Packaging Glass with a Hierarchically Nanostructured Surface: A Universal Method to Achieve Self-Cleaning Omnidirectional Solar Cells

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Supporting Information

ABSTRACT: Fused-silica packaging glass fabricated with a hierarchical structure by integrating small (ultrathin nanorods) and large (honeycomb nanowalls) structures was demonstrated with exceptional light-harvesting solar performance, which is attributed to the subwavelength feature of the nanorods and an efficient scattering ability of the honeycomb nanowalls. Si solar cells covered with the hierarchically structured packaging glass exhibit enhanced conversion efficiency by 5.2% at normal incidence, and the enhancement went up to 46% at the incident angle of 60°. The hierarchical structured packaging glass shows excellent self-cleaning characteristics: 98.8% of the efficiency is maintained after 6 weeks of outdoor exposure, indicating that the nanostructured surface effectively repels polluting dust/particles. The presented self-cleaning omnidirectional light-harvesting design using the hierarchical structured packaging glass is a potential universal scheme for practical solar applications.

KEYWORDS: solar cells, antireflective coatings, nanorods, nanowalls, hierarchical, self-cleaning

Photon management at the nanoscale has been important for boosting the efficiency of a wide range of optical devices for photovoltaics, light emission, photodetection, and photocatalysis. For solar applications, a nanostructure design to significantly suppress the reflectance and efficiently enhance the light propagation length of guided mode couplings in wide ranges of wavelengths would advance solar cell efficiencies, possibly breaking the Shockley–Queisser limit. These photon management schemes by employing nanostructures include (i) coating antireflective (AR) layers on the surface and (ii) confining light inside the active layers (achieved by scattering and resonance). First of all, inspired by the hexagonal nanostructures of a moth’s eye, nanostructural AR coatings with excellent broadband and omnidirectional properties have been demonstrated. In these AR nanostructures, the Fresnel reflection is greatly reduced by various methods of photon management. For example, texturing the surface with subwavelength features (including diameter, length, surface profile, and interface roughness control) results in smooth transition of the refractive index at the air/device interface, eliminating the reflection through destructive interferences among the waves reflected at different depths from the interface. Second, as the light enters the cell, it must be efficiently absorbed. The light-scattering effect and resonance absorption can increase the light–medium interaction, enabling a breakthrough over the conventional Lambertian limit. By applying the scattering effect, the effective optical thickness can be enlarged due to extensive scattering angles, giving rise to an increase of the near and below band gap absorption. As the scattering angle is larger than the critical angle of total internal reflection, light can be effectively confined within the active layer, which is strongly favorable for a solar cell. Resonance absorption including dielectric and metallic resonance and photonic crystals can redirect and confine the light at active regions to enhance absorption. For example, maximizing photon absorption can be realized by building a nanoscale resonator with a properly selected cavity length, allowing the formation of standing waves and thus magnifying optical intensities in the active region.

Very recently, a new-generation AR hierarchical structure integrating two or three types of nanostructures was proposed to achieve the extremely low reflection that is not reachable...
with a single-layer structure. The advanced AR nanostructures hierarchically combine the peculiar properties of different antireflective structures, further expanding the working range in wavelengths and incident angles. The enhanced omnidirectionality of hierarchical AR nanostructures is vitally important for high efficiency photovoltaic devices, whose solar harvesting often requires a costly tracking system to avoid the considerable efficiency loss at high incident angles. In addition, the hierarchical structure is also expected to exhibit improved hydrophobicity considering the dramatically reduced contact area on the nanostructured surface. AR nanostructures with superior self-cleaning capability are crucial to the sustainability and performances of solar cells in harsh environments, such as deserts or cities with severe air pollution, where the power conversion efficiency (PCE) can be hampered by up to 68% because of dust accumulation.

