Supporting information for

Enhanced water-resistant performance of Cu-BTC through polyvinylpyrrolidone protection and its capture ability evaluation of methylene blue

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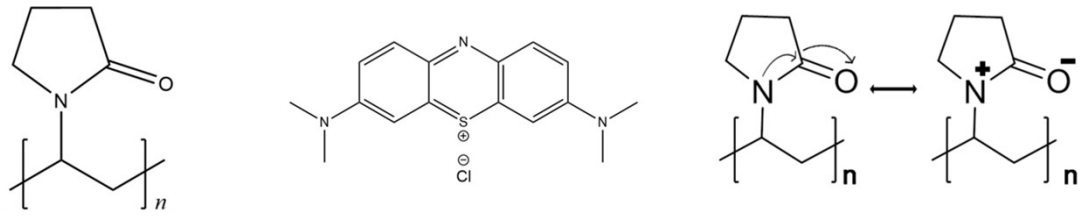
Section I:

Chemicals: Copper nitrate trihydrate ($Cu(NO_3)_2{\cdot}3H_2O$) (Shanghai Aladdin Biotechnology Co., Ltd.), Benzene-1,3,5-tricarboxylic acid (H_3BTC) (Sinopharm Chemical Reagent Co., Ltd.), polyvinylpyrrolidone K30 ($(C_6H_9NO)_n$) (Sinopharm Chemical Reagent Co., Ltd.), absolute ethanol (C_2H_6O) (Sinopharm Chemical Reagent Co., Ltd.), deionized water (generated at 25 ^oC, 18.25m$\Omega{\cdot}cm^{-1}$), sodium hydroxide (NaOH) (Sinopharm Chemical Reagent Co., Ltd.), hydrochloric acid (HCl) (Sinopharm Chemical Reagent Co., Ltd.), methylene blue (MB) (Sinopharm Chemical Reagent Co., Ltd.).

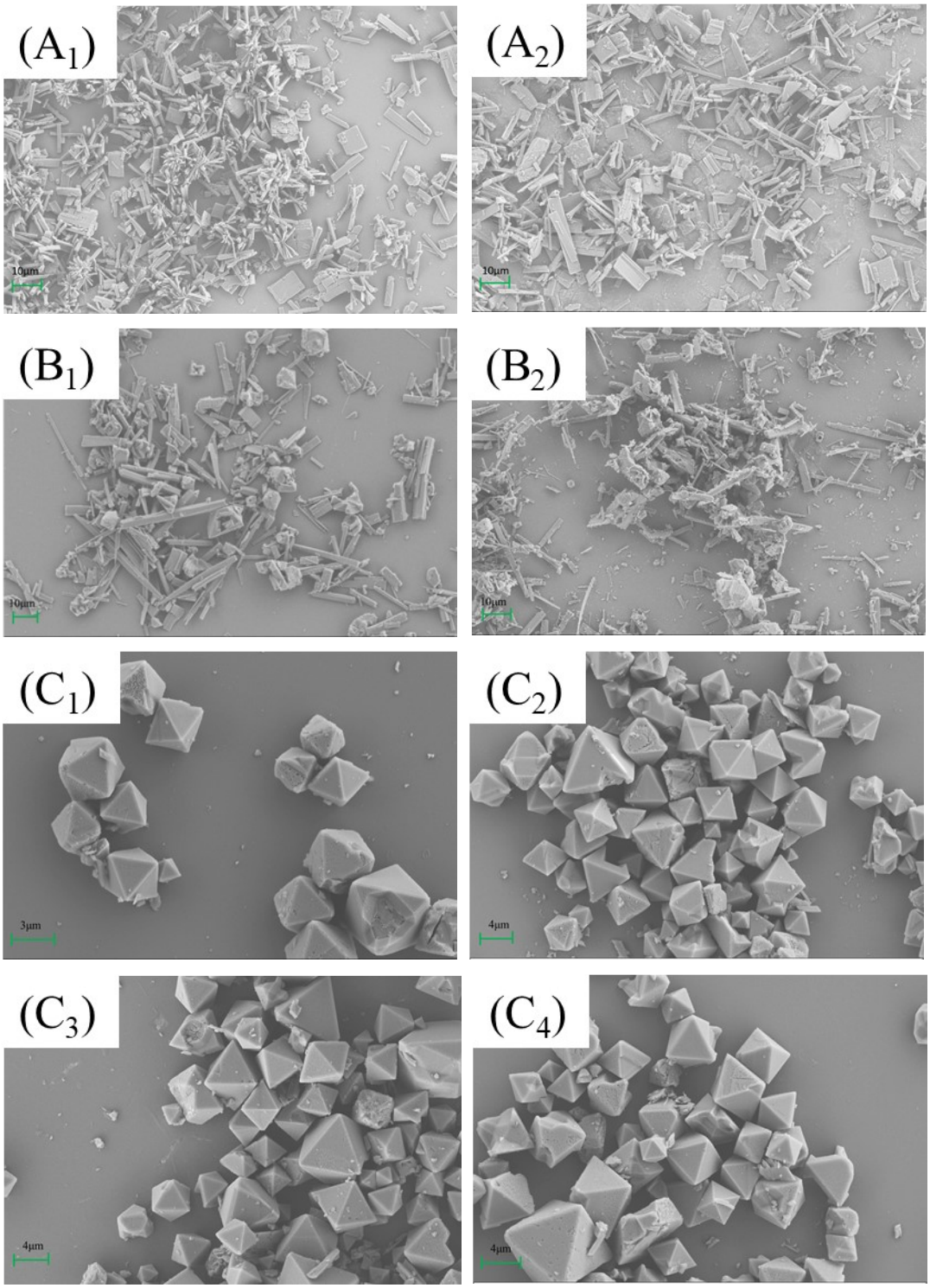
Apparatus: SEM images are scanned by electron microscope using Hitachi S4800 equipped with EDAX energy dispersion detector (Zeiss Gemini SEM 300). D8 Advance X-ray diffractometer of Bruck AXS GMBH is used to scan the crystal phase

