

Supporting Information

High throughput production of self-floating MIL-88A(Fe)@polyurethane sponge for efficient oil/water separation

Xiao-Hong Yi, Guang-Chi Liu, Hong-Yu Chu, Ya Gao, Chong-Chen Wang* and Peng Wang

Text S1 Chemical reagents

All reagents were used without any further purification. Polyvinyl butyral (PVB, 97%) was purchased from Shang Hai Yingjia Industrial Development Co., Ltd. Iron(III) chloride (FeCl_3 , 97%), and fumaric acid (FA, 99%) were purchased from Jinan Jinsheng New Material Co. LTD. Potassium chloride (KCl, 99%), magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 99%), sodium sulfate (Na_2SO_4 , 99%), calcium sulfate (CaSO_4 , 99%), hydrochloric acid (HCl, 36%), sodium hydroxide (NaOH, 95%) and tetrachloromethane (CCl_4 , 99.5%) were provided by Sinopharm Chemical Reagent Co., Ltd. Ethanol (99%) was obtained from Tianjin Yongda Chemical Reagent Co., Ltd.

Text S2 Characterization methods

Powder X-ray diffraction (PXRD) patterns were recorded on a Dandonghaoyuan DX-2700B diffractometer in the range of $2\theta = 5^{\circ}$ – 50° with Cu K_{α} radiation. The morphology of the materials was measured by scanning electron microscopy (SEM) (TM3030Plus Main Unit). X-ray photoelectron spectroscopy (XPS) was observed using a Thermo ESCALAB 250XI. The metal ions leaching and content of elements of Fe were performed by inductively coupled plasma (ICP-5000, Focused Photonics Inc.).

Text S3 Preparation of MIL-88A(Fe)@sponge

The room-temperature preparation spindle-like MIL-88A(Fe) was carried out according to the method previously reported by Fu et al.¹ Specifically, 600 mmol of industrial grade FeCl_3 (69.6 g) and 600 mmol of industrial grade fumaric acid (97.3 g) were dissolved in 2 L of pure water and 2 L of 95% ethanol, respectively. Then the two solutions were mixed completely and stirred at room temperature for 24 h to obtain MIL-88A(Fe) nanoparticles, which was separated rapidly from the mother liquor with the aid of PVDF hollow fiber membrane.² The prepared MIL-88A(Fe) was further washed with pure water and 95% ethanol until colorless and set aside.

EtOH and H_2O were successively used to clean 30 pieces of polyurethane sponge carriers ($10.0 \text{ cm} \times 10.0 \text{ cm} \times 1.0 \text{ cm}$, see in Fig. S1a) with assistance of an ultrasonic bath, and the treated sponge were dried in an oven at 60°C overnight for further modification.

MIL-88A(Fe) (52.5 g) and polyvinyl butyral (1.0 g) was ultrasonically dispersed in ethanol (1.0 L) for 30.0 min and then the sponge (52.5 g) was added to the suspension. Subsequently, the sponge absorbed MIL-88A(Fe) (MIL-88A(Fe)@sponge, MS) was dried at 60°C (Video 1). To remove the instable absorbed nanoparticles, the coated sponge was washed gently using ultra-water, until the coating rates were stable ($\sim 0.07 \text{ g/g}$). And the procedure was repeated twice ($\sim 0.14 \text{ g/g}$), the photo was shown in Fig. S1b. Subsequently, the MS with the size of $2.0 \text{ cm} \times 2.0 \text{ cm} \times 1.0 \text{ cm}$ was utilized for oil/water separation (Fig. S1c).

