Membranes

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CO_2-Responsive Nanofibrous Membranes with Switchable Oil/Water Wettability**

*Hailong Che, Meng Huo, Liao Peng, Tommy Fang, Na Liu, Lin Feng, Yen Wei, and Jinying Yuan**

Dedicated to Professor Xinde Feng on the occasion of his 100th birthday

Abstract: *Responsive polymer interfacial materials are ideal candidates for controlling surface wetting behavior. Here we developed smart nanostructured electrospun polymer membranes which are capable of switching oil/water wettability using CO_2 as the trigger. In particular, the combination of CO_2-responsiveness and porous nanostructure enables the as-prepared membranes to be used as a novel oil/water on–off switch. We anticipate that the promising versatility and simplicity of this system would not only open up a new way of surface wettability change regulation by gas, but also have obvious advantages in terms of highly controlled oil/water separation and CO_2 applications.*

Understanding and manipulating the surface properties of advanced materials has been the subject of intense research recently due to their versatile potentials in many fields.[1] Wettability is of great importance to interfacial materials and is largely controlled by the surface structure and chemical composition of the materials.[2] In this respect, stimuli-responsive membranes capable of changing surface wettability derived from changes in the materials' environment have found wide range of applications, including controlled drug delivery, reversible cells capture, catalysis, and oil/water separation.[3] With the development of nanotechnology, surface chemistry and polymer science, a growing number of smart surfaces with switchable wettability for both oil and water have been developed by alternating external conditions such as pH, light, temperature and electric fields.[3d,4] In particular, smart surfaces based on stimuli-responsive polymer systems make it possible to realize the perfect control of surface wettability and act as reversible on–off switches, since their well-designed structures can be readily available, and their reversible physical properties change can be easily achieved upon exposure to surrounding stimulation. For example, Gao and Hou et al. prepared temperature-sensitive surfaces by direct casting of polymethylmethacrylate-*b*-poly(*N*-isopropylacrylamide) (PMMA-*b*-PNIPAAm) solution onto a common industrial steel mesh, which exhibited temperature switchable oil/water wettability.[5] Wang et al. reported functionalized materials that were able to adjust the surface wettability between superoleophilicity and superoleophobicity in aqueous media by grafting a pH-responsive poly(2-vinylpyridine)-based polymers on non-woven textiles and polyurethane sponges.[6] The membranes showed a strong pH-dependent oil/water wettability by adjusting the pH of media. Despite of these progresses, it still suffers from critical issues to apply these systems in on–off switches. For instance, physical stimuli especially high-energy ultraviolet (UV) irradiation may damage the system to a certain extent. When adding acids and bases to the solution, inevitable salt accumulation and progressive dilution accompanied with repetitive regulation of the aqueous pH give rise to a complex and weak cycling process. Hence, from these perspectives, to devise new functional surfaces possessing well-controlled oil/water wettability triggered by environmentally friendly and cost-effective stimuli still remains a challenge.

In this regard, we aim to realize the surface wettability change regulation by a "green" gas, and explore how the gas can act on oil/water on–off switches. Carbon dioxide (CO_2) has emerged as a widespread, nontoxic, inexpensive, and renewable resource, and has attracted great interests.[7] Amidine, a type of CO_2-responsive molecule, can react with CO_2 in water to form a charged amidinium bicarbonate and this reaction is reversible by bubbling with Ar or N_2. A series of CO_2 controlled on–off switches based on amidine functionality have been developed by Jessop's group including solvents, solutes and surfactants.[8] Our group have previously constructed the "breathing" vesicles in aqueous solution with reversible distinctive volume expansion and contraction in size by alternating treatment with CO_2 and Ar, respectively. The vesicles were formed by the self-assembly of an amphiphilic diblock copolymer consisting of hydrophilic poly(ethylene oxide) (PEO) and CO_2-sensitive poly(*N*-amidino)dodecyl acrylamide (PAD).[9] Another type of CO_2-responsive polymer containing amine groups, such as poly(*N*,*N*-dimethylaminoethyl methacrylate) (PDMAEMA)

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[*] H. Che, M. Huo, L. Peng, T. Fang, Prof. J. Yuan
Key Lab of Organic Optoelectronics & Molecular Engineering of Ministry of Education, Department of Chemistry
Tsinghua University, Beijing, 100084 (P.R. China)
E-mail: yuanjy@mail.tsinghua.edu.cn

