

Electronic Supplementary Information

Impact of the particle size of a metal-organic framework for sulfur storage in Li-S batteries

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Synthesis of ZIF-8 of ~2 μ m

ZIF-8 of ~2 μ m was prepared in ethanol without modulating agent. Typically, zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 2.975 g, 10 mmol) was dissolved in 100 mL of ethanol. A second solution was prepared by dissolving 2-methylimidazole (2-MeIM, 3.284 g, 40 mmol) in 100 mL of ethanol. The two solutions were combined under stirring, and the stirrer was stopped after 1 min. The mixed solution was kept at room temperature for 12 h, before the resulting white products were centrifuged and washed with plenty of ethanol. After the products were dried under vacuum at 60 °C overnight, white powders were obtained.

Synthesis of ZIF-8 of ~800 nm

ZIF-8 of ~800 nm was prepared in methanol with sodium acetate as the modulating agent. Typically, zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 2.975 g, 10 mmol) was dissolved in 100 mL of methanol. A second solution was prepared by dissolving 2-methylimidazole (2-MeIM, 3.284 g, 40 mmol) and sodium acetate trihydrate ($\text{NaOAc} \cdot 3\text{H}_2\text{O}$, 5.443 g, 40 mmol) in 100 mL of methanol. The two solutions were combined under stirring, and the stirrer was stopped after 1 min. The mixed solution was kept at room temperature for 12 h, before the resulting white products were centrifuged and washed with plenty of ethanol. After the products were dried under vacuum at 60 °C overnight, white powders were obtained.

Synthesis of ZIF-8 of ~200 nm

ZIF-8 of ~200 nm was prepared in methanol without modulating agent. Typically, zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 2.975 g, 10 mmol) was dissolved in 200 mL of methanol. A second solution was prepared by dissolving 2-methylimidazole (2-MeIM, 6.568 g, 80 mmol) in 200 mL of methanol. The two solutions were combined under stirring, and the stirrer was stopped after 1 min. The mixed solution was kept at room temperature for 48 h, before the resulting white products were centrifuged and washed with plenty of ethanol. After the products were dried under vacuum at 60 °C overnight, white powders were obtained.

Synthesis of ZIF-8 of ~70 nm

ZIF-8 of ~70 nm was prepared in methanol without modulating agent. Typically, zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 2.975 g, 10 mmol) was dissolved in 100 mL of methanol. A second solution was prepared by dissolving 2-methylimidazole (2-MeIM, 3.284 g, 40 mmol) in 100 mL of methanol. The two solutions were combined under stirring, and the stirrer was stopped after 1 min. The mixed solution was kept at room temperature for 12 h, before the resulting white products were centrifuged and washed with plenty of ethanol. After the products were re-dispersed in water and freeze-dried for 48 h, white powders were obtained. The use of freeze-drying instead of drying under vacuum or by heating prevents severe agglomeration of the fine powders.^{1, 2} We note that the freeze-

dried 70 nm ZIF-8 powders can be easily re-dispersed in polar solvents by mild sonication, in contrast to the previous report, in which similar ZIF-8 nanoparticles cannot be re-dispersed any more after a drying step at 40 °C in air.³

