Supporting information for

Well-construction approach of exceptional water stable (mesoporous SiO_2)-on-(microporous Cu-BTC) composite for methylene blue efficient capture

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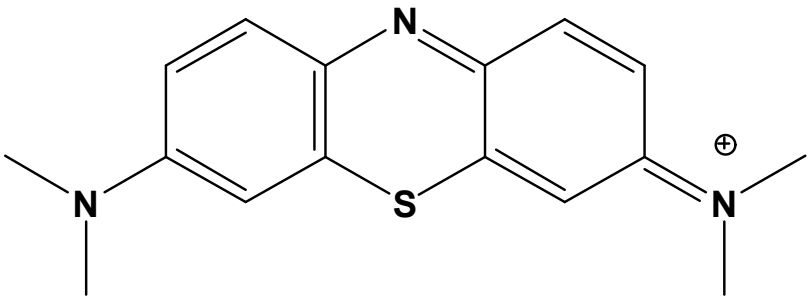
Section I

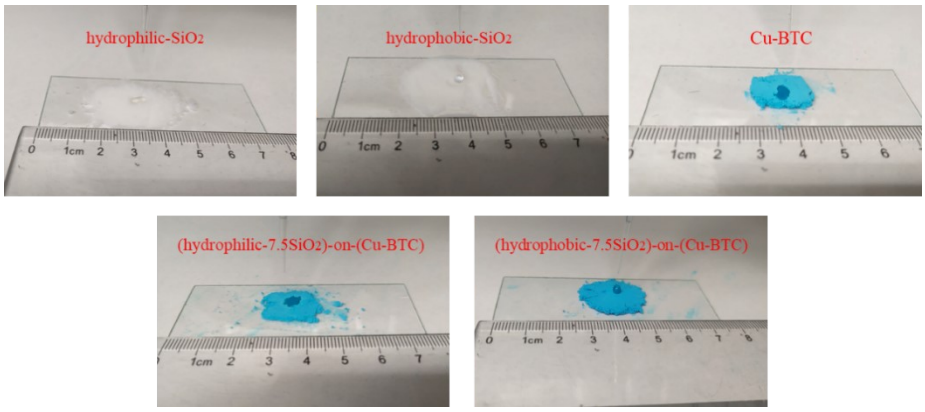
Chemicals. Reagents required include ethanol (CH_3CH_2OH, ⩾99.7%), Polyvinylpyrrolidone (PVP), 1,3,5-Benzenetricarboxylic acid (H_3BTC, 98%), N,N-Dimethylformamide(DMF, ⩾99.5%), Methylene blue (MB), which were supplied by Sinopharm Chemical Regent Co., Ltd. Copper nitrate hydrate ($Cu(NO_3)_2 \cdot 3H_2O$, 99%),

which was supplied by Shanghai Aladdin Biochemical Technology Co., Ltd. Nano SiO_2. All chemicals selected for this work are not purified in any way.

