

Supplementary Information

Preparation of magnetic, superhydrophobic/superoleophilic polyurethane sponge: Separation of oil/water mixture and demulsification

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Experimental

Materials and reagents

High-density polyethylene (HDPE) pellets (MW=125.000), $\text{FeCl}_2 \times 4\text{H}_2\text{O}$, $\text{FeCl}_3 \times 6\text{H}_2\text{O}$, ammonium hydroxide, acetone, ethanol, toluene, xylene, *n*-hexane, chloroform, dichloromethane, Pluronic F-127, sodium chloride (NaCl) and sodium sulfate (Na_2SO_4) were purchased from Sigma-Aldrich and used as received. The polyurethane (PU) sponge was obtained from a local supermarket. Milli-Q water (18 M Ω) was used for cleaning and rinsing throughout all experiments.

Synthesis of magnetic Fe_3O_4 nanoparticles

The Fe_3O_4 magnetic nanoparticles (MPs) were prepared as reported previously [20]. In short, $\text{FeCl}_2 \times 4\text{H}_2\text{O}$ (0.34 g, 1.7 mmol) and $\text{FeCl}_3 \times 6\text{H}_2\text{O}$ (0.95 g, 3.5 mmol) were dissolved in deaerated water (20 mL) and subsequently added to a nitrogen-protected three-necked flask under sonication. The resulting mixture was heated at 50 °C for 30 min. Then concentrated ammonium hydroxide (2 mL) was added dropwise and kept at 50 °C for 30 min. The system was finally cooled to room temperature and the solid product was isolated *via* a non-uniform magnetic field generated by a Nd–Fe–B permanent magnet. The resulting Fe_3O_4 nanoparticles were washed six times with Milli-Q water to remove unreacted chemicals and then dried by freeze-drying (CHRIST, Germany, Alpha 2-4 LSCbasic) at -86.8 °C for 24 h.

Characterization

Scanning electron microscopy (SEM) images were recorded and elemental compositions were analyzed using an electron microscope ULTRA 55 (Zeiss, France) equipped with an energy dispersive X-ray (EDX) analysis device (Bruker AXS Microanalysis GmbH, Berlin, Germany). The samples were coated with a thin film of platinum to decrease charging effects.

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) analysis of the prepared Fe_3O_4 nanoparticles were carried out by using an FEI, TECNAI G2 F20 instrument operated at an accelerated voltage of 300 kV ($C_s = 0.6$

mm, resolution 1.7 Å). For the TEM analysis, the sample was prepared by drop casting 10 µL of Fe₃O₄ nanoparticles (1 mg) dispersed in 5 mL isopropyl alcohol over a carbon coated 200 mesh Cu grid. The Fe₃O₄ nanoparticles drop casted Cu grid was dried and the prepared sample was used for the imaging purpose.

X-ray photoelectron spectrometer (XPS) analysis was conducted on a Model PHI 5300, Physical Electronics, USA) with 250 W Mg K α ($\lambda = 0.9891$ nm) X-ray being the excitation source.

Magnetic properties were assessed using an MPMS-XL SQUID magnetometer. The magnetization measurements were performed using an ADE EV9 Vibrating Sample Magnetometer (VSM). Cycles were performed from 20KOe to -20KOe and back. To ensure a quantitative measurement of magnetization, the VSM was carefully calibrated using a 8 mm nickel disk with known magnetization. Sponge samples were subsequently cut in disk shape with the same diameter as the calibrating nickel disk and weighted prior to measurement.

Wetting properties were evaluated by contact angle (CA) measurements using a DIGIDROP (GBX Company, Ltd. France) apparatus at ambient temperature using a water droplet of 8 µL.

UV-vis spectrophotometry (Perkin Elmer Lambda UV-Vis 950 spectrophotometer) was used for the determination of the toluene content in the separated toluene/water emulsion. The size of micro-drops in these emulsions was characterized by MICROSCOPE NIKON (ECLIPSE Ti2-U).

