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Self-cleaning properties of SiO₂ doped TiO₂ thin films

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ABSTRACT

In this study, SiO₂ doped TiO₂ thin films were deposited on glass substrates using a sol-gel dip-coating process and calcinations at the temperature of 500 °C for 2 h with the heating rate of 10 °C/min. SEM and AFM techniques were used to characterize the structural, chemical and physical properties of the thin films. The water contact angle on the thin films surface was measured under UV light by a water contact angle analyzer. The results indicated the SiO₂ doping had a significant effect on the self-cleaning properties of TiO₂ thin films.

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INTRODUCTION

In practice, surface cleaning of building materials like tiles, facades and glass panes causes considerable trouble, high consumption of energy and chemical detergents and, consequently, high costs. To realize self-cleaning materials surface there are two principal ways: the development of so-called super-hydrophobic or super-hydrophilic surfaces (Benedix *et al.*, 2000). Self-cleaning applications using titanium dioxide (TiO₂) thin film have become a subject of an increasing interest especially in recent years. The self-cleaning property has been known to be a combined effect between super-hydrophilicity and photo-catalysis (Guan *et al.*, 2003; Mokhtarimehr *et al.*, 2013; Sayilkan *et al.*, 2009). The photo-catalytic property helps decompose many type of bacteria, organic and inorganic compounds that come into contact with the surface and thus prevents them from building up (Aguado *et al.*, 2006). The super-hydrophilic property of the TiO₂ thin films on the surface allows water to spread completely across the surface rather than remain as droplets, thus making the surface easy to wash (Boroujeny *et al.*, 2012; Wang *et al.*, 2009). Therefore, the photo-catalytic and hydrophilic properties of the TiO₂ coated surface allow the water to move easily wash away deposited particles (Shokuhfar *et al.*, 2012; Sikong *et al.*, 2010).

In the present study, SiO₂ doped TiO₂ thin films with different amounts of SiO₂ content were prepared by sol-gel process and were coated on glass substrate. The phase structure and hydrophilic or self-cleaning properties of SiO₂ doped TiO₂ thin films were measured.

Experimental Detail:

Reagents and Materials:

Titanium (IV) isopropoxide (TTIP, 99%, Fluka Sigma-Aldrich) and Tetraethyl Orthosilicate (TEOS, 99%, Fluka Sigma-Aldrich) were used as starting materials. Ethanol (C₂H₅OH, 99.9%, Merck Germany) was used as a solvent.

Preparation of Thin Films:

The sol-gel method was used to prepare the TiO₂ doped with SiO₂ thin films containing 0, 1, 2 and 3 mol% SiO₂ from the mixtures of TiO₂ and TiO₂ precursor sols (Sangchay *et al.*, 2013). Firstly, TEOS and TTIP with fixed at 10 ml were mixed into 150 ml of ethanol and the mixture was vigorously stirred at room temperature for 15 min. The pH of mixed solution was adjusted to about 3-4 by 3 ml of 2 M nitric acid (HNO₃). Finally, it was vigorously stirred at room temperature for 45 min until clear sol was formed. For this work the SiO₂ doped TiO₂ thin films containing 0, 1, 2 and 3 mol% SiO₂ from the mixtures were designated as T, T1S, T2S and T3S, respectively.

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Before coating, the glass substrates were ultrasonically cleaned in ethanol (Mokhtarimehr *et al.*, 2013). The thin films were obtained by dip coating method and withdrawn at a speed of 1.25 mm/s. The gel films were air dried for 24 h, and then calcined at 500 °C for 2 h with a heating rate of 10 °C/min in air atmosphere. The typical procedure of SnO₂ doped TiO₂ thin films preparation by sol-gel dip coating method is show in Figure 1.

