Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information

Intelligent sponge with reversibly tunable super-wettability: robust for effective oil-water separation as both absorber and filter tolerating fouling and harsh environments

Lingjie Li[a, ‡], *Lei Liu*[a, ‡], *Jinglei Lei*[a*], *Jianxin He*[a], *Nianbing Li*[b], *Fusheng Pan*[c]

a. School of Chemistry and Chemical Engineering, Chongqing University, Chongqing, 400044 PR China;

b. School of Chemistry and Chemical Engineering, Southwest University, Chongqing, 400715 PR China;

c. School of Materials Science and Engineering, Chongqing University, Chongqing, 400044 PR China

‡ Equal contribution.

* Corresponding author. *JLLei@cqu.edu.cn; Fax: +86 2365112328; Tel: +86 13983064116*

Discussion on wettability reversible conversion mechanism

Generally, the wettability of a surface is considered to be strongly dependent upon the surface morphology and chemical composition.[1-3] To thoroughly understand the wettability reversible conversion mechanism of the sponges under UV light irradiation and thermal treatment, the surface morphology and chemical composition of the sponges after UV irradiation and heat treatment are characterized. Figs. S2 and S3 show the FESEM images and XPS survey spectra of the sponges after different processes, respectively. All the samples show little morphological changes (Fig. S2) but visible changes on chemical composition (Fig. S3), indicating that the compositional changes are the major factor for the super-wettability transition.

Furthermore, the XPS high-resolution spectra are detected. As shown in Fig. S4a, the O 1s high-resolution spectrum of the as-prepared sponge can be fitted by four peaks centered at binding energies of 529.9, 530.9, 531.7, 532.4 eV, respectively, which are attributed to O–Ti (belonging to TiO_2), O–C (including O=C–O and O–C=O, belonging to the octadecanoic acid) and NCOO (belonging to polyurethane). After UV irradiation, the O 1s high-resolution spectrum (Fig. S4b) of the sample can be fitted by five peaks centered at binding energies of 529.9, 530.9, 531.7, 532.4 and 532.7 eV, respectively. The new fitting peak at 532.7 eV (attributed to C-O-H) appears due to the water (hydroxyl groups) adsorption. The increased hydroxyl groups can enhance surface hydrophilicity. Further after heat treatment for 20 h, the O 1s high-resolution spectrum (Fig. S4c) of the sample can be resolved into four components with the binding energies of 529.9, 530.9, 531.7, 532.4 eV, respectively.

The fitting peak at 532.7 eV (attributed to C-O-H) disappears, suggesting that the hydroxyl groups reduce and the surface hydrophobicity is strengthened.

As well known, TiO_2 is photosensitive. When the sponge is irradiated by UV light, the photogenerated holes can react with the lattice oxygen of the anchored TiO_2 nanoparticles to form Ti^{3+} and surface oxygen vacancies.[4] As shown in Fig. S5, The Ti atoms (as Ti^{3+}) have seven electrons in their outer orbital, which are electron-deficient. Thus, to obtain a stable state, Ti atoms are prone to building hydrogen bonds with interfacial water molecules, leading to a hydrophilic hydration structure.[5] After the UV irradiated surface is heated at 120℃ for 20 h, the absorbed water (hydroxyl groups) is eliminated, the hydrophilic surface converts to the hydrophobic one.

