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Trans. Nonferrous Met. Soc. China 17(2007) 1082−1086
Transactions of Nonferrous Metals Society of China
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Shape-controlled synthesis of nanocubic Co_3O_4 by hydrothermal oxidation method

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Received 30 December 2006; accepted 9 April 2007

Abstract: The nanocubic Co_3O_4 was synthesized by hydrothermal oxidation method. The effects of cobalt salt, precipitating agent, surfactant, solvent, pH value of the suspension and the amount of oxidant H_2O_2 on the morphology and structure of Co_3O_4 were investigated. The Co_3O_4 powders were characterized by transmission electron microscope and X-ray diffraction. The results show that the morphology of Co_3O_4 is closely dependant on the anion in cobalt salts, but it is not so sensitive to the precipitating agents and solvents. The amount of H_2O_2 is the key factor to obtain Co_3O_4 with spinel crystal structure. The optimum synthetic conditions of uniform shape-controlled Co_3O_4 nanocubes are as follows: $Co(CH_3COO)_2{\cdot}4H_2O$ as cobalt salt, KOH as precipitating agent, polyethylene glycol with relative molecular mass of about 20 000 as surfactant, water−*n*-butanol as solvent system, pH value of 8−9, the molar ratio of H_2O_2 to Co^{2+} above 2.5:1.0, hydrothermal temperature of 160 ℃ and hydrothermal holding time of 10 h. The tap density and apparent density of nanocubic Co_3O_4 obtained with the average particle size of 20 nm are 1.01 g/cm^3 and 0.70 g/cm^3, respectively.

Key words: Co_3O_4; nanocubes; shape-controlled; hydrothermal oxidation

1 Introduction

The tricobalt tetraoxide Co_3O_4 belongs to the normal spinel crystal structure based on a cubic close packing array of oxide atoms, in which Co^{2+} ions occupy the tetrahedral 8a sites and Co^{3+} ions occupy the octahedral 16d sites. In recent years, Co_3O_4 has attracted attention due to its wide applications in catalysts[1], magnetic semiconductors[2], electrode material[3−5], gas sensors[5] and pressure sensitive ceramics[6]. Various methods, such as the thermal decomposition of solid phase[7−8], sol-gel method[9], hydrothermal method[10−11], solvothermal decomposition[12], chemical vapor deposition[13], liquid-control-precipitation method[14] and spray pyrolysis[15], were attempted to synthesize nanosized spinel Co_3O_4. It is well-known that the behaviors of nanophase materials strongly depend on the shape and size of the particles[5]. And hydrothermal oxidation method is an efficient technique for preparing fine uniform particles of metal oxides[16].

ZHANG et al[10] studied the effects of hydrothermal synthetic conditions, such as the starting concentration of $Co(NO_3)_2$ solution, pH value, hydrothermal temperature, holding time and the stocking mode, on the shape and size of Co_3O_4 cubes in $Co(NO_3)_2$-$NH_3{\cdot}H_2O$ system. The Co_3O_4 and β-$Co(OH)_2$ mixtures were obtained when the temperature was below 180 ℃ and hydrothermal holding time was 1−36 h, and the cubic Co_3O_4 could be obtained by calcining the mixtures in air. JIANG et al[11] reported that $Co(OH)_2$ gel, which was prepared using $CoSO_4{\cdot}7H_2O$ and $NH_3{\cdot}H_2O$ as starting materials, could be oxidized to nanocrystalline Co_3O_4 by hydrogen peroxide in a hydrothermal system at 180 ℃ for 24 h. Although $Co(OH)_2$ gel was filtered using vacuum filtration and washed by distilled water for several times until no SO_4^{2-} and NH_4^+ remained, the morphology of nanocrystalline Co_3O_4 was irregular. In order to synthesize uniform shape-controlled Co_3O_4 nanocubes, the effects of anion in cobalt salt, precipitating agent, surfactant, solvent, pH value of the suspension, and the amount of oxidant H_2O_2 on the morphology and structure

Foundation item: Project(50542004) supported by the National Natural Science Foundation of China; Project(ZE097) supported by Creative Program of Central South University, China
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of Co_3O_4 were investigated in this study.

