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Preparation of cobalt nanoparticles by electron beam irradiation

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Abstract Cobalt nanoparticles were synthesized by electron beam irradiation without any catalysts at room temperature and ambient pressure. The nanoparticles were characterized by X-ray diffraction, transmission electron microscopy, vibrating sample magnetometer, and laser scattering particle size distribution analysis. Average size of the nanoparticles was about 32 nm with a narrow size distribution. Melting point of the nanoparticles was about 451.3℃.

Key words Cobalt, Nanoparticles, Electron beam, Irradiation

1 Introduction

Nanoparticles have unique catalytic, optical, electronic and magnetic properties[1–9]. And potential applications of metal nanoparticles have arose great research interests in their synthesis in solid-state chemistry. For synthezing better dispersed nanoparticles, a big challenge indeed, efforts have been made to prepare stable metal nanoparticles by various techniques, including hydrogen arc plasma[10], borohydride reduction of metal salts[11], extraction of transition metals from wood pulp fibers using supercritical carbon dioxide[12], radiolytic system, sonochemical and thermal decomposition of organic metal complexes[13,14], and electrode position on alumina template[15]. They are effective for synthesizing the transition metals.

Radiolytic synthesis of nanocrystals from metal ions in solution can provide a wide variety of mono and multi-metallic systems of different structures. In this paper, we use electron beams to synthesize nano-particles in an aqueous solution. It is known that bombarding water with electron beams produces hydrated electrons in addition to other species of radicals, and a hydrated electron has a standard electrochemical potential of –2.77 V, which is much lower than the standard potential of cobalt ion (–0.277 V for Co^{2+}/Co)[16]. Therefore, under E-beam irradiation, the reduction of cobalt ions occurs to produce cobalt nanoparticles.

2 Experimental

2.1 Chemical reagent

All the chemicals, including $CoSO_4 \cdot 7H_2O$, polyvinyl alcohol (PVA), isopropyl alcohol (IPA) and ammonia ($NH_3 \cdot H_2O$), were of analytical grade, and were used without further purification. Distilled water was used to dissolve the $CoSO_4$. PVA was added in the solution for controlling the size of nanoparticles and preventing them from aggregation. And IPA, as scavenger of oxidative radicals (OH·), was added in appropriate proportions. Ammonia solution was added as precipitator. It also controlled pH value of the solution, which was finally bubbled with nitrogen gas to eliminate dissolved oxygen.

2.2 E-beam irradiation

The solution was irradiated by 1.75 MeV, 2 mA electron beams from an accelerator at Institute of Radiation Applications, Shanghai University. The absorbed dose was about 550 kGy. Plastic film dosimeters were used to measure the dose and dose distribution.

2.3 Product collection

Color of the solution irradiated changed from pink to black gray. This is an indication of the radiation-induced Co nanoparticles in the solution. The residual

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PVA was removed by repeated washing with distilled water and ethanol (99.7%, ρ = 0.79 g/mL) until no suspended particles. After 10-hour vacuum-drying at room temperature, Co nanoparticle powders were obtained.

2.4 Product characterization

Structure of the Co nanoparticles was determined by X-ray diffraction (D/max 2550, Rigaku, Japan). The morphology was examined by transmission electron microscopy (JEM-200CX, JEOL, Japan). The particle size distribution was analyzed by laser scattering (380ZLS Zeta Potential/ Particle Sizer, Nicomp, USA). The melting point was checked with a differential scanning calorimeter (DSC) of STA 409 PG/PC (Netzsch, Germany). The magnetic properties were tested with a vibrating sample magnetometer (Model 155, EGG Princeton Applied Research, USA).

3 Results and discussion

Fig.1 shows XRD patterns of the Co nanoparticles. The peaks at 2θ=44.32°, 51.52°, 76° and 92.4° agree with the JCPDS card number of Co-15-0806. From the Scherrer formula[17], average size of the Co nanoparticles at 2θ = 44.32° is about 32 nm.

From TEM images of the Co nanoparticles (Fig.2), it can be seen that the Co nanoparticles dispersed in different solvents aggregated differently in morphology. They were better dispersed in chloroform than in ethanol, because the interaction between the Co nanoparticles and chloroform is stronger. The particle size measured from the TEM images agreed well with the XRD results. The electron diffraction pattern in Fig.3 reveals that the particles are of single crystal structure.

Size of the Co nanoparticles in solvent was analyzed by laser scattering. The mean diameter peak of the cobalt nanoparticles dispersed in chloroform is about 20 nm (Fig.4), which is in good agreement with the results of XRD and TEM.

Cobalt has magnetic properties. The σ-H hysteresis loop of the prepared Co nanoparticles was measured at room temperature and ambient pressure (Fig.5). Its coercivity is about 50.5 Oe.

