Janus Polymer/Carbon Nanotube Hybrid Membranes for Oil/Water Separation Postprint

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Abstract

A robust and simple method is provided to fabricate Janus polymer/carbon nanotube (CNT) hybrid membranes for oil/water separation. Starting from CNT membranes formed by dispensing, hydrophobic poly(styrene) (PS) and hydrophilic poly(N,N-dimethylaminoethyl

Full Text

Preamble

Janus Polymer/Carbon Nanotube Hybrid Membranes for Oil/Water Separation

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*S Supporting Information

ABSTRACT: A robust and simple method is provided to fabricate Janus polymer/carbon nanotube (CNT) hybrid membranes for oil/water separation. Starting from CNT membranes formed by dispensing, hydrophobic poly(styrene) (PS) and hydrophilic poly(N,N-dimethylaminoethyl methacrylate) (PDMAEMA) were grafted from different sides of the photoactive CNT membranes via self-initiated photografting and photopolymerization (SIPGP) to achieve Janus polymer/CNT hybrid membranes. The obtained membranes exhibit excellent oil/water selectivity in the removal of oil from water. Moreover, they can effectively separate both surfactant-stabilized oil-in-water and water-in-oil emulsions because of the anisotropic wettability of the membranes.

KEYWORDS: Janus polymer/CNT membrane, SIPGP, superhydrophobic, hydrophilic, oil/water separation

1. INTRODUCTION

With increasing industrial oily wastewater and frequent oil spill accidents, oil-contaminated water has become a worldwide problem. Oil/water separation, especially emulsified oil/water separation, presents significantly urgent environmental and economic demands. Materials with special wettability that can effectively separate oil/water mixtures have received broad attention in recent years. However, most of these materials can realize immiscible oil/water separation but are not effective in separating oil/water emulsions, particularly surfactant-stabilized emulsions with droplet sizes below 20 m. For selective and effective separation of oil/water emulsions, materials capable of separating both oil-in-water and water-in-oil emulsions with high separation efficiency and good recyclability are highly desired.

Janus materials, with different properties on opposite sides of the same object, have attracted tremendous attention over the past 20 years because of their remarkably interesting surface activities and potential applications as novel sensors, optical probes, and surfactants. Among various Janus materials, two-dimensional (2D) Janus nanosheets or membranes deserve special attention due to their highly anisotropic shape and asymmetric chemistry. For instance, inorganic Janus nanosheets can serve as solid surfactants to stabilize emulsion droplets. Apart from their remarkable stabilization effect, the anisotropic wettability of Janus membranes makes them attractive candidates for applications such as oil/water separation, catalyst supports, sensors, and so on.

Carbon nanotubes (CNTs), with three-dimensional (3D) network structures and outstanding mechanical, thermal, and electrical properties, have been extensively investigated and have shown promising applications in supercapacitors and other fields. The application of CNTs as oil/water separation materials has attracted extensive attention because of their low density, high porosity, and hydrophobic properties. For instance, single-walled CNT network films could be used for the separation of emulsified oil/water mixtures with higher flux than commercial filtration membranes, and hybrid foams of graphene and CNTs can selectively remove oils and organic solvents from water with high absorption capacity. By taking advantage of both Janus materials and CNTs, we herein present a broadly applicable method for designing Janus polymer/CNT hybrid membranes for highly effective removal of oils and separation of various surfactant-stabilized oil-in-water and water-in-oil emulsions.

There are many methods to grow polymers from CNTs. In this work, the Janus hybrid membranes were fabricated by respectively grafting hydrophobic polymer such as poly(styrene) (PS) and hydrophilic polymer such as poly(N,N-dimethylaminoethyl methacrylate) (PDMAEMA) from different sides of CNT membranes via self-initiated photografting and photopolymerization (SIPGP;

Figure 1 [FIGURE:1]). The obtained Janus PS−CNT−PDMAEMA hybrid membranes can selectively absorb a wide range of organic solvents and maintain high sorption capacity even after 10 repeated separation experiments. The unique Janus wettability endows the membranes with switchable transport performance, enabling them to effectively separate both surfactant-stabilized oil-in-water and water-in-oil emulsions. These Janus hybrid membranes have great potential for practical oil/water separation applications.

