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A facile two-step fabrication of nano-wrinkled double-layer moth-eye-like antireflection surface by integrating cage-like silsesquioxane nanoislands with fluoroacrylate

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ABSTRACT

Nano-wrinkled double-layer moth-eye-like antireflection coating (ARC) surfaces were fabricated by coupling octakis(methacryloxypropyl) silsesquioxane-based polymeric surface onto silsesquioxanes rigid layer on the quartz substrate. Octakis(aminophenyl) silsesquioxane (OAPS) reacted with decakis (methacryloxypropyl) silsesquioxane (CMSQ-T_{10}) through Aza-Michael addition and octakis(methacryloxypropyl) silsesquioxane (CMSQ-T_8) polymerized with hexafluorobutyl acrylate (HFBA) through radical polymerization in the rigid layer and top layer, respectively. Compressive stress, caused by mismatch of the different volumetric shrinkages between top layer and rigid layer, led to the wrinkled nanopatterned structures. Besides, the silsesquioxanes layer could offer as an in situ template and scaffold for the top polymeric surface. The reflectance was decreased to 3.5% (transmittance 98.5%) and the resulting ARC surfaces showed obvious hydrophobicity. We expect these ARC surfaces can find wide-spread applications in solar cells, camera lenses, and other photovoltaic components.

1. Introduction

Fresnel reflection happens at the interface when light travels from air to another media [1]. A total reflection loss of the light is about 8% over much of the spectrum while incident light transmits the uncoated glass. The existence of reflection can result in many issues for optical components, such as reflection ghost images, stray light, and energy loss [2]. To address these issues, many researchers have exploited ARC surfaces to eliminate the reflection. Recently, biomimetic ARC surfaces inspired by moth-eyes have drawn enormous attention due to their low reflection and energy-efficient properties [3–6]. Nanoparticles, such as Si, SiO_2, TiO_2 and GaAs, have been applied to generate arrays of nanostructures to emulate moth-eyes, however, the transmittance of incident light may also be affected that results in more energy loss at the same time. Thus, the fabrication of moth-eye-like ARC surface based on nanoparticles in a more robust and energy-efficient way is stilled needed.

Silsesquioxane cages, embodying a hybrid cage-like structure and functional groups at corners, have been extensively used as 3-D building blocks to construct well-defined nanocomposites [7,8]. For example, methacryl or acryl functionalized cage-like silsesquioxanes can polymerize with acrylic monomers to prepare hybrid polymers [9]. Suppose that if we prepare one-layer silsesquioxane-based polymeric surface onto a rigid silsesquioxane layer with different reactions occurring between top layer and rigid layer, compressive stress could be caused as a result of the different volumetric shrinkages, which might further trigger the formation of wrinkled nanostructures [10,11]. Besides, these silsesquioxane-based wrinkled nanostructures probably provide us an alternative approach to emulate moth-eyes for antireflection purpose.

In this work, we proposed a facile two-step fabrication of nano-wrinkled double-layer moth-eye-like ARC surface. First, a rigid layer was constructed through Aza-Michael addition [12] of decakis(methacryloxypropyl) silsesquioxane (CMSQ-T_{10}) and octakis(aminophenyl) silsesquioxane (OAPS). Subsequently, a top layer was coated on the rigid layer by radical polymerization of octakis(methacryloxypropyl) silsesquioxane (CMSQ-T_8) and hexafluorobutyl acrylate (HFBA). It is expected that wrinkled nanopatterned structures could be generated due to the existence of silsesquioxane cages and compressive stress. Such silsesquioxane-based moth-eye-like ARC surfaces provide as

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potential applications in solar cells, camera lenses, and other photovoltaic components.

2. Experimental section

2.1. Materials

Quartz substrates were supplied by Congyuan Co. Ltd (Guangzhou, China) and cut into 2.5×2.5 cm samples. Hexafluorobutyl acrylate (HFBA) was purchased from Zhejiang Chemicals (China) and purified by the reduced pressure distillation before usage.The used octakis (methacryloxypropyl) silsesquioxane (CMSQ-T_8) and T_{10} analogues (CMSQ-T_{10}) were prepared as described in our previous work [13]. Octakis(aminophenyl) silsesquioxane (OAPS) was prepared by following Laine's method with modifications [14] (See supplementary data). The chemical structures of the used cage-like silsesquioxanes and HFBA were shown in Figure S1.

Table 1
Sample designation and formulation of the double-layer ARCs.