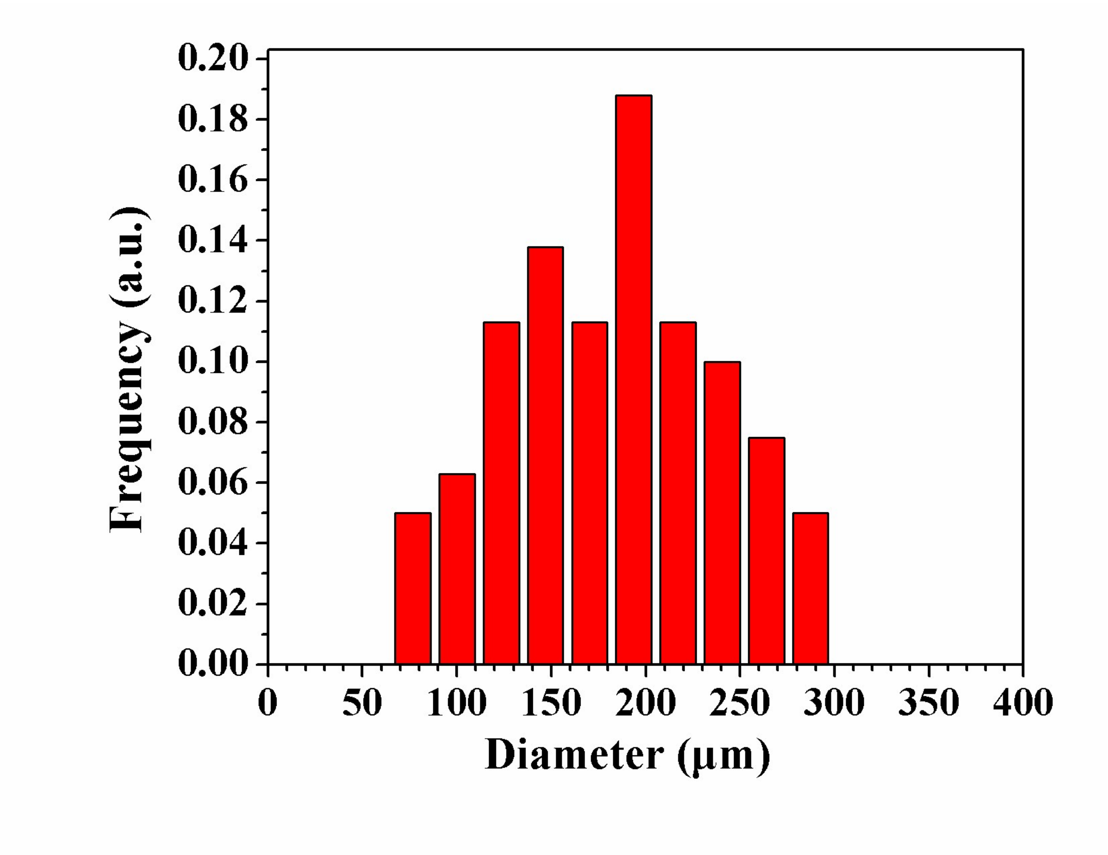

Fig. S1 Histogram of the pore diameter distribution of the sponge based upon a statistical analysis of the SEM image shown in Fig. 1a.

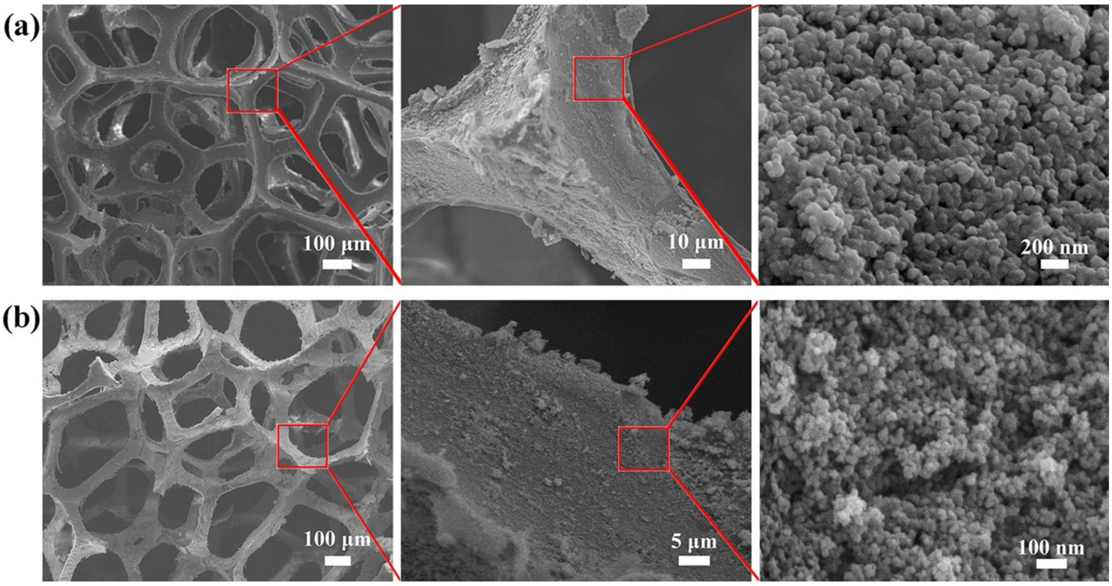

Fig. S2 FESEM images of the sponges after different processes: (a) UV irradiation, and (b) UV irradiation and subsequent 120℃ heat treatment.