2. EXPERIMENTAL SECTION

2.1. Materials

General chemicals in chemical reagent grade were used as received from Sinopharm Chemical Reagent. Styrene (99%) and N,N-dimethylaminoethyl methacrylate (DMAEMA) were obtained from Alfa Aesar China (Tianjin) Co., Ltd., and were purified by neutral Al_2O_3 column and dried with 0.4 nm molecular sieves at room temperature for 3 days. The raw multiwall CNTs (diameter: ~10−30 nm; length: ~10−30 m; −OH content: ~2%) with a purity of over 90% were purchased from Chengdu Organic Chemistry Co., Ltd., and were rinsed thoroughly with anhydrous ethanol and dried in a stream of nitrogen before use. Glass substrates were cleaned in a mixture of H_2O_2/H_2SO_4 (1:3, v/v) at 80 °C (“piranha solution”) for 2 h and washed thoroughly with Milli-Q-grade water. (Caution: Piranha solution reacts violently with organic matter!)

2.2. Preparation of Janus Polymer/CNT Hybrid Membranes

First, 2 mg of purified CNTs was dispersed in 1 mL of ethanol and sonicated for 3 h. The mixture was then dropped uniformly onto a glass substrate. After drying, the membrane was placed in a glass tube containing degassed styrene monomer and irradiated with a UV fluorescent lamp with a spectral distribution between 300 and 400 nm ($\lambda\_\{max\}$ = 350 nm, 210 mW/cm^2) under N_2 atmosphere for 1 h. After SIPGP, the as-prepared membrane was rigorously rinsed with toluene and ethyl acetate to remove physisorbed polymer and monomer. The PS-grafted CNT membrane was then etched from the glass substrate by NaOH (10 wt %). The released membrane was turned over and deposited onto another glass substrate. The subsequent photografting followed the same steps as PS grafting, with styrene replaced by DMAEMA. After SIPGP, the Janus polymer/CNT membrane was rinsed with ethanol to remove physisorbed polymer and monomer.

2.3. Sorption of Organic Solvents

First, 4 mg of oil red (an organic dye used to color organic solvents red) was added to 15 mL of hexane, and the mixture was sonicated for 10 min to form a homogeneous solution. Next, 1 mL of oil red-dyed hexane was added to the water surface. Due to its lower density, the oil droplet formed a homogeneous

layer on top of the water. Finally, a Janus PS−CNT−PDMAEMA membrane was placed in contact with the dyed hexane until the hexane was completely absorbed by the membrane. In this process, the PS side of the Janus CNT membrane faced upward while the PDMAEMA side contacted the water. The sorption of other organic solvents was performed following the same procedure. We emphasize that tests should be conducted quickly to avoid evaporation of the absorbed organic solvents, especially those with low boiling points. After the absorption process, the Janus PS−CNT−PDMAEMA membrane was immersed in ethanol for 1 h to extract the organic solvent from the membrane.

2.4. Preparation of Oil-in-Water and Water-in-Oil Emulsions

For oil-in-water emulsions, Tween 80 (HLB = 15, an oil-in-water emulsifier; 1.2, 1.1, and 0.8 g of Tween 80 for toluene-in-water, chloroform-in-water, and hexane-in-water emulsions, respectively) was added to 120 mL of water, followed by addition of 4 mL of oil. The mixture was stirred for 3 h. For water-in-oil emulsions, a certain amount of Span 80 (HLB = 4.3, a water-in-oil emulsifier; 0.8, 1.2, and 1.0 g of Span 80 for water-in-toluene, water-in-chloroform, and water-in-hexane emulsions, respectively) was added to 114 mL of oil, followed by addition of 1 mL of water. The mixture was stirred for 3 h. All prepared emulsions were stable for 24 h, and no demulsification was observed. The composition of various emulsions is summarized in Table S1 (Supporting Information). The density and viscosity of all oils used in this work are summarized in Table S2 (Supporting Information).

