

Electronic Supplementary Material (ESI) for New Journal of Chemistry.

This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2020

## Supporting information

### Autocatalytic route of CuO/Co<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> Nanocapsules as Excellent Performance Supercapacitor Materials

Yu Chen, Fang Cui\*, Qinghai Ma, Zhenhui Li, Linxu Xu, Jiajia Zhang, Zhiyi Chai,  
Wenlu Ma, and Tieyu Cui\*

School of Chemistry and Chemical Engineering, Harbin Institute of Technology,  
Harbin, 150001, P.R. China

Content	Page No.
Figure.S1	4
Figure.S2	5
Figure.S3	7
Figure.S4	8

Email address: cuifang@hit.edu.cn, cuit@hit.edu.cn

## **Experimental section**

**Reagents and apparatus.** All chemicals were used as received.  $C_6H_{12}O_6 \cdot H_2O$ ,  $Cu(Ac)_2$  and ethanol were purchased from Sinopharm group chemical reagent co. LTD.  $CoCO_3$  and hexadecyl trimethyl ammonium Bromide (CTAB) were purchased from Aladdin Industrial Corporation.  $C_2H_3BrO_2$ , (3-aminopropyl) triethoxysilane (APTES) and tetraethyl orthosilicate (TEOS) were purchased from Sigma-Aldrich Industrial Corporation.

The surface morphology was characterized by scanning electron microscopy (SEM, JSM-6700F, JEOL) and transmission electron microscopy (TEM, JEOL-2010, JEOL). The crystal structures of the metal oxides in nanocapsules were characterized by X-ray powder diffraction (XRD, D5005, Siemens) with  $Cu K\alpha$  irradiation. The characteristic peaks of materials were analyzed by Fourier transform infrared spectroscopy (FT-IR). The instrument was an AVATER 360 FT-

IR infrared spectrometer with potassium bromide as the reference tablet. In the test, KBr was taken as the background, the background peak is removed, and then scanning was carried out in the range of 400-4000  $\text{cm}^{-1}$  to obtain the corresponding infrared spectrogram. The electrochemical measurements including cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), galvanostatic charge/discharge (GCD) and Cyclic stability experiments were carried out by using a CHI 660e electrochemical workstation (CH Instruments, Inc., China).

**Synthesis of Cu@C nanosphere template.** The preparation of Cu@C nanosphere template adopted the method of hydrothermal carbonization. The 3.75 g (18.9 mmol)  $\text{C}_6\text{H}_{12}\text{O}_6 \cdot \text{H}_2\text{O}$  and 0.38 g (1.89 mmol)  $\text{Cu}(\text{Ac})_2$  were dissolved in 30 mL deionized water to form a  $\text{C}_6\text{H}_{12}\text{O}_6 \cdot \text{H}_2\text{O}$  solution (0.63 M), and then the solution was putted into a reaction kettle to react for 12 h at 180 °C. After centrifugal washing for many times by deionized water and ethanol (EtOH), Cu@C nanospheres template were obtained by drying for 8 h at 60 °C.

**Synthesis of CuO/Co<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanocapsules.** 0.40 g Cu@C nanosphere template, 0.30g as-prepared CoBA<sub>2</sub> (CoCO<sub>3</sub> and C<sub>2</sub>H<sub>3</sub>BrO<sub>2</sub>) and 0.26 g CTAB were dissolved in a mixed solvent (75 ml EtOH and 10 ml deionized water). After 30 min magnetic stirring and 30 min sonication, 0.4 ml APTES and 0.4 ml TEOS were added into system. Then the reaction was stirred at room temperature for 8 h. Finally, the sample was separated by centrifugation, and washed alternately with water and ethanol, then dried at 60 °C for 24 h. The brown sample was heated up to

550 °C by 10 °C/min in the muffle furnace for calcination, keeping for 90 min, and then cooled down naturally. Finally, the CuO/Co<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> was prepared.

**Synthesis of Co<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanocapsules.** First, 0.500 g of PVP was dissolved in 35 mL of ethanol, 0.400 g of carbon nanospheres (hydrothermal) was added as a template, 0.260 g of CTAB was used as a pore-forming agent, 0.400 mL APTES and 0.400 mL TEOS as a mixed silicon source. After the addition, ultrasonication and the mechanical agitation is alternately processed and fully dispersed in the solvent. 0.300 g of CoBA<sub>2</sub> precursor powder was dissolved in 10 mL water and 35 mL ethanol, and it was slowly released into the system then the reaction was stirred at room temperature for 8 h at room temperature. After the reaction, the solid product was separated by centrifugation, washed alternately with water and alcohol, and dried to obtain a reddish brown CoBA<sub>2</sub>@SiO<sub>2</sub>/C core shell intermediate powder. The prepared CoBA<sub>2</sub>@SiO<sub>2</sub>/C powder was calcined in a muffle furnace at a heating rate of 2 °C/min to 550 °C in air, kept for 90 min, and naturally cooled to room temperature. Co<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanocapsules were obtained.