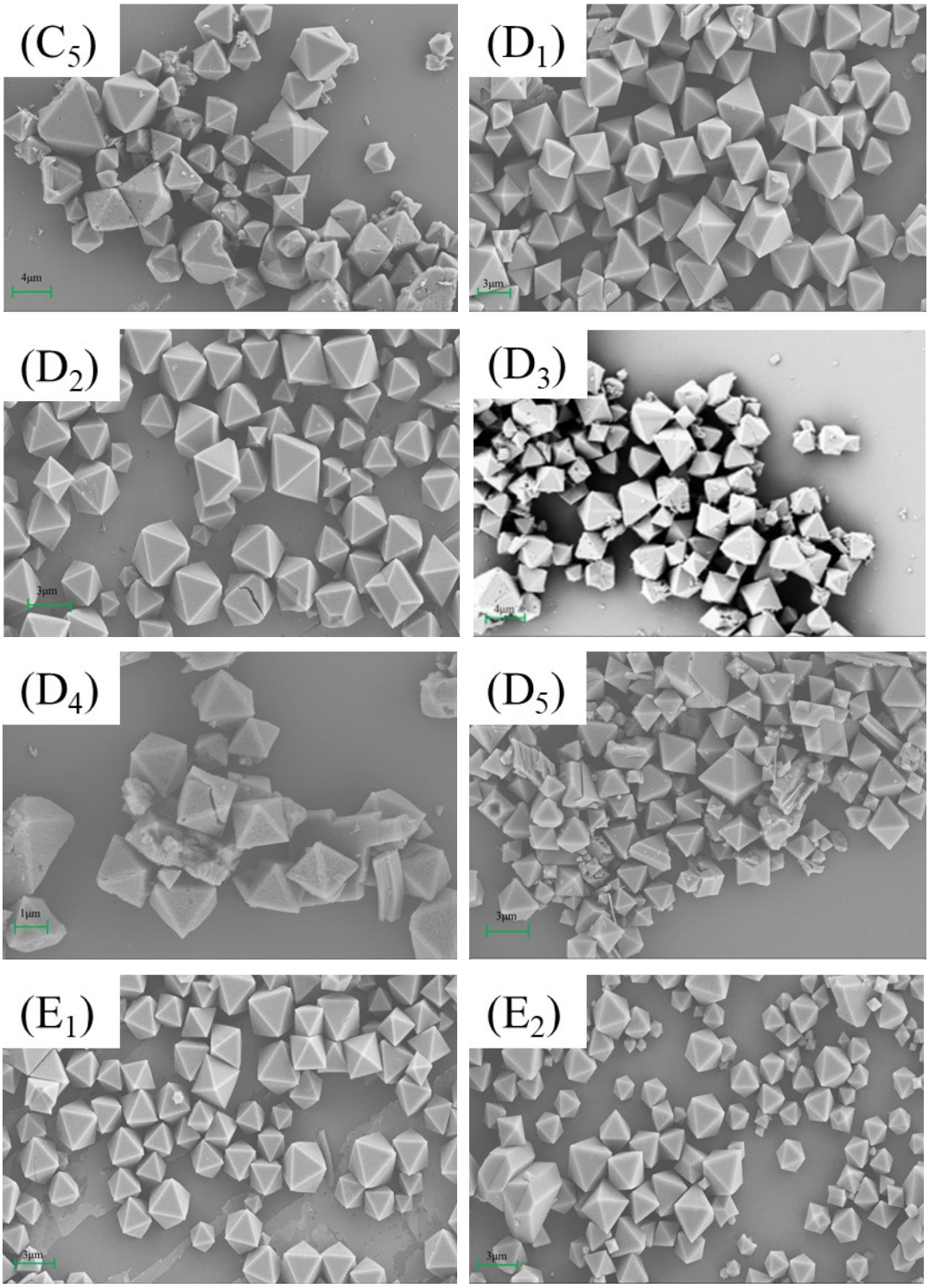
of the material (2θ = 5~30°). The specific surface area and average pore diameter of the material are measured by Autosorb-iQ physical adsorption instrument of Kanta Instrument Co., Ltd. (The samples were degassed at 120°C for 5h and The N_2 adsorption-desorption isotherms were recorded at -196℃). The average particle size of samples are measured by Mastersizer 3000E laser particle size analyzer from Malvern Instruments Co., Ltd. The thermal gravimetric analysis (TGA) was determined using a STA 449 F5 thermal gravimetric analyzer from 20 to 850℃. The functional groups were analyzed by a Fourier transform infrared spectrometer (FT-IR, Thermo Nicolet NEXUS-670). Sample absorbance was measured by Shimadzu UV-3600 spectrophotometer at 664nm.

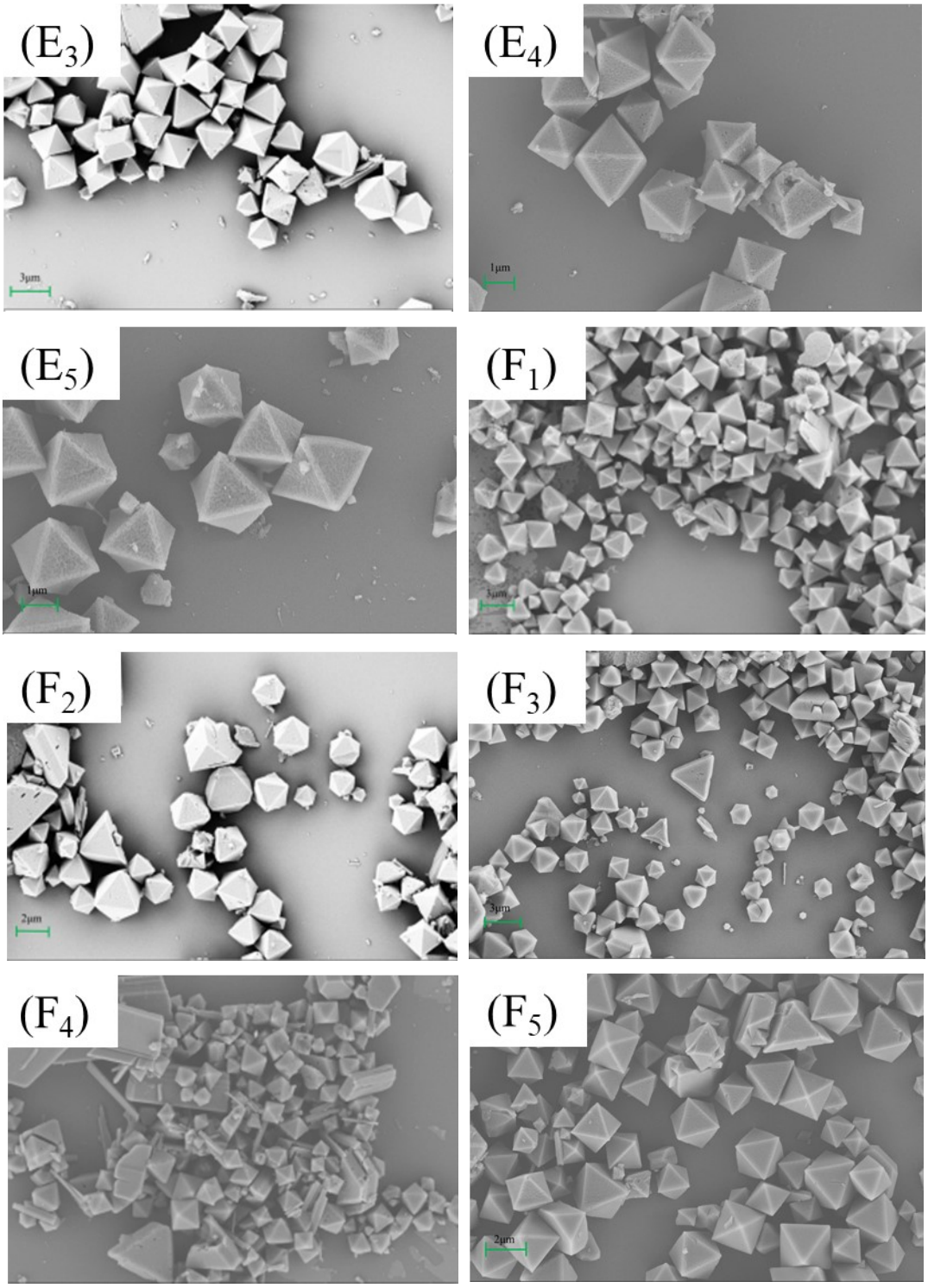


(A) (B) (C)

Scheme S1. Molecular formula of PVP and MB, and the resonance structure of PVP (A: Molecular formula of PVP; B: Molecular formula of MB; C: the resonance structure of PVP)


