Electronic Supplementary Information for

Preparation of self-assembled cobalt hydroxide nanoflowers and the catalytic decomposition of cyclohexyl hydroperoxide

Min Wang, [a,b] *Jiping Ma,* [a,b] *Chen Chen,* [a] *Xi Zheng,* [a,b] *Zhongtian Du* [a] *and Jie Xu* *[a]

[a]State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian

116023 (P.R. China)

[b]Graduate University of Chinese Academy of Sciences, Beijing 100049 (P.R. China)

*Corresponding author: E-mail: **xujie@dicp.ac.cn**

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1. Materials

Cobaltous nitrate ($Co(NO_3)_2 \cdot 6H_2O$, 99%), cobaltous chloride ($CoCl_2 \cdot 6H_2O$. 99%), *n*-butanol (C_4H_9OH, 99%), cyclohexane (C_6H_{12}, 99%), aqueous ammonia (NH_3, 25-28%), ethanol (C_2H_5OH, 99.5%), sodium chloride (NaCl, 99%), hexamethylenetetramine (HMT, 99%), urea (99%), acetone (C_3H_6O, 99.7%) n-butylamine (99%) triethylamine(99%) and tri-n-butylamine(99%) were obtained from Tianjin Kermel Chemical Reagent Development Center, China. Poly (oxyethylene) nonylphenol ether (NP-7, Industrial Grade) was purchased from Dalian chemical ctl. Deionized water used in all experiments was obtained from a Milli-Q system (Millipore). Raw material of CHHP was a cyclohexane solution provided by Liaoyang Synthetic Fiber Co. Ltd. (China). After purification, it contains CHHP (0.309 mmol mL^{-1}) and adipic acid (0.017 mmol mL^{-1}).

2. Preparation of cobalt hydroxide

The synthesis of cobalt hydroxide samples utilized two water-in-oil microemulsions[1]. Microemulsion I was composed of NP-7 as the surfactant, *n*-butanol as the cosurfactant, cyclohexane as the hydrocarbon phase, and 1.8 M cobalt nitrate solution as the aqueous phase. The molar ratio of the microemulsions was: 1(NP-7)/4.32(n-Butanol) /15(cyclohexane)/15.56(water). Microemulsion II had the same constituents as microemulsion I except that the aqueous phase was a solution of aqueous ammonia instead of cobalt nitrate. Microemulsion II was slowly dripped to microemulsion I under mechanical stirring at room temperature, and stirred for 12 hours followed by addition of acetone to break the microemulsion. The resulting precipitate was centrifuged and subsequent washed a couple of times with ethanol to remove surfactants. The precipitate was dried at 80 °C in air. When organic amine was used as alkaline precipitant, organic amine was directly added to the emulsion containing 1.8 M cobalt nitrate solution. The molar ratio of organic amine to cobalt nitrate solution is 2.

The cobalt hydroxide microplatelet was prepared as reported.[2] Typically, $CoCl_2$, NaCl and hexamethylenetetramine (HMT) were dissolved in 200 mL of 9:1 mixture of deionized water and ethanol to give the final concentration of 10, 50 and 60 mM, respectively. The obtained precipitate was washed three times with ethanol and dried at 60 °C.

The microscale hierarchical sisal-like cobalt hydroxide was prepared as reported.[3] Typically, 2 mmol $CoCl_2$, 6 mmol urea and hexamethylenetetramine (HMT) were dissolved in 24 mL distilled water. The solution was then transferred into a stainless steel autoclave and heated in an oven at 100 °C for 10 h. After the autoclave was air-cooled to room temperature, the resulting product was filtered, washed with distilled water and absolute ethanol for several times, then dried under dried at 60 °C.

3. Decomposition of CHHP

The reaction was carried out in a 50ml stainless steel autoclave under magnetic stirring. In a typical procedure, 0.01 g catalysts and 10 mL cyclohexyl hydroperoxide solution were added in the reactor. The reaction was conducted at a temperature ranging from 70 to 120 °C for 30 min under N_2 atmosphere. The recycle tests were conducted at 110 °C for 30 min and the recycled catalyst were washed with ethanol before used. The products were identified by an Agilent 6890N GC/5973 MS detector and quantitated by an Agilent 7890D GC equipped with a OV-1701 column (30 m × 0.25 mm × 0.3 μm) and titration. After transformation of the hydroperoxide into cyclohexanol by adding triphenylphosphine to the reaction mixture, cyclohexanol and cyclohexanone were determined by internal standard method using nonane as an internal standard. The concentration of CHHP was determined by iodometric titration and the acid and ester by acid-base titration. The selectivity of cyclohexanol and cyclohexanone was calculated by combining the result of GC of cyclohexanol or cyclohexanone and the iodometric titration of CHHP.

