Communication

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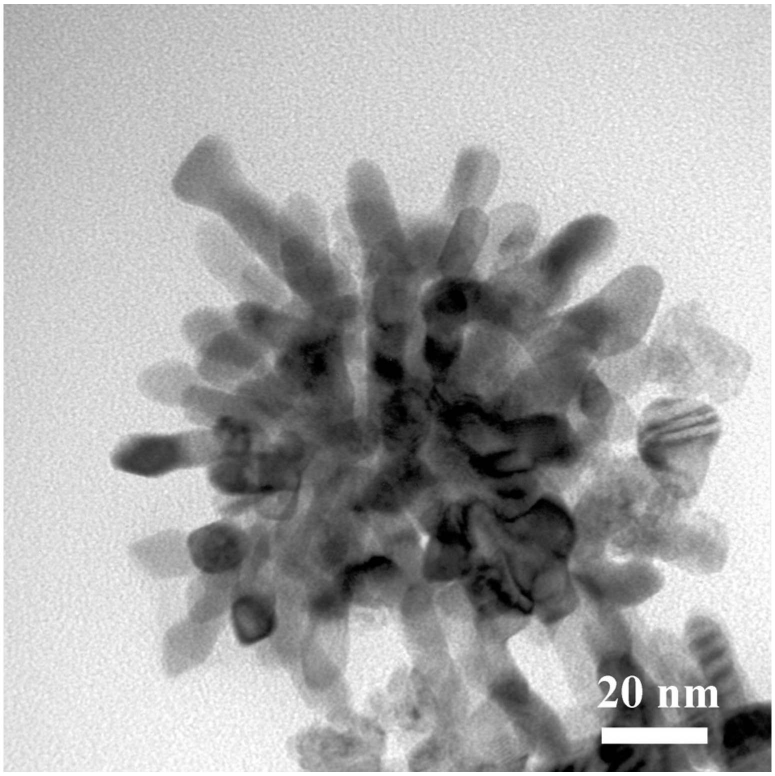

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Synthesis and Characterization of 3D CoPt Nanostructures

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Controlling the size and shape of nanocrystalline materials is a key issue in current nanoscience research. Synthetic chemical methods have proved very effective for the production of monodispersed nanocrystals with a tight size distribution and a wide spectrum of morphological features including spheres, wires, rods, etc. These nanostructures exhibit very interesting magnetic, electrical, optical, and chemical properties, which cannot be achieved by the corresponding bulk materials.[1−3] CoPt nanoparticles are excellent candidates for ultrahigh-density magnetic recording applications because they are chemically stable and have very high magnetocrystalline anisotropy, ($K_u = 4 \times 10^7$ erg/cm^3).[4] CoPt 1D and 2D nanostructures have previously been successfully synthesized in solution-phase process by the use of a high boiling point coordinating solvent such as dioctyl ether, diphenyl ether, or ethylenediamine,[5] a reducing agent mainly 1,2-hexadecanodiol, polyethylene glycol[6] or metal hydrides ($NaBH_4$, $LiBEt_3H$),[7] and nonionic surfactants such as oleic acid, oleylamine, alkylphosphines, or alkylphospines oxides that play the role of growth controllers and offer solubility in nonpolar organic solvents. An alternative method is the thermal decomposition of an organometallic precursor $Co_2(CO)_8$[8] or $Co(\eta3\text{-}C_8H_{13})(\eta4\text{-}C_8H_{12})$[9] which provides directly, without the use of reducing agent, the Co partner for the formation of the CoPt bimetallic nanoparticles. Very recently was described the synthesis of CoPt nanorods in ionic liquids.[10] Here, we report for the first time a successful one-pot chemical synthesis of a new, interesting 3D ferromagnetic CoPt polypod-like nanostructure by direct thermolytic reduction of $Pt(acac)_2$ and $Co(CH_3COO)_2$ in refluxing commercial (70%) oleylamine which plays the role of high boiling point coordinating solvent, reducing, and capping agent.

