



# Synthesis of $\text{Co}_3\text{O}_4$ nanocubes by hydrothermal route and their photocatalytic property

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MS received 15 May 2016; accepted 1 August 2017; published online 2 February 2018

**Abstract.** Monodispersed  $\text{Co}_3\text{O}_4$  nanocubes were prepared by a simple hydrothermal route with sodium pentanesulphonate, employing  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{NH}_3 \cdot \text{H}_2\text{O}$  (28 wt%) as the starting reactants. The final product was characterized by powder X-ray diffraction, energy-dispersive X-ray spectrometry, scanning electron microscopy and transmission electron microscopy. The as-prepared  $\text{Co}_3\text{O}_4$  nanocubes could photocatalytically degrade organic dye Rhodamine B under irradiation of 365 nm ultraviolet light.

**Keywords.**  $\text{Co}_3\text{O}_4$  nanocubes; Rhodamine B; photocatalysis; degradation.

## 1. Introduction

Over the past three decades, dyes from the textiles and plastics industries have been polluting the environment due to the discharge of coloured and carcinogenic wastewater, and therefore they have become an issue of worldwide concern. The release of these dye effluents also causes eutrophication and perturbs humans and other living organisms. Steps to prevent dye wastewater pollution to the environment are urgently needed. Advanced oxidation processes, such as sonolysis, radiolysis and photocatalysis can be carried out at ambient conditions, and they have the ability to completely degrade many organic pollutants, including dyes [1–4].

As an important magnetic p-type semiconductor, trivalent cobalt tetraoxide ( $\text{Co}_3\text{O}_4$ ) has attracted enormous research interest due to its unique catalysis [5,6], energy storage [7,8], sensors [9] and supercapacitors properties [10–13]. Recently,  $\text{Co}_3\text{O}_4$  was found to be an active agent for the photocatalytic degradation of organic pollutants under ultraviolet (UV) light irradiation, as a p-type semiconductor with a bandgap of about 2.07 eV [14,15]. To date,  $\text{Co}_3\text{O}_4$  nanomaterials with different morphologies have been synthesized, including nanoparticles [16], nanowires [17,18], nanobelts [19], nanocubes [2] and nanoplates [20].

In the current work, we successfully prepared monodispersed  $\text{Co}_3\text{O}_4$  nanocubes via simple hydrothermal route in the presence of sodium pentanesulphonate, employing cobalt nitrate hexahydrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) and ammonia ( $\text{NH}_3 \cdot \text{H}_2\text{O}$ ) as the starting reactants. Compared with the reported methods to prepare  $\text{Co}_3\text{O}_4$  nanocubes, the present route is simple, quick, safe and environment friendly. It was found that the as-prepared monodispersed  $\text{Co}_3\text{O}_4$  nanocubes

could be used as a UV light photocatalyst for the degradation of organic dye Rhodamine B (RB) at room temperature.

## 2. Experimental

All chemical reagents were analytically pure and used as received without further purification. Sodium pentanesulphonate was purchased from Alfa Aesar and the others from Sinopharm Chemical Reagent Co. Ltd., Shanghai, China.

### 2.1 Synthesis of $\text{Co}_3\text{O}_4$ nanocubes

In a typical experimental procedure, the appropriate amount of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (2 mmol, 0.582 g) was dissolved in 15 ml of deionized water under stirring. Sodium pentanesulphonate (4 mmol, 0.697 g) was dissolved in 20 ml of deionized water under stirring until it became transparent. Later, the aqueous cobalt nitrate solution was added dropwise into the aqueous sodium pentanesulphonate solution, with vigorous magnetic stirring, to form a homogeneous solution. Subsequently, 2 ml  $\text{NH}_3 \cdot \text{H}_2\text{O}$  (28 wt%) was added dropwise to this solution under vigorous stirring to obtain a colloidal solution. After the mixture was vigorously stirred for 20 min at room temperature, the as-prepared solution was poured into a Teflon-lined stainless-steel autoclave of 50 ml capacity. The autoclave was sealed and maintained at 160°C for 8 h. After this, the autoclave was allowed to cool down to room temperature naturally. The black precipitates were collected, washed with deionized water and absolute ethanol several times to remove the impurities and finally dried in vacuum at 60°C for 12 h.