2 Experimental

15 mmoL cobalt salt was dissolved into distilled water containing certain surfactant and organic solvent, and then excessive amount of precipitating agent was added with electromagnetic stirring at 30 ℃ during the formation of $Co(OH)_2$ precursor. The pH value of the suspension after precipitation reaction was monitored to 8−9. A certain amount of 30% (mass fraction) H_2O_2 was dropped into the suspension. Finally, all of them were transferred into a Teflon-lined stainless steel autoclave with the volume of 100 mL, and the autoclave was filled with distilled water up to 70% of the total capacity. The sealed autoclave was heated to 160 ℃ and maintained for 10 h, then cooled to room temperature in air naturally. The black powders were centrifuged and washed with distilled water and absolute ethanol for three times, respectively, and dried in an oven at 80 ℃ for 6 h.

The morphology and size of the obtained powders were determined by using a Japan JEOL JEM−1230 transmission electron microscopy(TEM). The X-ray diffraction(XRD) patterns of the powders were obtained with a Japan Rigaku D/max−2500 X-ray diffractometer using Cu K_α radiation in the 2θ range from 10° to 80°.

3 Results and discussion

3.1 Effect of cobalt salt and precipitating agent

Fig.1 shows the TEM images of Co_3O_4 using different cobalt salts and precipitating agents in the presence of polyethylene glycol with relative molecular mass of about 20 000(PEG 20 000) and water−*n*-butanol solvent system. It can be seen from Figs.1(a) and (d) that the morphologies of Co_3O_4 are irregular nanocubes using $Co(NO_3)_2·6H_2O$ as cobalt salt and KOH or NH_3-NH_4Cl buffer solution as precipitating agent. For comparison typical spherical Co_3O_4 and nanocubic Co_3O_4 are obtained when the cobalt salts are $CoSO_4·7H_2O$ and $Co(CH_3COO)_2·4H_2O$, respectively, as shown in Figs.1(b) and (c). It can be concluded that the morphologies of Co_3O_4 are closely dependant on the anion type in cobalt salts. In other words, the anion type in cobalt salt plays a

