Synthesis of octahedral Co_3O_4 via carbon-assisted method

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Octahedral Co_3O_4 (~1 μm) was synthesised by a one-step carbon-assisted method using degreasing cotton and cobalt chloride as precursors. The characterisation results show that the calcination temperature, calcination time, reaction precursor, oxygen environment and reactants ratio of the precursor play important roles in fabricating the Co_3O_4 powders. The result of the UV-vis spectrum also shows that the octahedral Co_3O_4 obtained can be applied in photocatalytic water splitting under visible light irradiation.

1. Introduction: Cobalt tetroxide (Co_3O_4) exhibits excellent performance in magnetism, diffusivity, conductivity and catalytic areas. Thus, Co_3O_4 has been widely applied in magnetic carriers, varistors, sensors, supercapacitors and catalysis [1–5]. Owing to its wide applications, much research on the synthesis of Co_3O_4 has been performed [6–10]. It has been demonstrated that the anions have significant impact on the morphology of Co_3O_4 [11–14]. Specifically, the chloride anion is the key element for the synthesis of octahedral product [15].

On the basis of the formation mechanism of Co_3O_4, the carbon-assisted method was employed in our work. The advantages of this one-step method lie in its simple process, low pollution, low cost and adaptation for large-lot production. The reactants of this novel method are only degreasing cotton and cobalt chloride. The cobalt ions and chloride ions were absorbed into the surface of the degreasing cotton, and the Co_3O_4 powders were obtained after a reaction at high temperature. The powders obtained were characterised through scanning electron microscopy (SEM) and X-ray diffraction (XRD). Then the necessary experimental conditions and the compulsory role of degreasing cotton were confirmed through the analysis of the characterisation results. Interestingly, the results of the UV-vis spectrum demonstrate that the Co_3O_4 obtained can be applied in photocatalytic water splitting under visible light irradiation.

2. Experiment: Cobalt chloride (AR) was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Commercial degreasing cotton was used as the reactant. Deionised water of 18.25 MΩ was purified through an ultra-pure (UPR) system.

Cobalt chloride and degreasing cotton in mole ratios of 4.4:1, 6.6:1 and 8.8:1 were used as reactants, respectively. The degreasing cotton was immersed in cobalt chloride solutions for 2 h, then the treated degreasing cotton was collected and transferred into a quartz Petri dish in a tube furnace (OTF-1200X-III) and kept at 600°C for 2, 3, 4 and 5 h, respectively. The powders were cooled to room temperature naturally in the furnace after calcining in air.

The Co_3O_4 powders in microsize were obtained after the solid product was milled using an agate mortar.

The Co_3O_4 powders obtained under different experimental conditions were characterised by SEM measurements (HitachiS-4800 SEM) and advanced XRD system (a Bruker D8) using Cu K radiation of wavelength 1.5406 Å.

3. Results and discussion

3.1. Confirmtion of the experiment parameters: Fig. 1 shows the XRD spectra of the samples obtained in different ratios of reactants at 600°C for 5 h. All the diffraction peaks in Fig. 1 are in agreement with the standard XRD pattern of cubic spinel Co_3O_4 (PDF No.01-074-1656). This result confirms that the products are all cubic spinel Co_3O_4 when the mole ratio of cobalt chloride and degreasing cotton are 4.4:1, 6.6:1 and 8.8:1, respectively.

The morphology of the samples obtained with different ratios of reactants is characterised by SEM. All the samples in Fig. 1 are octahedral microparticles. The surfaces of the particles in Figs. 1*a* and *b* are very rough. It is clearly seen that the crystals of the obtained particles in the ratio of 4.4:1 are undergrown in shape. The synthesised symmetric particles with smooth surfaces can be seen in Figs. 1*c* and *d*, and generally the size of the samples

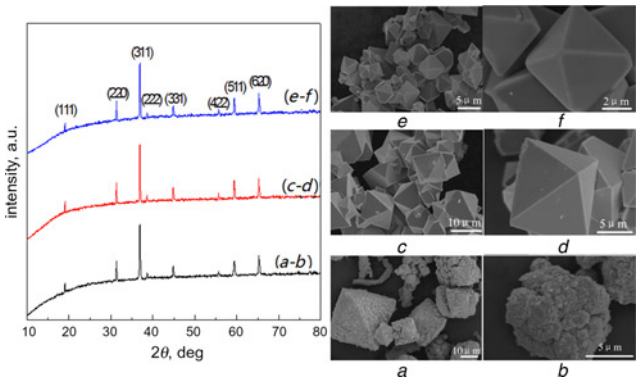

Figure 1 *XRD patterns and SEM of the samples obtained under different conditions*
a, *b* Sample obtained using cobalt chloride and degreasing cotton with mole ratio of 4.4:1
c, *d* Sample obtained using cobalt chloride and degreasing cotton with mole ratio of 6.6:1
e, *f* Sample obtained using cobalt chloride and degreasing cotton with mole ratio of 8.8:1

