Front. Chem. China 2009, 4(2): 154–159
DOI 10.1007/s11458-009-0022-y

RESEARCH ARTICLE

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Effect of sodium citrate on preparation of nano-sized cobalt particles by organic colloidal process

Abstract Nano-sized cobalt particles with the diameter of 2 nm were prepared via an organic colloidal process with sodium formate, ethylene glycol and sodium citrate as the reducing agent, the solvent and the complexing agent, respectively. The effects of sodium citrate on the yield, crystal structure, particle size and size distribution of the prepared nano-sized cobalt particles were then investigated. The results show that the average particle diameter decreases from 200 nm to 2 nm when the molar ratio of sodium citrate to cobalt chloride changes from 0 to 6. Furthermore, sodium citrate plays a crucial role in the controlling of size distribution of the nano-sized particles. The size distribution of the particle without sodium citrate addition is in range from tens of nanometers to 300 or 400 nm, while that with sodium citrate addition is limited in the range of (2±0.25) nm. Moreover, it is found that the addition of sodium citrate as a complex agent could decrease the yield of the nano-sized cobalt particle.

Keywords sodium citrate, cobalt, organic colloidal process, nano-sized material, complexation

1 Introduction

In recent years, magnetic nanomaterials attracted wide attention because of their great potential applications including ultra high density information storage [1], GMI [2] and biomedical [3], etc.. As its excellent electrical, magnetic, catalytic properties and a variety of crystalline structure, nanometer cobalt material is particularly eye-catching in a large number of magnetic nanomaterials. At present, there are many synthesis methods of nano-sized cobalt particles, such as cobalt carbonyl-pyrolysis [4] reported in literature. However, this method required a large amount of toxic organic solvents, and the reactants ($Co_2(CO)_8$) and the carbon monoxide products are toxic. So, it is not benign for the environment. In addition, there are some of other methods, such as a γ-ray irradiation method [5], lithography-vapor deposition [6], gas synthesis [7] method and so on. But all these methods have problems such as equipment demands, high operating costs, a complicated process, all of which are not favorable for large scale production. In contrast, using chemical reducing agents to reduce the cobalt salts in solution for obtaining cobalt nanocrystals (NCs) have some of advantages such as simple operation and low cost. It is reported that reducing agents such as polyol, $NaBH_4$, $LiBEt_3H$, N_2H_4 and Mg can reduce cobalt salt to obtain cobalt NCs in appropriate reaction conditions [8]. Sodium formate is a mild reducing agent, which usually was used to prepare noble metal and its alloys nanoparticles. However, sodium formate as a reducing agent to produce cobalt NCs has not reported yet.

Here, we report an organic colloidal process with sodium formate as a reducing agent, ethylene glycol as the solvent and sodium citrate as the complex agent to prepare cobalt NCs and it is focused on the influence of sodium citrate on obtained cobalt NCs.

2 Experimental

2.1 Chemicals

Ethylene glycol, cobalt chloride, sodium citrate, sodium formate and sodium hydroxide were purchased from the Tianjin Yongda Chemical reagents and development centers, Tianjin Kemiou chemical and real development centers, Chengdu joint chemical reagents Institute, Tianjin Chemical reagent factory (I) and Tianjin Baishi Chemical Co., Ltd., respectively. All chemicals used are analytical reagents.

Translated from *Journal of South China University of Technology*, 2008, 36(3) (in Chinese)

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2.2 Cobalt NCs synthesis

A certain amount of sodium citrate and 2.5 mmol of Cobalt (II) chloride hexahydrate were dissolved in 70 mL of ethylene glycol (EG) with strong stirring. Then, 20 mL of 1 mol/L of NaoH/EG solution was added dropwise into the system. Afterwards, 10 mmol of sodium formate were added and dissolved in the system with stirring. The above solution was heated to 180°C and kept for a certain period of time for the reaction. Cooling followed after the reaction, and the solution was filtrated and solid product was collected, following washed. It was then washed several times with distilled water and acetone, and lastly dried at 70°C in a vacuum oven for 12 h.

2.3 Characterization of synthesized cobalt NCs

The crystalline structure of NCs was characterized by X-ray power diffraction (XRD) using a Shimadzu XD-3A diffractometer. The measurement was conducted with Cu Kα radiation, Ni filter, 0.15418 nm ray wavelengths, 35 kV of tube voltage and 30 mA of tube current. Transmission electron microscopy (TEM) images were taken with a Philips CM300 at an acceleration voltage of 200 kV.

