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Superhydrophilic self-cleaning surfaces based on TiO_2 and TiO_2/SiO_2 composite films for photovoltaic module cover glass

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Abstract

Self-cleaning surfaces have excelled in recent years in energy and environmental fields. In particular, in solar energy area, these surfaces are used to avoid soiling accumulation on photovoltaic (PV) modules. So far TiO_2 has been widely used due to its photocatalytic activity and photo-induced superhydrophilicity. However, this oxide has some limitations since it reduces the glass transmittance and it rapidly reestablish the water contact angle in dark environments. In order to circumvent these limitations, composites TiO_2/SiO_2 have been proposed. For photovoltaic application, besides a good transparency in the wavelength region 300–1800 nm and self-cleaning properties, the coating should also present long durability and adequate adhesion to endure the outdoor conditions. Aiming at developing a coating with these properties, in this work, TiO_2/SiO_2 composites containing different titanium content have been synthesized and compared with pure TiO_2 films in relation to adhesion, transparency and hydrophilicity. Both films have been deposited over low iron float glass substrates by sol–gel dip-coating technique and different calcination temperatures (400, 500, 600°C) and Si/Ti molar rates ($Si_{86}Ti_{14}$, $Si_{40}Ti_{60}$) have been considered. TiO_2/SiO_2 films showed higher transmittance in visible range compared with pure TiO_2. TiO_2/SiO_2 films showed superhydrophilic character before and after ultraviolet irradiation, with water contact angles near to 0°. Furthermore, as predicted, TiO_2/SiO_2 films could keep the superhydrophilic character in dark environments, in contrast with pure TiO_2 films. Both TiO_2 and TiO_2/SiO_2 films exhibited good adherence and it is shown that higher calcination temperatures and higher titanium content enhance such property. All films presented abrasion resistant property in contact with sponge and detergent. It has been demonstrated that high transmittance, self-cleaning and adherent composite has been obtained by a simple sol–gel route presenting good potential to be applied on photovoltaics systems.

Keywords: TiO_2; TiO_2/SiO_2 composite; Thin film; Sol–gel; Self-cleaning surfaces; Superhydrophilicity

Background

TiO_2 is widely used as a photocatalyst and it can be applied in environmental and energy fields, including self-cleaning surfaces, air and water purification systems, anti-fogging surfaces, among others [1]. The self-cleaning property of TiO_2 is provided by two photo-induced phenomena [2]. The first one is the photocatalysis, wherein organic contaminants adsorbed on film surface are decomposed under ultraviolet light [3]. This property allows TiO_2 to be applied in air and water purification systems as well as for self-cleaning surfaces. The second one is the photo-induced superhydrophilicity, wherein contaminants and dirt are washed off the surface by the film of water on it [4]. On the superhydrophilic surface, a very small water contact angle is formed ($\theta \leq 5°$), as the water tends to spread completely across the surface rather than forming droplets. This makes the surface anti-fogging and easy- washing [1,3]. Commercial self-cleaning and anti-fogging surfaces are usually made of TiO_2 thin films [5]. However, TiO_2 thin films have some limitations, for example, they reduce the glass transmittance due to the high refractive index of TiO_2 [6]. Moreover, in dark environments TiO_2 films have a rapid reestablishment of hydrophobicity, which affects negatively the self-cleaning efficiency [7]. TiO_2/SiO_2 composite films can circumvent these limitations, slowing down the increase of water contact angle in dark environments and presenting higher transmittance with respect TiO_2, which is essential for the application as a self-cleaning surface in solar energy area [2,6,7]. Self-cleaning surface are indeed important for PV application, *since* the dust, pollution, and other particles accumulation reduce the transparency of the PV module cover glasses and consequently decrease the electrical performances of the modules. In particular for CPV modules, the soling effect is particularly severe, since such modules mainly collect the sun direct light which can be strongly reduced by the dust accumulation on the module. Performance degradation up to 30% has been measured [8]. Several studies have been made to address the severity of deposited particles (like dust, water stains, carbon from smoke, and pollen from agricultural regions) on the efficiency reduction of solar devices, which results in additional costs either from oversizing the system or from cleaning them [9]. For photovoltaic application, besides the self-cleaning properties, the coating should present adequate adhesion and transparency in the wavelength region 300–1800 nm. Several techniques have been reported for the deposition of TiO_2 and SiO_2 thin films, like CVD [10], sputtering [11-13], electron beam evaporation [14] and sol–gel process [2,6,7,15]. Sol–gel method has the advantage of offering small and large area deposition at a low cost [15]. In literature, however, detailed analyses of the anti-soling film in term of structural properties, transparency, robustness and cost are still missing. In this work, pure TiO_2 and TiO_2/SiO_2 composite films containing different titanium content have been deposited over glass substrates by sol–gel dip-coating method aiming at obtaining super hydrophilic, adherent and transparent coating. The influence of the titanium content and the calcination temperature has been evaluated. The coatings have been compared and characterized regarding their optical, mechanical and microstructural properties.

