

# Supplementary Information

## **Self-crosslinking Procedure to Yolk-Shell Au@Microporous Porous Carbon Nanospheres for Lithium–Sulfur Battery**

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## Experimental section

### Materials

All chemical reagents were employed directly without any further purification before use: Chloroauric acid ( $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ , analytical purity, Aladdin); Sodium citrate ( $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ , analytical purity, Aladdin); Polyvinylpyrrolidone ( $(\text{C}_6\text{H}_9\text{NO})_n$ , PVP, analytical purity, Aladdin); Ammonia aqueous solution ( $\text{NH}_3 \cdot \text{H}_2\text{O}$ , 25%, Guangzhou Chemical Reagent); Tetraethyl Orthosilicate ( $\text{Si}(\text{OC}_2\text{H}_5)_4$ , TEOS, Shanghai Reagent); 3-(methylacryloyl) propyltrimethoxy silane ( $\text{C}_{10}\text{H}_{20}\text{O}_5\text{Si}$ , KH-570, 97%, Aladdin); Sodium dodecyl benzene sulfonate ( $\text{C}_{12}\text{H}_{25}\text{C}_6\text{H}_4\text{SO}_3\text{Na}$ , SDBS, analytical purity, Damao Chemical Reagent); Sodium bicarbonate ( $\text{NaHCO}_3$ , analytical purity, Guangzhou Chemical Reagent); Chloromethylstyrene ( $\text{C}_9\text{H}_9\text{Cl}$ , CMS, analytical purity, Xiya Reagent); Divinylbenzene ( $\text{C}_6\text{H}_4(\text{CH}_2)_2$ , DVB, 80%, Aladdin); Tetrahydrofuran ( $(\text{CH}_2)_4\text{O}$ , THF); Ferric trichloride ( $\text{FeCl}_3$ , analytical purity, Fuchen Chemical Reagent); Dichloroethane ( $\text{C}_2\text{H}_4\text{Cl}_2$ , DEC, analytical purity, Chenyu Chemical Reagent); Acetone ( $\text{CH}_3\text{COCH}_3$ , analytical purity, Guangzhou Chemical Reagent); Hydrochloric acid ( $\text{HCl}$ , analytical purity, Guangzhou Chemical Reagent).

### Synthesis and modification of Au@SiO<sub>2</sub> core-shell nanoparticles

Typically, 237.5 mL of deionized water was vigorously stirred under reflux and 0.0216 g of  $\text{HAuCl}_4$  was added. The resultant solution was stirred until its boiling point was reached again. Then, 0.125 g of sodium citrate dissolved in 12.5 mL of deionized water was added, followed by refluxed for 30 min and then cooled down to room temperature. Subsequently, 0.0042 g of PVP dissolved in 1 mL of deionized water was added to the above mixture and stirred for 24 h at room temperature. The resulting

dispersion was centrifugated and the supernatant was removed. The volume of the concentrated colloid was then adjusted to 6 mL by dilution with water. For SiO<sub>2</sub> coating, 6 mL of the as-obtained Au nanoparticles in water was mixed with 19 mL of ethanol, followed by an ultrasonic mixing for 30 min. Then 0.8 mL of ammonia aqueous solution was added and mechanically stirred. After 10 min, a solution of 1.6 mL of TEOS in 19 mL of ethanol was injected into the above solution at the dropping rate about 1.0 mL min<sup>-1</sup> with a microinjector. The reaction was performed for 12 h. Subsequently, the obtained Au@SiO<sub>2</sub> nanospheres solution was added to 1.4 mL ammonia aqueous. After magnetic stirring for 10 min, a solution of 2 mL KH570 in 100 mL of ethanol was injected into the above solution at the dropping rate of 0.2 mL min<sup>-1</sup> with a microinjector. The amine-modified Au@SiO<sub>2</sub> nanoparticles were obtained by stirring at room temperature for 36 h. The product was collected by centrifugation, washed with ethanol for several times, and dispersed into 10 mL of a nanospheres ethanol solution.

