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Effective balance of antireflection and self-cleaning properties via hollow silica nanospheres-based surface coated with scattered titania nanoparticles

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Abstract

Antireflective (AR), self-cleaning, and anti-fogging bilayer coatings were prepared using a new structure and design concept. The bottom layer has a lower refractive index of 1.07–1.13 and was obtained from hollow silica ($HSiO_2$) nanoparticles, while the top layer has a high refractive index but good photocatalytic activity via titania (TiO_2) nanoparticles. The two layers give rise to a reasonable refractive index close to the ideal value of 1.22 and thus high transmittance (99.73% at maximum) in the visible region. The hardness of the TiO_2 layer is a protective cover to prevent mechanical damage. This endows the surface with self-cleaning properties. In addition, the mechanical strength of the coatings was further improved due to the formation of Ti–O–Si chemical bond between TiO_2 and $HSiO_2$. The coatings also exhibit excellent super-hydrophilic and anti-fogging properties. These excellent performance features make this coating promising for applications in harsh outdoor environments. Furthermore, the coating process is simple, low-cost, and time-efficient.

Keywords: Antireflective; Self-cleaning; Hollow silica; Titania

1. Introduction

Antireflective (AR) coatings are critical to increase optical efficiency of concentrating solar thermal (CST) systems. The losses from surface reflection for an uncoated PV module is as high as 36–37%—this significantly limits the photoelectric efficiency (Chhajed et al., 2008; Hidalgo et al., 1996). However, coating both sides of the solar thermal glass tubes can reduce the reflection loss from the active components of the solar collector in the range of 10–12%. Calculations have shown that the yearly energy produced in a solar heating plant (where the temperature of the solar collector fluid is 100 °C) can be increased by about 20% via AR-coated solar glass covers (Zettl, 2014). Considering multi-constraints in applications, AR coatings also must offer good abrasion resistance and self-cleaning properties—critical requirements for deploying CST plants on a massive scale in low-water desert type environments (Tuvshindorj et al., 2014; Yildirim et al., 2013).

There are two approaches to endow surfaces with the self-cleaning properties. One is to construct super-hydrophobic surfaces including micro-/nano-hierarchical structures like the lotus leaf. The tops of these structures are then coated with a thin layer with low surface energy material (organosilicon system) (Geng et al., 2013; Li et al., 2010). However, Manca et al. reported that TMS silica-based nanoparticles produce a super-hydrophobic

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coating that was completely removed after 2000 h of environmental exposure (Manca et al., 2009). Obviously, such a treated surfaces shows poor durability in practical application.

The second approach is to coat a thin layer of TiO_2 to fabricate super-hydrophilic surfaces (Kesmez et al., 2009; Nakata et al., 2011). The self-cleaning capacity of the TiO_2 surface derives from its two unique photo-induced phenomena: photo-catalysis and photo-induced superhydrophilicity (Liu et al., 2008). This approach offers additional advantages because of the hardness of the TiO_2 layer. However, high refractive index anatase TiO_2 will inevitably increase the reflection of incident light, and consequently dramatically reduce the transmittance of the coating. Although the reflective loss can be avoided by precisely controlling the thickness of TiO_2 layer, the low TiO_2 content is unfavorable for the photo-catalytic activity. In addition, Marco et al. prepared double-layered coatings with the dual functions of self-cleaning and antireflection by using a porous top layer of TiO_2 (Faustini et al., 2010). Unfortunately, the porous surface is prone to adsorb water vapor and contaminants in humid or wild surroundings. This gives rise to degradation of the AR property and the mechanical performance (Vicente et al., 2011).