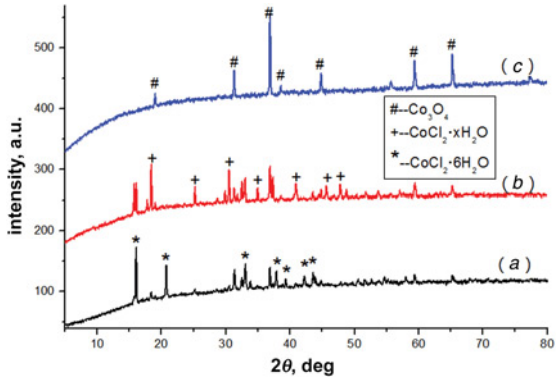

Figure 2 *XRD patterns of the samples obtained under different temperature (a, 400; b, 500; and c, 600°C)*

obtained is uniform. The regular octahedral particles are also shown in Figs. 1*e* and *f*; however, the particles' sizes become larger. Overall, the mole ratio of 6.6:1 of the reactants is acceptable for this method to synthesise the perfect octahedral Co_3O_4 with uniform morphology.

The influence of the calcination temperature studied through XRD and the results of the samples obtained under different temperatures (*a*, 400; *b*, 500; and *c*, 600°C) are shown in Fig. 2. The components of the powders synthesised at 400°C are $CoCl_2{\cdot}6H_2O$ and Co_3O_4, which is shown as curve *a*. The diffraction peaks of $CoCl_2{\cdot}xH_2O$ and Co_3O_4 are shown in curve *b*. Interestingly, pure Co_3O_4 can be observed in curve *c*. Comparing these three curves, it is concluded that the dehydration of the $CoCl_2{\cdot}6H_2O$ completely occurred at 600°C. The appropriate calcination temperature for the preparation of Co_3O_4 powders via the carbon-assisted method is 600°C.

The calcination time is another key element in the synthesis of Co_3O_4. The SEM results of calcination time are 2 (Fig. 3*a*), 3 (Fig. 3*b*), 4 (Fig. 3*c*) and 5 h (Fig. 3*d*). Most of the particles are still not formed as shown in Fig. 3*a*. This result illustrates that the calcination time in this method should be more than 2 h. It is clear that the particles grow bigger with the increase of calcination time. Comparing Figs. 3*c* and *d*, the size of the octahedral particles in Fig. 3*b* is more uniform. All the SEM results in Fig. 3

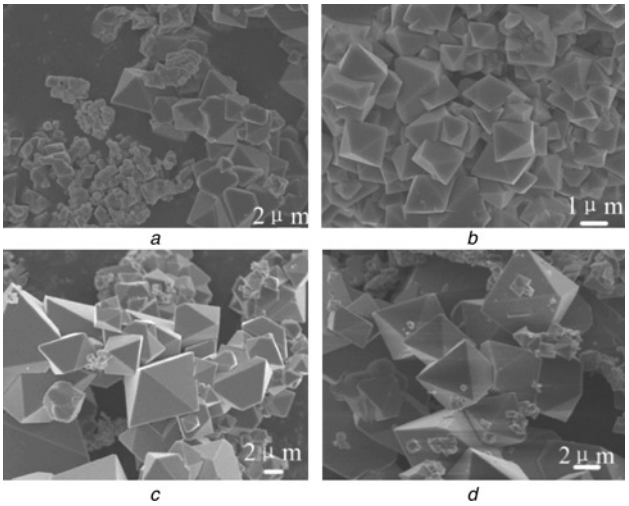

Figure 3 *SEM of the samples obtained under different calcination times*
a 2 h
b 3 h
c 4 h
d 5 h

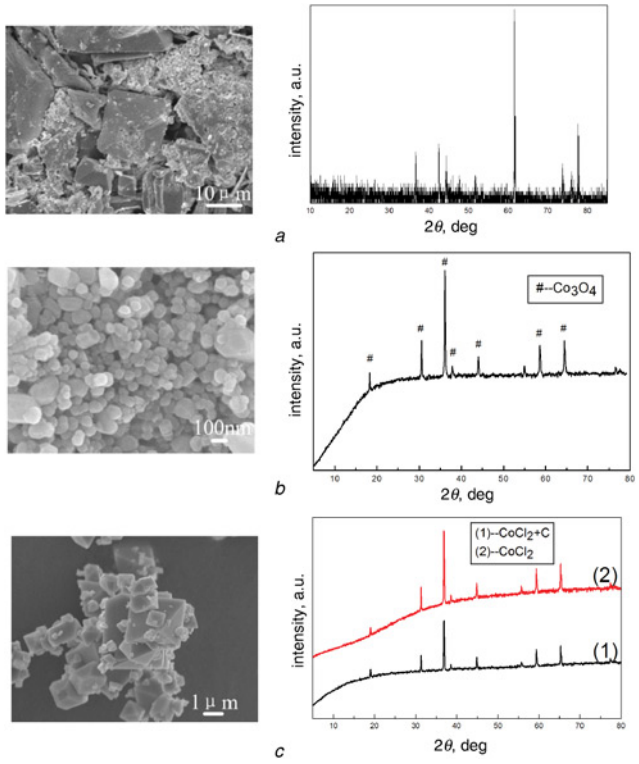

Figure 4 *SEM and XRD patterns of the samples obtained under different conditions*
a Sample obtained under hypoxemia condition
b Sample obtained using cobalt nitrate as reactant
c Sample obtained without adding degreasing cotton

demonstrate that uniformly octahedral particles (~1 μm) can be synthesised through calcination at 600°C for 3 h.