2.5. Separation of Oil-in-Water and Water-in-Oil Emulsions

The separation experiments were carried out with a vacuum-driven filtration system at a vacuum degree of 0.09 MPa (Figure S1, Supporting Information). The filter diameter was 10 mm.

2.6. Characterizations

Static water contact angle (WCA) measurements were performed at room temperature using an OCA-20 DataPhysics instrument. The water (Milli-Q) droplet volume was 3 L, and an average of three measurements was used to determine surface wettability. Transmission electron microscopy (TEM) measurements were performed with a JEOL JEM-2100F microscope. Scanning electron microscopy (SEM) measurements were carried out using a JEOL JMS-6700F scanning microscope. X-ray photoelectron spectroscopy (XPS) analysis was performed on a Shimadzu Axis Ultra DLD spectroscope using Mg Kα as the radiation source. Thermogravimetric analysis (TGA) measurements were conducted with a Netzsch TG 209F1 instrument at a heating rate of 10 °C/min under N_2 atmosphere. Raman measurements were recorded on a Dilor LabRam-1B multichannel confocal microspectrometer with 532 nm laser excitation. Optical microscopy images were taken on a BX 51TF Instec H601. Dynamic light scattering (DLS) measurements were performed on a Zetasizer Nano ZS. The water

content in collected filtrates was determined using a Karl Fischer moisture titrator (KF831). UV−vis spectra were recorded with a Lambda 950 spectrometer.

3. RESULTS AND DISCUSSION

3.1. Wetting Behavior

To preliminarily test whether hydrophobic PS and hydrophilic PDMAEMA were successfully attached to opposite sides of the CNT membrane, we performed WCA measurements to investigate the surface wettability of the hybrid membrane. As shown in Figure 2A [FIGURE:2], the WCA of the original CNT membrane is approximately 62°. After modification with PS, the WCA of the PS−CNT membrane increases to approximately 153° (Figure 2B). Grafting PDMAEMA from the lower surface (opposite side of the PS brushes) decreases the WCA to approximately 17° (Figure 2C). To more directly demonstrate the Janus membrane' s anisotropic surface wettability, two water drops were applied to opposite sides of the Janus membrane. The WCA difference reaches as high as approximately 130°, which demonstrates dramatic disparity between the surface properties of the two sides (Figure 2C). The anisotropic surface wettability of the obtained membrane suggests that PS and PDMAEMA were successfully grafted from the upper and lower surfaces of the CNT membrane, respectively.

3.2. Surface Morphology

SEM and TEM were applied to further characterize the surface morphology of the Janus PS−CNT−PDMAEMA membrane. The cross-sectional SEM image of polymer brushes grafted onto a Janus CNT hybrid membrane is shown in Figure 3A

. The thickness of the as-prepared hybrid membrane is about 5 m. Although the presence of PS and PDMAEMA brushes cannot be seen clearly in Figure 3A, the attachment of PS and PDMAEMA onto CNTs can be observed through further magnification of the hybrid membrane surface. After modification with PS and PDMAEMA, the average diameters of PS-grafted CNTs (Figure 3C) and PDMAEMA-grafted CNTs (Figure 3D) are relatively larger than that of original CNTs, indicating successful grafting of PS and PDMAEMA onto CNTs. The TEM results are consistent with the SEM results (Figure S3, Supporting Information). These results illustrate that PS and PDMAEMA were uniformly grafted from the upper and lower surfaces of the CNT membrane by SIPGP, respectively, with almost no agglomeration among CNTs.