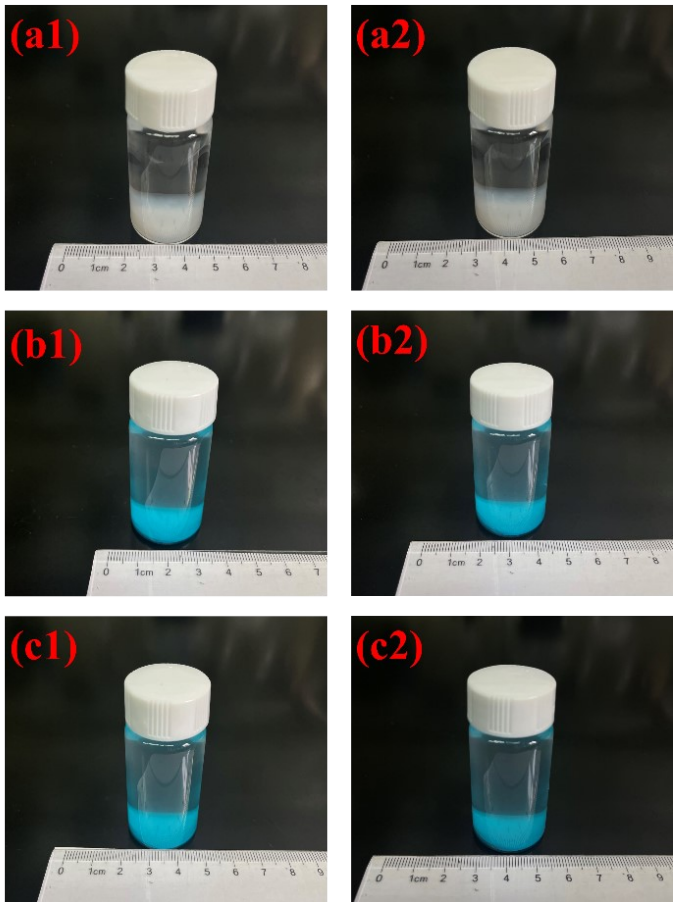
Instruments. The N_2 adsorption isotherms at -196℃ were calculated using the physical adsorption device (ASAP 2020), and the total surface area and pore size of the prepared MOFs and composites were calculated. Isotherms were measured using samples heated for 6 hours in a vacuum at 120℃. SEM images were obtained by electron microscope (SEM, Gemini 300). XRD (D2 Phaser, Bruker, Cu Kα radiation) was used to analyze the crystal phase of the samples. FT-IR data of potassium bromide particles were recorded by Nicolet Nexus 470 spectrometer. XPS analysis was performed using the Physical Electronics PHI 5700 spectrometer with nonmonochromatic Mg Kα radiation (300 W, 15 kV, 1253.6eV) for the core level signals of Cu2p and Si2p were analyzed using a multichannel detector. The spectra of the powder samples were recorded at 29.35 eV by using a 720-um diameter analysis region. THE PHI has access to ESCA-V6. F software package was used for acquisition and data analysis. The Shirley-type background is subtracted from the signal. In order to determine more accurately the binding energies of the core energy levels of different elements, the recorded spectra are always fitted with gaussian Lorentz curves. The estimated error of BE is about 0.1 eV. Thermogravimetric analysis (TG-DSC) is performed on a NETZSCH STA-449C thermal analyzer in the atmosphere of nitrogen.



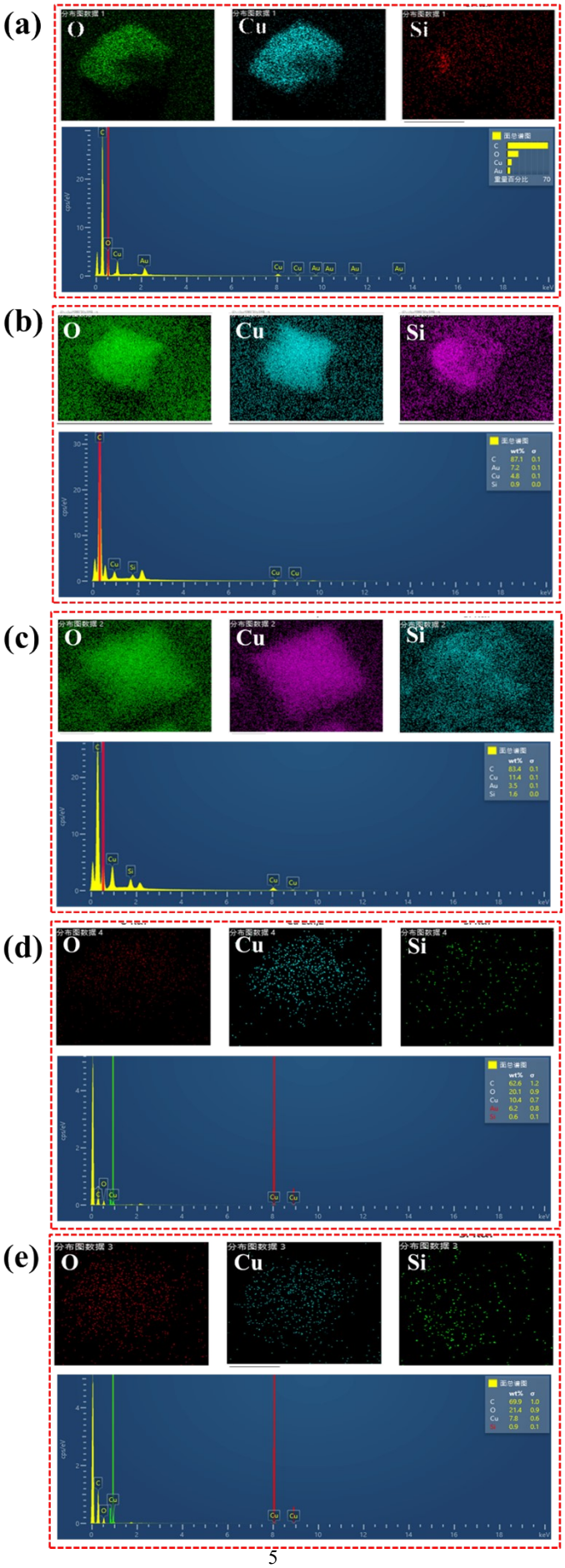
Scheme S1 Structure of methylene blue.



