# Thermo and pH Dual-Responsive Materials for Controllable Oil/Water Separation

Yingze Cao, Na Liu, Changkui Fu, Kan Li, Lei Tao, Lin Feng,* and Yen Wei

Department of Chemistry, Tsinghua University, Beijing 100084, P. R. China

Ⓢ Supporting Information

ABSTRACT: Thermo and pH dual-controllable oil/water separation materials are successfully fabricated by photo initiated free radical polymerization of dimethylamino ethyl methacrylate (DMAEMA). The PDMAEMA hydrogel coated mesh shows superhydrophilicity and underwater superoleophobicity at certain temperature and pH. Due to the double responsiveness of PDMAEMA hydrogel, the as-prepared mesh can selectively separate water from oil/water mixtures and make water and oil permeate through the mesh orderly and be collected separately by adjusting the temperature or pH. Water can pass through the as-prepared mesh under 55 °C (pH 7) and pH less than 13 (T = 25 °C) while oil is kept on the mesh. When the temperature is above 55 °C or pH is larger than 13, the water retention capacity of PDMAEMA hydrogel is significantly reduced and the swelling volume is decreased. Therefore, oil can permeate through the mesh and be collected in situ. Additionally, this material has excellent potential to be used in practical applications and has created a new field for water/oil separation in which the process can be diversified and more intelligent.
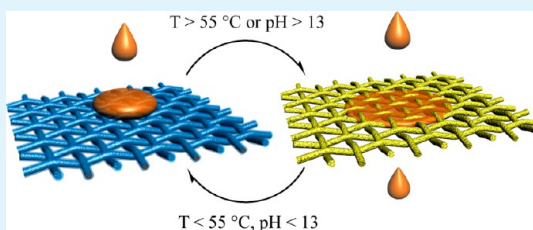
KEYWORDS: thermoresponsive, pH-responsive, controllable oil/water separation, PDMAEMA hydrogel, smart materials

1. INTRODUCTION

Stimulus-responsive (SR) polymers have attracted broad attention and been widely studied over the recent years because of their promising potential in fabricating intelligent controllable materials. SR polymers can display controlled changes in response to physical or chemical changes of the external environment, such as temperature, pH, light, electricity, and magnetism.[1−7] In the biomedical field, the SR polymers have numerous applications, for example, light-, pH-, and temperature-responsive dendrimer systems with different chemical compositions and architecture can be used to encapsulate and release drugs.[8−10] SR polymers also have potential application in many other fields like sensors, enzyme immobilization, and changing wettability. For example, some typical SR polymers are chosen to build smart surfaces with reversibly switchable wettability including poly (N-isopropyla-crylamide) (PNIPAAm) has been used for fabricating thermosensitive surfaces that can change from superhydrophilic to superhydrophobic by heating.[11] The electroresponsive polyaniline (PANI) nanowire film with reversible super-oleophobicity has achieved controlled transport of tiny volume of liquid.[12]

Oil/water separation has always been an important and urgent issue because of the discharge of oily wastewater from industries and frequent oil spill accidents.[13−16] Special wettability to solve this problem has become the focus of research in recent years.[17−20] Generally, there are three types of separation materials which can be concluded as: "oil-removing" type materials with superhydrophobicity and superoleophilicity, "water-removing" type materials with superhydrophilicity and

superoleophobicity, and the smart controllable separation materials.[21−26] Compared with the other two types of materials, the smart controllable separation materials have more advantages in simplifying separation devices, accelerating separation rate, and reducing energy use.[27−29] However, up to now, only a few works have reported smart controllable separation materials, such as mixing Fe_3O_4 with oil absorption substance (magnetic control)[30,31] and synthesizing block copolymer comprising pH-responsive poly(2-vinylpyridine) and oleophilic/hydrophobic polydimethylsiloxane blocks (pH control).[32]