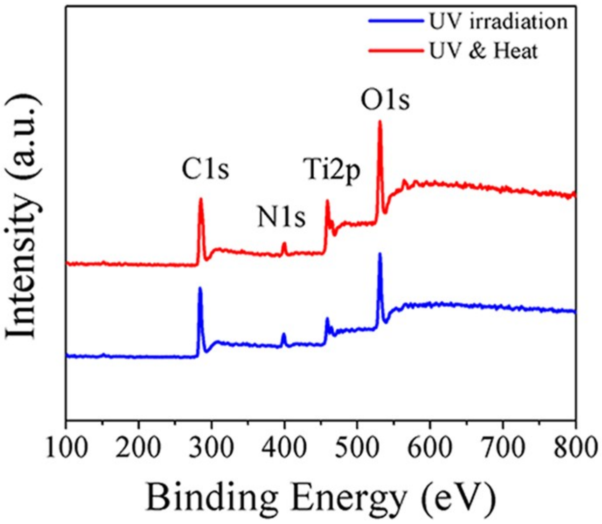

Fig. S3 XPS survey spectra of the sponges after different processes: (a) UV irradiation, and (b) UV irradiation and subsequent 120℃ heat treatment.

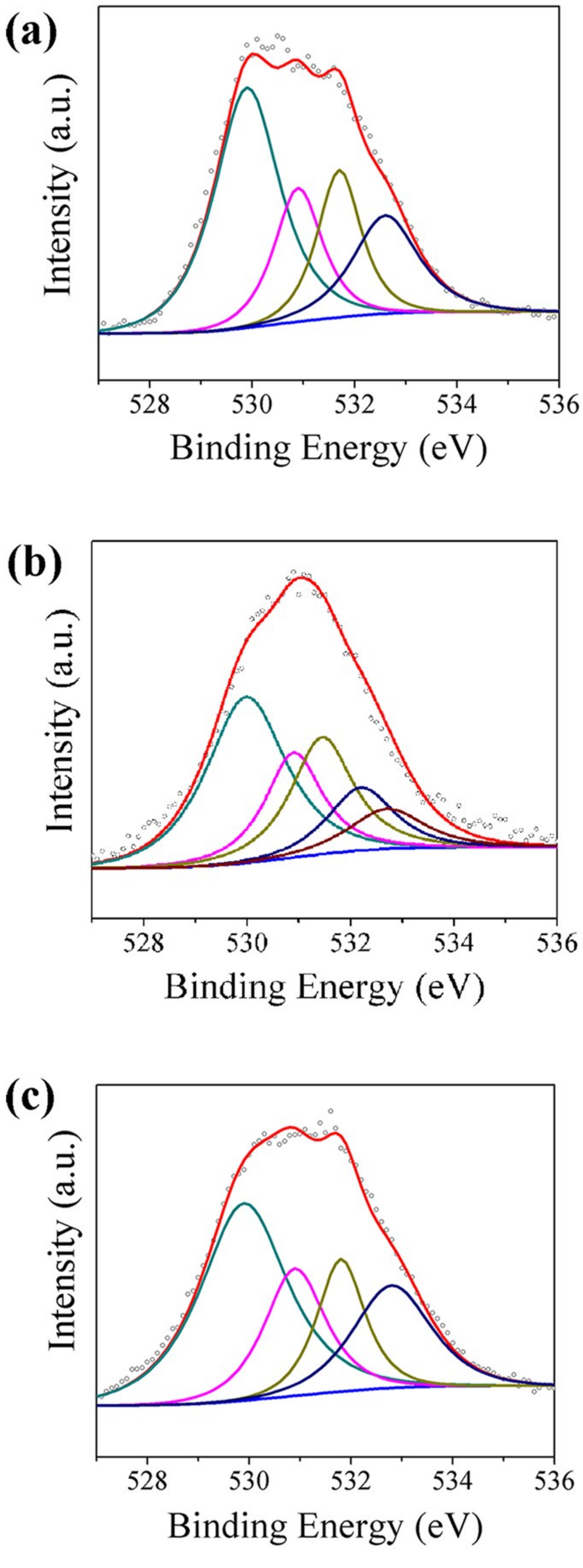

Fig. S4 XPS O 1s high-resolution spectra of the sponges: (a) as-prepared; (b) after UV irradiation for 6 h; (c) after UV irradiation and subsequent 120℃ heat treatment for 20 h.