2.4 The calculation of the yield and particle sizes

The yield of cobalt NCs was determined by the formula $Y = (m/m_0) \times 100\%$, where m and m_0 were the actual quality of the dried cobalt powder and the theoretic quality, respectively. And the particle size distribution was established from the TEM images.

3 Results and discussion

3.1 The influence of sodium citrate on the particle size and size distribution

TEM images in Fig. 1 and Fig. 2 show the different of particle size and size distribution of cobalt NCs when different molar ratio of sodium citrate to cobalt chloride was used. It can be seen that the cobalt NC sizes were larger without sodium citrate than those with sodium citrate added in the preparation process. The average cobalt particle size without sodium citrate in the preparation process is about 200 nm as a rough estimate, and with a broad size distribution, from tens of nanometer to three or four hundred nanometer. The size of cobalt NCs become significantly smaller with a narrower size distribution when sodium citrate was added in the preparation process. When the molar ratio of sodium citrate to cobalt chloride is four, most of the particles range from 7 nm to 20 nm and the average particle size is about 12 nm. Furthermore, when the molar ratio of sodium citrate to cobalt chloride is six, the particle size is smaller, and most of particle sizes range within 2±0.25 nm as shown in Fig. 2. These results show that adding sodium citrate reduced the cobalt NCs size and their size distribution significantly, and this effect became more marked with increased sodium citrate.

This is because of the fact that as the concentration of freed cobalt ions in the solution might be high without sodium citrate in the reaction system, the related reduction rate of cobalt ions and growth rate of cobalt NCs must be faster. So that, the obtained cobalt particle size is large since the NCs are apt to aggregate at high temperature without a surfactant in the reaction system. When a certain amount of sodium citrate was added, cobalt ions can be reduced slowly and equally. As a result, the cobalt ion reduction rate can be controlled by complex formation of sodium citrate agent in the reaction system. The cobalt NCs can be stable in the reaction system and could not be aggregated together after the completion of the reduction reaction. The citric acid ion can be absorbed on the surface of cobalt (0) NCs chemically which reduced the surface energy and consequently, reduced the growth rate of NCs, as well as caused steric hindrance and charge repulsion. As a result, added sodium citrate can reduce the size of cobalt NCs. At the same time, as the molar ratio of sodium citrate to cobalt chloride increased, the size of cobalt nanoparticle decreased markedly. This means that the higher concentration of sodium citrate is, the smaller size of cobalt

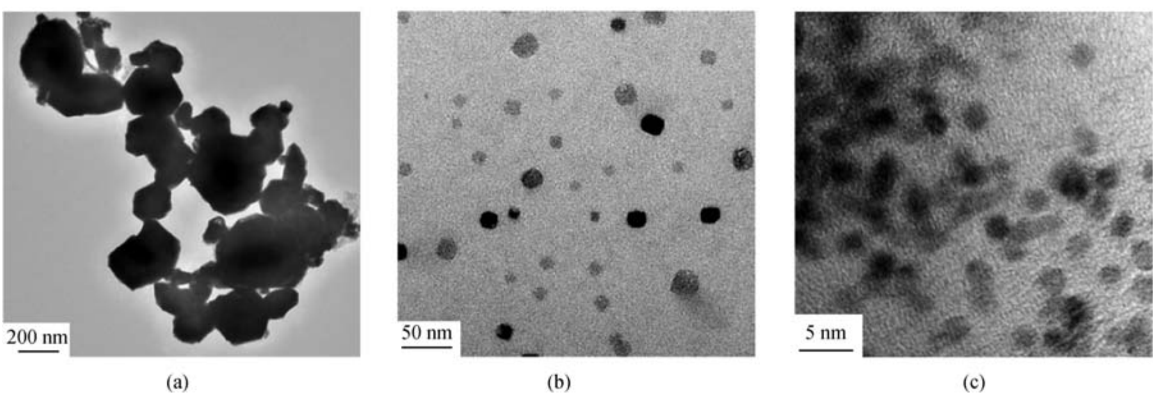

Fig. 1 TEM images of cobalt nanoparticles prepared in different molar ratios of sodium citrate to cobalt chloride