In this work, a thermo and pH double controllable oil/water separation material has been developed through photo initiated free radical polymerization. The stainless steel mesh as substrates was coated with poly (dimethylamino) ethyl methacrylate (PDMAEMA) hydrogel by simple immersion in a mixed pregel solution. It contains DMAEMA monomer, N,N′-methylene bisacrylamide (BIS) as the chemical cross-linker, and polyacrylamide (PAM) as thickener (Figure 1a). The stainless steel mesh was then drawn out horizontally from the solution and exposed under UV-light for in situ free radical polymerization. PDMAEMA, as one of the most promising SR polymers, has been extensively researched for its thermo and pH dual-responsive characteristic. The lower critical solution temperature (LCST) of PDMAEMA is ranging from 30 to 50 °C with different pH, molecular weight, and salt concen-
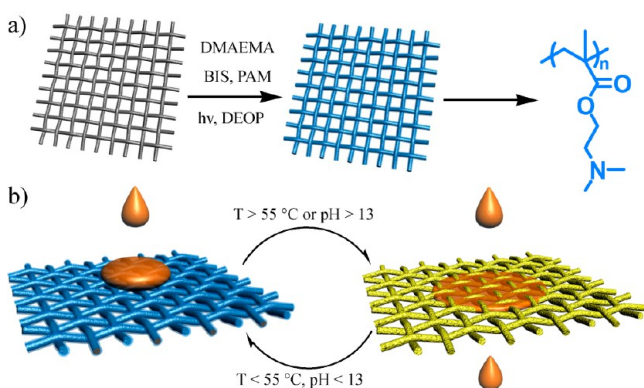
Figure 1. Schematic description of the preparation of PDMAEMA hydrogel coated mesh and the opposite wettability of the mesh when contacted with oil. (a) The stainless steel mesh as substrates was coated with PDMAEMA hydrogel which polymerized by DMAEMA monomer, N,N′-methylene bisacrlamide (BIS) as the chemical cross-linker, and polyacrylamide (PAM) as thickener under UV light. (b) Under 55 °C (pH 7) and pH less than 13 ($T = 25$ °C), oil cannot permeate though the mesh, whereas when the temperature is above 55 °C or pH is larger than 13, oil can pass through the mesh easily.

tration.[11] By simply adjusting the pH of the aqueous solution of PDMAEMA, the phase separation temperature can easily be turned. Because the protonation degree of the tertiary amine group in PDMAEMA varies depending on pH of the aqueous solution, hydrophilicity/oleophilicity of PDMAEMA will be diverse at different pH.

As shown in Figure 1b, the as-prepared mesh is super-hydrophilic and underwater superoleophobic that can selectively separate water from oil/water mixtures. Water can pass the mesh but oil cannot at less than 55 °C (pH 7) and pH less than 13 ($T = 25$ °C). When the temperature is greater than 55 °C or pH is larger than 13, oil can permeate through the mesh since the water retention capacity of PDMAEMA hydrogel is significantly reduced and the swelling volume is decreased. The change in water retention capacity and volume is the macroscopic performance of transition of intra- and inter-molecular hydrogen bonds in PDMAEMA hydrogel. Depending on the dual-responsive characteristic, oil and water can sequently permeate through the mesh, thus we can in situ collect them separately by adjusting temperature and pH.

2. EXPERIMENTAL SECTION

2.1. Materials and Measurements. Dimethyl amino ethyl methacrylate and N, N′-methylene bisacrylamide purchased from J&K and 2, 2′-diethoxyacetophenone purchased from Alfa Aesar were used as received. All other agents and solvents were purchased from Sinopharm Chemical Reagents and used directly without further purification. SEM images of the PDMAEMA hydrogel coated mesh were obtained using a field-emission scanning electron microscope (JSM-6700F, Japan). Contact angles were measured on an OCA20 machine (Data-Physics, Germany) at ambient temperature. The oil droplets (DCE, 2 μL) were dropped onto the prepared mesh under water. The average value of five measurements performed at different positions on the same sample was adopted as the contact angle. TGA analysis were carried out using a TA Instrument (TGA Q50) in air atmosphere (flow rate 60 mL/min) at a heating rate of 5 °C/min from room temperature to 110 °C and kept isothermal for 15 min.

2.2. Electrodeposition of Copper on the Substrate. Stainless steel mesh with pore size approximately 40 μm was chosen as substrates. Cu electrodeposition was carried out on mesh surface at a constant potential (1.5 V) for 400 s twice at room temperature and the electrolyte was an aqueous solution of 0.5 mol/L CuSO₄. The working

electrode was copper mesh and cathode were stainless steel mesh. After the deposition, the samples were rinsed with deionized water and dried.

