Self-cleaning effect of highly water-repellent microshell structures for solar cell applications†

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A self-cleaning effect developed through the use of a superhydrophobic and water-repellent surface was demonstrated for solar cell applications. A perfectly ordered microshell array was fabricated on a transparent and flexible polydimethylsiloxane (PDMS) elastomer surface. This microshell PDMS showed an excellent water-repellent property with a contact angle (CA) higher than 150° and a hysteresis of lower than 20°, even without the aid of a low surface energy chemical coating. Fabricated superhydrophobic microshell PDMSs showed a superior dust cleaning effect compared to that of flat PDMS, preventing the degradation by dust particles of solar cell efficiency. This transparent, flexible, and superhydrophobic microshell PDMS surface provides feasibility for a practical application of superhydrophobic surfaces in solar cells.

Superhydrophobic surfaces such as the leaves of the lotus plant show high hydrophobicity and extremely low wettability.1 This special wettability of the surface has garnered much attention over the past decades for its use in promising applications including microfluidics, or fog-resistant and self-cleaning surfaces.2–9 Various studies have been conducted to realize superhydrophobic surfaces by forming microstructures10–12 or nanostructures13–15 based on the Cassie and Baxter16 and Wenzel17 models. As a result, researchers have been able to obtain a surface with extremely superhydrophobic properties and its CA is larger than 173°.18 Nevertheless, most studies regarding superhydrophobic surfaces have focused mostly on enhancing the non-wetting property itself. It is still a question of whether such a superhydrophobic surface can be practically applicable in areas such as self-cleaning surfaces on solar cells. Further studies are needed to verify the feasibility of superhydrophobic surfaces in real world application.

It is commonly claimed that the self-cleaning property of a superhydrophobic surface can be used in solar cell applications. Accumulation of airborne dust or particles on solar cell panels has been reported to cause the degradation of solar cell efficiency. Eliminir et al. showed that a solar cell installed at a 45° angle accrues a decrease in the output power of about 17.4% per month due to airborne dust.19 This situation is aggravated if the solar cell is installed at a lower tilting angle, a case which is favorable for higher efficiency in power generation. Although rainfall can partly remove the dust from the panel, it can adversely leave other debris on the panel when the panel dries. Considering that solar cell modules are often the power supply for remote or rarely visited areas such as unmanned lighthouses and observatories, efficiency degradation due to panel dust can be problematic. Particularly in locations where access is difficult, like desert sites, the accumulation of dust on the solar cell panel can be a serious concern because it eventually lowers the solar cell efficiency. Applying a transparent superhydrophobic surface to the solar cell panel has been expected to prevent the efficiency degradation caused by the accumulation of dust particles. However, while this concept is commonly mentioned,20 so far, there have been no reports showing exactly how beneficial the self-cleaning effect of a superhydrophobic surface is when applied to a solar cell panel.

The concept of self-cleaning on a superhydrophobic surface (as shown in Fig. S1†) was first demonstrated by Barthlott and Neinhuis, who studied water-repellent plants in nature.21 According to their work, when particles exist on a smooth (flat) surface, a water droplet merely redistributes the particles as it slides down, or, in the worst case, does not roll off from the surface, yielding no cleaning effect. In contrast, particles on a superhydrophobic surface are removed by a droplet rolling off from the surface. This is possible because a superhydrophobic surface has low CA hysteresis, whereas a flat surface has high CA hysteresis, which disables the droplet from rolling off. By adopting this cleaning principle, Bhushan et al. demonstrated a self-cleaning efficiency on various types of artificial superhydrophobic surfaces.22 Although their research was a thorough investigation of the cleaning efficiency for various surfaces, neither of the surfaces they studied were practically applicable for solar cell panels. On the other hand, Zhu et al. demonstrated the self-cleaning effect of nanodome solar cells by using nanoscale morphology.23 Although this work provided some insight into the idea of self-cleaning solar cells created by altering the structural morphology of the solar cells, the results are difficult to apply in practice on large-sized and commercialized solar cells. Moreover, the absence of comparison with the reference data (cleaning effect on a flat solar cell surface) may cause readers to question the necessity of self-cleaning surfaces on solar cells. Therefore, a highly transparent superhydrophobic surface with a simple fabrication process, a superior cleaning effect compared to that of conventional flat surface solar panels, and a practicability for use in commercialized solar cells are the things demanded for future applications.