Methods

Thin film deposition

Low iron float glass (LIFG) substrates 4 mm thick(Pilkington Optiwhite Low Iron) were ultrasonically cleaned with ethanol (EtOH) and air dried. Titanium isopropoxide (TIPT), tetraethyl orthosilicate (TEOS) and isopropanol (IspOH) (99%w/w) were used as precursors and solvent for sol gel solution. TiO_2/SiO_2 composite films were prepared with different Si/Ti molar rate mixed solutions. The abbreviation $Si_{86}Ti_{14}$, $Si_{40}Ti_{60}$ is used to express the Si/Ti molar rate mixed solutions used to prepare the composite composed by the mixture of SiO_2 and TiO_2 oxides. TIPT:IspOH:H_2O molar ratio was 1:97:0,5 and TEOS:IspOH:H_2O molar ratio was 1:47:2. Film deposition was performed using the dip-coating equipment Marconi (MA 765) at room conditions (20°C, relative air humidity lower than 30%). LIFG substrates were immersed and emerged with a speed of 3,6 mm/s. Then, films were treated in muffle furnace at 400, 500 and 600°C for 2 hrs under air.

Film characterization

Light transmittance (T) of the samples was measured by JASCO V-670 spectrophotometer in the range of 200–2100 nm. Surface hydrophilicity was evaluated by water contact angle (WCA) measurements using a KRUSS DS100 goniometer connected to a video camera at room temperature (25°C, relative air humidity lower than 50%). For these measurements, deionised water droplets volume was fixed at 2 μL, 2 drops per sample and 3 replicates were used. WCA measurements were performed before and after ultraviolet (UV) light irradiation (15 W mercury lamp–Techlux emitting 254 nm wavelength).The samples were exposed to light irradiation, 5 cm far from the light source. Adherence was evaluated by measuring the critical load in the point where the first coating delamination occurs. Load application and scratch formation were performed by VTT Tech Scratch Tester equipment. Scratch test parameters were: translation speed:10 mm/min, loading speed: 100 N/min, initial load: 0-1 N and final load: 40 N. Abrasion test was performed in a tribometer Biceri equipment. Abrasion test was carried out between a mobile probe fixed in a carriage with reciprocal movement and a fixed pin. The pin was manufactured by gluing a piece of 50 x 50 mm yellow part of a Scotch Brites ponge on a standard pin. Before testing, the sponge was lubricated with commercial diluted detergent (MISTOL 66% + 33% distilled water). Test time was 7 hrs, corresponding to 25.000 cycles of movement of the mobile surface. All the mechanical tests were carried out at room conditions (25°C, 30% relative air humidity). After abrasion test the light transmittances was measured. The film thickness and microstructure was evaluated by surface imaging and RMS roughness measurements using an atomic force microscope (AFM) Asylum Research - MFP-3D in tapping mode. RMS roughness values were calculated by spectral analysis on 1 μm^2 areas. This analysis have been carried out at room conditions (20°C, 20% relative air humidity) using C160TS-R3 probe (silicon, elastic constant = 26 N/m) and the software MFP3D (version 13). Raman spectra were collected on a Horiba JobinYvon LABRAM-HR 800 spectrograph, equipped with a 633 nm helium-neon laser, 20 mW of power, attached to an Olympus BHX microscope equipped with 10, 50, and 100X lenses.