According to the principle of optical interference, the complete transmission of light requires a coating material with a refractive index of ca. 1.22 for the case of a single-layer coated glass (Goswami et al., 2011). However, the silica that is often used as a building block for AR coatings has a refractive index as high as 1.45. Thus, to guarantee its AR property, some porosity should be introduced into the coating. The refractive indices of coating in the presence of certain porosity can be ~1.22. Normally, the relationship between refractive index and porosity can be described by the following equation:

$$n_p^2 = (n^2 - 1)(1 - p) + 1 \tag{1}$$

in which n_p and n are the refractive indices of porous and nonporous materials, respectively, and p is the percent porosity (Zhang et al., 2014a). Thus, the refractive index n_p of 1.22 for a silica coating corresponds to a porosity of 56%. If the coating is using solid silica ($SSiO_2$) nanoparticles as a building-block, then the porosity may arise from the random packing of particles.

Hollow silica ($HSiO_2$) nanoparticles have a lower refractive index than $SSiO_2$ nanoparticles because they are hollow. As a result, the $HSiO_2$-based thin coating possesses a lower refractive index than the $SSiO_2$-based thin coating assuming identical particle packing and porosity. Furthermore, $HSiO_2$ is surprisingly beneficial at offsetting the increase in the refractive index derived from the introduction of TiO_2. Recently, Li et al. fabricated a hierarchically structured antireflective and self-cleaning particulate coating consisting of raspberry-like SiO_2/TiO_2 nanoparticles by a one-pot sol–gel method (Li and He, 2013). It turns out that the random dispersion of TiO_2 nanoparticles on the surface of $SSiO_2$ core without agglomeration has a lower impact on the refractive index of coating than the overall package. Meanwhile these dispersive TiO_2 nanoparticles can also guarantee the photo-catalytic property of coatings.

To achieve the desired results, we used thin layers of TiO_2, but these can have minimal impact on the reflection when used on AR coatings. Herein, we programmed a double-layered $TiO_2/HSiO_2$ coating that consisted of a bottom layer of $HSiO_2$ nanoparticles and a top layer of scattered TiO_2 nanoparticles. The bottom $HSiO_2$ layer has a low refractive index. It is critical for creating AR properties. The top TiO_2 layer is photocatalytic and superhydrophilic and is employed to provide a self-cleaning function. Through this innovative design, the best balance between antireflection and self-cleaning properties can be reasonably achieved. The transmittances and abrasion-resistance of the coatings were regulated by altering the concentrations of TiO_2 nanoparticles on the surface of the coatings. Furthermore, after coating, 1H,1H,2H,2H-perfluorooctyltrimethoxysilane (POTS) modification for a double-layered coating surface was applied to obtain hydrophobicity and to characterize its self-cleaning performance by decomposing the hydrophobic alkyl chain under UV light.

2. Experimental

2.1. Preparation of $HSiO_2$ nanoparticles Sols

Hollow silica nanoparticles sols were prepared by a sol-gel process using polyacrylic acid (PAA, Mw $\approx$ 5000, 30%) as a template and tetraethylorthosilicate (TEOS, 99%) as a precursor. The 0.24 g of PAA were first dissolved in 6 mL aqueous ammonia (NH_4OH, 28%) followed by slow addition of 200 mL of absolute ethanol (EtOH, 99.9%) and the injection of five TEOS aliquots totaling 2 mL over 10 min with vigorous magnetic stirring at room temperature. After 10 h, 50 nm $HSiO_2$ nanospheres formed. The sediments were separated from the solution by centrifugation (10,000 rpm, 8 min), washed with distilled water and ethanol several times successively, and finally dispersed in ethanol to form a colloidal solution with a particle concentration of about 1.5 wt%.

2.2. Preparation of TiO_2 Nanoparticles Sols

In a typical procedure, a mixture of 6 mL of titanium tetraisopropoxide (TTIP, 97%) and 1 mL of 2-propanol (C_3H_8O, 99.7%) was added to 36 mL of distilled water with vigorous stirring. A white precipitate formed during the hydrolysis. Within 10 min of the alkoxide addition, 0.4 mL of nitric acid (HNO_3, 65%) was added to the hydrolysis mixture with vigorous stirring. The mixture was then stirred for 8 h at 80 °C to yield a transparent colloidal suspension. The size of the colloidal particles was ca. 7 nm. Finally the resulting sol was diluted with deionized