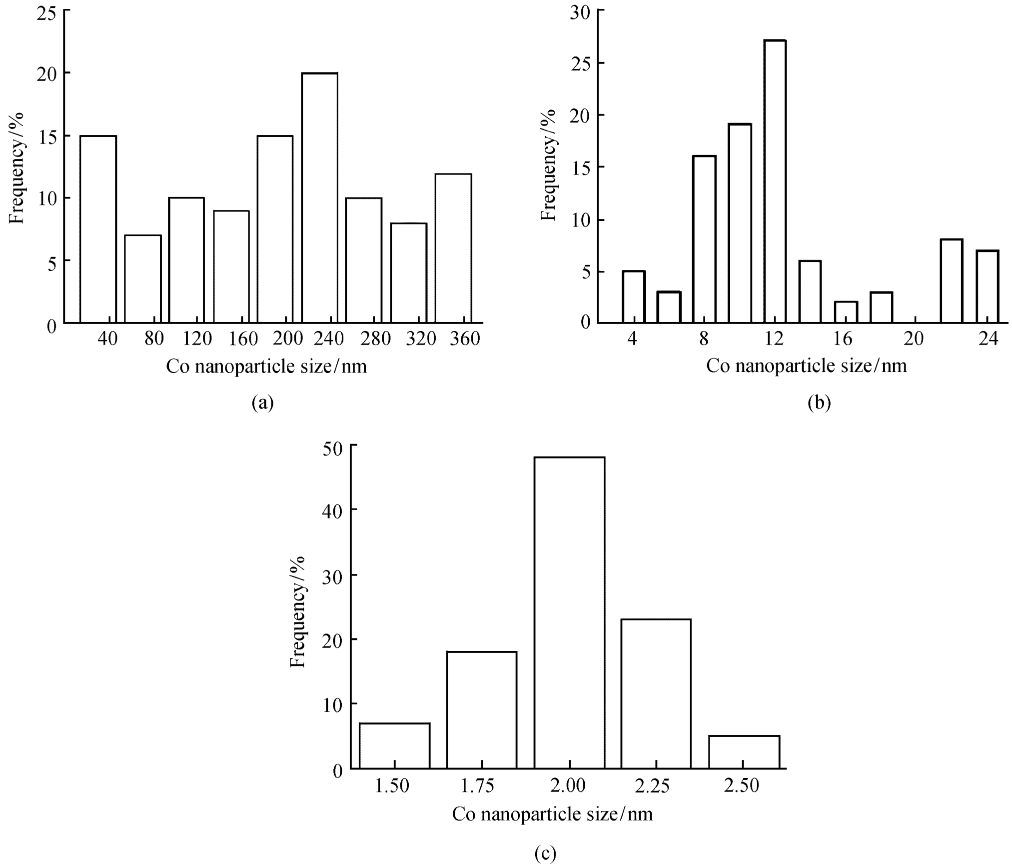

Fig. 2 Size distribution of cobalt nanoparticles prepared in different molar ratio of sodium citrate to cobalt chloride

nanoparticle can be achieved within a certain range of concentration.

3.2 The influence of the amount of sodium formate on the yield of cobalt NCs

The result list in Table 1 shows the influence of molar ratio of sodium citrate to cobalt chloride on the yield of cobalt NCs with a different amount of sodium formate.

As can be seen from the Table 1, cobalt (II) salt can be reduced into cobalt (0) by ethylene glycol without the addition of sodium formate and sodium citrate and the yield was as high as 85.7%. But particle sizes of cobalt obtained were large and they have a wide distribution range. When sodium citrate was added into the reaction systems, the reductive ability of ethylene glycol was restricted and the yield decreased dramatically until the yield was zero when the molar ratio of sodium citrate to cobalt chloride was four. However, while sodium citrate was added in the reaction systems with sodium formate as the reducing agent, the yield was kept high, though slightly decreased with the amount of sodium citrate increased, which indicates that sodium citrate restrained the reduction reaction of cobalt chloride as citrate ions could coordinate with cobalt ions to form $[Co(C_6H_5O_7)_2]^{4-}$ complexes [9]. According to thermodynamics point of view, the formation of the complex reduced Co(II) redox potential resulted in a yield decreased. For the dynamics, the formation of the complex reduced the concentration of Co^{2+}, so that the lower rate of reaction can also reduce the yield in a certain time.

In addition, one can see from Fig. 1 that the higher dosage of sodium citrate is, the smaller size of cobalt nanoparticles obtained, which would reduce the yield. Furthermore, the smaller size of NCs can be increased the loss of product during the filtration and treatment process.

