Electronic Supplementary Information (ESI)

Facile Synthesis of ZnO@ZIF Core-shell Nanofibers: Crystal Growth and Gas Adsorption

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S1. Synthesis Procedure

Materials. PVP (MW: 1, 300, 000), $Zn(NO_3)_2 \cdot 6H_2O$ were purchased from the Sigma-Aldrich Chemicals company. *N, N*-dimethylformamaide (DMF) was obtained from VWR Corporation. 2-methylimidazole and 4-methyl-5-imidazolecarboxaldehyde were purchased from Acros Organics. All the chemicals were used without further treatment

Fabrication of ZnO and ZnO@ZIF nanofiber. In a typical procedure, 3 g of PVP was dissolved in 38 mL ethanol, and then mixed with 10 mL DI water containing 4 g of $Zn(NO_3)_2 \cdot 6H_2O$. The mixture was subjected to magnetic stirring for ca. 1 hour to obtain a transparent solution. Subsequently, the solution was loaded into a glass syringe equipped with a stainless steel needle (Inner diameter: 250 μm), which was connected to high voltage supply. The feeding rate was controlled by the syringe pump. The PVP-$Zn(NO_3)_2$ nanofibers were obtained by electrospinning at a voltage of 15 kV, an electrospinning distance of 10 cm and a feeding rate of 1.0 mL/h. A piece of alumina foil was used to collect the electrospun nanofibers. The temperature and humidity during the electrospinning process were controlled at 25 °C and 30%, respectively. The as-spun nanofibers were then subjected to calcination in a muffle furnace at 500 ºC (ramping rate: 2 ºC/min) in air for 1 hour to remove the PVP and decompose $Zn(NO_3)_2$ to synthesize ZnO nanofibers. The as-prepared ZnO nanofibers were placed in a glass bottle, in which 2-methylimidazole was dissolved in DMF with a concentration of 0.08 mol/L. The molar ratio of ZnO nanfiber to the ligands was controlled at 0.03. After the mixture was heated in the oven at 70 ºC for 3 h, the nanofibers were taken out and immersed in methanol for 1 hour to remove the residuals. After that, ZnO@ZIF-8 core-shell nanofibers were obtained. The same procedures were carried out for the synthesis of ZnO@ZIF-93, except that 4-methyl-5-imidazolecarboxaldehyde was used as a ligand instead of 2-methylimidazole.

Synthesis of pure ZIF-8 particles. The following procedure was slightly modified from a previous report.[1] A solution of 1.4622 g $Zn(NO_3)_2 \cdot 6H_2O$ (4.92 mmol) in 100 mL methanol was rapidly added to a solution of 1.6248 g 2-methylimidazole (19.8 mmol) and 0.1676 g sodium formate (2.46 mmol) in 100 mL methanol under stirring with a magnetic bar. The stirring was turned off after one minute and the solution slowly turned turbid. After 24 hours, the ZIF-8 particles were collected by centrifugation at 7000 rpm for 10 minutes, and then washed with fresh methanol three times.

S2.   Characterization and DRIFTS Analysis

Sample Characterization. The morphology and diameter distribution of the nanofibers were observed by SEM (Su-70, Hitachi) and TEM (Libra 120, Zeiss).The phase identification was obtained using a PANalytical X'Pert Pro MPD X-ray diffractometer equipped with a Cu-Kα radiation source (λ=1.5401 Å). Fourier Transform Infrared (FTIR) spectrometer (Nicolet iS50, Thermos Scientific), which is equipped with an attenuated total reflectance (ATR) accessory, was used to analyze the vibrational properties of the samples. The Micromeritics ASAP 2020 Plus Physisorption system was used to determine the N_2 physisorption isotherms and BET surface areas of the samples.

