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Hydrophilic, self-clean and anti-fog SiO_2-TiO_2 thin film photocatalyst under visible light irradiation

Scientific research paper

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ABSTRACT

Silicon dioxide-titanium dioxide (SiO_2-TiO_2) thin films with super-hydrophilic properties and photocatalytic activity were deposited on glass substrates by a simple dip-coating method. Morphological, structural and optical properties of the SiO_2-TiO_2 thin films were characterized using field emission scanning electron microscopy (FESEM), X-Ray diffraction (XRD) patterns, and UV-Vis spectroscopy. The XRD patterns indicate decrease in the crystallite size from 51.0 nm to 22.7 nm with addition of SiO_2 to the TiO_2 structure. Moreover, the estimated band gap from optical measurements has a reduction from 3.13eV to 2.63eV for the SiO_2-TiO_2 sample. Water Contact Angle (WCA) measurements showed that SiO_2-TiO_2 thin film has super-hydrophilic property and self-cleaning, rainproof, anti-fog properties which can be effectively controlled by visible light illumination. An improved photocatalytic performance compared to TiO_2 in terms of higher efficiency (~100%) in degradation of methylene blue (MB) pollutant under visible light was achieved.

1 Introduction

Self-cleaning is an attractive property of a surface for removing the contaminants such as dirt, organic and inorganic pollutants, and microbes. The super-hydrophilic property is commonly accounted as an effective parameter for keeping the surface clean through reducing the contact angle of water to spread it thoroughly on the surface. If this property gets combined with visible photocatalytic activity, a surface with ability to be used for self-cleaning and anti-fog applications will be obtained [1-3]. Organic and inorganic pollutants in water have become serious concerns in recent decades due to their damage to environment. Dyes are accounted as important sources of water pollutions that affect human health. Methylene blue (MB) is one of the dyes which its removal by using photocatalysts has been of interest to the researchers [4,5].

Titanium dioxide (TiO_2) as a wide band gap metal oxide provides a super-hydrophilic surface with photocatalytic activity under UV illumination. Since UV radiation is harmful to the human health and covers just 4-5% of solar irradiation, application of TiO_2 is limited. Moreover, TiO_2 suffers from the rapid

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recombination of electron-hole pairs. Therefore, addition of materials in the form of elemental and composite doping like carbon (C), silver (Ag), silicon dioxide (SiO_2), and so on [6,7] for increasing the photocatalytic and super-hydrophilic properties of TiO_2 in the visible range have been reported. Ge et al. presented the fabrication of mesoporous SiO_2-TiO_2 composite for improving effective surface area of the catalyst. They used this structure for pollutant treatment and emulsion separation. The highest percentage of its photocatalytic degradation was achieved for rhodamine B dye at about 99.3% [8]. The other research group [9] suggested SiO_2/TiO_2 core/shell microspheres with sol-gel process for different shell thicknesses. The results showed the best decomposition of methyl orange in the thickness of 61 nm under UV light after 160 minutes.

Addition of SiO_2 to TiO_2 provides large specific surface area through creating suitable porous structure and reducing particle size. It also improves the light transmittance of TiO_2 which is favorable for a wide range of applications such as domestics and industry [3, 10-11]. Fateh et al. investigated the effect of adding SiO_2 into TiO_2 in the form of SiO_2-TiO_2 thin films on polycarbonate (PC) substrates for the photocatalytic activity and super-hydrophilic properties under UV light. They reported improved photocatalytic degradation for SiO_2-TiO_2 thin film compared to pure TiO_2 [1]. In these studies, the used photocatalyst based on the TiO_2 is in the form of powder. Although the powder has higher potential for photocatalytic degradation, its removal from the solution is a main issue. In addition, photocatalytic and super-hydrophilic properties of the reported structure in this research in the visible range compared to other papers is accounted as an advantage.

In the present research, SiO_2-TiO_2 thin films were deposited by a facile dip-coating method. During synthesis process, formation of Si-O-Ti bonds changes the structural and optical properties of TiO_2. These bonds cause the reduction of the crystallite size to increase the effective surface area and shift the TiO_2 band gap toward the visible spectrum through creation defects. Moreover, the acidic property of the Ti-O-Si bonds enhances density of hydroxyl radicals for improvement of the photocatalytic and super-hydrophilic properties. Therefore, this research investigates the improvement of TiO_2 photocatalytic and hydrophilicity properties by addition of SiO_2 via a simple and cost-effective method.

2 Experimental

2.1 Materials

To prepare SiO_2-TiO_2 thin films, 30 mL ethanol was mixed with 4 mL of Titanium Tetra Isopropoxide (TTIP, Merck) and nitric acid was added gradually. Then, Tetraethyl Orthosilicate (TEOS, Merck) (2.7% in volume) was added to the solution and stirred for 1 hour. Sodium Hydroxide (NaOH) and Methylene Blue (MB) were utilized for photocatalytic degradation.

2.2 preparation of SiO_2-TiO_2 thin films

The glass slides [25 mm × 75 mm × 1 mm] were immersed in the prepared solution with a speed of 1 mm/s and heated in an oven for an hour at 100 °C. At last, the samples were annealed at 500°C for another hour. The pure TiO_2 thin films were coated by the same process without addition of TEOS to the precursor solution.