3.3. Chemical Composition

The attachment of PS and PDMAEMA was further confirmed by XPS. As shown in Figure 4

, the XPS survey spectrum of the PDMAEMA-grafted surface reveals an N 1s peak at 398 eV, which can be assigned to the tertiary amine group in

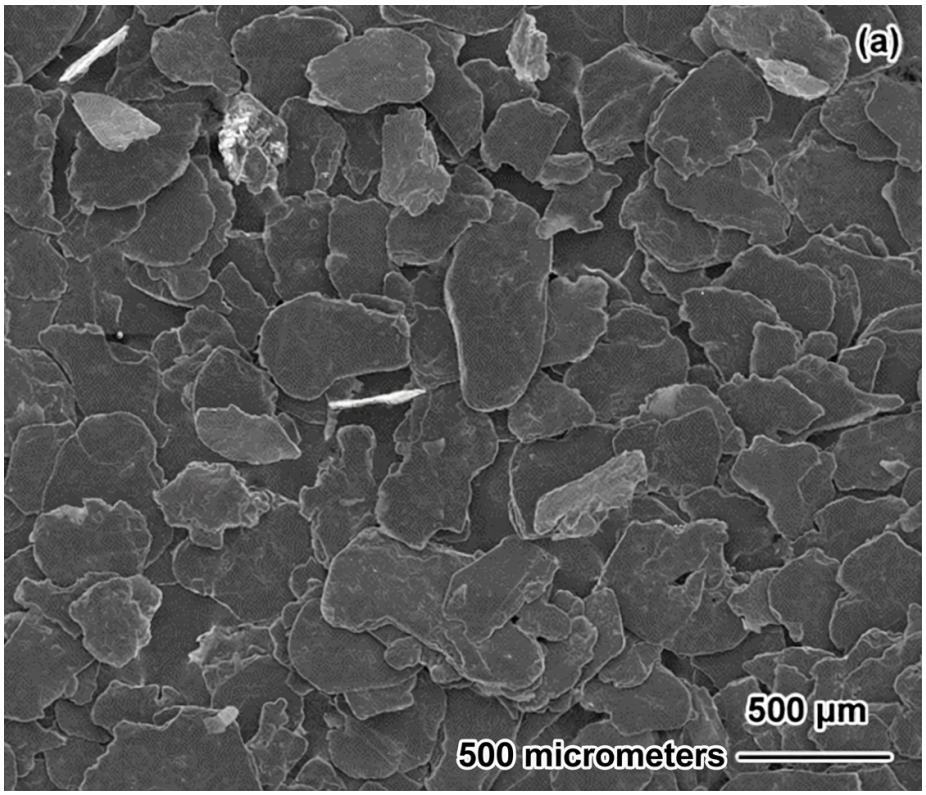

Figure 1: Figure 3

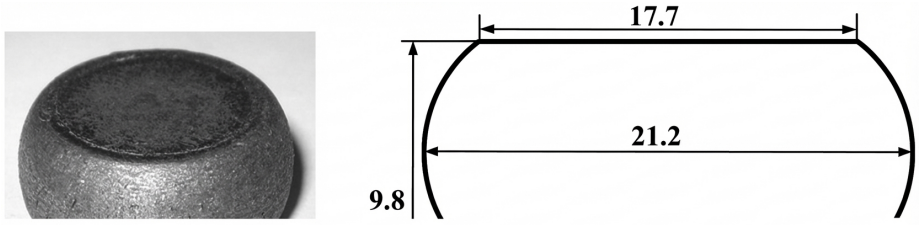

Figure 2: Figure 4

PDMAEMA. Since nitrogen is the characteristic element distinguishing PS and PDMAEMA, the two sides can be identified by nitrogen content. C 1s spectra for both surfaces of the Janus membrane are shown in Figure 4B,C. The C 1s spectrum of the PDMAEMA-grafted surface is deconvoluted into five component peaks. The intensity ratios of these peaks are approximately [A]:[B]:[C]:[D]:[E] = 2:1:3:1:1, which is in good agreement with the stoichiometric ratio of the corresponding carbon atoms in the chemical structure of PDMAEMA. The C 1s spectrum of the PS-grafted surface includes a main hydrocarbon peak at a binding energy of 284.8 eV and $\pi-\pi^*$ shakeup satellites at 291.5 eV. In addition, the mass content of both surfaces is comparable with the theoretical atomic content (Table S3, Supporting Information). The XPS results provide direct evidence of successful covalent attachment of PS and PDMAEMA brushes to the CNT membrane. The attachment of PS and PDMAEMA on CNTs is also confirmed by Raman and TGA results (Figure S4, Supporting Information).

3.4. Sorption of Organic Solvents

The Janus polymer/CNT membranes show great potential in the removal of organic contaminants from water. As shown in Figure 5A [FIGURE:5], hexane dyed with oil red was dropped onto the water surface, and a piece of the Janus polymer/CNT membrane was then brought into contact with the hexane layer. Hexane was fully absorbed within a few seconds, leaving an almost transparent region on the water surface. To quantitatively study the sorption capacity, we defined weight gain (wt %) as the weight of absorbed substance relative to the dried Janus polymer/CNT membrane. Various organic liquids were studied. As shown in Figure 5B, the Janus polymer/CNT membrane can uptake these organic liquids at 200−450 times its own weight. Moreover, the recyclability of the Janus polymer/CNT membrane was evaluated. As shown in Figure 4C, the sorption capacity for chlorobenzene varies only slightly during repeated experiments and always remains above 300 times the original weight of the Janus polymer/CNT membrane, indicating good recyclability of our material.

