Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Towards new multifunctional coatings for organic photovoltaics

Peter Šiffalovič [a], Matej Jergel [a,*], Monika Benkovičová [a], Andrej Vojtko [a], Vojtech Nádaždy [a],
Ján Ivančo [a], Michal Bodík [b], Maxym Demydenko [a,c], Eva Majková [a]

[a] Institute of Physics, Slovak Academy of Sciences, Dúbravská cesta 9, 845 11 Bratislava, Slovakia
[b] Faculty of Mathematics, Physics and Informatics, Comenius University, Mlynská dolina, 842 48 Bratislava, Slovakia
[c] Sumy State University, 2 Rymskogo-Korsakova st., 40007 Sumy, Ukraine

ARTICLE INFO

ABSTRACT

A cost-effective procedure for hydrophobization of commercial silica nanoparticles by octadecyltrichlorosilane or trichloro (1H,1H,2H,2H-perfluorooctyl) silane was developed. The functionalized nanoparticle solution could easily be applied on a glass surface by Langmuir-Schaefer deposition or spincoating to create a superhydrophobic surface with the contact angle above 170°. A hydrophobization driven formation of nanoparticle clusters resulted in multiscale hierarchical surface roughness as evidenced by the stylus profilometry and atomic force microscopy. Consequently, optical measurements in the vis-NIR region revealed enhanced forward diffuse scattering and reduced reflectance in a broad interval of the incidence angles. A small sliding angle far below 1° suggests additional coating functionalities such as the self-cleaning and anti-icing. The coating was tested on a front surface of an organic photovoltaic device. A more than 6% enhancement of the photoconversion efficiency comparing with the uncoated device was achieved which may be even larger in real operation conditions considering the air pollution and humidity.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Superhydrophobic surfaces hold great potential in shipbuilding, automotive and aerospace industry (drag reduction), in construction (self-cleaning facades) as well as in preparation of tailored smart coatings such as those for anti-corrosion, anti-biofouling or electrowetting applications [1–6]. A convention defines the superhydrophobic surface as the one with the water contact angle larger than 150°. It is known that while a low surface energy is sufficient to achieve the values up to $\approx 120°$ (hydrophobic surface), further contact angle enhancement is possible only by a special surface morphology [7,8]. In particular, a hierarchical multiscale surface roughness must be introduced to promote the effect of hydrophobic terminal groups such as -CH$_3$ or -CF$_3$. Therefore, the superhydrophobicity results from an interplay between physical and chemical factors. Inspiration comes from nature where a lotus leaf with the contact angle larger than 162° is a typical example [9].

The Wenzel [10] and Cassie-Baxter [11] models provided the first mathematical descriptions of the water contact angle of a rough surface. While the former suggests a perfect wetting, the latter postulates a water droplet sitting on the apex of the roughness nanostructure with air pockets in the roughness walleys. Later on, several modifications of the Cassie-Baxter model were introduced to analyze the contact angle behavior observed experimentally in the superhydrophobic regime [9,12–18]. This behavior may vary depending on the hysteresis between the advancing and receding droplet contact angle which is closely related to the droplet ability to slide on a tilted surface. A small sliding angle (for lotus leaf 2°) accompanies a small hysteresis while a red rose petal is an example of the perfectly sticky superhydrophobic surface (contact angle 152.4°, sliding angle 180°) [19].

Usually, a two-step physico-chemical surface treatment is applied to achieve artificial superhydrophobicity [20]. Transparent silica nanoparticles, which are hydrophilic and must be functionalized before application, are often used. For example, a superhydrophobic surface was prepared from trimethylsiloxane functionalized silica nanoparticles deposited onto a precoated polyurethane layer [21]. Hexamethyldisilazane modified 20 nm silica nanoparticles were incorporated into polytetrafluoroethylene emulsion [22]. Silica nanoparticles were deposited onto a flat/patterned (regular pillar-like) substrate to enhance the surface roughness which was further modified by a self-assembled fluorosilanated monolayer [7]. A simpler and faster one-step process consisting of deposition of functionalized nanoparticles, such as *e.g.* silica nanoparticles hydrophobized with hexadecyl trimethoxysilane [23]

or monodisperse 120 nm silica nanoparticles functionalized with fluoroalkylsilane [24], is often sufficient to achieve the contact angle above 150°. Here, spin coating (single or multiple to optimize the contact angle) and spraying of a nanoparticle solution onto glass, silicon, aluminum or aluminum oxide are the most frequent techniques. A study of Son et al. [25] showed a slight decrease in the photoconversion efficiencies of monocrystalline solar cells when used with various superhydrophobic coatings. Recently, superhydrophobic coatings with high transmittance for application on solar cells have been proposed, however, without any measurements of solar cell efficiencies [26].

In this work, a cost-effective hydrophobization of commercial silica nanoparticles is introduced with the aim to prepare a functionalized nanoparticle solution that can be applied easily in a simple one-step process to create a superhydrophobic surface. Applying octadecyltrichlorosilane (OTS) or trichloro (1H,1H,2H,2H-perfluorooctyl) silane (OTSF) as the surfactant, excellent superhydrophobicity combined with a small sliding angle was achieved while enhanced diffuse scattering and suppressed reflectance in the vis-NIR region in a broad interval of the incidence angles suggest antireflective properties. A pilot coating application to an organic photovoltaic device showed a positive effect on the photoconversion efficiency. The potential applications comprise multifunctional organic solar panels (*e.g.* self-cleaning, anti-icing) and other organic photovoltaic elements with enhanced properties.

