Surface Chemistry

Deutsche Ausgabe: DOI: 10.1002/ange.201411283
Internationale Ausgabe: DOI: 10.1002/anie.201411283

A Superamphiphobic Coating with an Ammonia-Triggered Transition to Superhydrophilic and Superoleophobic for Oil–Water Separation**

Zhiguang Xu, Yan Zhao, Hongxia Wang, Xungai Wang, and Tong Lin*

Abstract: *Superhydrophilic and superoleophobic materials are very attractive for efficient and cost-effective oil–water separation, but also very challenging to prepare. Reported herein is a new superamphiphobic coating that turns superhydrophilic and superoleophobic upon ammonia exposure. The coating is prepared from a mixture of silica nanoparticles and heptadecafluorononanoic acid-modified TiO_2 sol by a facile dip-coating method. Commonly used materials, including polyester fabric and polyurethane sponge, modified with this coating show unusual capabilities for controllable filtration of an oil–water mixture and selective removal of water from bulk oil. We anticipate that this novel coating may lead to the development of advanced oil–water separation techniques.*

Surfaces with a special wettability, either "superoleophilic and superhydrophobic" or "superhydrophilic and superoleophobic", are very attractive for separating oil–water mixtures in applications like oil spill cleanup, oily wastewater treatment, and fuel purification. The existing materials for oil–water separation mostly have a superoleophilic–superhydrophobic surface,[1–6] which is easily fouled with oil, especially when the oil has a high viscosity. The difficulty to clean the membranes significantly increases material and operating costs. Additionally, when the separation membrane is set horizontally, water tends to settle down onto the membrane surface due to its higher density than oil, and thus forms a barrier layer that prevents oil permeation.

Materials with superhydrophilic and superoleophobic property are seldom reported, but are ideal for oil–water separation, in which water permeates through the membrane whereas oil is retained. In theory, surfaces that simultaneously have superhydrophilicity and superoleophobicity are energy unfavorable. Since water has a significantly higher surface tension than oils, a surface that is repellent to an oil fluid is usually also water-repellent, and on such a surface the water static contact angle (θ_{water}) normally is higher than the oil static contact angle (θ_{oil}). A few papers have reported the opposite case in which $\theta_{water} < \theta_{oil}$.[7–15] This unusual wetting behavior was achieved by designing the surface to produce specific interactions with water. However, the surfaces in most of these studies were wettable to both water and oils (i.e., $\theta_{water} < \theta_{oil} < 90°$).[7–12] Only two papers reported surfaces that can simultaneously display superhydrophilic and superoleophobic properties, but these surfaces have shown time-dependent behavior; it took more than 9 min for the water contact angle to decrease from its initial value (> 150°) to 0°.[13,14] Such a slow response is undesirable especially for oil–water separation by affinity absorption.

Herein, we report a new superamphiphobic coating, on which a water droplet remained stable ($\theta_{water} > 150°$) over time in air, but spread completely within three seconds ($\theta_{water} \approx 0°$) upon exposure to ammonia vapor. On the contrary, oil droplets placed on this coating remained stable ($\theta_{oil} > 150°$) during the ammonia exposure. We further demonstrate that such a unique wetting behavior is very useful for controllable filtration of oil–water mixture. Porous materials modified with this coating can selectively absorb and collect water from bulk oil, which is completely different to the conventional techniques that selectively remove oils from bulk water.[16–27] It is also noted that our coating is superoleophobic both in air and under water. This feature makes it distinct from the widely reported underwater superoleophobic materials,[28–35] which lack selective oil/water absorption capability.

Figure 1 a illustrates the procedure to prepare the superamphiphobic coating. A heptadecafluorononanoic acid-modified TiO_2 sol (HFA-TiO_2), in which both titanium carboxylate coordination complexes and Ti−O−Ti networks existed, was mixed with silica nanoparticles (NPs) in ethanol to form a coating solution. A simple dip coating method was then used to apply the coating solution onto porous substrates including polyester fabric and polyurethane sponge.