Scheme S2 Comparisons of hydrophilic and hydrophobic properties of hydrophilic-SiO_2, hydrophobic-SiO_2, Cu-BTC, (hydrophilic-7.5SiO_2)-on-(Cu-BTC), and (hydrophobic-7.5SiO_2)-on-(Cu-BTC) samples, respectively.



Scheme S3 Particles morphologies comparisons of as-prepared samples before (1) and after (2) being soaked in strong alkali (pH=12) aqueous solution for 24 h at room temperature (25 ^{o}C). (a): Cu-BTC; (b): (hydrophilic-7.5SiO_2)-on-(Cu-BTC); (c): (hydrophobic-7.5SiO_2)-on-(Cu-BTC).


(a)
O
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Si
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Si
(c)
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Cu
Si
(d)
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Cu
Si
(e)
O
Cu
Si

Fig. S1 EDX images of Cu-BTC (a), (hydrophilic-7.5SiO_2)-on-(Cu-BTC) (b), (hydrophobic-7.5SiO_2)-on-(Cu-BTC) (c), and EDX images of (hydrophilic-7.5SiO_2)-on-(Cu-BTC) (d), (hydrophobic-7.5SiO_2)-on-(Cu-BTC) (e) after soaking in alkaline solution for 24 h at room temperature (25°C).

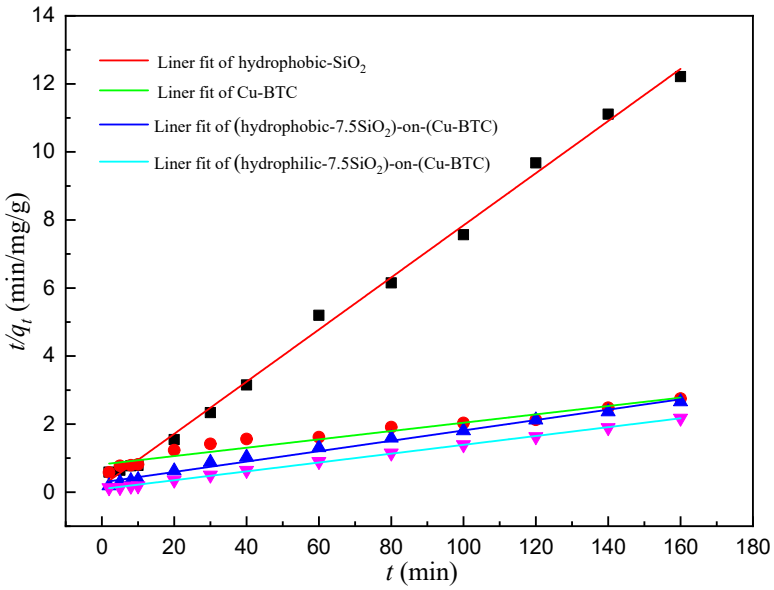

Fig. S2 Pseudo second-order fitting plots for MB adsorption onto hydrophilic-SiO_2, Cu-BTC, (hydrophilic-7.5SiO_2)-on-(Cu-BTC), and (hydrophobic-7.5SiO_2)-on-(Cu-BTC) samples.

