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Sol-gel preparation of self-cleaning SiO_2-TiO_2/SiO_2-TiO_2 double-layer antireflective coating for solar glass

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Self-cleaning SiO_2-TiO_2/SiO_2-TiO_2 double-layer antireflective (AR) coating is prepared by sol-gel process. SiO_2 sol is prepared by using tetraethyl orthosilicate (TEOS) as precursor and ammonia as catalyst, while TiO_2 sol was prepared by using tetrabutyl orthotitanate (TBOT) as precursor and hydrochloric acid as catalyst. The effect of TiO_2 content on refractive index, abrasion-resistance and photo-catalytic activity of SiO_2-TiO_2 hybrid thin films or powders is systematically investigated. It is found that the refractive index of SiO_2-TiO_2 hybrid thin films increases gradually from 1.18 to 1.53 as the weight ratio of TiO_2 to SiO_2 increased from 0 to 1.0. The SiO_2-TiO_2 hybrid thin film and powder possesses good abrasion-resistance and photo-catalytic activity, respectively, as the weight ratio of TiO_2 to SiO_2 is 0.4. The degradation degree of Rhodamine B by SiO_2-TiO_2 hybrid powder is 88.3%. Finally, SiO_2-TiO_2/SiO_2-TiO_2 double-layer AR coating with high transmittance, abrasion-resistance and self-cleaning property is realized.

Introduction

Photovoltaic (PV) power is one of the renewable energies, which has been developing rapidly in China because of the environmental problem. PV installations were installed outdoors and even in the sun-baked deserts. Therefore, glass covers are essential for preventing PV cells from damage of physical shock and corrosion. The refractive index of glass covers is approximately 1.52. The difference between air and glass cover results in about 8% reflection on the surfaces of cover glass. This reduces the efficiency of the PV cells. Antireflective (AR) coatings have been widely used in optical devices and energy-related applications to reduce transmission losses [1–4]. An ideal homogeneous AR coating can realized 100% transmittance at a specific wavelength when its refractive index is equal to $(n_a n_s)^{1/2}$, where n_a and n_s are the refractive indices of air and substrate, respectively [5,6]. This indicates that the refractive index of AR coating for cover glass should be about 1.22.

Sol-gel silica AR coatings have attracted much attention due to their advantages of low cost, simple operation process and controllable microstructure [7,8]. Sol-gel silica AR coatings can be prepared from both base-catalyzed silica sol and acid-catalyzed silica sol. Base-catalyzed silica AR coatings possess almost 100% transmittance [9]. The base-catalyzed silica AR coatings possess high transmittance but poor abrasion-resistance, while the acid-catalyzed silica AR coatings possess high abrasion-resistance [10] but poor transmittance. The AR coatings used for cover glasses must have both high transmittance and abrasion-resistance. The above mentioned single-layer sol-gel silica AR coatings cannot meet the requirement of cover glasses. To realize high transmittance as well as high abrasion-resistance, $\lambda/4$-$\lambda/4$ and $\lambda/4$-$\lambda/2$ double-layer AR coatings have been designed and prepared by sol-gel process [11–13]. In this work, we also prepared a $\lambda/4$-$\lambda/4$ double-layer AR coating by sol-gel process. The thin films for double-layer AR coating were the SiO_2-TiO_2 hybrid thin films which were deposited from the SiO_2-TiO_2 hybrid sols. In addition to the high abrasion resistance, the SiO_2-TiO_2 hybrid thin films also possess photo-catalytic activity and hence self-cleaning property. Finally, the SiO_2-TiO_2/SiO_2-TiO_2 double-layer AR coating with high transmittance, abrasion-resistance and self-cleaning property was prepared by the sol-gel process. This AR coating can find great application in cover glasses of PV installations.

Experimental section

Preparation of sols

Preparation of SiO_2 sol

Tetraethyl orthosilicate (TEOS, 164 g) was mixed with anhydrous ethanol (1385 g), ammonia water (25–28%, 8.7 g), and

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deionized water (40 g). The solution was left in a closed glass container and stirred at 30 °C for 2 h and aged at 25 °C for 7 days. Finally, the aged SiO_2 sol was refluxed for 24 h to remove ammonia.

