Supporting Information

Amphiphilic, Ultralight, and Multifunctional Graphene/Nanofibrillated Cellulose Aerogel Achieved by Cation-Induced Gelation and Chemical Reduction

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Experimental section

Materials

The cellulose material (Celish MFC KY100-S) was purchased from Daicel Chemical Industries, Ltd., Japan. Graphite powder was obtained from Qingdao Black Dragon graphite Co., Ltd., China. TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy, free radical) was purchased from sigma Aldrich and used as received. Sodium hypochlorite (NaClO) solution (reagent grade, available chlorine 8%), potassium permanganate ($KMnO_4$), sulfuric acid (H_2SO_4 98%), hydrogen peroxide (H_2O_2), sodium nitrate ($NaNO_3$), sodium hydroxide (NaOH) and aluminum nitrate nonahydrate ($Al(NO_3)_3.9H_2O$) were purchased from Kermel Chemical reagent plant (Tianjin, China) and used as received.

Preparation of nanofibrillated cellulose (NFC) dispersion

Microfibrillated cellulose was used as raw material and treated with TEMPO-oxidized system.[1] The microfibrillated cellulose was first dispersed in deionized water in which sodium bromide (NaBr) and TEMPO were dissolved (1 and 0.1 mmol per gram of MFC, respectively). The concentration of the MFC in deionized water was 2 wt%. The reaction was started by adding the desired amount of the sodium hypochlorite (5 mmol per gram of MFC) dropwise into the dispersion. The pH was maintained at 10.5 by adding 0.5 M NaOH using a pH stat until no NaOH consumption was observed. The TEMPO-oxidized cellulose was filtered and then dispersed in water at a concentration of 1 wt% followed by adjusting to PH 2-3 with 0.1 M HCl and kept starring at 500 rpm for 1 h. Finally, the resulting cellulose was filtered and washed several times until the filtrated solution was neutral. The nanofibrillated cellulose dispersion was stored at 4 °C before use.

Synthesis of graphene oxide (GO)

GO was prepared by Hummers' method. Briefly, graphite (2 g) was mixed with $NaNO_3$ (1 g) and H_2SO_4 (50 ml) at 0 °C, then $KMnO_4$ (6 g) was slowly added over 1 h. The mixture was kept at 0 °C for 2 h. After removal of the ice-bath, the mixture was stirred at 35 °C for 30 min. Distilled water was (100 ml) was then slowly added to the reaction, keeping the temperature at 98 °C for 3 h. Finally, the mixture was further treated with 5% H_2O_2 (50 ml) at room temperature to reduce the residual permanganate and manganese dioxide until the slurry turned golden yellow. Wet graphene oxide was obtained after centrifugation and washing with deionized water repeatedly to remove residual salts and acids. Then graphene oxide was added to a given amount of deionized water, and the mixture was treated with ultrasonication for 1 h before further use.

Hydrogelation

Hydrogels of NFC, graphene oxide (GO), and graphene oxide/NFC (GO/NFC) were prepared by addition of metal salt solution to the top of the aqueous dispersion without stirring. Specifically, the prepared NFC (9.75 mg g^{-1}) and GO (6.65 mg g^{-1}) solution in a glass container were degased via 15 min ultrasonication, then 50 mM aqueous solution of aluminum nitrate nonahydrate was added dropwise along the wall of the container into the solution without stirring. For preparation of GO/NFC hydrogels, a variety of graphene oxide dispersions were added to a quantitative amount of nanofibrillated cellulose aqueous solution under continuous magnetic stirring to yield a homogeneous dispersion, degased via 15 min ultrasonication, then metal salt solution was added as did above. Gelation occurred promptly upon the addition of aluminum nitrate nonahydrate solution. After standing for overnight, the metal salt solution on the top was decanted and the resulting hydrogels were soaked and rinsed with deionized water several times to remove unbounded ions. By changing the loading of NFC from 50, 30 and 10 wt%, the final hydrogels was coded as NFC/GO-50, GO/NFC-30 and GO/NFC-10, respectively.