N. Liu, Prof. L. Feng, Prof. Y. Wei
Key Lab of Bioorganic Phosphorus Chemistry & Chemical Biology of Ministry of Education, Department of Chemistry
Tsinghua University, Beijing, 100084 (P. R. China)

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and poly(*N*,*N*-diethylaminoethyl methacrylate) (PDEAEMA), have been reported by Zhao et al.[10] The tertiary amine groups in PDEAEMA can react with CO_2 in water, exhibiting an extended hydrophilic chain conformation.[11] Upon exposure to N_2 to remove CO_2, it recovers its hydrophobic aggregate state. These exciting results prompted us to select the CO_2-sensitive polymers for the gas-controlled surface wettability study.

Here we report a simple method to fabricate smart nanostructured membranes (SNMs) with a high interface-to-volume area by electrospinning,[12] which is a powerful and cost-effective technique for generating nanofibers. The membranes can adjust their oil/water wettability between hydrophobicity/oleophilicity and hydrophilicity/oleophobicity under an alternating CO_2/N_2 stimulation. We have found that the smart surfaces can be utilized as a promising class of materials suitable for the dual oil/water on–off switch adjusted by a gaseous trigger without deteriorating the system.

Figure 1 illustrates the process for fabricating SNMs. It is based on the combination of polymerization reactions and the technique of electrospinning. In order to keep the membrane stable in water with high sensitivity to CO_2, a water-insoluble component is required to be incorporated into the polymer system. The combination of PMMA, a sufficiently stable polymer in water, can effectively improve the stability of the nanofibers. In this work, firstly, we synthesized PMMA-*co*-PDEAEMA copolymers by radical copolymerization reactions (Supporting Information (SI), Figure S1). Next, continuous polymer nanofibers were prepared by electrospinning. To observe the formation of continuous nanofibers, we used scanning electron microscopy (SEM) to inspect the size and morphological variations of the nanofibers at different copolymer concentrations (SI, Figure S2). Appropriate polymer concentration (25 wt%) could avoid the breakup of the stable jet to generate very fine bead-free nanofibers with the average diameter of about 700 nm (Figure 1 b). The representative cross-sectional view of the nanofibrous membranes (SI, Figure S3) has shown that a SNM thickness of around 100 μm was acquired after 10 h of electrospinning. It is a fact that electrospun nanofibrous membranes are one of the best choices to develop smart surface materials due to their excellent characteristics such as high porosity and large surface-to-volume ratio. In this study, the membranes had a visibly large number of micropores between fibers which play a significant role in effectively alleviating the mass transfer resistance of liquid. Moreover, continuous nanostructured fibers assembled in random networks can greatly increase the roughness of the surfaces.

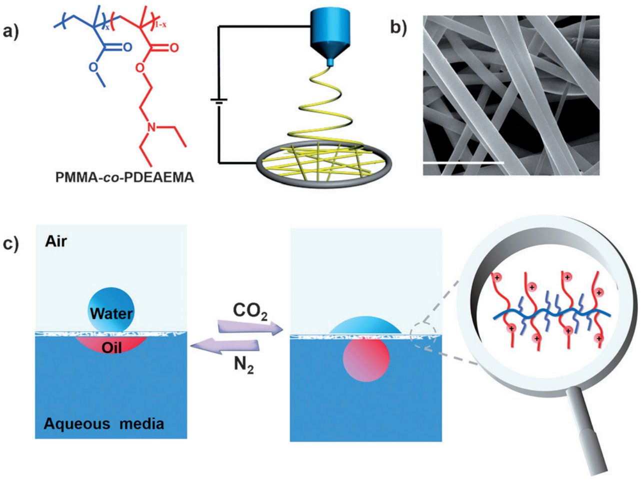

Figure 1. Fabrication process and CO_2 switchable oil/water wettability of the smart nanostructured membranes. a) Diagram of the electrospinning process for fabricating PMMA-*co*-PDEAEMA nanofibers. b) SEM images of a representative porous membranes with a diameter of 700 nm. Scale bars, 5 μm. c) Illustration of the CO_2 switchable oil/water wettability between hydrophobicity/oleophilicity and hydrophilicity/oleophobicity.