After coating, silica NPs were uniformly distributed on the coated fiber surface (Figure 1 b), and the textile structure remained unchanged (see also Figure S1). The enlarged view of a single fiber (Figure 1 c) shows that the thickness of thin HFA-TiO_2 layer was less than the diameter of silica NPs (100–170 nm). The root-mean-square (RMS) roughness of the coating surface was measured by atomic force microscope (AFM) to be about 33 nm (Figure S2). The coated fabric was also characterized by Fourier transform infrared (FTIR) spectroscopy and thermogravimetric analysis (TGA; Figure S3).

On the coated fabric, droplets of water, hexadecane, soybean oil, paraffin oil, and diesel oil all stayed nearly spherical (Figure 2 a), and both θ_{water} and θ_{oil} were above 150° (Figure 2 b). The coated fabric remained superamphiphobic over time in contact with these liquids (Figure S4). Such

---

[*] Dr. Z. Xu, Dr. Y. Zhao, Dr. H. Wang, Prof. X. Wang, Prof. T. Lin
Institute for Frontier Materials
Deakin University, Geelong, Victoria 3216 (Australia)
E-mail: yan.zhao@deakin.edu.au

[**] Dr. Y. Zhao thanks the Australian Research Council (ARC) for an Australian Postdoctoral (APD) fellowship under Discovery Project DP110101315. We also thank Dr. Yichao Wang of RMIT University and Dr. Haijin Zhu of Deakin University for help with the XPS and NMR test, respectively.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201411283.

© 2015 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

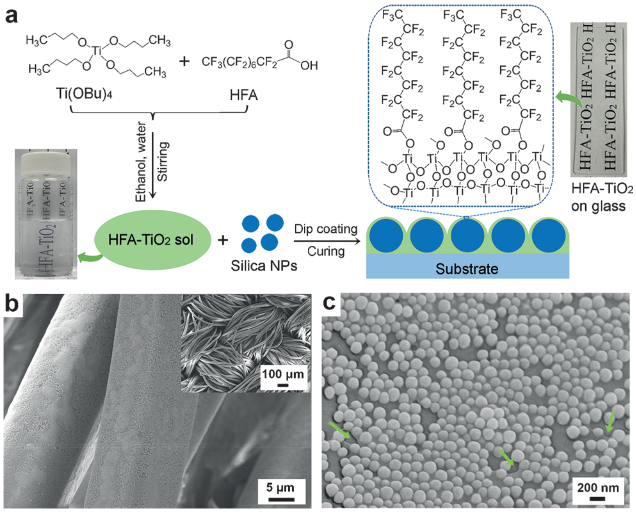

Figure 1. a) Schematic illustration of the preparation procedure for superamphiphobic coating (HFA-TiO_2 sol and its coating on a glass slide were transparent). b) SEM image of the polyester fibers coated with silica NPs/HFA-TiO_2. Inset: large-area view of the treated polyester fabric. c) Enlarged SEM view of the coated fiber surface (green arrows indicate HFA-TiO_2 thin layer).

a superamphiphobic surface exhibited slippery superhydrophobic and sticky superoleophobic characteristics (Figure S5). The pristine polyester fabric was wettable by these liquids (Figure S6). Besides the fluorinated alkyl chain of HFA, both the micro-scale roughness of the fabric weave structure and the nanoscale roughness of silica NPs contributed to the development of superamphiphobicity (Figure S7).

Upon exposure to ammonia vapor, the coated fabric turned water-wettable ($\theta_{water} \approx 0°$), but was still highly oil-repellent ($\theta_{oil} > 150°$; Figure 2a,b). Figure 2c shows the contact angle change during the ammonia exposure process. A water droplet on the fabric decreased its contact angle from 152° to 0° within just three seconds, while the oil droplet did not change its contact angle ($\theta_{oil} = 151°$) during the entire process. In addition to ammonia vapor, basic solutions can also trigger the superhydrophobic to superhydrophilic transition, but the coating is stable against acidic and high ionic strength solutions (Figure S8).