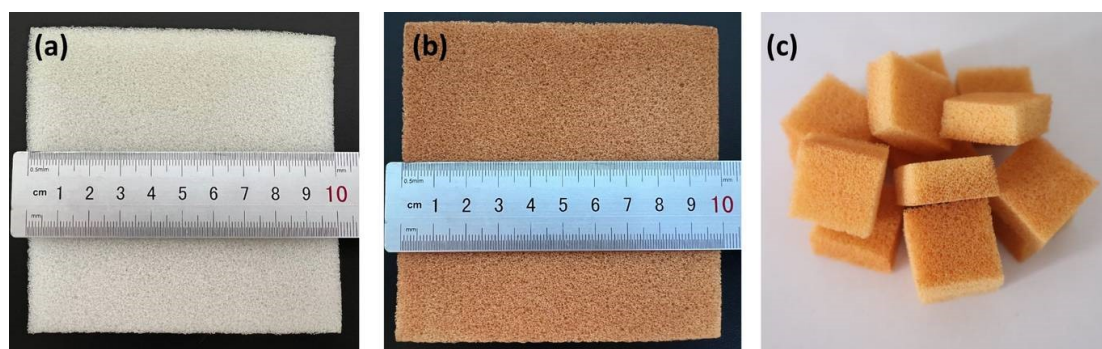


Fig. S1 The photos of (a) pristine sponge, MIL-88A(Fe)@sponge: (b) $10.0 \text{ cm} \times 10.0 \text{ cm} \times 1.0 \text{ cm}$ and (c) $2.0 \text{ cm} \times 2.0 \text{ cm} \times 1.0 \text{ cm}$.

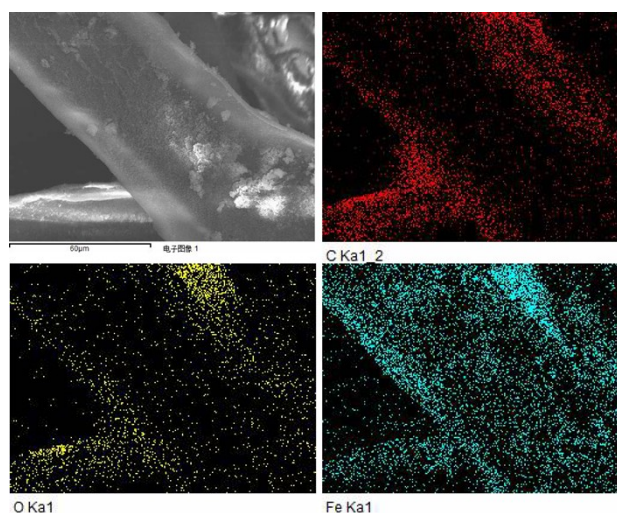


Fig. S2 The EDS elemental mappings of MS.

Text S4 XPS analysis of MIL-88A(Fe)@sponge

XPS investigation was conducted to evaluate the chemical species on the surface of MS. The XPS survey spectra of the MS clearly showed the C 1s, N 1s, O 1s and Fe 2p peaks for polyurethane sponge and MIL-88A(Fe), respectively (Fig. S3a). In Fig. S3b, the C 1s spectrum fits for MS showed six peaks: C-C at 284.8 eV,³ C-H at 285.32 eV,⁴ C-O at 285.89 eV,⁵ C=O at 286.83 eV,⁵ C=N at 287.58 eV⁶ and O=C-O at 289.22 eV.⁷ For the O 1s peaks were shown as Fig. S3c, the peaks at 531.06 eV and 533.46 eV binding energy corresponded to the C=O and O-H, respectively.⁸ And the peaks at 532.44 eV corresponded to the Fe-O of MIL-88A(Fe).⁹ The Fe 2p map can be deconvoluted into four peaks (Fig. S3d), with the Fe 2p^{3/2} orbit at 711.95 eV, Fe 2p^{1/2} orbit at 725.34 eV, and the satellite peak at 717.19 eV and 730.00 eV, confirming the trivalent state of Fe in the MIL-88A(Fe).¹⁰ For the N 1s XPS spectrum of MS, two peaks identified as C-N=C (398.76 eV) and N=N (400.38 eV) of polyurethane sponge were obtained after classifying (Fig. S3e).^{11, 12}

