Preparations of Nickel, Cobalt, and Iron Nanoparticles through the Rapid Expansion of Supercritical Fluid Solutions (RESS) and Chemical Reduction

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Nanoscale materials have attracted a great deal of attention for their interesting chemical and physical properties and potential technological applications.[1−5] The preparation of nanoscale materials with desired properties represents a significant challenge. Many different techniques have been developed for preparations of nanoparticles, especially semiconductors such as cadmium sulfide.[2,4] However, preparations of some metal nanoparticles including nickel, cobalt, and iron are more difficult.[6−18] For the generation of polymer stabilized iron nanoparticles, sonochemical decomposition of iron-containing complexes such as $Fe(CO)_5$ is by far the most successful method.[11−14] In addition to the sonochemical preparation, chemical reduction reactions of nickel and cobalt ions in solution have been used to produce nickel and cobalt nanoparticles.[6,8,9] Along with the effort to develop the existing experimental procedures into mature techniques, new methods that are more controllable with respect to particle properties and more amenable to large-scale production are being explored. Here we report a facile and flexible method for preparing stable suspensions of polymer-protected nickel, cobalt, and iron nanoparticles. The method is based on the rapid expansion of supercritical fluid solutions (RESS), coupled with chemical reduction. The metal nanoparticles thus prepared were characterized using X-ray powder diffraction and transmission electron microscopy (TEM) methods. The TEM results show that the metal nanoparticles have reasonably narrow size distributions.

The RESS technique has been used in the production of polymer particles and fibers of narrow size distributions.[19] In a classical rapid expansion into vacuum or air, the supercritical fluid solution is transferred rapidly to subcritical pressures. The “solution droplets” from the rapid expansion through a nozzle are extremely unstable, resulting in rapid solute precipitation. It is this rapid solute precipitation from supercritical solution upon very rapid pressure reduction in the expansion that provides the basis for the RESS processing in particle and fiber production.[19] The same processing conditions may be achieved in the RESS into a liquid solution. Because of the high velocity of the expanding supercritical fluid solution, the microscopic conditions at the end of the expansion nozzle are little affected by the receiving medium, air or liquid. In the process of RESS into a liquid solution, the receiving liquid solution “captures” the nanoscopic “solute droplets” (from the “solution droplets”) produced in the rapid expansion. For the preparation of metal sulfides such as cadmium sulfide, the nanoscopic “droplets” produced in the RESS process contain cadmium cations, which are captured by sulfide anions in the receiving liquid solution to form cadmium sulfide nanoparticles.[20] Similarly, nanoscopic metal ion “solute droplets” produced in the RESS process may be chemically reduced in the receiving liquid solution to form metal nanoparticles. The suspension of nanoparticles thus formed can be stabilized by protective polymers.

Nickel nanoparticles were prepared in a rapid expansion of a nickel chloride ($NiCl_2$) solution in near-critical ethanol into a room-temperature solution of $NaBH_4$ in DMF that also contains poly(*N*-vinyl-2-pyrrolidone) (PVP) polymer for particle protection. In a typical experiment, a solution of $NiCl_2$ in ethanol, dried using molecular sieves and deoxygenated by bubbling with argon gas for ∼30 min, was loaded into a syringe pump. Before the rapid expansion, the solution of $NiCl_2$ in ethanol was heated and equilibrated at 230 °C in the heating zone, which consists of a stainless steel tubing coil and a stainless steel cell of high heat capacity in a tube furnace. A 60 mL portion of the ethanol solution with $NiCl_2$ concentration of 8 mg/mL was expanded rapidly into 10 mL of deoxygenated room-temperature

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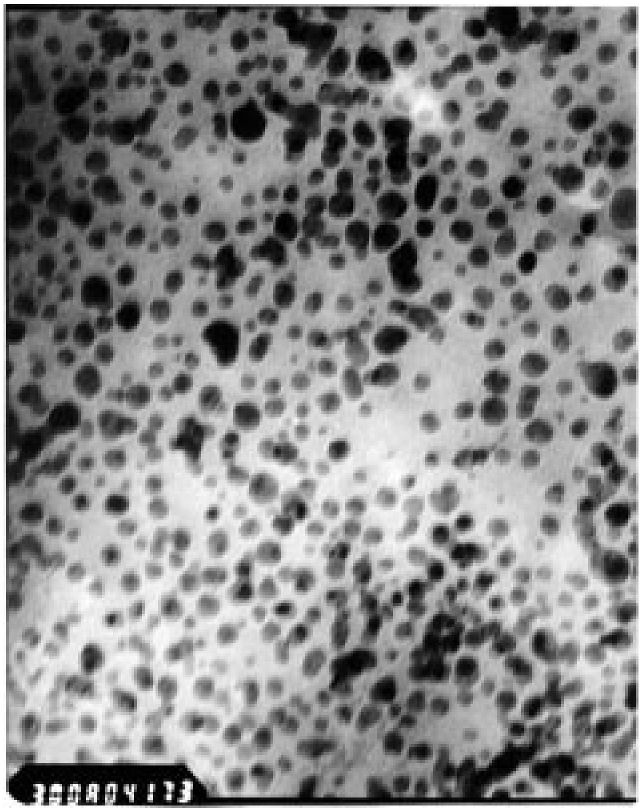