2.3. Preparation of PDMAEMA Hydrogel-Coated Mesh. Dimethyl amino ethyl methacrylate (DMAEMA), N, N′-methylene bisacrylamide (BIS), 2, 2′-diethoxyacetophenone (DEOP), and PAM (number average molecular weight M_n = 3 000 000), as the precursor, cross-linker, initiator, and adhesive agent (38:1:0.0.5: (7×10^{-5}) by mole) were dissolved in deionized water and stirred for 12 h to form a homogeneous solution. The stainless steel mesh was immersed in the mixed pregel solution, then slowly taken out with the sticky solution adhered on the surface of steel wires. The mesh with pregel solution was placed under the 365 nm UV light for 120 min to form PDMAEMA hydrogel coated mesh. Pregel solutions contained different mole ratios of monomer and crosslinker have been prepared to observe the effects of different crosslinking degree on oil/water separation process (see details in the Supporting Information).

2.4. Separation of Oil/Water Mixtures. The as-prepared mesh stored in water before separation was fixed between two Teflon fixtures. Both of the fixtures were attached with glass tubes and placed vertically. The diameter of the tube was 25 mm. The oil/water mixtures (30 v/v%) were poured onto the as-prepared mesh. The separation was achieved by the weight of the liquids. The separation efficiency was determined by testing the content of the oil before and after separation and calculated by oil rejection coefficient (R (%)) according to

$$R(\%) = \left(1 - \frac{C_p}{C_0}\right) \times 100\% \tag{1}$$

where C_o and C_p are the oil concentration of the original oil/water mixture and the collected water after the first separation. The oil content was measured by the infrared spectrometer oil content analyzer (CY2000, China)

3. RESULTS AND DISCUSSIONS

3.1. Mesh Morphology. Figure 2 shows the scanning electron microscopy (SEM) images of PDMAEMA hydrogel coated mesh. Figure 2a is a typical image of stainless steel mesh as a substrate with pore diameter of approximately 40 μm (400
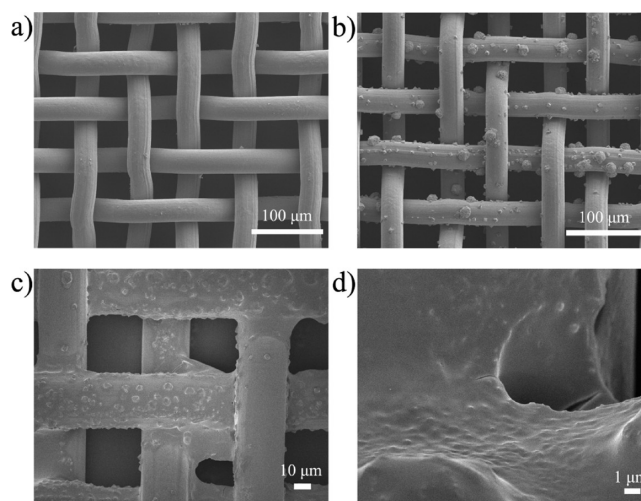
Figure 2. SEM images of the as-prepared mesh: (a) the stainless steel mesh as substrates with an average diameter of approximately 40 μm; (b) the substrates after electro-deposition of copper and rectangular pyramid-shaped copper can be observed which intended to increase the surface roughness; (c) large-area view of the PDMAEMA hydrogel-coated mesh; (d) the high-magnification image of hydrogel coated mesh, in which the nanostructured papillae can be clearly seen.

2027

dx.doi.org/10.1021/am405089m | ACS Appl. Mater. Interfaces 2014, 6, 2026−2030

mesh size). The surface of the substrate is clean and smooth. Figure 2b is the image of the substrate after electro-deposition of copper which is intended to increase the surface roughness. The electrodeposition was achieved under potentiostatic and thermostatic control at 1.5 V for 400 s twice (see details in the Experimental Section). The electro-deposited copper can be observed in the shape of rectangular pyramid which could continue to pile up to form larger cluster. Both form of copper help store the pregel solution for better polymerization on the mesh. Figure 2c demonstrates that the PDMAEMA hydrogel coatings cover the steel uniformly and a few of hydrogel exists in the pores of the mesh which has less influence on the pass of water through the as-prepared mesh. A rough surface with nanostructured papillae can be clearly observed on the enlarged view of a single wire (Figure 2d).