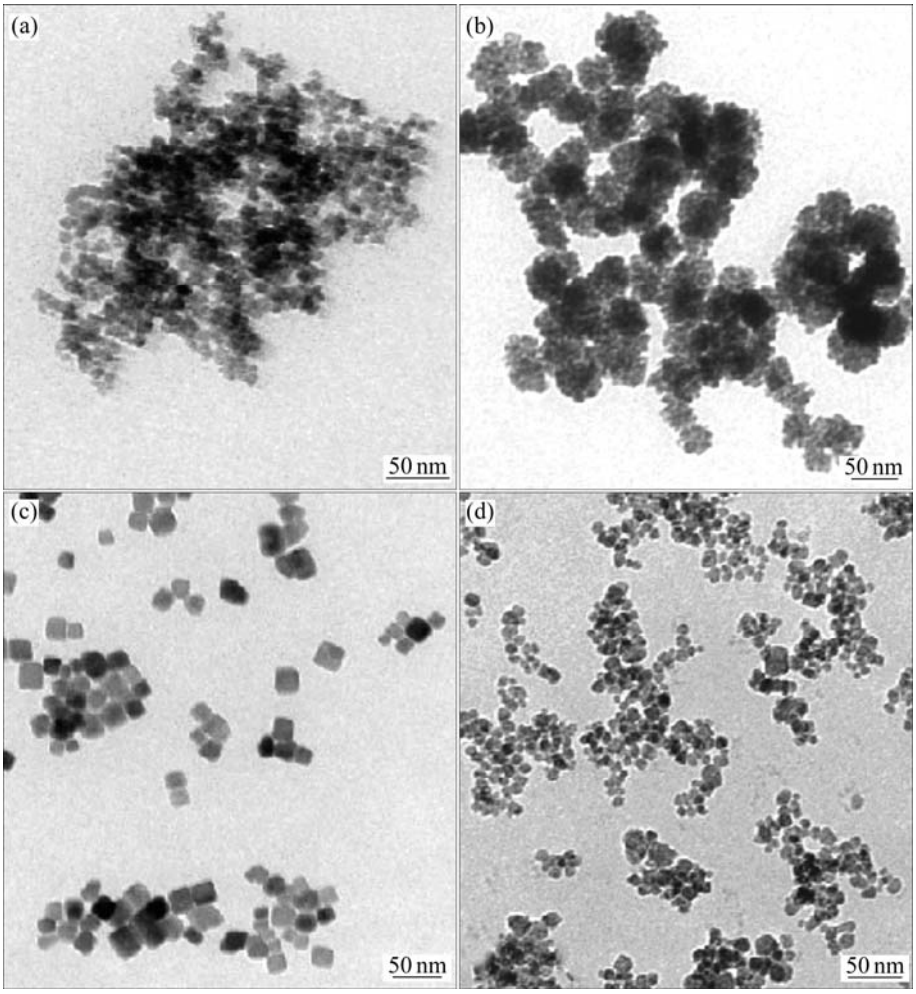

Fig.1 TEM images of Co_3O_4 synthesized with different cobalt salts and precipitating agents: (a) $Co(NO_3)_2$ and KOH; (b) $CoSO_4$ and KOH; (c) $Co(CH_3COO)_2$ and KOH; (d) $Co(NO_3)_2$ and NH_3-NH_4Cl buffer solution

key role in the morphology of Co_3O_4, while the influence of precipitating agent on the morphology of Co_3O_4 is very limited. Therefore, $Co(CH_3COO)_2·4H_2O$ and KOH are chosen as cobalt salt and precipitating agent to synthesize nanocubic Co_3O_4, respectively.

3.2 Effect of surfactant

Fig.2 shows the effects of surfactant on morphology of Co_3O_4 in water−*n*-butanol solvent system. It can be seen that nanocubic Co_3O_4 synthesized in the presence of non-ionic surfactant PEG 20 000 is highly dispersed and shows excellent uniformity, while Co_3O_4 nanoparticles obtained from anionic surfactant sodium dodecyl benzene sulfonate(SDBS) are agglomerated in irregular shapes. This may be due to the interface retarding effect of PEG 20 000. The relative molecular mass of PEG 20 000 is greater than that of SDBS. As a result, PEG 20 000 is chosen as the surfactant in the synthesis of nanocubic Co_3O_4.

3.3 Effect of pH value

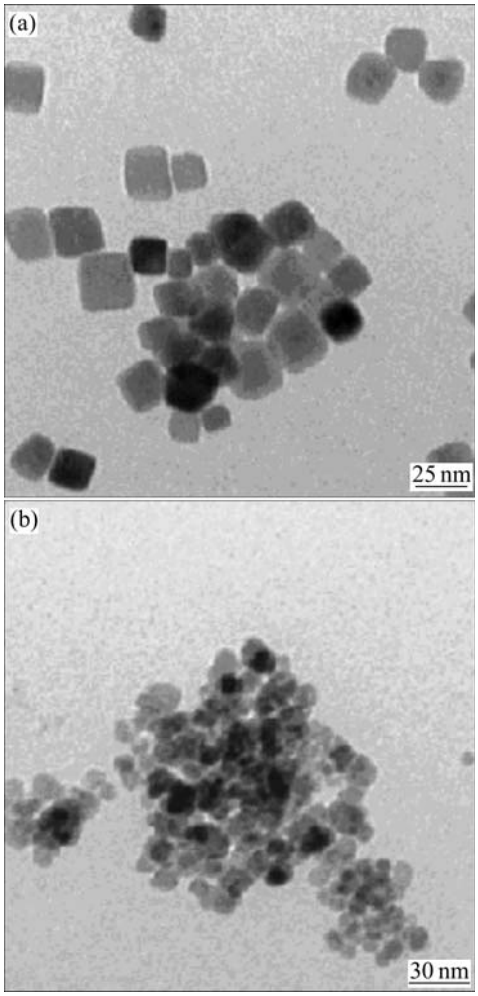

Fig.2 TEM images of Co_3O_4 synthesized with different surfactants: (a) Polyethylene glycol 20 000; (b) Sodium dodecyl benzene sulfonate

Fig.3 shows the TEM image of Co_3O_4 synthesized in suspension of pH 11−12 after precipitation reaction. Compared Fig.1(c) with Fig.3, it is very obvious that nanocubic Co_3O_4 with the average particle size of 20 nm is formed when pH is 8−9, and when pH goes up to 11−12 irregular Co_3O_4 including some grains recombined in the products becomes serious. Because the condensation reaction of $Co(OH)_2$ precursor can easily occur at higher pH value, agglomeration of the nanoparticles occurs.