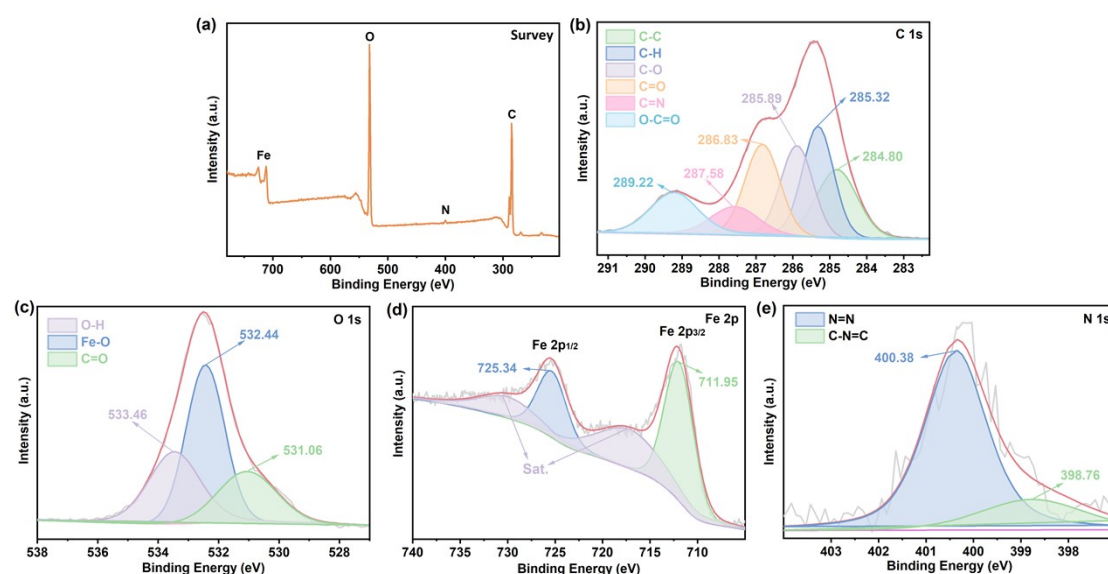


Fig. S3 XPS spectra of (a) Survey, (b) C 1s, (c) O 1s, (d) Fe 2p and (e) N 1s of MS.

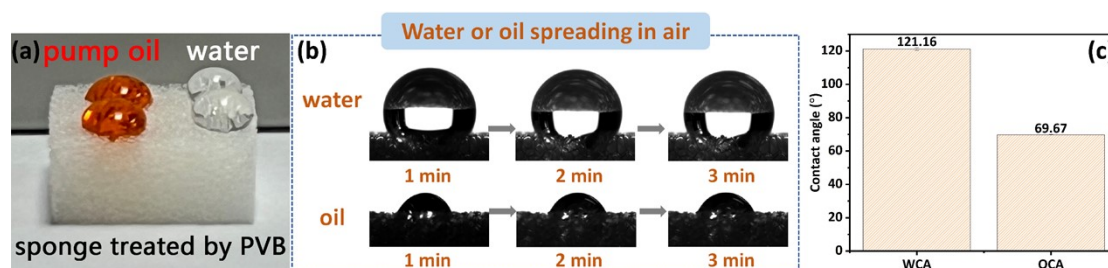


Fig. S4 (a) The image, (b) dynamic and (c) static WCA and OCA of water and oil adsorption of sponge treated by PVB in air.