***In-situ* DRIFTS Analysis (CO_2 adsorption and desorption).** This analysis was conducted in a DRIFTS chamber. **(1) Adsorption:** Firstly, the chamber loaded with nanofibers was purged with ultrapure helium gas (purity > 99.995 %, Praxair) with a flow rate of 30 mL/min at 150 °C for 30 min. Subsequently, the heater was turned off to allow the temperature to cool down to room temperature and an IR background spectrum was collected. Then, CO_2 gas (10%, helium as balance gas, Praxair) was continuously introduced to the chamber with a flow rate of 4 mL/min. Meanwhile, the IR spectra were collected to record the CO_2 adsorption as a function of time. **(2) Desorption:** After the completion of the adsorption process, helium gas (4 mL/min) was introduced into the chamber instead of CO_2 gas. The temperature was kept constant at room temperature. Then, the IR spectra were collected to record CO_2 desorption process as a function of time.
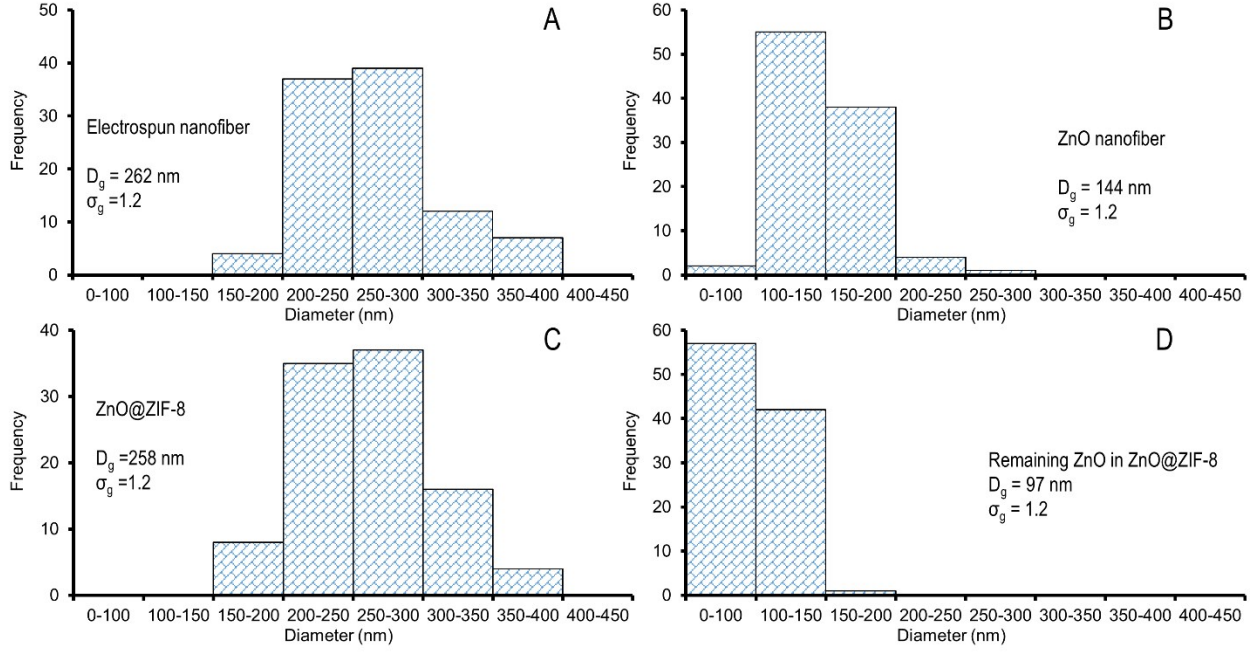
S3. Diameter Distribution Analysis

Figure S1. Diameter distribution of as-prepared nanofibers.

The distribution was attained by measuring the diameters of 100 nanofibers at random from the corresponding SEM image. Then, Equation (1) and Equation (2) were applied to calculate the geometric mean diameter (D_g) and standard deviation (σ_g), respectively.[2]

$$D_g = e^{\frac{\sum ln D_i}{N}}$$

(1)

$$\sigma_g = e^{\left(\frac{\sum (lnD_i - \ln D_g)^2}{N}\right)^{0.5}}$$

(2)

where D_i means the diameter of individual nanofiber and N represents the total number of counted nanofiber.

Based on the changes in diameters of ZnO nanofibers before and after the ZIF growth, the molar ratio of ZIF-8 shell to ZnO core can be calculated assuming 100% conversion of consumed ZnO to ZIF-8. The calculation was detailed as below:

Original diameter of ZnO nanofiber: 144 nm;

Diameter of remaining ZnO core: 97 nm;

Mole number of consumed ZnO (equal to the mole number of ZIF-8 shell):

$$\text{n(ZIF-8)} = \frac{\rho_{ZnO} L \pi \left(\left(\frac{144}{2} \right)^2 - \left(\frac{97}{2} \right)^2 \right)}{M(ZnO)} \tag{3}$$

where, ρ_{ZnO} is the density of ZnO, 5.61 g/cm³; L is the length of the nanofiber, which is considered as a constant; $M(ZnO)$ is the molar weight of ZnO, 81.41 g/mol.

