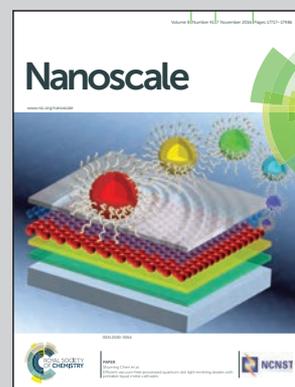


Showcasing research from the Institute of Nanoscience and Nanotechnology, School of Physical Science and Technology, Lanzhou University, Lanzhou, China.

A new kind of transparent and self-cleaning film for solar cells

A highly optically transparent and flexible self-cleaning superhydrophobic film (SSF) is developed. This SSF exhibits a very rough surface morphology with hierarchical structure, which makes it have a contact angle of 154.6° and a sliding angle of smaller than 1° , and the SSF can also be self-cleaned in the wind. By covering a commercial solar cell with this SSF, with the assistance of environmental wind or rain, the solar cell could be greatly relieved of the degradation caused by dust covering.

As featured in:



See Yong Qin et al., *Nanoscale*, 2016, 8, 17747.



www.rsc.org/nanoscale

Registered charity number: 207890



Cite this: *Nanoscale*, 2016, **8**, 17747

Received 2nd May 2016,
 Accepted 12th July 2016

DOI: 10.1039/c6nr03537j

www.rsc.org/nanoscale

A new kind of transparent and self-cleaning film for solar cells†

Qi Xu,^a Qi Zhao,^a Xiaofei Zhu,^a Li Cheng,^a Suo Bai,^a Zenghua Wang,^a Leixing Meng^a and Yong Qin^{*a,b}

A kind of one step and *in situ* etching method is developed to fabricate a highly optically transparent and flexible self-cleaning superhydrophobic film (SSF). This SSF exhibits a very rough surface morphology with hierarchical structure, which makes it have a contact angle of 154.6° and a sliding angle of smaller than 1°. And the SSF can also be self-cleaned in the wind. The SSF hierarchical structure scatters the incident light, but it almost doesn't attenuate the light. So the SSF has antireflection properties and a high light transmittance of 94%. The excellent self-cleaning property, high light transmittance and antireflection property mean that the SSF greatly enhances the performance of solar cells in practical working conditions. The solar cell's efficiency maintains at 95.8% of its initial value after covering with the SSF, which is about 1.7 times higher than that of the solar cell covered with dust, as in practical conditions.

Introduction

Due to the increase of fossil fuels shortage and environmental pollution, searching for clean and renewable energy sources such as wind, tidal, geothermal, and solar energy, is more and more urgent. Compared with the others of the above mentioned energy types, solar energy is the most abundant. Solar energy reaches the surface of earth at a rate of 1.2×10^{17} W.¹ The IEA estimated that in 2013 the world energy consumption was 5.7×10^{20} joules. So if the solar energy reaching the earth can be fully collected, one day's energy from the sun can meet the whole world's energy consumption for more than twenty years. Moreover, unlike the regional distribution of wind, tide, and geothermal energies, solar energy is ubiquitous. Since the photovoltaic effect was first experimentally demonstrated in

1839, using solar cells to harvest solar energy has attracted tremendous attention.^{2–8} Nowadays, solar cells have been widely used in residential, commercial and utility-scale areas. Up to now, the solar cells' maximum efficiency has reached 46%.⁹ However, in practical applications, the solar cell's outdoor working environment is rather more dirty than the cleaning room, which will greatly decrease the conversion efficiency of solar cells because of reduced light transmittance. Just as increasing the ideal efficiency of solar cells in the cleaning room is important, maintaining their practical efficiency in practical working conditions is equally important because both of them determine the final efficiency of solar cells. In practical conditions, the gradual degradation of the transmittance caused by the accumulation of surrounding dust can largely decrease the solar cell's performance.^{10–14} A research conducted by Hamdy K. Elminir showed that the output of a solar cell installed at a tile angle of 45° decreases at a rate about 17.4% per month.¹⁵ So keeping a high efficiency in dusty environments is quite important. On rainy days, when the dust covered solar cell panel meets with rain, it will be partly cleaned, but the sludge formed will stick on the panel, and this sludge is even more difficult to clean. And because the areas with abundant sunlight usually are drier and short of rain, the solar cell is rarely cleaned by the rain. But there are abundant wind resources in these areas, so if the solar cell can be self-cleaning in rain and wind, it will contribute greatly to increasing the performance of the solar cell in all areas.

