In situ synthesis of zeolitic imidazolate frameworks /carbon nanotubes composites with enhanced CO_2 adsorption

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SUPPORTING INFORMATION

1. Theoretical product yield in ideal reaction

In ideal reaction, the theoretical product yield $W_{(ZIFs)}$ can be calculated by Eq. (S1):

$$W_{(ZIFs)} = \frac{Mw_{(ZIFs)} \times W_{(zinc\ nitrate)}}{Mw_{(zinc\ nitrate)}} \quad \text{(S1)}$$

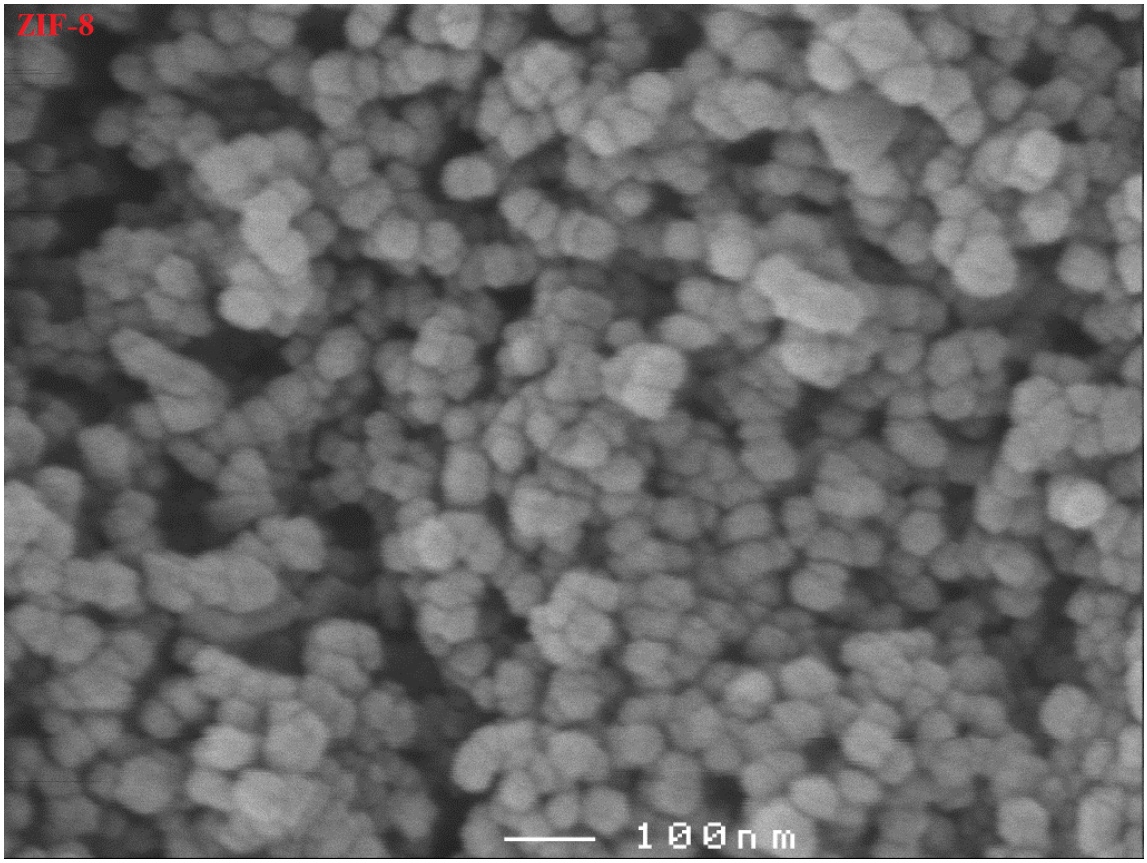
Where $Mw_{(ZIFs)}$ and $Mw_{(zinc\ nitrate)}$ are the molecular weight of ZIF-8 and $Zn(NO_3)_2{\cdot}6H_2O$, respectively. When $W_{(zinc\ nitrate)}$ is equal to 0.5866 g, the value of $W_{(ZIFs)}$ can be obtained as 0.4527 g.