3.5. Separation of Oil/Water Emulsions

Besides its absorption of organic liquids, the simultaneous superhydrophobicity and hydrophilicity makes the Janus polymer/CNT membrane a very promising candidate for oil/water separations. The water-repellency and oil-repellency of the Janus membrane in complex under-oil or under-water environments were evaluated (Figure S5, Supporting Information). The observed distinct oleophobicity and superhydrophobicity of the membrane provides an excellent basis for its application in separating both oil-in-water and water-in-oil emulsions. Due to uniform CNT dispersion, the solution could easily form a uniform CNT membrane over a large area by dropping or spin coating; the polymer/CNT hybrid membrane was thus designed to match the size and shape of a filter. The subsequent separation was carried out at 0.09 MPa using a filter with a diameter of 10 mm (Figure S1, Supporting Information). A series of oil/water mixtures, includ-

ing surfactant-stabilized oil-in-water and water-in-oil emulsions, were prepared to evaluate the separation capability of the membrane.

For separating oil-in-water emulsions, the PDMAEMA side (hydrophilic) was in contact with the feed emulsions, and the membrane only allowed the continuous water phase to pass through because of the oil-repellency of the PDMAEMA side. For separating water-in-oil emulsions, the PS side (superhydrophobic) was in contact with the feed emulsions, and only oil could pass through the membrane due to the water-repellency of the PS side. Figure 6 [FIGURE:6] shows the separation results for Tween-80-stabilized toluene-in-water and Span-80-stabilized water-in-toluene emulsions as examples. In both cases, the collected filtrate (Figure 6C, right) is transparent compared with the original milky white feed emulsion (Figure 6C, left). Optical microscopy was applied to examine the separation effectiveness by comparing the feed with the collected filtrate (Figure 6C). Numerous densely packed droplets are visible in the feed solution, but no droplets are observed in the collected filtrate throughout the entire view, indicating excellent separation properties of the Janus polymer/CNT membrane.

