Supporting Information

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

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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 ($MgCl_2·6H_2O$, 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.

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Text S2 Characterization methods

Powder X-ray diffraction (PXRD) patterns were recorded on a Dandonghaoyuan DX-2700B diffractometer in the range of 2ϑ = 5°–50° with Cu K_α radiation. The morphology of the materials was measured by scanning electron microscopy (SEM) (Qtanta250FEG, FEI Company). Fourier transform infrared (FTIR) spectroscopy was observed using a Nicolet 6700. X-ray photoelectron spectroscopy (XPS) was observed using a Thermo ESCALAB 250XI. The water contact angle (WCA) and oil contact angle (OCA) of materials were measured by a Thermo SCI3000F. Rapid determination of moisture in MS with an infrared moisture meter (Sartorious LMA100P). The cyclic compressive stress curves for MS were measured by a universal testing machine (Instron 5942). 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 cm × 10.0 cm × 1.0 cm, see in Fig. S1a) with assistance of an ultrasonic bath, and the treated sponge were dried in an oven at 60 ^oC 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 (~0.07 g/g). And the procedure was repeated twice (~0.14 g/g), the photo was shown in Fig. S1b. Subsequently, the MS with the size of 2.0 cm × 2.0 cm × 1.0 cm was utilized for oil/water separation (Fig. S1c).

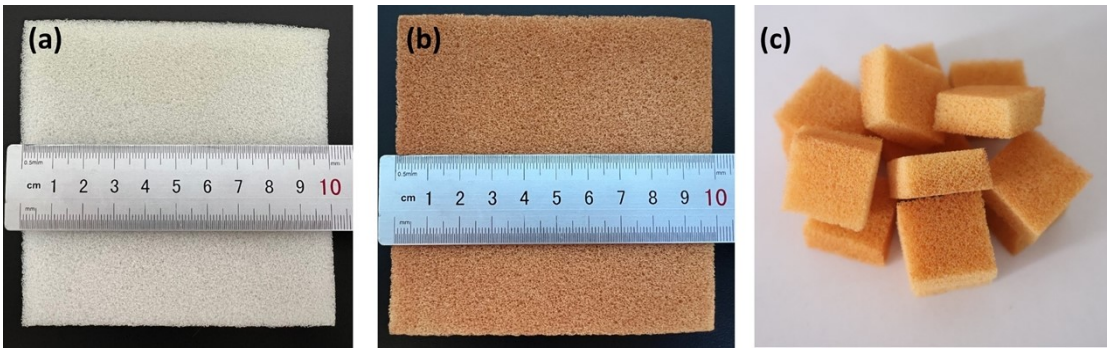

Fig. S1 The photos of (a) pristine sponge, MIL-88A(Fe)@sponge: (b) 10.0 cm × 10.0 cm × 1.0 cm and (c) 2.0 cm × 2.0 cm × 1.0 cm.

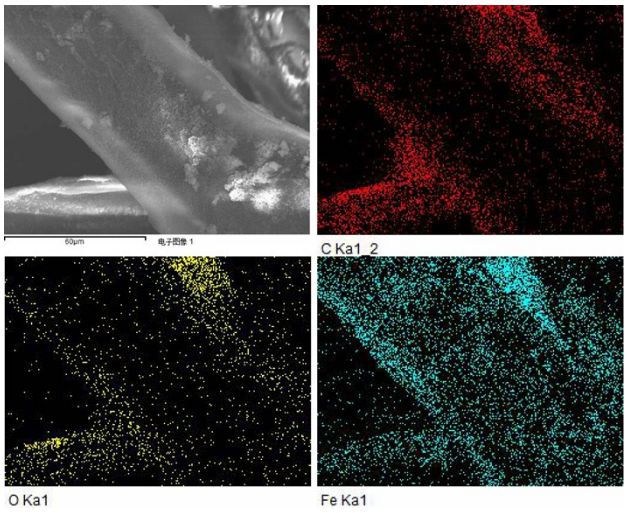

Fig. S2 The EDS elemental mappings of MS.