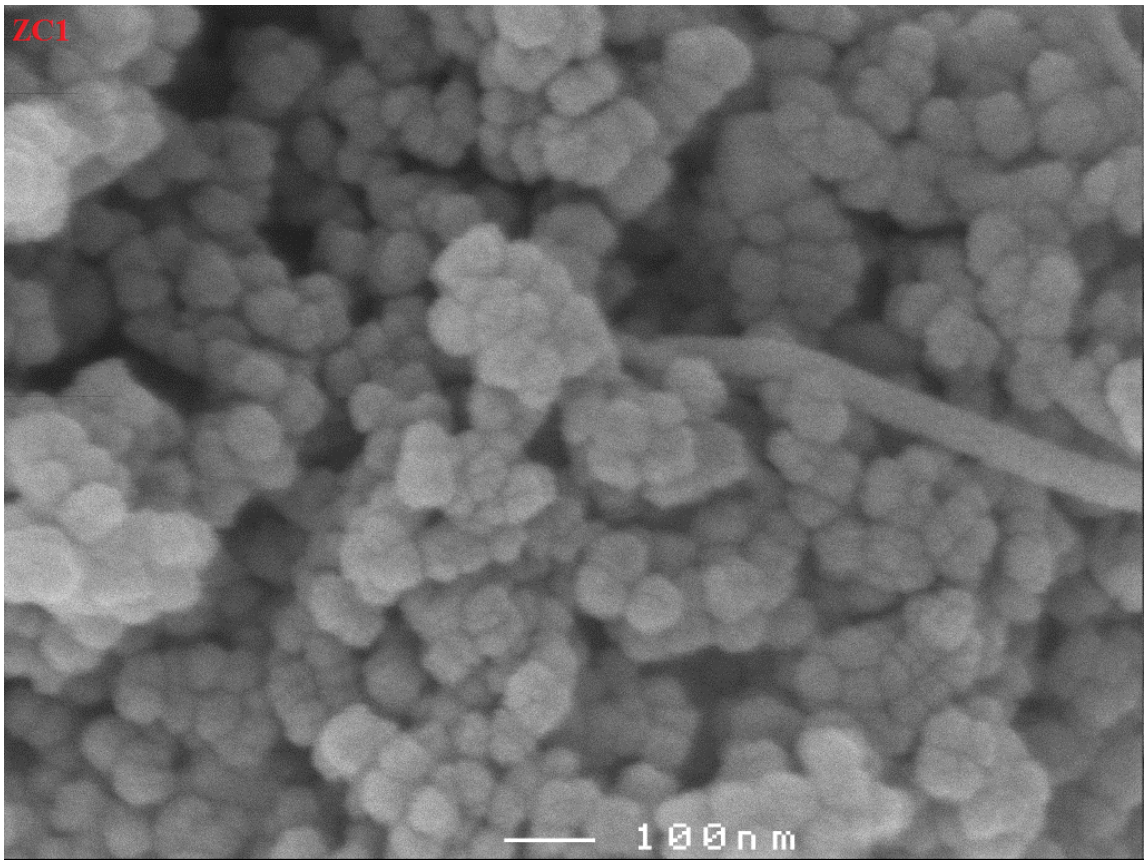
2. The corresponding percentage of incorporated CNTs in the composites

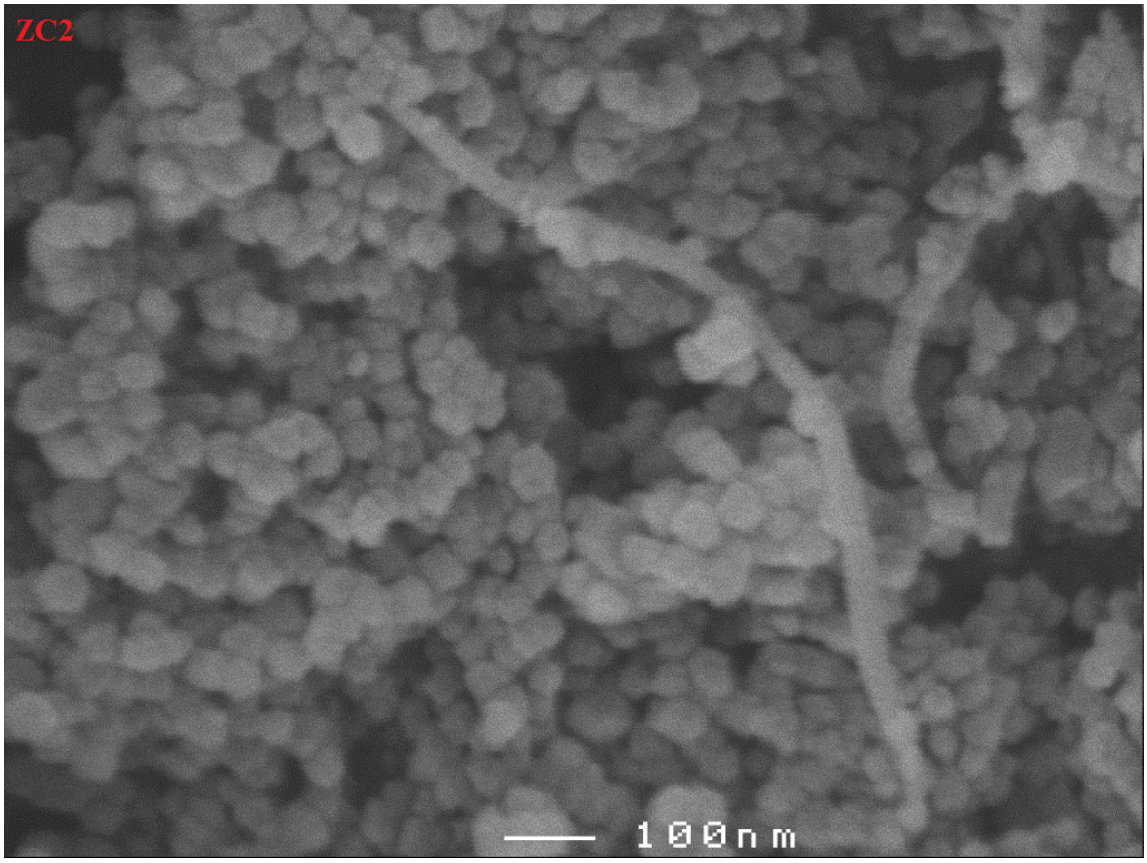
The corresponding percentage of incorporated CNTs can be calculated by Eq. (S2), and the values are 1.11, 3.13, 6.28, 10.01, 14.89 and 20.88 wt.% of the theoretical final product, respectively. The synthesized ZIF-8/CNTs composites are referred to as ZCn with n from 1 to 6, for the different CNTs contents (5.1, 14.7, 30.5, 50.6, 79.6 and 120.1 mg, respectively)