For self-cleaning in flowing water, superhydrophilic films and superhydrophobic films are very promising technical solutions. Superhydrophilic films realize the cleaning process by spreading over the surfaces a sheet of water to carry away the dirt. A practical hydrophilic glass fabricated by directly patterning a glass surface without any further surface chemical treatment has been reported.¹⁶ This film shows a high transmittance of 94–94.3%. Solar cells with this film show a relatively constant performance during the monitoring period. However, under aggressive fogging conditions, these surfaces may exhibit frost formation or excess and nonuniform water condensation, this will result in poor optical performance

^aInstitute of Nanoscience and Nanotechnology, School of Physical Science and Technology, Lanzhou University, Lanzhou, 730000, China.

E-mail: qinyong@lzu.edu.cn

^bThe Research Institute of Biomedical Nanotechnology, Lanzhou University, Lanzhou, 730000, China

†Electronic supplementary information (ESI) available. See DOI: 10.1039/c6nr03537j

of the coating. Compared with the superhydrophilic films, superhydrophobic films have the property to reduce the accumulation of snow and to even eliminate the formation of ice on solid surfaces,¹⁷ which can be ascribed to the hydrophobic film's small surface energy.¹⁸ Therefore, superhydrophobic films have a broader working environment in self-cleaning areas. Over the past decades, there has been a burst in research on self-cleaning superhydrophobic surfaces due to their potential applications in anti-dust, water repellent, anti-corrosion, antifog, microfluidic devices.¹⁹ Compared with a large contact angle, a small sliding angle is more important for self-cleaning films' practical applications.²⁰ Inspired by nature such as lotus leaves, butterfly wings, and water strider legs, films with hierarchical structure can greatly reduce the sliding angle.^{21–23} When a droplet rolls off from the films, it will carry away the dust covered on the films. As for solar cells, in order to maintain their output power, the films should possess high optical transparency. Moreover, considering the solar cells' complicated working situations, the film should also possess mechanical flexibility to realize a conformal covering. Although, there are a lot of reports focusing on either flexibility^{24,25} or transparency.^{26–28} Reports addressing both the transparency and flexibility have been rarely reported. Recently, a mechanically flexible, optically transparent self-cleaning surface fabricated *via* UV imprinting and subsequent etching of the transferred porous alumina membrane has been reported.²⁹ The fabricated film has an optical transparency higher than 82% at 550 nm, contact angle hysteresis smaller than 3.5°, and a static contact angle bigger than 170°. However, the low light transmittance and complicated process limited its applications in solar cells. Developing a kind of flexible film with high light transmittance, antireflection properties and excellent self-cleaning properties under not only water flushing but also wind blowing is greatly desirable for enhancing the performance of solar cell in practical working conditions.

In this paper, we developed a SSF with high light transmittance through a one-step reactive ion etching (RIE) method. The fabricated SSF exhibits high self-cleaning properties and light transmittance. The SSF has a contact angle of 154.6°, a sliding angle smaller than 1°, and a light transmittance of 94%. The dust on the SSF can be easily washed out by water, and more importantly, it can also be moved out by a gentle wind. By covering a commercial solar cell with this SSF, the solar cell could be greatly relieved of the degradation caused by dust covering, its efficiency stays at 95.8% of its initial after a self-cleaning process in a dusty environment.

Results and discussion

The solar cell's practical outdoor working environment is very different from the cleaning room which is commonly used as the standard testing environment of solar cells in the literature. Compared with the cleaning room, there is lots of floating dust in the outdoor working environment due to vehicular exhausts, civil construction activities and so on.

The clean solar cell panel is easy to get dirty as shown from the contrast between Fig. 1a and b. When the light is projected on the solar panel, the areas covered by dust as shown in Fig. 1b will either scatter or absorb the light. For these areas in which the light can't penetrate into the solar cell, they can be considered as ineffective areas of solar cell panels. As the dust gradually accumulates on the solar panel, the effective areas are reduced, and the output of the solar cell decreases accordingly. Developing an effective way to clean the surface of the solar cell panels is urgently needed.