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 eV [6] 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 deconvolved 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]

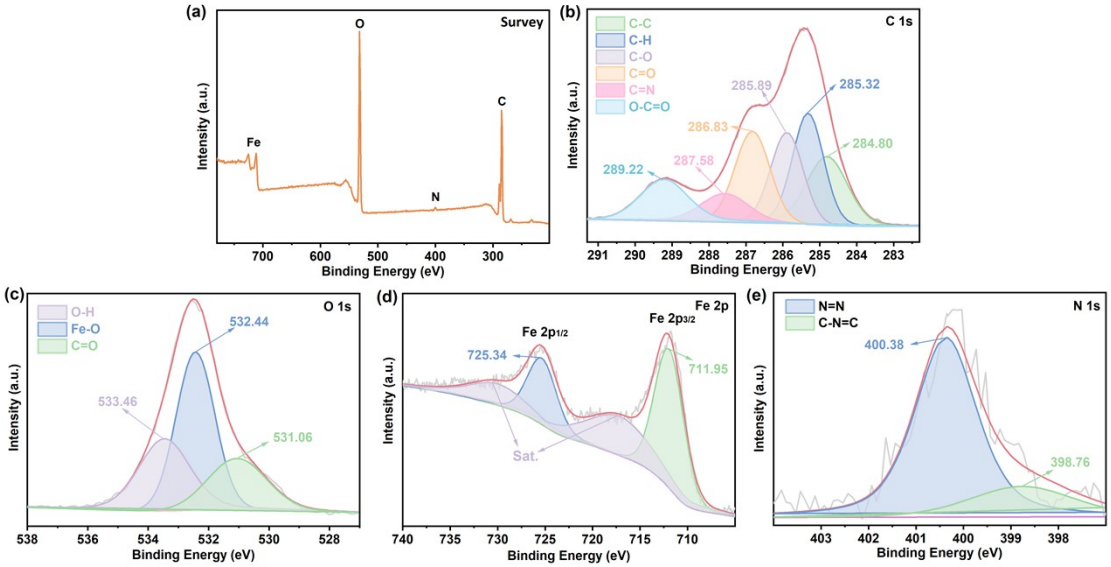

Fig. S3 XPS spectra of (a) Survey, (b) C 1s, (c) O 1s, (d) Fe 2p and (e) N 1s of MS.

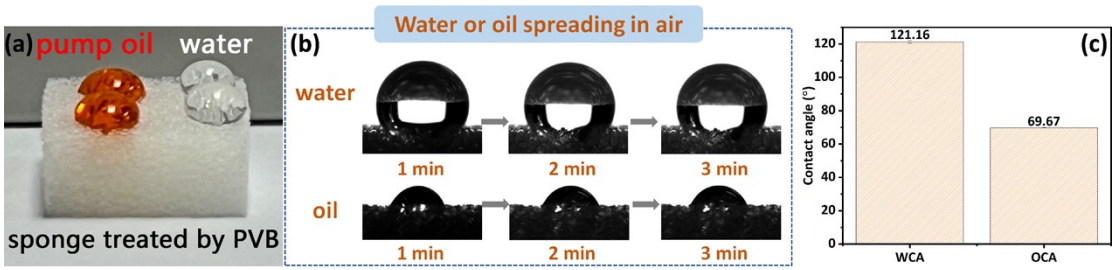

Fig. S4 (a) The image, (b) dynamic and (c) static WCA and OCA of water and oil adsorption of sponge treated by PVB in air.

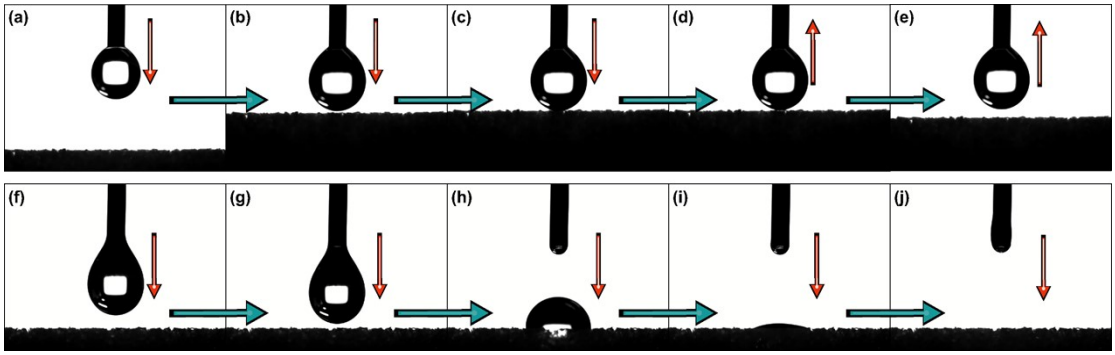

Fig. S5 Dynamic adhesion performance test: (a-e) water and (f-j) oil.

