

Preparation and characterization of Co_9S_8 nanocrystalline and nanorods

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Abstract. Hexagonal Co_9S_8 nanocrystal and nanorods were synthesized using cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), dimethyl sulfoxide (DMSO) and non-aqueous alcohol as the starting materials, and taking dimethyl sulfoxide as both sulfur source and strong infiltrator in nanorods preparation. The Co_9S_8 samples were characterized by X-ray diffraction (XRD), scanning tunneling microscope (SEM), transmission electron microscope (TEM), vibrating sample magnetometer (VSM) and laser Raman spectrometer. The results show that the as-prepared Co_9S_8 nanocrystal with a size of 6 nm take on weak paramagnetism at room temperature. The lengths and diameters of the nanorods were about 4 μm and 200 nm, respectively. The reason for the relative lower synthesis temperature of nanorods was discussed and a ‘micro-autoclave reactor’ model was suggested as well.

Keywords. DMSO; nanostructures; annealing; infiltration.

1. Introduction

Cobalt sulfides such as CoS , Co_3S_4 , CoS_2 and Co_9S_8 , usually have many stable phases and intricate structures (Rau 1976; Wold and Dwight 1993), however, for obtaining novel physical properties, Co_9S_8 with nanocrystalline and one-dimension nanostructures have attracted so much attention recently (Chauke *et al* 2002). For example, Co_9S_8 is of importance in hydrodesulfurization catalysts and magnetic devices (Yamada *et al* 1998; Igor *et al* 2004). Besides, among several transition metal sulfides, Co_9S_8 was found to have the highest catalytic activity for O_2 reduction in acidic solution (Baresel *et al* 1974; Behret *et al* 1975). Thus, it is promising for Co_9S_8 to be a sort of a catalyst towards electroreduction of O_2 (Sidik and Anderson 2006).

So far, various sulfur source agents have been employed for the preparation of Co_9S_8 , such as sulfur element (Schneemeyer and Sienko 1980), hydrogen sulfide (Pasquariello *et al* 1984), sodium sulfite (Zhang *et al* 2004), thiourea (Liu 2005) and sodium sulfide (Yu *et al* 2002). However, it usually needs a relatively high temperature to synthesize cobalt sulfides by using the reported sulfur source agents. For example, Co_9S_8 was prepared with anhydrous cobalt sulfate salt in a flowing gas of hydrogen sulfide and hydrogen at 525°C (Pasquariello *et al* 1984).

In this paper, Co_9S_8 nanocrystal and nanorods were successfully prepared by using cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$),

dimethyl sulfoxide (DMSO) and non-aqueous alcohol as reactants. For obtaining a facile and relative lower temperature procedure to synthesize Co_9S_8 nanorods, here, DMSO was employed not only as a sulphur source but also as a strong infiltrator at atmospheric pressure instead of vacuum decompression (Chakravarti and Vetter 1993; Chen *et al* 2000; Holzinger *et al* 2003; Nath *et al* 2003; Chin *et al* 2005).

2. Experimental

2.1 Preparation of nanocrystalline Co_9S_8

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was added to DMSO and $\text{C}_2\text{H}_5\text{OH}$ (volume ratio of 7 : 3) mixed solvent and the concentration of the mixture solution was 0.5 M. A pot with appropriate mixture solution was put into a quartz tube oven keeping a constant flow rate of argon gas, initially at a temperature of 150°C for 5 min and then increased to 300°C for 4 h, and finally cooled to room temperature naturally. After being washed with absolute ethanol and distilled water, the black product was dried at a low temperature (sample 1).

2.2 Preparation of Co_9S_8 nanorods

The precursor solution preparation was the same as those of Co_9S_8 nanocrystal. The mixture with Co^{2+} 0.5 mol/L was slowly dropped onto two sides of the AAO template, and the infiltration time was about 2 h. Then, the tem-

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plate was put into a quartz tube oven, in which temperature was maintained at 150°C for 15 h (sample 2), and annealed at 250°C for 5 h (sample 3), and finally cooled to room temperature naturally. Argon gas flow rate was kept constant in all procedures.

The X-ray powder diffraction (XRD) patterns were carried out on a Switzerland X'TRA mode X-ray diffractometer with CuK α radiation. Transmission electron microscopic (TEM) images were taken with a JEM-200CX mode transmission electron microscope. Scanning tunneling microscopy (STM) was performed on JSM-5610LV-VANTAGE mode scanning tunnelling microscope. The Raman spectrum was measured with a JY-HR800 laser Raman spectrometer at room temperature. The magnetic properties were studied using a Lakeshore 7307-9309 vibrating sample magnetometer (VSM).