Results and discussion

Pure TiO_2 and TiO_2/SiO_2 transmittance spectra in 200–2100 nm range is shown in Figure 1.

TiO_2/SiO_2 composite films showed high %T (>85%) in visible-NIR range, which is fundamental for solar energy application [14]. $Si_{86}Ti_{14}$ composite film treated 400°C and 500°C presented the best result of %T with value ~ 1% lower compared to the uncoated glass. Whereas, both samples, $Si_{40}Ti_{60}$ composite and TiO_2 treated at 400°C

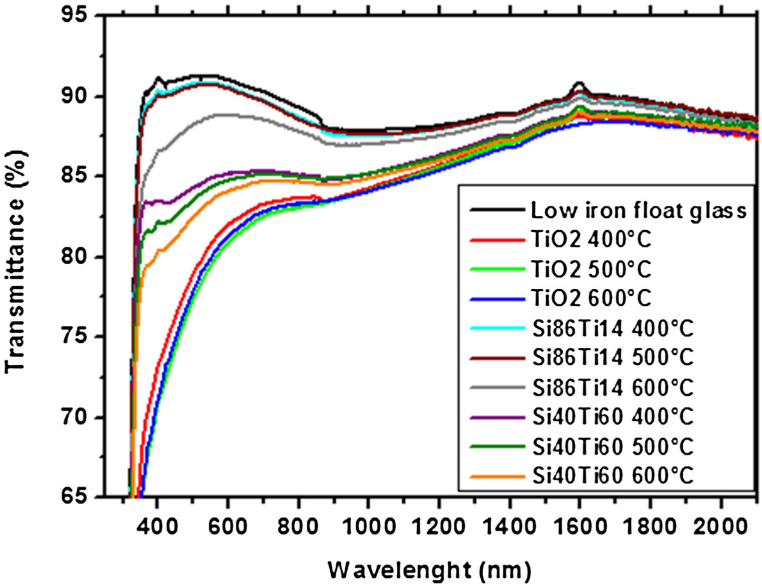

Figure 1 % Transmittance spectra of pure TiO_2 and TiO_2/SiO_2 composite film treated at 400, 500 and 600°C.

presented a transmittance of 6% and 11% lower than the uncoated glass respectively. It is possible to notice that all composite samples show an improvement in transmittance compared to pure TiO_2 films. It is possible also to assess (Figure 1) the effect of the calcination temperature on the thin film transmittance. For all the coatings, higher temperature resulted in lower %T due to the densification of the coatings and to the increase of the refractive index value [15]. While titanium content increases, %T of the thin film decreases. This can be explained by the fact that TiO_2 has higher refractive index (RI) ($n \approx 2{,}5$) than SiO_2 ($n \approx 1{,}45$). Consequently, higher RI results in lower %T of the coatings [15].

Table 1 shows WCA of all samples before and after UV irradiation for 30 min. WCA measurements were performed with 2 weeks and 3 months aged samples and the results of superhydrophilic state were similar. Pure TiO_2 films did not maintain the superhydrophilic state ($\text{angle} < 5^0$) after 2 weeks in the darkness, whereas composite films did. At dark environments, TiO_2 films tends to re-establish the hydrophobicity quickly, while TiO_2/SiO_2 slows down this reestablishment [2,7]. After UV irradiation, all samples presented superhydrophilic behaviour ($\text{angle} < 5°$), except uncoated glass, showing how coating applications were efficient to give superhydrophilic property to the glass. Superhydrophilic surface is promising for photovoltaic module due to its self-cleaning effect.

