

Polymer-stabilized Co Nanocrystals.

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Abstract Polymer-coated cobalt nanocrystals were prepared in a polar solvent at high temperature through an organometallic thermal-decomposition route in the presence of poly (N-vinyl-2-pyrrolidone) as a protective polymer. The as-synthesized PVP-coated cobalt nanocrystals were 20 to 80 nm cubic/hexagonal shapes. HCP was further determined as a main phase in these samples. For comparison purposes, we have also prepared PVP-cobalt nanocrystals using the seed-mediated thermal decomposition method. It revealed that PVP plays a significant role in the synthesis of cubic-structured cobalt nanocrystals. It was also noted that the formation of Co nanocrystals and their magnetic properties were dependent not only on the PVP component but also in the synthetic route. The saturation magnetization (M_s) determined from the seed-mediated sample is lower than that of the conventional sample. The coercivity of the former (610 Oe at 5 K), however, is double that of latter (300 Oe at 5 K), indicating that coercivity strongly depends on the crystallinity of the cobalt.

Introduction

Nanostructured transition metal crystals are excellent samples of advanced materials. Their physical properties are highly dependent on the nature of the surface [1]. Interestingly, polymer-coated magnetic nanoparticles also have great potential in many technological fields, including biological and environmental applications. However, only a few groups reported to employ linear polymers in processing magnetic nanoparticles [2, 3]. In this paper, we focused on the synthesis of polymer-coated cobalt nanocrystals and investigated various influences on its magnetic properties. Our research samples were prepared in a polar solvent through organometallic thermal-decomposition at a high temperature, with the presence of poly (N-vinyl-2-pyrrolidone) (PVP) as a protective polymer. Although Sun, et al. has produced PVP-coated FePt nanocrystals [4], in which capping agents (hydrocarbons with short chains such as oleic acid/oleyl amine) were exchanged with linear polymers, our process was different. We directly used PVP as a stabilizing agent and produced the samples in a polar solvent system.

Experimental Section

All reactions were conducted using standard airless procedures and commercially available reagents. Cobalt octacarbonyl was purchased from Gelest, poly (N-vinyl pyrrolidone) (PVP, $M_w \approx 2500$) from Polysciences, trioctylphosphine (90 %) from Aldrich, and ethylene glycol (98 %) from EM Science. The reagent grade ethyl alcohol was employed as a solvent.

In a typical synthesis, poly(N-vinyl pyrrolidone) (0.06g), dissolved in 10 mL ethylene glycol, was injected into 16 mL ethylene glycol at 45 °C. This was done under an Ar atmosphere while being agitated vigorously. 5×10^{-2} g of $\text{Co}_2(\text{CO})_8$ were then added to the above solution at 50 °C. The temperature was steadily increased to 160 °C within 1hr and maintained at 160 °C for an additional 20 min. From a transparent color, it changed into black, indicating the formation of cobalt particles. The reaction mixture was then allowed to cool at room temperature under an argon

atmosphere and the cobalt particles were separated through centrifugation. In the comparative study on the effect of PVP, the same procedure was used except this time, PVP was added.

In seed-mediated synthesis, 0.3×10^{-3} g of $\text{Co}_2(\text{CO})_8$ was dissolved in a mixture of diethyl ether and ethanol. This solution was injected into 16 mL ethylene glycol at 50 °C under an argon atmosphere while being stirred vigorously. The temperature of this system was heated to 160 °C within 20 min and maintained at 160 °C for additional 20 min. The mixture was then allowed to cool at room temperature. 0.06 g of PVP and 5×10^{-2} g of $\text{Co}_2(\text{CO})_8$ dissolved in 10 mL ethylene glycol was injected into the above seed solution after it was re-heated at 50 °C. The temperature of this reaction mixture was then increased to 160 °C within 1hr and was maintained for 20 min. The recovery procedure is the same as that described above.

TEM images were taken on a JEOL 2010 microscope (80 kV). The magnetic susceptibility and magnetization hysteresis loops were recorded using a Quantum Design MPMS SQUID magnetometer. The phase characterization of the nanostructured composites was performed using the Philips X'pert-systems (Cu-K α radiation).