We also preexposed the dry superamphiphobic fabric to an ammonia atmosphere for 30 seconds and then tested the contact angles. After ammonia treatment, the fabric became highly hydrophilic and a water droplet completely spread within just 198 milliseconds, whereas a hexadecane droplet stayed stable (Figure 2d). For a flat glass slide coated with only HFA-TiO_2, $\theta_{water} \approx 22°$ and $\theta_{oil} = 71°$ under the same ammonia treatment (Figure S9). It is known that surface roughness makes the apparent contact angle lower when the intrinsic contact angle is $< 65°$, whereas higher when the intrinsic contact angle is $> 65°$.[36] So the superhydrophilicity and superoleophobicity of the coated fabric also arose from the amplification effect of the surface roughness on wettability.

The superhydrophobic to superhydrophilic transition can be attributed to the formation of ammonium carboxylate ions in the presence of ammonia based on cleavage of titanium carboxylate coordination bonding.[37] The presence and absence of ammonium ions in the HFA-TiO_2 coating were confirmed by FTIR spectra (Figure 3), in which the bands at 1405 cm^{-1} and 3180 cm^{-1} corresponding to ammonium ions appeared after ammonia exposure.[37] After the coating was heated at 120 °C for 20 min, these bands disappeared, indicating the decomposition of ammonium carboxylate ion bonding. Correspondingly, the superhydrophilicity and superhydrophobicity could be switched by ammonia exposure and heating (Figure S10). For comparison, fluoroalkylsilane coatings were subjected to the same ammonia treatment, but showed no change in superhydrophobicity (see Figure S11).

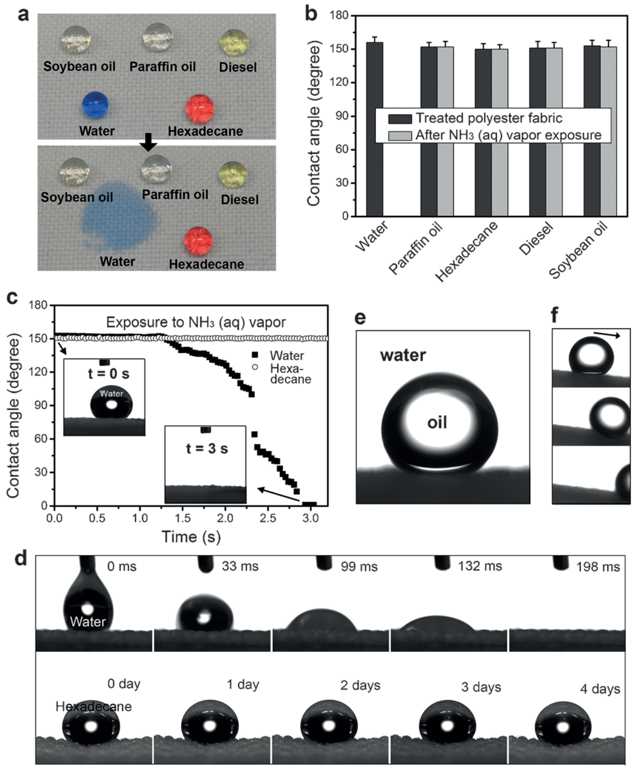

Figure 2. a) Photos of liquid droplets on the coated polyester fabric before (top panel) and after (bottom panel) ammonia exposure (see also Movie S1). Water and hexadecane were colored with acid blue 25 and oil red O, respectively. b) Contact angles of coated polyester fabric to various liquids before and after ammonia exposure. c) Time-dependence of contact angle for a water droplet and a hexadecane droplet placed on the coated polyester fabric upon exposure to ammonia vapor. d) Evolution of water and hexadecane droplets placed on the ammonia preexposed fabric with time. e) Shape of a DCE droplet placed on the coated and ammonia-exposed polyester fabric in water (contact angle 153 ± 2°). f) Sliding of the DCE droplet shown in panel (e).