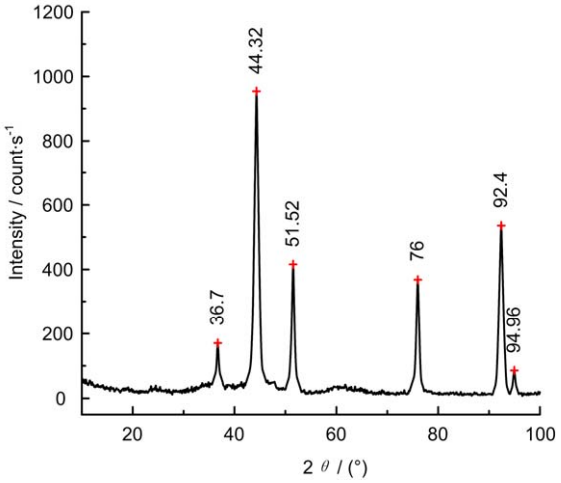

Fig.1 XRD patterns of the E-beam irradiation-induced Co nanoparticles.

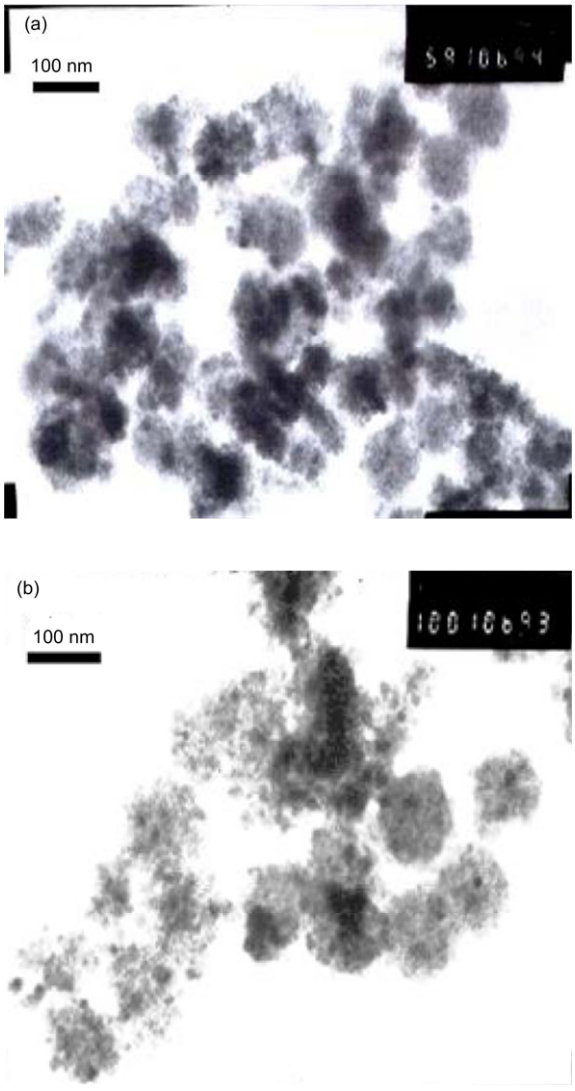

Fig.2 TEM images of the Co nanoparticles dispersed in ethanol (a) and chloroform (b).

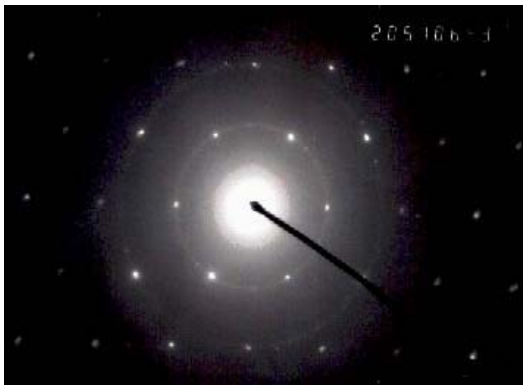

Fig.3 Electron diffraction pattern of the cobalt nanoparticles.

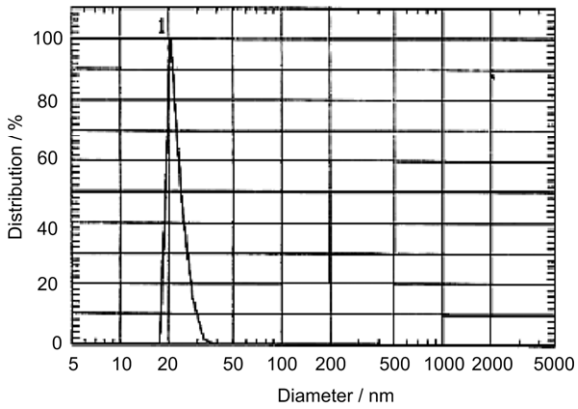

Fig.4 Size distribution curve of cobalt nanoparticles dispersed in chloroform.