Figure 1. TEM image of the PVP-protected nickel nanoparticles (1 mm = 2.5 nm).

DMF solution of $NaBH_4$ (concentration of 16 mg/mL) for the formation of nickel nanoparticles. The DMF solution also contains 20 mg/mL of PVP polymer with an average molecular weight M_W of ~360 000 for stabilizing the suspension of nickel nanoparticles thus produced. For the rapid expansion, a fused silica capillary nozzle with an inner diameter of 77 μm was employed. The system pressure was maintained at close to 3000 psia during the rapid expansion by use of the syringe pump. The suspension of PVP-protected nickel particles in DMF−ethanol is stable with respect to gravity, showing no signs of precipitation. The as-prepared nickel particles were deposited on a collodion film for TEM measurement. Shown in Figure 1 is a typical TEM image of the PVP-protected nickel particles. A statistical analysis of the TEM image yields an average size of 5.8 nm in diameter, with a size distribution standard deviation of 0.54 nm (Figure 2).

The nickel nanoparticles can be precipitated from the suspension by placing a magnet under the beaker. Upon complete removal of the solvent, the solid, black sample was washed with water and acetone for X-ray powder diffraction characterization.[21] The nickel nanoparticles thus obtained are apparently amorphous, exhibiting an extremely broad diffraction pattern.[22] To identify the nanoparticles using X-ray powder diffraction, an increase in the crystallinity of the nickel nanoparticles was achieved by heat-treating[22] the solid sample in an oven at 500 °C for ~4 h under argon atmosphere. The X-ray diffraction pattern of the heat-treated nickel particles is shown in Figure 3, which corresponds to face-centered cubic (fcc) nickel. On the basis of the band broadening in the X-ray diffraction pattern,[23] the average size of the heat-treated nickel particles is 19 nm, significantly larger than those of as-prepared nickel particles.

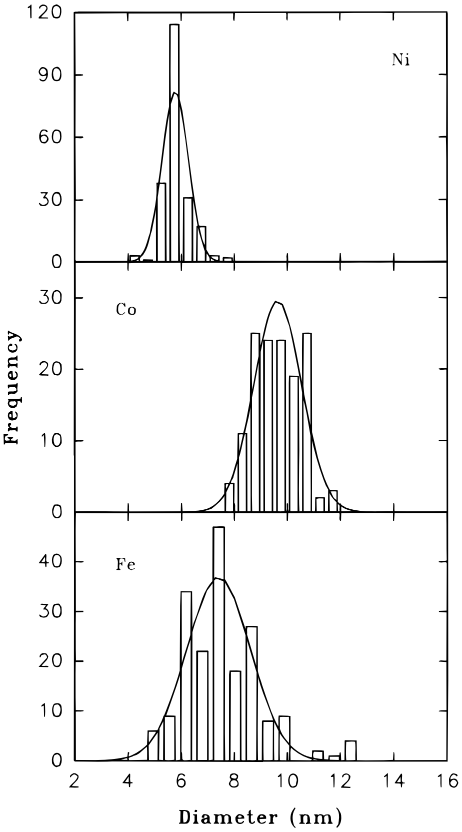

Figure 2. Histograms from the TEM images of the nickel (209 particles), cobalt (137 particles), and iron (187 particles) nanoparticles. The curves are results from the Gaussian distribution analyses.[25]

PVP-protected cobalt nanoparticles were prepared in a similar fashion. A solution of $CoCl_2$ in dry THF (2.6 mg/mL) was used in the rapid expansion, and $NaBH_4$ in DMF (3 mg/mL) was used as the reducing agent. The suspension of the cobalt particles in DMF−THF in the presence of PVP polymers is also stable with respect to gravity, showing no signs of precipitation. The TEM analysis of the as-prepared cobalt particles yielded an average size of 9.8 nm in diameter, with a size distribution standard deviation of 1.1 nm (Figure 2). The black, solid sample of the PVP-protected cobalt particles is amorphous, resulting in an extremely broad X-ray diffraction pattern. However, a clear pattern corresponding to fcc cobalt was obtained (Figure 3) upon heat-treatment of the sample at 540 °C for ~16 h under an argon atmosphere. On the basis of band broadening in the X-ray diffraction pattern, the average size of the heat-treated cobalt particles was estimated to be 20 nm in diameter,[23] which is again significantly larger than those of the as-prepared cobalt particles.