It has to be noticed that chemical etching or photolithography are common methods of decreasing the surface reflectance and enhancing the diffuse scattering in crystalline silicon solar cells. For the same reason, textured transparent conducting oxide electrode is used in inorganic thin film solar cells with the active layer thickness amounting to 1–2 μm. Though these approaches might be more effective in terms of the wide-angle diffuse light scattering, they are inapplicable in organic solar cells with the active layer thickness of ≈ 100 nm. Hence, the nanoparticle superhydrophobic coating reported here is a promising alternative to standard surface patterning in the case of organic solar cells.

2. Experimental details

2.1. Nanoparticle functionalization and coating deposition

Aerosil® 150 fumed silica nanoparticles (Evonik Industries) with 14 nm mean diameter and (150 ± 15) m^2/g specific surface were used. These nanoparticles are produced in large quantities for polymer industry. The nanoparticle functionalization followed basically the procedure published by Manca et al. [27]. In particular, 1.5 g of the nanoparticle powder was annealed at 120 °C for 24 h to remove water adsorbed on the nanoparticle surface. Subsequently, the nanoparticles were dissolved in 50 ml of toluene (Mikrochem) and a surfactant was added. Except for 25 ml of hexamethyldisilazane (HMDS) used in the original recipe, addition of 2 g of octadecyltrichlorosilane (OTS) or trichloro (1H,1H,2H,2H-perfluorooctyl) silane (OTSF) from Sigma-Aldrich was also tested. The reaction took place at 50 °C for 24 h under permanent stirring. Subsequently, abundant surfactant was repeatedly separated by centrifugation and removed (3 times at least). Finally, the nanoparticles were dried at 150 °C for 5 h.

In order to prepare a well-defined nanoparticle coating suitable for a detailed characterization, a modified Langmuir-Schaefer (LS) deposition was chosen. Briefly, the synthesis product was dissolved in chloroform (Sigma-Aldrich) in 15 mg/ml concentration and spread on deionized water surface (18.2 MΩ cm, Elga, Bucks) in a Langmuir-Blodgett (LB) trough (KSV, Nima Technology) by a microsyringe. The surface pressure–area (Π-*A*) isotherms for different surfactants measured with a Wilhelmy plate during barrier movement in the
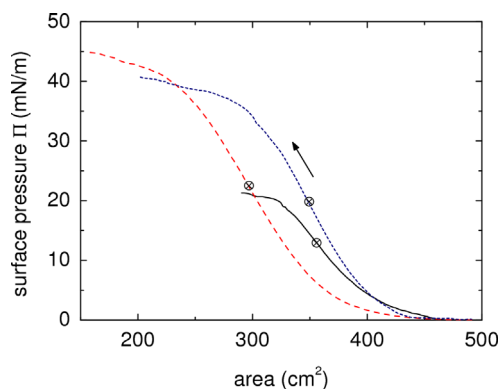

Fig. 1. Surface pressure–area isotherms for HMDS (full line), OTF (dashed line) and OTSF (dotted line) functionalized nanoparticle solutions measured during compression in the LB trough as indicated by the arrow. The symbols indicate the working pressures used for the modified LS deposition of monolayers while bilayers were formed at high pressures where the isotherms tend to saturation.

Table 1
Parameters of the LS deposited nanoparticle coatings on glass functionalized with different surfactants.

Surfactant type	Π_{dep}* 1 ML* (mN/m)	Average thickness (nm)	Rms roughness (nm)	Contact angle 1 ML* (°)	Contact angle 2 ML* (°)
HMDS	12.8	602	147	171 ± 3.0	173 ± 2.0
OTS	22.5	513	96	172 ± 3.0	173 ± 3.0
OTSF	19.6	1351	680	171 ± 0.4	175 ± 3.0

* Π_{dep}— Working pressure for deposition, 1 ML—Monolayer, 2 ML—Bilayer.

LB trough are shown in Fig. 1. The working pressure for the modified LS deposition was chosen in the middle of the linear part of the (Π-*A*) plot where a closed monolayer of the synthesis product was formed. Here, the compression was stopped and the Langmuir film was transferred onto a float glass substrate (Visiontek) by a slow regulated removal of the water subphase. For comparison, the modified LS deposition was applied also at a high surface pressure where the (Π-*A*) isotherm tends to saturation and a bilayer is formed.

2.2. Coating characterization

Thickness of the monolayer coating on the glass for different surfactants was measured by stylus profilometry (Dektak) with a tip of 12.5 μm radius and a contact force of 300 μN. The monolayer thickness is directly related to the average size of the entities grown during the synthesis of the hydrophobic nanoparticles while the root-mean-square (rms) thickness deviation provides information on the coating roughness. The thickness is slightly larger than 0.5 μm for HMDS and OTS surfactants with -CH$_3$ terminal groups and more than 1 μm large for OTSF surfactant with -CF$_3$ terminal groups (Table 1). The rms roughness ranges from 20% (OTS) to 50% (OTSF) of the thickness. These large thickness and roughness values suggest aggregation of silica nanoparticles into much larger irregular clusters during their hydrophobization.

Atomic force microscopy (AFM) (Bruker AXS) provided information on the coating morphology. AFM height images of the OTS functionalized monolayer coating scanned in the tapping mode over various areas confirm presence of irregular nanoparticle clusters which are obviously stable once being formed and give rise to a complex multiscale surface roughness (Fig. 2).

The contact angle measurements (KSV Instruments, CAM 200) of the monolayer and bilayer coatings show excellent superhydrophobicity (Fig. 3) with the contact angle values larger than 170°