

Supporting Information

Insights into catalytic roles of noble-metal-free catalysts Co_xS_y for reduction of 4-nitrophenol

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Preparations of Catalysts

Co_9S_8 catalyst was synthesized by a facile hydrothermal method. In a typical process, 0.2 mol of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and 0.2 mol thiourea were dissolved into 40 mL deionized water, respectively. After being stirred for 30 min, the solution was transferred into a 50 mL Teflon lined stainless steel autoclave, sealed and maintained at 180°C for 24 h. After being cooled to room temperature, the black precipitate was centrifuged, washed three times with deionized water and ethanol, followed by drying at 60°C overnight. The as-prepared powder was calcined at 330°C for 1 h in H_2/Ar atmosphere to obtain Co_9S_8 particles. Synthesis of CoS and CoS_2 has been reported in previous works.^{1,2}

Typically, dissolving $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (2.5 mmol) into a mixture solution of deionized water (20 mL) and ethylene glycol (5 mL), and then thiourea (10 mmol) was added. After stirring for 10 min, the mixed solution was transferred into a 50 mL Teflon-lined stainless steel autoclave, and heated for 15 h at 180°C. Finally, the autoclave was cooled to room temperature, and the black powder of CoS was collected by centrifugation, washed several times with deionized water and ethanol, and dried for 12 h at 50°C under vacuum conditions.

The $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2 mmol) was firstly dissolved in 30 mL of deionized water to obtain solution A, and solution B was prepared by dissolving 2 mmol of L-cysteine in 30 mL of deionized water. After solution A was added into solution B under constant and vigorous stirring for 15 min, the resulting mixture was sealed in a Teflon-lined stainless steel autoclave, which was maintained at 190°C for 6 h, followed by cooling down to room temperature. Subsequently, the as-obtained CoS_2 products were collected, completely washed, and dried at 60°C overnight.

Characterizations

UV-vis absorption spectra were monitored by using a Thermo Fisher evolution 300 spectrophotometer. N_2 adsorption-desorption isotherms were performed on Autosorb-iQ-C apparatus (Quantachrome Instruments). X-ray diffraction patterns (XRD) were recorded on a Rigaku D/max-2500PC apparatus with graphite monochromatized $\text{Cu K}\alpha$ irradiation, operated at 40 kV and 200 mA in the 2θ range from 10° to 80°. Morphologies of samples were obtained by scanning electron microscope (SEM, Hitachi S4800). Surface chemical compositions of catalysts were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo Fisher K-Aepra ESCA). H_2 -temperature programmed desorption (H_2 -TPD) was performed on a Micromeritics Auto Chem II 2920 apparatus, equipped with a thermal conductivity detector (TCD). Prior to the test, the catalysts were temperature programmed from room temperature to 200°C for 30 min in Ar (30 mL min^{-1}). After cooling down to 40°C in Ar flow, the sample was adsorbed with 10% H_2/Ar (30 mL min^{-1}) for 30 min. Subsequently, H_2 -TPD was then carried out by increasing the temperature to 850°C with a ramp rate of 10°C min^{-1} in Ar flow.

The electrochemical impedance spectroscopy (EIS) were carried out in a standard three electrode system on a CHI 760E electrochemistry workstation (CH instruments, Chenhua Inc., Shanghai, China) in 0.5 M PBS buffer solution ($\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4$) as an electrolyte, where platinum wire and Ag/AgCl were used as counter and reference electrodes. Work electrode was prepared as follow: 5 mg catalyst was ultrasonically dispersed in a mixture solution containing 400 μL of

ethanol, 100 μL of isopropanol and 20 μL of 5 wt% Nafion, yielding a homogeneous ink. 10 μL of the ink was loaded onto a glassy carbon electrode (GC, 3 mm in diameter, 0.071 cm^2) with a constant catalyst loading of 0.5 mg/mL. After fully dried at room temperature, the electrode was finally used as the working electrode. The EIS tests were scanned from 0.1 Hz to 100 kHz at 1.5 V with AC amplitude of 5 mV.