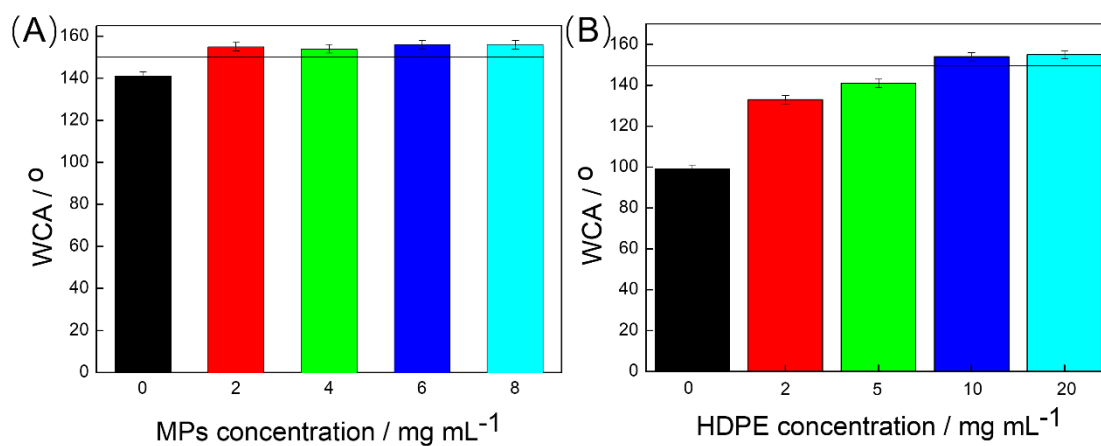


Figure S1: (A) Effect of MPs concentration added to HDPE/toluene/ethanol solution (200 mg HDPE/20 mL toluene) and immersion/heating cycles on the water contact angle of the MSS-PU sponge; (B) Effect of HDPE concentration on the water contact angle of the MSS-PU sponge.

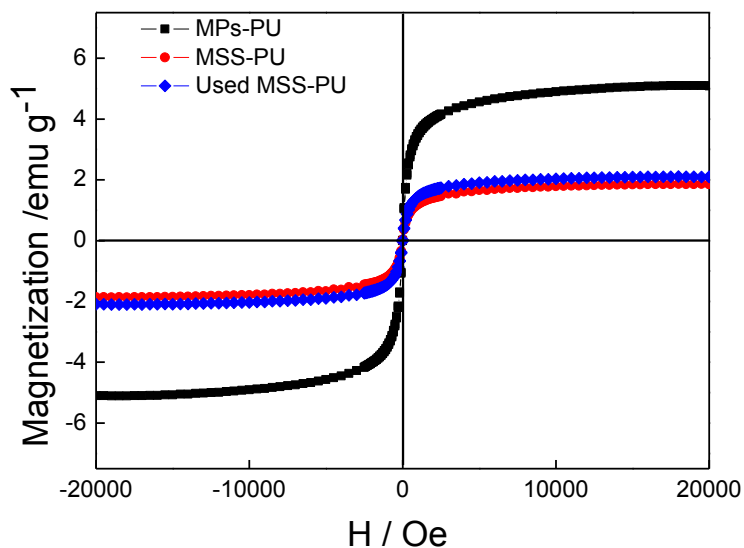


Figure S2. Magnetic hysteresis curves recorded at 300 K of MPs-PU (black), fresh (red) and stored MSS-PU samples.

Investigation of the contact angle (CA) and surface energy of MSS-PU

The surface energy of MSS-PU was investigated using the Owens-Wendt equation:

$$\gamma_L(1 + \cos \theta) = 2(\gamma_S^d \cdot \gamma_L^d)^{1/2} + 2(\gamma_S^p \cdot \gamma_L^p)^{1/2}$$

where γ_L^d , γ_L^p and γ_L represent the dispersive force, polar force and surface tension of the testing liquid, θ is the contact angle (CA) of the liquid on the solid surface.

Accordingly, the surface energy of MSS-PU (γ_S^p and γ_S^d) could be determined by testing different combinations of one polar liquid and one non-polar liquid (water, glycerol, glycol, ethanol, diiodomethane, and hexadecane). The combination of water/diiodomethane, glycerol/hexadecane, water/hexadecane, and glycerol/diiodomethane indicated that the estimated surface energy (γ_S) of MSS-PU was $51.8 \text{ mN}\cdot\text{m}^{-1}$ ($\gamma_S^p = 13.7 \text{ mN}\cdot\text{m}^{-1}$ and $\gamma_S^d = 38.2 \text{ mN}\cdot\text{m}^{-1}$). Moreover, for hydroxyl containing liquids (water, glycerol, glycol, and ethanol), it was found that the cosine of CA ($\cos \theta$) of such liquids follows a linear function with their surface tension (γ_L). Briefly, the CA increased with increasing of the surface tension, as shown in **Figure S6**. This indicates that the MSS-PU is able to maintain a superhydrophobic state towards the liquid with high surface tension like water. Therefore, the majority of organics, especially non-polar ones, could be extensively absorbed by the MSS-PU, while the water was repelled due to its high surface tension. This property is mandatory for efficient separation of oil/water mixtures.

Table S1. Surface tension of different liquids and their corresponding contact angles (CAs) on the MSS-PU sample.