The superhydrophilicity of the ammonia-treated surface can be ascribed to the migration of the ammonia salt of HFA formed upon ammonia exposure from the solid–air interface to the water–air interface, and even the water phase. This migration will not only increase solid-surface free energy but also simultaneously reduce water surface tension locally, thus leading to the observed superhydrophilicity. The driving force for the migration could be the attraction between the ions of HFA ammonia salt and the permanent dipole of water

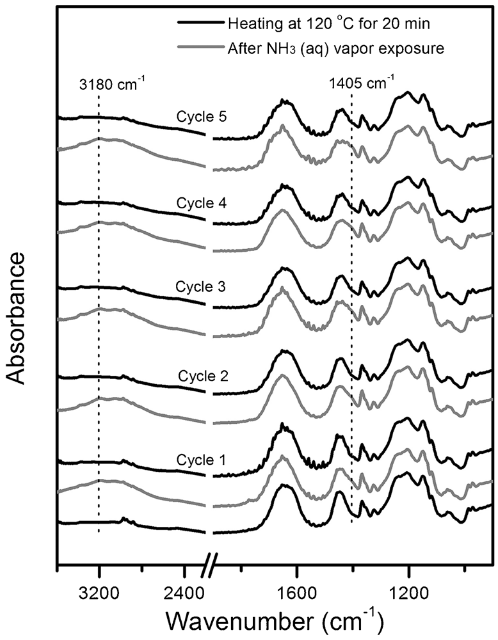

Figure 3. FTIR spectra of the HFA-TiO_2 coating on KBr pellet over five cycles of exposing the coated fabric to ammonia and heating at 120 °C for 20 min.

molecules, which might cause either the rotation of HFA ammonia salt or the penetration of water molecules through the array of fluorinated chains to meet the ions. Since hexadecane is nonpolar, there is no such driving force for HFA ammonia salt to migrate, and hence, the ammonia-treated surface was still superoleophobic.

Upon heating, the inner bonded HFA can migrate toward solid–air interface so as to minimize the surface free energy, which could be the reason for the recovery of superhydrophobicity. However, by increasing the number of ammonia exposure/heating cycles, θ_{water} of the superhydrophobic state decreased from 156° to less than 150° in the fifth cycle (Figure S10), which indicates the gradual loss of HFA ammonia salt from the solid surface. This result, in turn, provides evidence for the explanation given above. In addition, the migration of the HFA ammonia salt from the solid surface to water phase was also verified by examining the solid surface and the liquid phase using X-ray photoelectron spectroscopy (XPS) and nuclear magnetic resonance (NMR) spectroscopy, respectively (Figure S12).

The underwater oil wettability of the ammonia-exposed fabric was tested using 1,2-dichloroethane (DCE) as probe oil. Contact angle measurements showed that the fabric had an underwater superoleophobic property with a DCE contact angle of ca. 153° (Figure 2e). The DCE droplet had a quite low adhesion with the fabric and could slide off when the fabric was slightly tilted (sliding angle $< 10°$; Figure 2f).

In view of the above-demonstrated peculiar wettability toward water and oil, our coating is expected to be useful for oil–water separation. As a proof of concept, we separated an oil–water mixture using the coated fabric (Figure 4a). A mixture of hexadecane and water (1:1, v/v) was poured onto the fabric that was mounted between two glass tubes. Because of the superamphiphobicity of the fabric, both hexadecane and water were retained. To trigger the separation, ammonia vapor was introduced into the lower tube through a syringe needle. Upon ammonia exposure, the fabric allows water penetration but retains hexadecane. To our knowledge, such an ammonia-triggered, on-demand separation of an oil–water mixture has not been reported before.