Catalytic experiments

Reduction of p-NP to p-AP by excess NaBH_4 was carried out at room temperature in a standard 4 mL quartz cell. Typically, 2.5 mL of fresh NaBH_4 (0.01 M) was added into 25 μL of 4-NP aqueous solution (0.01 M) in the quartz cell. Then, 5 mg catalyst was added into the above solution quickly to start the reaction, and the absorption spectra in scanning range of 200-500 nm were monitored by UV-vis spectrophotometer at a 1.5 min interval. After 3 min of reaction time, the catalyst was separated from the reaction solution with a magnet, thoroughly washed with deionized water and ethanol, and then dried at 60°C overnight. The recovered catalyst was used for the next cycling reaction to investigate its reusability and stability.

1. H. Yang, J. Zha, P. Zhang, Y. Xiong, L. Su and F. Ye., *RSC Adv.*, 2016, **6**, 66963-66970.
2. J. Jin, X. Zhang and T. He., *J. Phys. Chem. C*, 2014, **118**, 24877-24883.

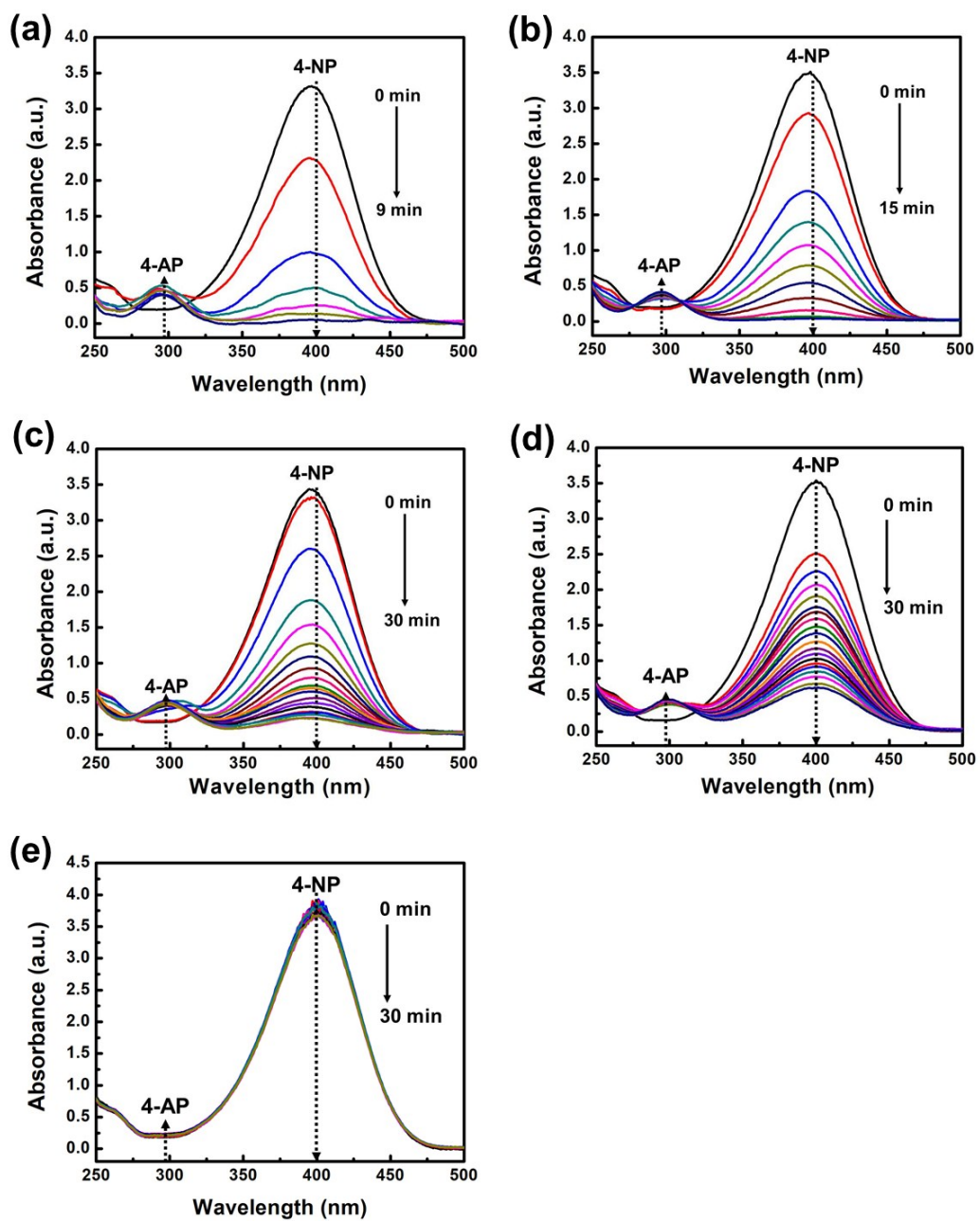


Fig. S1 Time-dependent UV-Vis spectra of 4-NP catalyzed by CoS (a), CoS₂ (b), Co₃O₄(c), commercial CoS (d), and no catalyst (e).

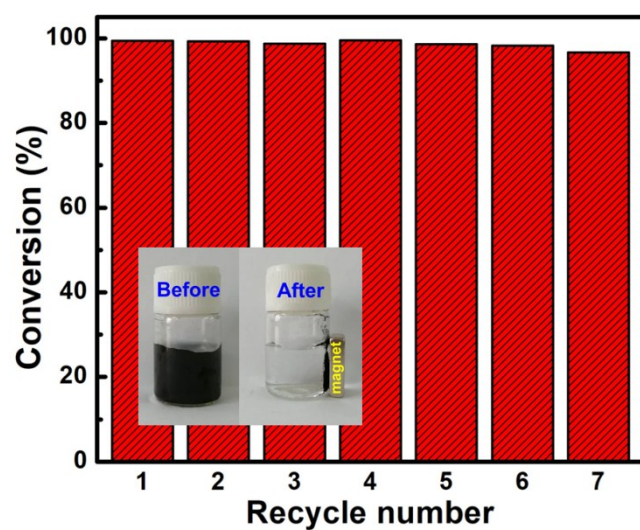


Fig. S2 Cycling activity of Co_9S_8 for 4-NP reduction (5 mg catalyst, 2.5 mL of fresh NaBH_4 (0.01 M), and 25 μL of 4-NP aqueous solution (0.01 M). Reaction time is 3 min. Inset shows separated process of Co_9S_8 using a magnet.

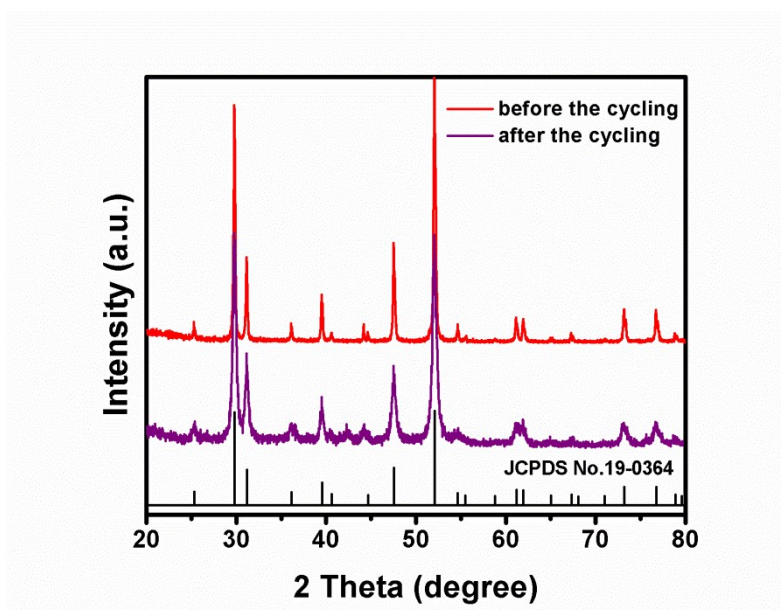


Fig. S3 XRD patterns of Co_9S_8 before and after the cycling.