3.2. Mesh Wettability.
The wettability and oil-adhesion properties of the PDMAEMA hydrogel coated mesh were characterized by the contact angle measurement. Figure 3a
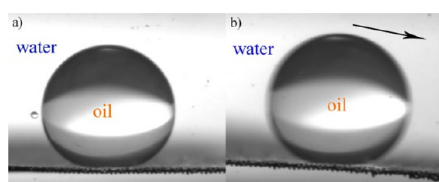
Figure 3. As-prepared mesh shows special wettability with both underwater superoleophobic and low oil-adhesion characteristics in oil/water/solid three-phase system: (a) the photograph of a 1,2-dichloroethane droplet (2 μL) on the coated mesh in water with a contact angle of 151.0 ± 0.8° and (b) sliding angle of 3.0 ± 0.8°.

displays the shape of a 1,2-dichloroethane droplet on the mesh underwater, and in this case the oil contact angle (OCA) is about 151.0 ± 0.8°. Water can be absorbed by hydrogel and trapped in the rough nanostructure, resulting in great decrease of the contact area between oil droplet and the mesh. Therefore, the mesh shows underwater superoleophobic property in the oil/water/solid three-system. The triple-phase contact line (TCL) is not continuous in this composite contact mode so that oil droplet can easily roll off the mesh.[12] Figure 3b illustrates the photograph of a 1,2-dichloroethane droplet on the as-prepared mesh with a sliding angle of 3.0 ± 0.8° that indicates the oil-adhesion of the mesh is quite low in neutral solution at ambient temperature. The oil contact angles under aqueous solutions at different pH value have been presented in Figure S2 in the Supporting Information.

3.3. Thermoresponsive Controllable Separation.
The PDMAEMA-coated mesh shows different wettability with oil at different temperature and pH since PDMAEMA is a thermo- and pH sensitive polymer. A series of proof-of-concept studies have been carried out to test the controllable oil/water separation capacity. The oil/water separation procedure was performed as shown in Figure 4. The mesh was fixed between two Teflon fixtures. Both of the fixtures were attached with a glass tube and placed vertically. When pouring the mixture of gasoline and water, water passed through the mesh rapidly while gasoline was repelled and kept in the upper glass tube. During the separation, no external force was used except their own weight (Figure 4a−c). After the separation, the water was collected in the beaker below for further analysis. Meanwhile, we in situ heated the mesh with a 1000 W hair dryer for 2.5 min. When PDMAEMA reached its LCST, the coated mesh's
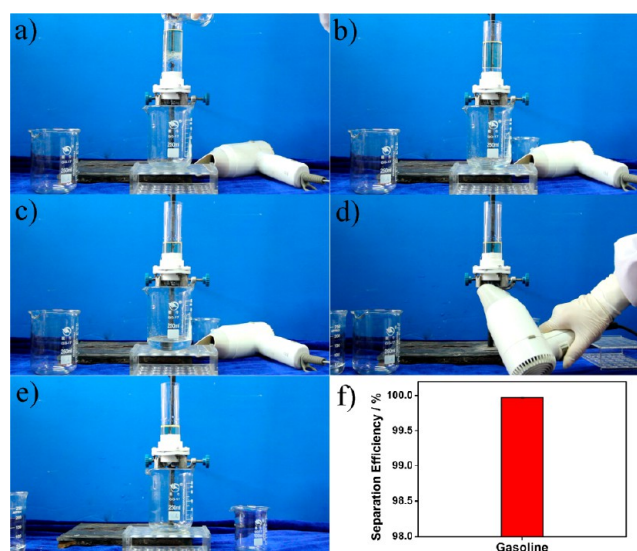
Figure 4. Studies of the temperature-controllable oil/water separation. (a) The mesh was fixed between two Teflon fixtures. Both of the fixtures were attached with a glass tube and placed vertically. A mixture of gasoline and water was poured into the upper glass tube. (b) Water passed through the mesh quickly, while the gasoline was kept in the upper glass. (c) The separation was accomplished and water was collected in the beaker below for further analysis. (d) The mesh was in situ heated by a hair dryer until PDMAEMA hydrogel reached its LSCT. Then gasoline started to permeate the mesh and (e) was collected in another beaker. (f) The separation efficiency for gasoline and water mixtures.

water retention capacity was significantly reduced and the swelling volume of the hydrogel was greatly decreased (see details in the separation video in the Supporting Information). Then gasoline could permeate and be collected afterward (Figure 4d, e).