To prove the CO_2-induced wettability of the as-prepared smart membranes, we carried out static water contact angle (WCA) measurements in atmospheric environment. For comparison, PMMA-*co*-PDEAEMA films were simultaneously fabricated by spin-coating copolymer solution onto a glass slide. As shown in Figure 2 a, a water droplet remained stable on the SNMs for 5 min with the WCA of about 140°, while the corresponding spin-coated film exhibited a relatively lower WCA of 90° (SI, Figure S4a). The distinct difference between these two phenomena is influenced by the different surface roughness. For the electrospun membranes, the presence of random fiber networks during the process of electrospinning highly increased their roughness. Additionally, the air/water interface could be remarkably improved due to the nanostructure of the electrospun membranes and higher density of micropores on the surfaces which enabled gas to penetrate through, thus substantially reduced the water contact area. After purging CO_2 for 15 min, the SNMs were endowed with a significant transition from hydrophobicity to hydrophilicity with the WCA slowly decreasing from 140° to 36° (Figure 2 b) in 5 min.

This phenomenon could be explained by the protonation and deprotonation effects of amine groups in PDEAEMA. Obviously, at neutral aqueous media, the initial PDEAEMA chains maintained in a dehydrated, collapsed form. Upon exposure to CO_2 in water, some PMMA domains were overlaid by the mobilizable, swollen and chain-extended PDEAEMA chains, which exposed themselves on the surface exterior making the material favorable for water capture. Meanwhile, after N_2 bubbling, the wettability of the membranes could return to the initial hydrophobic state.

After demonstrating the water wettability of the PMMA-*co*-PDEAEMA nanofibers on exposure to CO_2 or N_2, we also investigated the oil wettability of SNMs underwater which is one of the key factors to affect their applications in aqueous surrounding. In fact, unlike air media where hydrophobic mesh is surrounded by gas allowing oil to penetrate (SI, Figure S5), the oil wettability of the surfaces in aqueous environment is more complex. This is because a barrier layer could be formed underwater that prevents oil permeation, and the superoleophilic property of the material may not be maintained. A PMMA-*co*-PDEAEMA spin-coated film with a oil contact angle (OCA) of about 38° (SI, Figure S4b) indicated PMMA-*co*-PDEAEMA is oleophilic. The porous structure of the electrospun membranes, which traps air into the smart surfaces underwater, plays a crucial role in its oil

