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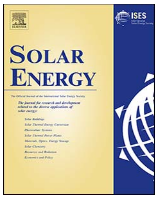

Leaf-structure patterning for antireflective and self-cleaning surfaces on Si-based solar cells

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ABSTRACT

As the naturally evolved sunlight harvester, plant foliage is gifted with dedicated air-leaf interfaces countering light reflections and ambient ruins, yet offering antireflective and self-cleaning prototypes for manmade photovoltaics. In this work, we report on an ecological and bio-inspired coating strategy by replicating leaf structures onto Si-based solar cells. Transparent photopolymer with leaf surface morphologies was tightly cured on Si slabs through a facile double transfer process. After bio-mimicked layer coverages, sunlight reflection drops substantially from more than 35% down to less than 20% once lotus leaf was employed as the master. Consequentially, 10.9% gain of the maximum powers of the photovoltaic is obtained. The leaf replicas inherited their masters' hydrophobicity which is resistant to acidic and basic conditions. Physically adhered dusts are easily removed by water rolling. Lightwave guidance mechanism among air-polymer-Si interfaces is explicated through optical simulations, while wettability through the morphological impacts on hydrophobic states. Taking advantages of varieties of foliage species and surface structures, the work is hoped to boost large-scale industrial designs and realizations of the bionic antireflective and superhydrophobic coating on future solar cells.

1. Introduction

Light exhibits reflection when it impinges on interface between two media with different refractive indices. Such a reflection rate of sunlight reaches more than 35% on the surface of polished silicon, the dominant material to harvest sunlight in photovoltaic (PV) modules. Bare silicon slab is physically brittle and easily oxidized with time. The physical property poses survivals of modules in different ambiences, whilst the latter leads to surface recombination loss in the cells and decrease of PV efficiency (Hirst and Ekins-Daukes, 2011). In most cases, PV modules are exposed to various natural weather conditions. They are easily covered by dusts and organic wastes from plant, animal, and industrial pollutants (Said et al., 2015). The unwanted light reflection and dirt ask for proper shielding materials onto the bare Si slabs. For practical applications, such materials should be antireflective (AR), transparent, protective, durable and self-cleaning. Furthermore, the material synthesis route should be easy and cheap, featuring in large-scale industrial fabrication.

In a typical Si-PV module, the silicon slab is folded by a glass shield above an encapsulation layer of ethyl vinyl acetate (EVA). Patterning the glass will not only need additional treatments to the chemically inert glass itself, but also ask for a clear clue in selecting patterns from tremendous micro- and submicro-types. Another route is to directly engineer the Si surface with AR structures, such as through colloidal lithography (Dev et al., 2014), wet-etching processes (Adamian et al., 2000), and ion etching (Bien et al., 2012). Various micro- and submicro-structures have been used in PV cells (Zang et al., 2013), or on the Si slabs too (Bichotte et al., 2017; Jovanov et al., 2017). Albeit successes in antireflection designs, surface structure durability and wettability remain unclear within these treatments. Additionally, the costs and limits of pattern types bar practical applications in large scales.

When talking about solar energy conversions, the primary function of plant foliage shall never be neglected. Photosynthesis on leaves supplies both oxygen and organic matters on earth. After millions of years of natural evolution, surface morphologies are not only benefiting solar radiance harvesting, but also apt to protections and environmental adaptations. The upper epidermis "shields" of the natural sunlight harvesting systems play a similar but crucial role to these of the ideal covers on manmade PV systems. The rich plant species further provide a large library for the coating types. Recently, these bio-inspired structures have been proved efficiently enhancing solar energy

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conversions on PV cells, thanks to their lightwave guidance nature (Huang et al., 2015, 2016a,b). However, the bio-structures are mainly patterned onto soft species such as transparent polymers which are further folded onto possible active units (Chen et al., 2015). Later, direct replicating biostructures on to PV unit was also reported, but the functional sizes of the surfaces were very much limited due to the tiny leaf masters (Vüllers et al., 2016). Besides, physical mechanisms of the antireflective property and hydrophobicity were not revealed. A facile, precise and reliable route to replicate the bioinspired structures directly onto large inorganic Si slab is required, together with understanding of physical origins beyond multi-functionalities of the structures.

In this paper, we report on replicating leaf surface structures directly onto bare silicon surfaces to form antireflective and self-cleaning coatings through a facile double transfer method. Light reflection on the patterned surface is suppressed lower around 20% determined via UV–Visible spectroscopy. Consequentially, a gain of more than 10% for the maximum power was reached on the patterned silicon photovoltaics. Benefiting from the AR and wettability of the master leaves and physical and chemical advances of the cured photopolymer, a maximum value of 150(± 0.5)° is found for the static water contact angle (CA) from the Lotus replica, and 20(± 0.5)° for the rolling angle from the same replicated surface. Thanks to morphological advances, hydrophobicity is resistant to ambient liquid pH values. Lightwave guidance mechanism was clarified through optical simulations, and wettability through hydrophobic state analysis. Such an ecological and bio-inspired method paves a route for large-industrial scale fabrications of the reliable coatings with antireflective, transparent and self-cleaning properties.