## 2.2 Characterization

Powder X-ray diffraction (XRD) patterns of the products were obtained using a DX-2600 X-ray diffractometer (Dandong, China) equipped with Cu K $\alpha$  radiation ( $\lambda = 0.1542$  nm), at a voltage of 40 kV, a current of 30 mA and a scanning rate of  $0.02$  s $^{-1}$  in  $2\theta$  ranges from 10 to 80°. Scanning electron microscopy (SEM) images and X-ray energy-dispersive spectrometry (EDS) of the product were obtained using a Hitachi S-4800 field emission scanning electron microscope (FESEM), employing the accelerating voltage of 5 and 15 kV, respectively. Transmission electron microscopy (TEM) images were obtained using a FEI Tecnai G $^2$  20 transmission electron microscope, employing an accelerating voltage of 200 kV.

## 2.3 Photocatalysis experiments

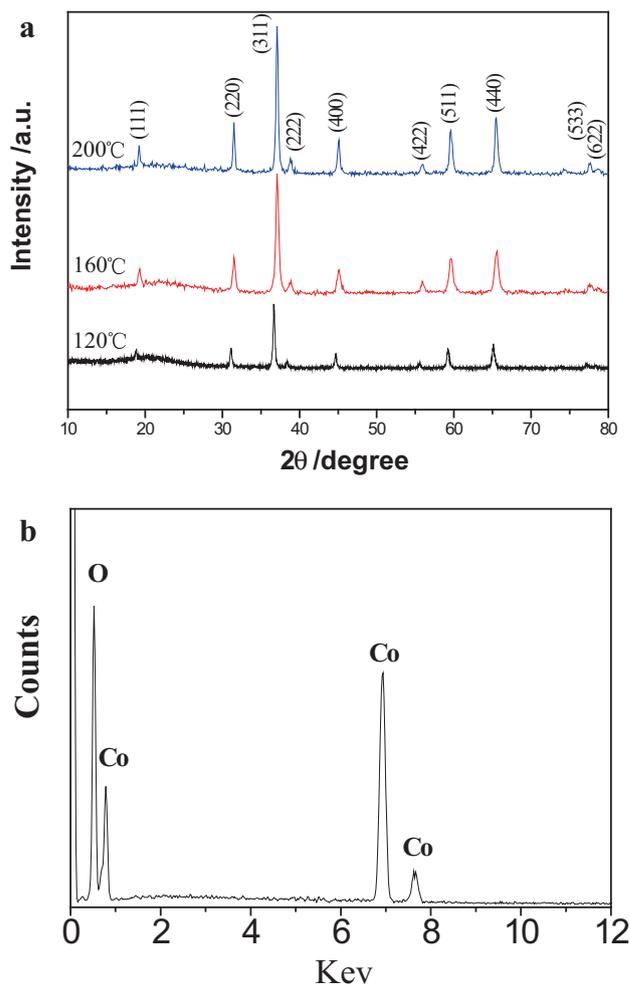
Catalysis activity of the as-prepared Co $_3$ O $_4$  nanocubes under UV light was investigated, against the organic dye RB, used as the pollutant mode. In a typical experimental process, 20 mg of Co $_3$ O $_4$  nanocubes was firstly dispersed in 50 ml RB solution with an initial concentration of 10 mg l $^{-1}$  under ultrasonic assistance. Later, the mixed system was stirred in dark for another 30 min to ensure a sorption–desorption equilibrium. The catalytic degradation of RB was measured at room temperature under irradiation with a 15 W UV lamp (365 nm) at a distance of about 25 cm. The concentration changes of RB solution were measured using a Hitachi U-3010 UV–visible absorption spectrophotometer.