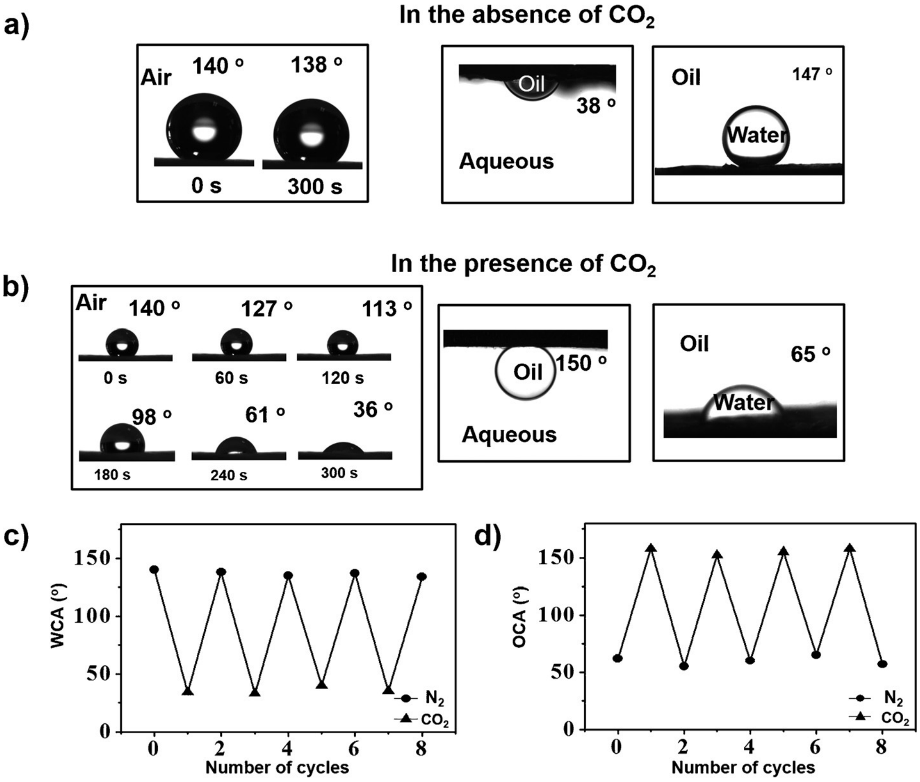

Figure 2. Wetting behavior of water and oil on the SNMs. a) Oil/water behavior of the surfaces before CO_2 treatment. Left: Still images of the water droplet on the as-prepared surfaces in air within 300 s. Middle: An oil droplet (hexane) with the OCA of about 36° on the surfaces in aqueous solution. Right: A water droplet with the WCA of about 147° on the surfaces in hexane solution. b) Oil/water behavior of the surfaces after CO_2 treatment. Left: Still images of the CO_2 bubbled water droplet on the as-prepared surfaces in air with the WCA decreased to 36° within 300 s. Middle: An oil droplet (hexane) with the OCA of about 155° on the surfaces in aqueous solution. Right: A water droplet with the WCA of about 65° on the surfaces in hexane solution. c, d) Reversible wettability of the as-prepared surfaces for water and oil droplets triggered by CO_2 and N_2.

affinity and water un-wetting performance. The oil-wetting behavior in aqueous media can be seen in Figure 2a. An oil droplet (hexane) with the OCA of about 36° on the surfaces in aqueous solution was rapidly absorbed by the surfaces in less than 3 s after it contacted the membrane, demonstrating its oleophilicity in neutral aqueous environment (SI, Figure S6). Remarkably, the oil wettability of the membranes was totally reversed after bubbling CO_2 into the aqueous solution for 15 min. Figure 2b illustrates the formation of an oil droplet sphere with an OCA of about 150°, indicating a CO_2-induced superoleophobic property of the material. Meanwhile, we immersed the membrane into hexane (oil) solution to survey its oleophilicity and hydrophobicity in the absence and presence of CO_2 to better understand the CO_2-switchable oil/water wettability (Figure 2a and b, right). Obviously, after CO_2 stimulation, SNMs changed from hydrophobic/oleophilic to hydrophilic/lipophobic in hexane solution.

As for oil wettability in aqueous media, PMMA-*co*-PDEAEMA exhibited a collapsed conformation due to its oleophilicity. Thus, an oil-trapped surface was generated to prevent the access of water. Upon purging CO_2 into the solution, hydrated and swollen PDEAEMA chains stretched out into the water on the exterior of the SNMs, exhibiting a high affinity to water. Therefore, a water-trapped surface can be formed in such a water media to prevent the oil from being absorbed into the membranes. After removing CO_2 by passing N_2 for 15 min, the oil was absorbed again by the surfaces, demonstrating its recovering oleophilicity from the superoleophobic state. This reversible shift from oil-trapped to oil-repelled state could be repeated for many times upon exposure to CO_2 and N_2 in the solution (Figure 2c and d). We explored the variation of ^{1}H NMR spectra of DEAEMA monomer after bubbling with CO_2, which could be used as a model to support this process as well (SI, Figure S7 and Supplementary Discussion). Therefore, we can conclude that the gas-sensitive electrospun PMMA-*co*-PDEAEMA membranes provides a novel system in which selective oil/water wettability can be effectively realized by manipulating alternative CO_2/N_2 treatment.

From what has been discussed above, chemical composition and surface morphology are two important factors to influence the surface oil/water wettability.[13] The polymer responsiveness and nanostructures of the electrospun membranes jointly enhance the CO_2 switchable oil/water wettability. Figure 3 displays the atomic force microscope (AFM) images of PMMA-*co*-PDEAEMA single nanofiber before and after treatment with CO_2. In the absence of CO_2, the surface of the nanofiber is smoother compared with that stimulated by CO_2. Corresponding to the profile images, Figure 3c is the height fluctuation of the nanofiber which represents the roughness of the surface. Clearly, the curve demonstrates a relatively large fluctuation after bubbling CO_2, revealing a rougher surface. These results are consistent with the three-dimensional (3D) images of the nanofiber (insets in Figure 3a and b). This interesting phenomenon is related to the CO_2-sensitivity of PDEAEMA. It is likely due to the role of PDEAEMA component that can react with CO_2 after stimulation, while PMMA cannot. Thus the surface is no longer flat, and a fluctuating surface appears. We have also explored the quantitative relationship between roughness and olephilicity/lipophobicity of the nanofibers (SI, Figure S8). Increasing CO_2 stimulation time (from 0 min to 15 min), the surface roughness of the nanofiber was gradually enhanced and the nanofibers became more hydrophilic and lipophobic. From these results, we deduced that CO_2 can effectively adjust the level of the roughness and oil/water wettability of the nanofibers, and there exists quantitative relationship

