Shape-controlled synthesis of nanocubic Co$_3$O$_4$ by hydrothermal oxidation method

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Abstract: The nanocubic Co$_3$O$_4$ 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$_2$O$_2$ on the morphology and structure of Co$_3$O$_4$ were investigated. The Co$_3$O$_4$ powders were characterized by transmission electron microscope and X-ray diffraction. The results show that the morphology of Co$_3$O$_4$ 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$_2$O$_2$ is the key factor to obtain Co$_3$O$_4$ with spinel crystal structure. The optimum synthetic conditions of uniform shape-controlled Co$_3$O$_4$ nanocubes are as follows: Co(CH$_3$COO)$_2$·4H$_2$O 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$_2$O$_2$ to Co$^{2+}$ above 2.5:$1.0$, hydrothermal temperature of 160 $^\circ$C and hydrothermal holding time of 10 h. The tap density and apparent density of nanocubic Co$_3$O$_4$ 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$_3$O$_4$; nanocubes; shape-controlled; hydrothermal oxidation

1 Introduction

The tricobalt tetraoxide Co$_3$O$_4$ 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$_3$O$_4$ 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$_3$O$_4$. 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$_3$O$_4$ cubes in Co(NO$_3$)$_2$-$\beta$-Co(OH)$_2$ system. The Co$_3$O$_4$ and $\beta$-Co(OH)$_2$ mixtures were obtained when the temperature was below 180 $^\circ$C and hydrothermal holding time was 1–36 h, and the cubic Co$_3$O$_4$ could be obtained by calcining the mixtures in air. JIANG et al[11] reported that Co(OH)$_2$ gel, which was prepared using CoSO$_4$·7H$_2$O and NH$_3$·H$_2$O as starting materials, could be oxidized to nanocrystalline Co$_3$O$_4$ by hydrogen peroxide in a hydrothermal system at 180 $^\circ$C 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$_3$O$_4$ was irregular. In order to synthesize uniform shape-controlled Co$_3$O$_4$ nanocubes, the effects of anion in cobalt salt, precipitating agent, surfactant, solvent, pH value of the suspension, and the amount of oxidant H$_2$O$_2$ on the morphology and structure...
of Co$_3$O$_4$ 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 °C 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$_2$O$_2$ 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 °C 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 °C 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$_\alpha$ 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$_3$O$_4$ 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$_3$O$_4$ are irregular nanocubes using Co(NO$_3$)$_2$·6H$_2$O as cobalt salt and KOH or NH$_3$−NH$_4$Cl buffer solution as precipitating agent. For comparison typical spherical Co$_3$O$_4$ and nanocubic Co$_3$O$_4$ are obtained when the cobalt salts are CoSO$_4$·7H$_2$O and Co(CH$_3$COO)$_2$·4H$_2$O, respectively, as shown in Figs.1(b) and (c). It can be concluded that the morphologies of Co$_3$O$_4$ 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$_3$O$_4$ synthesized with different cobalt salts and precipitating agents: (a) Co(NO$_3$)$_2$ and KOH; (b) CoSO$_4$ and KOH; (c) Co(CH$_3$COO)$_2$ and KOH; (d) Co(NO$_3$)$_2$ and NH$_3$−NH$_4$Cl buffer solution](image-url)
3.2 Effect of surfactant

Fig.2 shows the effects of surfactant on morphology of Co₃O₄ in water−n-butanol solvent system. It can be seen that nanocubic Co₃O₄ synthesized in the presence of non-ionic surfactant PEG 20 000 is highly dispersed and shows excellent uniformity, while Co₃O₄ 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 Co₃O₄.

3.3 Effect of pH value

Fig.3 shows the TEM image of Co₃O₄ synthesized in suspension of pH 11−12 after precipitation reaction. Compared Fig.1(c) with Fig.3, it is very obvious that nanocubic Co₃O₄ with the average particle size of 20 nm is formed when pH is 8−9, and when pH goes up to 11−12 irregular Co₃O₄ 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.

The condensation reaction of Co(OH)₂ can be expressed as

$$\text{Co}^{2+} + \text{CO}_3^{2-} + \text{H}^+ \rightarrow \text{Co}^{3+} + \text{Co}^{2+} + \text{H}_2\text{O}$$

(1)

In order to synthesize nanocubic Co₃O₄, the pH value of suspension should be strictly controlled at 8−9.

3.4 Effect of solvent

The XRD patterns of Co₃O₄ 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 Co₃O₄. No impurity peaks are observed, which indicates that the final product synthesized is Co₃O₄ with spinel crystal structure under hydrothermal oxidation condition. Based on Scherrer formula, the average particle sizes of Co₃O₄ 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 Co₃O₄ synthesized in water and water−alcohol solvent systems using Co(CH₃COO)₂·4H₂O as cobalt salt. Compared Fig.1(c) with Fig.5, it can be seen that nanocubic Co₃O₄ particles are all obtained in these solvent systems. While Co₃O₄ synthesized in water−n-butanol solvent system shows a
3.5 Effect of amount of H$_2$O$_2$

In order to get Co$_3$O$_4$ with spinel crystal structure, the amount of oxidant H$_2$O$_2$ should be enough. The chemical reaction in the hydrothermal oxidation process can be expressed as

$$3\text{Co(OH)}_2 + \text{H}_2\text{O}_2 \rightarrow \text{Co}_3\text{O}_4 + 4\text{H}_2\text{O} \quad (2)$$

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

Fig.6 shows the XRD patterns of the samples obtained with adding different amount of H$_2$O$_2$. When the molar ratio of H$_2$O$_2$ to Co$^{2+}$ is 2.0:1.0, the impurity Co(OH)$_2$ still exists. While the molar ratio of H$_2$O$_2$ to Co$^{2+}$ is increased to 2.5:1.0, Co$_3$O$_4$ with cubic spinel crystal structure is obtained. So in order to obtain Co$_3$O$_4$ with spinel crystal structure, the molar ratio of H$_2$O$_2$ to Co$^{2+}$ should be higher than 2.5:1.0.

4 Conclusions

1) The uniform shape-controlled spinel Co$_3$O$_4$ nanocube is prepared by hydrothermal oxidation method. The optimum synthetic conditions of Co$_3$O$_4$ nanocubes are as follows: Co(CH$_3$COO)$_2$·4H$_2$O as cobalt salt, KOH as precipitating agent, polyethylene glycol 20 000 as surfactant, pH value of 8~9, molar ratio of H$_2$O$_2$ to Co$^{2+}$ above 2.5:1.0, hydrothermal temperature of 160 $^\circ$C and hydrothermal holding time of 10 h.

2) The morphology of Co$_3$O$_4$ is closely dependant on the anion in cobalt salts. The nanocrystalline, spherical and uniform nanocubic Co$_3$O$_4$ particles are obtained using Co(NO$_3$)$_2$·6H$_2$O, CoSO$_4$·7H$_2$O and Co(CH$_3$COO)$_2$·4H$_2$O as cobalt salts, respectively.

3) The precipitating agent and solvent system have little influence on morphology of Co$_3$O$_4$. The Co$_3$O$_4$ nanocubes are all synthesized in water, water–alcohol.
and water–$n$-butanol solvent systems, and the average particle sizes of Co$_3$O$_4$ are calculated to be 27, 10 and 15 nm, respectively. The tap density and apparent density of uniform shape-controlled Co$_3$O$_4$ 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$_2$O$_2$ is the key factor to obtain Co$_3$O$_4$ with spinel crystal structure. The molar ratio of H$_2$O$_2$ to Co$^{2+}$ should be higher than 2.5:1.0.

References