Membrane permeability was comprehensively investigated (Figure 7 [FIGURE:7]). For oil-in-water emulsions, because our membrane only allows the continuous water phase to pass through, if the oil density is higher than that of water, the rejected oil droplets will accumulate and form a barrier layer on the membrane surface, impeding water permeation. Therefore, the permeate flux of the membrane heavily depends on the oil' s density. For water-in-oil emulsions, our membrane only allows the continuous oil phase to pass through, so it is reasonable that membrane flux is higher for oils with lower viscosity. Because chloroform is the densest oil and toluene is the most viscous oil studied in this work (Table S1, Supporting Information), chloroform-in-water presents the lowest flux in oil-in-water emulsions, and water-in-toluene presents the lowest flux in water-in-oil emulsions.

The purity of purified water and oil was investigated by UV−vis spectrometer and coulometer, respectively (Figure S6 and Table S4, Supporting Information). For the toluene-in-water emulsion, the characteristic peak of toluene was not observed in the filtrate spectrum (Figure S6A, Supporting Information). For the water-in-toluene emulsion, the purity of the recovered toluene was above 99.98%. The separation results for toluene-in-water and water-in-toluene emulsions effectively illustrate the high separation efficiency of our membrane. Similar effective separations were also achieved for other emulsion systems, including chloroform-in-water (S-2), hexane-in-water (S-3), water-in-chloroform (S-5), and water-in-hexane (S-6; Figures S7 and S8, Supporting Information).

4. CONCLUSIONS

In summary, we have demonstrated a facile and versatile approach to prepare Janus polymer/CNT hybrid membranes for emulsified oil/water separation. The polymer/CNT hybrid membranes were constructed by SIPGP, grafting hy-

drophobic PS and hydrophilic PDMAEMA from different surfaces of the CNT membranes. The obtained Janus polymer/CNT membranes can selectively remove a wide range of organic solvents from water with high absorption capacity and good recyclability. Furthermore, the Janus polymer/CNT membranes can effectively separate both surfactant-stabilized water-in-oil emulsions and oil-in-water emulsions due to the anisotropic wettability of the membranes, displaying high separation efficiency and promising flux. The high sorption capacity and remarkable recyclability make these membranes promising candidates for various practical applications such as controllable oil/water separation and selective oil absorption.

ASSOCIATED CONTENT

*S Supporting Information

SIPGP details, figures, tables, and flux calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Wang, L. K.; Chen, J. P.; Hung, Y.; Shammas, N. K., Eds. Membrane and Desalination Technologies. In *Handbook of Environmental Engineering*, Vol. 13; Humana Press: New York, 2010.

(2) Zhou, X. Y.; Zhang, Z. Z.; Xu, X. H.; Guo, F.; Zhu, X. T.; Men, X. H.; Ge, B. Robust and Durable Superhydrophobic Cotton Fabrics for Oil/Water Separation. *ACS Appl. Mater. Interfaces* **2013**, *5*, 7208−7214.

(3) Zhang, J. P.; Seeger, S. Polyester Materials with Superwetting Silicone Nanofilaments for Oil/Water Separation and Selective Oil Absorption. *Adv. Funct. Mater.* **2011**, *21*, 4699−4704.