Table 1 Water contact angles before and after ultraviolet irradiation for 30 minutes

Sample	**TiO_2 400°C**	**TiO_2 500°C**	**TiO_2 600°C**	**$Si_{86}Ti_{14}$ 400°C**	**$Si_{40}Ti_{60}$ 400°C**
Before UV (^{0})	(30,0 ± 0,2)	(27,0 ± 0,2)	(26,0 ± 0,2)	(6,0 ± 0,1)	(6,0 ± 0,1)
After UV (^{0})	(6,0 ± 0,2)	(4,0 ± 0,2)	(4,0 ± 0,2)	(1,0 ± 0,1)	(0,1 ± 0,1)
Sample	**$Si_{86}Ti_{14}$ 500°C**	**$Si_{40}Ti_{60}$ 500°C**	**$Si_{86}Ti_{14}$ 600°C**	**$Si_{40}Ti_{60}$ 600°C**	**Uncoated glass**
Before UV (^{0})	(1,0 ± 0,1)	(1,0 ± 0,1)	(1,0 ± 0,1)	(1,0 ± 0,1)	(32,0 ± 0,2)
After UV (^{0})	(0,1 ± 0,1)	(0,1 ± 0,1)	(0,1 ± 0,1)	(0,1 ± 0,1)	(30,0 ± 0,2)

Raman spectroscopy was used to characterize the phase transformation of titania at TiO_2 and TiO_2/SiO_2 films. The anatase phase and the rutile phase have different Raman active modes. The main peaks of anatase are at 143 (most intense), 396, and 639 cm^{-1}, while rutile peaks are at 447 and 610 cm^{-1} [15]. Figure 2 shows the Raman spectra of TiO_2 (Figure 2-A) and TiO_2/SiO_2 films (Figure 2-B) heat-treated at different temperatures. TiO_2 films have clearly showed anatase phase, presenting the main peaks at 143, 396, and 639 cm-, in this case, no rutile peaks were identified. Regarding the composite, only the $Si_{40}Ti_{60}$ composite exhibited anatase phase (Figure 2-B) with the peaks shifted, because the presence of SiO_2 that can affect anatase crystallization [16]. $Si_{40}Ti_{60}$ composite bands, at 396, and 639 cm-1, suggests anatase and rutile peaks combination (Figure 2-B). $Si_{86}Ti_{14}$ composite films did not show anatase/rutile peaks (Figure 2-B), probably, due to high Si/Ti molar rate [17]. Preliminar photocalyst test, not reported in this paper, suggest that both composite samples exhibited photocalytic