(A1)
10μm
(A2)
10μm
(B1)
10μm
(B2)
10μm
(C1)
3μm
(C2)
4μm
(C3)
4μm
(C4)
4μm


(C5)
4μm
(D1)
3μm
(D2)
3μm
(D3)
4μm
(D4)
1μm
(D5)
3μm
(E1)
3μm
(E2)
3μm


(E3)
3μm
(E4)
1μm
(E5)
1μm
(F1)
3μm
(F2)
2μm
(F3)
3μm
(F4)
(F5)
2μm

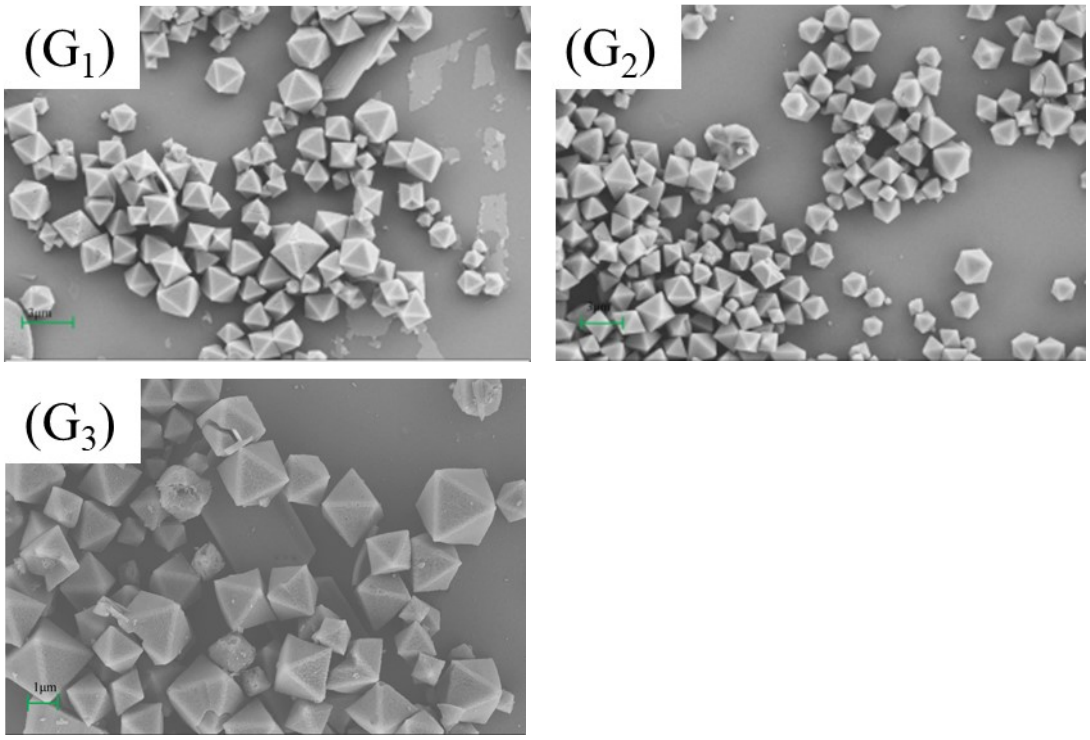
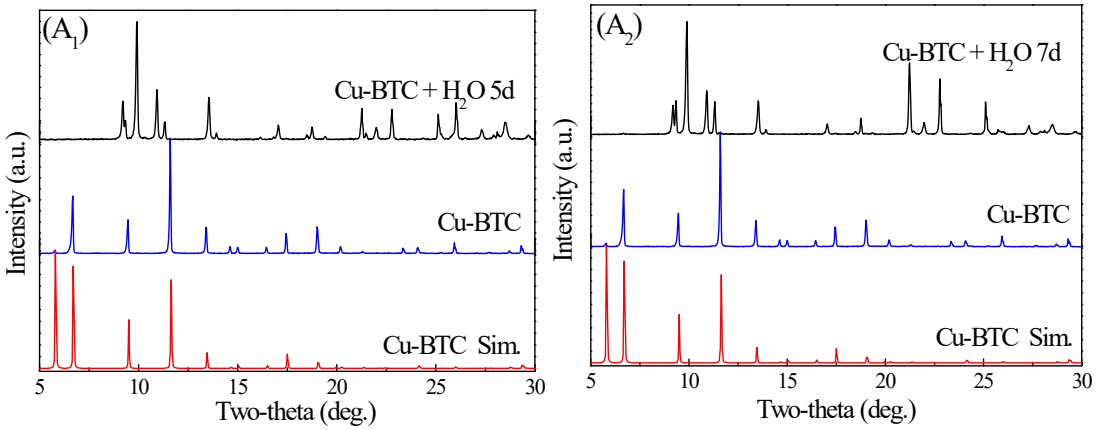
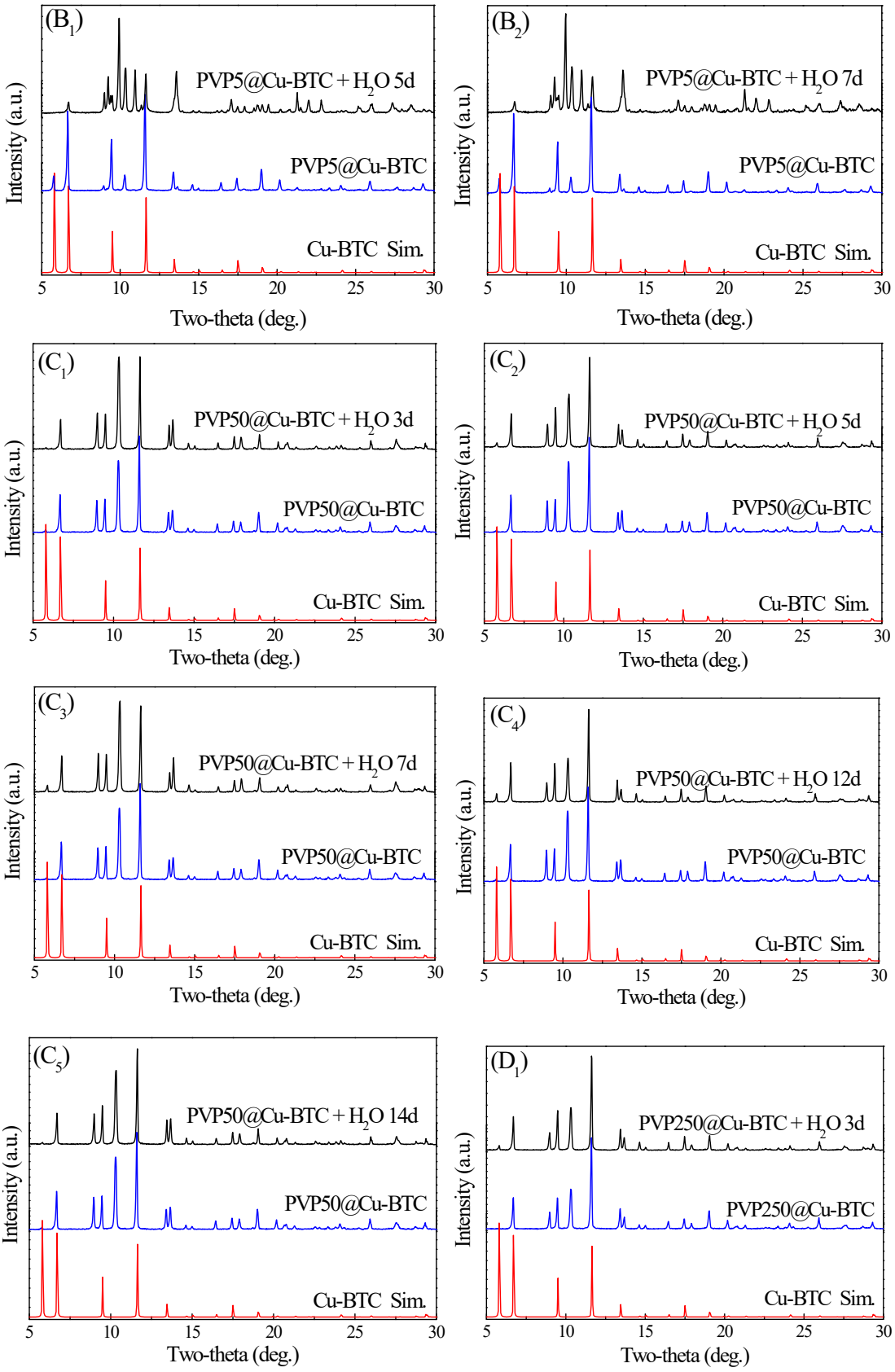
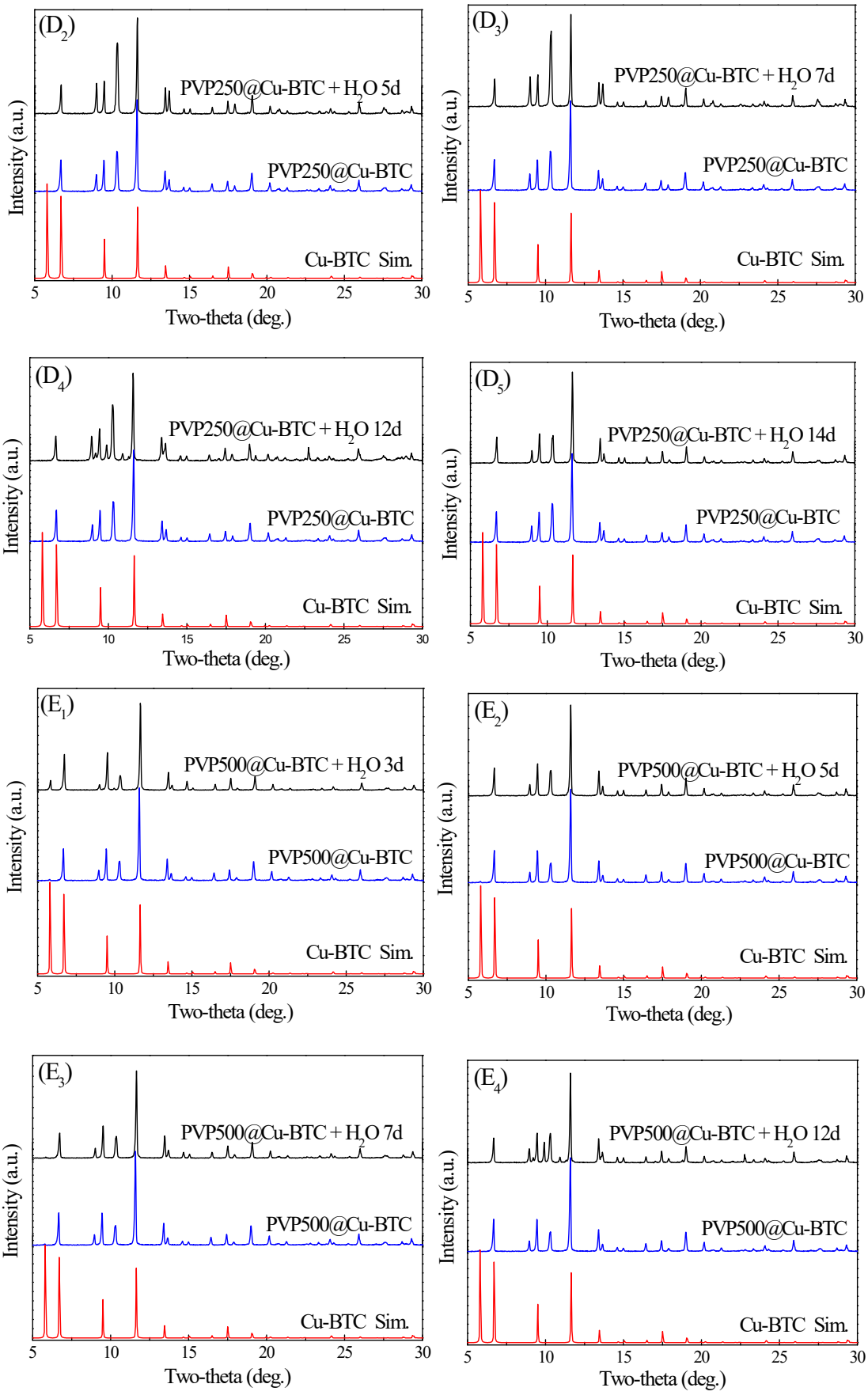
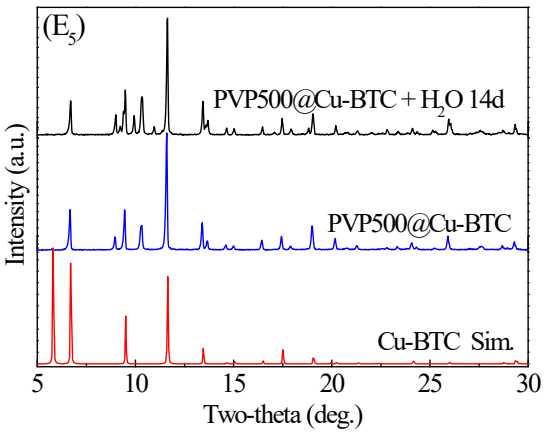