#### **Synthesis of Au@SiO<sub>2</sub>@PCMS nanospheres**

Briefly, 100 mL of deionized water was poured into a 250 mL round-bottom bottle with air guide tube, reflux condensation tube, mechanical stirring rod and vacuum plug. Nitrogen was used to remove oxygen for 10 min. Subsequently, 0.03 g of SDBS and 0.24 g of NaHCO<sub>3</sub> were added, and the mixture was thoroughly stirred until the system was homogeneous, and nitrogen gas was continuously supplied for 10 min. Then the ethanol solution of amine-modified Au@SiO<sub>2</sub> dispersed by ultrasound was added and stirred until the system was homogeneous. Next, 4.8 mL of CMS and 0.2 mL of DVB

were added and stirred for 36 h at 30 °C. After the reaction, the product was washed and centrifuged three times with THF and ethanol, and dried at 60 °C for 6 hours, the Au@SiO<sub>2</sub>@PCMS nanospheres were obtained.

### **Fried-Crafts hypercrosslinking Reaction of Au@SiO<sub>2</sub>@PCMS nanospheres**

The hypercrosslinking reaction was carried out in accordance with the ratio of Au@SiO<sub>2</sub>@PCMS nanospheres: FeCl<sub>3</sub>: DCE=1 (g): 1.1 (g): 80 (mL). Au@SiO<sub>2</sub>@PCMS was swelled in DCE for 12 h, then heated to 80 °C, and anhydrous FeCl<sub>3</sub> was quickly added for 24 h. The reaction was terminated by adding acetone: hydrochloric acid = 3:1 (volume ratio) mixed solvent and maintaining the temperature at 80 °C for 30 min, and then centrifuging to obtain a solid, followed by washing with a mixed solution of acetone and hydrochloric acid for 6 h, and then washing with ethanol several times and H<sub>2</sub>O until pH is neutral, dried in a vacuum oven at 60 °C to obtain Au@SiO<sub>2</sub>@xPCMS.

### **Synthesis of YS-Au@MCNSs**

The Au@SiO<sub>2</sub>@xPCMS nanospheres were heated to 900 °C at 5 °C min<sup>-1</sup> for 3 h under N<sub>2</sub> flow, thus obtaining the Au@SiO<sub>2</sub>@MCNSs core-shell-shell nanoparticles. The resulting nanocomposite was treated using HF aqueous solution to remove SiO<sub>2</sub>, washed, filtrated and then dried, leading to formation of YS-Au@MCNSs.

### **Characterization**

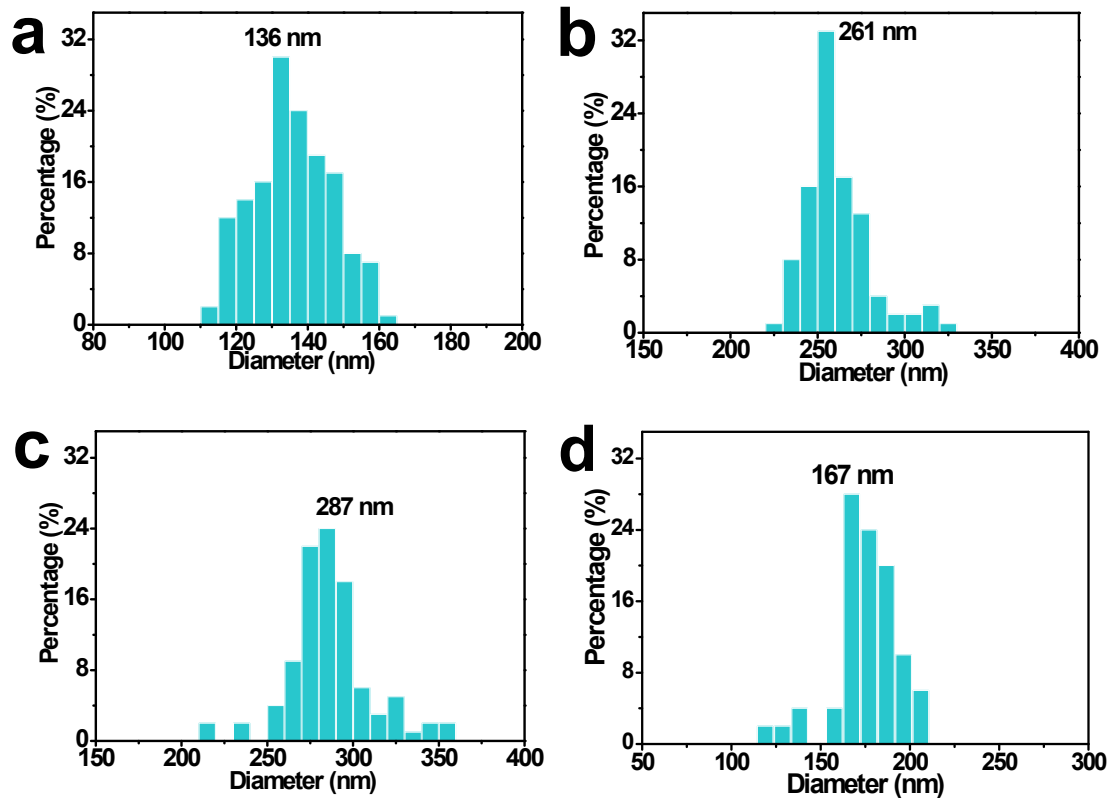
The microstructure of the samples was investigated by a JSM-6330F scanning electron microscope (SEM) and a FEI Tecnai G2 Spirit transmission electron microscope (TEM). About 100 nanoparticles in a SEM image were picked at random,