Results and Discussion

$\text{Co}_2(\text{CO})_8$, as a thermal-decomposition precursor, was first added into a warm polar solution (ethylene glycol, 50 °C) in the presence of PVP (polyvinylpyrrolidone, MW = 2500). Decomposition and nucleation occurred instantly when the temperature was increased, resulting in numerous small metal clusters (nuclei). Nanometer-sized cobalt crystals steadily grew from these clusters during a continuous heating treatment at 160 °C. Linear polymer, PVP, acted as a network and controlled the size and shape of these cobalt nanoparticles [2]. The functional group from the linear polymer, PVP, formed a cap around the metal nanocrystals and weakly bonded with the crystalline face of these nanocrystals [5], resulting in a small degree of agglomeration. Special crystal shapes may be observed depending on the polymer composition.

The TEM images of cobalt nanocrystals are illustrated in Fig. 1(a, b). It shows that the Co nanoparticles produced from the thermal-decomposition of cobalt octacarbonyl, in the presence poly (N-vinyl pyrrolidone) and ethylene glycol; mainly exist in cubic/hexagonal shapes. The average diameter of these polymer-coated particles is about 60 nm. The polymer (PVP) shell, exhibiting a layer 3-5 nm thick, can be clearly observed. Despite undergoing several washing treatments, the polymer shell still remained on the surface of the Co nanocrystals. The crystallinity of the Co was, thus, enhanced due to polymer layer restrictions. In order to further verify its contribution, an experiment was conducted without the presence of PVP under the same rest conditions. The experiment revealed that the absence of PVP resulted in irregular and aggregated Co particles, as illustrated in Fig. 1c. This demonstrates that PVP plays an important role in the formation of cubic/hexagonal cobalt nanocrystals.

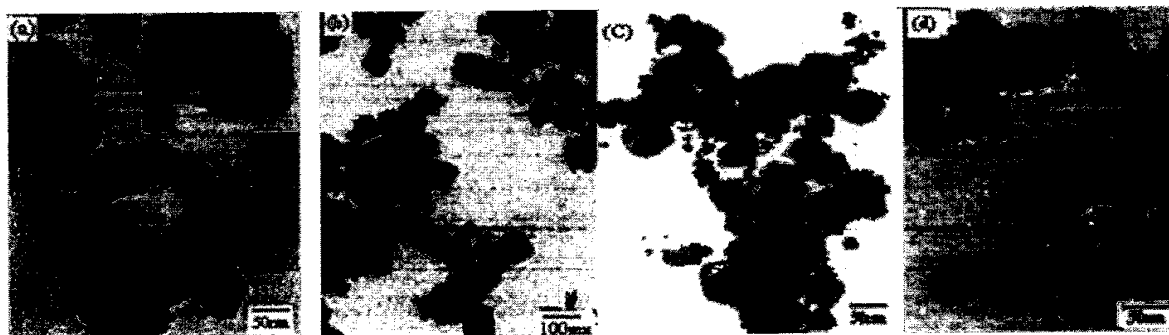


Fig. 1. TEM images showing (a,b) cubic/hexagonal-shaped Co nanoparticles synthesized with the presence of PVP (60 nm, 80 nm) (c) irregularly-shaped cobalt nanoparticles synthesized with the absence of the polymer. (d) cubic / hexagonal-shaped Co nanoparticles (60 nm) synthesized through seed mediated synthesis

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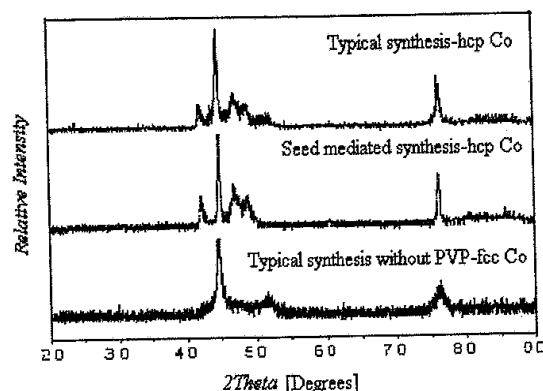