Synthesis of ZIF-8 of ~15 nm

ZIF-8 of ~15 nm was prepared in methanol with triethylamine as the modulating agent. Typically, zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 2.975 g, 10 mmol) was dissolved in 100 mL of methanol. A second solution was prepared by dissolving 2-methylimidazole (2-MeIM, 3.284 g, 40 mmol) and triethylamine (TEA, 4.048 g, 40 mmol) in 100 mL of methanol. The two solutions were combined under stirring, and the stirrer was stopped after 1 min. The mixed solution became turbid very soon and was kept at room temperature for 2 h, before the gel-like products were separated with high-speed centrifugation (20000 rpm*15 min). The products were washed with plenty of ethanol with sonication and centrifugation to fully remove the organic residues. After the products were re-dispersed in water and freeze-dried for 48 h, white ultrafine powders were obtained. The use of freeze-drying here is essentially important. Fig. S4 shows the difference in appearances and nitrogen adsorption properties between the freeze-dried sample (15 nm-F) and the one directly dried under vacuum in an oven (15 nm-V). In sharp contrast to 15 nm-F, being ultrafine white powders, directly drying under vacuum yielded transparent “crystals” (15 nm-V), which can be picked up by tweezers. It is not surprising that 15 nm-F can be easily re-dispersed in polar solvents simply by stirring or shaking, but 15 nm-V cannot (after ground) even with sonication. Nitrogen adsorption experiments show that 15 nm-F has more accessible micropores (higher adsorption volume in the low relative pressure range) than 15 nm-V, with much larger interparticle space (see Fig. S4b): both indicate a much looser packing of the nanoparticles given by freeze-drying. This feature plays an important role in ensuring the complete infiltration of molten sulfur in the following step to prepare the S@ZIF-8 composite. Using the 15 nm-V sample to prepare the S@ZIF-8 composite would leave obvious diffraction peaks of crystalline sulfur in the PXRD pattern (data not shown), indicative of an incomplete infiltration of molten sulfur and a considerable number of inaccessible micropores in the directly dried sample.

Synthesis of S@ZIF-8 composites

ZIF-8 prepared from an alcohol system has the advantage of being easy-to-activate.⁴ A 24 h degassing process at room temperature or a 6 h one at 120 °C is enough to achieve similar porosity with a 12 h one at 150 °C. To prepare the S@ZIF-8 composite, degassed ZIF-8 powders were first ground with sulfur of the desired ratio (see Table S2) in an argon-filled glove box, and then subjected to a heating process in a sealed autoclave at 155 °C for 12 h for the 2 μm , 800 nm and 200 nm ZIF-8, 6 h for the 70 nm one and 2 h for the 15 nm one (for stability concerns), respectively.

Characterization

The structure and morphology of the samples were characterized by powder X-ray diffraction (PXRD, Rigaku D/max 2000 diffractometer, Cu K α), scanning electron microscopy (SEM, Hitachi S4800) and transmission electron microscopy (TEM, JEM 2100, 200 kV). Nitrogen adsorption measurements were conducted on a NOVA gas sorption analyzer (Quantachrome Instruments) at 77 K. Brunauer-Emmett-Teller (BET) surface areas, pore volumes, and pore size distributions were obtained by analyzing the adsorption isotherms with Quantachrome NovaWin software (version 11.03). The fitting range for BET surface areas was $0.005 < p/p_0 < 0.05$.⁵ QSDFT equilibrium model was used to calculate the pore size distributions.

Electrochemistry

To prepare the working electrodes, 60 wt% S@ZIF-8 composite, 30 wt% conductive carbon black (CB) and 10 wt% poly(vinylidene fluoride) (PVDF) binder were mixed in N-methyl-2-pyrrolidinone (NMP) to form a slurry. Sonication was used to improve the dispersion. The slurry was then coated on aluminium current collectors and dried at 60 °C over 24 h. Coin cells of 2032-type with a metallic Li anode were assembled. 0.6 M bis-(trifluoromethanesulfonyl)imide lithium (LiTFSI) with 0.1 M LiNO₃ in a mixed solvent of 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) (v/v 1:1) was used as the electrolyte.⁶ The active material loading was about 1.0 mg cm⁻² and the total amount of electrolyte added to each cell was 60 μ L. The batteries were cycled between 1.8~2.8 V galvanostatically with LAND CT2001A instruments (Wuhan, China). To obtain sufficient statistical significance, at least five batteries for the same sample were always measured under identical conditions. Maximum capacities were recorded and averaged over batteries arithmetically. Capacity decays (in terms of mAh g⁻¹) in each cycle were recorded and averaged first over cycles (to get average decay for a certain battery) then over batteries arithmetically. Capacity retentions over 250 cycles for each battery were also calculated and averaged arithmetically.

