

Co₉S₈ nanotubes: facile synthesis and application in the catalytic reduction of 4-nitrophenol

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Abstract. Co₉S₈ nanotubes have been successfully synthesized via a facile two-step solvothermal method without the assistance of any template or surfactant, using cobalt sulphate (CoSO₄·7H₂O), urea and sodium sulphide (Na₂S·9H₂O) as starting reactants, and deionized water and glycol as the reactive medium. The phase and the morphology of the as-obtained product were characterized by means of powder X-ray diffraction, energy dispersive spectrometry and scanning electron microscopy. The result displays that the Co₉S₈ nanotubes have hexagonal cross-sections, the diameter of the nanotubes is about 200 nm and the wall thickness is of 50 nm. The experiments showed that the Co₉S₈ nanotubes could be used as new-type catalysts for the reduction of 4-nitrophenol. It was found that the as-obtained Co₉S₈ nanotubes contributed to the best catalytic activity.

Keywords. Co₉S₈ nanotubes; solvothermal; catalytic reduction; 4-nitrophenol.

1. Introduction

Over the past decade, design and synthesis of micro- and nanoscale inorganic materials with special morphologies or hierarchical structures have been receiving extensive research interest due to their potential applications in catalysis, optical, electronic materials and other properties [1–4]. As semiconductor compounds, cobalt sulphides with different stoichiometric ratios, such as CoS, CoS₂, Co₃S₄, Co₉S₈ and Co_{1-x}S, have attracted attention because of their unique catalytic, electrical, and their potential applications for catalysts, supercapacitors and Li-ion batteries [5–8].

In recent years, cobalt sulphide nanostructures of various morphologies have been applied in many different fields, such as CoS/CoS₂ nanoparticles for high rate hybrid supercapacitors [9,10], CoS nanowires for application in supercapacitors [11,12], CoS₂ nanopyramid array grown on 3D carbon fibre paper as an excellent electrocatalyst for hydrogen evolution [13], CoSn (Co₉S₈, Co₃S₄ and Co_{1-x}S) hierarchical microspheres exhibited great electrocatalytic activities [14], rose-like Co₉S₈ as cathode materials for application in lithium-ion batteries [15], flower-like Co_{1-x}S anode materials for lithium-ion batteries [16] and hierarchical hollow Co₉S₈ microspheres as electrocatalysts [17]. However, the above methods usually require high temperature, long time and even a series of complicated procedures. Obviously, it is still necessary and significant to develop a facile and efficient approach for the large fabrication of uniform cobalt

sulphide micro-/nanostructures and explore new properties and applications.

In this study, we designed a facile two-step solvothermal method to successfully synthesize three-dimensional (3D) Co₉S₈ nanotubes, employing CoSO₄·7H₂O, urea and Na₂S·9H₂O as starting reactants, and deionized water and glycol as the reactive medium. The experiments showed that the Co₉S₈ nanotubes could be used as new-type catalysts for the reduction of 4-nitrophenol by NaBH₄ and as-obtained Co₉S₈ nanotubes. It was found that the as-obtained Co₉S₈ nanotubes contributed to the best catalytic activity.

2. Experimental

2.1 Materials preparation

The precursor Co(CO₃)_{0.5}(OH)·0.11H₂O nanowires were synthesized by a facile solvothermal method. All reagents and chemicals were analytically pure, bought from the Shanghai Chemical Company and used as received without further purification. In a typical experimental procedure, 0.562 g CoSO₄·7H₂O was dissolved in 40 ml of mixture containing 30 ml of deionized water and 10 ml of ethylene glycol. After stirring for about 20 min, a transparent solution was obtained. Then 0.12 g urea was added into the above solution, with vigorous magnetic stirring at room temperature, to form a homogeneous solution. The as-prepared solution was poured into a Teflon-lined stainless steel autoclave of 50 ml capacity. Then, the autoclave was sealed and maintained at 100°C for 10 h. After that, the autoclave was

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allowed to cool down to room temperature naturally. The pink precipitates were separated by centrifugation at 7000 r.p.m., washed with deionized water and absolute ethanol several times to remove the impurities, and finally dried in vacuum at 60°C for 2 h.