Preparation of SiO_2-TiO_2 hybrid sol

Butyl titanate (TBOT) and HCl in molar ratio of 1:0.22 was added into SiO_2 sol and stirred for 2 h at 30 °C. The addition of TBOT and HCl was controlled to prepared SiO_2-TiO_2 hybrid sols with weight ratio of TiO_2 to SiO_2 to be 0, 0.1, 0.2, 0.3, 0.4, 0.6, 0.8 and 1.0.

Preparation of AR coatings

Glass substrates were cleaned by ultrasonication in acetone for 10 min, and then wiped carefully with cleanroom wipers. SiO_2-TiO_2 sols were deposited on the well-cleaned substrates sequentially at a relative humidity less than 20% by dip coating. Double-layer AR coating were prepared by depositing SiO_2-TiO_2 hybrid sols with weight ratio of TiO_2 of 1.0 and 0.4 on glass substrate with withdraw rate of 150 mm/min and 120 mm/min, respectively. The thin films and double-layer AR coating were heat-treated at 500 °C for 2 h.

Characterization

XRD measurements were performed by a D/max-RB X-ray diffractometer operating in the reflection mode with Cu-Kα radiation (40 kV, 80 mA) and diffracted beam monochromator, using a step scan mode with the step of 0.02° (2θ) and 6°/min. Transmittance spectrum of AR coating was measured with an UV–Vis spectrophotometer (Mapada, UV-3200PC). The refractive indices of the coatings were determined by ellipsometry (SENTECH SE850 UV). The abrasion-resistance of the resultant coatings was assessed in the abrasion test, in which the standard normal stress 25 kPa was applied with rotational shear (100 rpm for 0.5 h) on an abrasion-resistance machine (DZ-8103, Dongguan City Dazhong Instrument CO, Ltd.). The abrasion-resistance was characterized by contrasting the transmittance spectra before and after abrasion test. SiO_2-TiO_2 hybrid powders were prepared by heated the respective sols to 500 °C for 2 h. To evaluate the photo-catalytic activity of SiO_2-TiO_2 powder, 0.05 g SiO_2-TiO_2 powder was added into 100 mL rhodamine B solution with concentration of 2 mmol/L. Fig. 1 shows the schematic representation of photo-catalytic activity test. Before UV irradiation, the solution with SiO_2-TiO_2 powder was stirred for 1 h, and then irradiated for 2 h. 2 mL rhodamine B solution was taken every half hour to test its UV–Vis absorption spectrum.

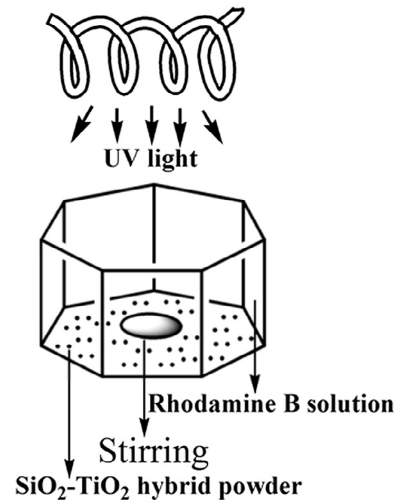

Fig. 1. Schematic representation of photo-catalytic activity test.

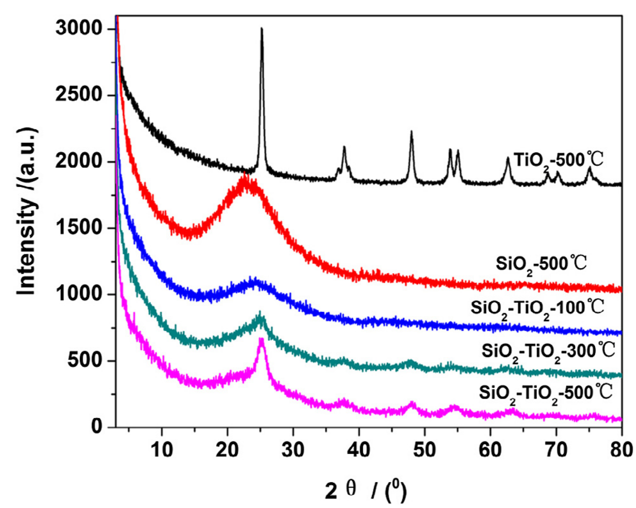

Fig. 2. XRD pattern of silica and TiO_2 annealed at 500 °C and SiO_2-TiO_2 hybrid powder with weight ratio of TiO_2 to SiO_2 of 0.4 annealed at 100 °C, 300 °C and 500 °C.