Iron nanoparticles were prepared similarly, except that a stronger reducing agent,[9,24] $LiB(C_2H_5)_3H$, was

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[21] Despite being washed with different solvents, the sample may still contain residual boron compounds,[9] which is a disadvantage of the reduction method based on boron hydrides.

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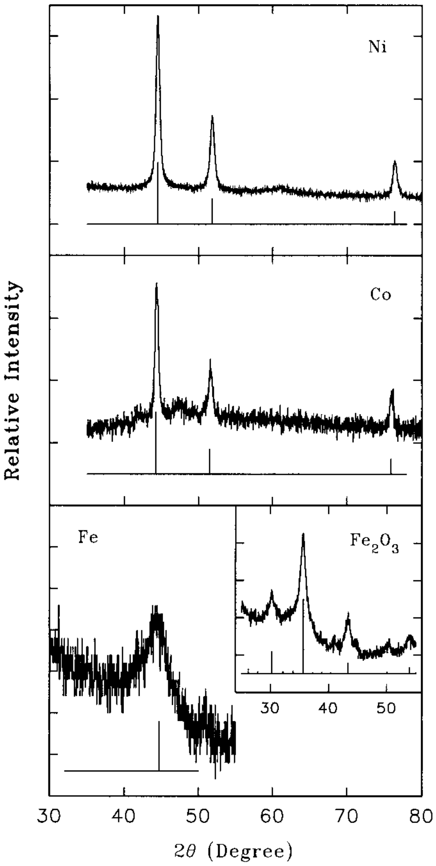

Figure 3. Results from X-ray diffraction measurements of iron particles and heat-treated nickel, cobalt, and Fe_2O_3 particles.

used because $NaBH_4$ is incapable of reducing iron ions. A solution of $FeBr_3$ in carefully dried THF (2 mg/mL) at close to the critical temperature was rapidly expanded into a room-temperature solution of $LiB(C_2H_5)_3H$ in carefully dried THF. Poly(ethylene oxide) (PEO) with an average molecular weight M_W of ~400 000 was used for particle stabilization. The use of carefully dried THF as the solvent and PEO as the protective polymer was necessary because $LiB(C_2H_5)_3H$ reacts with alcohol and water violently and also with PVP. The solutions were deoxygenated carefully to avoid the formation of iron oxides. The suspension of the iron particles in THF under the PEO polymer protection is also stable without precipitation. The TEM analysis shows that the as-prepared iron particles have an average size of 7.6 nm in diameter, with a size distribution standard deviation of 1.4 nm (Figure 2). The black, solid sample of the PEO-protected iron particles was obtained from the suspension in a glovebox. The X-ray powder diffraction pattern of the sample corresponds to largely amorphous α-Fe (body-centered cubic) (Figure 3).[13]

The iron particles are highly air-sensitive, both in the stable suspension and in the solid state, easily oxidizing into Fe_2O_3. The X-ray diffraction pattern of the heat-treated (350 °C for ~4 h) Fe_2O_3 particles from the oxidation is also shown in Figure 3.

The nickel, cobalt, and iron (also Fe_2O_3) particles prepared in this work are all magnetic in the sense that the particles may be precipitated from the suspensions in a magnetic field. The stable suspensions of the particles allow facile preparations of polymer (such as PMMA) thin films in which the metal particles are homogeneously dispersed. A systematic study of the magnetic properties of the nanoparticles will be pursued.

The technique of RESS into liquid solution may be developed into a general method for preparations of bulk quantities of stabilized nanoparticles.[20] Manipulating nanoparticle properties through varying RESS conditions is in progress. Preliminary results show that the size and size distribution of the metal nanoparticles are insensitive to the expansion nozzle inner diameter (50 μm vs 77 μm) and the concentration of the protective polymer. However, a parameter that appears to have some effect on the nanoparticle properties is the temperature of the supercritical fluid solution. Further experiments are needed for a more quantitative evaluation.

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