Mole number of remaining ZnO core:

$$n(ZnO) = \frac{\rho_{ZnO} L \pi \left(\frac{97}{2} \right)^2}{M(ZnO)} \tag{4}$$

Thus,

$$\frac{n(ZIF-8)}{n(ZnO)} = 1.2$$

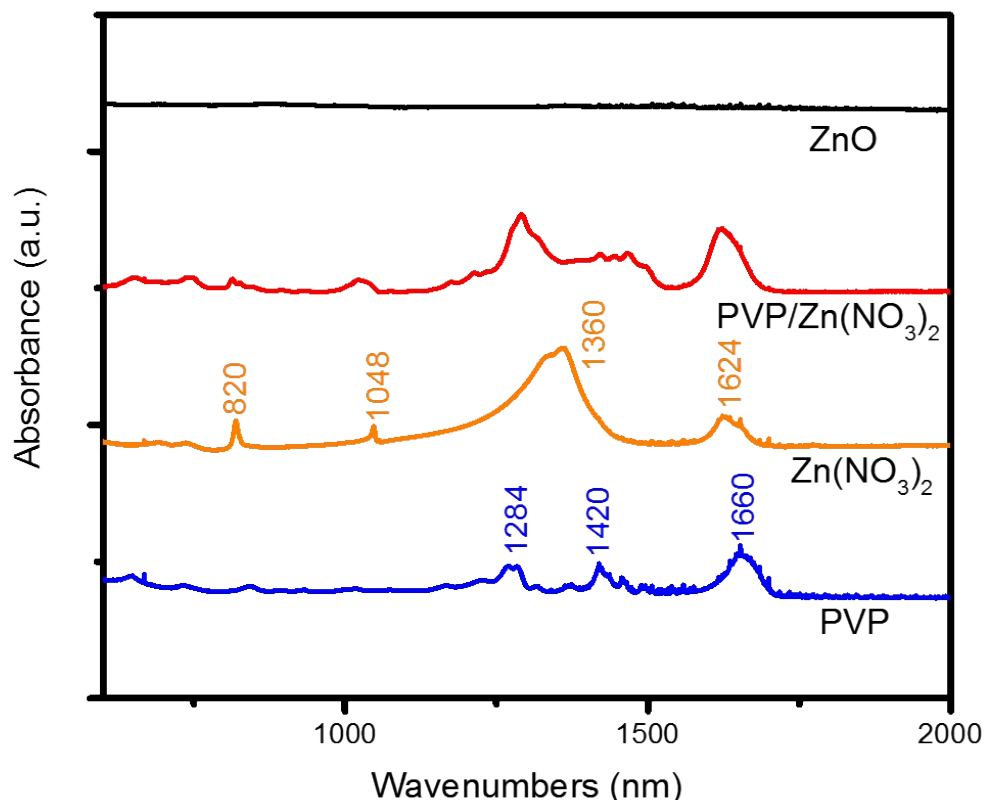## S4.   Verification of PVP Removal after Calcination

Figure S2. FTIR spectra of various samples: PVP, zinc nitrate hexahydrate, PVP/Zn(NO$_3$)$_2$ nanofiber and ZnO nanofiber.

