High efficient adsorbent design using Cu–BTC/CuO/Carbon fiber paper composite for CH_4/N_2 high selectivity

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Material characterization

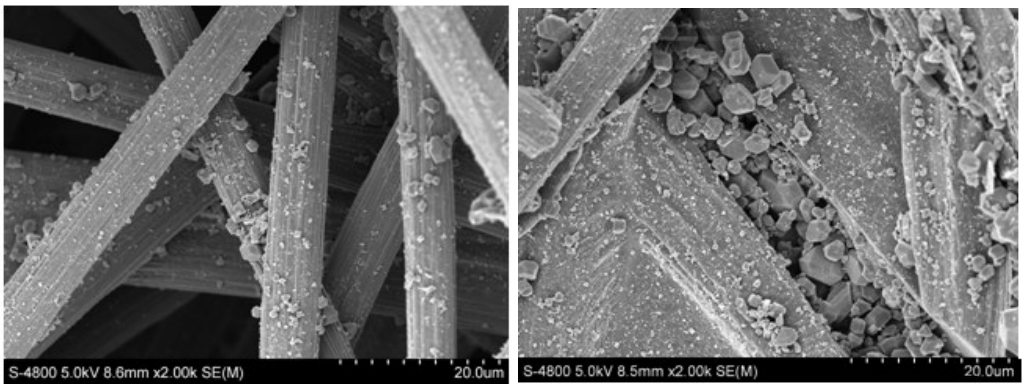
The SEM images of samples obtained at different synthesis times (3, 9, 18, and 24 h) are shown in Fig. S1. The pictures on the left show Cu–BTC (3, 9, 18,and 24 h) growing on carbon fiber, whereas the pictures on the right show Cu–BTC (3, 9, 18, and 24 h) grown on carbon sheet. The Cu-BTC crystal and CuO coating on the carbon fiber paper (CFP) are shown in Fig. S2 (a) and (b), respectively.

The adsorption isotherms of the gases (N_2 and CH_4) are measured using an automatic gas sorption analyzer (Quantachrome Autosorb IQ, USA). In the analysis, the samples were pretreated at 393.15 K under vacuum for 16 h to remove any physically adsorbed gases from the surface. N_2 is then used to measure the adsorption and desorption on samples at different relative pressures and at 77 K temperature to test the surface area and pore diameter distribution. Pore size distribution is estimated from nitrogen data by using a no-local density functional theory (NLDFT). The other gases (N_2 and CH_4) are used to measure the adsorption at different pressure and temperature (273.15 K) in an ice-water bath. The results of N_2 adsorption–desorption isotherms and the pore distribution are shown in Fig. S3 and Fig. S4, respectively. Fig. S5 shows the SEM of different concentrations of Cu-BTC and CuO on CFP. The dual-site Langmuir–Freundlich (DSLF) model is expressed as:

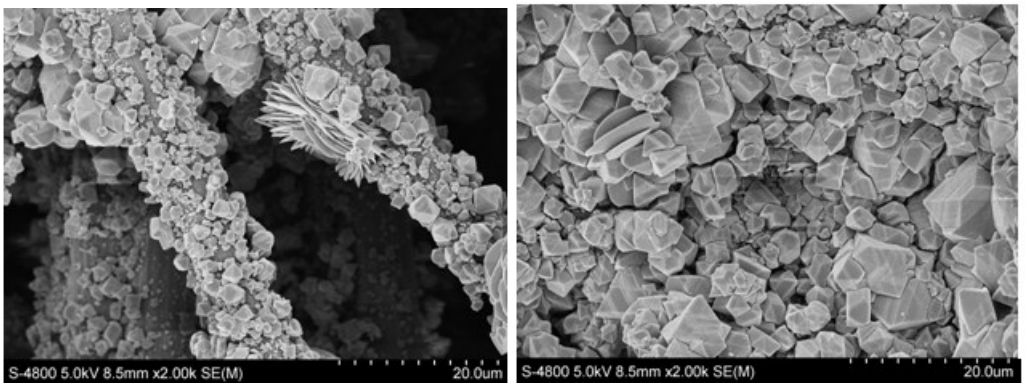
$$q = q_{m,1}\frac{b_1 p^{1/n_1}}{1+b_1 p^{1/n_1}} + q_{m,2}\frac{b_2 p^{1/n_2}}{1+b_2 p^{1/n_2}} \quad (1)$$

where $q_{m,1}$ and $q_{m,2}$ are the saturation capacities of the sites 1 and 2 (mol/kg) in the DSLF model, respectively; b_1 and b_2 are the affinity coefficients of sites 1 and 2(1/kPa) in the DSLF model,