and then a statistical analysis of the particle size distribution was carried out. The maximum in the resulting particle size distribution curve was referred to as the average diameter of nanoparticles. XRD patterns were recorded on a D-MAX 2200 VPC diffractometer using Cu K radiation. Nitrogen adsorption measurements were carried out using a Micromeritics ASAP 2020 analyzer at 77K.

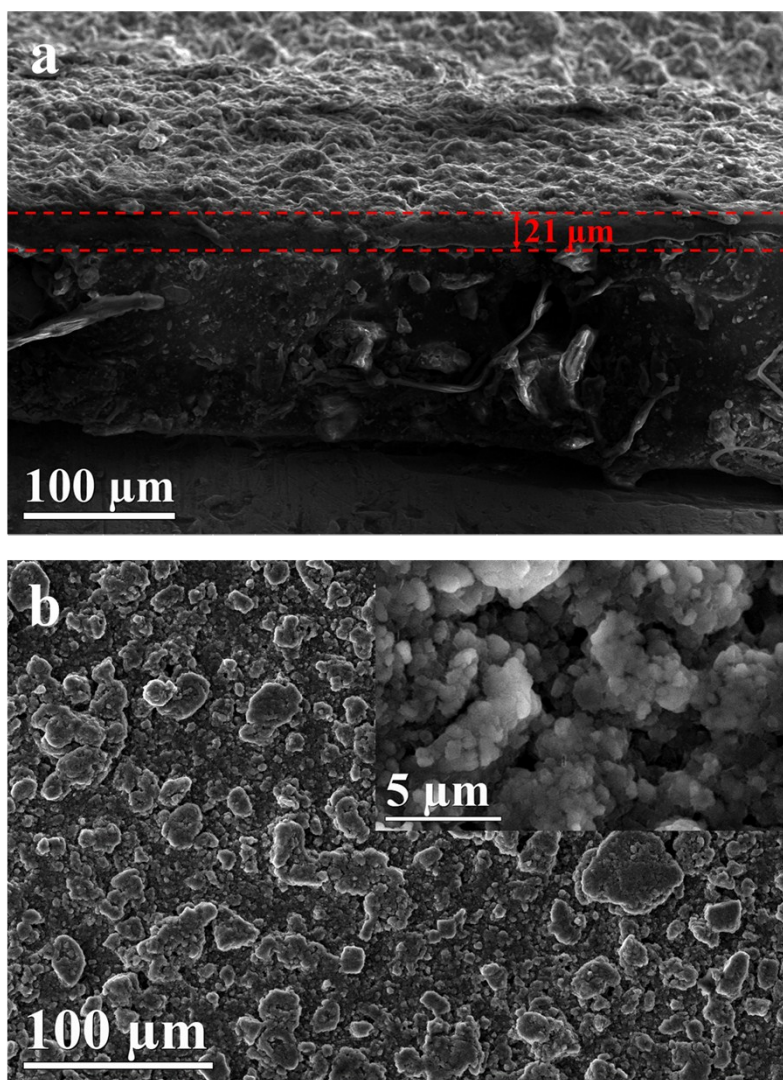
### **Cell fabrication and electrochemical measurements of lithium-sulfur batteries**