To confirm the necessary experimental conditions, the sample obtained in an oxygen-free environment or using different reactants was analysed through SEM and XRD characterisations. All these samples were obtained at 600°C for 3 h. There is no Co_3O_4 formed in an oxygen-free environment, which is shown in Fig. 4*a*. The results in Fig. 4*b* demonstrate that the chloride anions play a key role in the synthesis of octahedral Co_3O_4 powders. In contrast, without degreasing cotton, the size range of the Co_3O_4 is huge, as shown in Fig. 4*c*.

All the results in Fig. 4 demonstrate that the oxygen environment, chloride anions and degreasing cotton are necessary parts for the synthesis of Co_3O_4. The degreasing cotton plays an important role in the formation of uniform particles. Water molecules and cobalt chloride were evenly absorbed onto the surface of the cotton fibre before calcination. The cotton fibre can prevent the crystalloids from agglomeration. The octahedral Co_3O_4 is dispersed uniformly by the cotton fibre during the formation process. Thus, the particles obtained are of regular size. Furthermore, the calcination product of the degreasing cotton is carbon dioxide and water. Therefore, no polluted product is introduced in this method. The corresponding reaction processes are shown below [16]

$$6CoCl_2 \cdot xH_2O + (6-x)H_2O + O_2 = 2Co_3O_4 + 12HCl\uparrow \quad (1)$$

$$(C_6H_{10}O_5)_n + 6nO_2 \rightarrow 6nCO_2 + 5nH_2O \quad (2)$$

The H_2O in the solution is easily evaporated during the calcination process. On one hand, the H_2O in the solution absorbed into the cotton fibre evaporated more slowly. On the other hand, the H_2O produced by degreasing cotton combustion can act as a reactant

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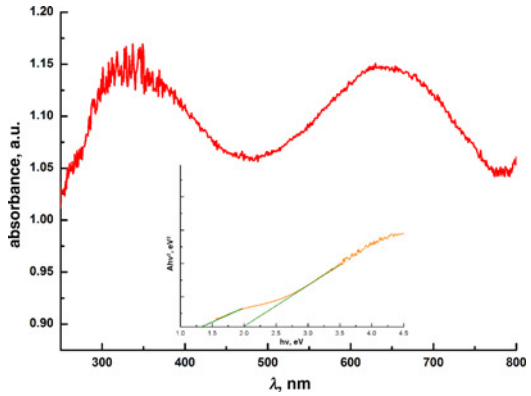

Figure 5 *UV-vis spectrum and $(Ahv)^2$–hv cure (insert) of the Co_3O_4 nanoparticles(hv is the photon energy (eV), A is the absorption coefficient)*

in reaction (1). On the basis of the analysis above, it is concluded that the participation of the absorbance cotton is indispensable. Overall, after the cobalt chloride and degreasing cotton (mole ratio in 6.6:1) were heated at 600°C for 3 h in an oxygen environment, the octahedral Co_3O_4 powders (~1 μm) were obtained successfully.

3.2. Optical properties of the Co_3O_4 particles: In Fig. 5, the bandgap E_g value calculated according to the UV-vis spectroscopy of octahedral Co_3O_4 powders is 1.35 (E_{g1}) and 2.0 eV (E_{g2}), respectively. This result indicates that the Co_3O_4 powders have good absorption in the region of visible light. In our future work, we will research visible light photocatalytic water splitting on the octahedral Co_3O_4 powders.

3.3. Repeatability calculation: The experiment has been repeated four times to confirm the repeatability of this method. 0.009 mol of degreasing cotton was immersed into 20 ml of 3 M cobalt chloride solution and 0.06 mol of the Co^{2+} was left after discarding the excess solution. Therefore, the theoretical mass of the sample is 4.82 g, while the experimental values are 4.67, 4.86, 4.78 and 4.76 g, respectively. The experimental mass values are basically consistent with that of theoretical values.

4. Conclusion: Octahedral Co_3O_4 (~1 μm) was prepared by an environmentally friendly one-step carbon-assisted method. Through the results of SEM and XRD characterisations, it is confirmed that the fabrication of perfect octahedral Co_3O_4 using this method must meet the following requirements: (i) using cobalt chloride and degreasing cotton with a mole ratio of 6.6:1, (ii) calcination temperature of 600°C, (iii) at least 3 h of calcination time; (iv) being in an oxygen environment and (v) having degreasing cotton as the dispersant agent. In addition, as the Co_3O_4 prepared has decent performance in visible light absorption, an experiment on its photocatalytic ability on water splitting will be undertaken shortly.

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