(4) Zhu, Q.; Chu, Y.; Wang, Z. K.; Chen, N.; Lin, L.; Liu, F. T.; Pan, Q. M. Robust Superhydrophobic Polyurethane Sponge as a Highly Reusable Oil-Absorption Material. *J. Mater. Chem. A* **2013**, *1*, 5386−5393.
(5) Zhu, Q.; Pan, Q. M.; Liu, F. T. Facile Removal and Collection of Oils from Water Surfaces through Superhydrophobic and Superoleophilic Sponges. *J. Phys. Chem. C* **2011**, *115*, 17464−17470.
(6) Wang, B.; Li, J.; Wang, G.; Liang, W.; Zhang, Y.; Shi, L.; Guo, Z.; Liu, W. Methodology for Robust Superhydrophobic Fabrics and Sponges from in Situ Growth of Transition Metal/Metal Oxide Nanocrystals with Thiol Modification and Their Applications in Oil/Water Separation. *ACS Appl. Mater. Interfaces* **2013**, *5*, 1827−2022.
(7) Cao, Y. Z.; Zhang, X. Y.; Tao, L.; Li, K.; Xue, Z. X.; Feng, L.; Wei, Y. Mussel-Inspired Chemistry and Michael Addition Reaction for Efficient Oil/Water Separation. *ACS Appl. Mater. Interfaces* **2013**, *5*, 4438−4442.
(8) Li, A.; Sun, H. X.; Tan, D. Z.; Fan, W. J.; Wen, S. H.; Qing, X. J. G.; Li, X.; Li, S. Y.; Deng, W. Q. Superhydrophobic Conjugated Microporous Polymers for Separation and Adsorption. *Energy Environ. Sci.* **2011**, *4*, 2062−2065.
(9) Zhang, J. P.; Seeger, S. Polyester Materials with Superwetting Silicone Nanofilaments for Oil/Water Separation and Selective Oil Absorption. *Adv. Funct. Mater.* **2011**, *21*, 4699−4704.
(10) Li, A.; Sun, H. X.; Tan, D. Z.; Fan, W. J.; Wen, S. H.; Qing, X. J. G.; Li, X.; Li, S. Y.; Deng, W. Q. Superhydrophobic Conjugated Microporous Polymers for Separation and Adsorption. *Energy Environ. Sci.* **2011**, *4*, 2062−2065.
(11) Shi, Z.; Zhang, W. B.; Zhang, F.; Liu, X.; Wang, D.; Jin, J.; Jiang, L. Ultrafast Separation of Emulsified Oil/Water Mixtures by Ultrathin Free-Standing Single-Walled Carbon Nanotube Network Films. *Adv. Mater.* **2013**, *25*, 2422−2427.
(12) De Gennes, P. G. Soft Matter (Nobel Lecture). *Angew. Chem., Int. Ed.* **1992**, *31*, 842−845.
(13) Liang, F. X.; Zhang, C. L.; Yang, Z. Z. Rational Design and Synthesis of Janus Composites. *Adv. Mater.* **2014**, DOI: 10.1002/adma.201305415.
(14) Lattuada, M.; Hatton, T. A. Synthesis, Properties, and Applications of Janus Nanoparticles. *Nano Today* **2011**, *6*, 286−308.
(15) Hu, J.; Zhou, S. X.; Sun, Y. Y.; Fang, X. S.; Wu, L. M. Fabrication, Properties, and Applications of Janus Particles. *Chem. Soc. Rev.* **2012**, *41*, 4356−4378.
(16) Jiang, S.; Granick, S. *Janus Particles: Synthesis, Self-Assembly, and Applications*; RSC: London, England, 2012.
(17) Yang, H.; Liang, F.; Wang, X.; Chen, Y.; Zhang, C.; Wang, Q.; Qu, X.; Li, J.; Wu, D.; Yang, Z. Z. Responsive Janus Composite Nanosheets. *Macromolecules* **2013**, *46*, 2754−2759.
(18) Liang, F. X.; Shen, K.; Qu, X. Z.; Zhang, C. L.; Wang, Q.; Li, J. L.; Liu, J. G.; Yang, Z. Z. Inorganic Janus Nanosheets. *Angew. Chem., Int. Ed.* **2011**, *50*, 2379−2382.