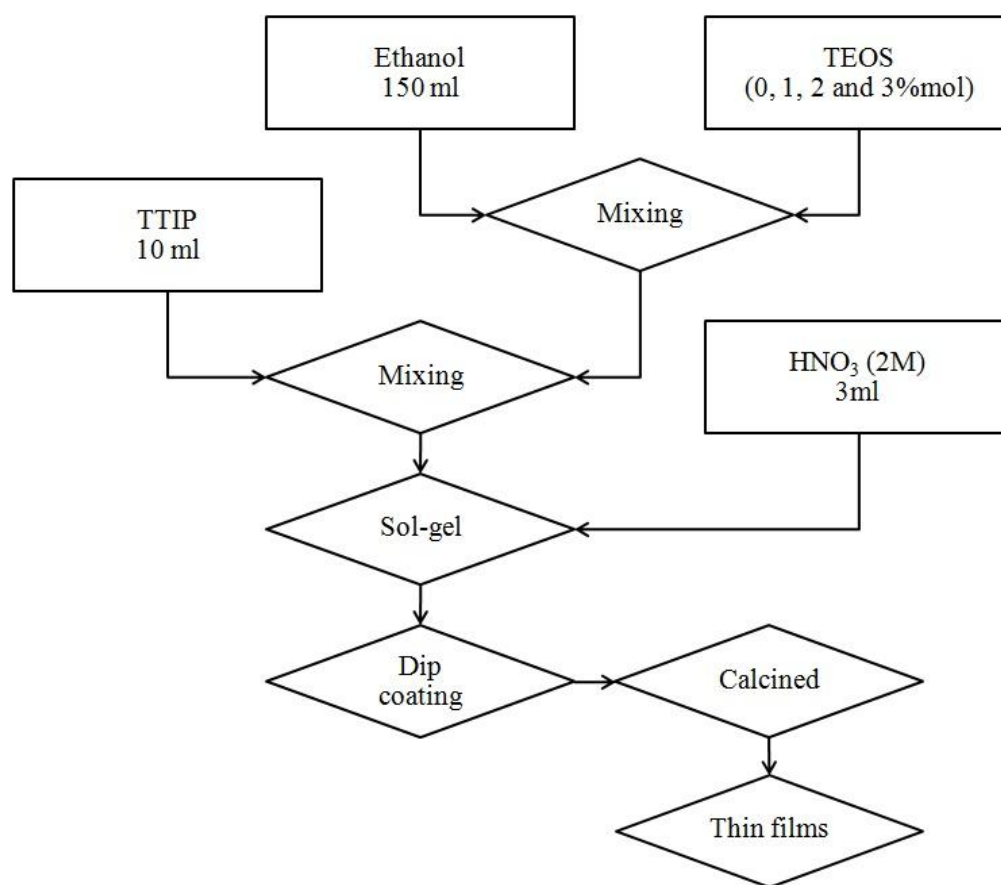


Fig. 1: Typical procedure of SnO₂ doped TiO₂ thin films preparation by sol-gel dip coating method

Thin Films Characterization:

The morphology of the synthesized thin films was characterized by Scanning Electron Microscope (SEM) (Quanta 400) and the surface roughness of thin films was measured by atomic force microscope (AFM) for an area of 1x1 μm².

Self-Cleaning Property Test:

The self-cleaning or hydrophilic property of thin films was evaluated by measuring the static contact angle between de-ionized water and thin films with and without UV irradiation using 110 W of black lamps at ambient conditions at room temperature. Water droplets were placed at 3 different positions for one sample and the averaged value was adopted as the contact angle.

RESULT AND DISCUSSION

Characterization:

SEM images obtained from different composites indicated that the thin film thicknesses are in micrometer range. Figure 2 shows SEM image of TiO₂ and SiO₂ doped TiO₂ thin films prepared under the same conditions. SEM observations showed that thickness of TiO₂ and SiO₂ doped TiO₂ thin films are about 0.25 μm. Their surfaces are dense and very smooth.

The morphologies of un-doped and SiO₂ doped TiO₂ thin films were monitored by AFM as show in Fig. 3. The AFM images reveal the existence of SiO₂ nanoparticles in the thin films. The surface roughnesses of thin films are 1.120, 0.147, 0.155 and 0.167 nm for TiO₂ doped with 0, 1, 2 and 3 mol% SiO₂, respectively. It was apparent that SiO₂ added in TiO₂ has significantly affected on surface roughness of thin films compared with un-doped condition. For SiO₂ added in TiO₂ thin films, the surface roughness of thin films evidently decreases

with increases SiO_2 doping content. It also indicates that TiO_2 doped with 1 mol% SiO_2 thin films exhibit higher surface roughness compared to TiO_2 and TiO_2 doped with 2 and 3 mol% SiO_2 thin films, respectively.