A SSF was fabricated *via* RIE on PDMS film which was previously spin coated and cured on a glass slide, without pre-defined masks. After etching for 1 minute *via* Ar, O₂, and CF₄, the surface of PDMS is still flat without any changes (Fig. S1(a)†). After etching for 5 minutes, the surface of PDMS generates corrugated fluctuations (Fig. S1(b)†). After etching for 10 minutes, the surface generates tiny protrusions (Fig. S1(c)†). After etching for 12 minutes, the protrusions increase (Fig. S1(d)†). In the joints of these protrusions, its height increases remarkably. After etching for another 4 minutes, the joints of the protrusions dominate, and its remaining parts diminish gradually (Fig. S1(e)†). After etching for 20 minutes, only the joints of protrusions are noticeable (Fig. S1(f)†). These joints of protrusions gradually form coned shape structures as the etching process continues. After etching for 1 h, the etching atmosphere is changed and the second step of the etching process begins. In this step, the etching process is dominated by physical etching, the cone shaped structures increase in height rapidly. Finally, the cone shaped structures lean against each other and form humps in the surface. Thus, a SSF was obtained. Typical scanning electron microscopy (SEM) images of the etched surface after the RIE process are shown in Fig. 2(a). The surface of the SSF is extremely rough and full of humps which are distributed non-regularly but evenly. These humps' non-regular but even distribution can guarantee the self-cleaning film's isotropic wetting properties. The enlarged SEM image shows that these humps are around 3–5 μm in height, 2 μm in width, and 1 μm in adjacent spacing. The cone shaped structures which compose the humps could be seen clearly. The diameter of these tips is around 100 nm. These cone shaped structures and humps constitute the SSF's hierarchical structure. These hierarchical structures can not only enlarge the SSF's roughness but also reduce the water drop's contact area with the SSF, which will lead to a large contact angle and small sliding angle.

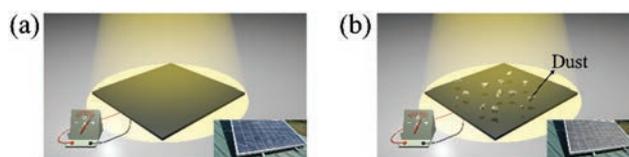


Fig. 1 Schematic of dust on the performance of solar cells. (a) The clean solar cell panel. The inset is a picture of an outdoor solar cell panel. (b) The dirty solar cell panel. The inset is a picture of an outdoor solar cell panel.

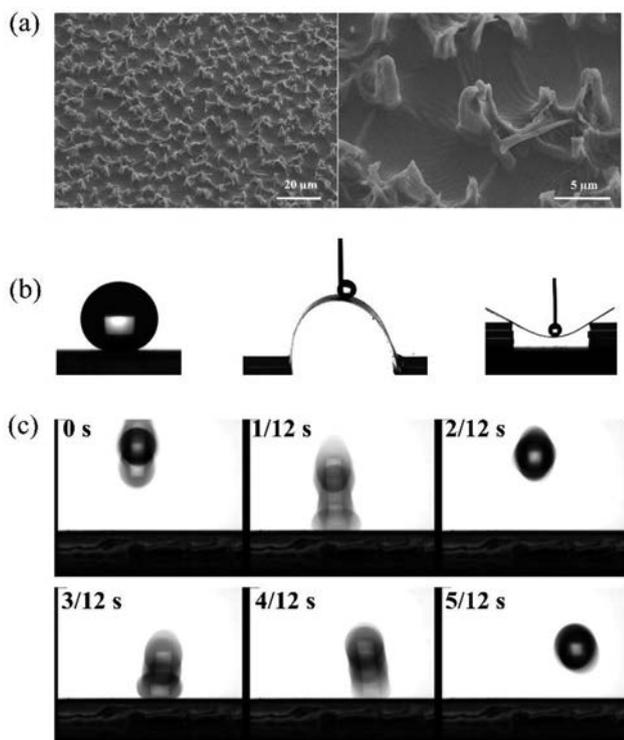


Fig. 2 The structure and performance characterization of the self-cleaning superhydrophobic film. (a) SEM images of the reactive ion etched surface. (b) The water droplet's contact status on flat and curved coatings. (c) The sequential digital images of a water droplet during the impingement test.