Table S1 All the chemicals used in this study

Chemicals	Purity	Manufactory
CH_3CH_2OH	≥99.7%	Sinopharm Chemical Regent Co., Ltd
Polyvinylpyrrolidone (PVP)	187.07	Sinopharm Chemical Regent Co., Ltd
1,3,5-Benzenetricarboxylic acid (H_3BTC)	98%	Sinopharm Chemical Regent Co., Ltd
N,N-Dimethylformamide(DMF)	≥95.5%	Sinopharm Chemical Regent Co., Ltd
Methylene blue (MB)	≥82%	Sinopharm Chemical Regent Co., Ltd
Copper nitrate hydrate ($Cu(NO_3)_2 \cdot 3H_2O$)	99%	Shanghai Aladdin Biochemical Technology Co., Ltd
Nano SiO_2	≥99%	Yuexu Technology Co., Ltd

Table S2 Textural properties of different materials, respectively.

Sample	S_{BET} (m^2/g)	V_{total} (cm^3/g)	Average pore diameter (nm)
SiO_2-hydrophilic	211.47	0.854	9.572
SiO_2-hydrophobic	187.07	0.784	7.343
Cu-BTC@(7.5)SiO_2-hydrophilic	645.62	0.455	2.823
Cu-BTC@(7.5)SiO_2-hydrophobic	605.65	0.440	2.905
Cu-BTC	1356.45	0.581	1.712
Cu-BTC@(15)SiO_2-hydrophilic	897.79	0.458	2.039
Cu-BTC@(5)SiO_2-hydrophilic	546.40	0.412	3.014

Table S3 Adsorption isotherm models used in this study and their linear forms

Isotherm	Nonlinear form	Linear form	Plot
Langmuir-I	$q_e = \frac{q_L K_L C_e}{1 + K_L C_e}$	$\frac{C_e}{q_e} = \frac{1}{q_L \cdot K_L} + (\frac{1}{q_L}) \cdot C_e$	$\frac{C_e}{q_e}$ versus C_e
Freundlich	$q_e = K_f C_e^{\frac{1}{n}}$	$\ln q_e = \ln K_f + (\frac{1}{n}) \cdot \ln C_e$	$\ln q_e$ versus $\ln C_e$
D–R	$q_e = q_s e^{(-K_D \varepsilon^2)}$	$\ln q_e = \ln q_s - K_D \varepsilon^2$	$\ln q_e$ versus ε^2

Where q_e is the maximum capacity of adsorption in mg/g; K_L is a constant related to the affinity of the binding sites in L/mg;'K_f' and 'n' are the measures of adsorption capacity and intensity of adsorption; q_s is the D-R isotherm constant in mg/g; K_D stands for the constant that is relevant with the adsorption energy in mol^2/kJ^2; ε represents the Polanyi potential constant in kJ/mol;

Table S4 Adsorption isothermal model fitting parameters of hydrophilic-SiO_2, Cu-BTC, (hydrophobic-7.5SiO_2)-on-(Cu-BTC) and (hydrophilic-7.5SiO_2)-on-(Cu-BTC).

Samples	Langmuir Model			Freundlich Model			D-R Model		
	q_L (mg/g)	K_L (L/mg)	R^2	K_f (L/g)	n	R^2	q_s (mg/g)	K_D (mol^2/kJ^2)	R^2
(hydrophilic-7.5SiO_2)-on-(Cu-BTC)	76.19	0.3917	0.9958	26.8923	3.35	0.6705	72.85	0.9099	0.9088
(hydrophobic-7.5SiO_2)-on-(Cu-BTC)	64.89	0.2774	0.9933	17.2415	2.72	0.7532	57.74	1.1331	0.9163
Cu-BTC	67.38	0.1358	0.9942	9.7817	1.96	0.8895	47.57	1.0008	0.8895
hydrophilic-SiO_2	13.81	0.4639	0.9985	5.7432	4.25	0.9335	12.38	0.4711	0.8567

Table S5 Kinetic parameters of MB adsorbed onto SiO_2-hydrophilic, Cu-BTC, Cu-BTC@(7.5)SiO_2-hydrophobic and Cu-BTC@(7.5)SiO_2-hydrophilic.