**Electrochemical measurements.** Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) analysis, and electrochemical impedance spectroscopy (EIS) were carried out using a Chi-660e electrochemical workstation at room temperature. The test system was using a three-electrode system with the platinum slice as counter electrode and the standard calomel electrode as reference electrode. The electrolyte was selected the 6 M KOH aqueous solution. EIS was conducted in the frequency

range from 0.01 Hz to 10000 Hz.

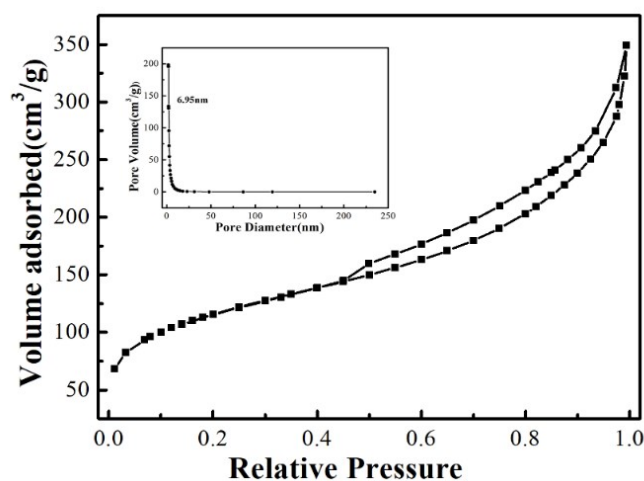


Fig.S1 N<sub>2</sub> adsorption/desorption isotherms and the corresponding pore size distributions(insets) of CuO/Co<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanocapsules

The N<sub>2</sub> physisorption-desorption tests of CuO/Co<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanocapsules was shown in Fig.S1. The isotherms of CuO/Co<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanocapsules could be categorized as type IV according to the IUPAC, indicating a mesoporous feature of the nanocapsules. The nanocapsule increased slightly with  $P/P_0=0.00-0.40$ . Faster adsorption increased was appeared at  $P/P_0=0.40-0.99$  due to capillary condensation. After the holes were filled, the adsorption isotherms reach equilibrium. Moreover, the big opening H<sub>4</sub> type hysteresis loop demonstrated the presence of large pores. The surface area of the nanocapsules was 396.20 m<sup>2</sup>·g<sup>-1</sup>, and the pore size was concentrated at 6.95 nm.

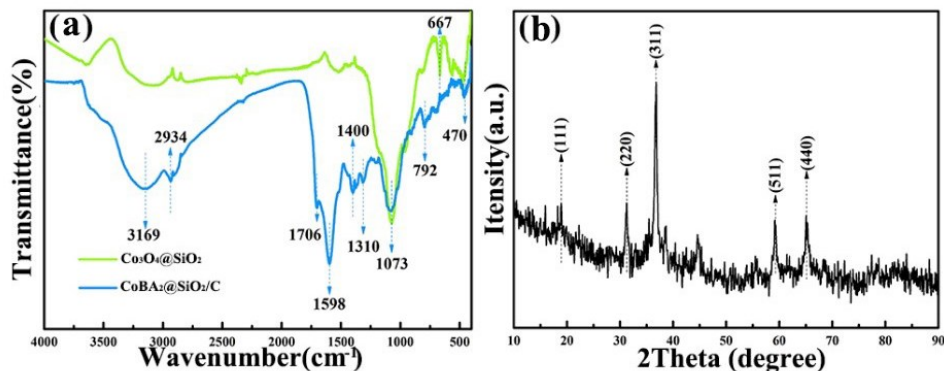


Fig.S2 FT-IR spectra (a) of  $\text{Co}_3\text{O}_4@\text{SiO}_2$  nanocapsules and  $\text{CoBA}_2@\text{SiO}_2/\text{C}$ ; XRD (b) of  $\text{Co}_3\text{O}_4@\text{SiO}_2$  nanocapsules after calcination