To characterize the SSF's superhydrophobic property, a water droplet with a volume of $5 \mu\text{L}$ was deposited on the SSF. From the optical microscope image shown in the left part of Fig. 2(b), the water contact angle on a flat SSF is measured to be 154.6° . Tilting the specimen stage to make it have a 1° angle with the horizontal plane, the droplet begins to move, so the sliding angle is smaller than 1° . In the practical working environment, the object to be covered is not always flat. Considering the PDMS's intrinsic flexibility, it is expected that the SSF would possess good hydrophobic properties even in a curved state. To test this, the SSF is bent upward, and a water droplet of $5 \mu\text{L}$ was in contact with the SSF, from the optical microscopic image (Fig. 2(b), middle), the sphere like droplet indicates the SSF still possesses good superhydrophobic character. On bending the film downward, and repeating the above test, the same result is obtained (Fig. 2(b), right). On lifting up the needle tip and letting the droplet drip on the SSF, the droplet moves back and forth on the concave SSF. The above results show that when the SSF is bent, it still possesses good superhydrophobic performance. In the practical application, the SSF need to have self-cleaning properties under rain, water rinsing and so on. In the above applications, there is a collision between the water and SSF. To mimic this, the SSF's water repellency was further characterized by the impingement test. The bounce process of a $5 \mu\text{L}$ water droplet was recorded

by a camera mounted on DSA100 equipment. Fig. 2(c) extracted from the recorded video shows the water's motion in 0.5 s. In the impact process, the droplet doesn't fragment into small pieces, and there are no anchoring places where there is residual water.

Next, the SSF's ability for self-cleaning is demonstrated. The SSF was placed on a desk with one side placed on a glass slide to provide a tilt angle. When a water droplet was deposited on the SSF, the water droplet will roll off the SSF and carry out the encountered dust in this process (Fig. 3(a), Movie S1†). The initial transparent water gradually becomes turbid due to the adhesion of dust. Repeating this process several times, the SSF will finally be cleaned. On the other hand, due to the low surface free energy and hierarchical surface structure of the SSF, the adhesion force between the dust and the SSF is small. So we speculate that maybe the SSF can also complete a self-cleaning process under the blowing of gentle wind. In order to confirm this, a pile of dust was shaken off on the SSF (Fig. 3b, middle). A gentle wind with a speed about 8.1 m s^{-1} generated by periodically squeezing a 5 mL plastic dropper was used to blow the SSF. After a few cycles, the dust on the SSF can be taken away completely (Movie S2†).

For the practical application on solar cells, the SSF must possess good light transmittance to maintain the solar cell's conversion efficiency. The SSF's light transmittance was tested using an ultraviolet-visible spectrophotometer. Fig. 4(a) shows that when the wavelength changes from 300 nm to 800 nm, the SSF's transmittance increases from 88% to 94%. After this, the SSF's optical transparency was tested by placing it on top of a A4 paper printed with logos of Lanzhou University. Through the sample, the details of the pattern in the paper can be seen clearly, there is no big difference in the logos' clarity between the covered pattern and uncovered pattern. And the ball like water droplet reconfirms the SSF's good superhydrophobic character.

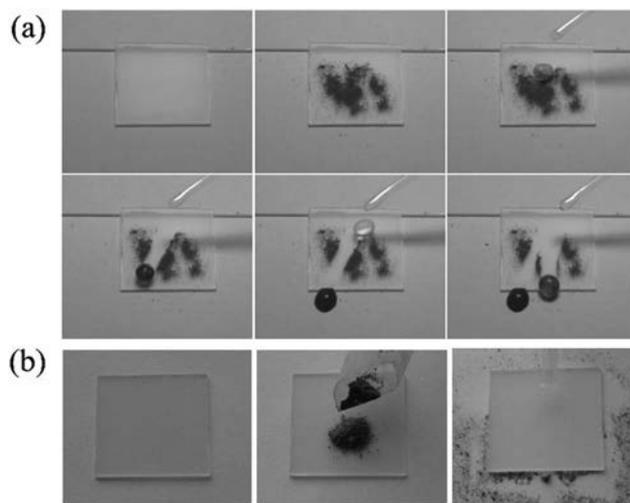


Fig. 3 (a) Self-cleaning process *via* water droplet. (b) Self-cleaning process *via* wind.