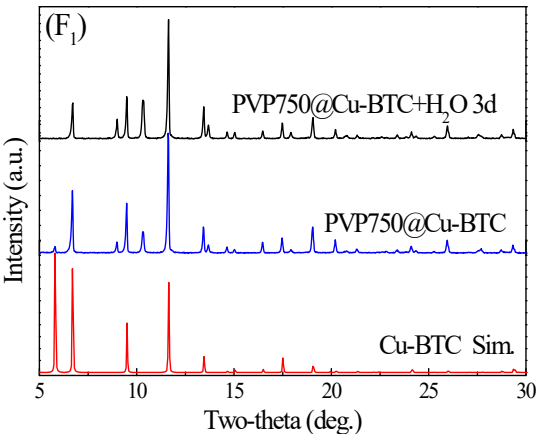
Fig. S1. SEM images of ((A_1) and (A_2)): Cu-BTC, ((B_1) and (B_2)): PVP5@Cu-BTC after being soaked accordingly in water for 5 and 7 days; ((C_1), (C_2), (C_3), (C_4) and (C_5)): PVP50@Cu-BTC; ((D_1), (D_2), (D_3), (D_4) and (D_5)): PVP250@Cu-BTC; ((E_1), (E_2), (E_3), (E_4) and (E_5)): PVP500@Cu-BTC, ((F_1), (F_2), (F_3), (F_4) and (F_5)): PVP750@Cu-BTC after being soaked in water for 3, 5, 7, 12 and 14 days; ((G_1), (G_2), and (G_3)): PVP1000@Cu-BTC after being soaked accordingly in water for 5, 7 and 12 days.

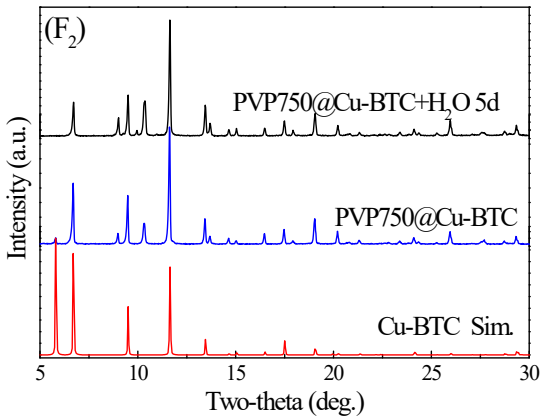


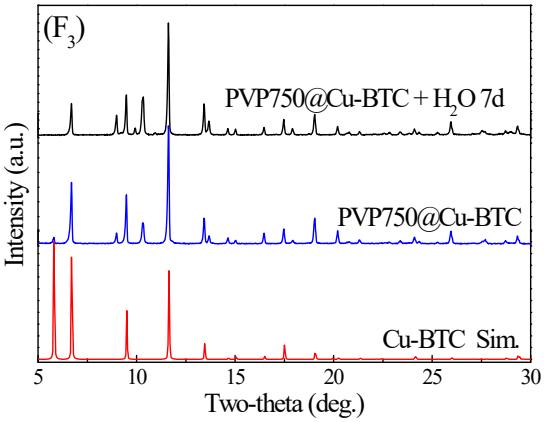

(B1)
PVP5@Cu-BTC + H2O 5d
PVP5@Cu-BTC
Cu-BTC Sim.
(B2)
PVP5@Cu-BTC + H2O 7d
PVP5@Cu-BTC
Cu-BTC Sim.
(C1)
PVP50@Cu-BTC + H2O 3d
PVP50@Cu-BTC
Cu-BTC Sim.
(C2)
PVP50@Cu-BTC + H2O 5d
PVP50@Cu-BTC
Cu-BTC Sim.
(C3)
PVP50@Cu-BTC + H2O 7d
PVP50@Cu-BTC
Cu-BTC Sim.
(C4)
PVP50@Cu-BTC + H2O 12d
PVP50@Cu-BTC
Cu-BTC Sim.
(C5)
PVP50@Cu-BTC + H2O 14d
PVP50@Cu-BTC
Cu-BTC Sim.
(D1)
PVP250@Cu-BTC + H2O 3d
PVP250@Cu-BTC
Cu-BTC Sim.
Intensity (a.u.)
Two-theta (deg.)
5
10
15
20
25
30