Fig.S2-a was the FT-IR spectrum of  $\text{CoBA}_2@\text{SiO}_2/\text{C}$  core shell intermediate and  $\text{Co}_3\text{O}_4@\text{SiO}_2$  nanocapsules sample before and after calcination. First, for the infrared spectrum of the  $\text{Co}_3\text{O}_4@\text{SiO}_2/\text{C}$  nanocomposite before calcination, the C-N stretching peak ( $1167\text{ cm}^{-1}$ ) belonging to the silicon source APTES and the imine peak at  $1125\text{ cm}^{-1}$  can be observed. In addition,  $2934\text{ cm}^{-1}$  was a characteristic peak of protonated amine groups; in addition,  $1706\text{ cm}^{-1}$ ,  $1598\text{ cm}^{-1}$  and  $1310\text{ cm}^{-1}$  were characterized as antisymmetric stretching vibrations, symmetric stretching vibrations and changes of carboxyl groups in intermediates, respectively. The angular vibration characteristic peak; in addition, regarding the silicon-containing organic functional group, the anti-symmetric stretching vibration peak of the Si-O bond at  $1073\text{ cm}^{-1}$ . At  $792\text{ cm}^{-1}$ , it was a stretching vibration peak of a silicon-carbon (Si-C) bond. At the same time, comparative analysis of the FT-IR spectrum of  $\text{Co}_3\text{O}_4@\text{SiO}_2$  nanocapsule samples, we can find that the characteristic peaks of organic groups such as proton amine and carboxyl group disappear, which indicated that the organic components in the  $\text{SiO}_2$  shell were completely removed after high temperature calcination treatment. The characteristic peak at  $667\text{ cm}^{-1}$

belonging to  $\text{Co}_3\text{O}_4$  appears, indicating the presence of  $\text{Co}_3\text{O}_4$  component in the calcined product; in addition, the antisymmetric stretching vibration belonging to the Si-O-Si network still appears at  $1073\text{ cm}^{-1}$ , indicating the  $\text{SiO}_2$  was stable and did not deteriorate during calcination; while the peak at  $792\text{ cm}^{-1}$  disappeared after the calcination process, indicating that the carbon sphere template had been removed from the interior of the nanocapsule. By comparing the material changes of the products before and after calcination, we found that the organic components in the nanocapsules were removed during the calcination process, leaving only the inorganic  $\text{SiO}_2$  shell and  $\text{Co}_3\text{O}_4$  nanoparticles, which was consistent with the expected results, which proved that we obtained the target product.

Fig.S2-b shown the XRD spectrum information of  $\text{Co}_3\text{O}_4@\text{SiO}_2$  nanocapsules. It can be seen that the crystal particles in the sample were cubic structures (JCPDS No.78-1970), the unit cell parameters were  $a = 8.085$ , and the  $2\theta$  value was  $18.9^\circ$ ,  $31.3^\circ$ ,  $36.8^\circ$ ,  $59.5^\circ$ ,  $65.2^\circ$ , corresponding to (111), (220), (311), (511), (440) crystal faces, respectively. These evidences indicated that the prepared nanocapsules were metal oxide particles are  $\text{Co}_3\text{O}_4$  crystal particles.