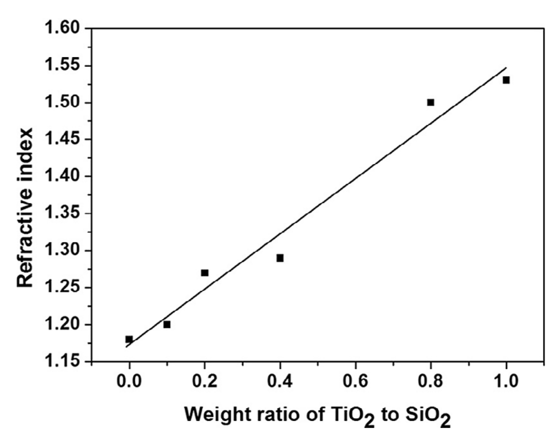

Fig. 3. Change in refractive index as a function of weight ratio of TiO_2 to SiO_2.

Results and discussion

XRD pattern of SiO_2-TiO_2 hybrid powders

XRD patterns of TiO_2, SiO_2 and SiO_2-TiO_2 hybrid powders are shown in Fig. 2. For SiO_2 powder annealed at 500 °C, a wide hump in the range of 2θ from 15° to 30° is typical for amorphous silica. XRD patterns exhibited strong diffraction peaks at 25.3°, 37.9°, 48°, 54°, 55° and 62.7° indicating that TiO_2 annealed at 500 °C is in the anatase phase. SiO_2-TiO_2 hybrid powder shows no anatase phase of TiO_2 as the calcination temperature is only 100 °C. As calcination temperature being increased to 300 °C and 500 °C, the diffraction pattern peaks for anatase TiO_2 appear and the intensity increases gradually with increasing calcination temperature. It is well-known that TiO_2 with anatase crystal structure has good photocatalytic property [14]. Therefore, to afford SiO_2-TiO_2 hybrid materials good photoactivity, the calcination temperature was controlled to be 500 °C.