3. Results and discussion

Figure 1a shows the XRD pattern of sample 1. Most of the peaks could be indexed to the phase of Co₉S₈. After refinement, the cell constant, $a = 9.865 \text{ \AA}$, was close to that of the reported value in the JCPDS cards (75-2023, hexagonal). The crystalline size of Co₉S₈ was about 6 nm calculated by half-width of peaks using the Scherrer equation. Figure 1b is the XRD pattern of sample 2, which

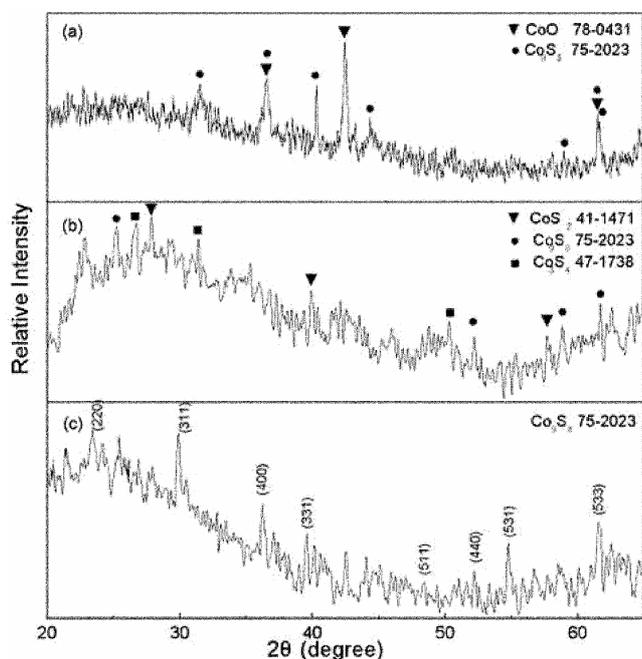
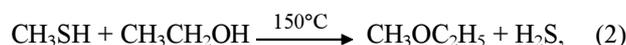


Figure 1. XRD patterns of Co₉S₈ nanocrystalline and nanorods: (a) Co₉S₈ nanocrystalline prepared by CoCl₂·6H₂O, non-aqueous alcohol and DMSO at 300°C for 4 h, (b) a mixed phase of Co₉S₈, CoS₂ and Co₃S₄ prepared by CoCl₂·6H₂O, non-aqueous alcohol and DMSO at 150°C for 15 h (sample 2) and (c) the single phase of Co₉S₈ prepared by annealing sample 2 for 5 h at 250°C (sample 3).

showed nanorods with a mixed phase of Co₃S₄, Co₉S₈ and CoS₂ (reflections at d spacings of 3.35, 2.85 and 1.81 Å corresponding to the 220, 311 and 511 planes of Co₃S₄, respectively, reflections at d spacings of 3.54, 1.75, 1.57 and 1.51 Å corresponding to the 220, 440, 620 and 533 Å planes of Co₉S₈, respectively and reflections at d spacings of 3.20, 2.52 and 1.60 Å corresponding to the 111, 211 and 222 planes of CoS₂, respectively). The XRD pattern of sample 3 is shown in figure 1c, in which Co₉S₈ nanorod was converted from sample 2 by annealing at 250°C for 5 h. As shown in figure 1c, all of the marked peaks could be indexed as the phase of Co₉S₈ (JCPDS 75-2023, hexagonal). It is clear that both phases, Co₃S₄ and CoS₂, in sample 2 converted to Co₉S₈ phase.

In the case of the formation of Co₉S₈ nanorods, the reaction process, we speculated, can be expressed in detail as follows



Co₉S₈ nanocrystalline (sample 1) with a mean size of 8 nm is as shown in figure 2a, which is in good agreement with that calculated using the Scherrer equation (6 nm). Besides, the greater Co₉S₈ nanocrystal with a diameter about 50 nm, as shown in figure 2b, is attributed to the growth of the small one, which is in a hexagonal shape.

TEM image of sample 2 (figure 2c) indicated that the nanorods were fragile for its poor crystallinity. The result was due to lower temperature. It was found that an increase in reaction temperature could improve the growth of Co₉S₈ nanocrystal obviously, as shown in figure 2d (sample 3). The improved Co₉S₈ nanorods were uniform and had a diameter of about 200 nm and length of up to 4 μm. The electron diffraction pattern (the inset in figure 2e) from a selected area of a Co₉S₈ nanorod (shown in figure 2e) revealed that the as-prepared Co₉S₈ nanorods were polycrystalline rods.