References

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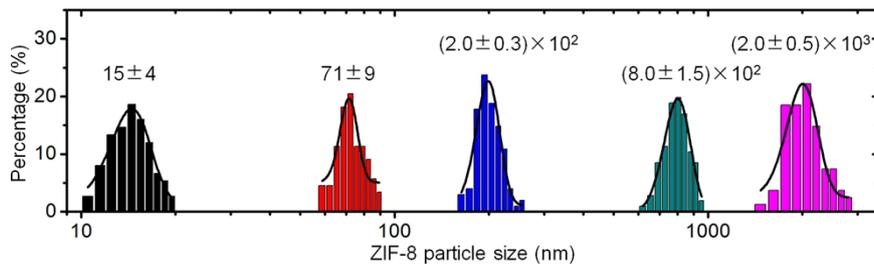


Fig. S1. Particle size distributions of the ZIF-8 samples. Obtained from analyses of ~ 100 particles for each size from the SEM or TEM images.

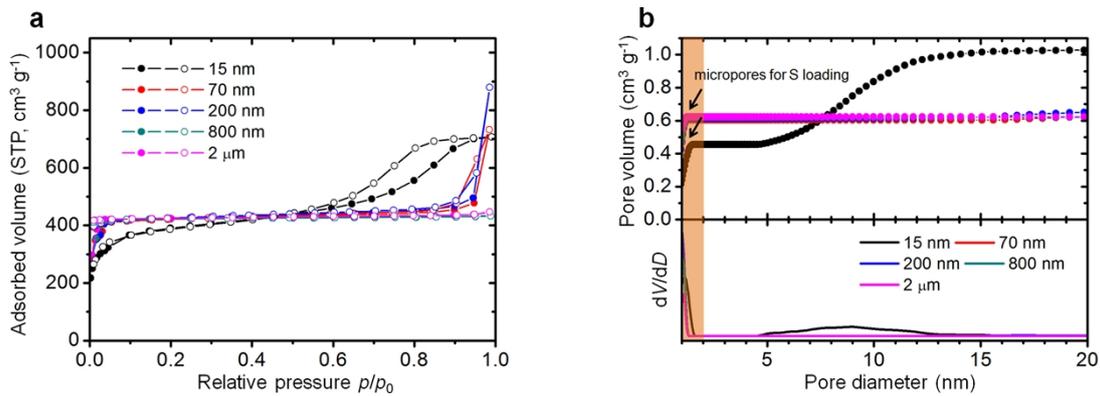


Fig. S2. Nitrogen adsorption measurements for the ZIF-8 samples at 77 K. (a) Adsorption isotherms. (b) Pore size distributions calculated by QSDFT equilibrium model. Sulfur loading was based on the micropore volumes of the samples.