Thermogravimetric analysis (TGA) of PDMAEMA hydrogel-coated mesh has been made to confirm the different ability of holding water. Samples were taken out from different water bath with temperature of 25 and 55 °C and hung up in the air for 5 min. As shown in Figure 5a, the water content of the coated mesh from a room temperature water bath is 18.6% while only 0.02% in the mesh from a 55 °C water bath. Moreover, we made some bulletlike PDMAEMA hydrogel to test the swelling property. After immersed in water bath at different temperature (25 and 55 °C), there is no visible change on the high-temperature hydrogel in contrast to an obvious swelling on the low temperature hydrogel (Figure 5c). With the two characteristics above, the as-prepared mesh can selectively separate water from oil/water mixtures at room temperature and let oil permeate after heating. Therefore, water and oil can pass through the mesh in turn and be collected separately simply by adjusting the temperature, implying the achievement of controllable oil/water separation. As shown in Figure 4f, the separation efficiency of gasoline can be up to 99.97 ± 0.01%.

3.4. pH-Responsive Controllable Separation.
To study the pH responsiveness of the PDMAEMA hydrogel coated mesh, a set of oil/water mixtures with different pH have been prepared. The aqueous solution was dyed by cresol red, which displays red in the solution with pH below 1.8, yellow between 1.8 to 8.0, and purple above 8.0. Before each separation, the as-prepared mesh has been immersed in the corresponding solution were respectively 0.1 M HCl solution, deionized water,
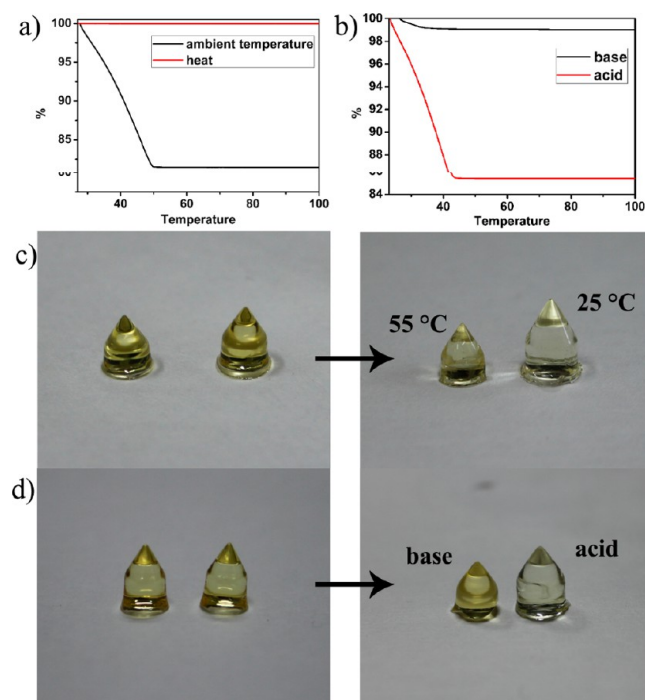
Figure 5. (a, b) TGA spectra of the PDMAEMA hydrogel coated meshes from different temperature and pH water bath. It clearly showed the water content of the coated mesh from a room-temperature water bath is 18.6%, whereas it is only 0.02% in the mesh from a 55 °C water bath and 15.0 and 1.0% for the mesh from 0.1 M HCl solution and 1 M NaOH solution, respectively. (c, d) Bulletlike PDMAEMA hydrogel was obviously swelled after immersed in a 25 °C water bath (or 0.1 M HCl aqueous solution), whereas there was no visible change after immersed in a 55 °C water bath (or 1 M NaOH aqueous solution).

and 1 M NaOH solution with pH of 1.0, 7.0, and 14.0. In Figure 6a, b, as pouring the mixtures of gasoline/0.1 M HCl solution and gasoline/water, water passed through the mesh quickly while gasoline was kept in the upper glass tube. It also indicated the mesh can be fully recovered after the thermo-responsive controllable separation process. However, the gasoline/1 M NaOH solution mixture permeated through the mesh altogether (Figure 6c). The different wettability of oil on the mesh is also caused by different water retention capacity and swelling volume. The water content of a coated mesh from 0.1 M HCl solution is 15.0 and 1.0% for the mesh from 1 M NaOH solution.(Figure 5b) Besides, the protonation degree of the tertiary amine group in PDMAEMA decreased from low pH to high pH solution. The bulletlike hydrogel gets a clear swell after immersed in the 0.1 M HCl solution while there is almost no change in volume in the 1 M NaOH solution. (Figure 5d). Therefore, the as-prepared mesh is confirmed to be pH responsive in oil/water separation.