The ZnO nanofibers were obtained by heating the PVP/Zn(NO$_3$)$_2$ nanofibers at 500 °C (ramping rate: 2 °C/min) in air for 1 h, which is a typical calcination process to remove PVP and obtain the metal oxide.[3] To further address any potential impurity concerns, we carried out additional FTIR analysis to verify the complete removal of PVP after the calcination process. As shown in **Figure S2**, the FTIR spectrum of pure PVP has peaks at 1284, 1420 and 1660 cm^{-1}, corresponding to C-N, CH$_2$ and C=O groups, respectively. Zn(NO$_3$)$_2$ has IR peaks at ~ 1360 and 1624 cm^{-1}. The electrospun PVP/Zn(NO$_3$)$_2$ nanofibers possess all the aforementioned IR peaks. After treating the PVP/Zn(NO$_3$)$_2$ nanofibers at 500 °C for 1 h, none of these peaks exist, indicating that all PVP was removed and all Zn(NO$_3$)$_2$ was converted to ZnO after the calcination process.
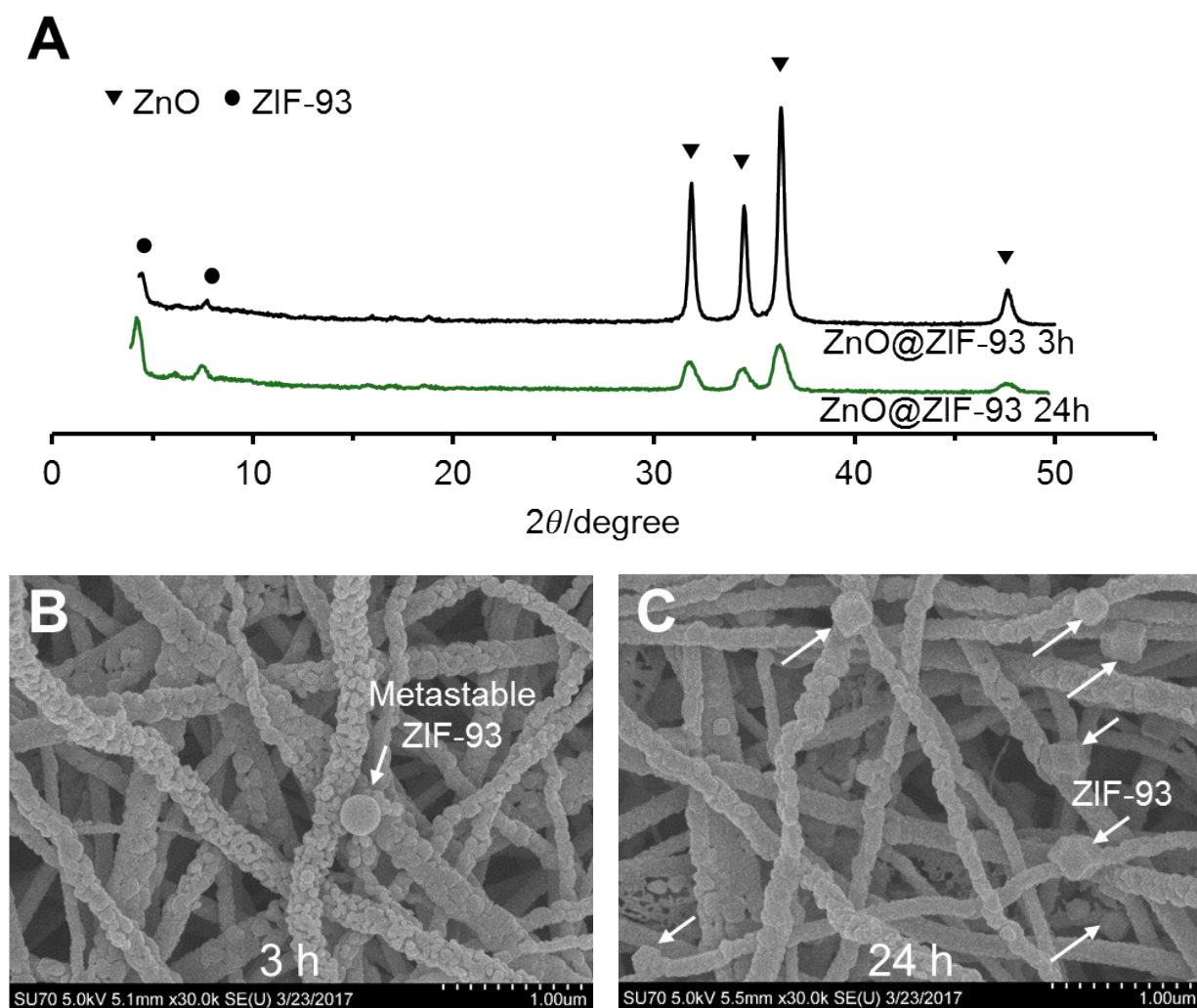
S5. Transformation of ZnO to ZIF-93