Recently, we have proposed a novel cylindrical nanoshell structure that shows a water-repellent property superior to that of the conventional pillar-like structure even without the aid of a low surface energy chemical coating.24 In this work, inspired by the structural properties of nanoshell array, superhydrophobic cylindrical microshell structures have been patterned on a transparent and flexible polydimethylsiloxane (PDMS) substrate. Herein, for the first time, a self-cleaning superhydrophobic surface was applied to a solar cell and its cleaning effect was investigated. This self-cleaning
The microshell PDMS surface is notable for its simple fabrication process, its excellent cleaning effect, and its practicability for use in commercialized solar cell panels. To verify these points, the self-cleaning efficiency of the microshell PDMS, in comparison to that of a flat PDMS, was demonstrated on the solar cell module. As a result of the evaluation, the microshell PDMS surface was found to have superior self-cleaning efficiency against dust particles compared to the flat PDMS; hence, the microshell PDMS shows remarkable improvement in the recovery of solar cell efficiency.

The fabrication process of the microshell PDMS array is shown in Fig. S2†. First, an array of oxide ring-like patterns was formed on a bulk silicon wafer by reactive ion etching (RIE). Then, using the oxide as a masking layer, a trench profile was obtained in the bulk silicon substrate by RIE. Subsequently, an anti-adhesion layer was formed on a silicon trench substrate to facilitate the detachment of PDMS replica from the silicon trench (see Fig. S2† for detail). Afterwards, the PDMS solution was cast on the silicon trench substrate. Finally, the PDMS replica was detached from the silicon wafer, forming microshell array patterns on the PDMS surface. It should be noted that the silicon mold is made by one-step photolithography and etching and can be recycled for the next PDMS replicas. Thus, a large-sized mold is available and the cost is also reduced. Fig. 1(a) shows an SEM image of the cylindrical silicon trench formed after the RIE of silicon, and Fig. 1(b) and (c) show the SEM of the microshell PDMS array. The structural dimensions of the microshell PDMS array were as follows: shell thickness ($T_o$) of 2 μm and shell height ($H_{shell}$) of 26 μm, as shown in Fig. 1. Diameter and pitch were measured at 16 μm and 25 μm, respectively. Apparent CA of 151° and CA hysteresis of 19° were measured on the fabricated microshell PDMS array with a water droplet (10 μL), as depicted in Fig. 1(d) and (e), respectively. Such an excellent hydrophobic property originates from the structural advantage of having a small solid/liquid area fraction. The fabricated microshell PDMS array showed a transparent property, as shown in the photograph given in Fig. S3(b)†. For reference, a photograph showing the transparency of the flat PDMS is shown in Fig. S3(a)†. The transmittance of the flat PDMS at wavelengths larger than 300 nm is reported to be higher than 80%, showing an even higher transmittance than that of a slide glass. Laboratory logos underneath both the flat PDMS and the microshell PDMS were legible without any blurring. This indicates that the flat PDMS and the microshell PDMS show excellent transparency characteristics.

The dust removal effect on the microshell PDMS array was tested by following the experimental procedures detailed in Fig. 2. First, dust was sprayed onto the microshell PDMS inside a contamination chamber. Carbon powder, of which size ranged from a few microns to a few hundred microns, was used as the source of the dust particles so that the experiment could mimic natural processes. After the deposition of the dust particles, the surface was tilted to 45°, which angle is used in many industrial weathering tests (International Standardization Organization reference number ISO 1514:2004(E)). With this tilt angle, droplets were released onto the surface to wash away the carbon dust, as shown in Fig. 2(c). The droplets were
released at a constant rate while gradually moving the sample to the left side of the stage. As a result, a droplet of volume 20 μL was released at spacing intervals of 1 mm to gradually wash away the carbon powder on the microshell PDMS array. Finally, the cleansed microshell PDMS array was carefully placed on a commercially available solar cell with an active area of 0.93 cm² to measure the efficiency. The flat PDMS surface was also tested by the same procedure for comparison with microshell array. The solar cell used in the experiment was a mono crystalline silicon solar cell with silver metal grid lines and SiNx anti-reflection coating. Detailed specifications of the solar cell module are summarized in Fig. S4†.

The self-cleaning effect for the microshell PDMS array was superior to that of the flat PDMS. Fig. 3 shows the current–voltage characteristics of the solar cell module, reflecting the cleaning efficiency of (a) the flat PDMS and (b) the microshell PDMS array. The photocurrent is superimposed on the current–voltage characteristics of the solar cell. Therefore, the existence of dust particles on the PDMS surface blocks the light and decreases the photocurrent level (short circuit current density, \( J_{sc} \)), eventually lowering the solar cell efficiency (\( \eta \)). Current density, shown in Fig. 3, is plotted by the absolute value. Solar cell efficiency for each of the cleaning steps is noted in the text label of each graph. The dashed line in each current–voltage curve shows the current measured on the solar cell before placing the PDMS substrate on it. \( J_{sc} \) and \( \eta \) were measured as 41.7 mA cm\(^{-2}\) and 11.57%, respectively. The solid line shows the initial state, when the PDMS sample was placed on the solar cell. Efficiency decreased slightly for both the flat PDMS (11.22%) and the microshell PDMS array (11.20%). This decrease can be attributed to the light loss in the PDMS layer due to reflection. This reflection loss is governed by the Fresnel equation, given as eqn S(1)†. Reflection loss is inevitable because of the refractive index mismatching of PDMS (\( n_{PDMS} = 1.4 \)) and because of the SiN\(_x\) anti-reflection coating layer (\( n_{SiN_x} = 1.9 \)) of the solar cell. Nevertheless, considering that no reflection occurs if the refractive index of the intermediate layer (i.e. the layer placed between the air and the original anti-reflection coating layer of SiN\(_x\)) is 1.38, the PDMS layer is a suitable choice for minimizing reflection. For further details, please refer to Fig. S5†, which is followed by a brief calculation of the reflective coefficient. No significant difference in \( \eta \) for the microshell PDMS or for the flat PDMS on the solar cell module indicates that the microstructures have no adverse effect on the transparency of the film.