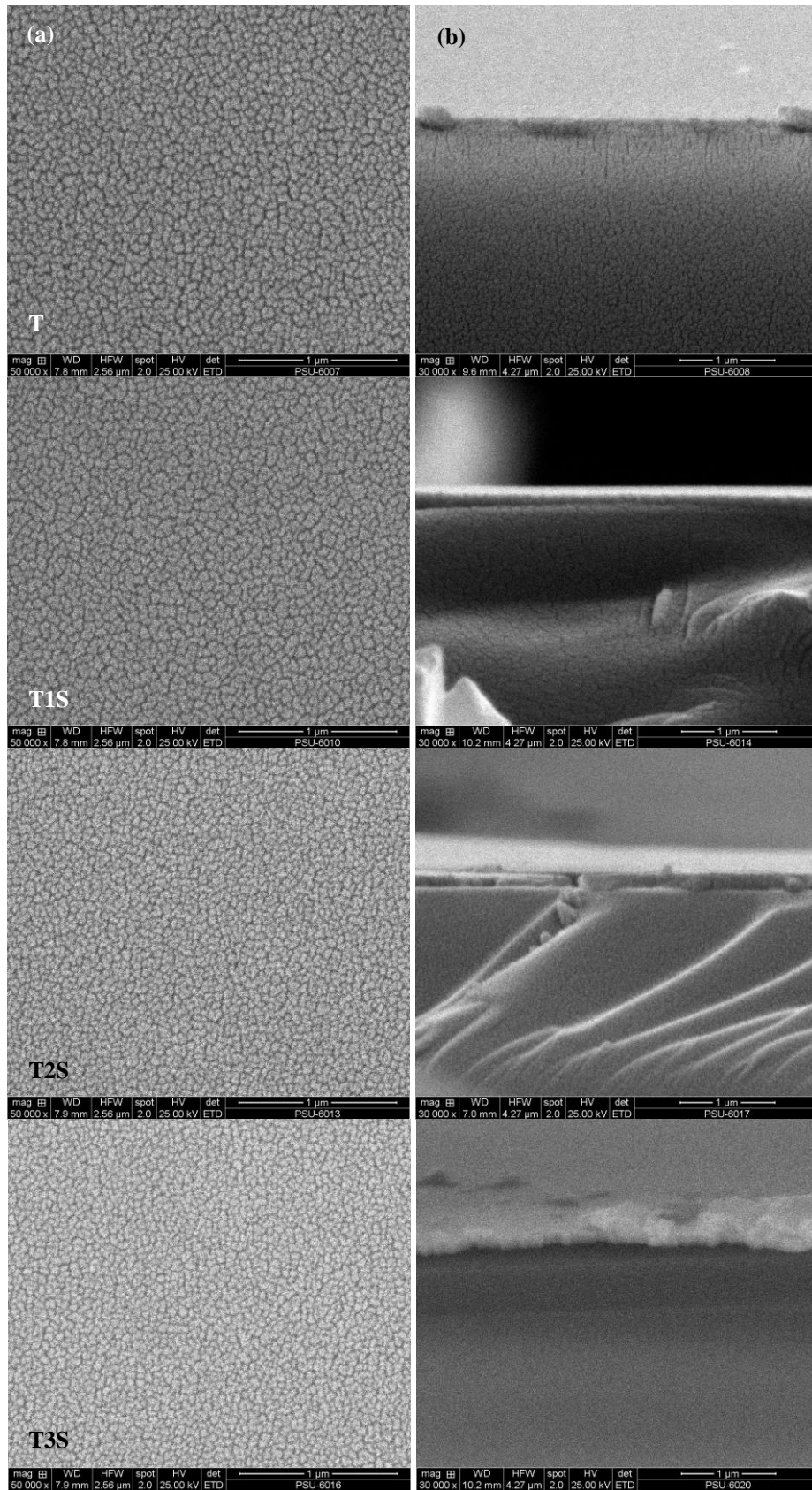