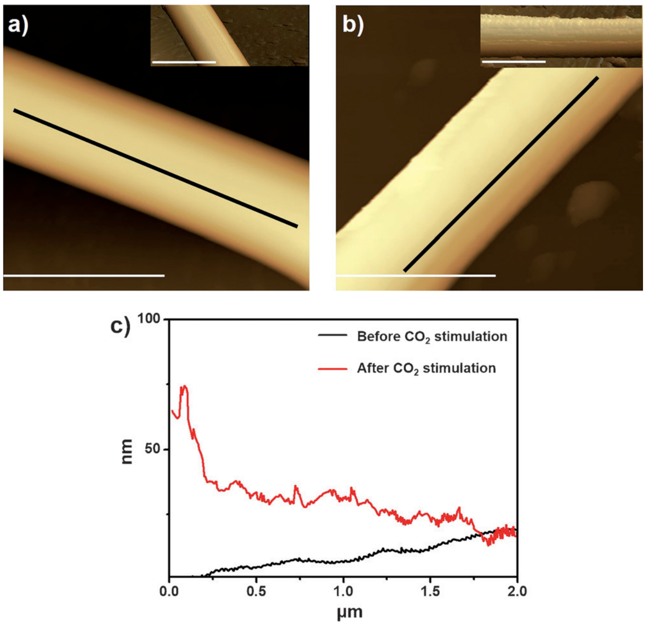

Figure 3. AFM imagines of single nanofiber a) before and b) after CO_2 stimulations. Scale bars, 1 μm. Insets in (a) and (b) are the corresponding 3D AFM images. Scale bars, 1 μm. c) Surface roughness curve of single nanofiber in the absence and presence of CO_2.

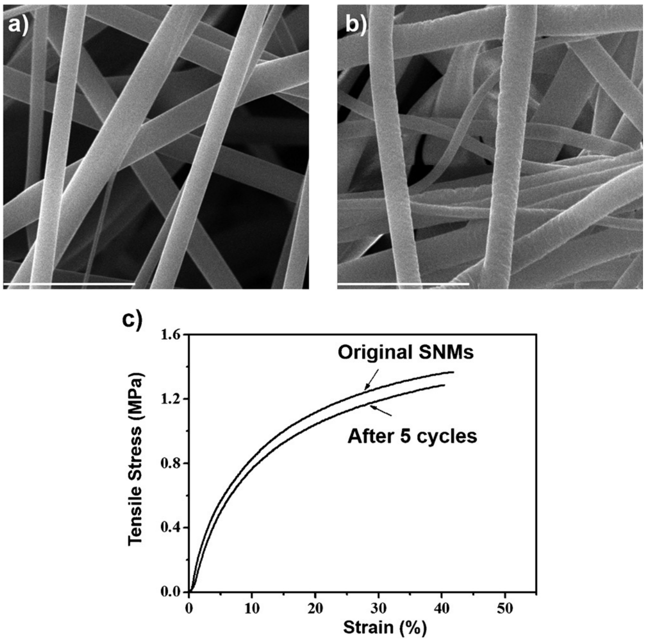

Figure 4. SEM images of the nanofibrous membranes a) in the absence and b) presence of CO_2. Scale bars, 5 μm. c) Stress–strain curves between the original SNMs and that after reversible stimuli for five times.