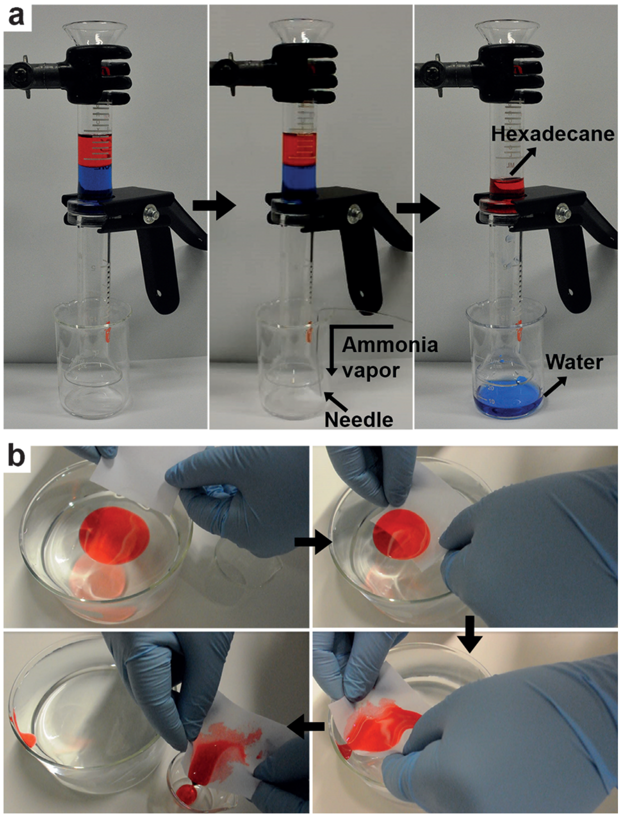

Figure 4. a) Oil–water separation by the functionalized polyester fabric (see also Movie S2). b) Snapshots showing the collection of hexadecane floating on the water surface using an ammonia-exposed, superhydrophilic, and superoleophobic polyester fabric.

In the case that triggered separation is not necessary, ammonia preexposure can be employed, and the superhydrophilic and superoleophobic fabric can be used directly. Unlike the widely reported superhydrophilic and underwater superoleophobic membranes,[16,28–35] which required to be prewetted before use, the ammonia preexposed fabric is superoleophobic both in air and under water so that the oil–water mixture can be poured onto a dry fabric and there is no need to prewet it. Furthermore, the superhydrophilic and superoleophobic fabric could provide an efficient way for oil spill cleanup (Figure 4b).

Our coating is also able to functionalize highly porous materials, e.g., polyurethane (PU) sponge (Figure 5a). As an absorbent, a dry, superhydrophilic, and superoleophobic sponge was used to separate water from bulk diesel (Figure 5b). Because of the superoleophobicity, an external force was needed to immerse the sponge into diesel and a concave (dimple) air–diesel interface was observed around the sponge. When the sponge touched the water in diesel, the water was

© 2015 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

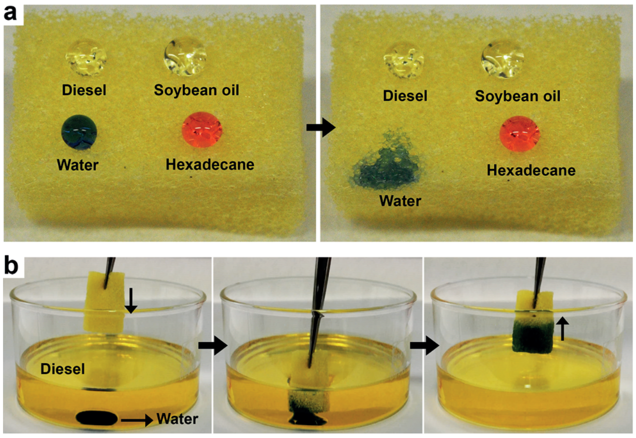

Figure 5. a) Photos of water and oil droplets placed on the functionalized PU sponge before (left panel) and after (right panel) ammonia exposure. b) Snapshots showing the absorption of water from bulk diesel by the ammonia-exposed, superhydrophilic, and superoleophobic sponge.