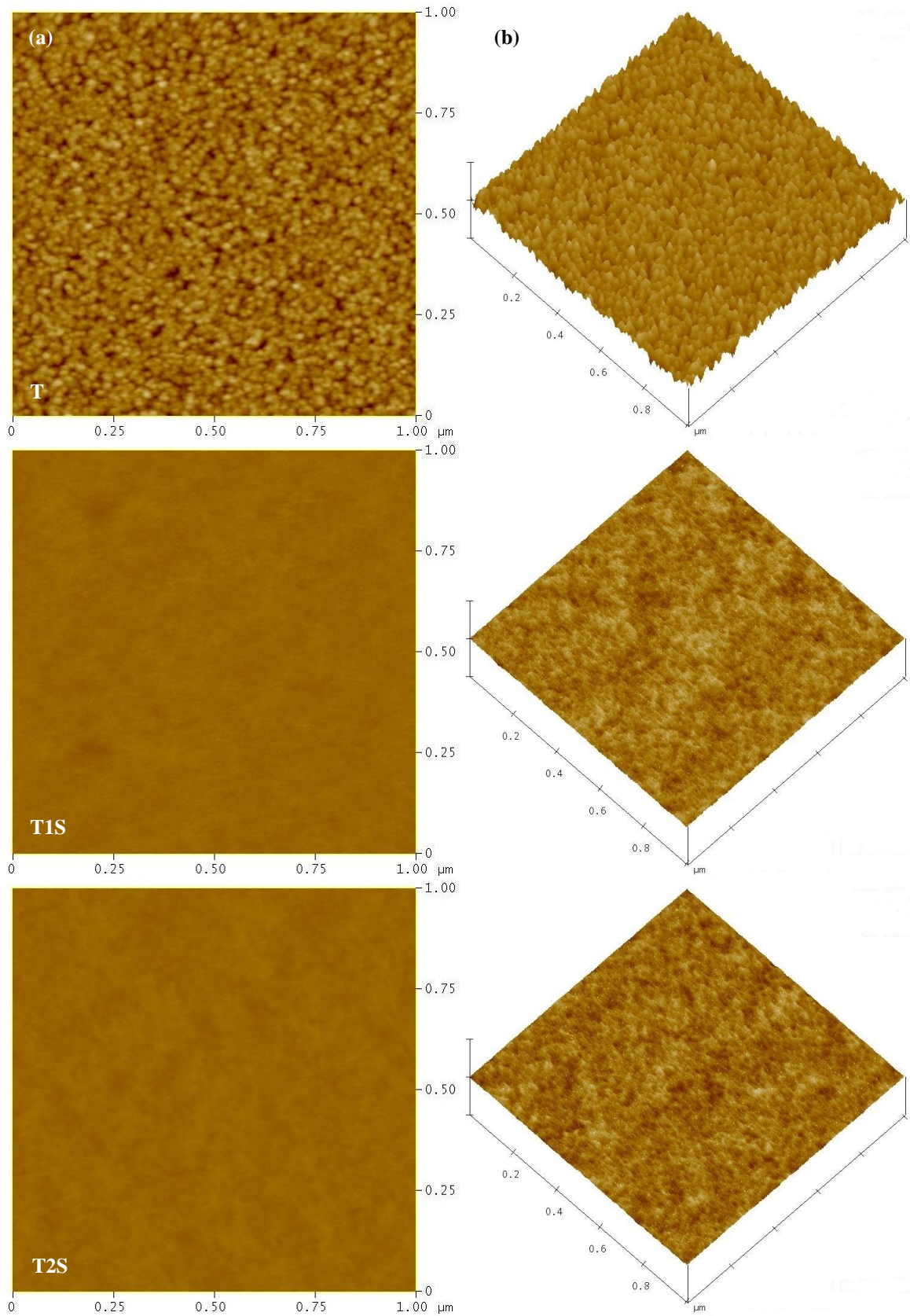