Nanocomposite aerogels of NFC, reduced graphene oxide (rGO) and reduced graphene oxide/NFC (rGO/NFC)

The as-prepared hydrogels of NFC, GO and GO/NFC were frozen in liquid nitrogen and then freeze-dried for 2 days to yield aerogels. Then, GO and GO/NFC aerogels were chemically reduced by immersing into hydroiodic acids (HI) solution at 100 °C for 10 min. The reduced aerogels were soaked and rinsed with ethanol several times to remove the residual HI solution and the iodine participating in the reducing reaction followed by transferring to deionized water. They were then freeze-dried as the approach mentioned above. Finally, the resulting aerogels were coded as rGO/NFC-50, rGO/NFC-30, rGO/NFC-10 and rGO, respectively.

Characterization

Scanning electron microscopy (SEM) images were taken by using a SEM (JEOL JSM-5900LV) at an accelerating voltage of 5 kV. Fourier transform infrared spectroscopy (FT-IR) spectra were recorded using a Thermo Nicolet 3700 spectrometer (U.S.A.). X-ray photoelectron spectroscopy was performed by Axis Ultra DLD (KRATOS Co., UK). X-Ray diffraction was carried out on a Philips X'Pert pro MPD X-ray diffractometer (Holland) with a Cu Kα radiation (λ = 1.5406

Å). Rheological tests were carried out with a rheometer TA AR2000ex operating in 40 mm parallel-plate configuration and 1 mm gap distance. Thermogravimetric analysis (TGA) was carried out with a TGA Q500 analyzer from room temperature to 800 °C at a scanning g rate of 5 °C min^{-1} under the protection of N_2. The compressive tests of the aerogels of NFC, rGO/NFC and rGO were performed by using the parallel plate compression clamps of TA Instruments Q800 DMA-analyzer. The strain ramp rate was maintained at 20 % per min for all the tests. The wetting properties of different samples were evaluated through contact angle tests, which were performed by OCA20 contact angle goniometer equipped with video capture (Dataphysics, Germany).

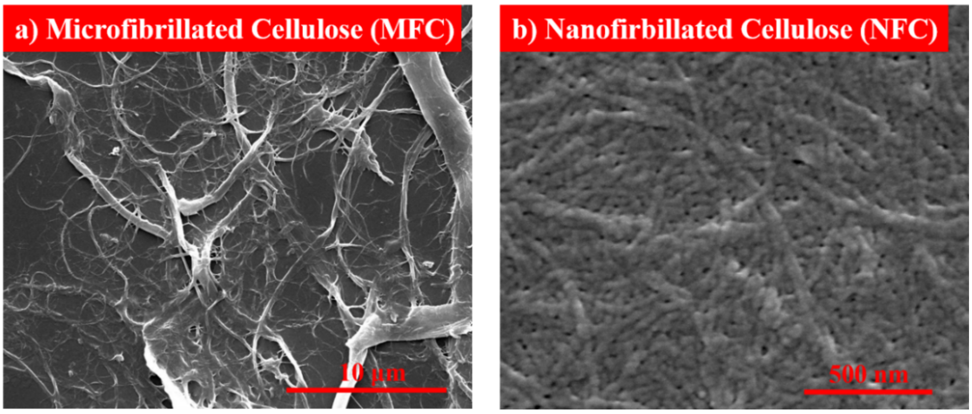

Figure S1. SEM images of original microfibrillated cellulose (a) and after TEMPO-oxidation (b).

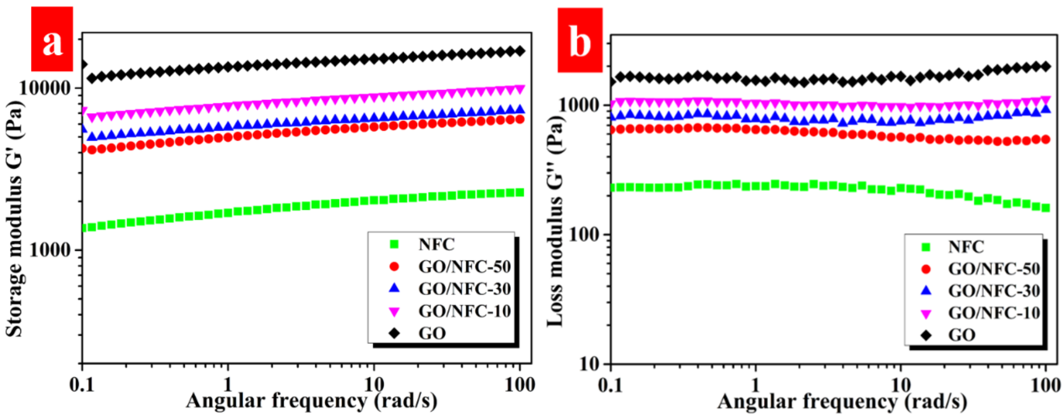

Figure S2. Dynamic properties of the GO/NFC hydrogels: dynamic frequency sweep (25ºC) of the gels at a strain rate of 0.5%. a) storage modulus plots, b) loss modulus plots.

