper grid covered with a carbon film. A thin film of a sample was prepared on a piece of silicon wafer for XRD studies.

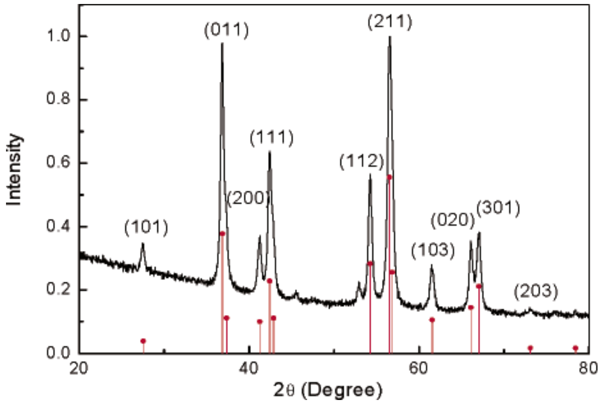

Figure 1. X-ray diffraction patterns (XRD) of CoP nanowires (ca. 7 nm in diameter and 400 nm in length). XRD were measured by using Philips PW 3020 with Co Kα radiation ($\lambda = 1.78897$Å) with an Fe filter.

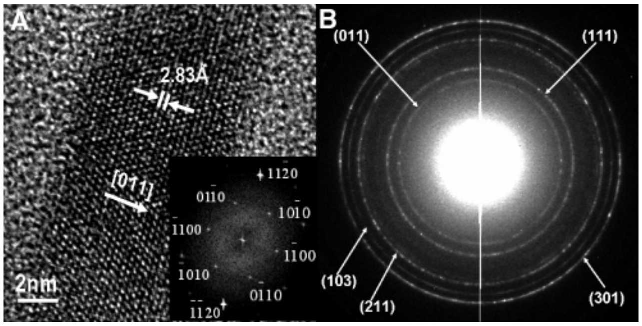

Figure 2. (A) HRTEM image of a 7 nm diameter CoP nanowire, (inset) FFT of the HRTEM image. (B) Selected area electron diffraction (SAED) pattern from the corresponding CoP nanowire assembly.

All of the prominent peaks in the XRD (Figure 1) can be exclusively matched to orthorhombic CoP (JCPDS No: 29-0497). Cell constants are calculated by Rietveld analysis(literature) $a = 5.074(5.077)$, $b = 3.279(3.281)$, $c = 5.585(5.587)$. The regularity of the lattice planes in the HRTEM image (Figure 2A) clearly indicates that the 7 nm CoP nanowires are single crystals. The space between adjacent planes is 2.83 Å, corresponding to the (011) planes of CoP. The preferred orientation of nanowires is parallel to the (011) plane. Fast Fourier transform (FFT) diffraction recorded from an individual CoP nanowire reveals that each nanowire is a single crystal. The diffraction spots can be matched to the characteristic

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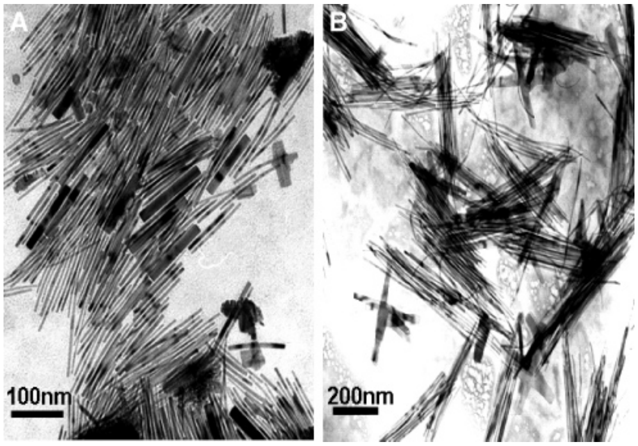

Figure 3. TEM images of CoP nanowires prepared with different weight ratios of HDA to TOPO: (A) 1:2 and (B) 1:1.

pattern associated with the wurtzite-orthorhombic crystalline structure of CoP. The reciprocal lattice peaks obtained by FFT of the lattice image are compatible with a lattice constant of 2.89 Å, which is in accordance with the result obtained from HRTEM. The indexed reciprocal lattices also reveal that the $[11\bar{2}0]$ direction is parallel with the nanowire axes. Strong ring patterns of SAED (Figure 2B) are consistent with the (011), (111), (211), (103), and (301) planes of the orthorhombic CoP structure.

Reaction temperature is a key factor in the formation of the CoP nanowires. At temperatures lower than 320 °C, no CoP was obtained. This result indicates that alkylphosphonic acid can serve as a source of phosphide only when the temperature is high enough to cleave bonds between carbon and phosphorus.[18] We also have found that CoP nanostructures can only be prepared from phosphonic acids with long-chain carbon substituents; the methyl or ethylphosphonic acids are more thermally stable.

It is well-known that technical grade TOPO contains alkylphosphonic acids as impurities.[19] The same amount of TOPO of this type (15 g, 90%, Aldrich) was used to replace pure TOPO and TDPA. Satisfactory CoP nanowires were obtained (Figure 3). Moreover, elemental analyses indicated a high yield of CoP (88 wt %), consistent with some TOPO and HDA incorporation in the product. It was concluded that the unpurified TOPO can serve as an effective capping agent and phosphorus source. This observation is significant as pure TOPO and alkylphosphonic acid are much more expensive than crude TOPO.

However, the reaction of [Co(acac)$_2$] with TOPO as the only solvent did not give any wires of CoP even at 360 °C over 3 h. Similar experiment in HDA alone gave only CoO nanoparticles. These experiments show that a mixed solvent system (HDA and TOPO) is essential for the growth of nanowires of CoP. The mixed ligand system has a remarkable role in promoting the anisotropic growth. Moreover, the diameter and length of the CoP nanowires depend on the ratio of HDA to TOPO. Increasing the concentration of HDA favors the formation of longer nanowires.[1] The formation of nanowires is generally governed by the differential growth of crystallographic surfaces. Their surface energies could be altered by coordination with HDA and/or TOPO.[1,20]

TEM images (Figure 3) of the CoP nanowires from this synthesis reveal the presence of straight nanowires with a uniform length distribution and a high aspect ratio. The nanowires made from the mixed solution with a 1:2 weight ratio of HDA to TOPO are found to be ca. 10 nm in diameter and 100 ± 10 nm in length (Figure 3A). When the ratio of HDA:TOPO is 1:1, the nanowires with higher aspect ratio were observed with 7 nm in diameter and 400 ± 20 nm in length (Figure 3B). These nanowires tend to arrange themselves with the long axes parallel to one another. Note, in Figure 3A, apparently the larger size nanowires were due to an overlap of the smaller nanowires.

In summary, a simple and reproducible method, from [Co(acac)$_2$] and long-chain alkylphosphonic acid in the presence of HDA and TOPO at high temperature, has been developed to prepare uniform single-crystalline CoP nanowires with a high aspect ratio. Technical grade TOPO can be replaced for the combination of alkylphosphonic acid and purified TOPO in the synthesis of CoP. We have also observed that the diameter and length of these single-crystal materials can be controlled by changing the ratio of HDA to TOPO. The CoP nanowires are promising materials for anodes, catalysts, or magnetic sensing.

Acknowledgment. We thank Dr. T. Hashimoto for assistance with HRTEM, Dr. I. Abrahams (Queen Mary College, London) for support with X-ray work, and Dr. Wang and Mr. L. Zhou for helpful discussions.

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JA055963I