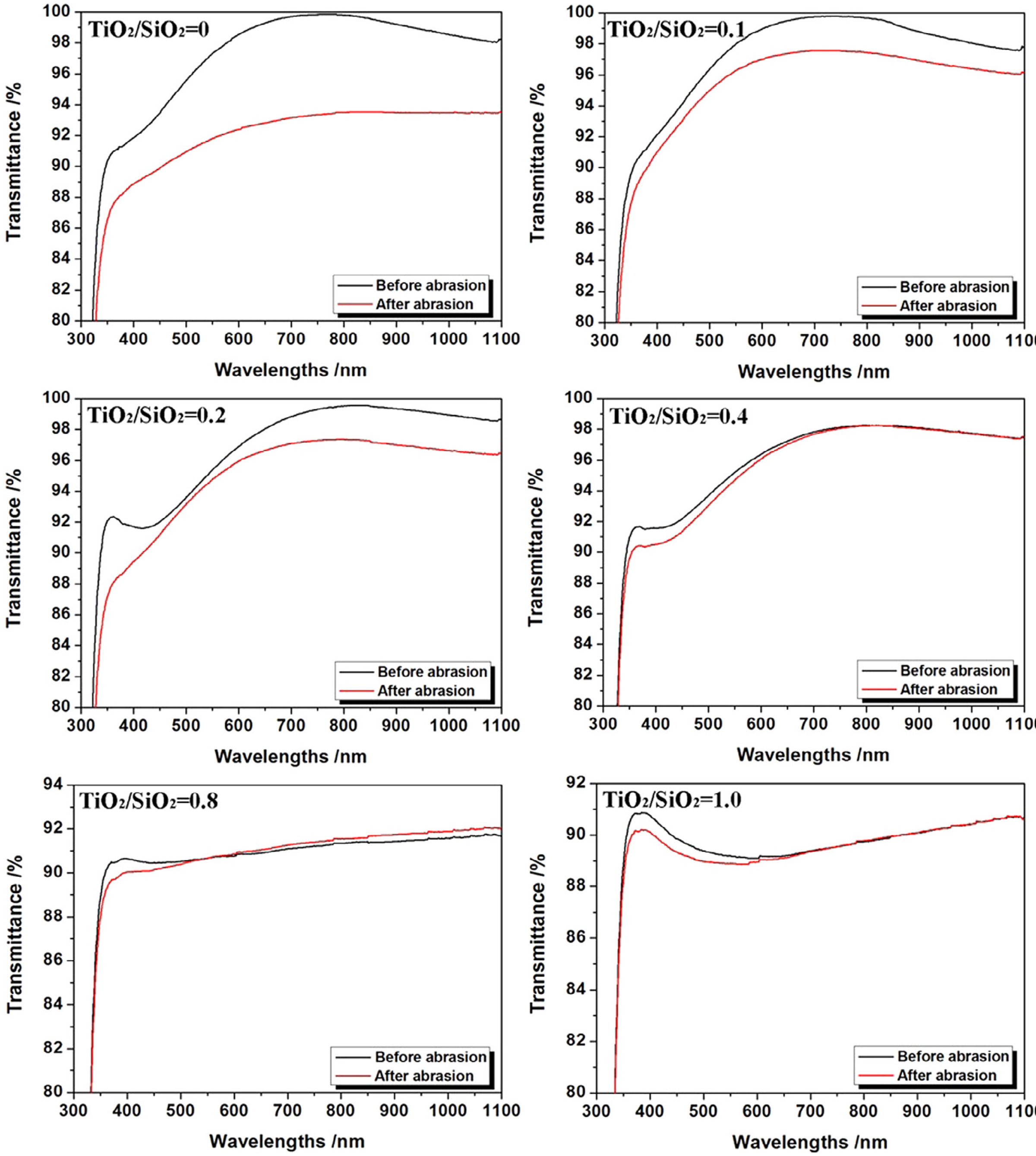

Fig. 4. Transmittance spectra of SiO_2-TiO_2 hybrid thin films with different weight ratio of TiO_2 to SiO_2 before and after abrasion-resistance test.

Refractive index of SiO_2-TiO_2 hybrid thin film

The refractive indices of SiO_2-TiO_2 hybrid thin films with different weight ratio of TiO_2 to SiO_2 are shown in Fig. 3. The refractive index of the thin films increases with the increasing weight ratio of TiO_2 to SiO_2. As the weight ratio of TiO_2 to SiO_2 increases from 0 to 1.0, the refractive indices increase from 1.18 to 1.53 continuously. TiO_2 has probably two effects on the refractive index of hybrid thin film. First, the refractive index of TiO_2 and SiO_2 thin film is 2.20 and 1.18, respectively. Theoretically, the refractive index of SiO_2-TiO_2 hybrid films can be controlled in the range of 1.18–2.20 by varying the weight ratio of TiO_2 to SiO_2. Second, SiO_2 thin film prepared by base-catalyzed method is consisted of a layer of silica particles randomly stacked on substrate's surface. There are lots of inter-particle voids in the thin film. The TiO_2 is likely incorporated into the spherical particles structure so that the porosity decreases. This also increases the refractive index of SiO_2-TiO_2 hybrid thin film.

Abrasion-resistance of SiO_2-TiO_2 hybrid thin film

For outdoors use such as the PV installations, the abrasion-resistance is very important for AR coatings because they have to endure abrasion process due to atmospheric conditions and cleaning process. The transmittance spectra of hybrid thin films before and after abrasion test were shown in Fig. 4. As the weight ratio of TiO_2 to SiO_2 increases, the reduction in the values of maximum transmittance decreases obviously, indicating an improvement of the abrasion-resistance of the hybrid thin films. The maximum