Despite the rapid progress of nanostructured solar cells in the past years, the enhancement of efficiency has not been as high as expected due to high recombination rates (low minority carrier lifetime), arising from the excessive bulk and surface defects significantly created during nanostructuring solar cells. Moreover, photon management of nanostructured solar cells always comes with complex and deliberate geometry design, which is contingent upon the different types of solar materials and cells. Solving this problem has become a most daunting challenge, and a universal method is needed for applying a variety of solar materials and cells.

In this study, a concept employing novel hierarchical light-harvesting structures comprising nanorods (NRs) and honeycomb nanowalls (HNWs) fabricated on the packaging glass is realized for achieving optimal photon management universally applicable to all types of solar modules. These hierarchical structures show impressive solar performance through merging the advantages of different feature sizes: the NR structure’s purpose is to realize an effective medium with smooth index transition from the air to the glass, while the purpose of the formation of HNWs is to create an effective scattering center to facilitate sunlight with extensive scattering angles into the solar device. It is found that the short-circuit current density ($J_{sc}$) of a Si solar cell covered with hierarchically structured packaging glass can be enhanced by 5.2%, as compared with the device under bare glass. More importantly, the solar cell with the hierarchical structured glass retained 98.8% of its original PCE after 6 weeks of outdoor exposure, while that with bare glass only kept 84.7% of its PCE. The superior photovoltaic performances brought by the hierarchical packaging glass are even manifested at high incident angles; for example, the PCE enhancement as high as 46% with respect to that measured with bare glass after long-term use can be obtained at the incident angle of 60°. These excellent light-harvesting properties, including boosted light penetration and magnified scattering waves, are theoretically analyzed with two-dimension (2D) and three-dimension (3D) finite-difference-time-domain (FDTD) methods. The universal light-harvesting and self-cleaning packaging glass proposed here paves a unique and promising way for practical solar module applications, benefiting a wide variety of photovoltaic devices.

**RESULTS AND DISCUSSION**

Figure 1a–c show top-view and cross-sectional scanning electron microscopy (SEM) images of NR, HNW, and hierarchical structures. The images were recorded with a JEOL JSM-6700f field-emission scanning electron microscopy (FESEM) system. Average heights of NR, HNW, and the hierarchical structures are 510, 480, and 470 nm, respectively. These dimensions are intentionally selected to maximize the absorption efficiencies of sunlight. The tapered tips of NRs shown in the inset of Figure 1a are attributed to the increased etching rate of SiO$_2$ underneath the shrunk polystyrene (PS) nanospheres. Nanostructures presented in Figure 1 are robust and well maintained during the fabrication processes.

To demonstrate light-harvesting and scattering properties of the prepared glasses, the spectra of total optical transmittance ($T_{total}$) and haze (defined as the ratio of diffused transmittance to $T_{total}$) at the wavelengths ranging from 450 to 1100 nm are presented in Figure 2a,b. One can see that $T_{total}$ values of NR and HNW are higher than that of the bare surface at the wavelengths above 470 and 506 nm, respectively. The decreased $T_{total}$ at short wavelengths is caused by the strong scattering waves, which is contingent upon the different types of solar materials and cells. The superior self-cleaning capability are crucial to the sustainability and performances of solar cells in harsh environments, such as deserts or cities with severe air pollution, where the power conversion efficiency (PCE) can be hampered by up to 68% because of dust accumulation.
reflective scattering.$^{34}$ In other words, the geometrical features of the nanostructures become increasingly resolved by the decreased wavelength, leading to a pronounced scattering effect and therefore a decreased total transmittance. To mitigate the size effect, Ho et al. fabricated SiO$_2$ NR arrays with diameters of 50 nm, much lower than the visible wavelengths, leading to very low reflectance in the range 330–570 nm.$^{26}$ Ho’s results explain the highest $T_{\text{total}}$ of the hierarchical surface, with which the reflection at long and short wavelengths is respectively suppressed by the stacking HNWs (period: 450 nm) and NRs (diameter: 75 nm).