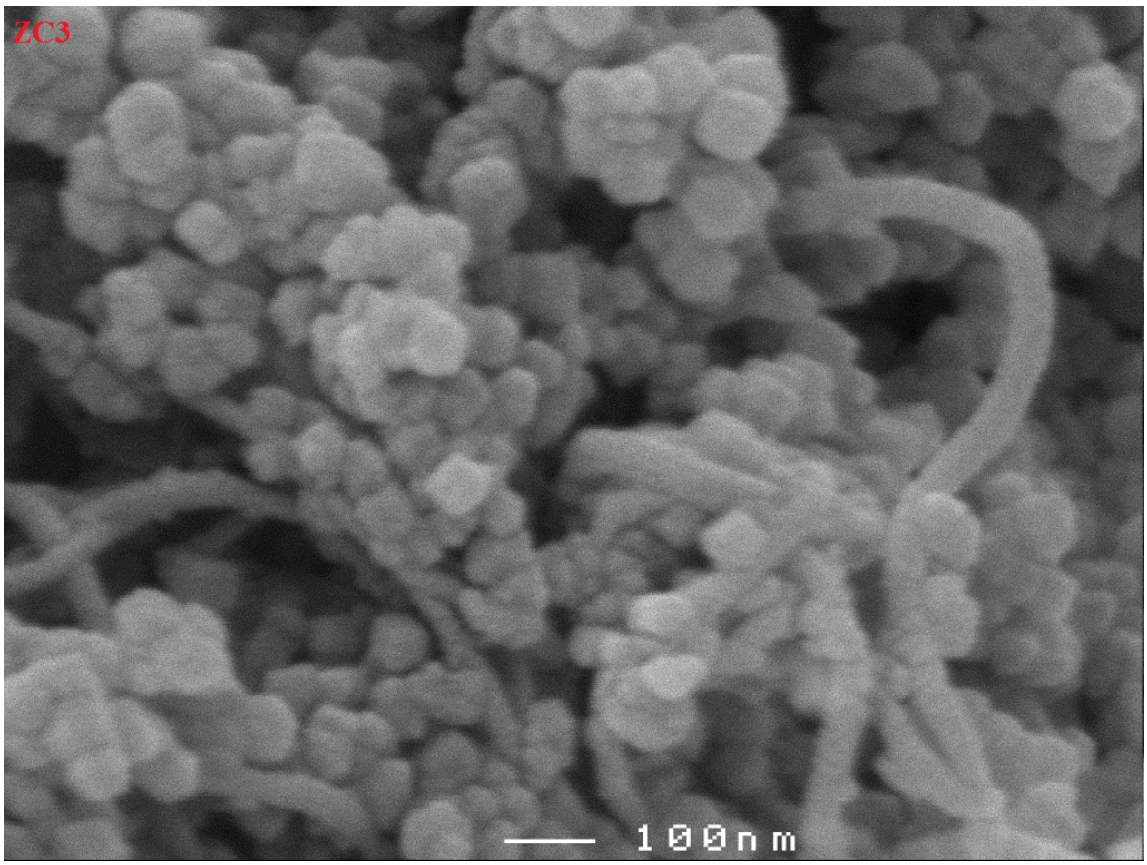
$$CNTs\% = \frac{W_{(CNTs)}}{W_{(CNTs)} + W_{(ZIFs)}} \times 100\% \quad \text{(S2)}$$