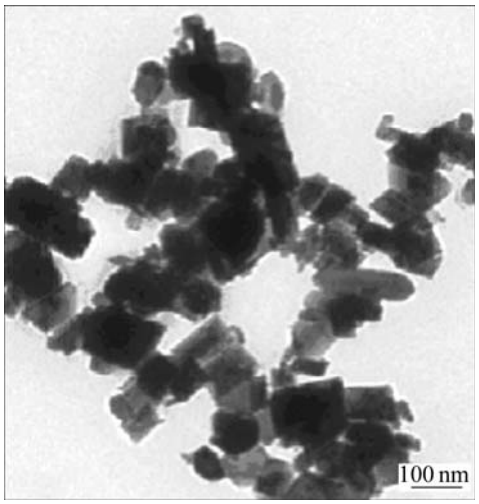

Fig.3 TEM image of Co_3O_4 synthesized in suspension of pH 11−12

The condensation reaction of $Co(OH)_2$ can be expressed as

$$—Co—O—H+H—O—Co—\rightarrow—Co—O—Co—+H_2O \quad (1)$$

In order to synthesize nanocubic Co_3O_4, the pH value of suspension should be strictly controlled at 8−9.

3.4 Effect of solvent

The XRD patterns of Co_3O_4 synthesized in different solvent systems are shown in Fig.4. All peaks shown in Fig.4 can be indexed to a cubic spinel crystal structure Co_3O_4. No impurity peaks are observed, which indicates that the final product synthesized is Co_3O_4 with spinel crystal structure under hydrothermal oxidation condition. Based on Scherrer formula, the average particle sizes of Co_3O_4 in water, water−alcohol and water−*n*-butanol solvent systems are calculated to be 27 nm, 10 nm and 15 nm, respectively.

Fig.5 shows the TEM images of Co_3O_4 synthesized in water and water−alcohol solvent systems using $Co(CH_3COO)_2·4H_2O$ as cobalt salt. Compared Fig.1(c) with Fig.5, it can be seen that nanocubic Co_3O_4 particles are all obtained in these solvent systems. While Co_3O_4 synthesized in water−*n*-butanol solvent system shows a

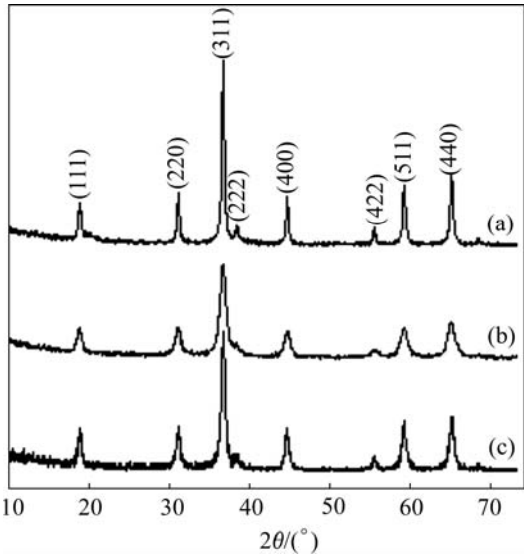

Fig.4 XRD patterns of Co_3O_4 synthesized in different solvent systems: (a) Water; (b) Water–alcohol; (c) Water−*n*-butanol

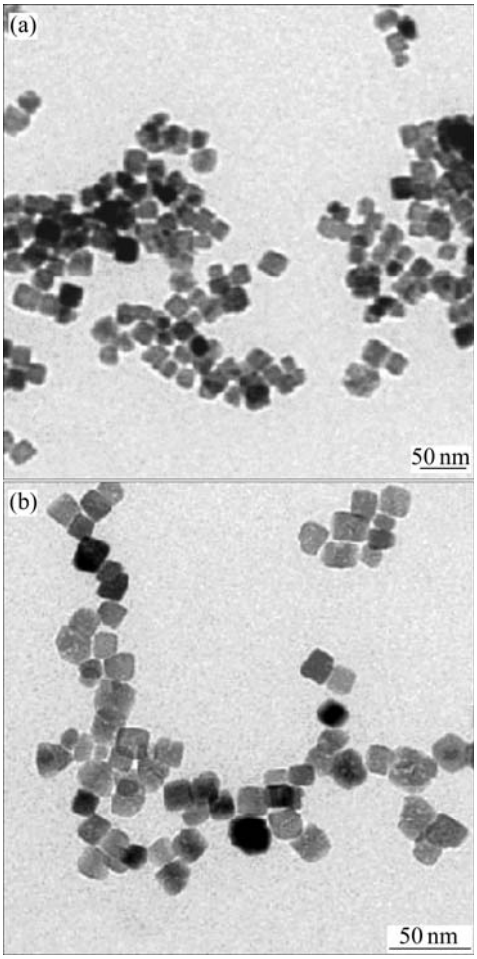

Fig.5 TEM images of Co_3O_4 synthesized in different solvent systems: (a) Water; (b) Water−alcohol

better monodisperse sign (Fig.1(c)), and the tap density and apparent density of uniform shape-controlled Co_3O_4 nanocubes are 1.01 g/cm^3 and 0.70 g/cm^3, respectively.