4. CONCLUSIONS

In summary, a novel thermo- and pH dual-responsive PDMAEMA hydrogel coated mesh was successfully fabricated in an oil/water/solid three-phase system. The as-prepared superhydrophilic and underwater superoleophobic mesh has realized controllable oil/water separation with high separation efficiency. It can selectively separate water from oil/water mixtures and make water and oil permeate through the mesh orderly and be collected separately by adjusting the temper-
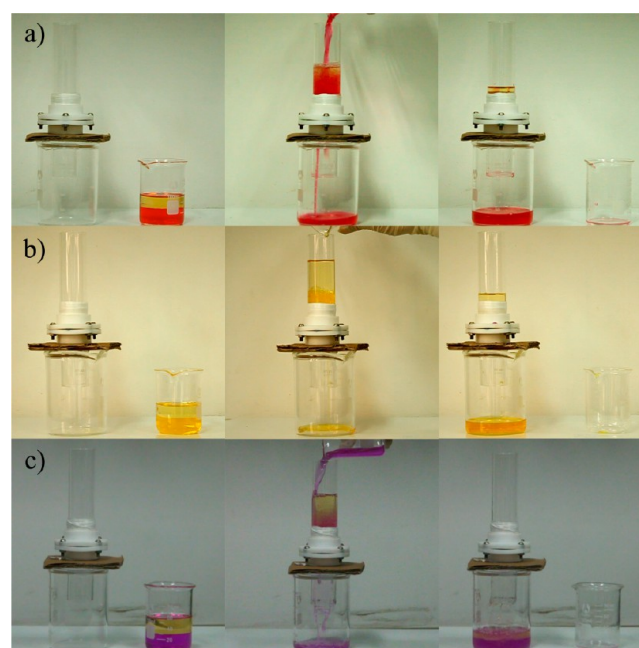
Figure 6. Studies of the pH-controllable oil/water separation: (a, b) Mixtures of gasoline/0.1 M HCl aqueous solution and gasoline/water were poured onto the mesh, water passed through the mesh quickly and gasoline was kept in the upper glass to achieve separation. (c) The mixture of gasoline/1 M NaOH aqueous solution passed through the mesh altogether. The water phase was dyed by cresol red.

ature or pH. This material has excellent potential to be used in practical applications because of its thermo- and pH dual-responsive property and biocompatibility. Moreover, this material has created a new field for water/oil separation in which the process can be diversified and more intelligent.

■ ASSOCIATED CONTENT

ⓢ Supporting Information
Video of thermoresponsive controllable separation at pH of 7 and effects of cross-linking degree et al. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: fl@mail.tsinghua.edu.cn.

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Das, S.; Ranjan, P.; Maiti, P. S.; Singh, G.; Leitus, G.; Klajn, R. Adv. Mater. 2013, 25, 422−426.
(2) Wang, D.; Jiao, P.; Wang, J.; Zhang, Q.; Feng, L.; Yang, Z. J. Appl. Polym. Sci. 2012, 125, 870−875.
(3) Liu, S.; Armes, S. P. Angew. Chem., Int. Ed. 2002, 41, 1413−1416.
(4) Shi, G.; Jin, S.; Xue, G.; Li, C. Science 1995, 267, 994−996.

(5) Deng, Y.; Yang, W.; Wang, C. C.; Fu, S. K. *Adv. Mater.* **2003**, *15*, 1729−1732.

(6) Sun, W.; Zhou, S.; You, B.; Wu, L. *J. Mater. Chem. A* **2013**, *1*, 3146−3154.

(7) Sun, W.; Zhou, S.; You, B.; Wu, L. *Macromolecules* **2013**, *46*, 7018−7026.

(8) Stuart, M. A. C.; Huck, W. T.; Genzer, J.; Müller, M.; Ober, C.; Stamm, M.; Sukhorukov, G. B.; Szleifer, I.; Tsukruk, V. V.; Urban, M. *Nat. Mater.* **2010**, *9*, 101−113.