When carbon powder was sprayed on each PDMS substrate, degradation of the efficiency down to 6.06% for the flat PDMS and to 6.10% for the microshell PDMS was observed (marked as dashed dotted lines in Fig. 3). When cleaning was done at a tilt angle of 45°, solar cell efficiency of the microshell PDMS recovered back to 9.76%, showing a 71.8% recovery rate, whereas the flat PDMS recovered to 6.76%, showing only a 13.6% recovery rate. These curves are marked as dotted lines in Fig. 3. Note in the graph that \( J_{sc} \) is the major contributor that affects the solar cell efficiency. Other solar cell parameters such as open-circuit voltage (\( V_{oc} \)) and fill factor (FF) did not show significant change in their values, supporting the idea that the degradation of solar cell efficiency is caused by the dust particles. This is because dust blocking the light decreases only the current level while having no effect on \( V_{oc} \) or on the series or shunt resistance of the solar cell. Photographs in the bottom of Fig. 3(a) and (b) show the PDMS surface before and after carbon powder spraying and cleaning. The cleaning efficiency of the microshell PDMS is superior to that of the flat PDMS, as is visible in these photographs. Nevertheless, complete recovery of efficiency to its initial value in the microshell PDMS was not observed because particles of sizes smaller than the pitch of the microshell residing between the structures are less likely to be washed away. Therefore, further optimization of the microshell array design is needed to prevent the particles from residing between the structures. However, actual raindrops falling at high speed should wash away the particles more effectively than the gently rolling droplets.

Fig. 4 shows the statistical data of the cleaning efficiency for (a) the flat PDMS and (b) the microshell PDMS after nine different trials. Before spraying the dust particles, the flat PDMS and the microshell PDMS showed average \( \eta \) values of 11.12% and 11.05%, respectively. When dust particles were on the surface, average degradation values of \( \eta \) down to 6.69% for the flat PDMS and to 6.56% for the microshell PDMS were observed. After the cleaning, the flat PDMS

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**Fig. 3** Cleaning effect on (a) flat PDMS and (b) microshell PDMS array through current–voltage characteristics, where solar cell efficiency (\( \eta \)) for each cleaning step is written in the text label of each graph. Below the current–voltage curve photographs before and after the cleaning of carbon powder are shown.
showed an average $\eta$ of 6.59%, which was lower than when the dust was initially on the surface. This is because after the cleaning process, water droplets remained on the surface and redistributed the dust particles as they dried. On the other hand, the microshell PDMS showed an average $\eta$ of 9.78% after the cleaning process. It is also noteworthy that, in the case of the flat PDMS surface, distribution of $\eta$ was spread wider than that for the microshell PDMS surface. These results demonstrate the non-uniform cleaning property of the flat surface.

In conclusion, inspired by the structural advantages of superhydrophobic cylindrical nanoshell array, a microshell array was formed on a transparent and flexible PDMS layer. The microshell PDMS showed excellent superhydrophobic and water-repellent properties at CA higher than 150° and CA hysteresis of lower than 20° even without the aid of a low surface energy chemical coating. These desirable characteristics were primarily attributed to the small solid area fraction in contact with the liquid. Therefore, droplets weakly adhere to the surface, resulting in droplet roll off at a slightly tilted angle. Utilizing this property of the microshell PDMS, the self-cleaning application of superhydrophobic surfaces in solar cell performance was studied. As a result, this work has demonstrated for the first time that a superhydrophobic surface can actually prevent the degradation of solar cell efficiency through a self-cleaning effect much superior to that of non-superhydrophobic surfaces. In detail, the microshell PDMS showed an excellent cleaning effect against dust particles residing on the surface, whereas a non-superhydrophobic flat surface showed a poor cleaning effect. This shows that the degradation of solar cell efficiency by airborne dust can be reduced by covering the solar cell module with superhydrophobic microshell PDMS array.

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References