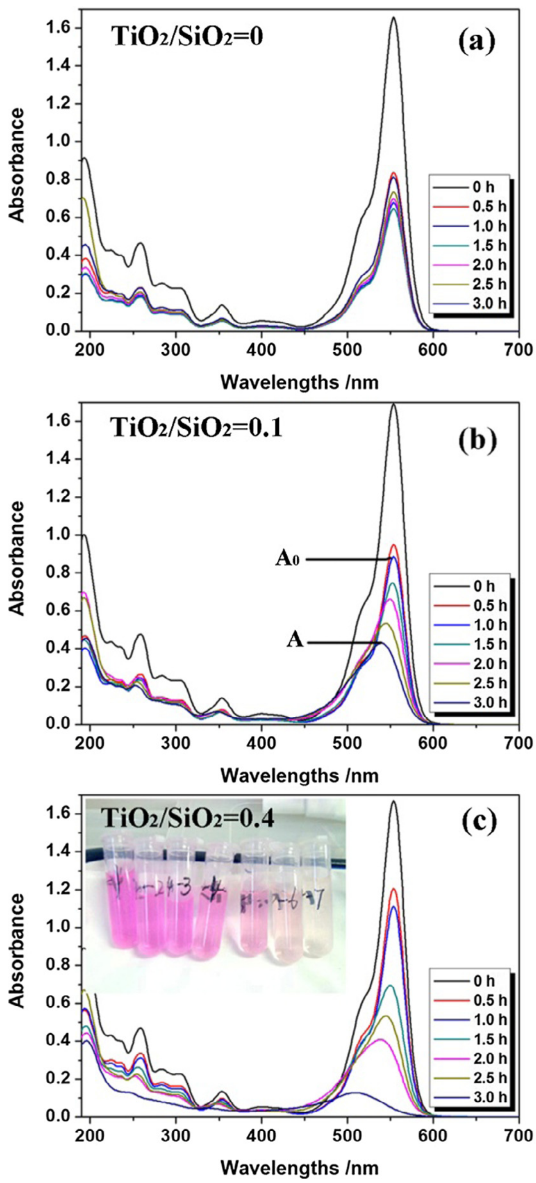

Fig. 5. Absorbance spectra of rhodamine B solution with SiO_2-TiO_2 powders under UV irradiation.

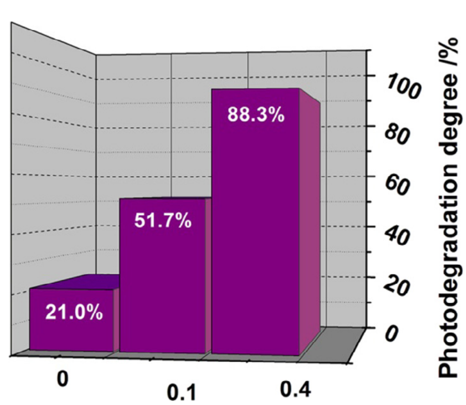

Fig. 6. Photodegradation degree of rhodamine B solution with SiO_2-TiO_2 hybrid powders under UV irradiation.

transmittance almost unchanged as the weight ratio of TiO_2 is 0.4. This indicates that the abrasion-resistance of SiO_2-TiO_2 is good as the weight ratio of TiO_2 is higher than 0.4.

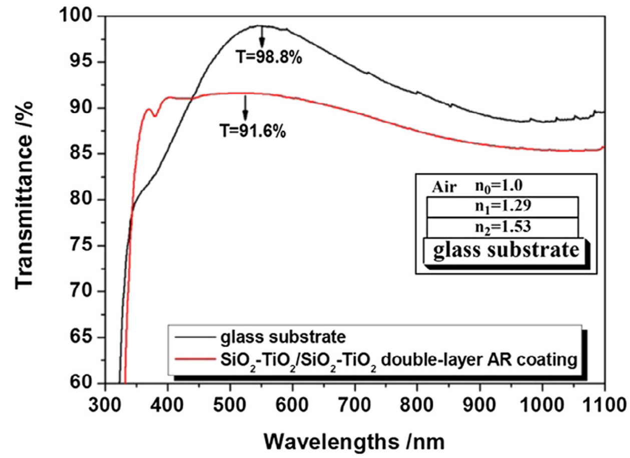

Fig. 7. Transmittance spectra of bare glass substrate and double-layer AR coating.

Photo-catalytic activity of SiO_2-TiO_2 hybrid powder

TiO_2 has good photocatalytic oxidation property and is the most important photo-catalytic material. This gives TiO_2 the ability of decomposition of organic substances under UV illumination [15,16]. In this work, TiO_2 was incorporated with SiO_2 to prepare SiO_2-TiO_2 hybrid thin film and to keep the surface of hybrid thin film free from organic contamination. Rhodamine B was adopted as the target compound to examine the photo-catalytic activity of the SiO_2-TiO_2 hybrid powders. Fig. 5 shows the decay of the absorbance band of rhodamine B as a result of the photodegradation caused by SiO_2-TiO_2 hybrid powders. SiO_2 powder prepared by sol-gel process has high surface area and can adsorb rhodamine B. Therefore, the rhodamine B solutions with SiO_2-TiO_2 hybrid powders were stirred for 1 h before UV irradiation to exclude influence of adsorption on the decay of absorbance band.