Figure S3. (A) XRD patterns ZnO@ZIF-93 after 3-hour and 24-hour reaction; SEM images of ZnO@ZIF-93 after (B) 3-hour and (C) 24-hour reaction.
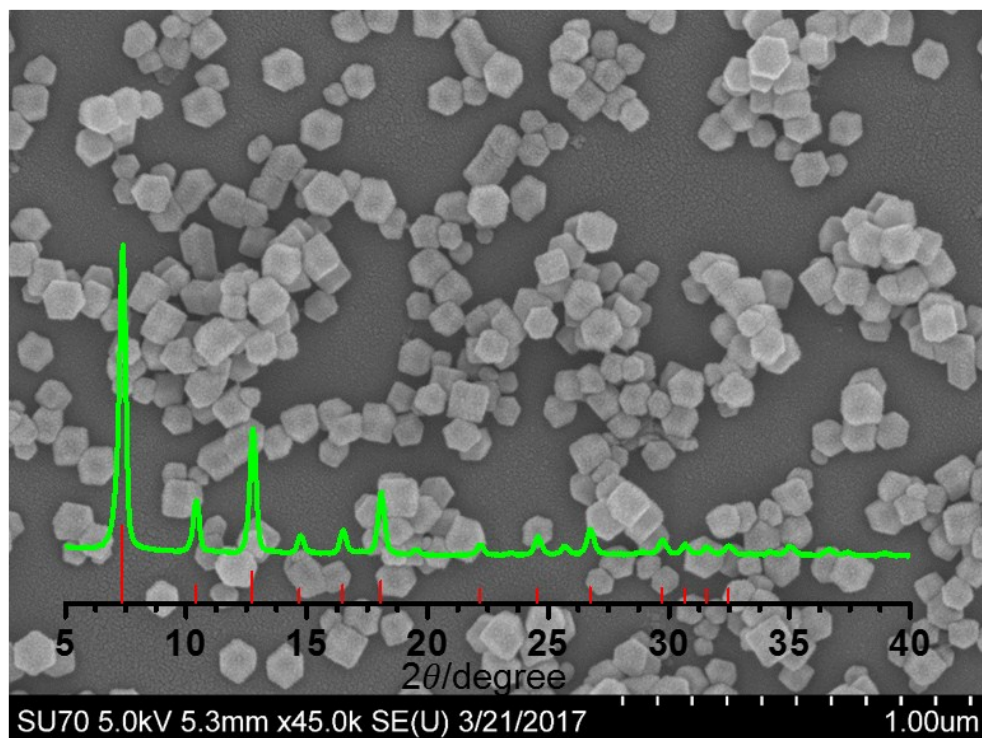
S6. Characterization of Pure ZIF-8 Particles

Figure S4. SEM image and the corresponding XRD pattern of pure ZIF-8 particles.
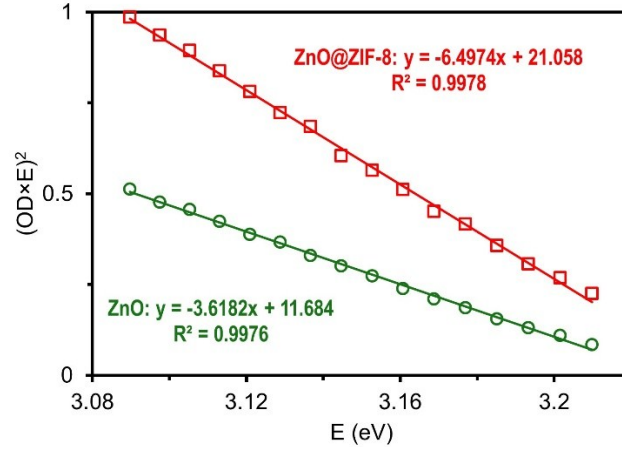
S7.   Band Gap Calculation

Figure S5. The plot of $(OD \times E)^2$ versus E.

The band gap of the samples were obtained based on the following equation.[4]

$$(\alpha E)^2 = B(E - E_g) \tag{5}$$

α is the adsorption cofficient and its value can be calculated from $\alpha = \dfrac{OD}{d}$. OD is the absorbance and d is the effective thickness, which is a constant for a specific sample. B is the proportionality constant. E is the photon energy ($E = 1239/\lambda$, λ is the wavelength). E_g is the band gap.