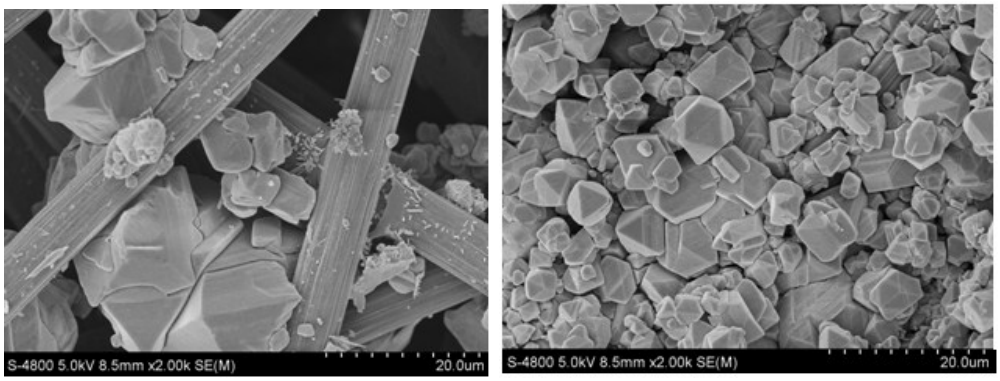
respectively; n_1 and n_2 are the corresponding deviations from an ideal homogeneous surface. The fitted parameters are shown in Table S1.



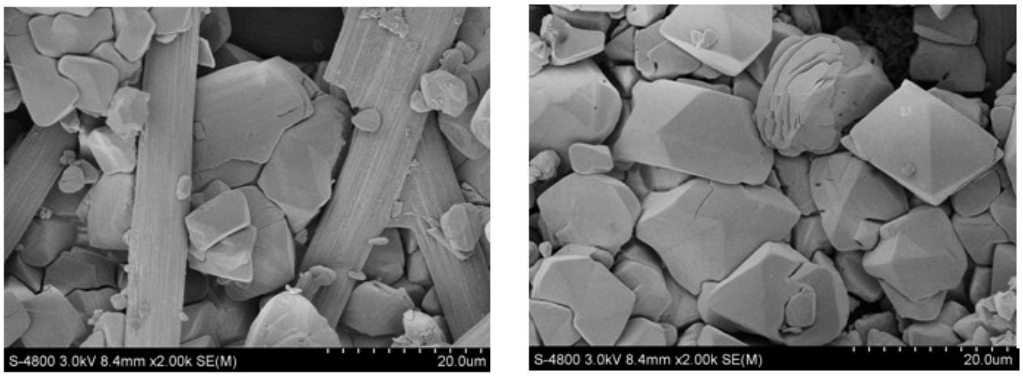
(a) Cu-BTC/CFP (3 h)



(b) Cu-BTC/CFP (9 h)