Fig. 2. XRD diffraction patterns of Co nanocrystals [top: Co nanoparticles synthesized through typical synthesis (hcp main phase), middle: Co nanocrystals through seed-mediated synthesis (hcp main phase), bottom: Co nanoparticles without PVP (pure fcc)]

Two cobalt samples, with PVP and without PVP, have been characterized and their XRD patterns are presented in Fig. 2. The XRD trace reveals that the Co sample with PVP exists in the hcp structure, [ICDD PDF cards (5-0727)] as a major phase (minor contribution of epsilon phase); whereas, the sample without PVP exists in the fcc-structure as a single phase.

The magnetic properties of both cubic and hexagonal-structured cobalt nanocrystals were determined using SQUID. The field cooling (FC) and zero field cooling (ZFC) curve are shown in Fig. 3a. The ZFC and FC curves measured at 100 Oe show a steady increase in magnetization as a function the temperature measuring up to 300 K. This suggests a ferromagnetic behavior [6], containing paramagnetic impurities at low temperatures. Based on the sample shown in Fig. 1a, as presented in Fig. 4a the coercivities were measured as 300 Oe (at 5 K) and 200 Oe (at 300 K), respectively.

Magnetization is not saturated at room temperature, probably because of the pinning of spins on the surface of the particles when a very high anisotropy field is present [7]. The release of the gaseous phase from decomposition, when the metal particles are formed, may result in some internal pores. This leads to spin canting in the volume of the particle and lowering of magnetization saturation.

To investigate the effect of PVP on the magnetic properties of Co nanocrystals, the FC and ZFC of both samples synthesized with and without the PVP medium were investigated from 5 K to 300 K. In the Co without PVP (Fig. 3b), the FC curve appears almost flat, suggesting a pure ferromagnetic behavior without paramagnetic impurities. The coercivity of this sample can reach up

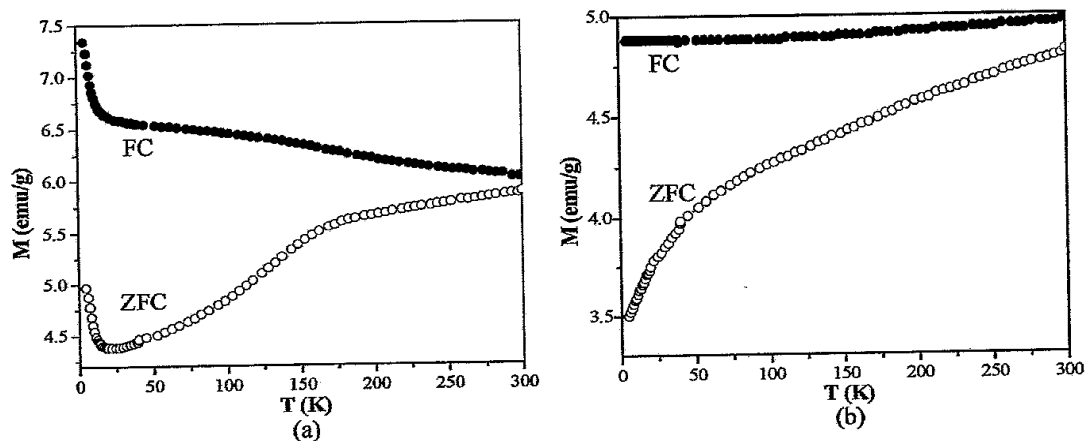


Fig. 3. Magnetization normalized by mass verse temperature for the 60nm cubic Co nanocrystals synthesized (a) with the presence of the polymer, (b) with the absence of the polymer in ethylene glycol, at an applied magnetic field of 100 Oe

to 260 Oe (at 5 K) and 160 Oe (at 300 K), respectively. Compared to the sample prepared with PVP medium, it is clear that the PVP-mediated Co nanocrystals possess a much higher coercivity than one without PVP, indicating that the magnetic disorder is confined to a very thin surface layer. This thin layer, however, where spin canting may exist due to the breaking of magnetic exchange pathways, appears to be sufficient in enhancing anisotropy, leading to a high blocking temperature. When there is surface spin disorder, surface anisotropy results in an enhanced coercivity [8].