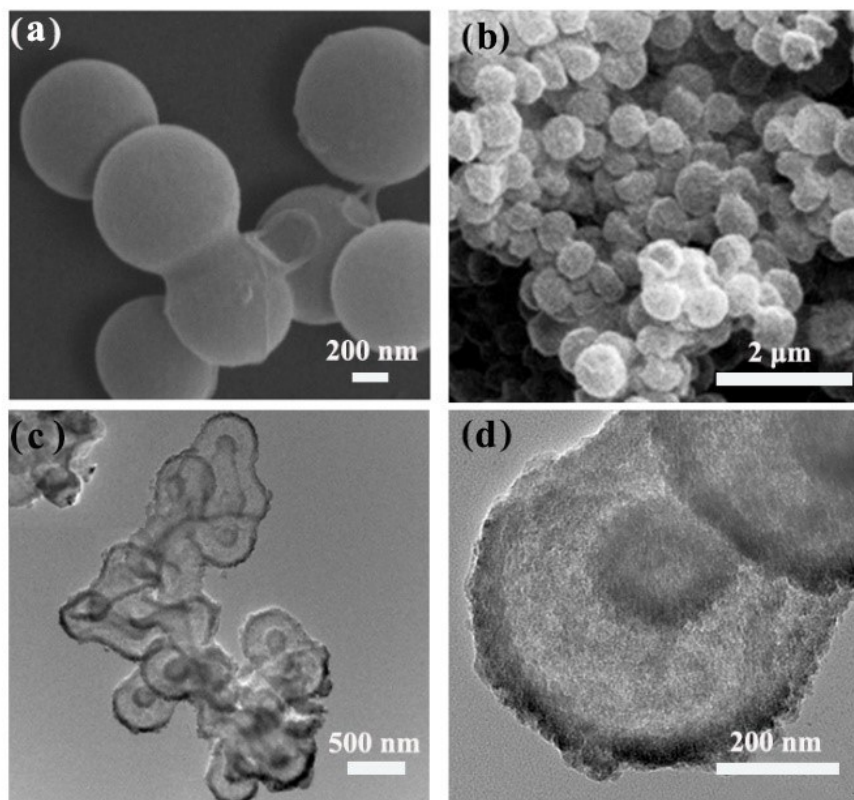


Fig.S3 SEM of  $\text{CoBA}_2@\text{SiO}_2/\text{C}$  intermediate (a),  $\text{Co}_3\text{O}_4@\text{SiO}_2$  nanocapsule (b) and TEM of  $\text{Co}_3\text{O}_4@\text{SiO}_2$  nanocapsule (c, d)

The microscopic surface morphology of  $\text{Co}_3\text{O}_4@\text{SiO}_2$  nanocapsules before and after calcination was shown in Fig. S3. Fig.S3-a was the SEM of the  $\text{CoBA}_2@\text{SiO}_2/\text{C}$  core shell intermediate, and Fig.S3-b was the SEM of the  $\text{Co}_3\text{O}_4@\text{SiO}_2$  nanocapsule . It can be known from the SEM photograph that after the  $\text{SiO}_2$  shell layer was deposited by sol-gel reaction on the surface of the C nanosphere, the spherical morphology of the core shell intermediate remains unchanged, the thickness of the shell layer increases slightly, and the rise roughness of the original smooth surface indicated that the surface of the template was coated with  $\text{SiO}_2$  shell. After calcination, the  $\text{Co}_3\text{O}_4@\text{SiO}_2$  nanocapsules still maintain a



good spherical morphology. The wall cracked or slightly collapsed during the calcination process, revealing the internal structure, and it was initially proved that the calcined material was a hollow structure. Therefore, preliminary conclusions indicated that a hollow  $\text{Co}_3\text{O}_4@\text{SiO}_2$  nanocapsule structure was experimentally prepared. It can be seen from the TEM Fig.S3-c and d of the nanocapsule that the product was a hollow nanocapsule structure, the particle size was mainly distributed at about 500 nm, and the thickness of the shell was about 15 nm.

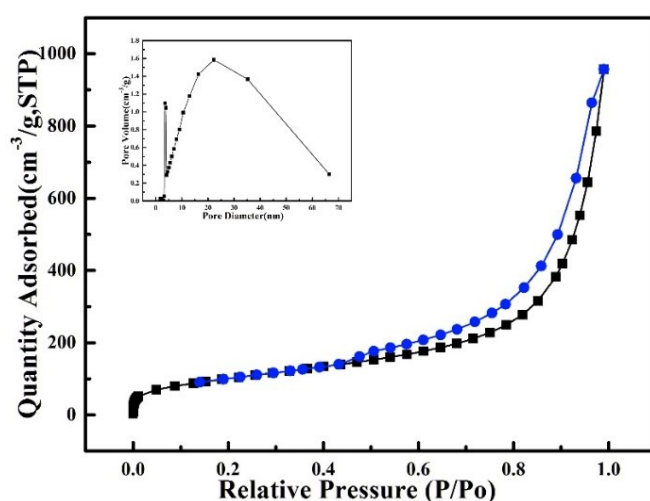


Fig. S4  $\text{N}_2$  adsorption and desorption curves and pore size distribution of  $\text{Co}_3\text{O}_4@\text{SiO}_2$  nanocapsules

The Fig. S4 proved that  $\text{Co}_3\text{O}_4@\text{SiO}_2$  nanocapsules pores were mesoporous pore structure types. In addition, the pore size distribution of  $\text{Co}_3\text{O}_4@\text{SiO}_2$  nanocapsules was shown in Fig. 4S. It can be seen that the pore size was concentrated at 3.538 nm and 22.285 nm. The smaller of the holes was the mesopores on the capsule wall, while the larger ones were the stacked holes between the capsules after the nanocapsules were brought together. Calculated by the BJH method, the

nanocapsule has a specific surface area of about 67.196 m<sup>2</sup>/g and an average pore diameter of about 6.293 nm.