A quantity of 0.108 g of the precursor was dispersed into 30 ml of deionized water, then 10 ml of 0.2 M $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ solution was added into the above solution in a Teflon-lined autoclave of 50 ml capacity under stirring. Then, the autoclave was sealed and maintained at 120°C for 2 h. After that, the autoclave was allowed to cool down to room temperature naturally. The black precipitates were separated by centrifugation at 7000 r.p.m., washed with deionized water and absolute ethanol several times to remove the impurities, and finally dried in vacuum at 60°C for 2 h.

2.2 Materials characterization

The chemical composition of the samples was determined by X-ray powder diffraction (XRD), Shimadzu XRD-6000 X-ray diffractometer equipped with $\text{CuK}\alpha$ radiation ($\lambda = 0.154060$ nm), employing a scanning rate of $0.02^\circ \text{ s}^{-1}$ and 2θ range from 10° to 80° . Field scanning electron microscopy (FESEM) images and energy dispersive spectrometry (EDS) of the products were obtained on a Hitachi S-4800 FESEM, employing the accelerating voltage of 5 and 15 kV, respectively. UV–vis absorption spectra were recorded on a Metash 6100 UV–vis absorption spectrophotometer.

2.3 Catalytic study

To investigate the catalytic activity of Co_9S_8 nanotubes for reduction of 4-nitrophenol, a certain amount of Co_9S_8 nanotubes was dispersed into proper amounts of deionized water to form a suspension. The aqueous solutions of 4-nitrophenol and NaBH_4 were freshly prepared. In order to induce the reaction, appropriate volumes of 4-nitrophenol solution, the catalyst suspension and NaBH_4 solution were injected into a cuvette. The final volume of the mixed system was kept at 3 ml. Here, the concentrations of various components were $1 \times 10^{-4} \text{ mol l}^{-1}$ (4-nitrophenol), $2.0 \times 10^{-2} \text{ mol l}^{-1}$ (NaBH_4) and 10 mg l^{-1} (Co_9S_8 nanotubes). The detailed reduction processes were monitored using a UV–vis spectrophotometer.

3. Results and discussion

3.1 Structural and morphology characterizations

XRD patterns of the precursor sample were obtained, which revealed the phase of the precursor sample as shown in figure 1a. All the identified peaks can be assigned to pure hexagonal phase $\text{Co}(\text{CO}_3)_{0.5}(\text{OH})\cdot 0.11\text{H}_2\text{O}$ (JCPDS card number 48-0083). The XRD pattern in figure 1b confirms that the heat-treated sample only contains pure cubic phase Co_9S_8 (JCPDS card number 86-2273). The absence of