The lowest reflection on the hierarchical structure can be further attributed to the following effects: (i) For wavelengths greater than the geometric size of the upper NR, the reduced reflectance is explained by the effective medium theory.$^{35}$ The subwavelength dimensions of the SiO$_2$ NR make the structure behave like an effective medium whose effective refractive index ($n_{\text{eff}}$) smoothly changes from 1 (air) to 1.55 (SiO$_2$). As the incident light is reflected at the nanostructure, the suppression of reflectance occurs through destructive interferences, where the waves with different phases partially (or wholly) cancel one another. (ii) For short wavelengths, i.e., comparable to the geometric size of the nanostructure, the reflectance is reduced through the resonance and/or scattering effect.$^{36}$ When light impinges on the bottom HNW, strong optical scattering can take place around the air/HNW interface, leading to prolonged optical paths on the surface and thus increasing the chances of light penetration into the active region. The combined effect of effective medium and light trapping leads to the highest transmittance exhibited by the hierarchical surface.

Figure 2b shows the haze spectra of the four types of surface. It can be seen that the haze gradually decays as the wavelength increases, which is ascribed to the fact that the nanostructures are mostly of dimensions less than 500 nm. With the incident wavelengths longer than the nanostructures, the surface features become less resolved, resulting in a decreased scattering effect and thus a reduced haze ratio. To extract the most photocurrents from a solar cell, the haze on the device surface should be maximized without sacrificing $T_{\text{total}}$. The surface with properly enhanced haze can enhance optical absorption of the solar cell via the aforementioned scattering effect, which has been demonstrated by other research groups.$^{37,38}$ It should be mentioned that a high-haze surface does not guarantee high $J_{\text{SC}}$ from a solar cell. A surface with high haze could be caused by severe reflective scattering, leading to decreased $T_{\text{total}}$, as depicted by the spectra of the NR surface in Figure 2a. The effect of haze on solar cell performance should be evaluated with $J–V$ characteristics and external quantum efficiency (EQE) spectra, which will be shown later.

Surface morphology of a packaging glass not only influences its optical properties but also plays an important role in its hydrophobic behavior. For practical applications, a packaging glass with excellent self-cleaning properties is desired to ensure the solar cell has a high $T_{\text{total}}$ and $J_{\text{SC}}$ over a long period of time. To evaluate the self-cleaning capability of the prepared surfaces, measurements of the contact angle (CA) were performed and are shown in Figure 3a–d. The wettability of all surfaces was characterized by the sessile drop method using a 3 μL water droplet at room temperature. The CA of water on the bare surface of fused-silica glass is 91°. NR, HNW, and hierarchical surfaces exhibit great surface hydrophobicity, with CAs of 104°, 101°, and 124°, respectively. The mechanism of the hydrophobic behavior can be explained by Cassie’s equation:$^{39}$

$$\cos \theta_w = w \cos \theta_i - (1 - w)$$  \hspace{1cm} (1)

where $\theta_w$ ($90^\circ < \theta_w < 180^\circ$ for a hydrophobic surface) is the measured CA on the structured surface, $\theta_i$ is the intrinsic CA on a bare surface, and $w$ and $(1 - w)$ are the fractions of the water/solid interface and water/air interface at the contact surface, respectively. The contact areas of water droplets are dependent on the filling fraction of the surface structures, which can be estimated from the SEM images in Figure 1. The filled fractions of NR, HNW, and hierarchical surfaces are 0.47, 0.54, and 0.08, respectively. Since the pillar-shaped NRs in the hierarchical structure are of high aspect ratio (length: 470 nm; diameter: 75 nm), the air space among the ultrasharp tips of the hierarchical structure is easily created, which results in the high fraction of the water/air interface, i.e. a large value of $(1 - w)$ and thus a large CA. The largest CA of the hierarchical surface is expected to sustain the performances of solar cells after long-term use.