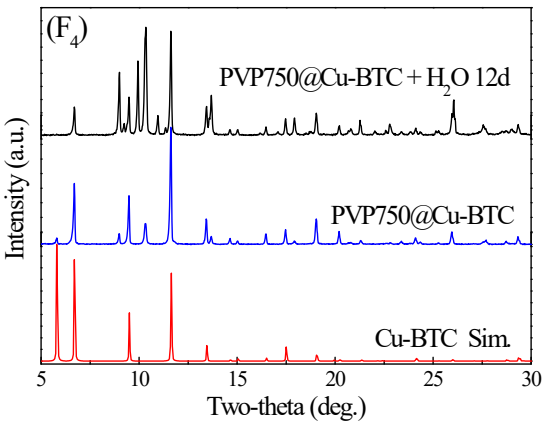

(D2)
PVP250@Cu-BTC + H2O 5d
PVP250@Cu-BTC
Cu-BTC Sim.
Intensity (a.u.)
Two-theta (deg.)
(D3)
PVP250@Cu-BTC + H2O 7d
PVP250@Cu-BTC
Cu-BTC Sim.
Intensity (a.u.)
Two-theta (deg.)
(D4)
PVP250@Cu-BTC + H2O 12d
PVP250@Cu-BTC
Cu-BTC Sim.
Intensity (a.u.)
Two-theta (deg.)
(D5)
PVP250@Cu-BTC + H2O 14d
PVP250@Cu-BTC
Cu-BTC Sim.
Intensity (a.u.)
Two-theta (deg.)
(E1)
PVP500@Cu-BTC + H2O 3d
PVP500@Cu-BTC
Cu-BTC Sim.
Intensity (a.u.)
Two-theta (deg.)
(E2)
PVP500@Cu-BTC + H2O 5d
PVP500@Cu-BTC
Cu-BTC Sim.
Intensity (a.u.)
Two-theta (deg.)
(E3)
PVP500@Cu-BTC + H2O 7d
PVP500@Cu-BTC
Cu-BTC Sim.
Intensity (a.u.)
Two-theta (deg.)
(E4)
PVP500@Cu-BTC + H2O 12d
PVP500@Cu-BTC
Cu-BTC Sim.
Intensity (a.u.)
Two-theta (deg.)

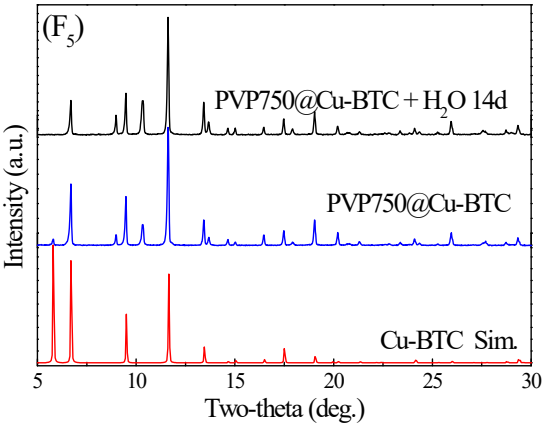

(E5)
PVP500@Cu-BTC + H2O 14d
PVP500@Cu-BTC
Cu-BTC Sim.
Intensity (a.u.)
5
10
15
20
25
30
Two-theta (deg.)

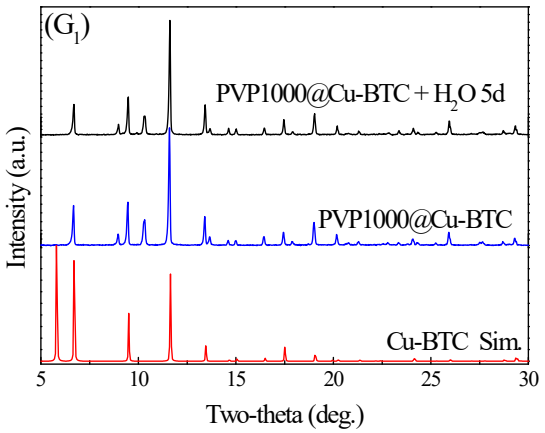

(F1)
PVP750@Cu-BTC+H2O 3d
PVP750@Cu-BTC
Cu-BTC Sim.
Intensity (a.u.)
5
10
15
20
25
30
Two-theta (deg.)

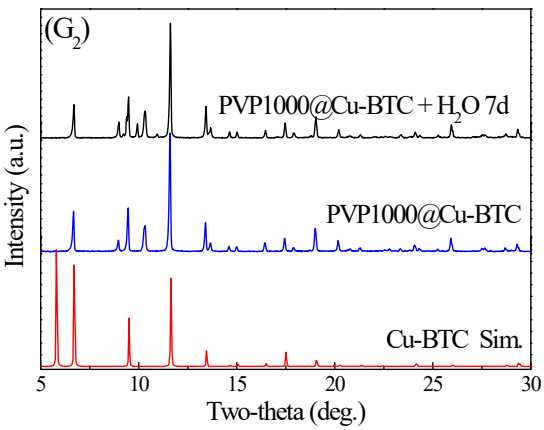

(F2)
PVP750@Cu-BTC+H2O 5d
PVP750@Cu-BTC
Cu-BTC Sim.
Intensity (a.u.)
5
10
15
20
25
30
Two-theta (deg.)


(F3)
PVP750@Cu-BTC + H2O 7d
PVP750@Cu-BTC
Cu-BTC Sim.
Intensity (a.u.)
5
10
15
20
25
30
Two-theta (deg.)


(F4)
PVP750@Cu-BTC + H2O 12d
PVP750@Cu-BTC
Cu-BTC Sim.
Intensity (a.u.)
5
10
15
20
25
30
Two-theta (deg.)


(F5)
PVP750@Cu-BTC + H2O 14d
PVP750@Cu-BTC
Cu-BTC Sim.
Intensity (a.u.)
5
10
15
20
25
30
Two-theta (deg.)


(G1)
PVP1000@Cu-BTC + H2O 5d
PVP1000@Cu-BTC
Cu-BTC Sim.
Intensity (a.u.)
5
10
15
20
25
30
Two-theta (deg.)


(G2)
PVP1000@Cu-BTC + H2O 7d
PVP1000@Cu-BTC
Cu-BTC Sim.
Intensity (a.u.)
5
10
15
20
25
30
Two-theta (deg.)

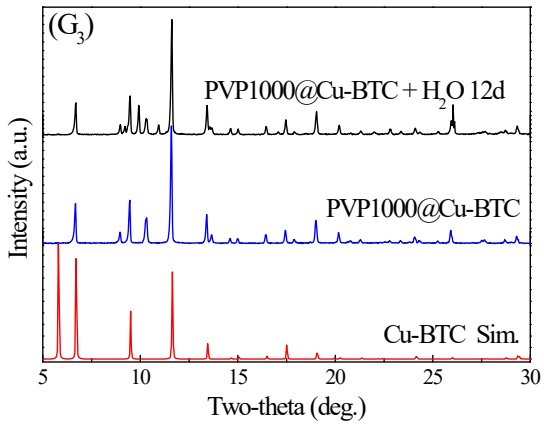
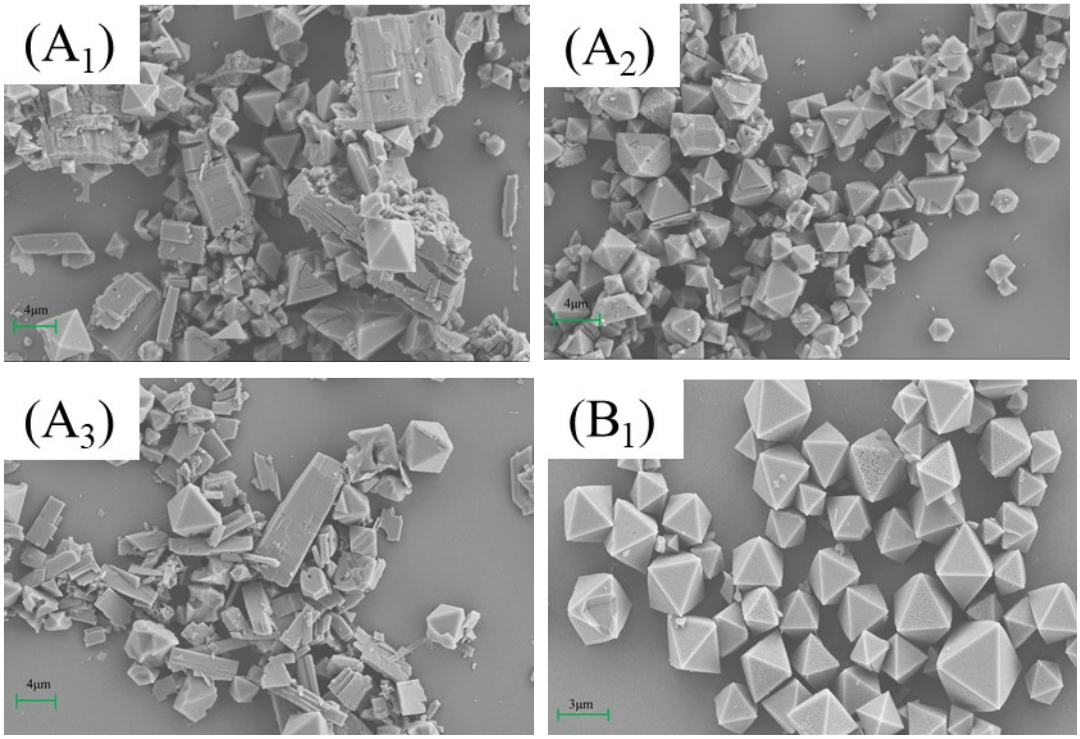