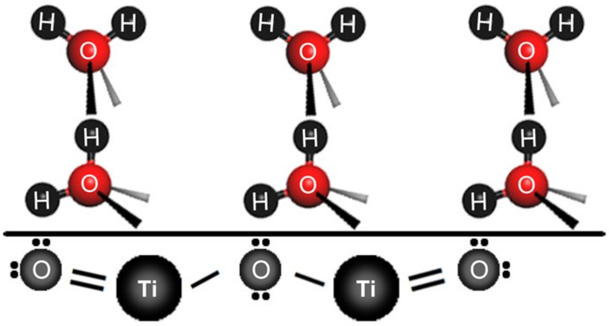

Fig. S5 Schematic of the orientation of water molecules next to the UV irradiated sample surface.

Table S1. Density, viscosity and surface tension values of six organic solvents for the absorption experiments.[6]

Organic solvents	Density ($g{\cdot}cm^{-3}$)	Viscosity（$mPa{\cdot}s$）	Surface tension ($N{\cdot}m^{-1}$)
hexane	0.66	0.29	0.0184
toluene	0.87	0.59	0.0284
dichloromethane	1.33	0.43	0.0265
tetrachloromethane	1.60	0.97	0.0295
isooctane	0.69	0.53	0.0235
dodecane	0.75	1.51	0.0254

Table S2. Comparisons on oil-absorption capacity of as-prepared TiO_2-coated sponge in this work with other reported sponge-based materials.

Ref.	Sponge-based materials	Absorption capacity
This work	Polyurethane sponge + octadecanoic acid + P25 TiO_2	27-60
7	Polyurethane sponge + GO + APTES	29-46
8	Polyurethane sponge + PDMS + CNTs	15-25
9	Polyurethane sponge + silica nanoparticles + DTMS	19.8-46.8
10	Chitin + urea	29-58
11	Graphite + glucose	23-35
12	Polyurethane sponge + Cu mesh + decanethiol	13-21
13	Polydimethylsiloxane	4.72-20
14	Polyurethane sponge + nanoparticles + n-dodecanethiol	18-26
15	Polyurethane sponge + oxazolidine	16-40
16	Polyurethane sponge + methyltrichlorosilane	15-26
17	Polyamide sponge + SiO_2 + PFA	25-60
18	Silicone sponges + Fe_3O_4 + SiO_2	7-17
19	Polyurethane sponge + HFTHTMS	15
20	Polyurethane sponge + CNT + PDA + ODA	22-34.9
21	Polyurethane sponge + ZnO + PA	44
22	Polymer sponge + SiO_2 + PDMS	Not mentioned
23	Melamine sponge + perfluorodecanethiol	Not mentioned

Movie Lists

Movie S1. Wettability and adhesion of the as-prepared sponge by water. An impacting water column bounces off the sample, leaving it completely dry.

Movie S2. Oil absorption by the as-prepared sponge under water. Due to the underwater superoleophilicity of the as-prepared sponge, the perchlormethane droplet (dyed red with sudan Ⅲ) is rapidly absorbed when the sponge contacts it.

Movie S3. Oil absorption and collection. The absorbed oils in the sponge can be collected by a simple squeezing process, and then the recovered sponge is reused for oil-water separation for next cycle.

Movie S4. Wettability of the as-prepared sponge after UV irradiation by oil under water. After UV irradiation, a wettability transition takes place from superoleophilicity to superoleophobicity under water.

Movie S5. The experimental set-up used for the oil/water separation. Due to the superhydrophilic and underwater superoleophobic of the sponge after UV irradiation, when the hexane−water mixture (hexane dyed red with Sudan Ⅲ) is poured onto the sponge, water quickly permeates through the sponge while the hexane retains above the sponge and finally the hexane-water mixture is separated successfully.

Movie S6. The experimental setup used for the oil-water separation. Superhydrophilic and underwater superoleophobic sponge was heated at 120℃ for 20 h, it reverted to its superhydrophobic and underwater superoleophylic state. When the perchlormethane-water mixture (water dyed blue with methylene blue) is poured onto the sponge, perchlormethane quickly permeates through the sponge while the water retains above the sponge and finally the perchlormethane-water mixture is separated successfully.