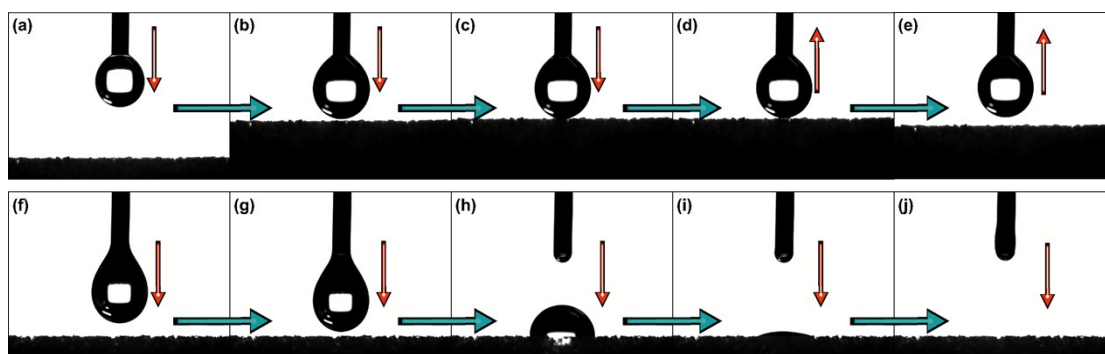


Fig. S5 Dynamic adhesion performance test: (a-e) water and (f-j) oil.

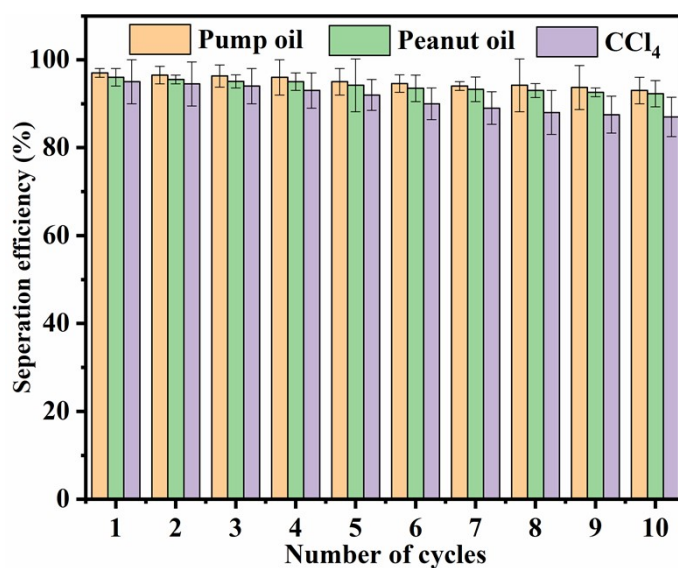


Fig. S6 Separation efficiencies of pump oil-water, peanut oil-water and CCl₄-water over MS.

Table. S1 Comparative performance of typical MOF&sponge for oil/water separation.

Samples	Wettability	Absorption substances	Adsorption capacity (g/g)	Recyclability (times)	Separation efficiency (%)	Ref.
sponge@HFGO@ZIF-8	162°	vegetable oil, Decaoctane, silicone oil, coconut oil, petroleum ether, chloroform	1.5-6.0	4	N.A.	13
ZIF-8@polyurethane sponge	129.2°	diesel, petrol, vegetable oil, chloroform, n-hexane	23-79	10	N.A.	14
UiO-66-(COOH) ₂ /polyurethane sponge	161°	n-hexane, tetrachloromethane edible oil, paraffin and N,N-Dimethylformamide	29-56	15	96	15
PDMS@H-MOF-5 sponge	156°	olive oil, silicone oil, n-hexadecane, and toluene	N.A.	10	98	16
Ce-MOF@polyurethane sponge	152.53°	dichloromethane, castor oil, engine oil, colza oil, dichloromethane, acetone	15.0-44.9	7	N.A.	17

			and n-hexane				
Co-HHTP@modified sponge	160.2°		n-hexane, petroleum ether, cyclohexane, kerosene, dichloromethane and chloroform	65-100	40	99.2	18
MIL-88A(Fe)@polyurethane sponge	135.5°		pump oil, peanut oil, and CCl ₄	32-34	60	95	This work