In a typical synthesis were dissolved $Pt(acac)_2$ (0.25 mmol) and $Co(CH_3COO)_2$ (0.25 mmol) in 20 mL of oleylamine at 100 °C under magnetic stirring. The reaction mixture was maintained at this temperature until a clear solution was obtained, and then the temperature was raised to 250 °C and kept at this temperature for 30 min. After reaction the mixture was cooled to room temperature, and the bimetallic particles were precipitated by the addition of 50 mL of ethanol. The black precipitate was isolated by centrifugation and washed with ethanol several times. To remove the excess of oleylamine the particles were dissolved in chloroform, precipitated by ethanol and isolated by centrifugation. Finally, the CoPt particles were dispersed in ethanol and dried at room temperature after being spread on a glass plate. All experimental procedures were performed open to the atmosphere.

Figure 1 shows bright-field TEM micrographs of the CoPt polypod-like nanostructures. The CoPt nanopolypods were derived from the assembly of nanorods that have an average diameter of 5 and 20 nm length. The selected area electron diffraction pattern, shown as the inset in Figure 1, indicates that the nanopolypods have a face-centered cubic structure. The nanopolypods have uniform sizes averaging at about 50 nm. Their mean chemical composition (atomic percent), determined by energy-dispersive X-ray microanalysis, is $Co_{40}Pt_{60}$ with the center of the nanopolypods richer in Pt. Structural analysis by XRD (Figure 2) indicates that the CoPt nanopolypods have a chemically disordered face-centered cubic (fcc) phase, in agreement with the TEM results. The reflections at 39.9°, 46.3,° and 67.7° 2θ values arise from the (111), (200), and (220) planes of the cubic Pt phase (Figure 2a). These peaks dominate the XRD pattern because of the high atomic weight effect.[11] We must point out that the bimetallic nanoparticles made by wet chemical methods that occur in the temperature range of 200−250 °C do not form a crystalline alloy. However, the possibility that the as-made material is a mixture of Co and Pt phases is not very likely on the basis of the observed coercivity of this phase, as presented later. By thermal treatment under reducing atmosphere (4% H_2 in Ar) at 700 °C the fcc phase transforms to a

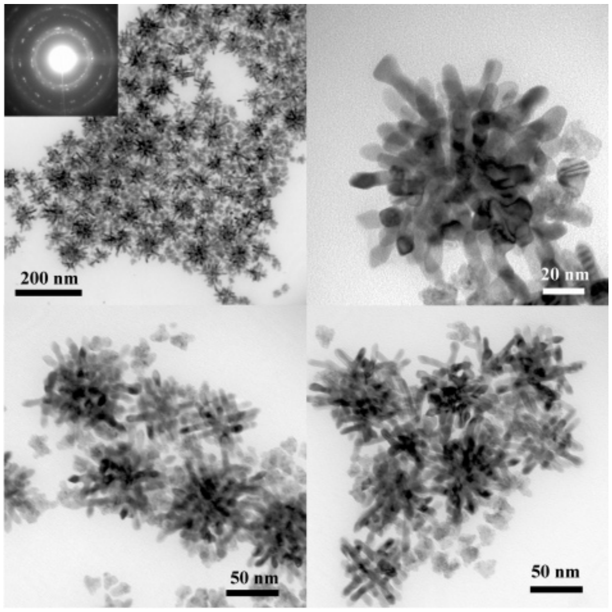

Figure 1. Bright field TEM micrographs of the CoPt nanopolypods. (Inset) Electron diffraction pattern.

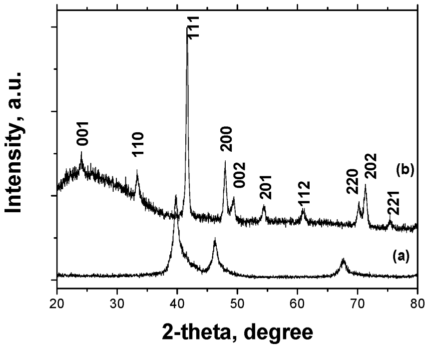

Figure 2. XRD patterns of CoPt nanoparticles, as made (a) and after annealing at 700 °C for 60 min (b) under reducing atmosphere (4% H_2 in Ar).