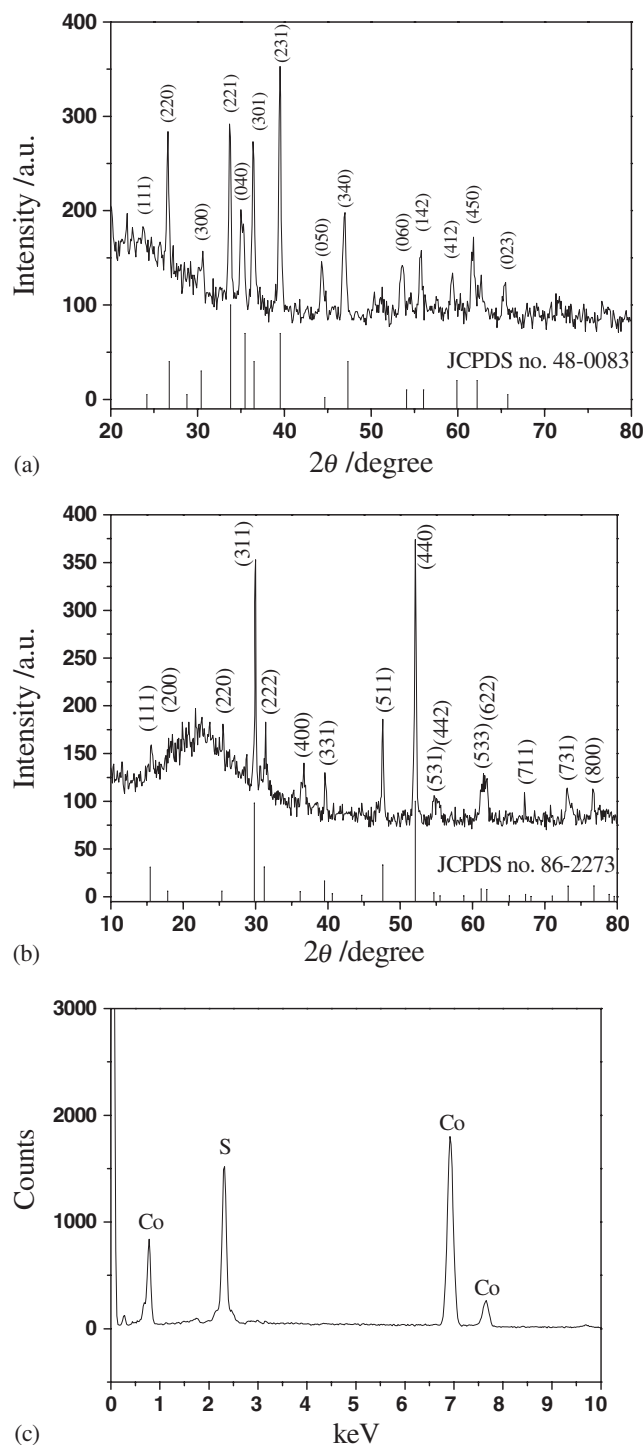


Figure 1. (a) The XRD pattern of the precursor. (b) The XRD pattern and (c) EDS analysis of Co_9S_8 .

peaks due to other phases indicates the high purity of the synthesized material. The very high peak intensity suggests that the material is well crystallized. This indicates the complete transformation of $\text{Co}(\text{CO}_3)_{0.5}(\text{OH})\cdot 0.11\text{H}_2\text{O}$ into the Co_9S_8 phase. Further evidence to form Co_9S_8 came from the EDS analysis of the as-prepared product. As shown in figure 1c, strong Co and S peaks are clearly visible. Based on

the calculation of the peak areas, the molar ratio of Co/S is very close to the stoichiometric ratio of Co₉S₈.

FESEM images of Co(CO₃)_{0.5}(OH)·0.11H₂O are shown in figure 2a and b and It is clear from the panoramic view (figure 2a) that the sample contains uniform nanowires. Under a higher magnification (figure 2b), these nanowires were shown to have a uniform width with a relatively smooth surface, and the diameter approximately 200 nm. FESEM images of Co₉S₈ are shown in figure 2c and d, these images indicate nanostructure morphology of the Co₉S₈ nanotubes. Co₉S₈ nanotubes surface was a bit rough around the edges, some of the nanotubes were broken, and they show hexagonal cross-sections as indicated in figure 2c. Higher magnification SEM image (figure 2d) shows the diameter of the nanotubes as about 200 nm, and the wall thickness as 50 nm.

The formation of Co₉S₈ nanotubes could be demonstrated by the Kirkendall effect, the Co(CO₃)_{0.5}(OH)·0.11H₂O nanowires were prepared and served as the templates. In aqueous, S²⁻ ions react with Co(CO₃)_{0.5}(OH)·0.11H₂O nanowires to produce a thin layer of Co₉S₈ nanoparticles on the surfaces of the Co(CO₃)_{0.5}(OH)·0.11H₂O nanowires. Then the direct conversion of the precursor core to the Co₉S₈ shell was therefore obstructed by the layer, so further reaction would continue by the diffusion of S²⁻ ions through the interface. Because the outward diffusion rate of the cobalt source was faster than the inward transport rate of S²⁻ ions through the Co₉S₈ shell, unequal diffusion of reacting species produces voids close to the interface [18]. According to the Kirkendall effect, the different diffusivities of the different components in a diffusion couple may lead to the

formation of Kirkendall voids close to the interface [19]. As the reaction continued, the Co₉S₈ shell was increased and the Co(CO₃)_{0.5}(OH)·0.11H₂O core was decreased gradually, finally Co₉S₈ nanotubes formed.

3.2 Catalytic property of 4-nitrophenol

In recent years, the reduction of aromatic nitrocompounds by sodium borohydride in the aqueous solution has made great progress [20–25]. Usually, the catalyst used was noble metal materials [26–28], transition metal materials [29,30] and so on. To date, there is no report on cobalt sulphide being used for the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP). To investigate the catalytic activity of the as-obtained Co₉S₈ nanotubes, an appropriate amount of hollow nanotubes was introduced into the system containing 4-NP and NaBH₄. Figure 3 exhibits the UV–vis absorption spectra of the 4-NP and NaBH₄ system in the presence of 30 mg l⁻¹ catalyst at various reaction times. A strong peak at 400 nm gradually decreased with increase in the reaction time. After 8 min, the peak at 400 nm almost disappears, indicating that the as-obtained Co₉S₈ nanotubes possess a good catalytic capacity for the reduction of 4-NP to 4-AP by NaBH₄. In the process of reaction, a new peak at 303 nm appeared, which belonged to the characteristic absorption peak indexed to 4-AP [31].