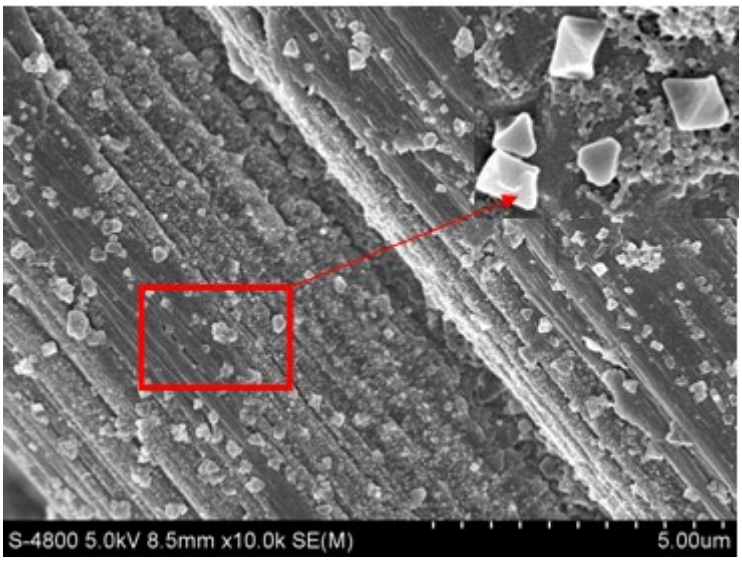


(c) Cu-BTC/CFP (18h)

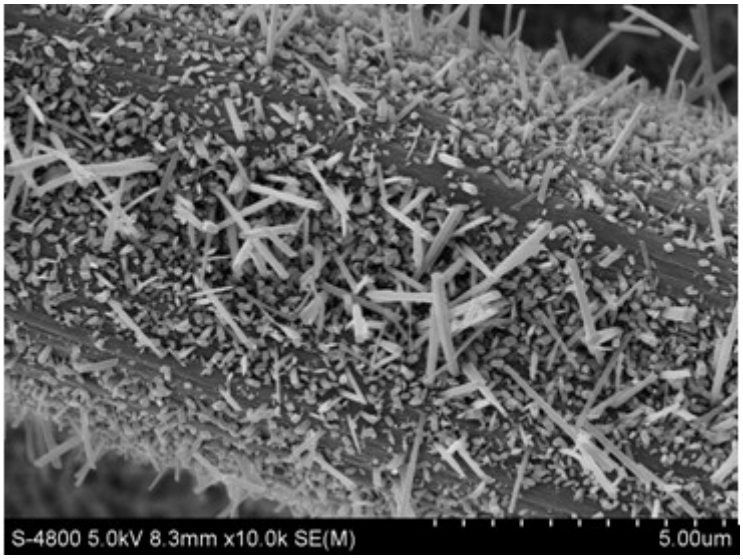


(d) Cu-BTC/CFP (24 h)

Fig. S1 SEM image of different samples.