Movies S7-S9. The experimental setups used for separation of hexane-10 M H_2SO_4 mixture, hexane-10 M NaOH mixture and hexane-saturated NaCl mixture, respectively. Here, H_2SO_4 solutions was dyed purple red with pyrocatechol violet, NaOH solutions was dyed rose red with rhodamine B and saturated NaCl solutions was dyed blue with methylene blue.

References

1 M. L. Ma and R. M. Hill, *Curr Opin Colloid Interface Sci*, 2006, **11**, 193.

2 X. M. Li, R. David and C. C. Mercedes, *Chem. Soc. Rev.*, 2007, **36**, 1350.

3 B. W. Xin and J. C. Hao, *Chem. Soc. Rev.*, 2010, **39**, 769.

4 W. Sun, S. X Zhou, B. You and L. M. Wu, *J. Mater. Chem. A*, 2013, **1**, 3146.

5 J. Y. Zheng, S. H. Bao, Y. Guo and P. Jin, *ACS Appl. Mater. Interfaces*, 2014, **6**, 1351.

6 Y. Gao, Y. S. Zhou, W. Xiong, M. M. Wang, L. S. Fan, H. R. Golgir, L. J. Jiang, W. J. Hou, X. Huang, L. Jiang, J. F. Silvain and Y. F. Lu, *ACS Appl. Mater. Interfaces*, 2014, **6**, 5924.

7 R. Tjandra, G. Lui, A. Veilleux, J. Broughton, G. Chiu, A. Yu, *Ind. Eng. Chem. Res.*, 2015, **54**, 3657.

8 C. F. Wang and S. J. Lin, *ACS Appl. Mater. Interfaces*, 2013, **5**, 8861.

9 J. T. Wang and G. H. Geng, *Marine Pollution Bulletin*, 2015, **97**, 118.

10 B. Duan, H. M. Gao, M. He and L. N. Zhang, *ACS Appl. Mater. Interfaces*, 2014, **6**, 19933.

11 R. H. Wu, B. W. Yu, X. Y. Liu, H. L. Li, W. X. Wang, L. Y. Chen, Y. T. Bai, Z. Ming and S. T. Yang, *Applied Surface Science*, 2016, **362**, 56.

12 F. J. Wang, S. Lei, C. Q. Li, J. F. Ou, M. S. Xue and W. Li, *Ind. Eng. Chem. Res.*, 2014, **53**, 7141.

13 X. Zhao, L. X. Li, B. C. Li, J. P. Zhang and A. Q. Wang, *J. Mater. Chem. A*, 2014, **2**, 18281.

14 Q. Zhu and Q. M. Pan, *ACS NANO*, 2014, **8**, 1402.

15 G. Wang, Z. X. Zeng, X. D. Wu, T. H. Ren, J. Han and Q. J. Xue, *Polym. Chem.*, 2014, **5**, 5942.

16 Q. Zhu, Y. Chu, Z. K. Wang, N. Chen, L. Lin, F. T. Liu and Q. M. Pan, *J. Mater. Chem. A*, 2013, **1**, 5386.

17 K. Q. Li, X. R. Zeng, H. Q. Li and X. J. Lai, *RSC Adv.*, 2014, **4**, 23861.

18 L. X. Li, B. C. Li, L. Wu, X. Zhao and J. P. Zhang, *Chem. Commun.*, 2014, **50**, 7831.

19 Y. Kim, J. Hwang, Y. Ahn, *Bull. Korean Chem. Soc.*, 2015, **36**, 2158.

20 H. Y. Wang, E. Q. Wang, Z. J. Liu, D. Gao, R. X. Yuan, L. Y. Sun and Y. J. Zhu, *J. Mater. Chem. A*, 2015, **3**, 266.

21 B. B. Li, X. Y. Liu, X. Y. Zhang, J. C. Zou, W. B. Chai and Y. Y. Lou, *J Chem Technol Biotechnol*, 2015, **90**, 2106.

22 J. Ge, Y. D. Ye, H. B. Yao, X. Zhu, X. Wang, L. Wu, J. L. Wang, H. Ding, N. Yong, L. H. He and S. H. Yu, *Angew. Chem. Int. Ed.*, 2014, **53**, 3612.

23 C. P. Ruan, K. L. Ai, X. B. Li and L. H. Lu, *Angew. Chem. Int. Ed.*, 2014, **53**, 1.