Liquid	γ_L^P/m N·m ⁻¹	$\gamma_L^d/mN\cdot m^{-1}$	$\gamma_L/mN\cdot m^{-1}$	CA ($\pm 1^\circ$)
Water	51.0	21.8	72.8	154
Glycerol	26.4	37	63.4	138
Ethylene-glyco 1	19.0	29.0	48.0	103
Ethanol	2.6	18.8	22.4	0
Diiodomethane	0.0	50.8	50.8	0
Hexadecane	0.0	27.6	27.6	0

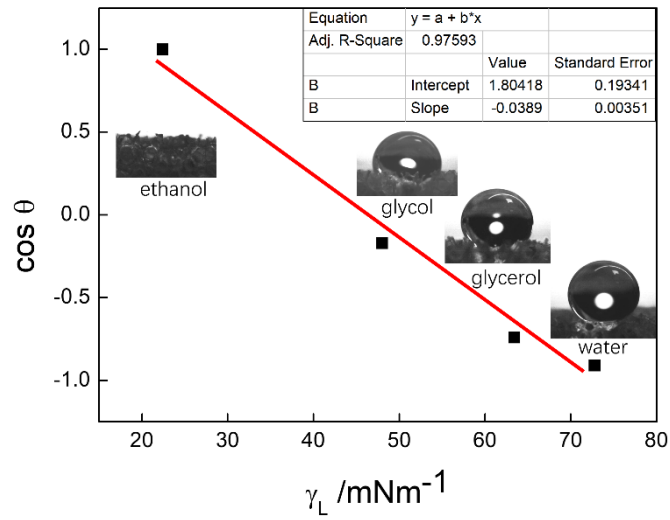


Figure S3: Change of the cosine of the CA as a function of the surface tension of different liquid droplets (water, glycerol, glycol, ethanol) on the surface of the MSS-PU. The insets are the photos of the corresponding CAs.

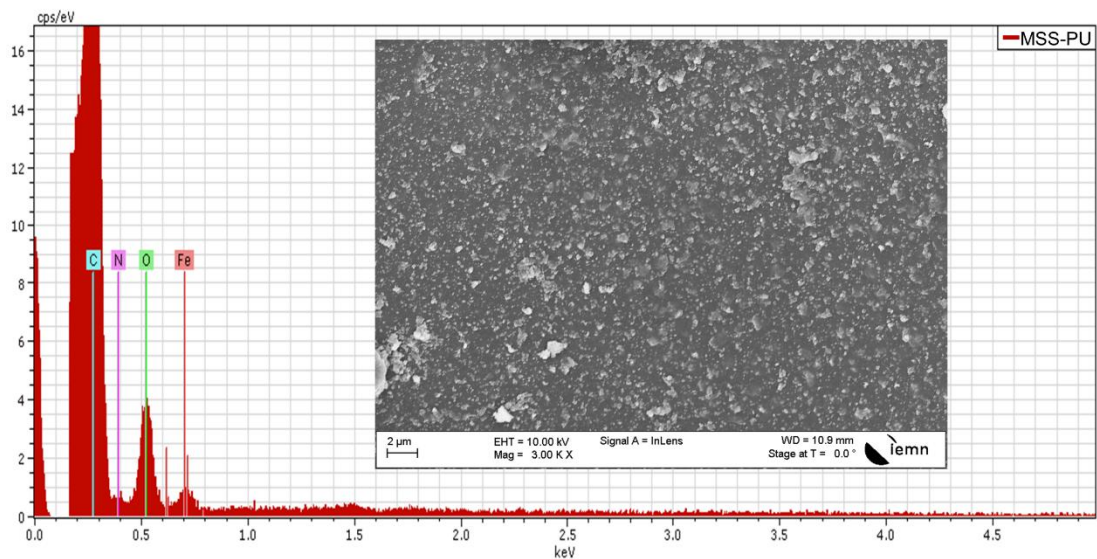


Figure S4: Energy dispersive X-ray (EDX) spectrum of MSS-PU.

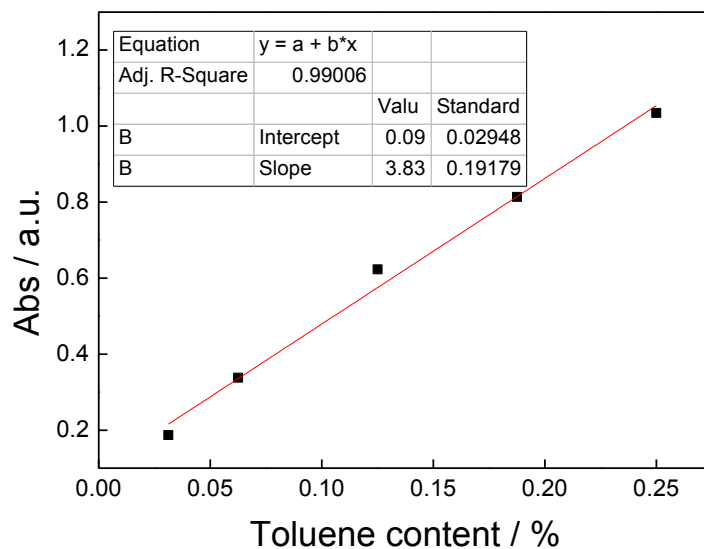


Figure S5: Calibration curve for the quantification of toluene by UV/vis spectroscopy using the absorbance of toluene at 260 nm. The calibration curve was generated by measuring the absorption of toluene in methanol/water (3/1, v/v) solution according to Lambert-Beer's law.