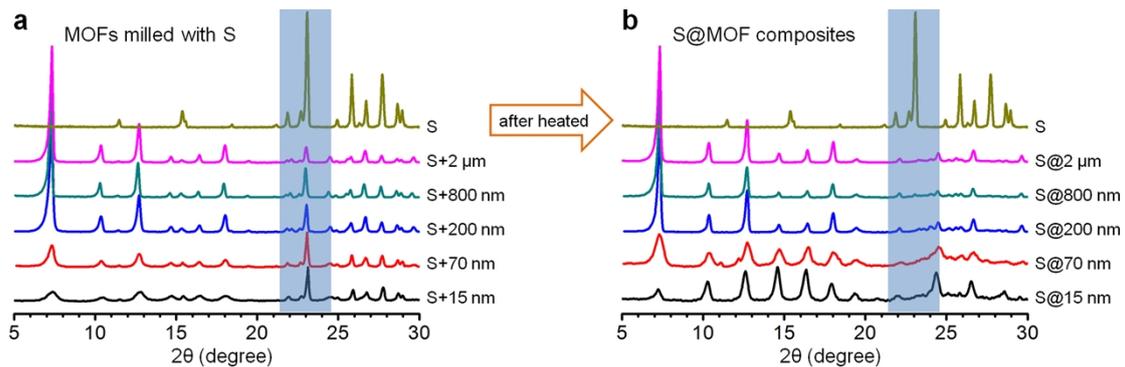


Fig. S3. Characterization of the sulfur loading for the ZIF-8 samples. PXRD patterns of sulfur and different ZIF-8 samples (a) after milled in the glovebox and (b) after heated at 155 °C. Crystalline sulfur becomes almost undetectable after the heating treatment while the structure of ZIF-8 is well-maintained.

Table S1. Pore characterization results given by nitrogen adsorption measurements at 77 K.

	S_{BET} ($\text{m}^2 \text{g}^{-1}$) ^a	V ($\text{cm}^3 \text{g}^{-1}$)	
		$p/p_0 = 0.05$ ^b	$d < 2 \text{ nm}$ ^c
15 nm	1393	0.50	0.46
70 nm	1662	0.64	0.60
200 nm	1672	0.64	0.61
800 nm	1678	0.65	0.62
2 μm	1679	0.65	0.62

^a Fitting range: $0.005 < p/p_0 < 0.05$

^b Calculated based on the adsorption volumes at $p/p_0 = 0.05$

^c Given by QSDFT calculation for reference

Table S2. Sulfur contents in the composites and in the cathodes.

	S/MOF (g g^{-1}) ^a	S content (%)	
		composite	cathode ^b
15 nm	0.91	48	29
70 nm	1.17	54	32
200 nm	1.17	54	32
800 nm	1.18	54	32
2 μm	1.19	54	33

^a S/MOF = (density of molten sulfur, 1.82 g cm^{-3}) \times (pore volume at $p/p_0 = 0.05$)

^b PVDF 10 wt% + CB 30 wt% + composite 60 wt%

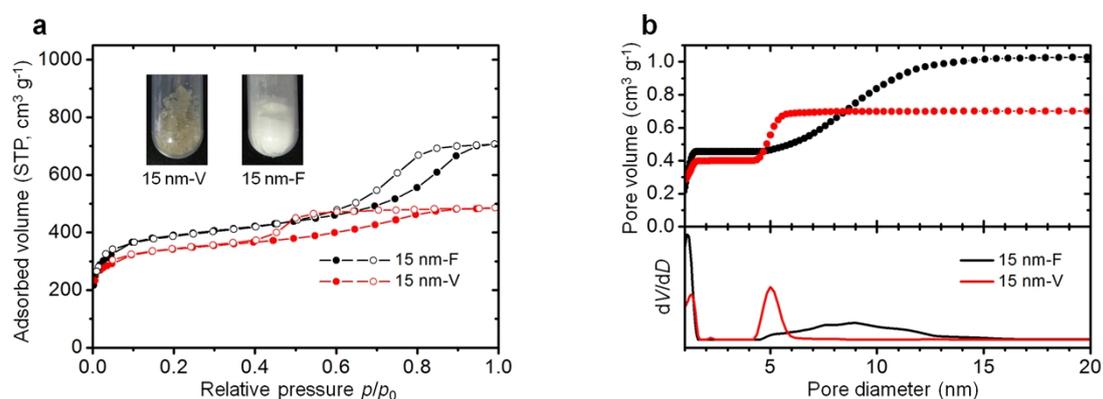


Fig. S4. Effects of drying methods in preparing ZIF-8 of 15 nm. (a) Nitrogen adsorption isotherms of the freeze-dried sample (15 nm-F) and the one directly dried under vacuum (15 nm-V). Insets are the appearances of the two samples. (b) Pore size distributions calculated by QSDFT equilibrium model. Freeze-drying method can help to prepare ultrafine MOF nanoparticles with looser packing and more accessible micropores than drying under vacuum or by heating.