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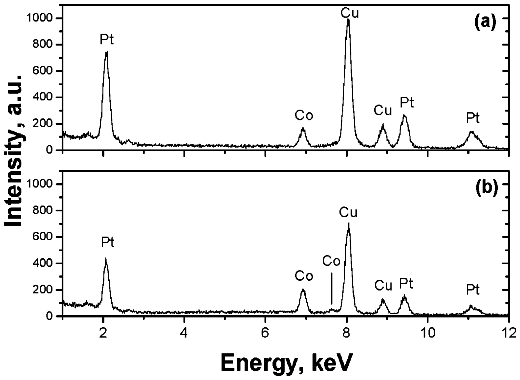

Figure 3. EDX data for the center (a) and shell (b) of the CoPt nanopolypods (Cu is from the TEM grid).

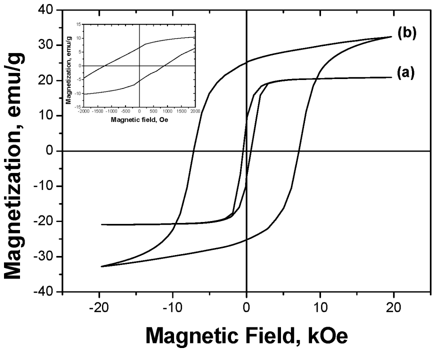

Figure 4. Room-temperature hysteresis loops of CoPt nanoparticles as made (a) and after annealing at 700 °C for 60 min under reducing atmosphere (4% H_2 in Ar) (b). (Inset) Hysteresis loop at 5 K for the as-made material measured by a SQUID magnetometer.

CoPt alloy with the highly ordered fct structure, as shown by XRD pattern (b) in Figure 2.

The as-made CoPt nanopolypods are ferromagnetic, soluble in nonpolar organic solvents such as toluene and chloroform and are well dispersed in hexane. Oleylamine seems to play an important role in the morphology of the final structure. In the presence of other capping agents that bind stronger than oleylamine with CoPt nanoparticles, like an equimolecular mixture of tri-octylphospine oxide and tri-octylphospine (TOPO-TOP), the final particles have spherical shape, as we observe in a separate experiment that not presented here. Oleylamine may act as ligand to form stable complexes with Pt^{2+} while temperature elevation leads to thermolytic reduction of the Pt complexes to the metal state. The initially formed tiny Pt seeds, possessing very negative redox potential,[12] can reduce Co^{2+} to the zero state followed by the generation of the CoPt nanoparticles. It is expected that in the core of these units the Pt atoms will predominate. This mechanistic aspect is in good agreement with the EDX data that confirm that the center of the nanostructure is richer in Pt, with % atomic composition $Co_{30}Pt_{70}$, and the shell, to a less extent, in Co with atomic composition $Co_{48}Pt_{52}$ (Figure 3).

The magnetic properties of CoPt nanopolypods have been studied by a vibrating sample magnetometer (VSM) and a superconducting quantum interference device (SQUID) magnetometer. Figure 4, shows the hysteresis loops of the as made and after annealing at 700 °C for 1 h CoPt nanopolypods. The inset picture displays the magnetization curve at 5 K measured by SQUID. The coercivity (H_c) is 525 Oe and 1.2 kOe at room temperature and 5 K, respectively, for the as-made CoPt sample, indicating ferromagnetic behavior and arguing against a mixture of pure Co and Pt phases. These values are higher compared with those of other CoPt shape anisotropy nanostructures such as nanowires.[5] After thermal treatment the room-temperature coercivity is 7.2 kOe, and the saturation magnetization is about 33 emu g^{-1}, values that are in good agreement with those reported in the literature for fct phase CoPt nanoparticles.[5,7] This result indicates complete transformation of the fcc to the fct structure.

In conclusion, the CoPt nanopolypods have been synthesized in high yield via a very simple and large-scale applicable thermolytic reaction. This methodology is expected to lead to new opportunities for the synthesis of new nanostructures. In fact, we have also synthesized FePt, NiPt alloys, and monometallic Ni, Co, Pt, Au, and Ag nanostructures using the same procedure. Research is in progress to study the morphological, chemical, and physical properties of these materials.

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