Sample code	Rigid layer OAPS: CMSQ-T_{10} (molar ratio)	Top layer CMSQ-T_8: HFBA (w/w)
1	1:1	1:50
2	1:4	1:50
3	1:8	1:50
4	1:1	1:100
5	1:4	1:100
6	1:8	1:100

2.2. Preparation of the double-layer ARC surface

CMSQ-T_{10} and OAPS mixture solution (A) and CMSQ-T_8 and PHFBA mixture solution (B) were prepared as described in supplementary data. The quartz was cleaned in 10 wt % HCl and acetone for 30 min under ultrasonic, respectively. CMSQ-T_{10} and OAPS mixture solution (A) was spin-coated on the quartz substrate using a spin processor

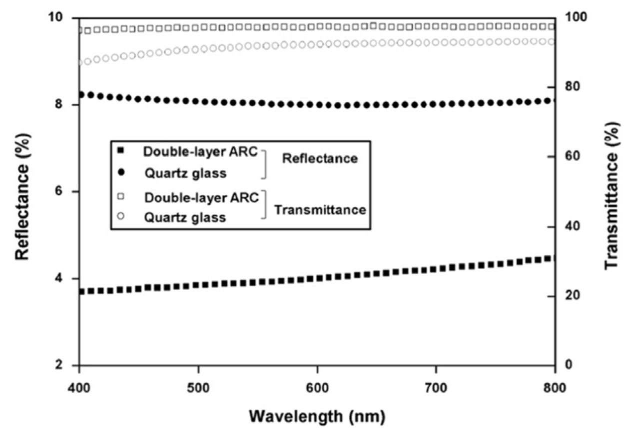

Fig. 2. Reflectance and transmittance spectra of the resulting double-layer ARC surface versus quartz glass.

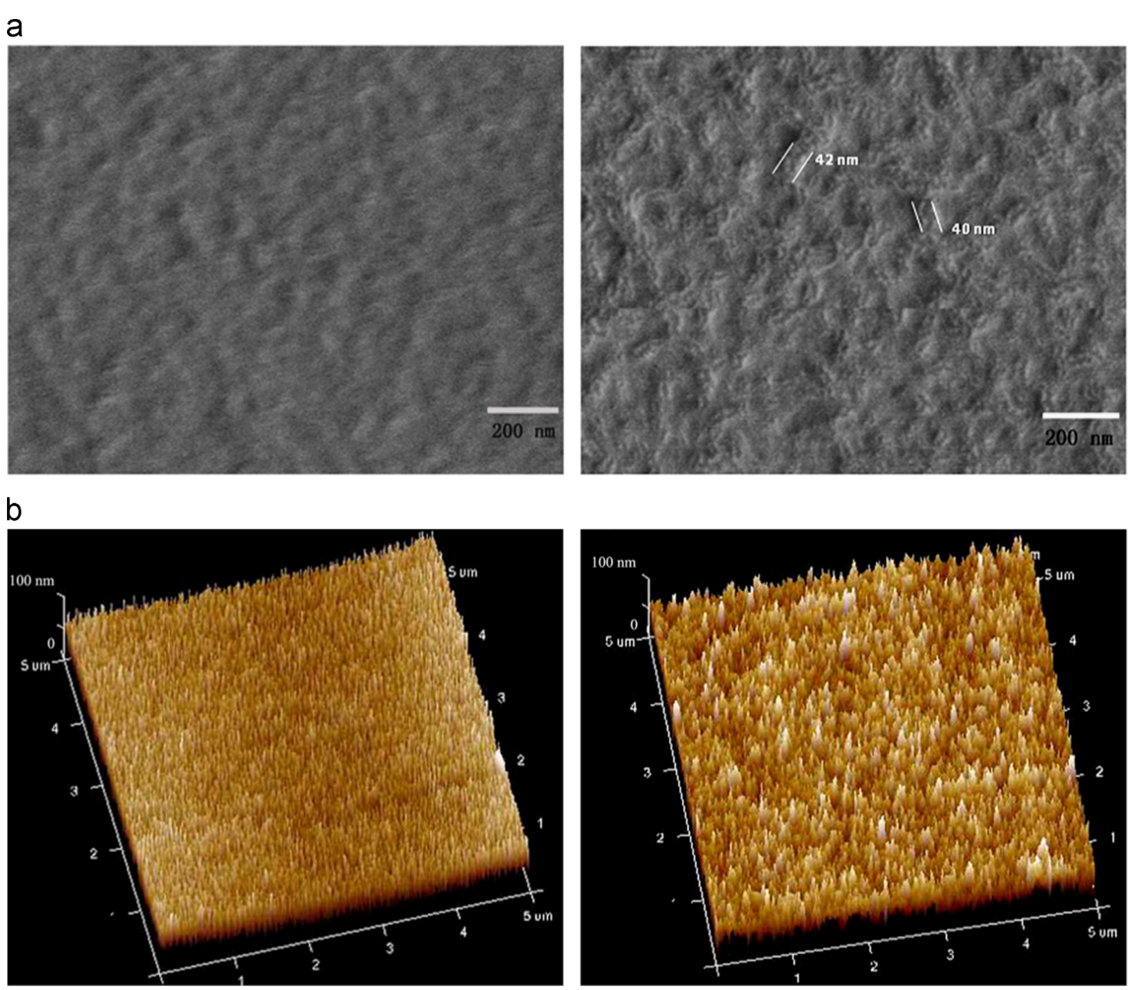

Fig. 1. SEM images and AFM 3D images of single surface layer (a) and the resulting double-layer ARC surface (b).