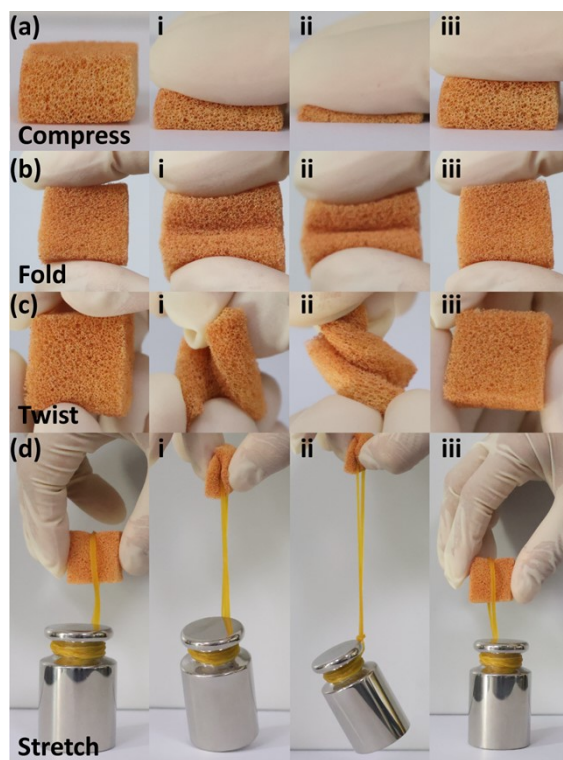


Fig. S7 Photographs of (a) compressing, (b) folding, (c) twisting, (d) stretching of MS.

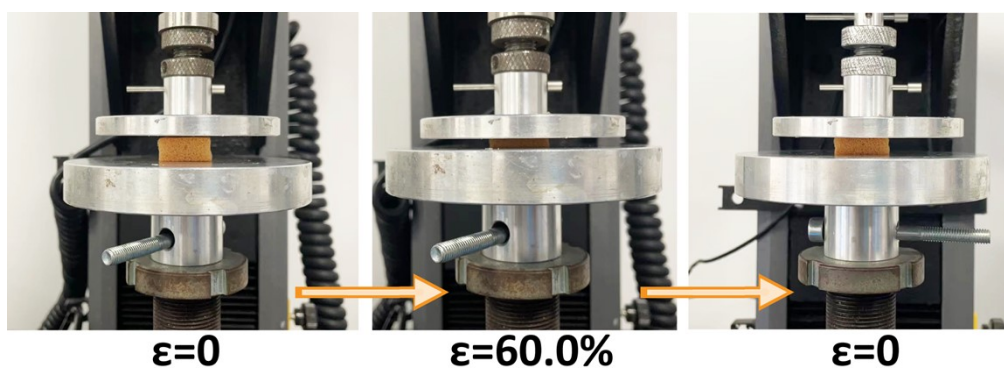


Fig. S8 Photographs for MS at strain of 60.0%.

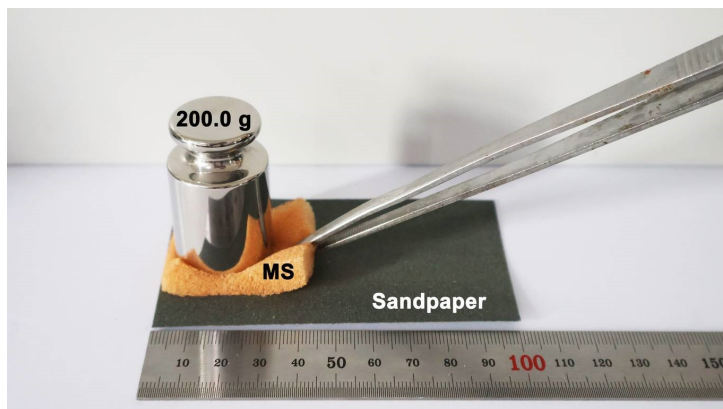


Fig. S9 Photograph for MS in the sandpaper abrasion test.