As reported earlier, bulk Co₉S₈ was prepared with anhydrous cobalt sulfate salt in a flowing gas of hydrogen sulfide and hydrogen at 525°C (Pasquariello *et al* 1984) and the transformation between Co₉S₈ and CoS in a H₂S atmosphere was above 600°C (Kiuchi and Nakamura 1983), the monosulfide form could be transformed into more sulfur richer forms after reacting with sulfur fume at temperatures of 300–400°C (Chung and Chung 2004); cubic phase nanocrystalline Co₉S₈ could be synthesized via a facile hydrothermal synthetic route in a sealed autoclave at 160°C for 24 h (Zhang *et al* 2004). However, a mixed phase of Co₉S₈, CoS₂ and Co₃S₄ was obtained at 150°C in our experiment. As shown in figure 3, it could be found that the channel entrance of the two sides of template was blocked by compact substance. As a result,

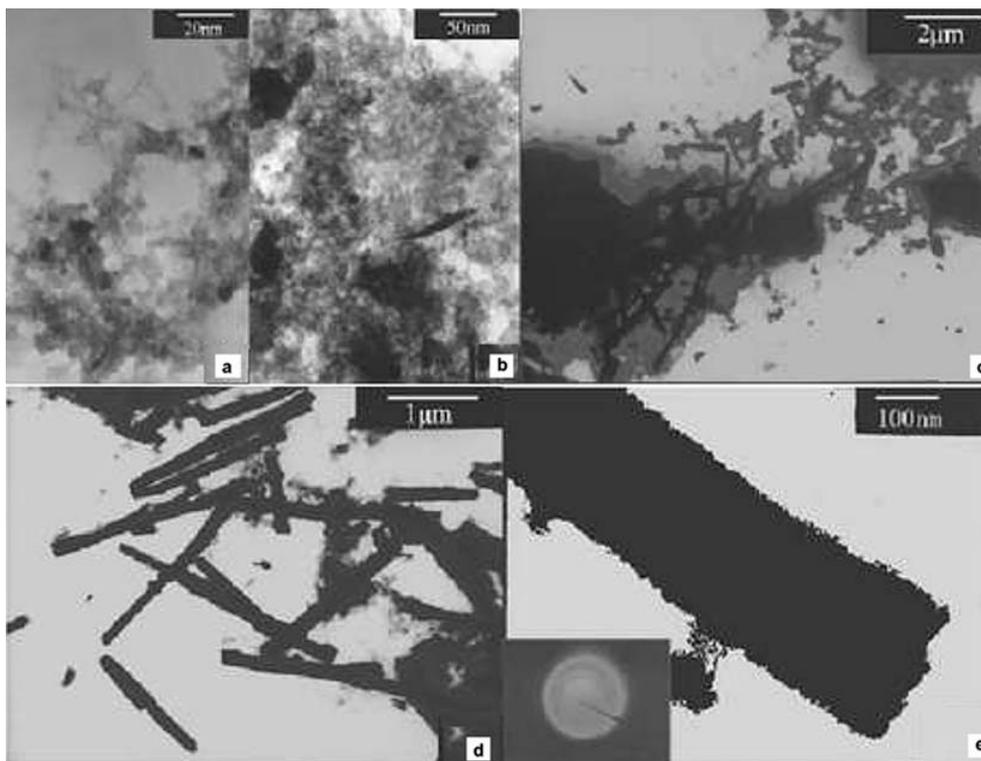


Figure 2. a–b. TEM images of Co_9S_8 nanocrystalline powders, and c–e. TEM images of nanorods by using $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, non-aqueous alcohol, DMSO under conditions c. at 150°C for 15 h, sample 2 (the mixed phase of Co_9S_8 , CoS_2 , and Co_3S_4), d. annealing sample 2 at 250°C for 5 h, sample 3 (the single phase of Co_9S_8), and e. amplificatory image of sample 3, the inset is the select electron diffraction pattern of Co_9S_8 nanorod.