Fig. 2: The SEM images of SnO_2 doped TiO_2 thin films with (a) surface and (b) cross section



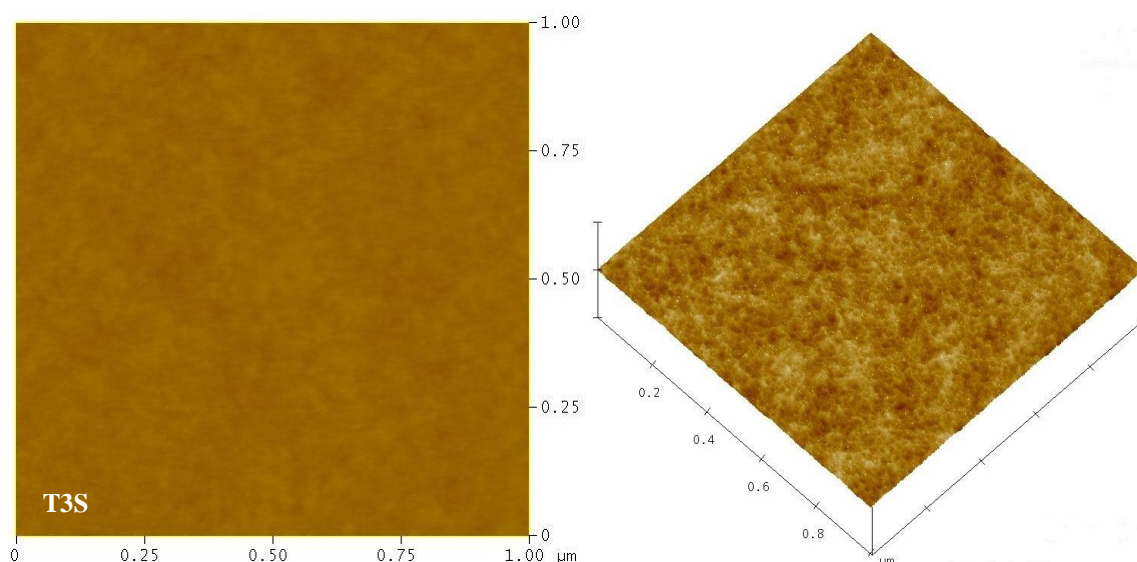


Fig. 3: The AFM images of SnO₂ doped TiO₂ thin films with (a) roughness and (b) 3D

Self-Cleaning Property:

Self-cleaning properties of thin films based on hydrophilic phenomenon can be considered in terms of contact angle of water droplets on the thin films. The contact angles of water droplets SnO₂ doped TiO₂ thin films coating on the glass substrate measured under UV irradiation for 0, 10, 20 and 30 min are shown in Table 1 and Figure 4. It was apparent that SiO₂ added in TiO₂ has significantly effect on contact angle under UV irradiation, with the contact angle decreases with increases SiO₂ doping due to have high surface roughness. We should note here that the all samples on contact angle for 30 min under UV irradiation prior to measurement. It found that the contact angle for water are 26.88°, 4.82°, 11.54° and 18.19° for the TiO₂ thin films with SnO₂ doping 0, 1, 2 and 3 mol%, respectively. It was found that TiO₂ doped with 1 mol% SiO₂ thin films show the best self-cleaning properties.

The result indicated that low doping of SiO₂ can improve the self-cleaning property of the TiO₂ thin films, most probably due to the increase of hydroxyl in the composites thin films. The image of water droplet contact angle of glass substrate and thin films (SiO₂ doping 0, 1, 2 and 3 mol%) measured during 30 min UV irradiation are illustrated in Figure 5.