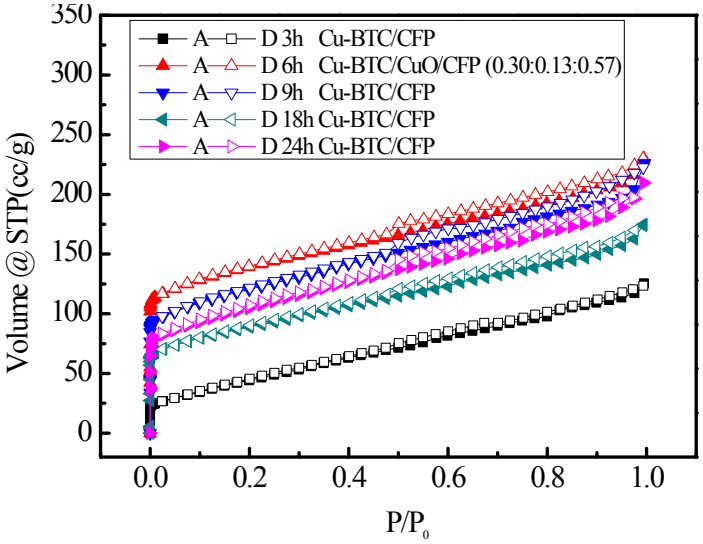


(a)The seeds coating on CFP

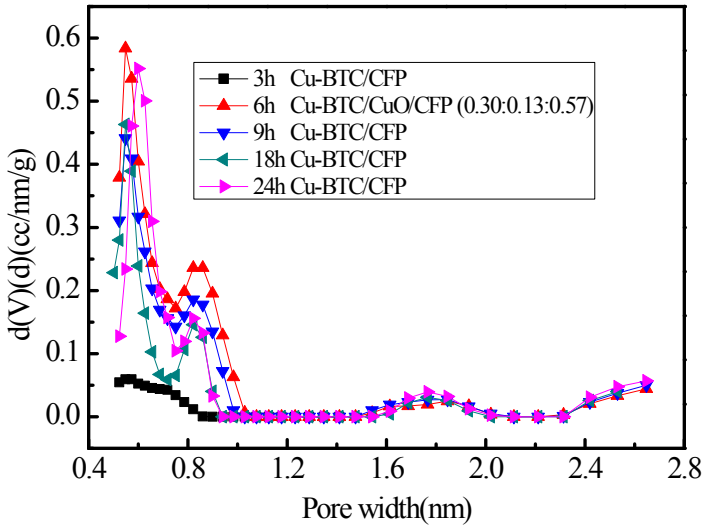


(b) CuO coating on CFP

Fig. S2 The SEM of Cu-BTC crystal and CuO coating on CFP.

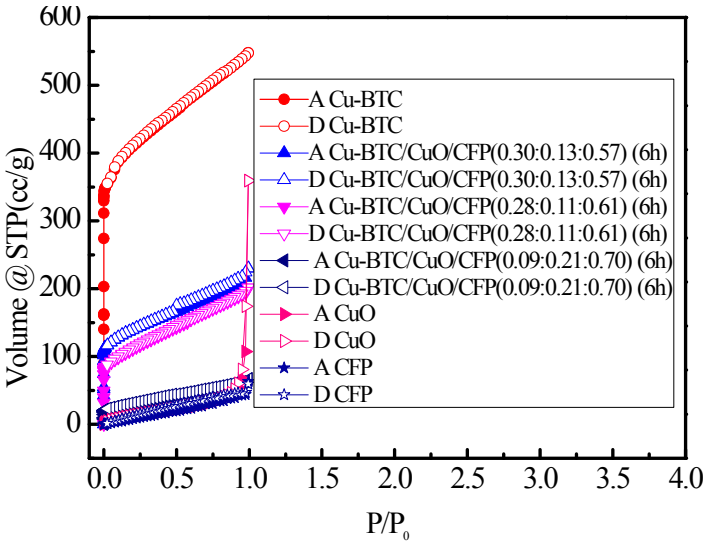


(a) N_2 adsorption isotherm at 77 K

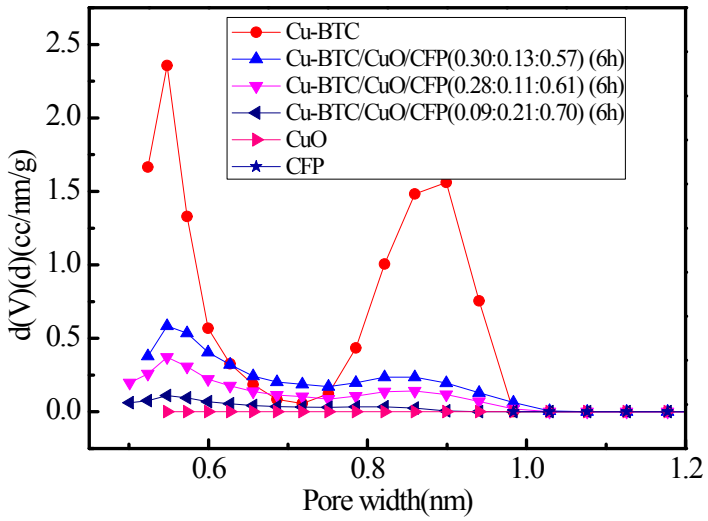


(b) Pore width distribution calculated by NLDFT

Fig. S3 Adsorption isotherm of N_2 and pore distribution.