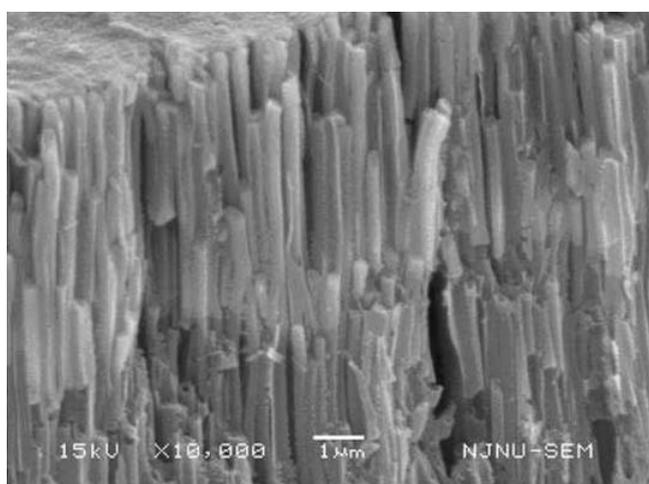


Figure 3. SEM image of Co_9S_8 nanorods prepared by annealing sample 2 for 5 h at 250°C .

the decomposed gas such as H_2S in channels provided a higher pressure which resulted in the great decrease of reaction temperature. By this, a suggested mechanism as same as ‘micro-autoclave reactor’ (MAR) was given. A schematic description of the formation of MAR is as shown in figure 4.

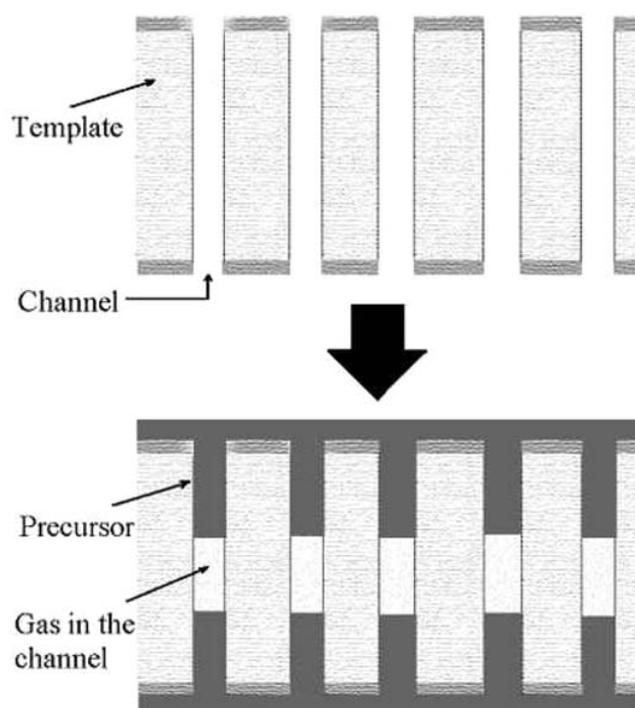


Figure 4. A schematic description of the formation of micro-autoclave reactor.

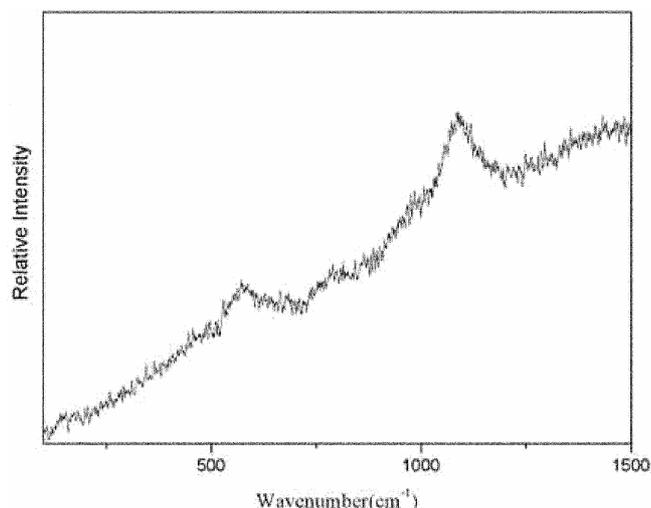


Figure 5. Raman spectrum measurement of Co_9S_8 nanorods.

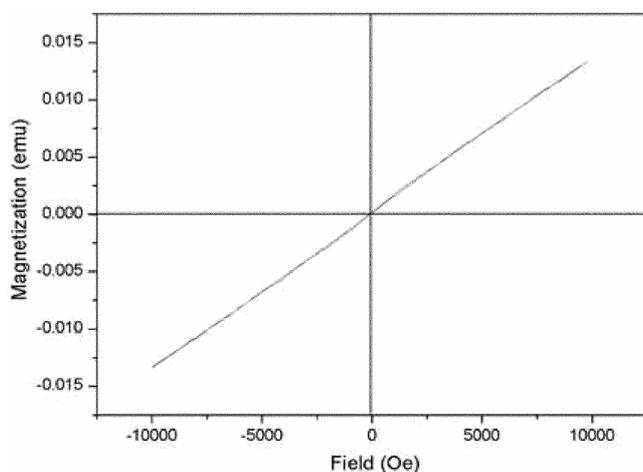


Figure 6. VSM pattern of Co_9S_8 nanocrystalline prepared at 300°C for 4 h.