(9) Chang, B.; Sha, X.; Guo, J.; Jiao, Y.; Wang, C.; Yang, W. *J. Mater. Chem.* **2011**, *21*, 9239−9247.

(10) Cabane, E.; Zhang, X.; Langowska, K.; Palivan, C. G.; Meier, W. *Biointerphases* **2012**, *7*, 1−27.

(11) Sun, T.; Wang, G.; Feng, L.; Liu, B.; Ma, Y.; Jiang, L.; Zhu, D. *Angew. Chem., Int. Ed.* **2004**, *43*, 357−360.

(12) Ding, C.; Zhu, Y.; Liu, M.; Feng, L.; Wan, M.; Jiang, L. *Soft Matter* **2012**, *8*, 9064−9068.

(13) Shannon, M. A.; Bohn, P. W.; Elimelech, M.; Georgiadis, J. G.; Marinas, B. J.; Mayes, A. M. *Nature* **2008**, *452*, 301−310.

(14) Gao, C.; Sun, Z.; Li, K.; Chen, Y.; Cao, Y.; Zhang, S.; Feng, L. *Energy Environ. Sci.* **2013**, *6*, 1147−1151.

(15) Feng, L.; Zhang, Z.; Mai, Z.; Ma, Y.; Liu, B.; Jiang, L.; Zhu, D. *Angew. Chem., Int. Ed.* **2004**, *43*, 2012−2014.

(16) Nguyen, D. D.; Tai, N.-H.; Lee, S.-B.; Kuo, W.-S. *Energy Environ. Sci.* **2012**, *5*, 7908−7912.

(17) Guo, L.; Yuan, W.; Li, J.; Zhang, Z.; Xie, Z. *Appl. Surf. Sci.* **2008**, *254*, 2158−2161.

(18) Li, M.; Xu, J.; Lu, Q. *J. Mater. Chem.* **2007**, *17*, 4772−4776.

(19) Cao, Y.; Zhang, X.; Tao, L.; Li, K.; Xue, Z.; Feng, L.; Wei, Y. *ACS Appl. Mater. Interfaces* **2013**, *5*, 4438−4442.

(20) Callies, M.; Quéré, D. *Soft Matter* **2005**, *1*, 55−61.

(21) Sun, W.; Zhou, S.; You, B.; Wu, L. *J. Mater. Chem. A* **2013**, *1*, 10646−10654.

(22) Xue, Z.; Wang, S.; Lin, L.; Chen, L.; Liu, M.; Feng, L.; Jiang, L. *Adv. Mater.* **2011**, *23*, 4270−4273.

(23) Crick, C. R.; Gibbins, J. A.; Parkin, I. P. *J. Mater. Chem. A* **2013**, *1*, 5943−5948.

(24) Zhou, X.; Zhang, Z.; Xu, X.; Guo, F.; Zhu, X.; Men, X.; Ge, B. *ACS Appl. Mater. Interfaces* **2013**, *5*, 7208−7214.

(25) Brugger, B.; Richtering, W. *Adv. Mater.* **2007**, *19*, 2973−2978.

(26) Zhang, S.; Lu, F.; Tao, L.; Liu, N.; Gao, C.; Feng, L.; Wei, Y. *ACS Appl. Mater. Interfaces* **2013**, *5*, 11971−11976.

(27) Kwon, G.; Kota, A.; Li, Y.; Sohani, A.; Mabry, J. M.; Tuteja, A. *Adv. Mater.* **2012**, *24*, 3666−3671.

(28) Janout, V.; Myers, S. B.; Register, R. A.; Regen, S. L. *J. Am. Chem. Soc.* **2007**, *129*, 5756−5759.

(29) Jin, M.; Wang, J.; Yao, X.; Liao, M.; Zhao, Y.; Jiang, L. *Adv. Mater.* **2011**, *23*, 2861−2864.

(30) Zhu, Q.; Tao, F.; Pan, Q. *ACS Appl. Mater. Interfaces* **2010**, *2*, 3141−3146.

(31) Zhang, L.; Wu, J.; Wang, Y.; Long, Y.; Zhao, N.; Xu, J. *J. Am. Chem. Soc.* **2012**, *134*, 9879−9881.

(32) Zhang, L.; Zhang, Z.; Wang, P. *NPG Asia Mater.* **2012**, *4*, e8.