Supporting Information

Fine-tuning of ZIF-67 Pore Sizes via Ligand Exchange: Optimal Active Site Interactions for Iodine Capture

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1. Experimental sections

1.1 Characterization

Powder X-ray diffraction (PXRD) patterns were collected at room temperature in a Rigaku D/MAX-2500PC diffractometer (Rigaku Co., Japan) using Cu $K\alpha_1$ radiation (λ = 0.15406 nm) operated at 40 kV and 100 mA. Field emission scanning electron microscopy (FE-SEM) images were taken at 5 kV with a SUPRA-55 microscope. Transmission electron microscopy (TEM) images were taken with a JEOL 2100 microscope. Thermogravimetric analysis (TGA) (SDTQ600) of the activated powder was performed from room temperature to 800 °C with a scan rate of 10 °C/min under a Nitrogen atmosphere. N_2 adsorption and desorption isotherms were measured at 77 K using a Micromeritics ASAP 2460 sorption analyzer. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas using adsorption data in a relative pressure range from 0.05 to 0.30. The pore size distributions and pore volume were derived from the desorption branches of the isotherms. X-ray photoelectron spectroscopy (XPS) analysis was conducted on a PHI 5000 VersaProbe II spectrometer equipped with an Al Kα X-ray source operating at 12 kV and 6 mA. UV-Vis absorption spectra were collected using a UV-Vis spectrophotometer (SPECORD® 210 PLUS) in the wavelength range from 200 to 700 nm.

Table S1 Pore structure parameters of ZIF-67 and ZIF-67-IM materials

Sample	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore diameter (nm)
ZIF-67	1327	0.74	2.24
ZIF-67-IM	1590	0.93	2.33

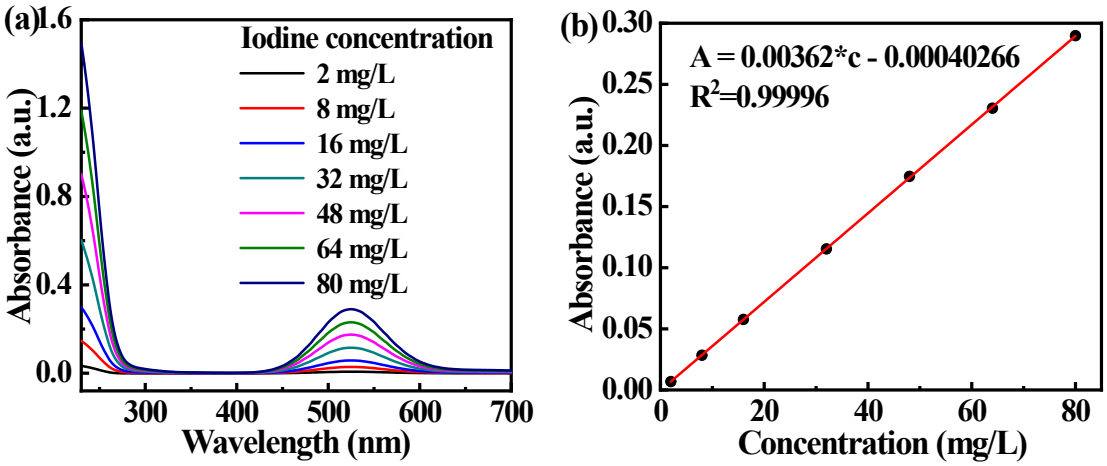

Fig. S1 (a) Absorption curves of standard iodine/cyclohexane solutions; (b) Absorbance/concentration standard curve.

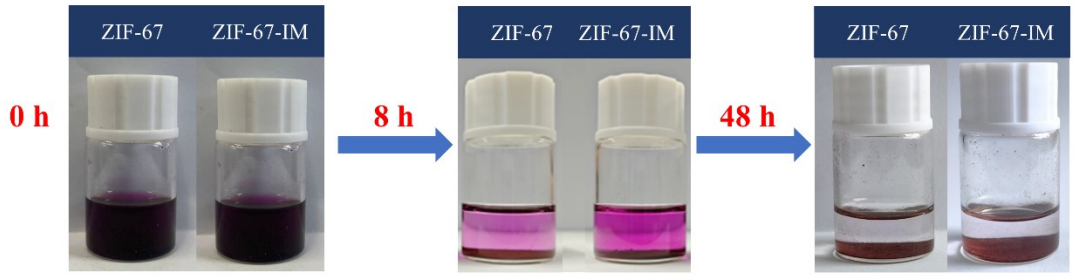

Fig. S2 The color change of solution during the adsorption of iodine by ZIF-67 and ZIF-67-IM (after 48 h of adsorption).