3.5 Effect of amount of H_2O_2

In order to get Co_3O_4 with spinel crystal structure, the amount of oxidant H_2O_2 should be enough. The chemical reaction in the hydrothermal oxidation process can be expressed as

$$3Co(OH)_2+H_2O_2 \rightarrow Co_3O_4+4H_2O \quad (2)$$

So the molar ratio of H_2O_2 to $Co(OH)_2$ is 1:3 in theory. However, H_2O_2 tends to decompose in the practical operation, therefore the amount of H_2O_2 is far more than the theoretical value.

Fig.6 shows the XRD patterns of the samples obtained with adding different amount of H_2O_2. When the molar ratio of H_2O_2 to Co^{2+} is 2.0:1.0, the impurity $Co(OH)_2$ still exists. While the molar ratio of H_2O_2 to Co^{2+} is increased to 2.5:1.0, Co_3O_4 with cubic spinel crystal structure is obtained. So in order to obtain Co_3O_4 with spinel crystal structure, the molar ratio of H_2O_2 to Co^{2+} should be higher than 2.5:1.0.

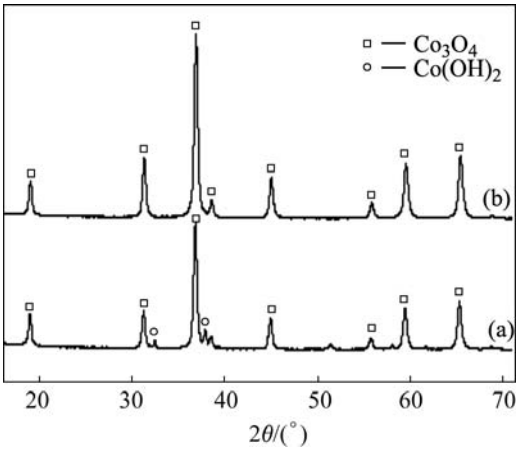

Fig.6 XRD patterns of Co_3O_4 synthesized with different molar ratios of H_2O_2 to Co^{2+}: (a) 2.0:1.0; (b) 2.5:1.0

4 Conclusions

1) The uniform shape-controlled spinel Co_3O_4 nanocube is prepared by hydrothermal oxidation method. The optimum synthetic conditions of Co_3O_4 nanocubes are as follows: $Co(CH_3COO)_2{\cdot}4H_2O$ as cobalt salt, KOH as precipitating agent, polyethylene glycol 20 000 as surfactant, pH value of 8−9, molar ratio of H_2O_2 to Co^{2+} above 2.5:1.0, hydrothermal temperature of 160 ℃ and hydrothermal holding time of 10 h.

2) The morphology of Co_3O_4 is closely dependant on the anion in cobalt salts. The nanocrystalline, spherical and uniform nanocubic Co_3O_4 particles are obtained using $Co(NO_3)_2{\cdot}6H_2O$, $CoSO_4{\cdot}7H_2O$ and $Co(CH_3COO)_2{\cdot}4H_2O$ as cobalt salts, respectively.

3) The precipitating agent and solvent system have little influence on morphology of Co_3O_4. The Co_3O_4 nanocubes are all synthesized in water, water−alcohol

and water−*n*-butanol solvent systems, and the average particle sizes of Co_3O_4 are calculated to be 27, 10 and 15 nm, respectively. The tap density and apparent density of uniform shape-controlled Co_3O_4 nanocubes synthesized in water−*n*-butanol solvent system are 1.01 g/cm^3 and 0.70 g/cm^3, respectively.

4) The amount of H_2O_2 is the key factor to obtain Co_3O_4 with spinel crystal structure. The molar ratio of H_2O_2 to Co^{2+} should be higher than 2.5:1.0.

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(Edited by LI Xiang-qun)