Table 1 The yields of cobalt nanoparticle prepared in different molar ratio of sodium citrate to cobalt chloride

Sample number	Molar ratio of sodium citrate to cobalt chloride	Molar ratio of sodium formate to cobalt chloride	Yield/%
1	0	0	85.7
2	2	0	25.0
3	4	0	0
4	0	4	91.2
5	2	4	69.2
6	4	4	55.7
7	6	4	46.2

3.3 The influence of reaction time on the yield of cobalt nanoparticle

In order to further reveal the influence of sodium citrate on the yield, the yield varied with the reaction time in different molar ratio(r) of sodium citrate to cobalt chloride was investigated as shown in Fig. 3. The results in Fig. 3 show that when the molar ratio of sodium citrate to cobalt chloride was in 0 to 2, cobalt (0) was found after two hours of the reaction, although the yield was low. Whereas there was no cobalt (0) can be found at two hours of the reaction when the molar ratio of sodium citrate to cobalt chloride was raised to four and six. However, at that time, the solution color was changed from transparent blue and purple to half transparent dark red and brown, which means that the reaction already began. It can be seen that an induction stage exist before the precipitation of the cobalt (0) NCs and the induction stage was extend when sodium citrate was added in the reaction system. According to the LaMer model [10], during the induction stage, the accumulated cobalt ions in the reaction system has not yet reached the critical concentration of supersaturation, there is no precipitation of cobalt nuclei. Once the precipitation of cobalt nuclei appeared, the following reaction will be triggered as the cobalt nuclei acts as a seed. It also can be seen that in Fig. 3, in the latter reaction stages (8 hr later), the slope of the curve declined obviously in the presence of sodium citrate which suggeted that the average reduction rate of cobalt chloride decreased. This may be due to the concentration of cobalt salt dropping along with the reaction, the molar ratio of sodium citrate to cobalt chloride became higher than that of in initial value, resulted in the slowness of the average reduction rate of cobalt salt in the latter reaction stages.

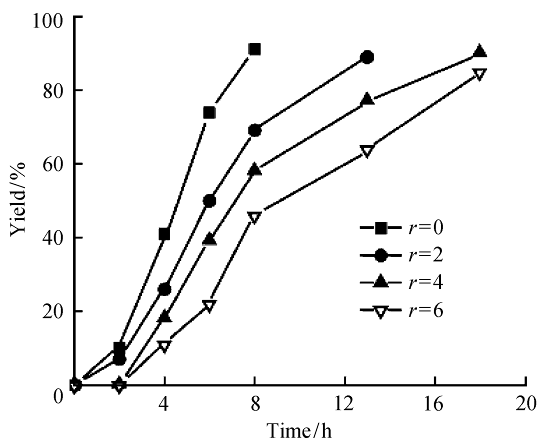

Fig. 3 Effect of reaction time on the yields of Co nanoparticles

3.4 The influence of sodium citrate on the crystal structure of cobalt nanoparticle

X-ray diffraction (XRD) patterns of the cobalt NCs prepared by the different molar ratio of sodium citrate to cobalt chloride and ethylene glycol as reducing agent were showed in
Fig 4. We can see that in Fig 4(a), the diffraction patterns of cobalt NCs obtained though the molar ratio of sodium citrate to cobalt chloride were 4 and 6. The peaks of the patterns were 41.4°, 44.3°, 47.3°, 75.8° of diffraction angle, which were attributed to (100), (002), (101) and (110) planes of hexagonal close–packed (hcp) structure of cobalt NCs, respectively [PDF#894308]. When the ratio dropped to 2 and zero, except for these peaks, a small diffraction peak of 51.7° appeared, which can be attributed to the face-centered cubic (fcc) crystal structure of cobalt (200) plane [PDF#894307], suggesting that the hcp and fcc crystal mixed in low value of molar ratio of sodium citrate to cobalt chloride. When the molar ratio of sodium citrate to cobalt chloride was 4 and 6, ethylene glycol in the reaction system played the role of the solvent. All cobalt chloride was reduced by sodium formate, indicated that pure hcp cobalt crystal was obtained as shown in Table 1.