2. I_2 adsorption studies

2.1 Adsorption kinetics

The quantitative basis of Spectrophotometry-Lambert-Beer law:

$$\mathrm{A} = \lg\frac{I_0}{I} = abc \tag{S1}$$

The calculation formulas for the removal rate of iodine molecules and the adsorption capacity of the adsorbent during the adsorption process are as follows:

$$\text{Removal efficiency}(\%) = \frac{C_0 - C_t}{C_0} \times 100\% \tag{S2}$$

$$q_t = \frac{\mathrm{V}\left(C_0 - C_t\right)}{m} \tag{S3}$$

The pseudo-first-order model is:

$$\frac{dq_t}{dt} = k_1\left(q_e - q_t\right) \tag{S4}$$

The linear expression of the pseudo-first-order kinetic equation obtained by integration is as follows:

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1}{2.303}t \tag{S5}$$

The pseudo-second-order model is:

$$\frac{dq_t}{dt} = k_2\left(q_e - q_t\right)^2 \tag{S6}$$

The linear expression of the pseudo-second-order dynamic equation obtained by integration is as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e{}^2} + \frac{t}{q_e} \tag{S7}$$

2.2 Adsorption equilibrium

The Langmuir model assumes that a uniform surface is formed by monolayer adsorption, and the equation is as follows:

$$q_e = \frac{q_{\max} k_L C_e}{1 + k_L C_e} \tag{S8}$$

The linear Langmuir model is expressed as the following equation:

$$\frac{C_e}{q_e} = \frac{1}{k_L q_{\max}} + \frac{C_e}{q_{\max}} \tag{S9}$$

The Freundlich equation is based on the assumption of non-uniform adsorption on the adsorbent surface, and the expression is as follows:

$$q_e = k_F C_e^{1/n_F} \tag{S10}$$

The Freundlich model is expressed as the following equation:

$$\ln q_e = \ln k_F + \frac{1}{n_F} \ln C_e \tag{S11}$$

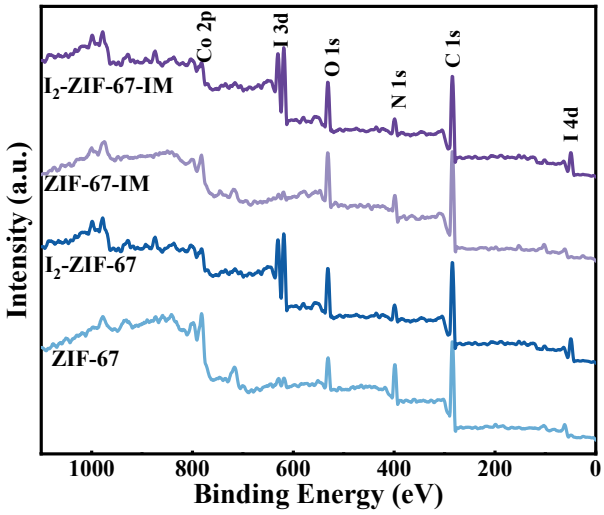

Fig. S3 XPS survey spectra of ZIF-67 and ZIF-67-IM before and after adsorption of I_2

Table S2 The pseudo-first-order kinetic and pseudo-second-order kinetic model parameters of the iodine adsorption process of ZIF-67 and ZIF-67-IM materials.

Sample	Pseudo-first-order model			Pseudo-second-order model		
	k_1 (h^{-1})	q_e ($mg \cdot g^{-1}$)	R^2	k_2 ($g \cdot mg^{-1} \cdot h^{-1}$)	q_e ($mg \cdot g^{-1}$)	R^2
ZIF-67	0.157	562.5	0.962	0.001	900.9	0.999
ZIF-67-IM	0.136	541.3	0.931	0.001	885.0	0.999

Table S3 Langmuir and Freundlich model parameters of ZIF-67 and ZIF-67-IM iodine adsorption isotherms.

Sample	Langmuir model			Freundlich model		
	k_L ($L \cdot mg^{-1}$)	q_{max} ($mg \cdot g^{-1}$)	R^2	k_F ($mg^{1-n} \cdot L^n \cdot g^{-1}$)	n_F	R^2
ZIF-67	0.020	2618.2	0.958	371.194	3.369	0.916
ZIF-67-IM	0.018	2560.9	0.958	326.618	3.224	0.938