As a reference, the absorbance spectrum of the rhodamine B solution with pure SiO_2 powder (i.e., SiO_2-TiO_2 hybrid powder with TiO_2 weight ratio of 0) is also shown in the Fig. 5(a). As shown in Fig. 5(a), the absorbance intensity decreases obviously by stirring for 0.5 h without UV irradiation. This is attributed to the adsorption of rhodamine B by SiO_2 powder. After stirring for another 0.5 h without UV irradiation, the absorbance intensity decreases very slightly, which indicates the adsorption of rhodamine B by SiO_2 powder reaches equilibrium. Finally, the rhodamine B solutions containing SiO_2 or SiO_2-TiO_2 hybrid powders with different weight ratio of TiO_2 to SiO_2 were irradiated by UV light for 2 h. The degradation degree of rhodamine B increases when the weight ratio of TiO_2 to SiO_2 increases from 0 to 0.4.

Fig. 6 presents the corresponding photodegradation degrees calculated from the final rhodamine B concentration. The photodegradation degree was calculated by the Eq. (1).

$$D = \frac{A_0 - A}{A_0} \times 100\% \qquad (1)$$

where A_0 and A are the absorbance intensity of rhodamine solutions before and after UV light irradiation. As shown in Fig. 6, pure SiO_2 powder presents a degradation degree of 21% at the end of the experiment. On the contrary, SiO_2-TiO_2 hybrid powders with weight ratio of TiO_2 to SiO_2 of 0.1 and 0.4 show much higher degrees (51.7% and 88.3%, respectively), due to the increase of photo-catalytic TiO_2 content. The SiO_2-TiO_2 hybrid powders were annealed at 500 °C to transform TiO_2 to anatase crystal structure which has good photocatalytic property [14].

Double-layer SiO_2-TiO_2/SiO_2-TiO_2 AR coating

As discussed before, SiO_2-TiO_2 hybrid thin film with weight ratio of TiO_2 to SiO_2 is 0.4 has good abrasion-resistance and photo-catalytic activity. Therefore, it was assigned as the top layer of double-layer AR coating to afford double-layer AR coating abrasion-resistance and anti-contamination property. The refractive index of inner layer of double AR coating can be calculated by the Eq. (2) [12].

$$R = \left(\frac{n_0 - (n_2/n_1)^2/n_s}{n_0 + (n_2/n_1)^2/n_s}\right)^2 = 0 \qquad (2)$$

where n_0, n_1, n_2 and n_s are the refractive indices of air ($n_0 = 1$), top-layer, inner layer and glass substrate ($n_s = 1.52$). The refractive index of top layer is 1.29, and that of inner layer should be about 1.59 according to Eq. (2). However, the highest refractive index of SiO_2-TiO_2 hybrid thin film prepared in this work is 1.53. This is of little important even there is a deviation in refractive index. This is because the theoretical transmittance of double-layer AR coating is also very high of 99.7% as the refractive index of inner layer is 1.53.

Fig. 7 shows the optical transmittance spectra of bare glass substrate and SiO_2-TiO_2/SiO_2-TiO_2 double-layer AR coating. The maximum transmittance of double-layer AR coating is 98.8% while that of bare glass substrate is only 91.6%. There is more than 7% increment in transmittance after depositing double-layer AR coating on glass substrate. Therefore, the double-layer AR coating possesses high transmittance, abrasion-resistance and anti-contamination property simultaneously.

Conclusions

SiO_2-TiO_2 hybrid thin films with refractive indices between 1.18 and 1.53 were prepared by sol-gel process. The abrasion-resistance and photo-catalytic activity of hybrid thin film increased with increasing TiO_2 content in the thin film. As the weight ratio of TiO_2 to SiO_2 is above 0.4, the hybrid thin film possessed good abrasion-resistance and photodegradation property simultaneously. SiO_2-TiO_2/SiO_2-TiO_2 double-layer AR coating was prepared by assigning SiO_2-TiO_2 hybrid thin film with weight ratio of TiO_2 to SiO_2 of 0.4 as the top layer. The transmittance of the double-layer AR coating is 98.8%. This SiO_2-TiO_2/SiO_2-TiO_2 double-layer AR coating with simultaneously high transmittance, abrasion-resistance and self-cleaning property can find great application in cover glass of PV installations.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.rinp.2017.12.058.

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