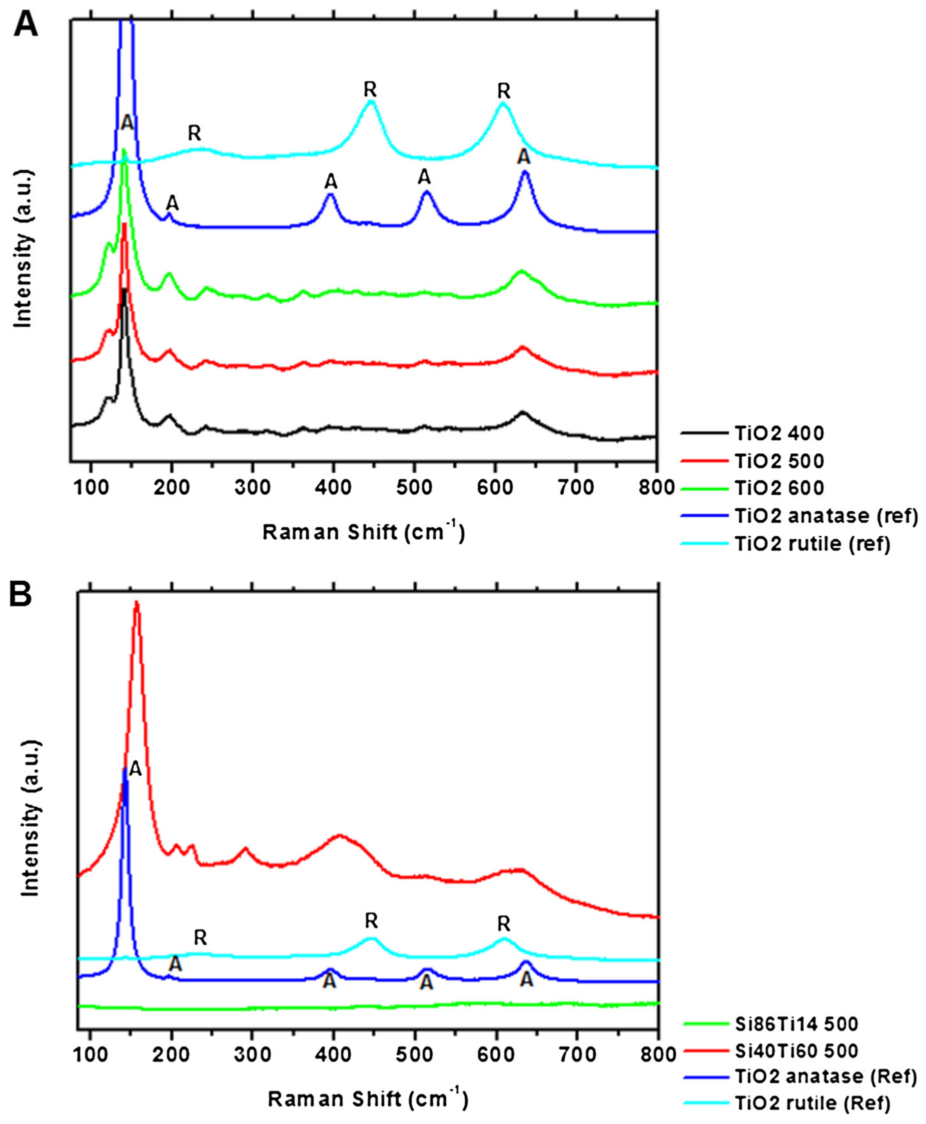

Figure 2 Raman spectra of pure TiO_2 and TiO_2/SiO_2 composite films heat-treated at different temperatures.

effect under UV light. The photocalytic effect was more pronounced on the sample that had higher Ti content. The $Si_{86}Ti_{14}$ composite exhibited good hydrophilicity and also photocatalylic effect according to our preliminar photocatalitic tests although the anatase phase was not present. Further studies will be conducted to understand better this phenomenon.

AFM images of TiO_2(TiO_2 400 °C) and TiO_2/SiO_2 ($Si_{40}Ti_{60}$ 400°C) samples are shown in Figure 3.

AFM analysis revealed that the composite thin film treated at 400°C is more porous than pure TiO_2 (Figure 3). Figure 3-A presents a typical morphology of TiO_2 400°C, crystalline with particle size = 6,2 nm. Figure 3-B shows clearly that TiO_2/SiO_2 film presents a sponge-like morphology with rather large cavities which indicates an important