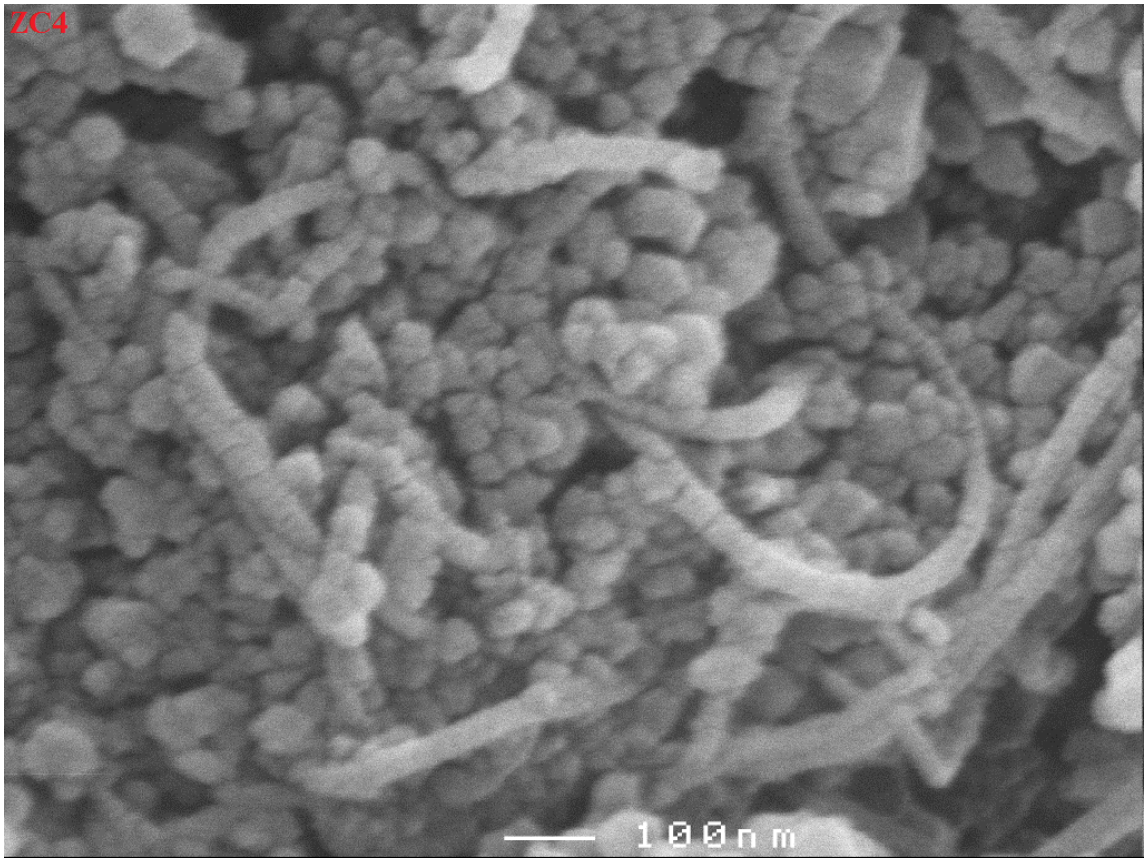
3. Bigger size of SEM images of ZIF-8 and ZIF-8/CNT composites






ZC2
100nm


ZC3
100nm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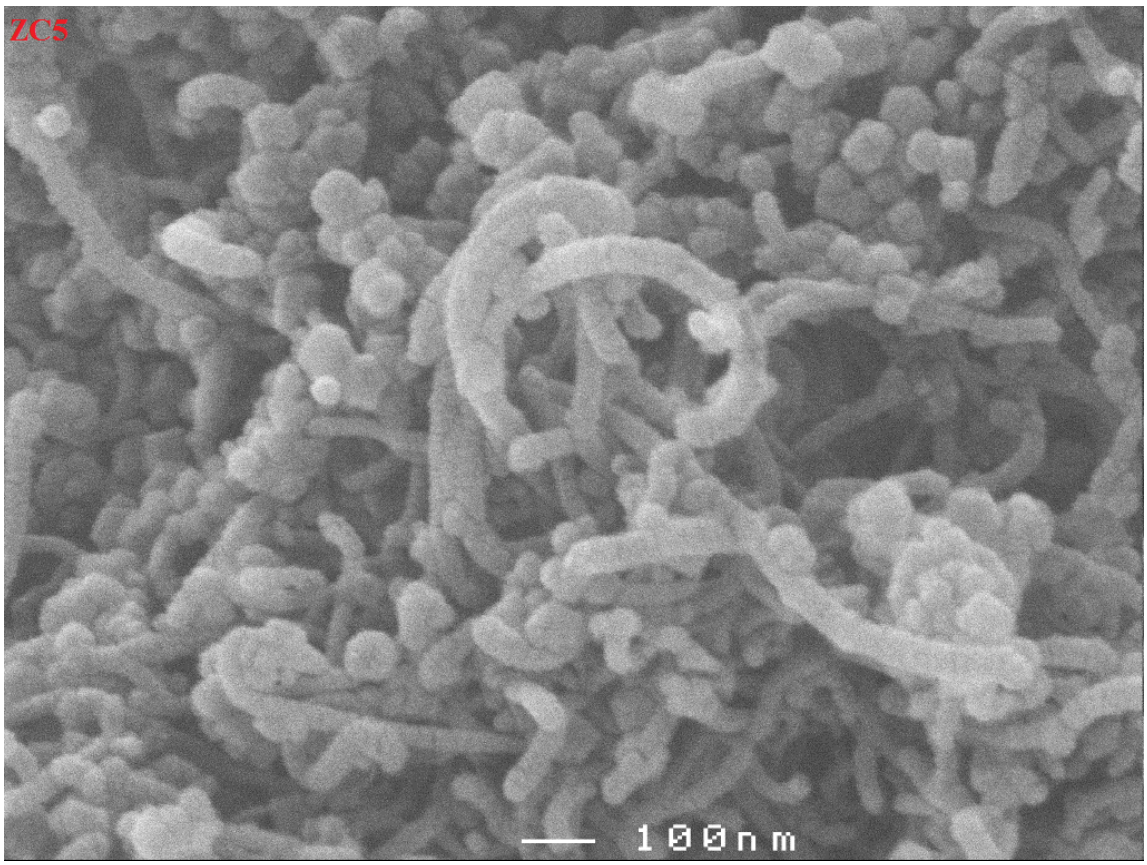
ZC5
100nm