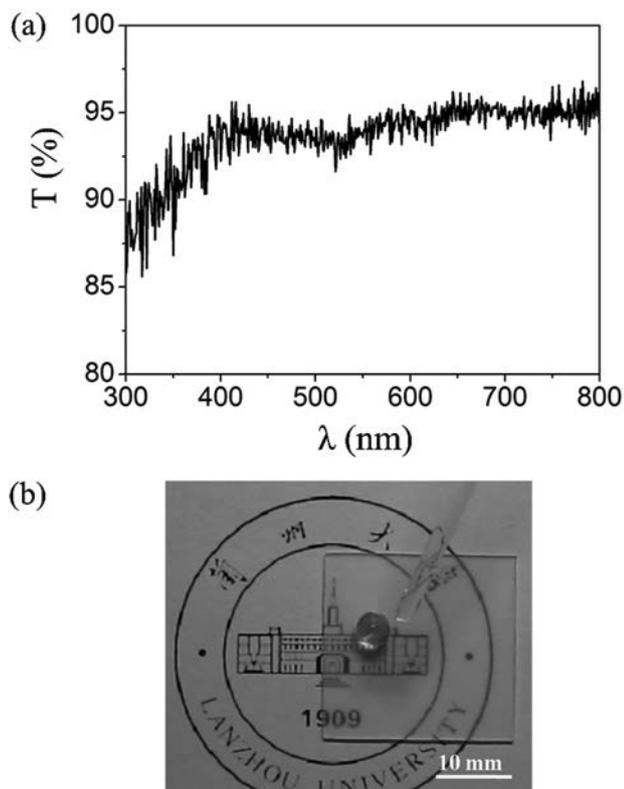


Fig. 4 (a) Light transmittance of the coating. (b) Photograph of the coating; the sphere like transparent matter is a water droplet.

After demonstrating the SSF's self-cleaning and optically transparent properties, the SSF is applied on a commercial solar cell to test its ability to maintain the solar cell's practical efficiency. During the test, the illumination intensity is kept at 100 mW cm^{-2} . The light is irradiated perpendicular to the solar cell. The tested J - V curves are shown in Fig. 5. The short circuit current density, open circuit voltage, fill factor, and efficiency are 31.6 mA cm^{-2} , 0.54 V , 0.70 , and 11.9% ,

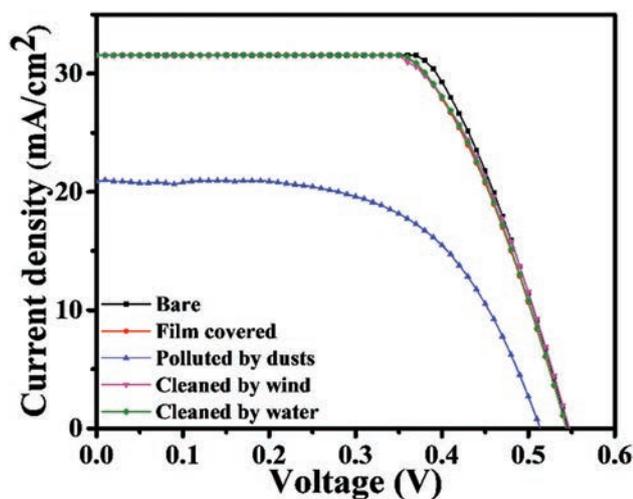


Fig. 5 The J - V curves for each testing step.

Table 1 The characteristic quantities of the solar cell in each testing step

	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	η (%)	η/η_{bare} (%)
Bare	31.6	0.54	0.70	11.9	1.00
Film covered	31.6	0.54	0.67	11.4	95.8
Polluted by dust	20.9	0.51	0.60	6.9	53.8
Cleaned by wind	31.6	0.54	0.66	11.3	95.0
Cleaned by water	31.6	0.54	0.67	11.4	95.8

respectively (Table 1). After covering the solar cell with a SSF, the current density and open circuit voltage haven't changed. The fill factor decreased slightly. On shaking dust onto the SSF, the solar cell's performance degrades severely, and compared with the short current density of the cleaned SSF, the short circuit current density changes from 31.6 to 20.9 mA cm^{-2} , which is a decrease of 30.7% . The other factors such as open circuit voltage and fill factor decrease slightly at the same time. The solar cell's efficiency changes from 11.4% to 6.9% , which is a decrease of 39.5% . Finally, the covering dust was washed out *via* a self-cleaning process by water or by wind. The efficiency recovers up to 99% when the cell was blown by a gentle wind generated by periodically squeezing a 5 mL plastic dropper, or 100% when the cell was washed by water.