(19) De Volder, M. F. L.; Tawfick, S. H.; Baughman, R. H.; Hart, A. J. Carbon Nanotubes: Present and Future Commercial Applications. *Science* **2013**, *339*, 535−539.
(20) Cao, Q.; Rogers, J. A. Ultrathin Films of Single-Walled Carbon Nanotubes for Electronics and Sensors: A Review of Fundamental and Applied Aspects. *Adv. Mater.* **2009**, *21*, 29−53.
(21) Hu, L. B.; Hecht, D. S.; Grüner, G. Carbon Nanotube Thin Films: Fabrication, Properties, and Applications. *Chem. Rev.* **2010**, *110*, 5790−5844.
(22) Schnorr, J. M.; Swager, T. M. Emerging Applications of Carbon Nanotubes. *Chem. Mater.* **2011**, *23*, 646−657.
(23) Dong, X. C.; Chen, J.; Ma, Y. W.; Wang, J.; Chan-Park, Mary B.; Liu, X. M.; Wang, L. H.; Huang, W.; Chen, P. Superhydrophobic and Superoleophilic Hybrid Foam of Graphene and Carbon Nanotube for Selective Removal of Oils or Organic Solvents from the Surface of Water. *Chem. Commun.* **2012**, *48*, 10660−10662.
(24) Homenick, C. M.; Lawson, G.; Adronov, A. Polymer Grafting of Carbon Nanotubes Using Living Free-Radical Polymerization. *Polym. Rev.* **2007**, *47*, 265−290.
(25) Paul, A.; Grady, B. P.; Ford, W. T. PMMA Composites of Single-Walled Carbon Nanotubes-Graft-PMMA. *J. Appl. Polym. Sci.* **2014**, DOI: 10.1002/app.39884.
(26) Jia, X.; Zhang, G. X.; Li, W.; Sheng, W. B.; Li, C. H. Tuning the Low Critical Solution Temperature of Polymer Brushes Grafted on Single-Walled Carbon Nanotubes and Temperature Dependent Loading and Release Properties. *J. Polym. Sci., Part A: Polym. Chem.* **2014**, *52*, 1807−1814.
(27) Xiao, P.; Gu, J. C.; Chen, J.; Han, D.; Zhang, J. W.; Cao, H. T.; Xing, B. R.; Han, Y. C.; Wang, W. Q.; Chen, T. A Microcontact Printing Induced Supramolecular Self-Assembled Photoactive Surface for Patterning Polymer Brushes. *Chem. Commun.* **2013**, *49*, 11167−11169.
(28) Steenackers, M.; Lud, S. Q.; Niedermeier, M.; Bruno, P.; Gruen, D. M.; Feulner, P.; Stutzmann, M. J.; Garrido, A.; Jordan, R. Structured Polymer Grafts on Diamond. *J. Am. Chem. Soc.* **2007**, *129*, 15655−15662.
(29) Xiao, P.; Gu, J. C.; Chen, J.; Zhang, J. W.; Xing, R. B.; Han, Y. C.; Fu, J.; Wang, W. Q.; Chen, T. Micro-Contact Printing of Graphene
(30) Chen, J.; Xiao, P.; Gu, J. C.; Han, D.; Zhang, J. W.; Sun, A. H.; Wang, W. Q.; Chen, T. A Smart Hybrid System of Au Nanoparticle Immobilized PDMAEMA Brushes for Thermally Adjustable Catalysis. *Chem. Commun.* **2014**, *50*, 1212−1214.
(31) Gupta, S.; Agrawal, M.; Conrad, M.; Hutter, N. A.; Olk, P.; Simon, F.; Eng, L. M.; Stamm, M.; Jordan, R. Poly(2-(dimethylamino)ethyl methacrylate) Brushes with Incorporated Nanoparticles as a SERS Active Sensing Layer. *Adv. Funct. Mater.* **2010**, *20*, 1756−1761.
(32) Ton-That, C.; Shard, A. G.; Teare, D. O. H.; Bradley, R. H. XPS and AFM Surface Studies of Solvent-Cast PS/PMMA Blends. *Polymer* **2001**, *42*, 1121−1129.

(33) Tao, M. M.; Xue, L. X.; Liu, F.; Jiang, L. An Intelligent Superwetting PVDF Membrane Showing Switchable Transport Performance for Oil/Water Separation. *Adv. Mater.* **2014**, *26*, 2943−2948.