Samples	Pseudo-first-order rate equation						Pseudo-second-order rate equation						Intra-particle diffusion model		
	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	K_1 (1/min)	R^2	$\triangle q$ (mg/g)	$\triangle q$ (%)	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	K_2 ($g \cdot mg^{-1} \cdot min^{-1}$)	R^2	$\triangle q$ (mg/g)	$\triangle q$ (%)	C (mg/g)	K_3 ($mg \cdot g^{-1} \cdot min^{-1/2}$)	R^2
SiO_2-hydrophilic	13.22	12.81	0.0138	0.3156	0.41	3.10	13.22	13.51	0.0326	0.9968	-0.29	-2.19	8.31	0.4610	0.3901
Cu-BTC	56.44	66.56	0.0383	0.9158	-10.12	-17.93	56.44	95.19	1.84E-04	0.9472	-38.75	-68.65	-5.30	5.2629	0.9889
Cu-BTC@(7.5)SiO_2-hydrophobic	60.24	55.18	0.0242	0.9571	5.06	8.39	60.24	63.34	8.09E-04	0.9887	-5.14	-8.53	10.44	4.2623	0.9691
Cu-BTC@(7.5)SiO_2-hydrophilic	73.94	68.90	0.0324	0.9229	5.04	6.82	73.94	75.09	1.86E-03	0.9991	-1.15	-1.56	31.76	3.9448	0.7665

Table S6 Diffusion coefficients of MB adsorbed onto SiO_2-hydrophilic ,Cu-BTC, Cu-BTC@(7.5)SiO_2-hydrophobic and Cu-BTC@(7.5)SiO_2-hydrophilic.

Samples	***K (s^{-1})***	***D_{iq} (cm^2/s)***
SiO_2-hydrophilic	0.1508	1.4004E-08
Cu-BTC	0.0135	4.0090E-11
Cu-BTC@(7.5)SiO_2-hydrophobic	0.0202	1.6327E-10
Cu-BTC@(7.5)SiO_2-hydrophilic	0.0253	2.1675E-10

Table S7 Mass comparisons of as-prepared samples before and after immersion in alkaline solution for 24 h at room temperature (25^{o}C).

Samples	Initial mass (*g*)	Final mass (*g*)	Loss rate (%)
SiO_2-hydrophilic	0.1000	0.0917	8
Cu-BTC@(7.5)SiO_2-hydrophilic	0.2000	0.1820	9
Cu-BTC@(7.5)SiO_2-hydrophobic	0.2000	0.1915	4

Table S8 Comparisons of Si contents derived from EDS before and after immersion in alkaline solution for 24 h at room temperature (25^{o}C).

Samples	Element	Initial (wt%)	Present (wt%)
Cu-BTC@(7.5)SiO_2-hydrophilic	Si	0.9	0.6
Cu-BTC@(7.5)SiO_2-hydrophobic	Si	1.6	0.9

Table S9 MB uptake capacities of different adsorbents.

Adsorbents	Uptake capacities (mg/g)	References
Cu-BTC	5	1
MIL-101	21	2
MIL-101	26	3
MIL-53	58	4
Zn-MOF	6	5
MIL-53(Fe)	25	6
MIL-88B(Fe)	23	6
Ni-MOF	18	6
ZIF-67	17	6
MIL-101(Fe)	16	6
Chitosan	27	7
CNT	46	8
OMWCNT	47	9
Core shell	34	10
Cellulose grafted	8	11
Magnetic chitosan/organic rectorite	25	12
Cu-BTC	54	This work
(hydrophilic-7.5SiO_2)-on-(Cu-BTC)	54	This work
(hydrophobic-7.5SiO_2)-on-(Cu-BTC)	61	This work

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