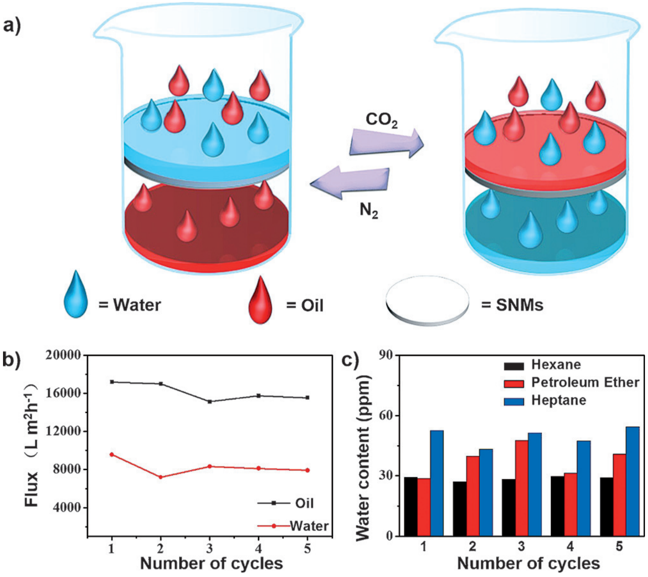

Figure 5. a) Representation of the CO_2 switchable oil/water on–off switch. b) Variations in the flux of oil and water in the absence and presence of CO_2, respectively. c) Water content in oil in the filtrate after permeating oil/water mixtures through the SNMs.

between roughness and olephilicity/lipophobicity of the nanofibers with different CO_2 stimulation time.

As expected, this kind of morphological difference can be confirmed by SEM images as well. As shown in Figure 4a and b, it is obvious that the roughness of the nanofibers can be enhanced upon exposure to CO_2. Undoubtedly, the roughness variation of the electrospun nanofibers is one of the essential elements that cannot be ignored during the surface wettability switch. These results present that the CO_2-responsive on–off oil/water switch is dependent on the combined effects of chemical composition and nano-structured rough surfaces.

Generally, the mechanical property of nanofibrous membranes is one of the most significant factors that influence their reusability for practical applications, and it is a combined result of the intrinsic strength of the fibers and the bonding among them.[14] Figure 4c demonstrates the typical tensile stress-strain curves of the membranes monitored by dynamic-mechanical analysis (DMA). For the original SNMs, an initial nonlinear elastic behavior can be observed, but later they displayed a typical linear increase until break. After repeating the reversible stimuli for five times, no obvious tensile stress decline of the membranes could be observed compared with the initial ones. Moreover, both initial and final state exhibited nearly the same strain of 42% and 44%, respectively. Thus, the stable mechanical property of the nanofibrous membranes presented above indicated its promising reusability.

The switching process between on and off for oil/water allowed us to utilize SNMs to switch selective oil/water separation. Figure 5a shows that in neutral aqueous media, when the mixture was poured into the upper glass tube, oil rapidly passed through the membranes while water could not, due to the hydrophobic/oleophilic surfaces (SI, Figure S9 and Video 1). By contrast, when the mesh was immersed in water with CO_2 bubbling for 15 min in a sealed environment (SI, Video 2) without subsequent drying, the complete opposite separation process could be observed. The water penetrated the membranes while oil retained on the nanofibers (SI, Video 3). Interestingly, the separation process was fully reversible after the removal of CO_2 from the solution upon exposure to N_2 for 15 min and dried over N_2 flow. These results demonstrate that using gas-responsive membranes, the selective oil/water separation was realized by bubbling and removing CO_2.

We measured the water and oil fluxes of the membranes by calculating the flow volume per unit time from the valid area of the membranes. Before CO_2 bubbling, the membranes exhibited a promising oil flux of 17000 $\mathrm{L\,m^{-2}\,h^{-1}}$. The highest values of 9554 $\mathrm{L\,m^{-2}\,h^{-1}}$ was achieved in terms of the flux of water after CO_2 treatment (Figure 5b). Moreover, the separation performance indicated the promising reusability of the membranes, with minimal flux fluctuation after five cycles despite of the relatively lower water flux compared to that of oil. Furthermore, the on–off switch also exhibited similar behavior for other oil types such as petroleum ether and *n*-heptane with high oil flux (SI, Figure S10). In addition, the water content in oil after every separation experiment for different oils was investigated. As shown in Figure 5c, the water content in hexane was below 30 ppm for five cycles, and the corresponding results for petroleum ether and *n*-heptane were 40 and 60 ppm, respectively. These unexpectedly high separation efficiencies demonstrate that these SNMs are good candidates for industrial oil spill cleanup and oil-polluted water disposal. Such smart membranes used for CO_2 controlled oil/water on–off switch, to the best of our knowledge, have not been reported before.