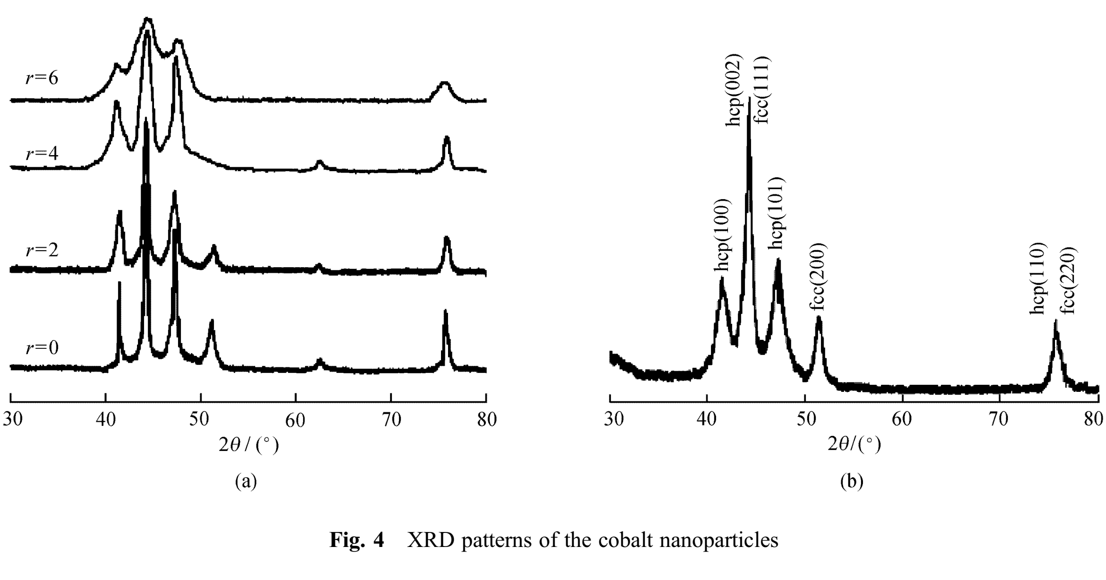

Fig. 4 XRD patterns of the cobalt nanoparticles

When the ratio are zero or two, cobalt crystals obtained were co-reduced by sodium formate and ethylene glycol. It is reported in Literature [11] that the different crystalline forms of cobalt nanocrystals could be obtained by adjust the concentration of sodium hydroxide. The crystal structures varied with the concentration of sodium hydroxide when cobalt NCs prepared by ethylene glycol reduced. And fcc and hcp mix of cobalt crystals were obtained by ethylene glycol reduced without sodium formate and sodium citrate added as shown in Fig. 4(b). Accordingly, the appeared fcc cobalt crystal was attributed to ethylene glycol participate in the reduction reaction when the molar ratio of sodium citrate to cobalt chloride are zero or two. Therefore, in this study, the influence of sodium citrate on the cobalt nanocrystals structures was realized by "selected" the reducing agents in the reaction systems.

3.5 Possible mechanism about the influence of sodium citrate on the cobalt NCs

According to the above discussion, sodium citrate present has a significant impact on the obtained cobalt NCs, including partide size and size distribution, which attribute to complexes forming. It is reported mechanism [12] that sodium citrate is a stabilizer in the preparation process of nanoparticles, which affects the particle size. In this study, the only possible mechanism for the effect of sodium citrate as a complex agent on the cobalt particle size distribution will be discussed.

According to the homogeneous nucleation theory based on the LaMer model [10], after the nuclei generation, the slow rate of particle formation is in favor of the narrow size distribution in the solution. In this study, after the first nucleation generated, the concentration of free cobalt ions in the solution is relative high without sodium citrate in the reaction systems. Accordingly, the growth rate of the cobalt atom is fast. If the growth rate of the cobalt particle is faster than that of the nucleation rate, the redundant cobalt particles in the solution accumulated. As long as the concentrations of particles exceed the critical supersaturation concentration in the solution, there will be re-nucleation. Some of the generated cobalt atoms make the original nuclear cobalt particles continuously grow and some of them will form the new nucleus. That is to say, the growth of NCs are not synchronized, and the particle size depends on the nucleation time. Larger particles will be obtained when the nucleation first formation and the smaller particles will be obtained when the nucleation is behind. Then, the particles size distribution is in a wide range. However, when sodium citrate was added into the reaction systems, they form a complex with cobalt ions and reduce the cobalt ions in the solution, thereby, reducing the generation rate of cobalt atom. This will keep the concentration of cobalt atom under the critical super-saturation concentration. Then, the original nucleus grows and there is no new nucleus generated after. Under these conditions, narrow size distribution of cobalt particles will be obtained and even monodispersed cobalt NCs can be gained.

4 Conclusions

Nano-sized cobalt particles with the diameter of 2 nm were prepared via an organic colloidal process at high temperature with sodium formate, ethylene glycol and sodium citrate as the reducing agent, the solvent and the complexing agent, respectively. Addition of sodium citrate could obviously reduce the particle size and yield of cobalt nanocrystals. When the molar ratio value of sodium citrate to cobalt chloride increases from zero to six, the average particle size of cobalt decreased from 200 nm to 2 nm, and the yield drops from 91.2% to 46.2%. At the same time, the particle size distribution of cobalt nanocrystals can be well controlled by sodium citrate addition. The cobalt particle sizes range is from tens of nanometers to three or four hundred nanometers without sodium citrate, and the cobalt nanoparticle is in diameter rang of 2 ± 0.25 nm by adding sodium citrate in the reaction systems.

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