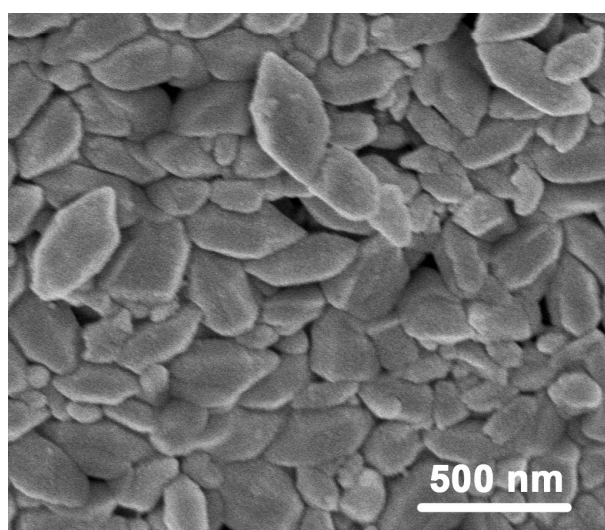


Fig. S10 SEM image of MS after 5 abrasion cycles.

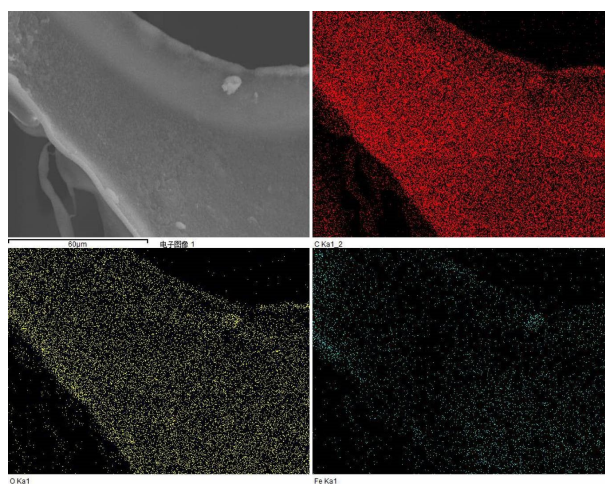


Fig. S11 EDS mapping of MS after the cyclic experiment.

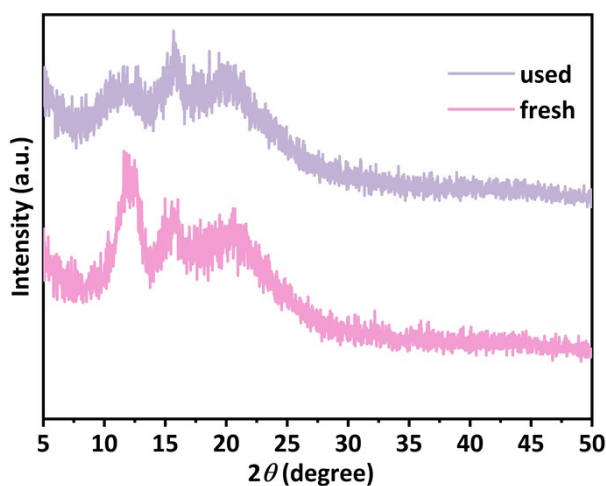


Fig. S12 XRD of MS after the cyclic experiment.

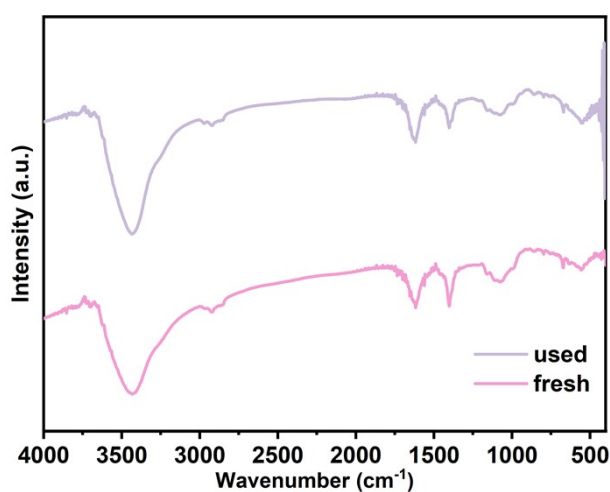


Fig. S13 FTIR of MS after the cyclic experiment.