To investigate the behavior of light propagation across the interfaces, 2D FDTD analysis of NR, HNW, hierarchical, and bare surfaces was carried out, through which light-harvesting capabilities of the four surfaces can be evaluated. Details on the simulated structures and optical parameters are described in Figure S1 in the Supporting Information. Figure 4a–d show the
time-averaged transverse electric (TE)-polarized ($E_y$) intensity distributions with the incident wavelength of 550 nm, which is close to the one with peak irradiance in the solar spectrum and generally considered as an important wavelength for various types of solar cells. In Figure 4a–c, it is clear that the periodic wave ripples in the glass are dispersed not only in the vertical direction (y-direction) but also in the horizontal direction (x-direction), indicating that the nanostructures behave as effective scattering centers. Compared with the case of the bare glass, the suppressed reflection on the nanostructured surfaces is confirmed by the lower $E_y$ intensities in the region bounded from $y = 0 \mu m$ to $y = 1 \mu m$ on the vertical axis, which are magnified in Figure S2 in the Supporting Information. Evidently, the greatest light-harvesting enhancement is achieved by the hierarchical structure. It is worth noting that the dimensions of the ultrathin tips in the hierarchical structure are much less than the incident wavelength, suggesting that the tip region should serve as an effective medium whose refractive index falls between those of air and SiO$_2$. The enhanced light harvesting can be quantitatively estimated by calculating the steady-state normalized $E_y$ intensities at $y = 3 \mu m$, which are 0.971, 0.981, 0.985, and 0.994 for bare, NR, HNW, and hierarchical surfaces, respectively. These calculated results are consistent with the previous discussion that the nanostructures, particularly the hierarchical one, can enhance optical transmission through a graded refractive index and strong scattering effect, leading to the increased $T_{total}$ shown in Figure 2a.

The cross-sectional $E_y$ distribution presented in Figure 4 shows the incident waves within the nanostructures. The scattering effect can be further manifested by the plain-view $E_y$ distribution shown in Figure 5, which is obtained by 3D FDTD simulation with the incident wavelength of 550 nm. Figure 5a–c display the instantaneous $E_y$ intensities for the three surfaces at $z' = 0.4 \mu m$ (where $z' = 0 \mu m$ corresponds to the position at the nanostructure/bulk interface, and $z' = 0.4 \mu m$ is 100 nm below the air/nanostructure interface, as indicated in Figure 5d). Dimensions of the simulated structures are the average values determined by the SEM images shown in Figure 1. In Figure 5a, one can see that $E_y$ is maximized within the NRs, indicating that incident waves are harvested within the nanostructured SiO$_2$. The light-trapping scenario is different for the case of the HNW, where strong scattering is observed around the sidewalls of the HNW, as shown in Figure 5b. The result shows that the HNW traps the incident light by forming scattering centers between the nanoholes. For the hierarchical structure presented in Figure 5c, it is found that the upper ultrathin NRs facilitate intensive waves into the lower HNWS and the strong scattered waves are observed in the lower HNWs, which is believed to increase the probability of optical absorption by the underneath solar cells. These simulation results indicate that the resonance effect induced within the nanostructure benefits optical harvest and should give rise to superior performances of the solar cells.

Aiming to evaluate the effect of the NR, the HNW, and the hierarchical surfaces on photovoltaic performances, we measured $J–V$ curves of commercial single-crystal Si solar cells covered with different types of packaging glass. Figure 6a presents the $J–V$ curves of the devices under air-mass (AM) 1.5G illumination at normal incidence, and the photovoltaic performances are summarized in Table 1. It is clear that the device with hierarchically structured packaging glass delivers the highest PCE, which is around 5.2% higher than that obtained with the bare glass. Similar efficiency improvement was also observed with the nanostructured glass applied to GaAs-based solar cells (Figure S3 in the Supporting Information). As indicated in Table 1, the improved PCE attained by the hierarchical surface mainly comes from the enhanced $J_{SC}$, which is due to the superior $T_{total}$ and haze discussed in Figure 2 and Figure 4. The improved optical absorption through the nanostructured surface is also confirmed by the EQE spectra measured in the wavelength range 400–1100 nm, which can be found in Figure S4 in the Supporting Information.