2. Experimental methods

2.1. Master leaf selection

The strategy debuts from carefully observations of natural leaves and their responses to ecological systems. Here, fresh master leaves were collected from the following 4 plants: lotus (Nelumbo nucifera), Indian shot (Canna indica), grape (Vitis vinifera L.) and bamboo (Phyllostachys edulis). Lotus leaf is famous for its superhydrophobic property. The structures leading to the property has been a research focus since the beginning of the century (Sun et al., 2005a,b). It's worth mentioning that such water repelling nature does not exclusively belong to aquatic plants. The Indian shot, a terrestrial plant from the Cannaceae family, is also superhydrophobic (Sharma and Mattaparthi, 2014), yet distinguishing themselves in tropic homegarden systems (Gajaseni and Gajaseni, 1999). As a typical liana plant, the grape possesses high solar energy harvesting efficiency in the photosynthesis for fruit production. We further notice that bamboo grows in warm moist environment, but the leaf surface feels coarser than many other tall wooden plants. This perennial evergreen plant features fast growth and prompt regeneration capacity, referring to very good light harvesting features. Furthermore, the leaf extract/main components are used as efficient inhibitors against stainless steel corrosions (Li et al., 2014).

2.2. Double transfer process

A schematic of fabrication steps for the coating is shown in Fig. 1. To start, fresh leaf masters were firstly cleaned with ethanol, and then dried with drier blow. Leaf types are selected to these with good hydrophobic properties, and with fast growth speed. They were then stuck in the die as shown in Fig. 1(b). Fig. 1(c) shows a mould with negative leaf structure was copied to the polydimethylsiloxane (PDMS). This undergoes the same procedure as described in our previous work (Huang et al., 2015). A negative master of PDMS was formed (Fig. 1(d)) and ready for photopolymer curing. Here, the Norland Optical Adhesive 63 (NOA63) photopolymer was employed as the coverage materials on polished bare silicon slab or Si PV cells without any coverage. Besides its feasibility in curing, the polymer also advances in stability in hierarchical structure moulding (Leem et al., 2016). The Si slabs were cut to as $1 \times 1\ \text{cm}^2$ to fit active regions of the plant leaves. The PV cells have a dimension of $5 \times 5\ \text{cm}^2$, nominal filling factor of 0.75, open-circuit voltages of 0.6 V and short-circuit current density of $24\ \text{mA/cm}^2$. In Fig. 1(e), the NOA63 liquid was evenly placed on the negative PDMS mould. The amount of NOA63 is enough to cover PDMS, and slight above the negative edges. Later, the silicon upper surface facing to the light was very gently placed to the photopolymer. Then, NOA63 was cured under UV radiation for 6–8 min until its solidification. The negative mould can be mechanically torn and detached from the PV surfaces, leaving the polymer with positive leaf structures ready on the Si surfaces as Fig. 1(f) shows.

2.3. Characterizations

Morphological determinations of the replicated photopolymers were carried out on a Hitachi S-4800 scanning electron microscope (SEM). For comparison purposes, corresponding master leaves were measured through the SEM too. Leaf samples were coated with carbon to increase conductivity during the measurement. All photos, except the one from real plant, in the present work were shot under fluorescence lighting with a Cannon digital camera without any correction through picture software. Optical properties of the coated surfaces were measured through a UV–Visible/NIR Spectrophotometer UH4150. The surface reflection and absorption curves were measured at a wavelength region from 300 to 800 nm, covering all visible light region of the solar spectrum. Analysis of the wettability was performed through a contact angle apparatus JY-82A from Chengde Dingsheng Testing Machine. Co. Ltd. By adding HCl or NaOH into water, the liquid was adjusted acidic or basic, and CA variations were measured at a pH range of 4–10. In the photovoltaic measurement, a solar simulator (SAN-EI ELECTRIC XES-40S1) under AM 1.5G illumination at $100\ \text{mW/cm}^2$ power density output was employed to obtain the I-V curves from silicon PV cells without and with the leaf structure coverages.

3. Simulations

To understand the physical mechanisms leading to AR nature, optical simulations were carried on the SiO_2 surface structures with the 0.05 μm Si substrates through the software of finite-difference-time-domain (FDTD) solutions™. The simulation time was set to 10,000 fs. A plane wave was selected as a simulated light source, and light wavelength covered range from 300 nm to 800 nm. The SiO_2 is employed here due to its wide application in PV cells, and similar refractive index to the one of NOA 63 above 380 nm. Its thickness is set to 15 μm, and refractive index of 1.55, very close to the value of 1.56 from NOA 63. Boundary condition are set as 'periodic' in X and Y axis direction, and 'perfectly matched layer' in Z axis direction. During the simulation, lightwave guidance mechanism among the interfaces was conducted by using an abstracted bamboo structure as the model. Based on the microscopic determinations, it is constructed by one micro-cone surrounded by four microspheres (see later in the text). Detailed computational methodology can be found e.g., in Huang et al. (2016a,b).

4. Results and discussion

4.1. Morphology

The SEM images of the master leaf surfaces are shown in Fig. 2(a)–(d), with the corresponding replicas in Fig. 2(e)–(h). Hereafter, we name the replica as PPR@PLN, where PPR refers to the photopolymer replica and PLN to the Plant Name. In general, the replica surface morphologies are almost identical to these of their masters, denoting the success of the direct transfer process.

Surface morphologies of the replicas vary from plant families. Lotus