From the UV-vis spectra (**Fig. 2D**), the photon energy (E) and corresponding absorbance (OD) values were obtained. The plot of $(OD \times E)^2$ versus E was depicted in **Fig. S5**, from which the band gap of each sample was acquired when $(OD \times E)^2$ equals zero.
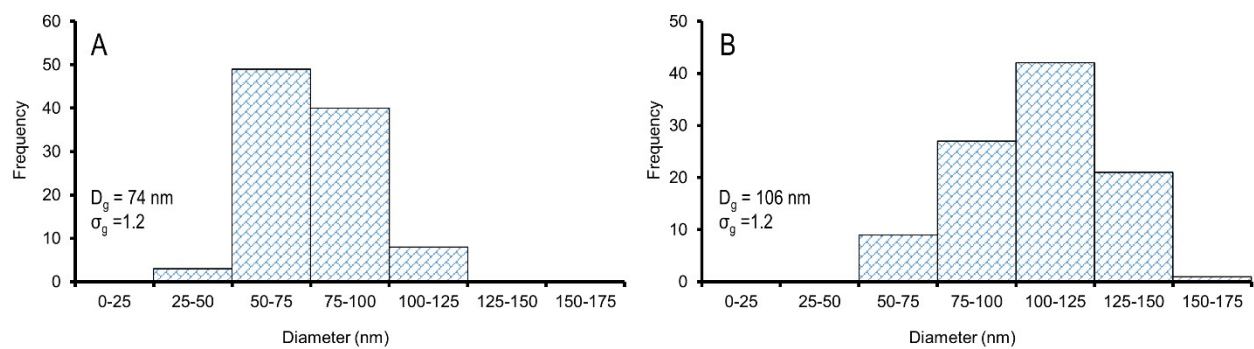
S8. Size Evolution of ZIF-8

Figure S6. Size evolution of the ZIF-8 as a function of reaction time: (A) 1 hour and (B) 2 hours.
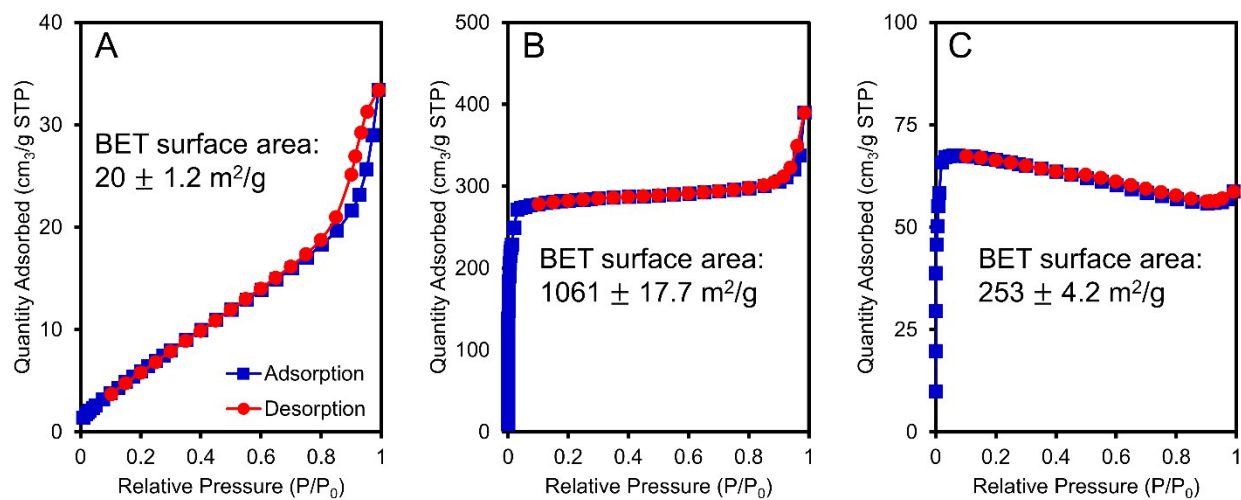
S9.   BET Analysis

Figure S7. N$_2$ physisorption isotherms at 77 K of (A) ZnO nanofibers, (B) pure ZIF-8, and (C) ZnO@ZIF-8 nanofibers.