Fig. S2. XRD patterns of ((A_1) and (A_2)): Cu-BTC, ((B_1) and (B_2)): PVP5@Cu-BTC after being soaked accordingly in water for 5 and 7 days; ((C_1), (C_2), (C_3), (C_4) and (C_5)): PVP50@Cu-BTC; ((D_1), (D_2), (D_3), (D_4) and (D_5)): PVP250@Cu-BTC; ((E_1), (E_2), (E_3), (E_4) and (E_5)): PVP500@Cu-BTC, ((F_1), (F_2), (F_3), (F_4) and (F_5)): PVP750@Cu-BTC after being soaked in water for 3, 5, 7, 12 and 14 days; ((G_1), (G_2) and (G_3)): PVP1000@Cu-BTC after being soaked accordingly in water for 5, 7 and 12 days.



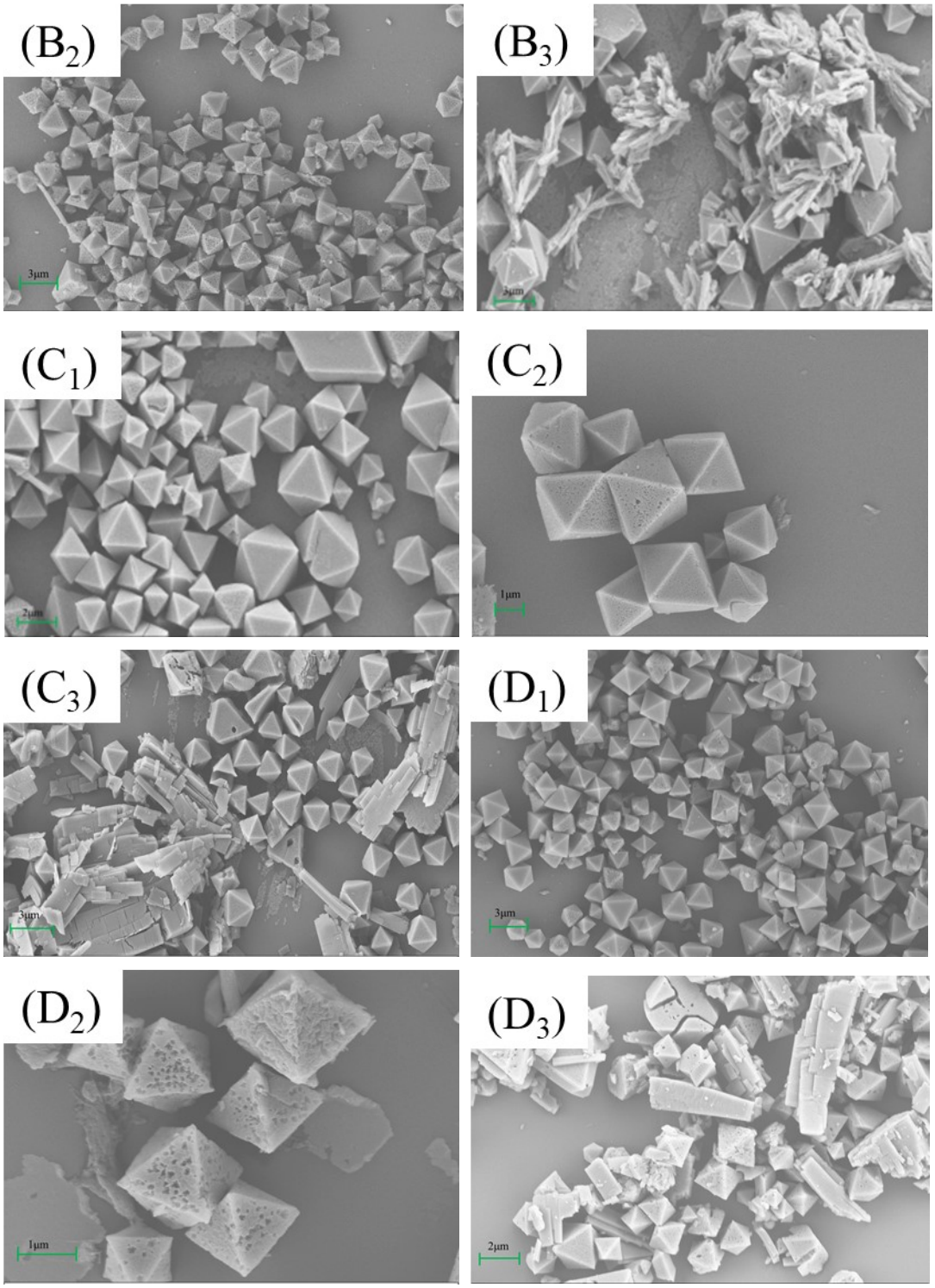
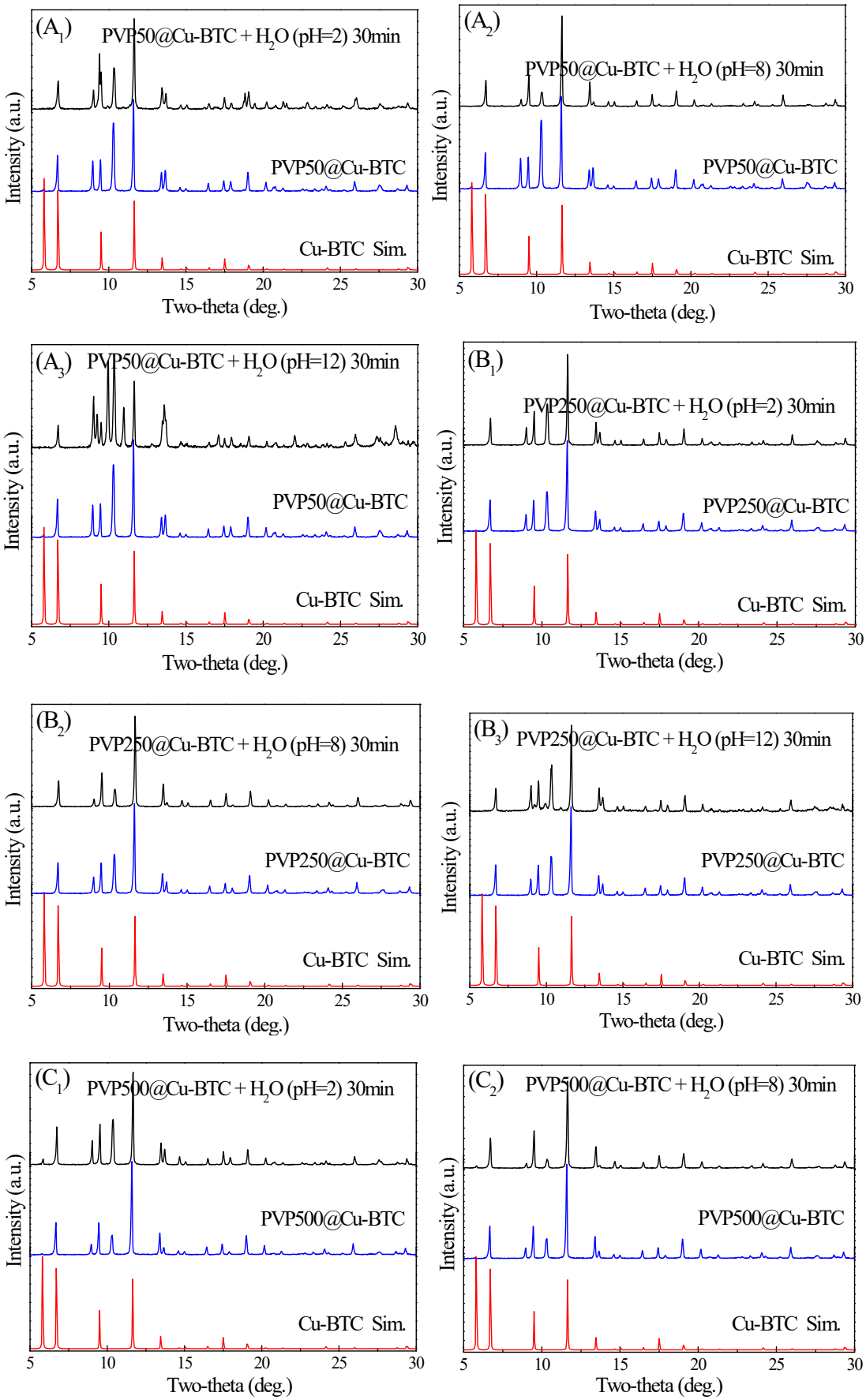