Conclusions

In summary, a highly optically transparent and flexible SSF with good self-cleaning properties under water rinsing or wind blowing was developed. Due to the large surface roughness and unique composition of the structure of humps, the SSF shows excellent non-wetting abilities. The water droplet on it can roll off easily even when it is tilted with a tiny angle of 1° . In addition, the dust on the SSF can also be taken away by gentle wind, this means that it can also realize a self-cleaning process practicable in windy areas where the rain is rare. Due to the inherent flexibility of PDMS, the SSF's self-cleaning property is well maintained even in the curved shape. On characterization by a light transmittance test, the SSF shows a relatively high light transmittance of about 94% in the visible light range. Finally, on covering the SSF on a solar cell, the solar cell's efficiency recovers up to 95.8% of the bare solar cell's efficiency. The solar cell could maintain its efficiency when the dust on the SSF is cleaned by water or gentle wind.

Experimental section

Preparation of SSF

The glass substrate was ultrasonically cleaned *via* acetone, ethanol, and deionized water for 15 minutes, respectively, to remove the organic and inorganic surface impurities. After that, clean air was used to blow the glass substrate dry. Curing agent was added to the polydimethylsiloxane (PDMS) with a mass ratio of $1:10$ and this was placed on a laboratory table for a period of time to remove the bubbles in it. The PDMS

was spin coated onto the substrate at a rotation speed of 500 rpm for 60 s. Then the substrate was placed onto a horizontal surface for 24 h. Next, it was placed in an oven to solidify for 2 h. The sample was put into a chamber for reactive ion etching, and the chamber was evacuated to a vacuum of 4×10^{-3} Pa. The flux of Ar and O₂ and CF₄ was adjusted to 15 sccm, 10 sccm, and 30 sccm, respectively. The chamber's pressure was tuned to make it stabilize at 5.0 Pa, and the radio frequency power set to 250 W. The PDMS was etched for 60 min then the CF₄ closed. The flux of Ar and O₂ was kept unchanged, then the chamber's pressure tuned to 2.0 Pa and the radio frequency power kept at 250 W. Etching was undertaken for another 20 min. The sample was taken out and immersed into hydrochloric acid for 5 h to remove the metal which inevitably comes from the inner wall of the RIE machine chamber during the etching process. Finally it was washed with deionized water and the SSF was peeled off from the substrate.

Characterization of the wetting properties and impingement test

The contact angle and sliding angle are measured using DSA100 from Krüss, Hamburg, Germany. Pictures of the self-cleaning behavior are taken with a camera. The impingement process was recorded by the camera mounted on DSA100.

Demonstration of the self-cleaning process

The SSF with a 2.5 cm × 2.5 cm sized glass slide as a substrate was placed on a horizontal table. One side of the substrate was placed on the edge of another glass slide to supply a small tilt angle. Dust was sprayed on the SSF and water droplets were dripped through a 5 mL plastic dropper.

Testing the solar cell

All of the *J-V* curves were tested using a solar simulator (Newport Corporation, 94023A) under 1 Sun illumination. During the test, the light intensity is set to be 100 mW cm⁻².

Acknowledgements

We sincerely appreciate the support from NSFC (no. 51322203, 51472111), the National Program for Support of Top-notch Young Professionals, the Fundamental Research Funds for the Central Universities (no. lzujbky-2014-m02, lzujbky-2015-118, lzujbky-2015-208), PCSIRT (no. IRT1251).