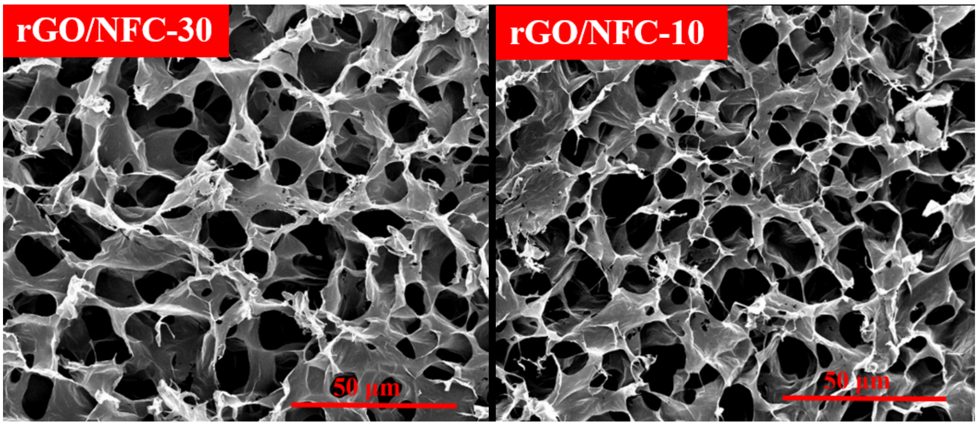

Figure S3. SEM images of rGO/NFC-30 and rGO/NFC-10 aerogels after hydroiodic acids reduction and freeze-drying.

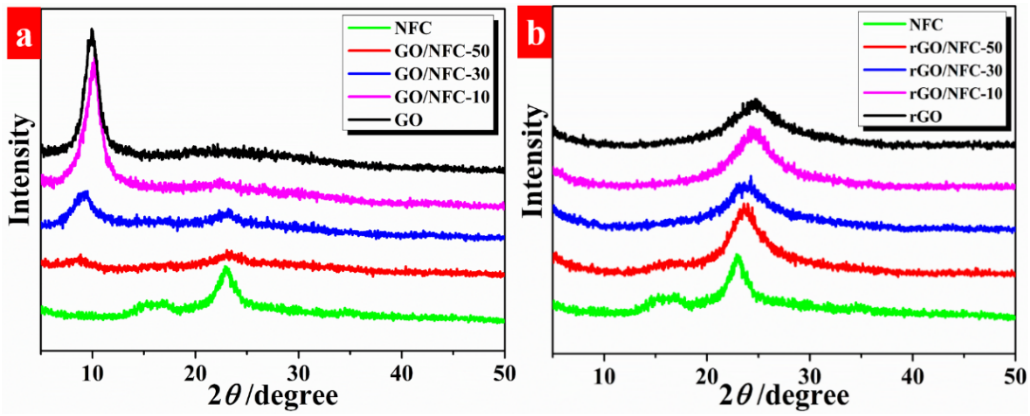

Figure S4. XRD pattern of (a) NFC, GO and GO/NFC, (b) NFC, rGO and rGO/NFC.

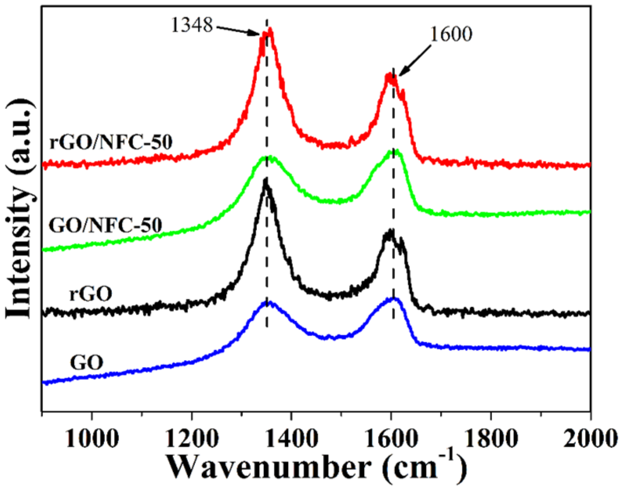

Figure S5. Raman spectra of GO, rGO, GO/NFC-50 and rGO/NFC-50 aerogels.