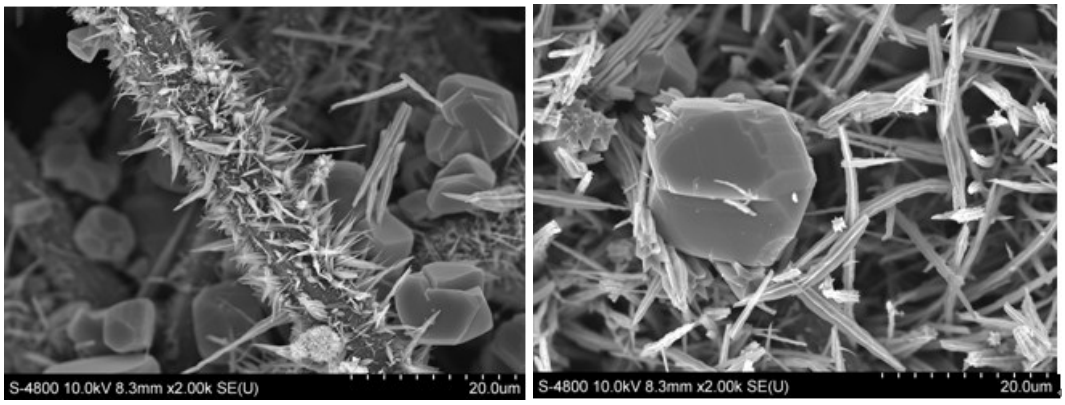


(a) N_2 adsorption isotherm at 77 K

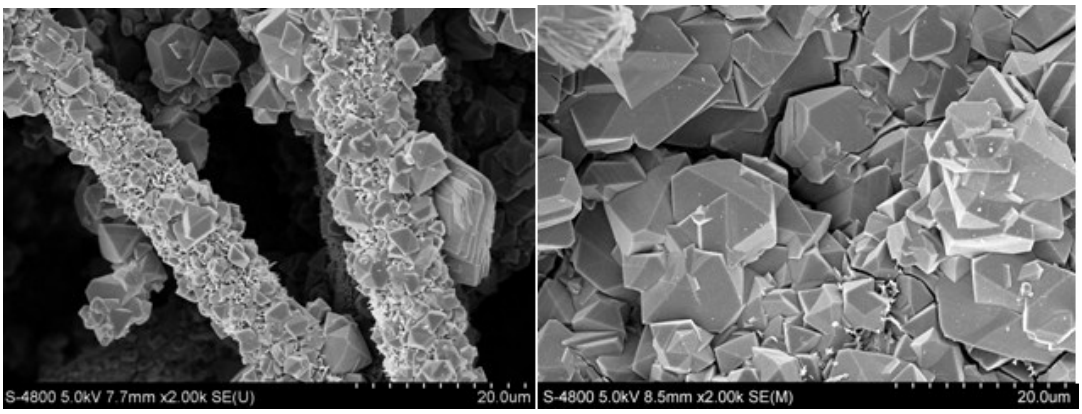


(b) Pore width distribution calculated by NLDFT

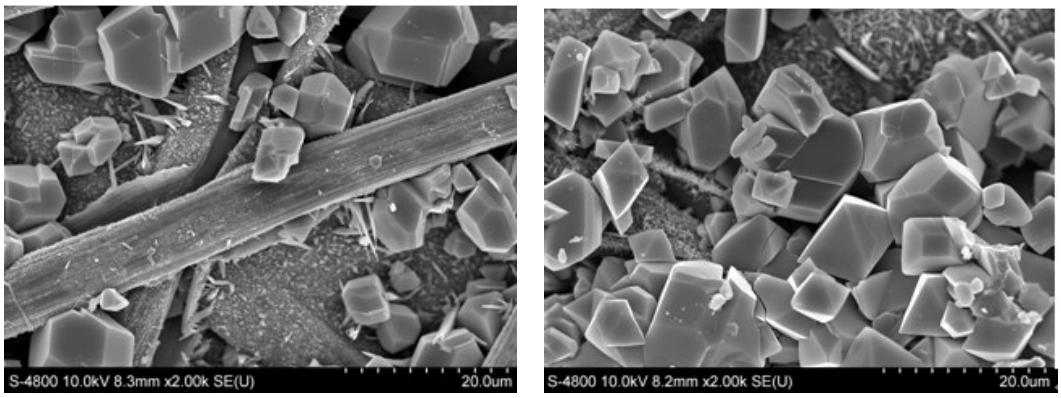
Fig. S4 Adsorption isotherm of N_2 and pore distribution.



(a) Cu-BTC/CuO/ CFP (0.09:0.21:0.70) (6h)



(b) Cu-BTC/CuO/CFP (0.30:0.13:0.57) (6h)



(c) Cu-BTC/CuO/CFP (0.28:0.11:0.61) (6h)

Fig. S5 The SEM of different concentrations of Cu-BTC and CuO on CFP.