## 3. Results and discussion

### 3.1 Structural and morphological characterizations

Figure 1a shows the XRD pattern of the product prepared at different temperatures. All the identified peaks can be assigned to pure cubic phase Co $_3$ O $_4$  specimens (JCPDS number 42-1467); no obvious peaks corresponding to other cobalt oxides are detected in the powder pattern. The average crystallite size roughly estimated on the basis of the Scherrer formula is about 50 nm for the Co $_3$ O $_4$  nanocrystals obtained at 120°C. Increasing the processing temperature would result in the increment of particle size. Figure 1a shows the XRD pattern of the Co $_3$ O $_4$  nanocrystals obtained at 160 and 200°C; here, sharper diffraction peaks can be observed. Figure 1b exhibits an EDS analysis of the as-prepared product. The strong peaks of Co and O can be easily seen. Based on a calculation of peak areas, the atomic ratio of Co/O in the final product is 0.741, which is very close to the stoichiometry of Co $_3$ O $_4$ .

The average crystallite sizes of the nanocrystals were calculated using the Scherrer equation ( $d = K\lambda/\beta \cos \theta$ ), from the major diffraction peaks, where  $K$  is a constant, equal to 0.9,  $\lambda$  is the wavelength of Cu K $\alpha$  radiation,  $\beta$  is the full-width at half-maximum of the diffraction peak in radians