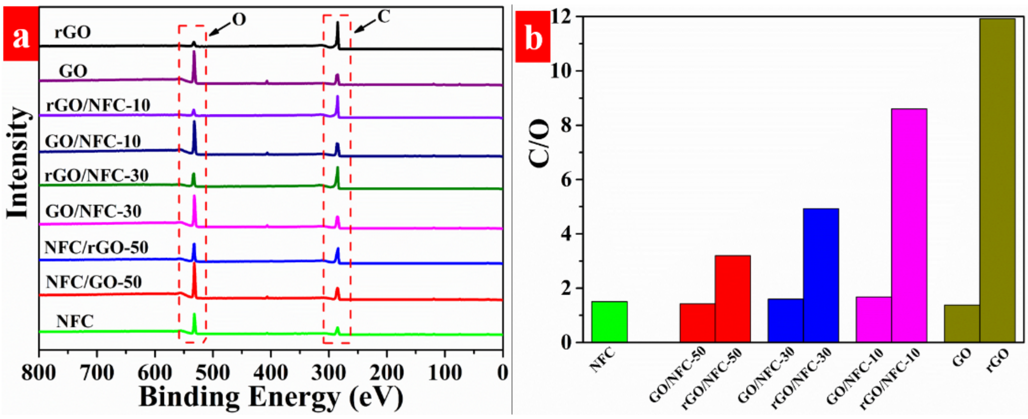

Figure S6. XPS spectra (a) and variation of the C/O atomic ratio (b) of the neat NFC aerogel and hybrid aerogels of before and after reduction by hydroiodic acids.

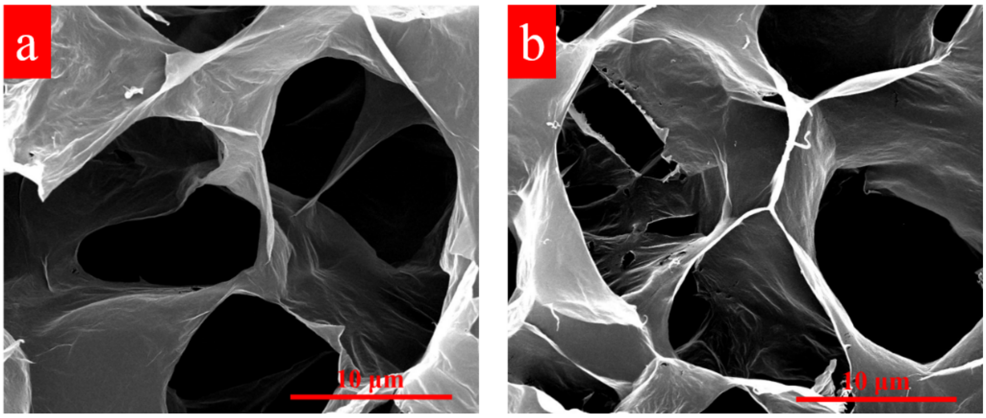

Figure S7. SEM images of the rGO/NFC-50 aerogel before (a) and after fatigue cyclic compression test (50 cycles, b), indicating that there are no obvious structural changes.