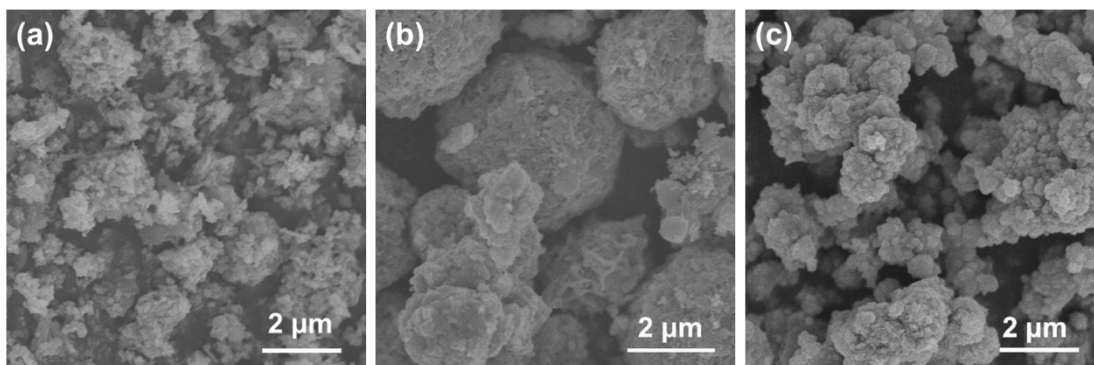


Fig. S4 SEM images of Co_9S_8 (a), CoS (b) and CoS_2 (c).

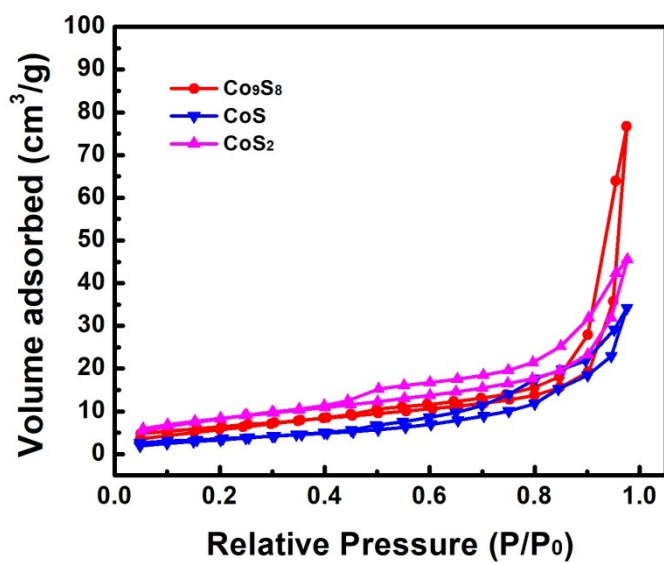


Fig. S5 N_2 adsorption-desorption isotherms of the Co_9S_8 , CoS and CoS_2 .

Table S1 Binding energy of Co 2p and S 2p.

Sample	Binding energy (eV)			
	Co^{3+}	Co^{2+}	S^{2-}	S_2^{2-}
Co_9S_8	778.4	780.7	161.5	-
	793.1	796.5	162.6	-
CoS	-	778.1	161.5	-
	-	793.1	162.6	-
CoS_2	-	778.1	-	162.8
	-	793.4	-	163.9