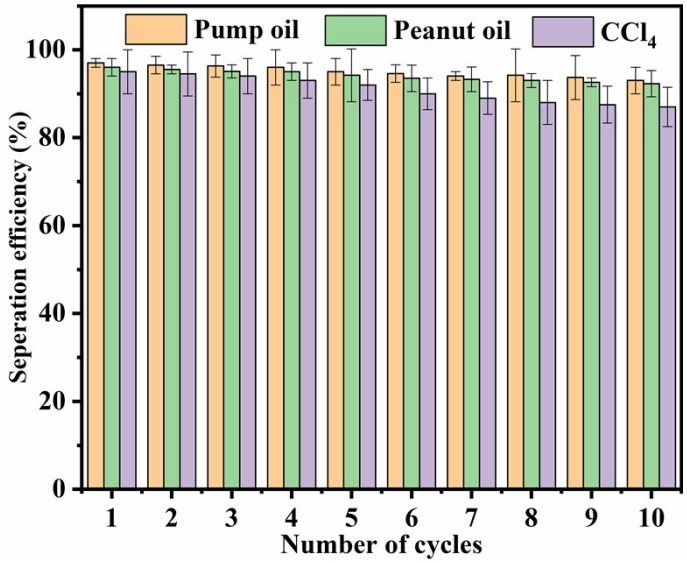

Fig. S6 Separation efficiencies of pump oil-water, peanut oil-water and CCl_4-water over MS.

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

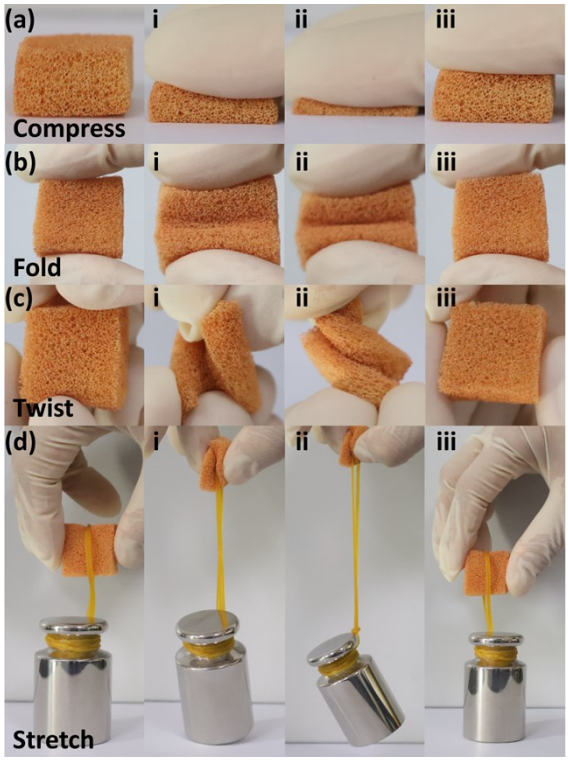

Fig. S7 Photographs of (a) compressing, (b) folding, (c) twisting, (d) stretching of MS.

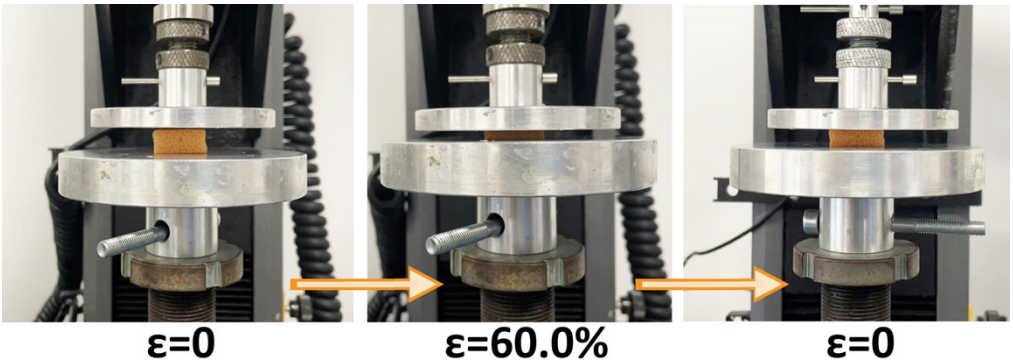

Fig. S8 Photographs for MS at strain of 60.0%.

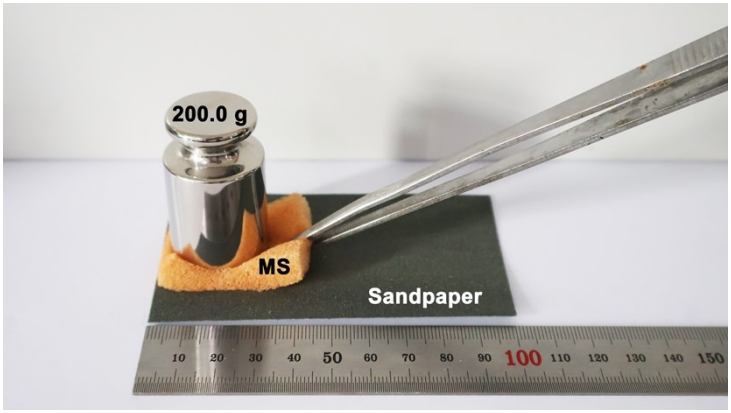

Fig. S9 Photograph for MS in the sandpaper abrasion test.