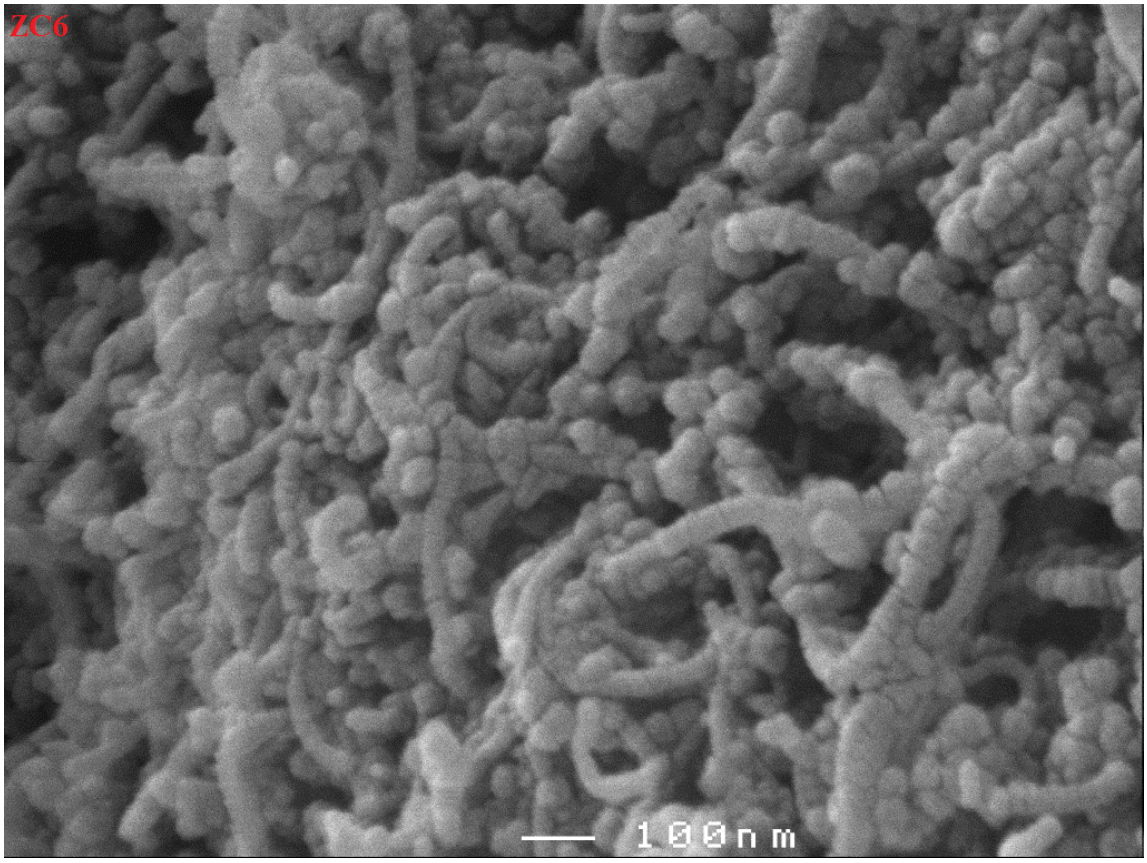

Figure S1. SEM image of ZIF-8 and ZIF-8/CNTs composites (bigger size)