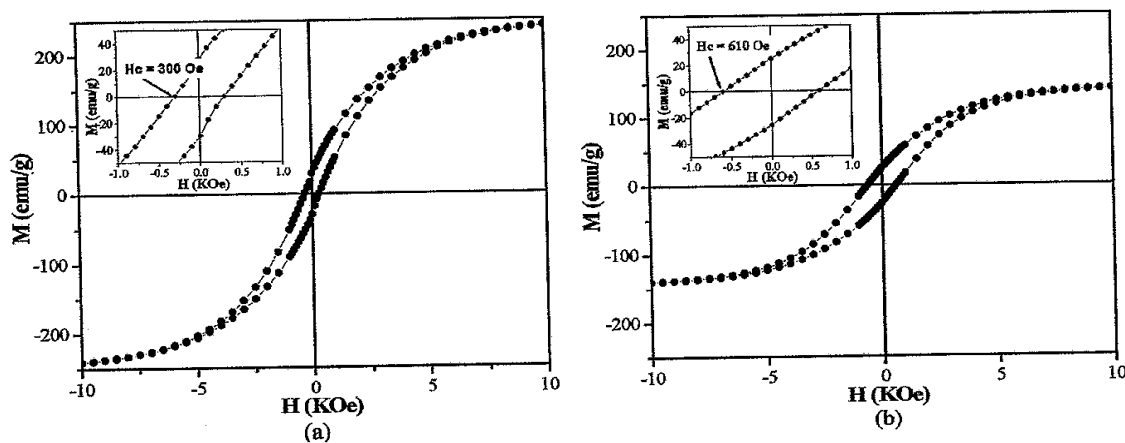


Fig. 4. Hysteresis loop for the 60nm cubic Co nanocrystals at a temperature of 5K (a) through typical synthesis, (b) through seed mediated synthesis [Insets: enlargement at low field]

In order to investigate the influence of seed on morphologies and physical properties, we induced a seed solution at the beginning of the conventional synthesis when octacarbonyl was thermally-decomposed in the presence of poly (N-vinyl) pyrrolidone and ethylene glycol. The TEM image of the cubic Co nanoparticles synthesized through the seed-mediated system is illustrated in Fig. 1d. It shows that the Co nanoparticles produced from this route mainly exist in cubic shapes with an average diameter of 60 nm. Sample synthesis via this route was also characterized using the XRD technique, revealing that the hcp phase (minor contribution from epsilon phase) are dominative, as shown in Fig 2. However, saturation magnetization (M_S) (not shown) was lower than that prepared from the conventional method. A double amount of coercivity (610 Oe at 5 K and 300 Oe at 300 K) can be determined from the seed-mediated sample, as shown in Fig. 4. The shifted hysteresis loops suggest that the surface spins are spin glasslike. The increase in coercivity can be attributed to the extra energy required in the switching of the core spins pinned by an exchange interaction with the frozen spin glasslike surface layer. The direct composition of the exchange interaction between surface and core spins lies at the origin of the large experimental value of the coercivity fields. To conclude, the unusually large value of the H_c is clearly seen in the case of the seed-mediated approach.

Conclusion

Polymer coated Co nanocrystals have been prepared in a one-step reaction through organometallic thermal-decomposition. PVP plays an important role in the formation of cubic/hexagonal Co nanocrystals. PVP shell coated onto the surface of metal particles cannot be completely washed out by using polar solvents such as ethanol or ethylene glycol.

The stability of such nanocomposites in a thermal environment is favorable in the application of PVP protected metal nanocrystals in biologics, nanoelectronics [9], and chemosensors [10].

The magnetic properties of cobalt nanocrystals are different when produced with seed-mediated and without seed-mediated processes. In a seed-mediated process, the saturation magnetization (M_S) is lower and coercivity is higher.

We are also carefully examining the influence of different solvents and capping agents (PVP and PVP + trioctylphosphine) on the formation of Co-crystals and related magnetic properties.

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