4. Characterizations

The X-ray powder diffraction (XRD) patterns were obtained using Rigaku D/Max 2500/PC powder diffractometer with Cu Kα radiation (λ = 0.15418 nm). Fourier transform infrared (FT-IR) spectra were collected on a Bruker Tensor 27 FT-IR spectrometer in KBr media. The thermal gravity analysis (TGA) measurements were carried out under N_2 flow on a NETZSCH STA 409 PC instrument. Samples were heated at a heating rate of 10 ^{o}C/min from 35 to 800 ^{o}C in an N_2 flow of 30 mL/min. N_2 physical adsorption–desorption measurement was carried out at 77 K on an Autosorb-1 Quantachrome instrument. Samples were pre-degassed at 80 °C for about 10 h to remove water and other physically adsorbed species. Microstructures of the materials were examined by transmission electron microscopy (TEM, JEOL JEM-2000EX). Morphology of the sample surfaces was observed by field-emission scanning electron microscopy (SEM, FEI Quanta 200F).

5. Fig. S1
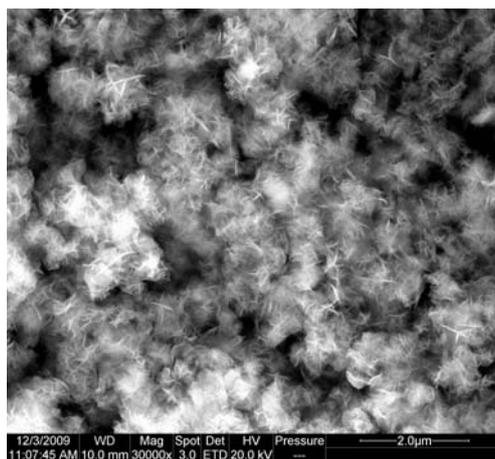
Fig. S1. Low magnification of SEM images of α-Co(OH)$_2$ nanoflowers
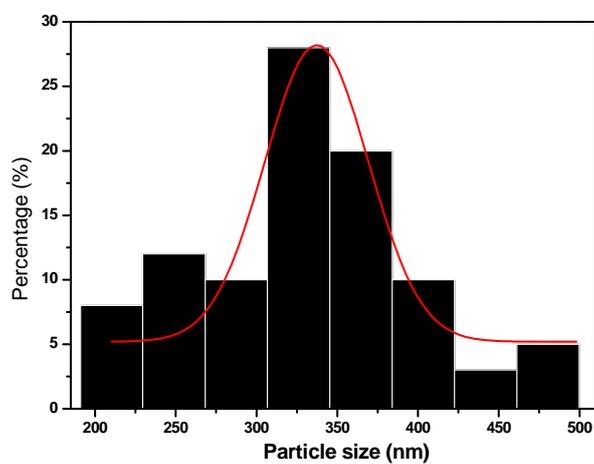
6. Fig. S2

Fig. S2. The particle size distribution of α-Co(OH)$_2$ nanoflowers

7. Fig. S3
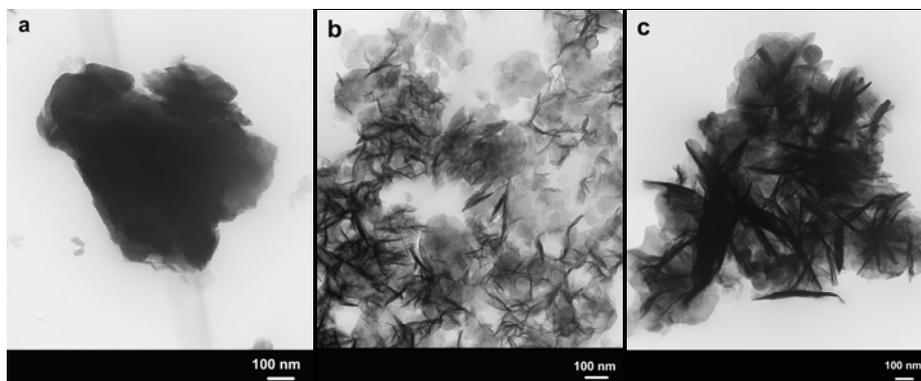
Fig. S3 TEM images of cobalt hydroxide prepared with different alkaline precipitant. a) n-butylamine; b) triethylamine; c) tri-n-butylamine.