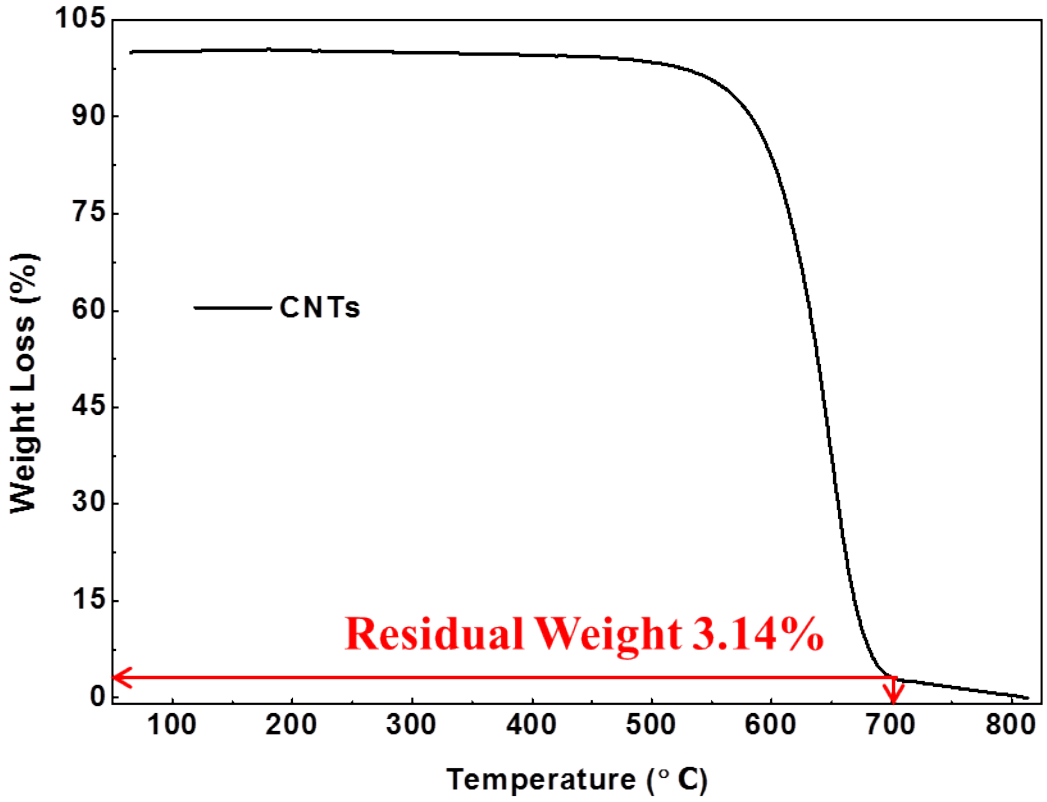

Figure S2. TGA curve of CNTs

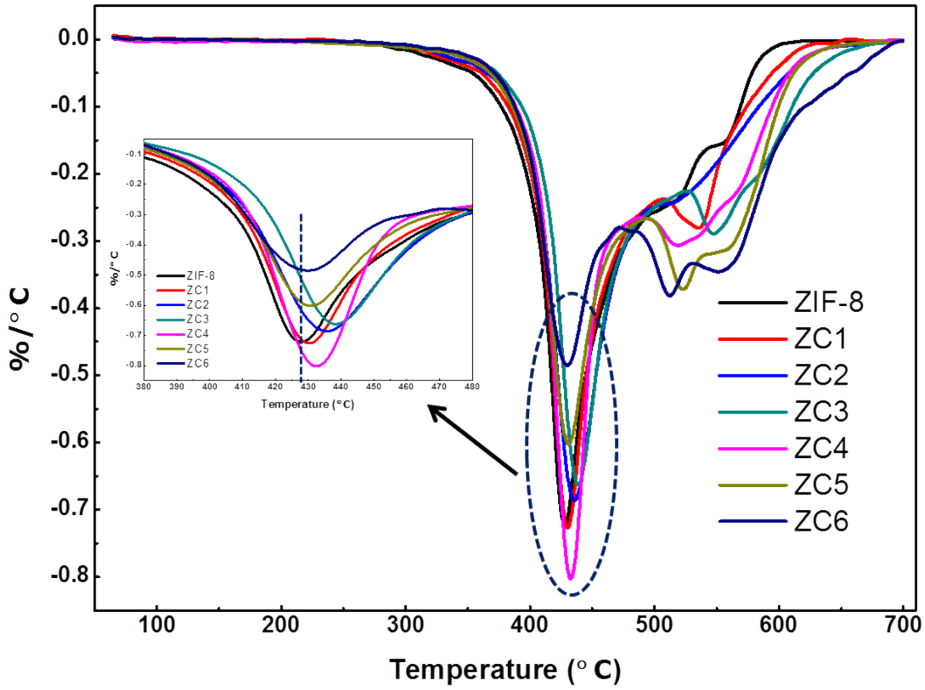

Figure S3. DTG curves of ZIF-8 and ZIF-8/CNTs composites

4. Calculation of CNTs and ZIF-8 percentages in the composites via TGA results

The percentages of ZIF-8 and CNTs in the composites were calculated by solving Eq. (S3) and Eq. (S4).

$$ZIFs\% + CNTs\% = 1 \quad \text{(S3)}$$

$$35.46\% \times ZIFs\% + 3.14\% \times CNTs\% = Residue\% \quad \text{(S4)}$$

Where ***ZIFs%*** and ***CNTs%*** are the weight percentages of ZIF-8 and CNTs in the composites, respectively, and ***Residue%*** is the weight percentage of residue in composites.