Laser Raman spectroscopy is an effective method to study the material structure, so it is suitable for exploring the structure of nanometer-sized crystals of Co_9S_8 . Up to now, there is little work on the Raman characterization of Co_9S_8 nanorods. The Raman spectra of the typical Co_9S_8 nanorods with diameter of about 200 nm and lengths of up to 4 μm at room temperature were shown in figure 5. Two well-resolved Raman peaks were seen at 573 cm^{-1} and 1085 cm^{-1} .

The magnetic properties of the Co_9S_8 nanocrystal prepared at 300°C for 15 h (figure 6) were evaluated by a vibrating sample magnetometer (VSM). In general, Co_9S_8 exhibits ferromagnetism at room temperature (Sidik and Anderson 2006). However, hysteresis loop of the as-prepared Co_9S_8 nanocrystal samples showed a weak superparamagnetic behaviour when measured at room temperature (gross weight of sample, 0.027 g). This might be attributed to size effect of the nanocrystal, by which the ferromagnetism was converted into superparamagnetism

when its diameter was under the critical size of single domains.

4. Conclusions

In summary, hexagonal Co_9S_8 nanocrystalline and nanorods were prepared by using cobalt chlorides, DMSO and non-aqueous alcohol. In our case, DMSO not only served as a sulphur source but also performed as a unique strong infiltrator for preparing Co_9S_8 nanorods. The VSM indicates that the nanocrystalline Co_9S_8 showed superparamagnetism. Both the Co_9S_8 nanorods were uniform and had diameters of about 200 nm and lengths of up to 4 μm . A so-called 'micro-autoclave reactor' model was suggested as the reason for lower synthesis temperature in our process.

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References

- Baresel D, Sarholz W, Scharner P and Schmitz J 1974 *Ber. BunsenGes.* **78** 608
- Behret H, Binder H and Sandstede G 1975 *Electrochim. Acta* **20** 111
- Chakravarti S K and Vetter 1993 *J. Micromech. Microeng.* **3** 57
- Chauke H R, Nguyen-Manh D, Ngoepe P E, Pettifor D G and Fries S G 2002 *Phys. Rev.* **B66** 155105
- Chen X R, Zhan H Y and Tian X Y 2000 *Liaoning Chem. Ind.* **29** 31
- Chin P P, Ding J, Yi J B and Liu B H 2005 *J. Alloys Compd.* **390** 255
- Chung J B and Chung J S 2004 *Ind. Eng. Chem. Res.* **43** 5318
- Holzinger M, Abraham J, Whelan P, Graupner R, Ley L, Hennrich F, Kappes M and Hirsch A 2003 *J. Am. Chem. Soc.* **125** 856
- Igor B, Pavel A and Michel D 2004 *J. Phys. Chem.* **B108** 7709
- Kiuchi H and Nakamura I 1983 *Nippon Kosyo Kaishi* **99** 401
- Liu X H 2005 *Mater. Sci. Eng.* **B119** 19
- Nath M, Choudhury A, Kundu A and Rao C N R 2003 *Adv. Mater.* **15** 2098
- Pasquariello D M, Kershaw R, Passaretti J D, Dwight K and Wold A 1984 *Inorg. Chem.* **23** 872
- Rau H 1976 *J. Phys. Chem.* **37** 931
- Schneemeyer L F and Sienko M 1980 *J. Inorg. Chem.* **19** 789
- Sidik R A and Anderson A B 2006 *J. Phys. Chem.* **B110** 941
- Wold A and Dwight K 1993 *Solid state chemistry* (New York: Chapman & Hall, Inc)
- Yamada H, Terao K and Aoki M 1998 *J. Magn. Magn. Mater.* **607** 177
- Yu Z R, Du J H, Guo S H, Zhang J Y and Matsumoto Y 2002 *Thin Solid Films* **415** 173
- Zhang Y G, Guo F, Wan S M and Zheng W W 2004 *J. Synth. Cryst.* **33** 927