sucked up into the sponge. Herein, we should emphasize that previous reports on oil–water separation by affinity absorption were mainly based on the selective removal of oil using "oil-absorbing" materials.[16–25] The opposite case, i.e., selective removal of water, has been seldom reported. Our work here provides a good example, which possesses great potential for applications in purification of water-containing oils.

In summary, we introduced a superamphiphobic coating, which turns superhydrophilic and superoleophobic upon ammonia exposure, and the use of this coating for functionalizing commonly used materials, including textiles and sponges, to perform unusual oil–water separations. We expect that this novel coating will lead to the development of advanced oil–water separation techniques and also aid in the design of smart interfacial materials.

Keywords: hydrophobic effects · oil-water separation · porous materials · superoleophobicity · surface chemistry

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 4527–4530
Angew. Chem. **2015**, *127*, 4610–4613

[1] L. Feng, Z. Zhang, Z. Mai, Y. Ma, B. Liu, L. Jiang, D. Zhu, *Angew. Chem. Int. Ed.* **2004**, *43*, 2012; *Angew. Chem.* **2004**, *116*, 2046.
[2] C. Wang, T. Yao, J. Wu, C. Ma, Z. Fan, Z. Wang, Y. Cheng, Q. Lin, B. Yang, *ACS Appl. Mater. Interfaces* **2009**, *1*, 2613.
[3] X. Tang, Y. Si, J. Ge, B. Ding, L. Liu, G. Zheng, W. Luo, J. Yu, *Nanoscale* **2013**, *5*, 11657.
[4] Y. Cao, X. Zhang, L. Tao, K. Li, Z. Xue, L. Feng, Y. Wei, *ACS Appl. Mater. Interfaces* **2013**, *5*, 4438.
[5] M. Huang, Y. Si, X. Tang, Z. Zhu, B. Ding, L. Liu, G. Zheng, W. Luo, J. Yu, *J. Mater. Chem. A* **2013**, *1*, 14071.
[6] W. Zhang, Z. Shi, F. Zhang, X. Liu, J. Jin, L. Jiang, *Adv. Mater.* **2013**, *25*, 2071.
[7] J. A. Howarter, J. P. Youngblood, *Adv. Mater.* **2007**, *19*, 3838.
[8] P. S. Brown, O. D. L. A. Atkinson, J. P. S. Badyal, *ACS Appl. Mater. Interfaces* **2014**, *6*, 7504.
[9] S. Hutton, J. Crowther, J. Badyal, *Chem. Mater.* **2000**, *12*, 2282.
[10] R. Lampitt, J. Crowther, J. Badyal, *J. Phys. Chem. B* **2000**, *104*, 10329.
[11] H. Sawada, Y. Ikematsu, T. Kawase, Y. Hayakawa, *Langmuir* **1996**, *12*, 3529.
[12] L. Li, Y. Wang, C. Gallaschun, T. Risch, J. Sun, *J. Mater. Chem.* **2012**, *22*, 16719.
[13] A. K. Kota, G. Kwon, W. Choi, J. M. Mabry, A. Tuteja, *Nat. Commun.* **2012**, *3*, 1025.
[14] J. Yang, Z. Zhang, X. Xu, X. Zhu, X. Men, X. Zhou, *J. Mater. Chem.* **2012**, *22*, 2834.