Fig. S3. SEM images of (A_1), (A_2) and (A_3): PVP50@Cu-BTC; (B_1), (B_2) and (B_3): PVP250@Cu-BTC; (C_1), (C_2) and (C_3): PVP500@Cu-BTC; (D_1), (D_2) and (D_3): PVP750@Cu-BTC being soaked accordingly in aqueous solutions at pH=2, 8 and 12 for 30 min.


(A1)
PVP50@Cu-BTC + H2O (pH=2) 30min
PVP50@Cu-BTC
Cu-BTC Sim.
(A2)
PVP50@Cu-BTC + H2O (pH=8) 30min
PVP50@Cu-BTC
Cu-BTC Sim.
(A3)
PVP50@Cu-BTC + H2O (pH=12) 30min
PVP50@Cu-BTC
Cu-BTC Sim.
(B1)
PVP250@Cu-BTC + H2O (pH=2) 30min
PVP250@Cu-BTC
Cu-BTC Sim.
(B2)
PVP250@Cu-BTC + H2O (pH=8) 30min
PVP250@Cu-BTC
Cu-BTC Sim.
(B3)
PVP250@Cu-BTC + H2O (pH=12) 30min
PVP250@Cu-BTC
Cu-BTC Sim.
(C1)
PVP500@Cu-BTC + H2O (pH=2) 30min
PVP500@Cu-BTC
Cu-BTC Sim.
(C2)
PVP500@Cu-BTC + H2O (pH=8) 30min
PVP500@Cu-BTC
Cu-BTC Sim.
Intensity (a.u.)
Two-theta (deg.)
5
10
15
20
25
30

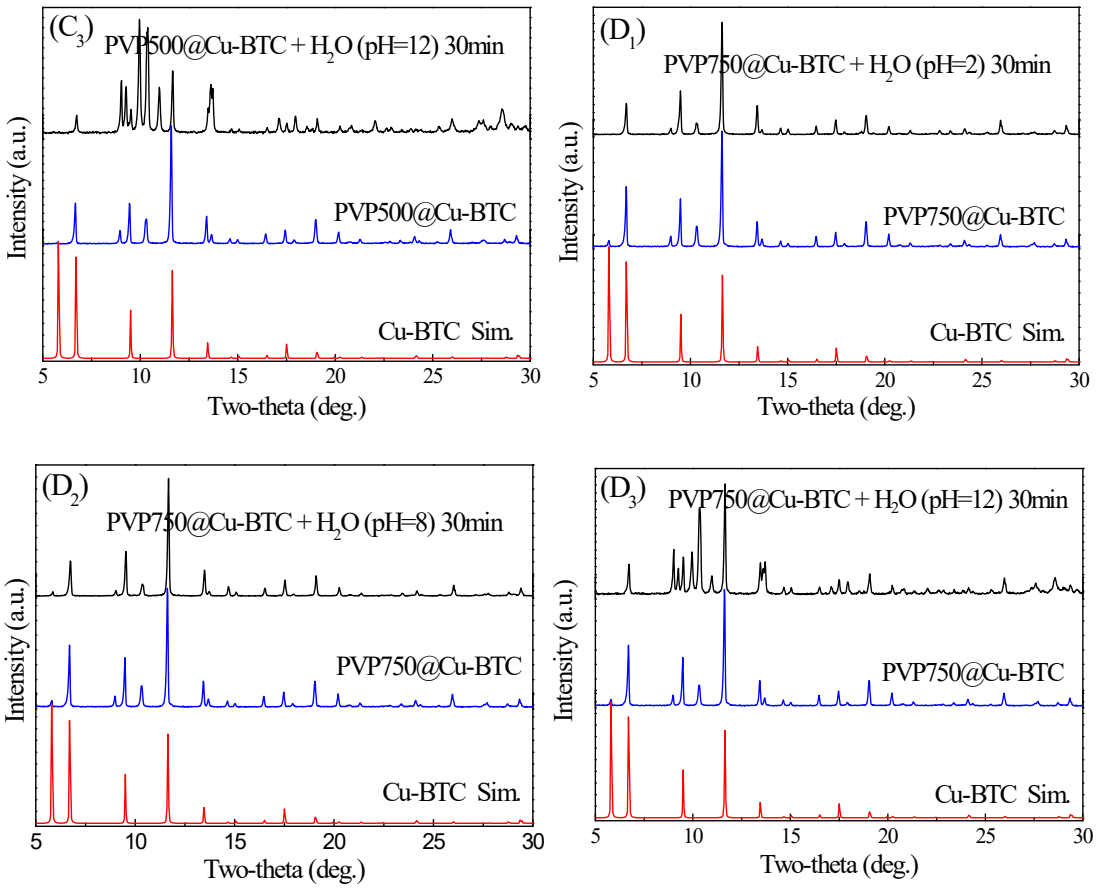
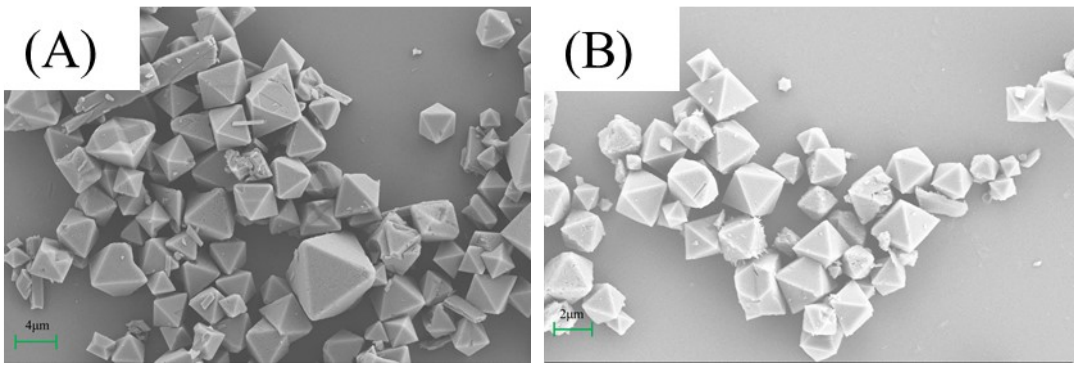


Fig. S4. XRD patterns of (A_1), (A_2) and (A_3): PVP50@Cu-BTC; (B_1), (B_2) and (B_3): PVP250@Cu-BTC; (C_1), (C_2) and (C_3): PVP500@Cu-BTC; (D_1), (D_2) and (D_3): PVP750@Cu-BTC being soaked accordingly in aqueous solutions at pH=2, 8 and 12 for 30 min.



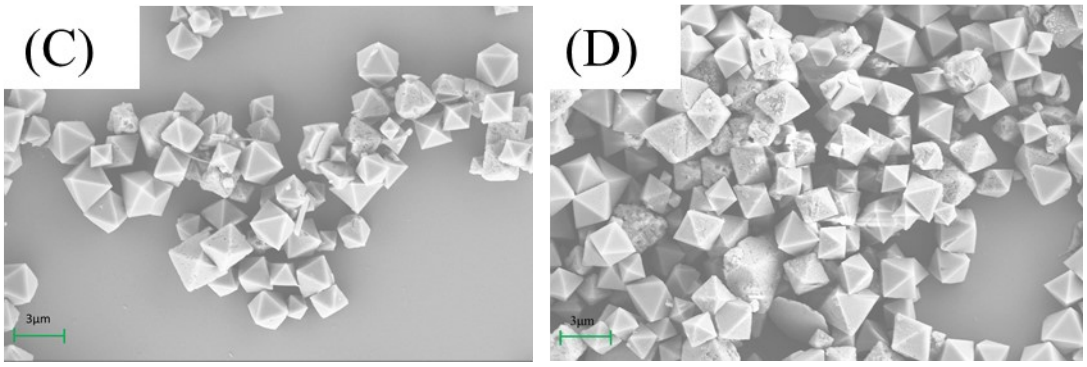


Fig. S5. SEM images of (A): PVP50@Cu-BTC, (B): PVP250@Cu-BTC, (C): PVP500@Cu-BTC, and (D): PVP750@Cu-BTC being soaked accordingly in water at 100 °C for 30 min.