Figure 4a shows the conversion-time curves of 4-NP in the presence of Co₉S₈ nanotubes. After 8 min, 4-NP conversion from orange to colourless transparent solution was almost complete.

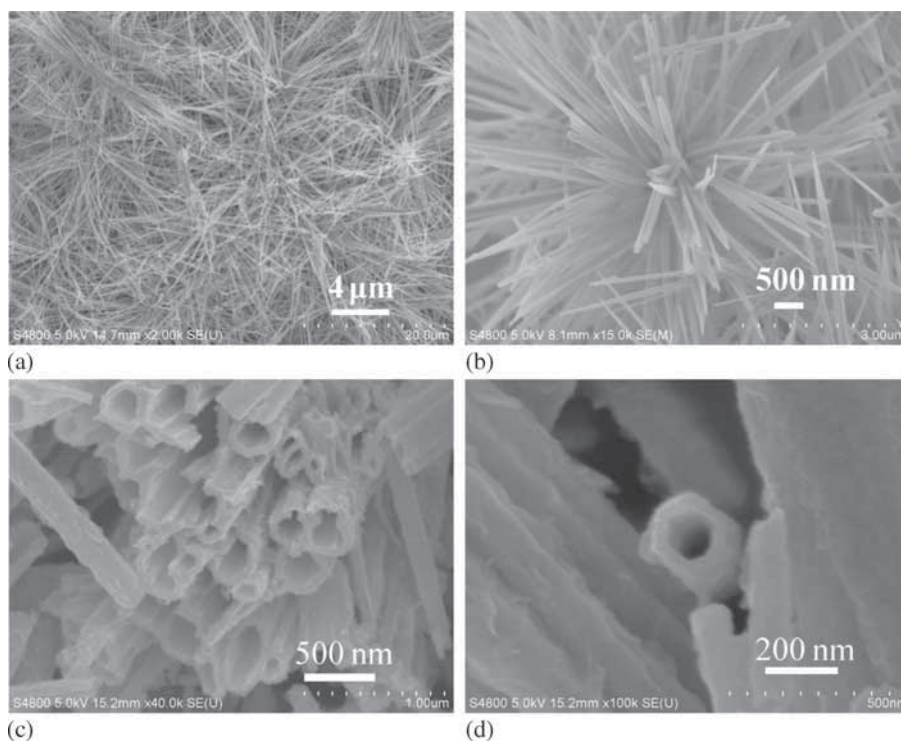


Figure 2. (a and b) The FESEM patterns of Co(CO₃)_{0.5}(OH)·0.11H₂O nanowires and (c and d) Co₉S₈ nanotubes.