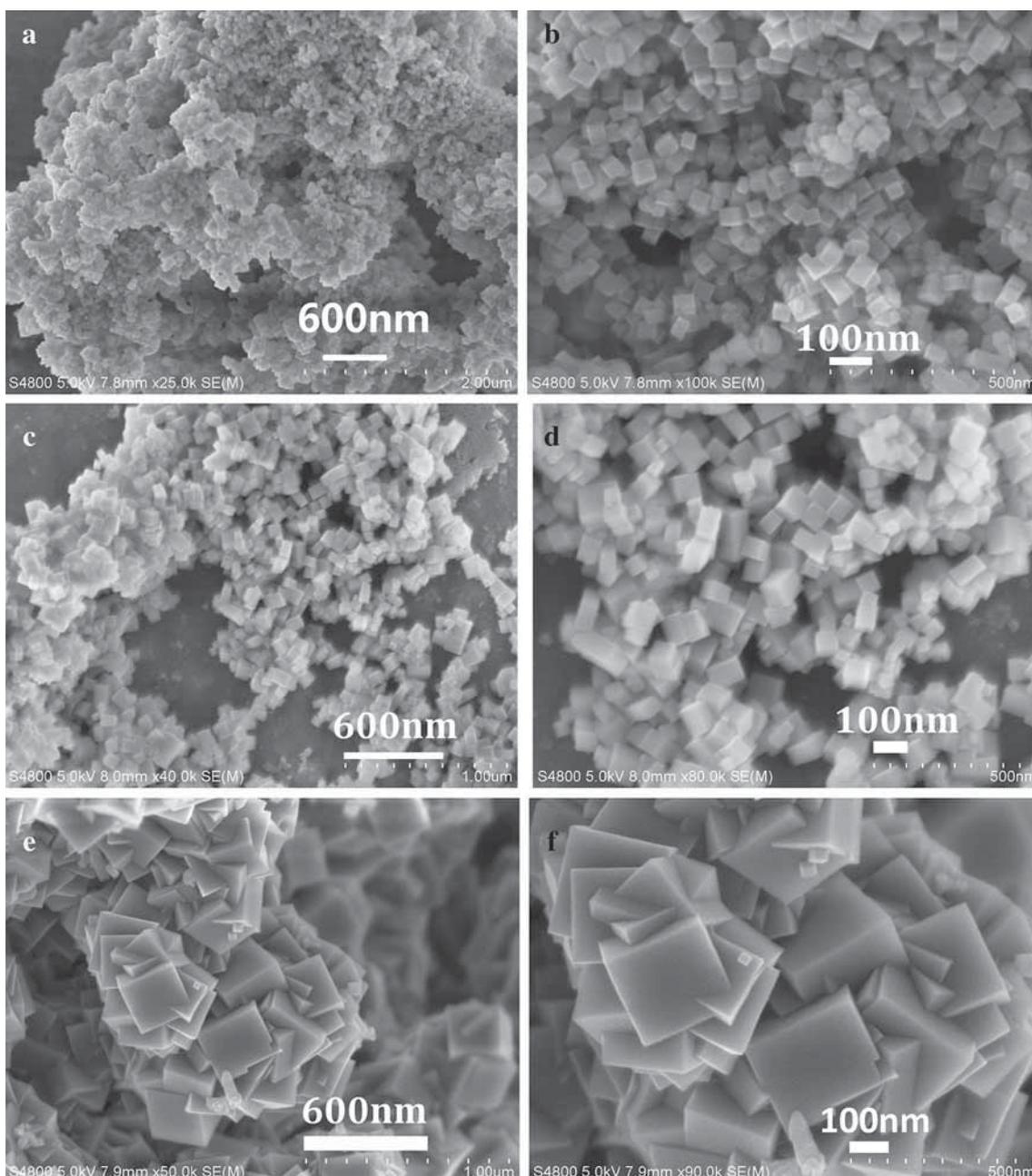


**Figure 1.** (a) XRD pattern and (b) EDS analysis of the as-prepared product.

and  $\theta$  are the Bragg angles of the main planes. The average crystallite sizes of the Co $_3$ O $_4$  nanocrystals obtained at 120, 160 and 200°C are 46.3, 50.1 and 112.5 nm, respectively.

The FESEM images of the as-prepared product synthesized at 120°C for 8 h are given in figure 2a and b. It can be seen that the samples consist of monodisperse nanocubes and the particle sizes of the nanocubes are about 50 nm, corresponding well to the XRD results. Upon increasing the processing temperature to 160°C, it is clear from the panoramic view (figure 2c) that the sample contains uniform nanocubes tens of nanometres in length. Under a higher magnification (figure 2d), Co $_3$ O $_4$  nanocubes are shown to have a uniform width of approximately 70 nm. However, with a further increase of temperature to 200°C, clustered nanocubes with a high degree of agglomeration are seen in figure 2e and f. The FESEM image shows that the Co $_3$ O $_4$  nanopolyhedrons obtained at 200°C are irregular.

Figure 3a shows the TEM image of the Co $_3$ O $_4$  nanocubes synthesized at 160°C for 8 h; it can be clearly seen that the size of Co $_3$ O $_4$  nanocubes is about 70 nm (figure 3a). The



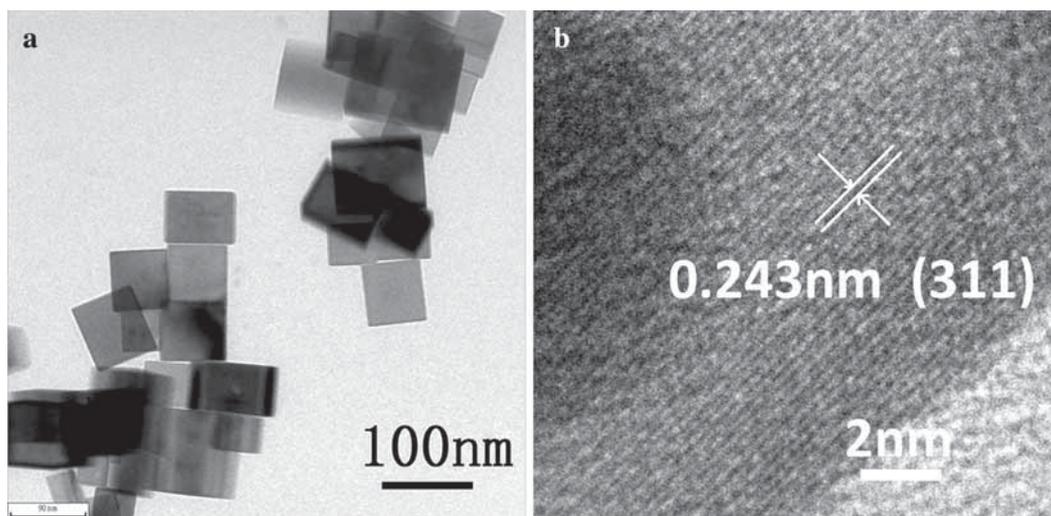
**Figure 2.** The FESEM patterns of the as-prepared products synthesized at (a, b) 120°C, (c, d) 160°C and (e, f) 200°C for 8 h.