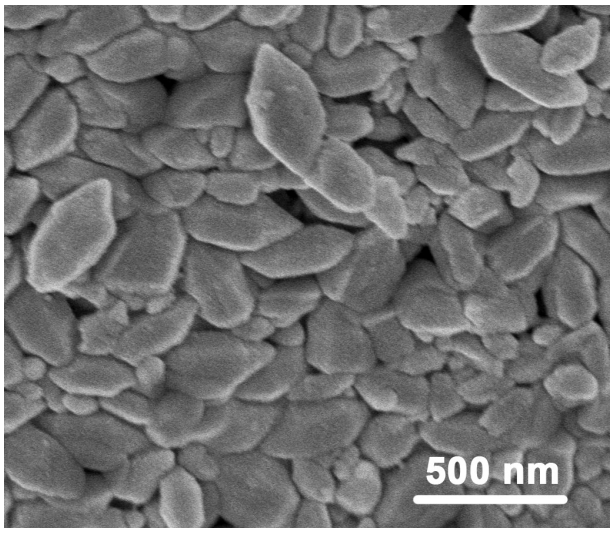

Fig. S10 SEM image of MS after 5 abrasion cycles.

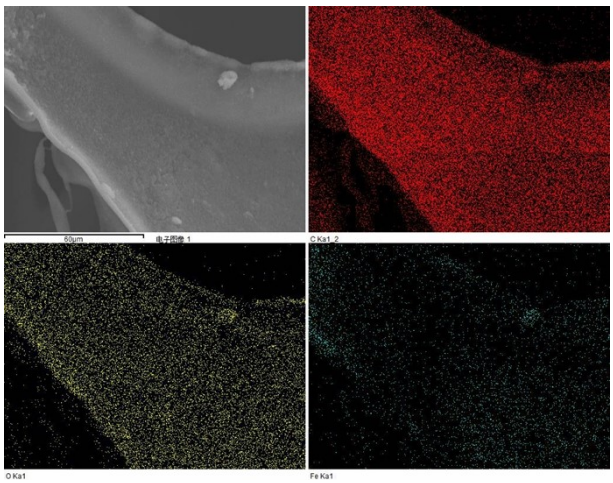

Fig. S11 EDS mapping of MS after the cyclic experiment.

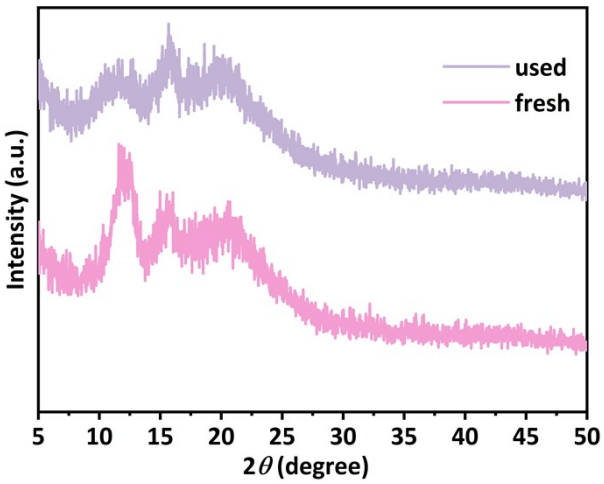

Fig. S12 XRD of MS after the cyclic experiment.

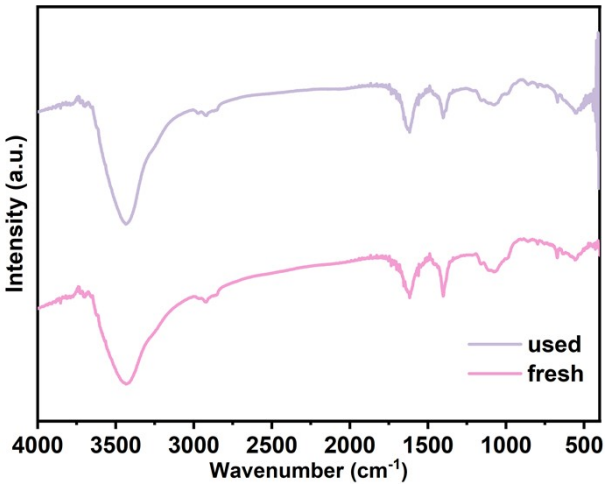

Fig. S13 FTIR of MS after the cyclic experiment.

Notes and references

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