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Organic colloid method to prepare ultrafine cobalt nanoparticles with the size of 2 nm

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Abstract

Ultrafine Co nanoparticles with the size of ca. 2 nm were prepared by an organic colloid method, in which sodium formate acted as reducing agent, ethylene glycol acted as solvent, sodium citrate acted as both complexing agent and stabilizing agent, respectively. X-ray diffraction (XRD) analysis indicated that the as-prepared Co nanoparticles were in hexagonal close-packed phase, and transmission electron microscope (TEM) images revealed that the size of the well-dispersed Co nanoparticles was as small as 2 nm, and the sizes were distributed in a very narrow region. The hysteresis loop of the as-prepared Co sample measured at room temperature showed a superparamagnetic behavior due to the extremely small size of the products. It was revealed that sodium citrate played a crucial role in decreasing the particle size and narrowing the size distribution. © 2007 Elsevier Ltd. All rights reserved.

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1. Introduction

Magnetic nanoparticles represent a particularly interesting class of materials for both scientific and technological explorations [1-4]. In recent years, one of the important goals in magnetic nanoparticle synthesis was to control the particle size and narrow the particle size distribution. It was reported that discrete magnetic nanoparticles with sizes ranging from 2 nm to 20 nm are of significant importance, because of the wide application in magnetic storage devices, ferrofluids, magnetic refrigeration system, magnetic carriers for targeting and catalysis [5]. As one of the most important magnetic materials, nanocrystalline Co has spurred intensive studies not only due to its multiple crystal structures, but also owing to its size-dependent magnetic, electronic and catalytic properties [6]. It was demonstrated in the literatures that Co nanoparticles with diameters of 5-20 nm could be fabricated by a wide variety of processes [7-12], while preparation of Co nanoparticles below 5 nm is still challenging and there are only

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a few successful examples on the synthesis of Co nanoparticles in this size regime [13–18]. It seems that the synthesis will be much more difficult if smaller Co nanoparticles are required. Recently, Javey et al. obtained 2 nm monodispersed Co nanoparticles using an electrobeam lithography technique [17]. However it is clear that scaling up of this synthetic procedure will be rather difficult because of both high operational cost and tedious synthetic steps. Ledo-Suárez et al. also synthesized 2 nm monodispersed Co nanoparticles via an electrochemical method [18]. But obviously, the usage of some environmentally unfriendly reagents, such as, acetonitrile, triphenylphosphine and heptane, in the process made the approach less attractive from the viewpoint of environment safety.

Recently, our group has reported the formation of ultrafine (ca. 1 nm) PtRuIr nanocatalyst using an organic colloid synthesis method [19]. We modified this method and applied it to the preparation of ultrafine Co nanoparticles. The results demonstrated that 2 nm Co nanoparticles with narrow size distribution could be obtained successfully by this route. In this novel and facile approach, sodium formate acted as reducing agent, ethylene glycol acted as solvent, sodium citrate acted as both complexing agent and stabilizing agent, respectively. The as-prepared Co nanoparticles were characterized by

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transmission electron microscopy (TEM), X-ray diffraction (XRD) and superconducting quantum interference device (SQUID) magnetometer.

2. Experimental section

All reagents were of analytic grade and used without further purification. In a typical synthetic procedure, 2.5 mmol cobalt chloride hexahydrate and a certain amount of sodium citrate were dissolved in 70 mL ethylene glycol under intense stirring, followed by adding 20 mL ethylene glycol solution of sodium hydroxide (1 M) to the above solution. For the sake of simplicity, we defined *R* as the molar ratio of sodium citrate to cobalt chloride in the present paper. 10 mmol sodium formate was then dissolved into the mixed solution. Subsequently, the temperature of the solution was elevated to 180 °C and held for 8 h. After reaction, the products were collected by centrifugation and washed with double-distilled water and acetone, then dried in a vacuum oven at 70 °C for 12 h.

X-ray powder diffraction patterns were recorded using a Shimadzu XD-3A X-ray diffractometer with Cu K α radiation ($\lambda = 1.5406$ Å). The transmission electron microscopy was carried out in a Philips CM300 transmission electron microscope operated at an accelerating voltage of 200 kV and room-temperature M/H hysteresis loop was recorded with a Quantum Design MPMS XL-7 superconducting quantum interference device (SQUID) magnetometer.

3. Results and discussion

The TEM images of cobalt nanoparticles prepared using different molar ratios of sodium citrate to cobalt chloride are shown in Fig. 1, which clearly indicated that the dosage of sodium citrate had a remarkable effect on the Co nanoparticles. As shown in Fig. 1a, when no sodium citrate was introduced to the reaction medium, most of the resulting Co nanoparticles were agglomerated together. In addition, the particle size was quite large and the size distribution was rather broad. With the increase in the molar ratio of sodium citrate to cobalt chloride, the particle size of prepared Co nanoparticles decreased remarkably. As R increased to 4, the Co nanoparticles were well-dispersed without agglomeration and the average particle size significantly decreased despite the fact that the size distribution from 7 to 20 nm was still somewhat large. And as R rose to 6, the diameter of the Co nanoparticles dropped further. High magnification TEM image (Fig. 1e) showed that the Co particles with an average size of 2 nm were predominantly spherical and of uniform size.