Notes and references

- O. Morton, *Nature*, 2006, **443**, 19–22.
- W. L. Ma, C. Y. Yang, X. Gong, K. Lee and A. J. Heeger, *Adv. Funct. Mater.*, 2005, **15**, 1617–1622.
- M. C. Scharber, D. Wuhlbacher, M. Koppe, P. Denk, C. Waldauf, A. J. Heeger and C. L. Brabec, *Adv. Mater.*, 2006, **18**, 789–794.
- J. Y. Kim, K. Lee, N. E. Coates, D. Moses, T.-Q. Nguyen, M. Dante and A. J. Heeger, *Science*, 2007, **317**, 222–225.
- J. Burschka, N. Pellet, S.-J. Moon, R. Humphry-Baker, P. Gao, M. K. Nazeeruddin and M. Graetzel, *Nature*, 2013, **499**, 316–319.
- M. A. Green, A. Ho-Baillie and H. J. Snaith, *Nat. Photonics*, 2014, **8**, 506–514.
- H. Zhou, Q. Chen, G. Li, S. Luo, T.-b. Song, H.-S. Duan, Z. Hong, J. You, Y. Liu and Y. Yang, *Science*, 2014, **345**, 542–546.
- N. J. Jeon, J. H. Noh, W. S. Yang, Y. C. Kim, S. Ryu, J. Seo and S. I. Seok, *Nature*, 2015, **517**, 476–480.
- M. A. Green, K. Emery, Y. Hishikawa, W. Warta and E. D. Dunlop, *Prog. Photovoltaics*, 2015, **23**, 1–9.
- H. Khonkar, A. Alyahya, M. Aljuwaied, M. Halawani, A. Al Saferan, F. Al-Khaldi, F. Alhadlaq and B. A. Wacaser, *Sol. Energy*, 2014, **110**, 268–275.
- F. A. Mejia and J. Kleissl, *Sol. Energy*, 2013, **95**, 357–363.
- S. Mekhilef, R. Saidur and M. Kamalisarvestani, *Renewable Sustainable Energy Rev.*, 2012, **16**, 2920–2925.
- D. Goossens and E. Van Kerschaever, *Sol. Energy*, 1999, **66**, 277–289.
- M. S. Elshobokshy and F. M. Hussein, *Sol. Energy*, 1993, **51**, 505–511.
- H. K. Elminir, A. E. Ghitas, R. H. Hamid, F. El-Hussainy, M. M. Beheary and K. M. Abdel-Moneim, *Energy Convers. Manage.*, 2006, **47**, 3192–3203.
- J. Son, S. Kundu, L. K. Verma, M. Sakhuja, A. J. Danner, C. S. Bhatia and H. Yang, *Sol. Energy Mater. Sol. Cells*, 2012, **98**, 46–51.
- B. Na and R. L. Webb, *Int. J. Heat Mass Transfer*, 2003, **46**, 3797–3808.
- S. A. Kulinich and M. Farzaneh, *Langmuir*, 2009, **25**, 8854–8856.
- X. Zhang, F. Shi, J. Niu, Y. Jiang and Z. Wang, *J. Mater. Chem.*, 2008, **18**, 621–633.
- W. Chen, A. Y. Fadeev, M. C. Hsieh, D. Oner, J. Youngblood and T. J. McCarthy, *Langmuir*, 1999, **15**, 3395–3399.
- L. Feng, S. H. Li, Y. S. Li, H. J. Li, L. J. Zhang, J. Zhai, Y. L. Song, B. Q. Liu, L. Jiang and D. B. Zhu, *Adv. Mater.*, 2002, **14**, 1857–1860.
- Z. Guo, W. Liu and B.-L. Su, *J. Colloid Interface Sci.*, 2011, **353**, 335–355.
- Y. Y. Yan, N. Gao and W. Barthlott, *Adv. Colloid Interface Sci.*, 2011, **169**, 80–105.
- T. Dong, Y. Zhou, D. Hu, P. Xiao, Q. Wang, J. Wang, J. Pei and Y. Cao, *J. Colloid Interface Sci.*, 2015, **445**, 213–218.
- M. Xu, N. Lu, H. Xu, D. Qi, Y. Wang, S. Shi and L. Chi, *Soft Matter*, 2010, **6**, 1438–1443.
- T. Li, M. Paliy, X. Wang, B. Kobe, W.-M. Lau and J. Yang, *ACS Appl. Mater. Interfaces*, 2015, **7**, 10988–10992.
- X. Liu, Y. Xu, K. Ben, Z. Chen, Y. Wang and Z. Guan, *Appl. Surf. Sci.*, 2015, **339**, 94–101.
- H. Yoon, H. Kim, S. S. Latthe, M.-w. Kim, S. Al-Deyab and S. S. Yoon, *J. Mater. Chem. A*, 2015, **3**, 11403–11410.
- T.-H. Kim, S.-H. Ha, N.-S. Jang, J. Kim, J. H. Kim, J.-K. Park, D.-W. Lee, J. Lee, S.-H. Kim and J.-M. Kim, *ACS Appl. Mater. Interfaces*, 2015, **7**, 5289–5295.