8. TGA of the cobalt hydroxide samples

All the cobalt hydroxide samples prepared in different conditions shows weight loss around 180-230 °C. The total mass loss is estimated all higher than the theoretical value (19%) calculated from the thermal decomposition of cobalt hydroxides: Co $(OH)_2$ = CoO + H_2O. This indicates those nitrate anions are interlay in the layer of all the cobalt hydroxide samples.
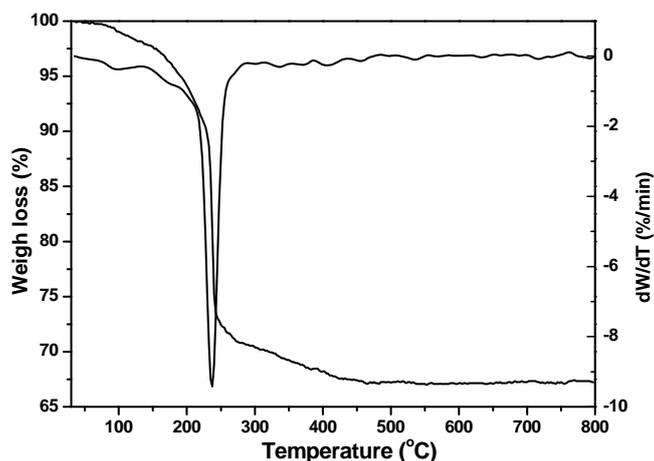
Fig. S4 TG-DTG curve of the samples prepared in the conditions: r=1, t=20 min.
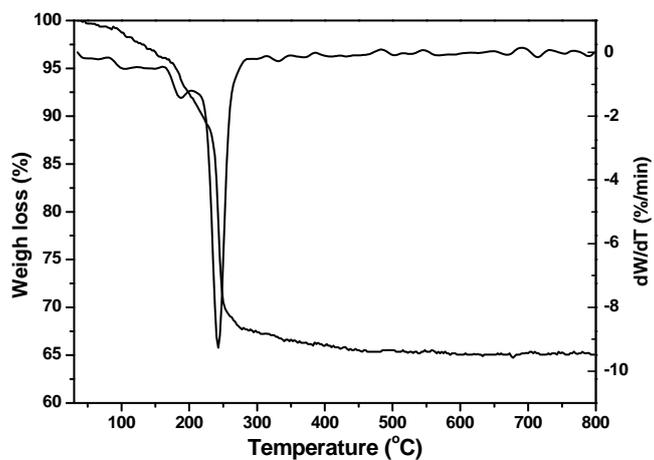
Fig. S5 TG-DTG curve of the samples prepared in the conditions: r=0.8, t=12 h.
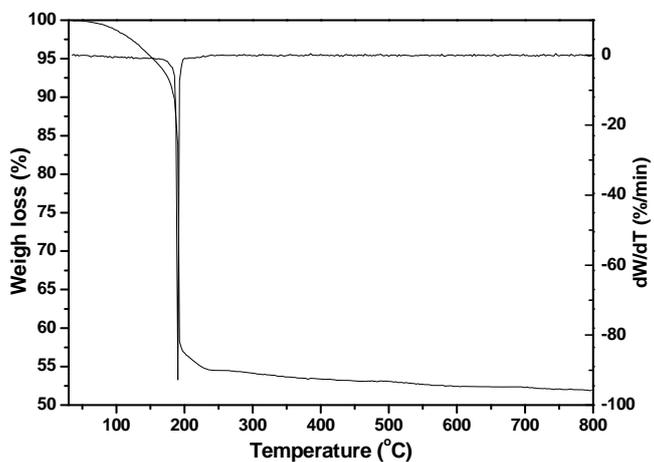
Fig. S6 TG-DTG curve of the samples prepared in the conditions: r=2, t=12 h.

9. Table S1

Table S1. Physic properties of the materials

Sample	BET surface areas (m^2/g)	Pore volume (cm^3/g)
Cobalt hydroxide microplatelets	43.5	0.15
Sisal-like cobalt hydroxides	27.7	0.06
Cobalt hydroxide nanoflowers	60.1	0.98

Reference

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3. B. X. Li, Y. Xie, C. Z. Wu, Z. Q. Li and J. Zhang, *Mater. Chem. Phys.*, 2006, **99**, 479.