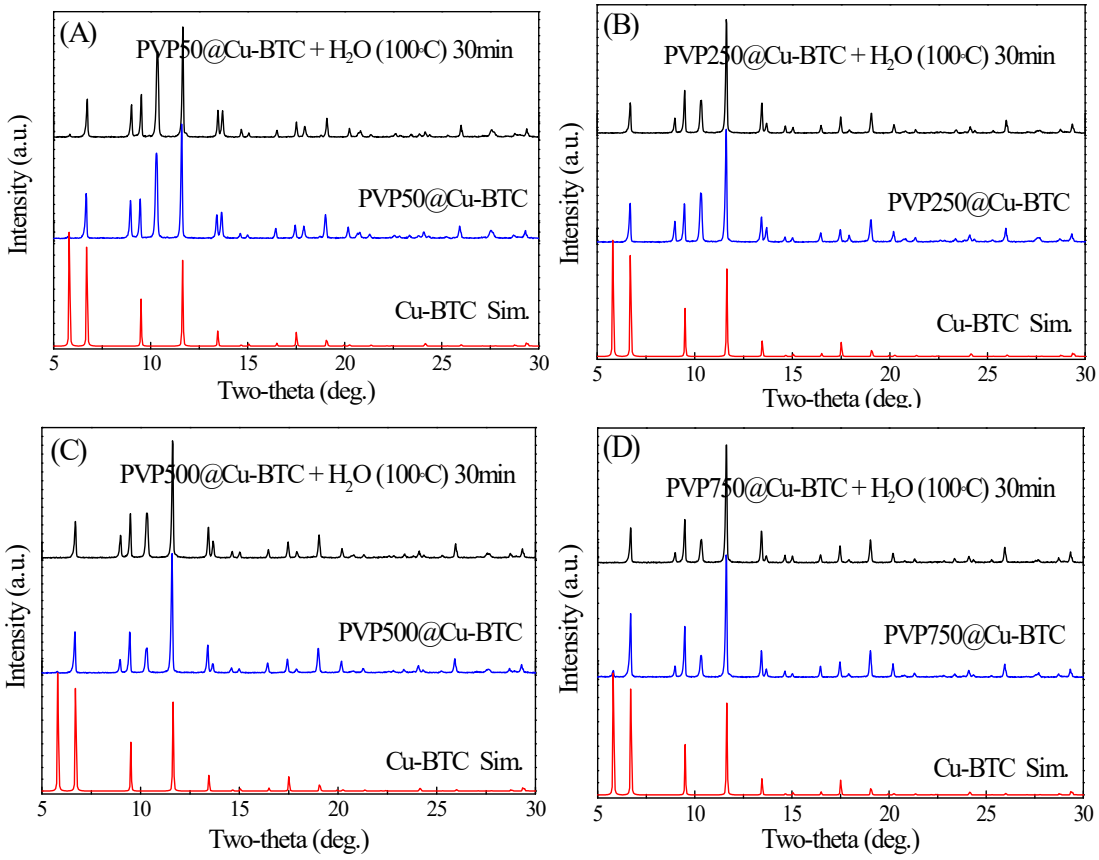


Fig. S6. XRD patterns of (A): PVP50@Cu-BTC, (B): PVP250@Cu-BTC, (C): PVP500@Cu-BTC, and (D): PVP750@Cu-BTC being soaked accordingly in water at 100 °C for 30 min.

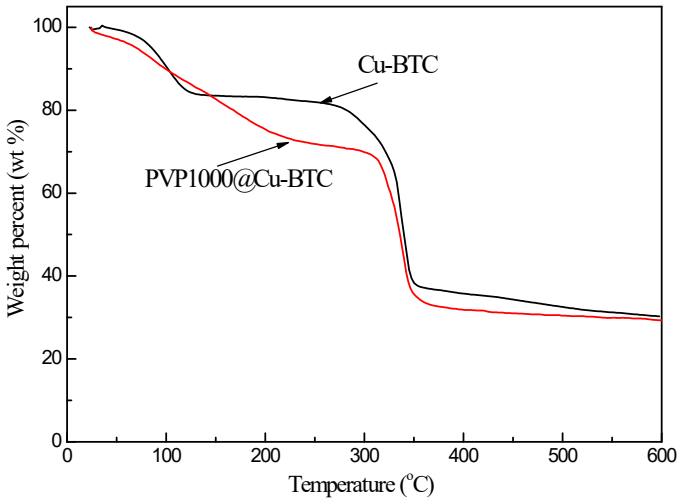


Fig. S7. TGA curves of Cu-BTC and PVP1000@Cu-BTC samples under nitrogen atmosphere.

Table S1. Summary of textural properties of the samples

Samples	S_{BET} ($m^2 \cdot g^{-1}$)	Pore volume ($cm^3 \cdot g^{-1}$)	Average pore size (nm)
Cu-BTC	970	0.37	0.57
PVP(0.00005)@Cu-BTC	1669	0.67	0.75
PVP(0.0005)@Cu-BTC	1166	0.47	0.52
PVP(0.0025)@Cu-BTC	1003	0.42	0.51
PVP(0.005)@Cu-BTC	1187	0.46	0.52
PVP(0.0075)@Cu-BTC	1306	0.49	0.55
PVP(0.01)@Cu-BTC	1162	0.44	0.61

Table S2. Comparison of the MB uptake capacity over different adsorbents

Adsorbent	MB uptake capacity (μmoL/g)	Reference
PVP750@Cu-BTC	240	this work
PVP1000@Cu-BTC	271	this work
M-Cu-BTC	1	1
MWCNT	184	2
MIL-101-Cr	63	3
MIL-53(Al)	63	4
Cu-BTC	28	5
Cu-BTC/GO	45	5
Fe_3O_4@ZIF-8	63	6
Co doped Fe-BDC MOF	75	7
Pine leaves	396	8
Citric Acid Modified Sawdust	348	9
Ce-UiO-66	344	10

References

1 A. R. Abbasi, M. Karimi and K. Daasbjerg, *Ultrason. Sonochem.*, 2017, **37**, 182–191.

2 S. B. Wang, C. W. Ng, W. T. Wang, Q. Li and Z. P. Hao, *Chem. Eng. J.*, 2012, **197**, 34–40.

3 T. T. Shen, J. M. Luo, S. Y. Zhang and X. B Luo, *J. Environ. Chem. Eng.,* 2015, **3**, 1372–1383.

4 C. Li, Z. H. Xiong, J. M. Zhang and C. S. Wu, *J. Chem. Eng. Data,* 2015, **60**, 3414–

3422.

5 L. Li, X. L. Liu, H. Y. Geng, B. Hu, G. W. Song and Z. S. Xu, *J. Mater. Chem. A*., 2013, **1**, 10292.

6 J. Zheng, C. Cheng, W. J. Fang, C. Chen, R. W. Yan, H. X. Huai and C. C. Wang, *Cryst. Eng. Comm.*, 2014, **16**, 3960–3964.

7 S. Soni, P. K. Bajpai, J. Mittal and C. Arora, *J. Mol. Liq.*, 2020, **314**, 113642.

8 M. T. Yagub, T. K. Sen and H. M. Ang, *Water, Air, Soil Pollut.*, 2012, **223**, 5267–5282.

9 W. Zou, H. B. S. Gao and K. Li, *Korean J. Chem. Eng.*, 2013, **30**, 111–122.

10 R. M. Rego, G. Sriram, K. V. Ajeya, H. Y. Jung, M. D. Kurkuri and M. Kigga, *Journal of Hazard. Mater.*, 2021, **416**, 125941.