crystallinity of the  $\text{Co}_3\text{O}_4$  nanocubes is shown in figure 3b; the obvious lattice fringes indicate the high crystallinity of the samples, and the interplanar distance of 0.243 nm, which corresponds to the distance between the (311) planes of  $\text{Co}_3\text{O}_4$  (JCPDS number 42-1467) crystal lattice.

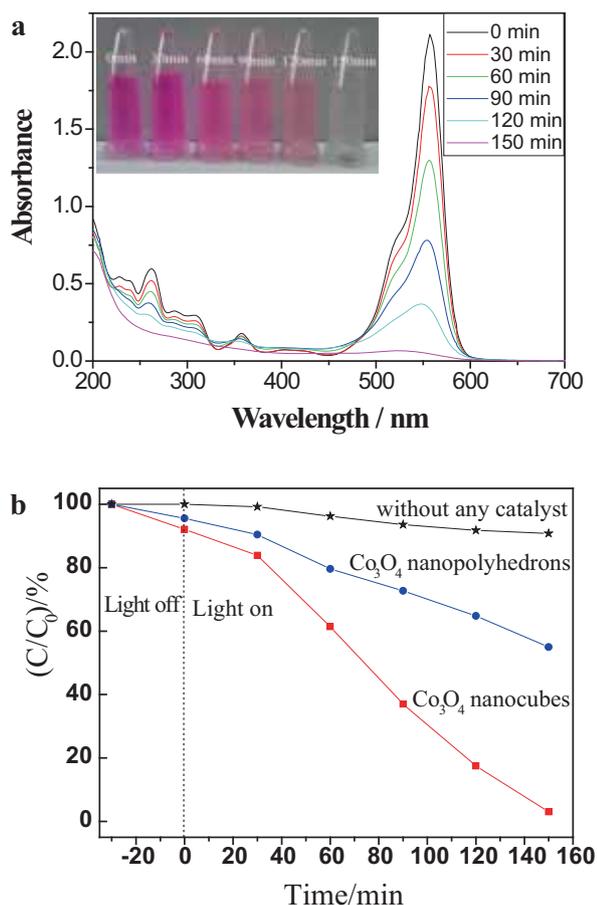
### 3.2 Photocatalytic activity

The photocatalytic activity of the catalysts was monitored by the degradation of RB under UV irradiation at room temperature. The relationship between absorbance and irradiation

duration of RB degradation using the  $\text{Co}_3\text{O}_4$  nanocubes synthesized at 160°C is shown in figure 4a. The strong absorption bands of RB located at  $\lambda = 557$  nm and  $\lambda = 262$  nm decreased gradually with increasing irradiation duration and the absorbance of RB was almost zero after 150 min of irradiation using the  $\text{Co}_3\text{O}_4$  nanocubes catalyst. The colour changes of RB solutions are displayed in the insets of figure 4a; the coloured RB solution became nearly transparent during the degradation process. In addition, the strong absorption bands of RB did not shift, indicating that the degradation of RB was due to the chromophore being destroyed. Within 150 min,



**Figure 3.** (a and b) TEM patterns of the  $\text{Co}_3\text{O}_4$  nanocubes synthesized at  $160^\circ\text{C}$  for 8 h.