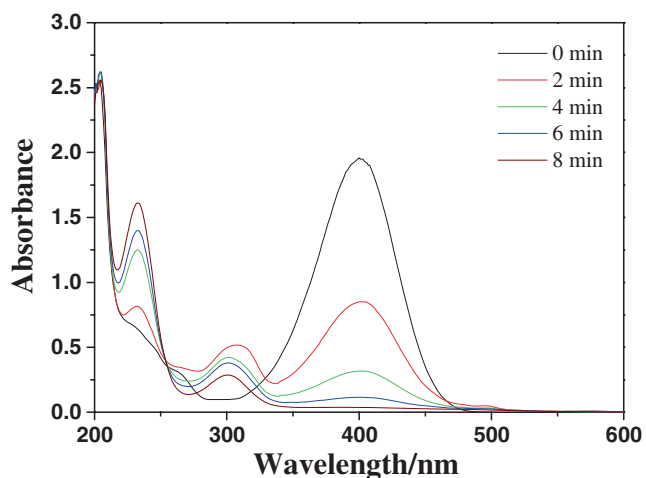
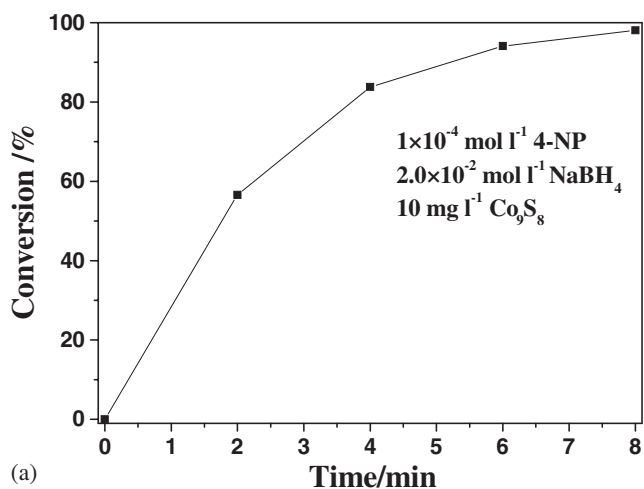
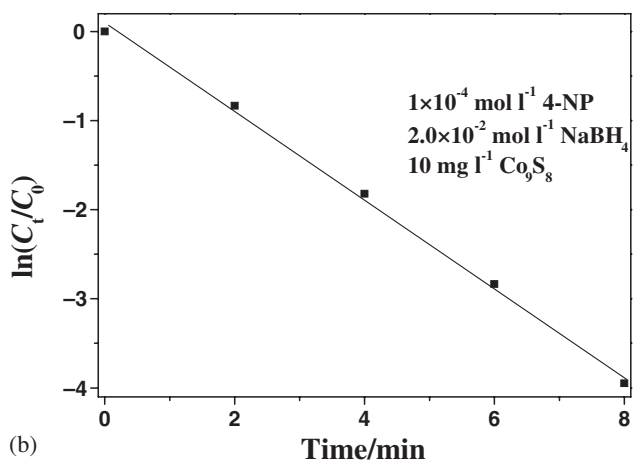


Figure 3. UV-vis absorption spectra of the system containing 4-nitrophenol and NaBH_4 in the presence of Co_9S_8 nanotubes for various durations.



(a)



(b)

Figure 4. (a) Conversion curves of 4-NP to 4-AP under the presence of Co_9S_8 nanotubes. (b) Inset shows the linear relationship between $\ln(C_t/C_0)$ and the reaction time in the presence of Co_9S_8 nanotubes.

Table 1. Comparison of catalytic performance of various catalyst materials for 4-NP reduction with different reported catalyst systems.

Catalyst materials and its amount	Kinetic rate constant, k (min^{-1})	Ratio constant, K ($\text{min}^{-1} \text{mg}^{-1}$)	Reference
$\text{Ni}_{33.8}\text{Co}_{66.2}$ dendrites	0.073	0.243	[22]
AgNPs composite nanofibres	0.372	12.4	[24]
Pure Pt	7.5×10^{-3}	0.025	[33]
Au@MIL-100(Fe) core-shell	0.33	11	[34]
Co_9S_8 nanotubes	0.4925	16.42	Present work

Since excess NaBH_4 was used in the experiment, the reduction reaction of 4-NP to 4-AP could be reasonably assumed to be pseudo-first-order kinetics with regard to 4-NP. This pseudo-first-order kinetics equation may be abbreviated as follows [32]:

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

Here, C_0 and C_t represent the initial and instantaneous concentrations of 4-NP, respectively, and k and t are the rate constant and the reaction time in turn. Figure 4b shows linear relationships between $\ln(C_t/C_0)$ and the reaction time in the presence of Co_9S_8 nanotubes. The rate constants of the reactions were calculated to be 0.4925 min^{-1} . Moreover, compared with some previous reports (see table 1), the present Co_9S_8 nanotubes also presented better catalytic activity for the reduction of 4-NP.

4. Conclusions

In summary, Co_9S_8 nanotubes have been successfully synthesized via a facile two-step solvothermal method without the need for any surfactant. The precursor $\text{Co}(\text{CO}_3)_{0.5}(\text{OH}) \cdot 0.11\text{H}_2\text{O}$ nanowires have been synthesized by employing $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and urea as starting reactants, and deionized water and glycol as the reactive medium. Later, by using $\text{Co}(\text{CO}_3)_{0.5}(\text{OH}) \cdot 0.11\text{H}_2\text{O}$ nanowires as templates, Co_9S_8 nanotubes were formed by the nanoscale Kirkendall effect. The experiments showed that the Co_9S_8 nanotubes could be used as new-type catalysts for the reduction of 4-nitrophenol. It was found that the as-obtained Co_9S_8 nanotubes contributed to the best catalytic activity.

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