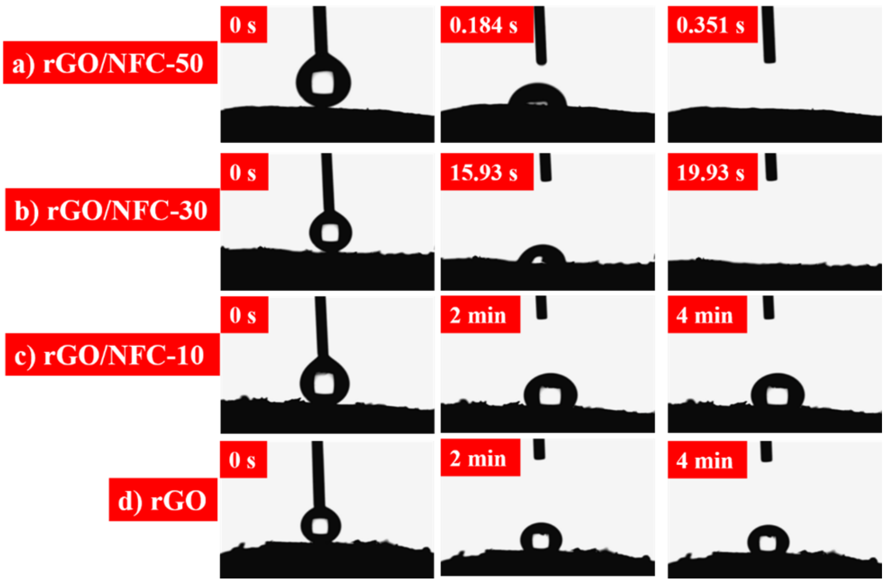

Figure S8. Photographs of a water droplet absorbed by (a) rGO/NFC-50 and (b) rGO/NFC-30 aerogel. Photographs of a water droplet supported on (c) rGO/NFC-10 and (d) rGO aerogel.

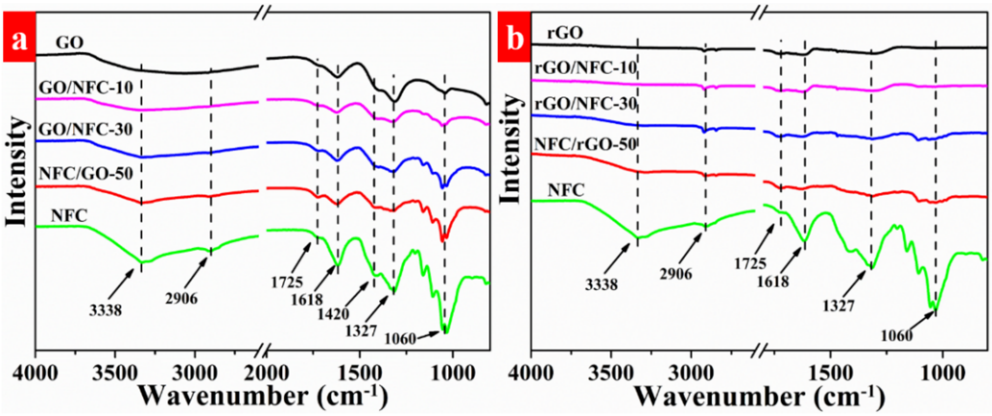

Figure S9. FT-IR spectra of the original NFC aerogel and GO, rGO, hybrid aerogels of before (a) and after (b) reduction by hydroiodic acids.

Table S1. Comparison of various absorbent materials.

Absorbent materials	Absorbed substances	Absorption capacities (times)	Surface wettability	Density (mg cm^{-3})	Ref.
Melamine-formaldehyde sponge	Oils and organic solvents	79-195	superhydrophobic	n.a.	[2]
Polydimethylsiloxane (PDMS) Sponge	Oils and organic solvents	4-11	hydrophobic	180-750	[3]
3D macroporous Fe/C	Lubricating oil, bean oil, crude oil, dodecane, and decane	4-10	superhydrophobic	n.a.	[4]
Graphene/α-FeOOH aerogel	Cyclohexane, toluene, gasoline, paraffin oil, phenoxin, and vegetable oil	12-27	superhydrophobic	n.a.	[5]
Nanocellulose aerogel	Hexane, petroleum benzene, octane, dodecane, hexadecane, octanol, paraffin oil, toluene, mineral oil, and chloroform	20-40	hydrophobic	20-30	[6]
Spongy graphene	Oils and organic solvents	20-86	hydrophobic	12±5	[7]
Hybrid gaphene/CNT foams	Compressor oil, sesame oil, chloroform,	80-130	superhydrophobic	n.a.	[8]

	dichloroform, toluene, and DMF				
Carbon nanotube sponges	Oils and organic solvents	80-180	Hydrophobic	5-10	[9]
Carbonaceous nanofiber aerogel	Gasoline, cyclohexane, ethanol, siesel oil, vegetable oil, chloroform, and phenoxin.	40-115	superhydrophobic	3.3-22	[10]
Carbon fiber aerogel	Oils and organic solvents	50-192	hydrophobic	n.a.	[11]
Ultra-flyweight aerogels (UFAs)	Oils and organic solvents	215-913	hydrophobic	1.4	[12]
Nitrogen-doped graphene foam	Oils and organic solvents	200-600	hydrophobic	2.1±0.3	[13]
Reduced graphene oxide foam	Motor oil, cyclohexane, chlorobenzene, petroleum, and toluene	5-40	hydrophobic	30	[14]
Graphene/NFC aerogel	Water, Oils and organic solvents	44-265	amphiphilic	6-8	present work