**Figure 4.** (a) UV–visible absorption spectra changes of an aqueous solution of Rhodamine B (RB) irradiated by 365 nm UV light in the presence of  $\text{Co}_3\text{O}_4$  nanocubes and (b) the degradation rate of RB in the presence of different catalysts under the irradiation of 365 nm light for different durations.

the colour of RB solution changed from red to colourless (see the inset in figure 4a). The photocatalytic behaviour of the  $\text{Co}_3\text{O}_4$  nanocubes catalyst was further evaluated by performing a comparison with the  $\text{Co}_3\text{O}_4$  nanopolyhedrons and without any catalyst, as shown in figure 4b. In order to ascertain the influence of adsorption on photocatalytic degradation, this experiment was repeated in dark for 30 min under the presence of the  $\text{Co}_3\text{O}_4$  nanocubes. The peak intensity had only a little decrease, indicating that the influence of adsorption on photocatalytic degradation can be ignored. The amount of RB decomposed was calculated using  $C/C_0$ , where  $C$  and  $C_0$  are the concentration based on the absorbance intensity of the sample at a specific time interval and the initial concentration, respectively. The decomposition of RB by the  $\text{Co}_3\text{O}_4$  nanocubes reached approximately 97% over 150 min, whereas 45% of RB was degraded with the  $\text{Co}_3\text{O}_4$  nanopolyhedrons (table 1).

The  $\text{Co}_3\text{O}_4$  nanocubes showed enhanced photocatalytic performance compared with that of the  $\text{Co}_3\text{O}_4$  nanopolyhedrons under UV irradiation. We consider that the enhanced performance of the  $\text{Co}_3\text{O}_4$  nanocubes may be ascribed to their ultrasmall size, large surface area and strong RB adsorption capacity. Thus they can provide more active sites for the photodegradation of RB.

**Table 1.** Comparison of catalytic performance of various catalyst materials for Rhodamine B.

Catalyst materials	Degradation efficiency of RB after 150 min (%)
$\text{Co}_3\text{O}_4$ nanopolyhedrons	45
$\text{Co}_3\text{O}_4$ nanocubes	97

**Table 2.** Comparison photocatalytic degrade for Rhodamine B with different reported catalyst systems.

Catalyst materials	Kinetic rate constant $k$ ( $\text{min}^{-1}$ )	Reference
$\text{WO}_3$	$4.15 \times 10^{-4}$	[21]
$\text{BiOBr}_{0.7}\text{Cl}_{0.3}$	$4.03 \times 10^{-3}$	[22]
$\text{Co}_3\text{O}_4$ nanorods	$1.92 \times 10^{-2}$	[23]
$\text{Co}_3\text{O}_4$ nanocubes	$2.34 \times 10^{-2}$	This work

The photocatalytic degradation obeys pseudo-first-order kinetics [21]

$$\ln(C_t/C_0) = -kt$$

Here,  $k$  and  $t$  are, respectively, the rate constant and the reaction time. The rate constants of the reactions were calculated to be  $2.34 \times 10^{-2} \text{ min}^{-1}$ . Moreover, when compared with some previous reports (see table 2), the present  $\text{Co}_3\text{O}_4$  nanocubes also presented better photocatalytic degradation for RB.

#### 4. Conclusions

In summary,  $\text{Co}_3\text{O}_4$  nanocubes have been synthesized by a simply hydrothermal route in the presence of sodium pentanesulphonate. The results indicated that the temperature during the hydrothermal route played a crucial role in the formation of  $\text{Co}_3\text{O}_4$  nanocubes. It was found that the as-prepared monodispersed  $\text{Co}_3\text{O}_4$  nanocubes could be used as a UV light photocatalyst for the degradation of organic dye RB at room temperature. The monodispersed  $\text{Co}_3\text{O}_4$  nanocubes show good catalytic efficiency for the degradation of RB, a model water contaminant, which may give rise to their potential application in wastewater treatment.

#### Acknowledgements

This work was financially supported by the Key projects of the Education Department of Anhui Province (Number KJ2015A271); Anhui Provincial Project of Outstanding Young Talents Fund in Universities (Number gxyqZD 2016342); the Opening Project of Anhui Key Laboratory

of Spin Electron and Nanomaterials (Number 2014YKF45, 2011YKF03); Innovation Project of College Students in Anhui Province (Number 201610379026) and Suzhou University professor research projects (Number 2017jb02, 2017jb03).

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