Based on TEM observation, it was apparent that sodium citrate, as a complex agent and stabilizer, played a crucial role in decreasing the particle size and narrowing the size distribution of the Co nanoparticles. It was generally acknowledged that the citrate ions could prevent the further growth of nanoparticle by the complexing of the carbonyl groups with metal ions and the adsorption on the surface of formed small metallic nanoparticles. Meanwhile, the adsorbed citrate ions could also act as a stabilizer and inhibit the agglomeration of nanoparticles by steric hindrance and/or Coulombic effects [20].

For comparison, we carried out another experiment, in which sodium tartrate acted as complexing agent instead, while other experimental conditions were kept unchanged. The TEM image of the resultant product is shown in Fig. 2. Nanosized Co particles could also be obtained, but the size distribution was large. Additionally, we also made an attempt to use some other complexing agents, such as ethylenediamine tetraacetic acid sodium (EDTA), sodium pyrophosphate in our synthesis route. But we failed to obtain ultrafine Co nanoparticles and the main products of these reactions were found to be Co(OH)₂. We thought this may result from either the poor solubility of these complexing agents in ethylene glycol or the low stability constants of the formed complexes. The role of complexing agents in this study is interesting but is not well-understood, and further investigation is still necessary.

It should be pointed out that reduction of divalent cobalt salts to metallic Co by polyols at elevated temperature (the so-called polyol process) has been well-documented in the literature [8]. However, the preliminary experiments showed that when Rwas 4 and 6, no cobalt nanoparticles were obtained without adding HCOONa to the reaction medium, so the possibility of reduction of cobalt (II) citrate complexes to metallic Co by ethylene glycol could be excluded in these cases. This revealed that it was HCOONa that initiated the reducing reaction and ethylene glycol was only used as a solvent at R = 4 and 6.

Fig. 3 shows the XRD patterns of the Co nanoparticles prepared using different molar ratios of sodium citrate to cobalt chloride.

As could be seen in Fig. 3, at R = 0 and 2, six peaks were observed at $2\theta = 41.4^{\circ}$, 44.4° , 47.2° , 51.5° , 62.4° and 75.8° in the XRD patterns, suggesting that these Co samples were present as both the hexagonal close-packed (hcp) and facecentered cubic (fcc) structures [21]. It was very interesting to note that the peak at $2\theta = 51.5^{\circ}$ disappeared as *R* increased to 4 and 6, indicating that the corresponding products were in pure hcp phase Co (space group: P63/mmc1(194); JCPDS: 05-0727, a = 2.503 Å, c = 4.060 Å). Also, we could see that the diffraction peaks gradually became broad and the intensities of the peaks decreased obviously as *R* increased, revealing a decrease in the mean size of Co nanoparticles, which was quite coincident with the TEM results.

Note that no diffraction peaks of impurities, such as, CoO and $Co(OH)_2$, were observed in all these XRD patterns, which implied that the Co nanoparticles prepared by our method were of high purity.

The M/H hysteresis loop (Fig. 4) of the 2 nm Co nanoparticles measured at room temperature (300 K) showed that the hysteresis and coercivity were nearly undetectable, suggesting that the prepared Co nanoparticles had superparamagnetic properties at room temperature. The saturation magnetization was 82.2 emu/g, which was much lower than that of bulk Co metal (168 emu/g).

It is known that the energy of a magnetic particle in an external field is proportional to its size or volume via the number of magnetic molecules in a single magnetic domain. When this energy becomes comparable to the thermal energy, thermal fluctuations will significantly reduce the total magnetic



Fig. 1. Typical TEM images of Co nanoparticles prepared using various molar ratios of sodium citrate to cobalt chloride: (a) R = 0, (b) R = 4, (c, d, e) R = 6, (f) particle size distribution at R = 6. Inset in Fig. 1e shows the magnified TEM image, in which fringe spacing of cobalt nanocrystals was clearly visible.

moment at a given field [22]. So the magnetic moment of the as-prepared Co nanoparticles significantly decreased compared with the corresponding value of bulk Co owing to its extremely small size. In addition, the electron exchange between ligand and surface atoms could also quench the magnetic moment [23]. In the present study, although the Co nanoparticles were washed before the magnetic measurement, it was possible that there were still a small amount of citrate ions adsorbing on the surface of Co nanoparticles, which could also cause the decrease in saturation magnetization.

4. Conclusion

In summary, 2 nm superparamagnetic Co nanoparticles with the hexagonal close-packed (hcp) structure were prepared by a novel and facile approach, in which sodium formate was used



Fig. 2. TEM image of Co nanoparticles prepared using sodium tartrate as complexing agent.



Fig. 3. XRD patterns of Co nanoparticles prepared at different *R*.



Fig. 4. The room-temperature (300 K) magnetic hysteresis loop of the asprepared 2 nm Co nanoparticles prepared at R = 6.

as reducing agent, ethylene glycol as solvent, sodium citrate as both stabilizing agent and complexing agent, respectively. It was revealed that sodium citrate played a crucial role in decreasing the particle size and narrowing the size distribution.

The very efficient route presented here, using only cheap inorganic reagents and ethylene glycol, should be very suitable for large-scale production of ultrafine Co nanoparticles with narrow size distribution due to the simplicity and low cost of the synthetic process. Furthermore, this approach may be extended to the preparation of the ultrafine nanoparticles of some other transition metals and alloys, such as Fe, Ni and their alloys, which is underway in our laboratory.

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