Notes and references

- 1 H. Fu, X.-X. Song, L. Wu, C. Zhao, P. Wang and C.-C. Wang, *Mater. Res. Bull.*, 2020, **125**, 110806.
- 2 H.-Y. Chu, M.-Y. Wang, C.-C. Wang, C.-Y. Wang, F.-X. Wang, X.-H. Yi, H. Fu, C. Zhao and P. Wang, *Sep. Purif. Technol.*, 2024, **340**, 126800.
- 3 X. Li, S. Chen, X. Hu and F. Zi, *Adv. Funct. Mater.*, 2024, **34**, 2307472.
- 4 S. Bag, C. Zhou, P. J. Kim, V. G. Pol and V. Thangadurai, *Energy Storage Mater.*, 2020, **24**, 198-207.
- 5 W. Feng, Z. Li, H. Gao, Q. Wang, H. Bai and P. Li, *Green Chem. Environ.*, 2021, **6**, 150-159.
- 6 F. Fang, Z.-T. Gong, L.-F. Yao, W. Pu, Y.-Q. Cai, Q.-L. Li, J.-J. Liu and S.-B. Xia, *J. Energy Storage*, 2023, **67**, 107521.
- 7 H. Li, Y. He, Q. Wang, S. Gu, L. Wang, J. Yu, G. Zhou and L. Xu, *Adv. Energy Mater.*, 2023, **13**, 2302901.
- 8 N. R. Singha, M. Mahapatra, M. Karmakar, H. Mondal, A. Dutta, M. Deb, M. Mitra, C. Roy, P. K. Chattopadhyay and D. K. Maiti, *ACS Omega*, 2018, **3**, 4163-4180.
- 9 D. Xie, S. Chu, S. Zhang, A. Ivanets, L. Zhang and X. Su, *J. Environ. Chem. Eng.*, 2022, **10**, 108805.
- 10 Y. Jiang, X. Chen, S. Yan, Y. Ou and T. Zhou, *Green Chem.*, 2022, **24**, 5987-5997.
- 11 J. Ren, S. Huo, G. Huang, T. Wang, J. Feng, W. Chen, S. Xiao and P. Song, *Chem. Eng. J.*, 2023, **452**, 139196.
- 12 Y. Yu, Q. Jin, D. Zhu and Y. Ren, *Adv. Funct. Mater.*, 2024, **34**, 2308706.
- 13 K. Jayaramulu, K. K. R. Datta, C. Rösler, M. Petr, M. Otyepka, R. Zboril and R. A. Fischer, *Angew. Chem. Int. Ed.*, 2016, **55**, 1178-1182.

- 14 T. Azam, E. Pervaiz, S. Javed, S. J. Amina and M. S. Khalid, *Chem. Phys. Impact*, 2020, **1**, 100001.
- 15 Z. He, H. Wu, Z. Shi, X. Duan, S. Ma, J. Chen, Z. Kong, A. Chen, Y. Sun and X. Liu, *Colloid. Surface A*, 2022, **648**, 129142.
- 16 S. Barthwal, Y. Jeon and S.-H. Lim, *Sustain. Mater. Techno.*, 2022, **33**, e00492.
- 17 J. F. Meng, B. Y. Song, F. Li and T. H. Li, *Mater. Today Chem.*, 2023, **28**, 101371.
- 18 X. He, J. Lu, J. Liu, Z. Wu, B. Li, Z. Chen, W. Tao and Z. Li, *J. Hazard. Mater.*, 2024, **469**, 134090.