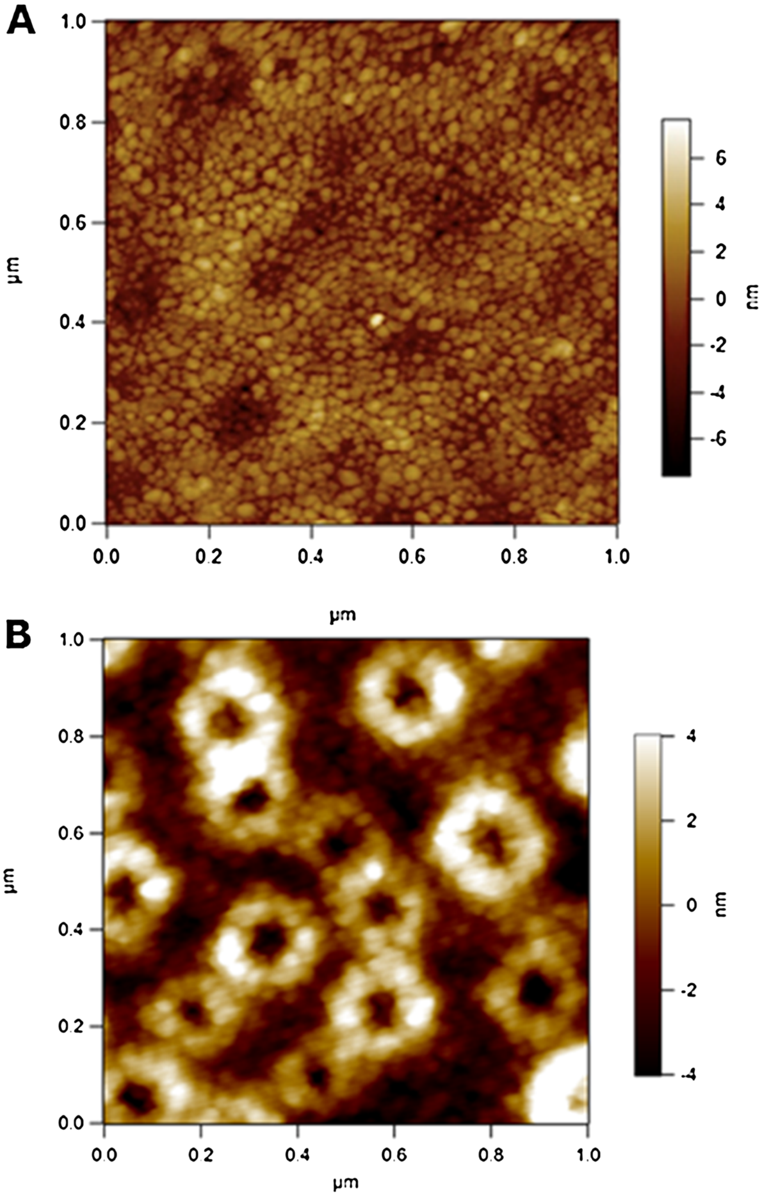

Figure 3 AFM images of films. A) TiO_2 calcined at 400°C and **B**) $Si_{40}Ti_{60}$calcined at 400°C.

surface porosity. Houmard et al.(2007) has shown similar morphology when it was prepared a TiO_2/SiO_2 composite by using a different sol composition and sol–gel spin-coating process [7]. The composite film shown in Figure 3-B is rougher (RMS = 2,7 nm) than TiO_2 film (RMS = 1,4 nm) in Figure 3-A, due to this morphology. The formation of this microstructure (Figure 3-B) is not yet completely understood, but it is speculated that modifications in the structure of –(O–Si)n– polymeric chains fixed on TiO_2 crystallites, which arise from modifications in the silica sol formulations, can lead to variations in the morphological properties of composite films [8]. The average thickness of the coating, measured by AFM in five points of the sample, has been estimated as 63 nm for $Si_{40}Ti_{60}$, 85 nm for $Si_{86}Ti_{14}$ and 45,5 nm for TiO_2.

Pure TiO_2 and TiO_2/SiO_2 composite films exhibited adherence in the range of 19–25 N (Figure 4). If calcination temperature increases, adherence is enhanced, because an increase the calcination temperature, promotes a greater densification of the film and hence improves the mechanical properties of the it [18]. This effect was more significant when temperature ranges from 400 to 500°C. The increase in titanium content also promotes a higher adherence of the film, but this effect is not as significant as the one provided by the increase of the temperature value. High calcination temperatures and high titanium content can thus provide films with good adherence, which affects directly the film durability. In fact, the durability of thin films is mainly dependent upon their adhesion to the substrate, because this determines the ease of removal. Therefore, TiO_2 and TiO_2/SiO_2 films with good adherence can maintain self-cleaning and anti-fogging properties for a long time under outdoor conditions [18].

Figure 5 shows %T in 300–1970 nm range of films before and after abrasion test with detergent and sponge.