[15] J. A. Howarter, J. P. Youngblood, *J. Colloid Interface Sci.* **2009**, *329*, 127.
[16] L. Zhang, Z. Zhang, P. Wang, *NPG Asia Mater.* **2012**, *4*, e8.
[17] X. Gui, J. Wei, K. Wang, A. Cao, H. Zhu, Y. Jia, Q. Shu, D. Wu, *Adv. Mater.* **2010**, *22*, 617.
[18] J. Yuan, X. Liu, O. Akbulut, J. Hu, S. L. Suib, J. Kong, F. Stellacci, *Nat. Nanotechnol.* **2008**, *3*, 332.
[19] M. Guix, J. Orozco, M. García, W. Gao, S. Sattayasamitsathit, A. Merkoçi, A. Escarpa, J. Wang, *ACS Nano* **2012**, *6*, 4445.
[20] Q. Zhu, Q. Pan, F. Liu, *J. Phys. Chem. C* **2011**, *115*, 17464.
[21] G. Hayase, K. Kanamori, M. Fukuchi, H. Kaji, K. Nakanishi, *Angew. Chem. Int. Ed.* **2013**, *52*, 1986; *Angew. Chem.* **2013**, *125*, 2040.
[22] W. Lei, D. Portehault, D. Liu, S. Qin, Y. Chen, *Nat. Commun.* **2013**, *4*, 1777.
[23] J. Zhang, S. Seeger, *Adv. Funct. Mater.* **2011**, *21*, 4699.
[24] P. Calcagnile, D. Fragouli, I. S. Bayer, G. C. Anyfantis, L. Martiradonna, P. D. Cozzoli, R. Cingolani, A. Athanassiou, *ACS Nano* **2012**, *6*, 5413.
[25] Z.-Y. Wu, C. Li, H.-W. Liang, Y.-N. Zhang, X. Wang, J.-F. Chen, S.-H. Yu, *Sci. Rep.* **2014**, *4*, 4079.
[26] C. Ruan, K. Ai, X. Li, L. Lu, *Angew. Chem. Int. Ed.* **2014**, *53*, 5556—5560; *Angew. Chem.* **2014**, *126*, 5662—5666.
[27] Z.-Y. Wu, C. Li, H.-W. Liang, J.-F. Chen, S.-H. Yu, *Angew. Chem. Int. Ed.* **2013**, *52*, 2925; *Angew. Chem.* **2013**, *125*, 2997.
[28] L. Zhang, Y. Zhong, D. Cha, P. Wang, *Sci. Rep.* **2013**, *3*, 2326.
[29] P.-C. Chen, Z.-K. Xu, *Sci. Rep.* **2013**, *3*, 2776.
[30] F. Zhang, W. B. Zhang, Z. Shi, D. Wang, J. Jin, L. Jiang, *Adv. Mater.* **2013**, *25*, 4192.
[31] Z. Xue, S. Wang, L. Lin, L. Chen, M. Liu, L. Feng, L. Jiang, *Adv. Mater.* **2011**, *23*, 4270.
[32] X. Gao, L. P. Xu, Z. Xue, L. Feng, J. Peng, Y. Wen, S. Wang, X. Zhang, *Adv. Mater.* **2014**, *26*, 1771.
[33] J. Zeng, Z. Guo, *Colloids Surf. A* **2014**, *444*, 283.
[34] W. Zhang, Y. Zhu, X. Liu, D. Wang, J. Li, L. Jiang, J. Jin, *Angew. Chem. Int. Ed.* **2014**, *53*, 856; *Angew. Chem.* **2014**, *126*, 875.
[35] Y. Zhu, F. Zhang, D. Wang, X. F. Pei, W. Zhang, J. Jin, *J. Mater. Chem. A* **2013**, *1*, 5758.
[36] Y. Tian, L. Jiang, *Nat. Mater.* **2013**, *12*, 291.
[37] S. Liu, G. Han, M. Shu, L. Han, S. Che, *J. Mater. Chem.* **2010**, *20*, 10001.

Received: November 20, 2014
Revised: January 6, 2015
Published online: February 18, 2015

© 2015 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim