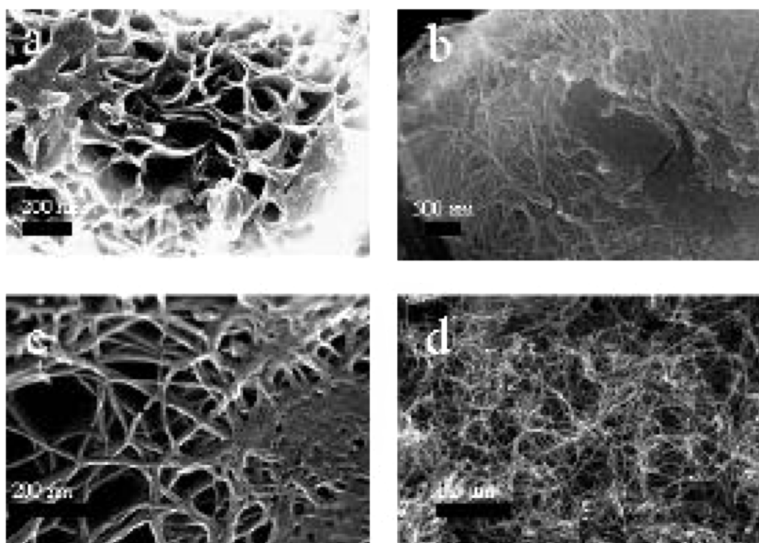## Communication

High-Yield Solvothermal Formation of Magnetic CoPt Alloy Nanowires

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High-Yield Solvothermal Formation of Magnetic CoPt Alloy Nanowires

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One-dimensional (1D) nanostructured materials have attracted much attention concerning their potential applications in both the investigation of mesoscopic physics and the fabrication of nano-devices.[1,2] In particular, 1D magnetic nanomaterials have been extensively exploited for their potential utilization in magnetic recording and spintronics.[3−6] The key synthetic methodologies developed so far include catalyzed high-temperature growth via the vapor−liquid−solid (VLS) mechanism,[7,8] templated synthesis,[9−11] organometallic precursors decomposed in solution,[12] and direct electrochemical precipitation.[13] Nevertheless, it remains a challenge to prepare free-standing magnetic nanowires in high yield. Solvo-thermal synthesis is one of the most powerful strategies employed for the crystallization of many unique compounds.[14] Under solvo-thermal conditions, many starting materials can undergo quite unexpected reactions, which are often accompanied by the formation of nanoscopic morphologies that are not accessible by classical routes. Buhro's group has reported the growth of the group III−V polycrystalline fibers and whiskers with small crystal dimensions by using simple organometallic reactions conducted at low tem-perature (−203 K) in hydrocarbon solvents.[15] Here, we report the first successful synthesis of an interesting 1D ferromagnetic CoPt alloy by direct decomposition of platinum acetylacetonate and cobalt carbonyl in ethylenediamine solvent through a solvothermal reac-tion. The CoPt alloy nanowires obtained have a tunable diameter of 10−50 nm and a length along the longitudinal axis of up to several microns, depending on crystallization temperature and time.

In a typical synthesis, under N_2 protection conditions, platinum acetylacetonate [Pt($CH_3COHCOCH_3$)$_2$, 0.39 g, 100 mmol] was dissolved and stirred in ethylenediamine (en, 40 mL) solvents. Cobalt carbonyl ($Co_2(CO)_8$, 0.34 g, 100 mmol) was added after the platinum acetylacetonate was completely dissolved. The mixture was stirred until a clear solution was obtained before being transferred to a Teflon-lined autoclave. The reaction was completed under an optimized temperature (160−200 °C) for 12−72 h. The products were filtered off, washed sequentially with ethanol, purified by ultrasonication in ethanol to remove residue ethylenediamine attached on the surface of nanowires, separated by centrifuge, and dried in a vacuum at 50 °C for 6 h.

Figure 1 shows the morphology images of the highly uniform (a) as-synthesized and (b) annealed CoPt nanowires that are acquired by a scanning electron microscope (SEM). The CoPt nanowires in Figure 1 have an average diameter of 30 nm, which is tunable by controlling the experimental conditions of reaction temperatures, times, and the concentrations of the precursors. The diameter of nanowires decreases with the increase of both reaction temperatures and reaction times. The higher the concentration of Co and Pt precursors is, the smaller the diameter of nanowires becomes. As
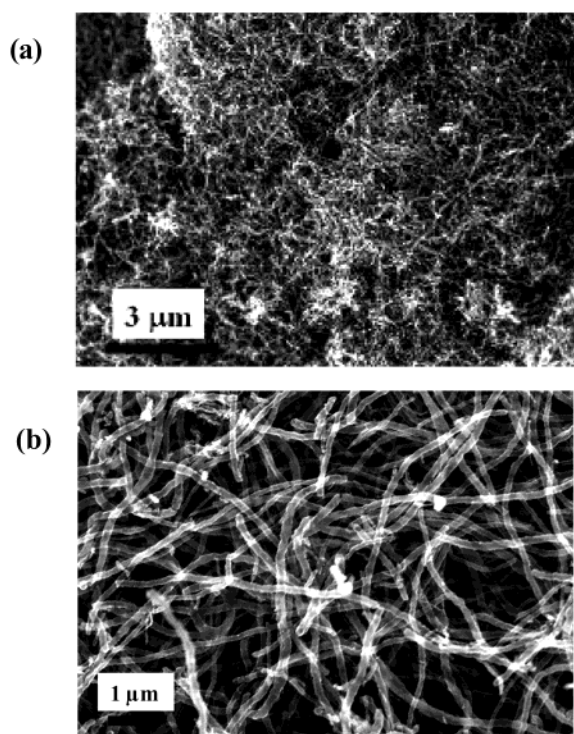
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Figure 1. (a) SEM image of uniform CoPt nanowires that were prepared via the solvothermal reaction. The wires have widths of 10−50 nm and lengths along the longitudinal axis of up to several microns. (b) SEM image of CoPt nanowires annealed at 580 °C.

seen in the figure, the length of the nanowires along the longitudinal axis can be up to several microns. The chemical concentration in the CoPt nanowires is determined by the energy dispersed X-ray spectrometer (EDX) using a Hitachi HF-2000 200 kV scanning transmission electron microscope (STEM). This EDX analysis demonstrates that the quantitative atomic ratio of Co and Pt in the corresponding nanowires is uniform and close to 53:47. Structural analysis by wide-angle X-ray diffraction (XRD) of the as-syn-thesized CoPt nanowires indicates a chemically disordered face-centered cubic (fcc) phase.[16,17] The chemical order can be improved partially by annealing the sample in a furnace at high temperature under a flowing Ar atmosphere (see Supporting Information).

The choice of solvent was found to play a key role in synthesizing the morphology of CoPt nanowires in our work. Solvent properties such as redox, polarity, softness, and viscosity strongly influence the solubility and transport behavior of the precursors involved in such heterogeneous liquid−solid reactions.[18] Recently, ethylene-diamine (en) has proven to be an ideal solvent for controlling the morphology of semiconductor materials in solvothermal synthe-sis.[11,19] Ethylenediamine molecules may act as a bidentate ligand to form a relatively stable complex ion [Pt(en)$_2$]$^{2+}$. With an increase
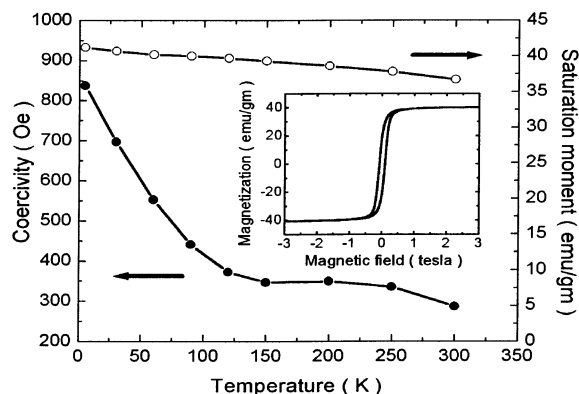
Figure 2. Temperature dependence of saturation magnetization (M_s, ○) and coercivity (H_c, ●) of the as-synthesized CoPt nanowires. The inset picture displays a typical magnetization curve acquired at 5 K by a SQUID magnetometer.

in the temperature, autoreduction of $[Pt(en)_2]^{2+}$ and the decomposition of $Co_2(CO)_8$ lead to the formation of the metallic CoPt nanophase.[20,21] The temperature was another factor affecting the growth of CoPt nanowires. No nanowires were obtained below 120 °C. The growth of nanowires was observed by raising the reaction temperature above 160 °C under auto pressure in the autoclave.

The successive processes occurring during the growth of CoPt nanowires under solvothermal conditions were investigated through the SEM imaging of the corresponding quenched samples at the different reaction stages. Initially, the formation of thin platelike nanostructures composed of many adjacent CoPt alloy sheets (<10 nm thick) was observed. Subsequently, the adjacent alloy sheets underwent extensive coarsening and ripening reactions under solvothermal conditions. Continuing phase transformation through coarsening and ripening reactions gave rise to an intermediate "spider" web morphological alloy phase. Further solvothermal treatment of the intermediate phase led to the controlled formation of high-yield crystallized CoPt nanowires. The whole transformation is reminiscent of the interesting surface restructuring phenomena discovered previously for Pt and its alloys at high temperature (−1000 °C) and under reactive gases such as ammonia and oxygen.[22] These processes are considered to be the key factors contributing to the loss of Pt catalysts in many catalytic reactions.[22]

The magnetic properties of the $Co_{53}Pt_{47}$ nanowires have been measured by a superconducting quantum interference device (SQUID) magnetometer. Figure 2 shows the temperature dependence of saturation magnetization (M_s, ○) and coercivity (H_c, ●) of the nanowires, with a magnetization curve being displayed as an inset. The H_c versus T curve shows a clear curvature instead of a linear dependence, which has also been observed in pure Fe, Co, and Ni nanowires.[23] The M_s versus T curve, although not complete due to the heating limitations of the SQUID magnetometer, clearly indicates that the Curie temperature of the $Co_{53}Pt_{47}$ nanowires is well above room temperature. The magnetic moment of the nanowires is approximately 1.18 μ_B per atom, which is reasonably in agreement with that of the bulk alloy (1.2 μ_B).[24]

In summary, the CoPt magnetic nanowires have been synthesized in high yield via a solvothermal synthesis. We expect that this methodology will lead to new opportunities to grow 1D and other

morphologically interesting nanomaterials through controlled restructuring of the precipitators generated in situ by solvothermal treatment. In fact, we have also successfully prepared FePt, NiPt, and CrPt alloy nanowires using the same approach. Research is underway to characterize magnetic properties of the corresponding single nanowire.

Supporting Information Available: EDX analysis spectra of the CoPt alloy nanowires; XRD patterns of the alloy nanowires after annealing for 1 h at various temperatures under flowing Ar atmosphere; SEM images of a successive transient process during the growth of alloy nanowires; SEM and HTEM images of the CoPt alloy nanowires annealed at 580 and 750 °C, respectively (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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JA035185Z