All TiO_2 and TiO_2/SiO_2 films have maintained transmittance after 25000 cycles in abrasion test, showing how these films would not be affected or scratched in a

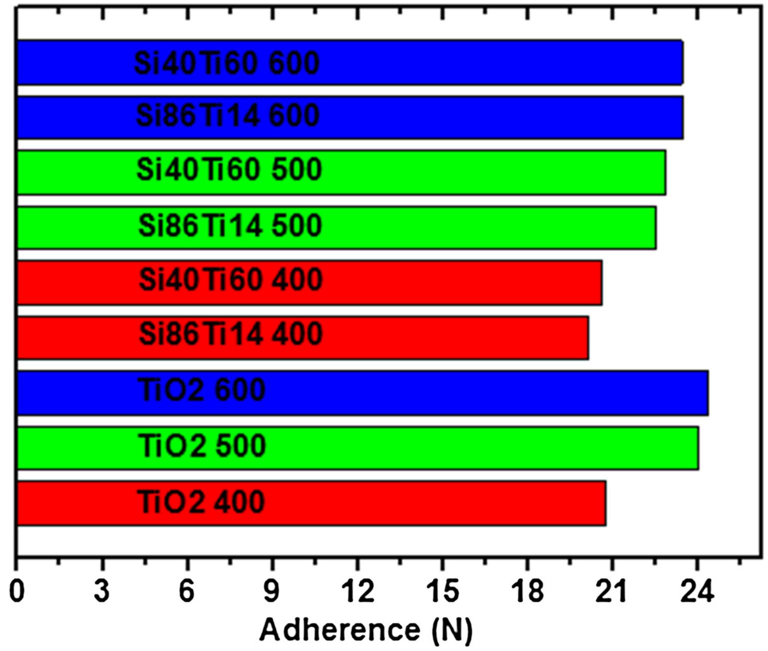

Figure 4 Adherence values of pure TiO_2 and TiO_2/SiO_2 composite film treated at 400, 500 and 600°C.

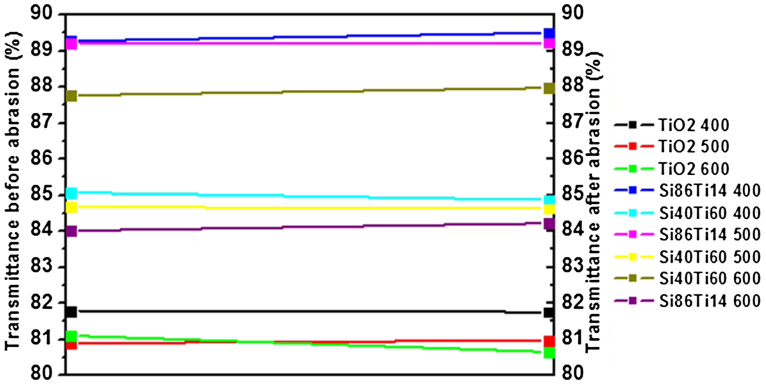

Figure 5 % Transmittance before and after abrasion testfor 400, 500 and 600°C heat-treated samples.

conventional cleaning process. These results corroborate with adherence results, showing how these films are well adhered to the substrate, and can support an abrasion procedure, like the one produced by cleaning. It is well known that wear is closely related to the adhesion of thin film to the substrates. If the film adherence is poor, the film will wear off quickly. If the film adherence is good, the film will resist to wear. Therefore, TiO_2 and TiO_2/SiO_2 films have exhibited good mechanical properties which are required for long durability in outdoor applications.

Conclusions

TiO_2/SiO_2 high transmittance, self-cleaning, abrasion resistant and adherent films were obtained by a simple sol–gel route. 500°C treated films showed better mechanical property with respect to 400°C treated films and better optical property with respect 600°C treated films. TiO_2/SiO_2 composite film presented an important surface porosity which is rougher than TiO_2 film. TiO_2/SiO_2 composite films presented higher transmittance, lower water contact angle and similar adherence/abrasive resistance compared to pure TiO_2 films. These properties are essential for application as a self-cleaning surface in solar energy area, when transparency and low water contact angles are required. TiO_2 and TiO_2/SiO_2 films have presented good mechanical properties which are required for outdoor applications and necessary to resist in harsh environmental conditions.

Competing interests

The authors declare that they have no competing interests.

Authors’ contributions

MAMLJ prepared the samples, performed the characterization and wrote the paper. JTSN developed the titanium solution route.GT is apartner that contributed with transmittance characterization and measurements methodology. PRPP gave support for contact angle measurements and AMF supervised the project, discussed all the results and raised funds for this study. All authors read and approved the final manuscript.

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