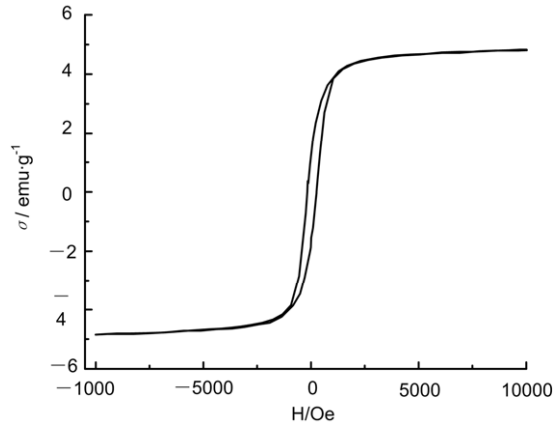

Fig.5 The σ-H hysteresis loop of the Co nanoparticles.

The results of DSC of the Co nanoparticles measured at 20℃·min^{-1} heating rate are shown in Fig.6. Melting point of the Co nanoparticles obtained from the DSC curve is about 451.3℃, which is far less than that of bulk cobalt (1490℃). Similar results were reported by other groups[18,19]. This is because of having been melted of nanoparticles below the equilibrium bulk melting point (T_m) due to the extremely high surface/volume ratio. The decreased melting point (ΔT_m) was proportional to the reciprocal particle size ($1/D$). Such particle size's dependence of melting point can be well interpreted by the classical thermodynamic theory. But such a dramatic decrease of over 1000℃ in our case is an unusual phenomenon, and further studies on it are needed.

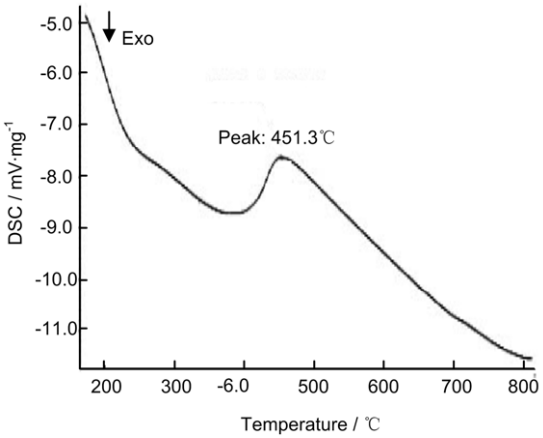

Fig.6 DSC spectra of the Co nanoparticles.

Yield rate (Fig.7) of the Co nanoparticle from the irradiated $CoSO_4$ solution shows that the conversion rate of the product increases with the dose, and reaching a balance at certain dose level under different irradiation conditions. Absorbed dose of the solution is a key parameter of the E-beam irradiation method. Therefore the selection of a proper dose level, accuracy and reproducibility of absorbed dose are very important. Irradiation conditions (such as voltage, current, power, beam scan frequency and width, conveyor speed, etc.) should be carefully selected and controlled, and it is also important to control the yield rate of Co nanoparticles.

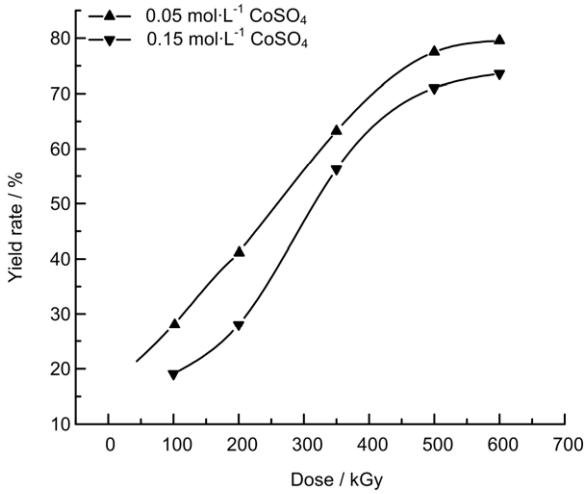

Fig.7 Yield rate of Co nanoparticle in CoSO4 solution irradiated to various doses by 1.75-MeV E-beams.

4 Conclusion

In this study, cobalt nanoparticles have been successfully prepared by electron beam irradiation of $CoSO_4 \cdot 7H_2O$ solutions with isopropyl alcohol as scavengers of oxidative radicals, without any catalysts, at room temperature and ambient pressure. Results show that the obtained cobalt nanoparticles have an average size of 32 nm with a narrow size distribution. The melting point of the cobalt nanoparticles has a dramatic decrease. Further studies are still needed to explore the different characteristics of the nanoparticles with various irradiation doses.

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