It should be emphasized that the hierarchical glass not only improves device performances but also renders excellent efficiency sustainability because of its superior self-cleaning capability. Figure 6b shows the daily integrated power density delivered by the Si solar cells with the prepared packaging glasses measured over 6 weeks of outdoor exposure. The daily integrated power is estimated by summing the output power of the solar cell from 8 A.M. to 4 P.M., and the summation is
The enhancement is particularly distinguished at high angles (from 5.2% at 0° to 27.7% at 60°). The PCE enhancement by the nanostructured glass is even evident after 6 weeks, which can be seen in Figure 7c,d. Comparing the results in Figure 7a and c, one can find that the significantly increased PCE enhancement displayed in Figure 7d is mainly due to the much degraded performance of the device with bare packaging glass, which can be explained by the greatly reduced $T_{\text{total}}$ of the bare glass after prolonged outdoor exposure, shown in Figure S5 in the Supporting Information. In Figure 7d, it is seen that the PCE enhancement achieved by the hierarchical glass is close to 46% at the AOI of 60°. In general, when optical waves reach the glass surface at a large AOI, the portion of the waves entering the glass is decreased, and thus the light-trapping effect becomes less pronounced. The weakened light-trapping effect often results in high reflectance at high AOIs, which can be seen in Figure S6 in the Supporting Information. In Figure 7d, the much improved PCE at AOIs indicates that the nanostructures can significantly enhance the light-harvesting effect by hierarchical structured glasses, as presented in Figure 5.

**CONCLUSIONS**

Packaging glass with hierarchical nanostructure is employed to improve the performances and lifetime of Si solar cells. The hierarchical nanostructure consists of ultrathin NRs and HNWs, providing a graded refractive index and strong optical scattering centers, respectively, and therefore harvesting photons in a wide range of wavelengths and AOIs. The hierarchical surface also exhibits excellent hydrophobic properties, which effectively sustain the photovoltaic performances in long-term use. After 6 weeks of outdoor exposure, the hierarchically structured glass results in a PCE enhancement as high as 46% at AOI = 60°, compared to that measured with the bare glass. The fabrication technique presented here holds great promise for various solar cells with superior antireflective and self-cleaning characteristics.

**METHODS**

The NR, HNW, and hierarchical surface textures were fabricated by dip-coating and PS nanosphere lithography techniques, as illustrated in Figure 8a–c. First, the fused-silica glass was dipped in a solution suspension of PS nanospheres (diameter: 450 nm) to be covered with a self-assembled monolayer. The monolayer nanospheres act as the
etching mask in the following RIE process. To create more space for etching, the PS nanospheres were shrunk by 50 sccm O2 gas flow for 30 s under a coil power of 50 W and a chamber pressure of 5 Pa. The remaining PS nanospheres were removed by tetrahydrofuran (THF).

To fabricate the HNW and hierarchical surfaces, the substrates with shrunk nanospheres were coated with 200 and 160 nm thick Ag by e-beam evaporation, as shown in Figure 1b,c. After removing the residual Ag by nitric acid, the hydrophobic surface was attained by immersing all samples in a 0.5 mM OTMS ethanol solution for 10 h. The samples were then rinsed with DI water and dried by N2.

ASSOCIATED CONTENT

* Supporting Information is available on the ACS Publications website at DOI: 10.1021/acsnano.5b05564.

Schematic diagram of three kinds of surfaces for FDTD simulations; magnified time-averaged, normalized TE electric field (Ez) distribution of Figure S; EQE spectra and the EQE enhancement factor of NR, HNW, and hierarchical surfaces; ftotal spectra of NR, HNW, and bare surfaces after 6 weeks of outdoor exposure; AOI-dependent specular reflectance of NR, HNW, and hierarchical surfaces at the wavelength of 550 nm (PDF)

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**Notes**
The authors declare no competing financial interest.

REFERENCES