For further confirming the CNT percentage in composites, elemental analysis (EA) was carried out on all the samples and the results were showed in Table S1.

Table S1. Comparison of CNTs percentage in the composites calculated by TGA and EA

Sample ID	ZIF-8	ZC1	ZC2	ZC3	ZC4	ZC5	ZC6
TG results	0	0.77	3.63	15.62	19.29	24.85	34.23
EA results	1.12	3.39	11.56	14.07	21.18	29.70	30.49

5. N_2 ads-desorption isotherms at 77 K

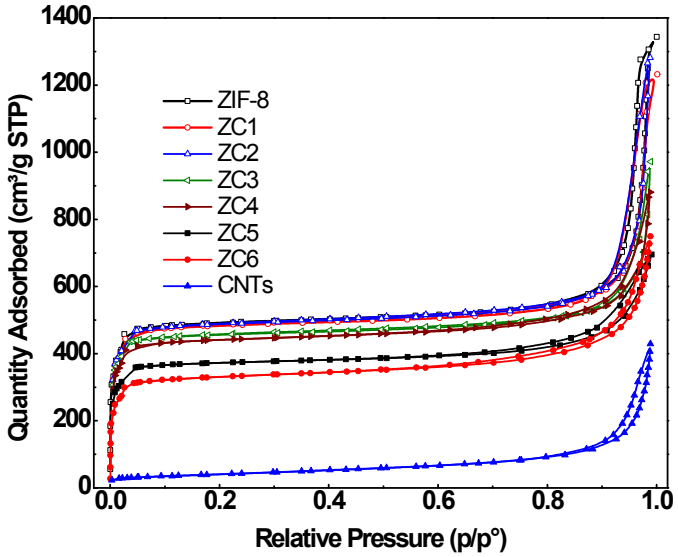

Figure S4. N_2 adsorption isotherms of all samples at 77 K

6. N_2 adsorption isotherms at 273 K

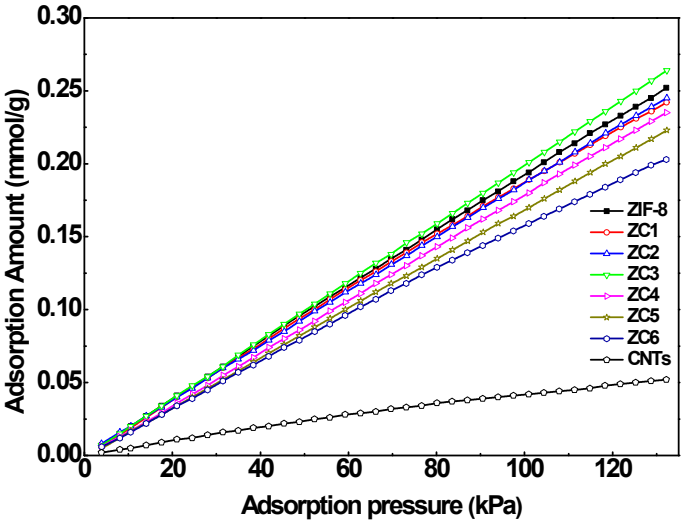

Figure S5. N_2 adsorption at 273 K on CNTs, ZIF-8 and ZIF-8/CNTs composites

7. Micropore volumes and BET surface areas calculation for hypothetical physical mixtures

Based on the content of ZIF-8 and CNTs in the composites (Table 1), the BET surface areas and micropore volumes of hypothetical physical mixture of ZIF-8 and CNTs are calculated by Eq. (S5) and Eq. (S6), respectively.

$$S_{BET}H = S_{BET}(CNTs) \times CNTs\% + S_{BET}(ZIFs) \times ZIFs\% \quad \text{(S5)}$$

$$V_{Mic}H = V_{Mic}(CNTs) \times CNTs\% + V_{Mic}(ZIFs) \times ZIFs\% \quad \text{(S6)}$$

Where $\boldsymbol{S_{BET}(CNTs)}$ and $\boldsymbol{S_{BET}(ZIFs)}$ are the BET surface areas of pure ZIF-8 and pure CNTs, respectively; ***ZIFs%*** and ***CNTs%*** are the weight percentages of ZIF-8 and CNTs in the composites, respectively; $\boldsymbol{V_{mic}(CNTs)}$ and $\boldsymbol{V_{mic}(ZIFs)}$ are micropore volumes of pure ZIF-8 and pure CNTs, respectively.