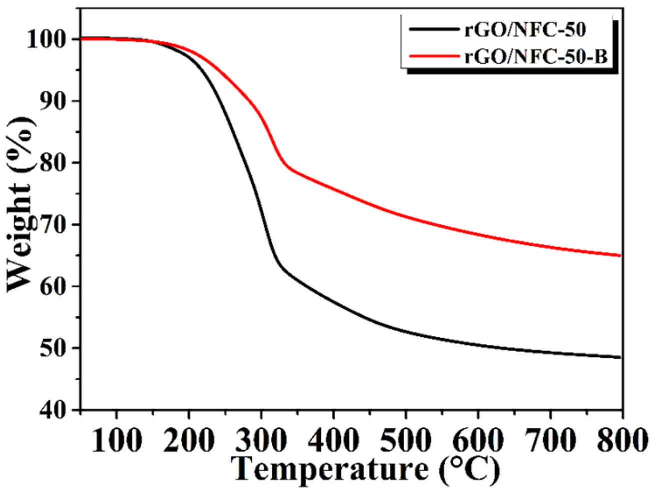

Figure S10. Thermo gravimetric analysis of rGO/NFC-50 aerogel in nitrogen before (rGO/NFC-50, black curve) and after (rGO/NFC-50-B, red curve) being recycled for five times sorption-combustion process.

References

1. T. Saito, S. Kimura, Y. Nishiyama, A. Isogai, *Biomacromolecules* 2007, **8**, 2485-2491
2. C. Ruan, K. Ai, X. Li, L. Lu, *Angew. Chem. Int. Ed.,* 2014, **53**, 5556-5560.
3. S. J. Choi, T. H. Kwon, H. Im, D. I. Moon, D. J. Baek, M. L. Seol, J. P. Duarte, Y. K. Choi, *ACS Appl. Mater. Interfaces,* 2011, **3**, 4552-4556.
4. Y. Chu, Q. Pan, *ACS Appl. Mater. Interfaces,* 2012, **4**, 2420-2425.
5. H. P Cong, X. C. Ren, P. Wang, S. H Yu, *ACS NANO,* 2012, **6**, 2693–2703.
6. J. T. Korhonen, M. Kettunen, R. H. Ras, O. Ikkala, *ACS Appl. Mater. Interfaces,* 2011, **3**, 1813-1816.
7. H. Bi, X. Xie, K. Yin, Y. Zhou, S. Wan, L. He, F. Xu, F. Banhart, L. Sun, R. S. Ruoff, *Adv. Funct. Mater.,* 2012, **22**, 4421-4425.
8. X. Dong, J. Chen, Y. Ma, J. Wang, M. B. Chan-Park, X. Liu, L. Wang, W. Huang, P. Chen, *Chem. Commun.,* 2012, **48**, 10660–10662.
9. X. Gui, J. Wei, K. Wang, A. Cao, H. Zhu, Y. Jia, Q. Shu, D. Wu, *Adv. Mater.,* 2010, **22,** 617-621.
10. H. W. Liang, Q. F. Guan, L. F. Chen, Z. Zhu, W. J. Zhang, S. H. Yu, *Angew. Chem. Int. Ed.,* 2012, **7**, 5101-5105.
11. H. Bi, Z. Yin, X. Cao, X. Xie, C. Tan, X. Huang, B. Chen, F. Chen, Q. Yang, X. Bu, X. Lu, L. Sun, H. Zhang, *Adv. Mater.,* 2013, **25**, 5916-5921.
12. H. Sun, Z. Xu, C. Gao, *Adv. Mater.,* 2013, **25**, 2554-2560.
13. Y. Zhao, C. Hu, Y. Hu, H. Cheng, G. Shi, L. Qu, *Angew. Chem.,* 2012, **124**, 11533 –11537.
14. Z. Niu, J. Chen, H. H. Hng, J. Ma, X. Chen, *Adv. Mater.,* 2012, **24**, 4144-4150.