In summary, by constructing the proposed nanostructured architecture, we developed "CO_2-modulable" PDEAEMA-based smart membranes that are able to reversibly regulate oil/water wettability of the surfaces. The continuous nanofibrous membranes have an important role in wetting behavior: offering randomly distributed nanofibers to facilitate the roughness of the membranes surfaces, and forming a great number of micropores within nanofibers for further improving the hydrophobicity in air and oleophilicity underwater. With the combination of conformational change of PDEAEMA chains and the roughness of the nanostructured surfaces of the membranes, we can successfully realize the CO_2-induced selective wetting behavior. Using CO_2 as driving force, the SNMs holds great promise in terms of dual oil/water on–off switches. On the basis of this understanding, we believe that this may open up new fields in industrial CO_2 applications. We anticipate that this process can also be employed easily to design and develop smart surfaces in myriad applications including wastewater treatment, biomedicine, microfluidics and nanoreactors.

Keywords: carbon dioxide · electrospinning · oil/water separation · stimuli-responsive materials · surface chemistry

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[1] a) D. G. Anderson, J. A. Burdick, R. Langer, *Science* **2004**, *305*, 1923–1924; b) P. M. Mendes, *Chem. Soc. Rev.* **2008**, *37*, 2512–2529; c) T. Sun, G. Wang, L. Feng, B. Liu, Y. Ma, L. Jiang, D. Zhu, *Angew. Chem. Int. Ed.* **2004**, *43*, 357–360; *Angew. Chem.* **2004**, *116*, 361–364; d) H. Y. Erbil, A. L. Demirel, Y. Avcı, O. Mert, *Science* **2003**, *299*, 1377–1380; e) R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni, E. Kojima, A. Kitamura, M. Shimohigoshi, T. Watanabe, *Nature* **1997**, *388*, 431–432.

[2] a) L. Feng, Z. Zhang, Z. Mai, Y. Ma, B. Liu, L. Jiang, D. Zhu, *Angew. Chem. Int. Ed.* **2004**, *43*, 2012–2014; *Angew. Chem.* **2004**, *116*, 2046–2048; b) H. Bai, X. Tian, Y. Zheng, J. Ju, Y. Zhao, L. Jiang, *Adv. Mater.* **2010**, *22*, 5521–5525.

[3] a) Y.-J. Kim, M. Ebara, T. Aoyagi, *Adv. Funct. Mater.* **2013**, *23*, 5753–5761; b) Y.-J. Kim, M. Ebara, T. Aoyagi, *Angew. Chem. Int. Ed.* **2012**, *51*, 10537–10541; *Angew. Chem.* **2012**, *124*, 10689–10693; c) W. Wu, Q. Zhang, J. Wang, M. Chen, S. Li, Z. Lin, J. Li, *Polym. Chem.* **2014**, *5*, 5668–5679; d) A. K. Kota, G. Kwon, W. Choi, J. M. Mabry, A. Tuteja, *Nat. Commun.* **2012**, *3*, 1025; e) S. Wang, X. Feng, J. Yao, L. Jiang, *Angew. Chem. Int. Ed.* **2006**, *45*, 1264–1267; *Angew. Chem.* **2006**, *118*, 1286–1289.

[4] a) M. A. C. Stuart, W. T. S. Huck, J. Genzer, M. Muller, C. Ober, M. Stamm, G. B. Sukhorukov, I. Szleifer, V. V. Tsukruk, M. Urban, F. Winnik, S. Zauscher, I. Luzinov, S. Minko, *Nat. Mater.* **2010**, *9*, 101–113; b) G. M. Whitesides, P. E. Laibinis, *Langmuir* **1990**, *6*, 87–96; c) J. Ge, Y. Yin, *Angew. Chem. Int. Ed.* **2011**, *50*, 1492–1522; *Angew. Chem.* **2011**, *123*, 1530–1561; d) B. Wang, Z. Guo, *Chem. Commun.* **2013**, *49*, 9416–9418.

[5] B. Xue, L. Gao, Y. Hou, Z. Liu, L. Jiang, *Adv. Mater.* **2013**, *25*, 273–277.

[6] L. Zhang, Z. Zhang, P. Wang, *NPG Asia Mater.* **2012**, *4*, e8.