YS-Au@MCNSs was mixed with sulfur (55%:45% by weight) and then ground in a glass bottle, followed by heating at 155 °C for 12 h under N<sub>2</sub> flow. After cooling, the YS-Au@MCNSs/S nanocomposite was generated. Cathodes were prepared by mixing the YS-Au@MCNSs/S nanocomposite as the active material, conductive carbon black and polyvinylidene fluoride binder (8:1:1 by weight) in N-methyl-2-pyrrolidinone (NMP). The obtained slurry was spread on aluminum foil using a coater, followed by removing NMP at 60 °C under vacuum. Cathode round plates with diameter of 12 mm were prepared. The electrolyte was composed of a 1.0 M bis (trifluoromethane) sulfonimide lithium salt in 1,3-dioxolane and 1,2-dimethoxyethane (50%:50% by volume) with 0.2 M LiNO<sub>3</sub> additive. The sufficient electrolyte/sulfur (E/S) ratio is about 75 μL/mg for filling the dead volume of coin cells and full dissolution of polysulfides. CR2032 coin-type cells composing of cathode, a separator membrane and lithium plate as anode were assembled in an argon-filled glove box. All electrochemical performances were measured at room temperature. The galvanostatic cycling performance tests were conducted on a LAND instrument (model: CT2001A) within a voltage range of 1.7-2.8 V vs. Li/Li<sup>+</sup>. The cyclic voltammogram measurement was

performed on a Chenhua CHI electrochemical workstation at a scan rate of 0.1 mV/s. Electrochemical impedance spectroscopy was conducted using Chenhua CHI electrochemical workstation in the frequency range from 100 kHz to 10 mHz. The specific capacity was calculated based on the weight of sulfur loaded in the cathode electrode; and for 1 C rate, the current density corresponds to 1675 mA/g.

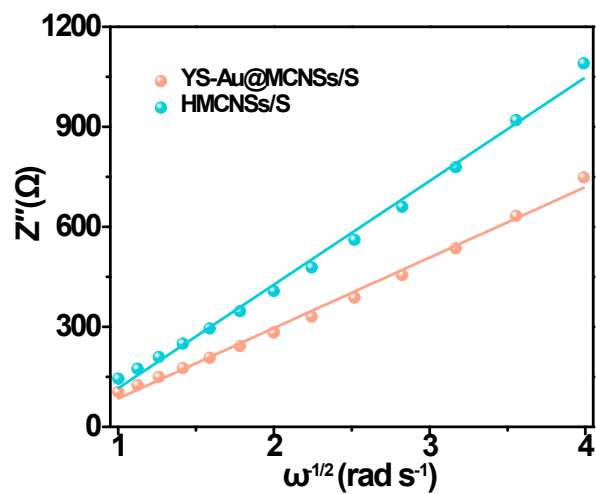


**Fig. S1.** Average diameter of (a) Au@SiO<sub>2</sub> (b) Au@SiO<sub>2</sub>@PCMS (c) Au@xPCMS and (d) YS-Au@MCNSs.



**Fig. S2.** (a) Cross-sectional view and (b) top view of the YS-Au@MCNSs/S electrode after 10 cycles at 0.1 C, the inset shows the top-view image in higher magnification.





**Fig. S3.** Plots of  $\omega^{1/2}$  versus- $Z''$  of different YS-Au@MCNSs/S and HMCNSs/S cathode.

**Table S1.** The kinetic parameter of YS-Au@MCNSs/S and HMCNSs/S cathode.

Key parameter	YS-Au@MCNSs/S	HMCNSs/S
$R_s$ ( $\Omega$ )	4.74	6.36
$R_{ct}$ ( $\Omega$ )	92.04	162.64
$\sigma$ ( $\Omega \text{ Hz}^{1/2}$ )	211.53	310.91
$D$ ( $10^{-19} \text{ cm}^2 \text{ s}^{-1}$ )	0.60	0.28