Table S1 Summary of equation parameters for the DSLF model

Adsorbate	Conditions	$q_{m,1}$	$q_{m,2}$	b_1	b_2	n_1	n_2	R^2
N_2	Cu-BTC/CP (3h)	2.35×10^{-1}	1.69×10^{-2}	1.3810^{-4}	1.81×10^{-4}	5.47×10^{-1}	3.68×10^{-1}	1.00
	Cu-BTC/CP (9h)	1.23	1.84×10^{-2}	4.89×10^{-4}	7.36×10^{-3}	8.31×10^{-1}	6.22×10^{-1}	1.00
	Cu-BTC/CP (18h)	4.05×10^{-1}	1.65×10^{-3}	1.39×10^{-3}	8.51×10^{-1}	8.33×10^{-1}	1.5×10^{-1}	1.00
	Cu-BTC/CP (24h)	8.39×10^{-1}	2.68×10^{-3}	1.44×10^{-4}	2.15×10^{-2}	6.54×10^{-1}	6.13×10^{-1}	1.00
	Carbon fiber	4.91×10^{-2}	4.91×10^{-2}	2.14×10^{-3}	2.14×10^{-3}	8.90×10^{-1}	8.90×10^{-1}	1.00
	Cu-BTC/CuO/CP(0.30:0.13:0.57)	6.00×10^{-1}	1.47×10^{-2}	7.97×10^{-4}	9.94×10^{-2}	7.44×10^{-1}	9.41×10^{-1}	1.00
	Cu-BTC/CuO/CP(0.28:0.11:0.61)	5.01×10^{-1}	1.00×10^{-5}	1.04×10^{-3}	7.06×10^{-2}	7.67×10^{-1}	6.70×10^{-1}	1.00
	Cu-BTC/CuO/CP(0.09:0.21:0.70)	1.24×10^{-1}	1.28×10^{-2}	4.26×10^{-4}	2.26×10^{-2}	6.51×10^{-1}	8.30×10^{-1}	1.00
	Cu-BTC	4.02	3.54×10^{-4}	1.07×10^{-3}	3.06×10^{-2}	9.46×10^{-1}	1.00	1.00
CH_4	Cu-BTC/CP (3h)	1.79×10^{-1}	6.40×10^{-4}	9.13×10^{-3}	8.51×10^{-1}	9.06×10^{-1}	1.5×10^{-1}	1.00
	Cu-BTC/CP (9h)	8.49×10^{-1}	1.47×10^{-2}	5.88×10^{-3}	7.98×10^{-1}	9.46×10^{-1}	1.49×10^{-1}	1.00
	Cu-BTC/CP (18h)	8.15×10^{-1}	2.05×10^{-2}	3.60×10^{-3}	8.51×10^{-1}	8.77×10^{-1}	1.5×10^{-1}	1.00
	Cu-BTC/CP (24h)	6.14×10^{-1}	1.16×10^{-2}	7.09×10^{-3}	8.51×10^{-1}	9.23×10^{-1}	1.5×10^{-1}	1.00
	Carbon fiber	5.08×10^{-2}	5.14×10^{-2}	1.25×10^{-3}	1.30×10^{-3}	8.49×10^{-1}	8.49×10^{-1}	1.00
	Cu-BTC/CuO/CP(0.30:0.13:0.57) (6h)	3.53	1.95	1.323×10^{-3}	6.62×10^{-3}	9.00×10^{-1}	1.36	0.999
	Cu-BTC/CuO/CP(0.28:0.11:0.61) (6h)	1.886	2.17×10^{-4}	2.23×10^{-3}	2.54×10^{-2}	9.68×10^{-1}	8.22×10^{-1}	1.00
	Cu-BTC/CuO/CP(0.09:0.21:0.70) (6h)	2.11×10^{-1}	1.99×10^{-2}	1.66×10^{-3}	5.58×10^{-2}	6.87×10^{-1}	8.71×10^{-1}	1.00
	Cu-BTC	4.60	1.15	2.754	8.01×10^{-3}	1.00	1.53	0.999