8. Heat of CO_2 adsorption

Adsorption Heat of CO_2 was calculated by the following virial equation Eq. (S7) and (S8):

$$lnP = lnq + \frac{1}{T} * \sum_{i=0}^{m} a_i \, Q^i \quad \text{(S7)}$$

$$Q_{st} = -R * \sum_{i=0}^{m} a_i q^i \quad \text{(S8)}$$

The above virial expression was used to fit the combined isotherm data for ZIF-8 and ZC2 at 273K and 298 K (Figure S3), where ***P*** is the pressure, ***q*** is the adsorbed amount, ***T*** is the adsorption temperature, $\boldsymbol{a_i}$ and $\boldsymbol{b_i}$ are virial coefficients, and ***m*** and ***n*** are the number of coefficients used to describe the isotherms. $\boldsymbol{Q_{st}}$ is the coverage-dependent enthalpy of adsorption and ***R*** is the universal gas constant.

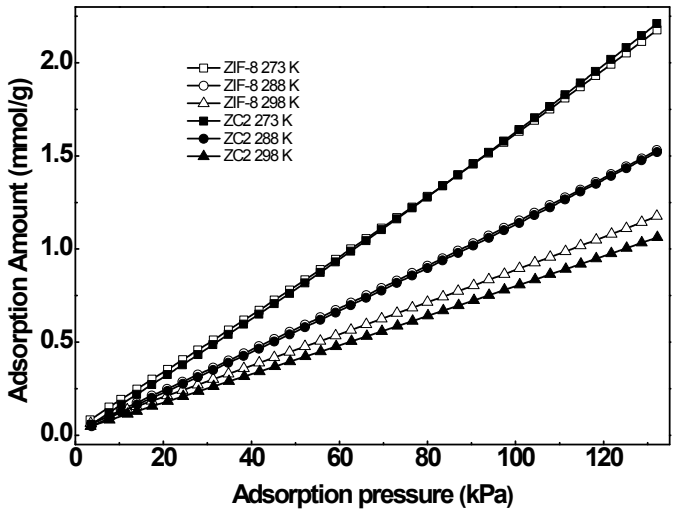

Figure S6. CO_2 adsorption on ZIF-8 and ZC2 at 273, 288 and 298K

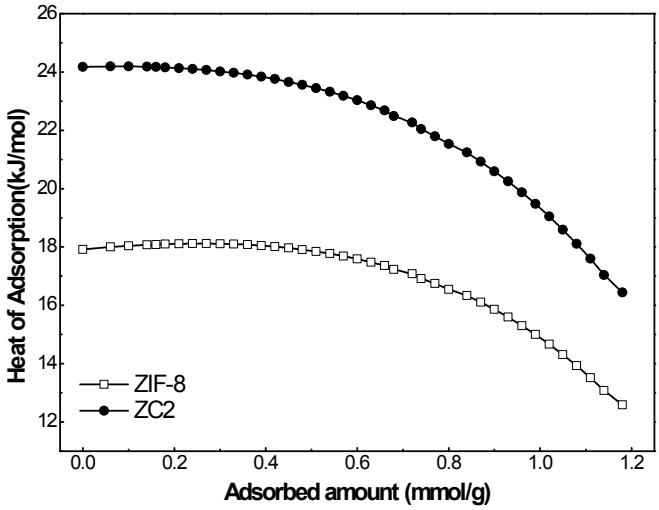

Figure S7. Heat of CO_2 adsorption on ZIF-8 and ZC_2 based on the isotherms at 288 and 298 K.

9. Langmuir fitting with CO_2 and N_2 adsorption isotherms

The CO_2 and N_2 adsorption isotherms of ZIF-8 and ZC2 were fitted by Langmuir equation Eq. (S9):

$$q = \frac{q_m bp}{1 + bp} \quad \text{(S9)}$$

Where q_m (mmol/g) and b (bar^{-1}) are the Langmuir isotherm equation parameters. They can be determined from the slope and intercept of a linear Langmuir plot of (1/q) versus (1/P).

The adsorption equilibrium selectivity α_{12} between components 1 and 2 is defined in Eq. (S10) and the Langmuir constants for ZIF-8 and ZC were showed in Table S2.

$$\alpha_{12} = \frac{x_1}{x_2} \times \frac{y_1}{y_2} \approx \frac{q_{m1} b_1}{q_{m2} b_2} \quad \text{(S10)}$$

Where component 1 is the stronger adsorbate and 2 is the weaker adsorbate. x_1 and x_2 are the molar fractions of components 1 and 2 on the adsorbent surface (or in the adsorbed phase), y_1 and y_2 are the molar fractions of components 1 and 2 in the gas phase. q_{m1}, q_{m2}, b_1, and b_2 are the Langmuir equation constants for components 1 and 2.

Table S2. Langmuir constants of CO_2 and N_2 adsorption at 308 K on ZIF-8 and ZC2

Samples	CO_2 adsorption at 308 K		N_2 adsorption at 308 K		α_{12}
	q_{m1} (mmol/g)	b_1 (bar^{-1})	q_{m2} (mmol/g)	b_1 (bar^{-1})	
ZIF-8	11.770	0.071	5.054	0.016	10.33
ZC2	13.013	0.061	2.546	0.025	12.47