[7] S. Lin, P. Theato, *Macromol. Rapid Commun.* **2013**, *34*, 1118–1133.

[8] a) P. G. Jessop, D. J. Heldebrant, X. Li, C. A. Eckert, C. L. Liotta, *Nature* **2005**, *436*, 1102–1102; b) Y. Liu, P. G. Jessop, M. Cunningham, C. A. Eckert, C. L. Liotta, *Science* **2006**, *313*, 958–960; c) P. G. Jessop, L. Kozycz, Z. G. Rahami, D. Schoenmakers, A. R. Boyd, D. Wechsler, A. M. Holland, *Green Chem.* **2011**, *13*, 619–623.

[9] a) Q. Yan, R. Zhou, C. Fu, H. Zhang, Y. Yin, J. Yuan, *Angew. Chem. Int. Ed.* **2011**, *50*, 4923–4927; *Angew. Chem.* **2011**, *123*, 5025–5029; b) Q. Yan, J. Wang, Y. Yin, J. Yuan, *Angew. Chem. Int. Ed.* **2013**, *52*, 5070–5073; *Angew. Chem.* **2013**, *125*, 5174–5177; c) Q. Yan, J. Yuan, *Chem. J. Chin. Univ.* **2012**, *33*, 1877–1885; d) A. Feng, Q. Yan, J. Yuan, *Prog. Chem.* **2012**, *24*, 1995–2003.

[10] a) D. Han, X. Tong, O. Boissière, Y. Zhao, *ACS Macro Lett.* **2011**, *1*, 57–61; b) Q. Yan, Y. Zhao, *J. Am. Chem. Soc.* **2013**, *135*, 16300–16303.

[11] a) S. S. Satav, S. Bhat, S. Thayumanavan, *Biomacromolecules* **2010**, *11*, 1735–1740; b) J. Zhang, D. Han, H. Zhang, M. Chaker, Y. Zhao, D. Ma, *Chem. Commun.* **2012**, *48*, 11510–11512; c) Z. Guo, Y. Feng, S. He, M. Qu, H. Chen, H. Liu, Y. Wu, Y. Wang, *Adv. Mater.* **2013**, *25*, 584–590; d) H. Thérien-Aubin, Z. L. Wu, Z. Nie, E. Kumacheva, *J. Am. Chem. Soc.* **2013**, *135*, 4834–4839; e) A. Feng, C. Zhan, Q. Yan, B. Liu, J. Yuan, *Chem. Commun.* **2014**, *50*, 8958–8961; f) B. Liu, H. Zhou, S. Zhou, H. Zhang, A. Feng, C. Jian, J. Jin, W. Gao, J. Yuan, *Macromolecules* **2014**, *47*, 2938–2946.

[12] a) D. Li, Y. Xia, *Adv. Mater.* **2004**, *16*, 1151–1170; b) J. T. McCann, M. Marquez, Y. Xia, *J. Am. Chem. Soc.* **2006**, *128*, 1436–1437; c) W. Wang, X. Lu, Z. Li, J. Lei, X. Liu, Z. Wang, H. Zhang, C. Wang, *Adv. Mater.* **2011**, *23*, 5109–5112; d) X. Lu, W. Zhang, C. Wang, T.-C. Wen, Y. Wei, *Prog. Polym. Sci.* **2011**, *36*, 671–712; e) X. Sui, J. Yuan, W. Yuan, M. Zhou, *Chem. Lett.* **2008**, *37*, 114–115; f) R. Hao, J. Yuan, Q. Peng, *Chem. Lett.* **2006**, *35*, 1248–1249.

[13] K. Li, J. Ju, Z. Xue, J. Ma, L. Feng, S. Gao, L. Jiang, *Nat. Commun.* **2013**, *4*, 2276.

[14] a) X. Tang, Y. Si, J. Ge, B. Ding, L. Liu, G. Zheng, W. Luo, J. Yu, *Nanoscale* **2013**, *5*, 11657–11664; b) B. Li, B. Jiang, D. J. Fauth, M. L. Gray, H. W. Pennline, G. A. Richards, *Chem. Commun.* **2011**, *47*, 1719–1721; c) H.-R. Kim, T. Ito, B.-S. Kim, Y. Watanabe, I.-S. Kim, *Adv. Eng. Mater.* **2011**, *13*, 376–382.

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