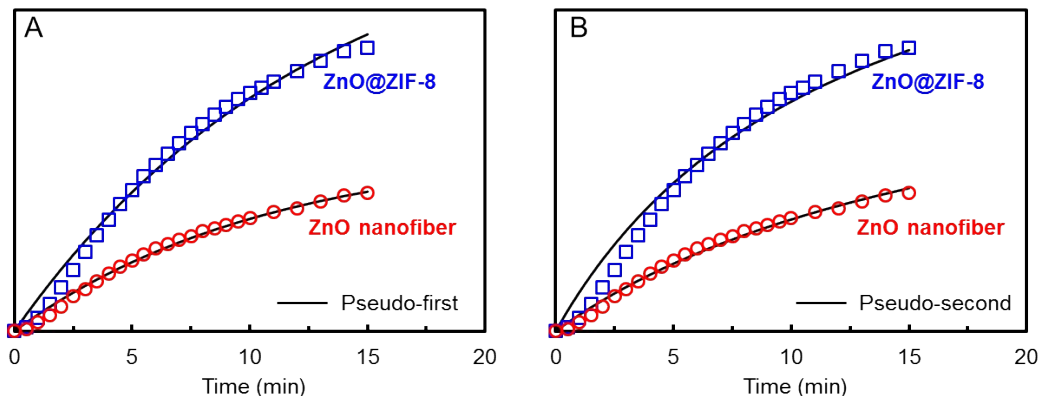# S10. Supplementary Kinetic Modelling of CO$_2$ Adsorption

Figure S8. Experimental adsorption kinetics and the corresponding fitting of the kinetics models: (A) Pseudo-first order and (B) Pseudo-second order.

Table S1. Adsorption kinetic constants and error calculated from the fitting of Pseudo-first order model and Pseudo-second order.

Sample	Pseudo-first order $q_t = q_e(1 - \exp(-k_f t))$			Pseudo-second order $q_t = q_e^2 k_s t/(1 + q_e k_s t)$		
	k_f	q_e	Error (%)	k_s	q_e	Error (%)
ZnO	0.093	40451	7.5	7.4×10^{-7}	70783	7.2
ZnO@ZIF-8	0.078	93825	11.5	7.4×10^{-7}	110997	18.6

q_t and q_e (IR peak area/g) are the adsorbed amount at given time (t, min) and equilibrium, respectively; k_f and k_s (min^{-1}) are the kinetic constants.

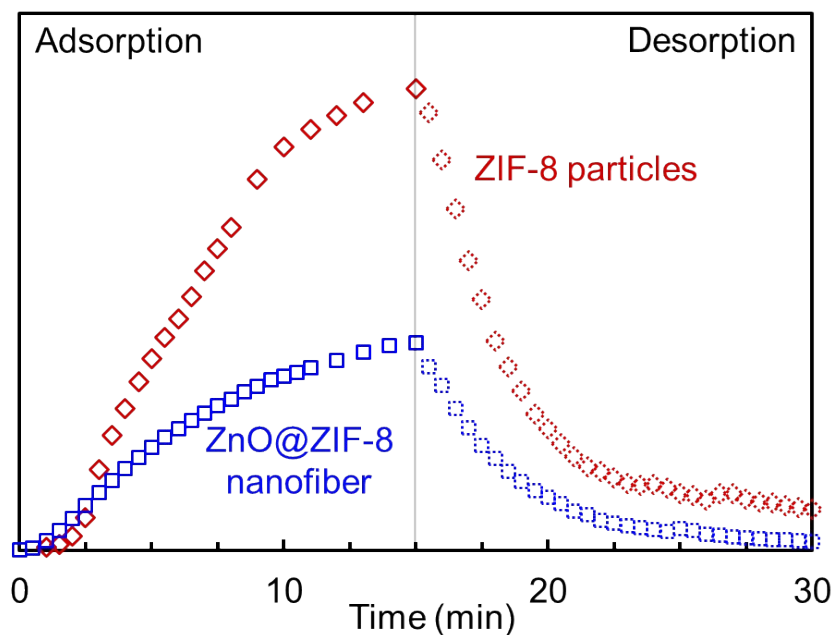# S11. Supplementary CO$_2$ Adsorption and Desorption

Figure S9. CO$_2$ adsorption and desorption performance of pure ZIF-8 and ZnO@ZIF-8 nanofibers.

S12. Supplementary References:

1   J. Cravillon, R. Nayuk, S. Springer, A. Feldhoff, K. Huber and M. Wiebcke, *Chemistry of Materials*, 2011, **23**, 2130-2141.

2   W. C. Hinds, *Aerosol technology: properties, behavior, and measurement of airborne particles*, John Wiley & Sons, 2012.

3   J. Liu, G. Zhu, M. Chen, X. Ma and J. Yang, *Sensors and Actuators B: Chemical*, 2016, **234**, 84-91.

4   Z. Yang, C. K. Chiang and H. T. Chang, *Nanotechnology*, 2008, **19**, 025604.