Table 1: The contact angles of water droplets SnO₂ doped TiO₂ thin films coating on the glass substrate measured under UV irradiation

Sample	UV irradiation time (min)			
	0	10	20	30
T	42.03	36.69	30.26	26.88
T1S	33.98	18.21	9.56	4.82
T2S	37.92	27.52	18.44	11.54
T3S	39.28	32.81	24.67	18.19

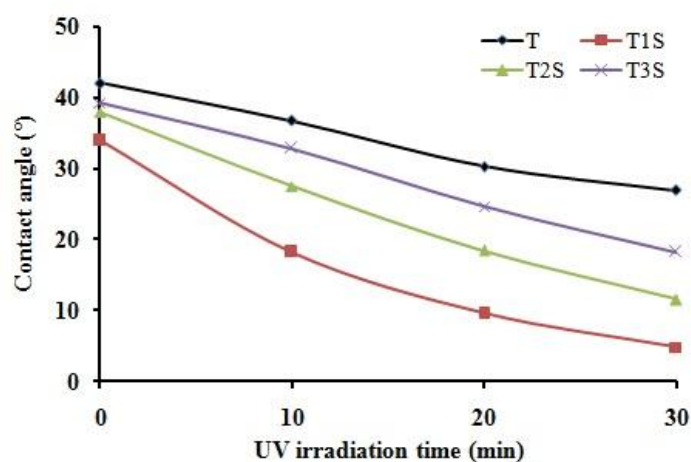


Fig. 4: The contact angles of water droplets SnO₂ doped TiO₂ thin films coating on the glass substrate measured under UV irradiation

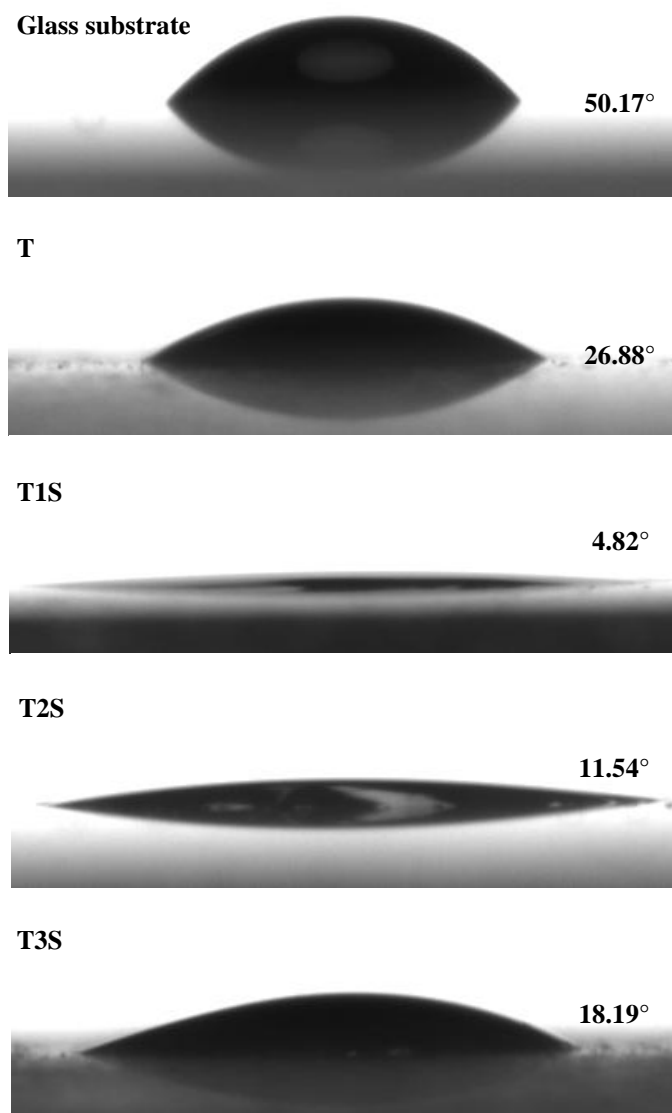


Fig. 5: The image of water droplet contact angle of glass substrate and SnO₂ doped TiO₂ thin films under with 30 min UV irradiation

Conclusion:

In this research, SiO₂ doped TiO₂ thin films were immobilized on the glass substrate using the dip coating process. The SiO₂ doped TiO₂ derived thin film has better contact angle than TiO₂ thin films, the hydrophilicity effect can show a great decrease in contact angle for TiO₂-SiO₂ surface. It was found that TiO₂ doped with 1 mol% SiO₂ thin films show the best self-cleaning properties. So, this product can be useful in exhibiting a self-cleaning effect for practical purposes such as constructional applications.

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