2.3 Characterization

The morphology and structure of the TiO_2 and SiO_2-TiO_2 thin films were investigated by field emission scanning electron microscopy (FESEM, MIRA3 TESCAN) and X-Ray diffraction (XRD, Rigaku Ultima IV with K_α radiation (λ=1.541871 Å)), respectively. The optical properties and photocatalytic degradation were determined using a UV-Vis spectrophotometer (Ocean Optics HR4000). For evaluation of hydrophilicity, Water contact angle (WCA) was measured under visible light with a wavelength of 542.38 nm.

2.4 Photocatalytic activity

Photocatalytic activity was investigated by using Methylene Blue (MB) as a model dye compound and analyzing its absorbance spectra in the presence of samples at the wavelength of 600 nm for different periods of time. At first, the dye solution was left in the dark for 20 minutes to reach equilibrium. Then, prepared thin films were immersed into 40 ml of 10 mg/L MB solution with PH=11 under visible light irradiation.

3 Results and discussion

3.1 Structure and morphology

FESEM images in Fig. 1 show the morphology of pure TiO_2 and SiO_2-TiO_2 thin films. In the TiO_2 thin film, particles accumulate and form dispersed large particles on the surface as shown in Fig. 1a. After addition of SiO_2, the size of particles increases to form islands in some places. Figures 1c-1d displays cross section images of TiO_2 and SiO_2-TiO_2 thin films.

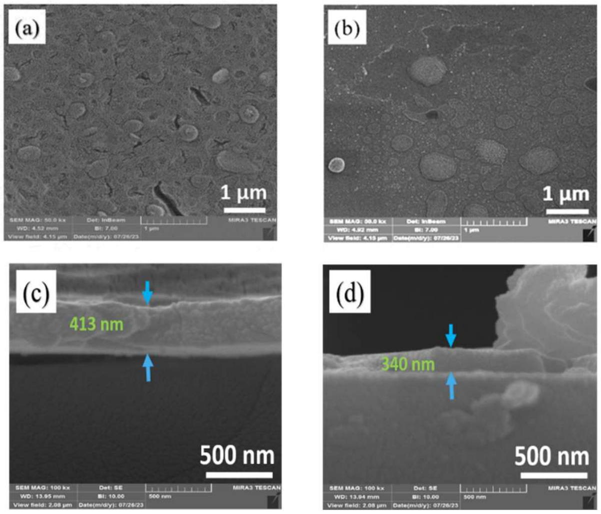


Figure 1. FESEM images of (a) TiO_2 (b) SiO_2-TiO_2 thin films and cross section images of (c) TiO_2 and (d) SiO_2-TiO_2 thin film.

The structural properties of TiO_2 and SiO_2-TiO_2 thin films were analyzed by XRD patterns in Fig. 2. According to the standard values in JCPDS card No. 9015929, the main crystalline phase in TiO_2 is anatase although the formation of rutile phase due to the presence of few peaks should be considered. After composition with SiO_2, the characteristic rutile peaks are disappeared. It is known that anatase phase shows higher photocatalytic activity. Therefore, it is expected that the addition of SiO_2 improves the photocatalytic activity of TiO_2 for degradation of dye pollutants like MB. Using Scherrer's formula [12], the crystallite size of SiO_2-TiO_2 thin film was obtained about 22.7 nm which was reduced compared to TiO_2 (i.e., 51 nm). This is due to this phenomenon that Si atoms prevent the growth of grains by entering into the crystalline lattice of TiO_2 [13]. In fact, a particle is composed of the crystallites so that if the particle is perfectly single crystallite, the crystallite size is equal to the particle size [14]. So that, the particles with the same size could be composed from crystallites with different sizes [14]. In this work, the synthesized structure is polycrystalline (as deduced from XRD), therefore increase of the particle size may be related to formation of some amorphous phases. In this structure, the intensity of XRD peaks which is indicative of crystallinity is lower which agrees well with the measured XRD results. With increasing the particle size, the probability of forming islands rises. Therefore, dispersed islands are seen on the surface of the SiO_2-TiO_2 sample in SEM images (Fig.1). According to the Bragg's relationship: $2d\sin\theta=n\lambda$, when the angle shifts towards the higher values, the distance between the crystalline planes reduces and TiO_2 structure becomes denser. As a result, crystallite size decreases. Also, presence of structural dislocations, defects and residual stress results in angle shift towards the higher values and reducing the intensities of peaks [14].

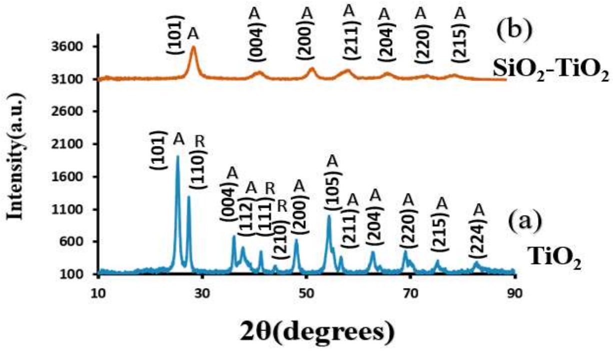


Figure 2 XRD patterns of (a) pure TiO_2 and (b) SiO_2-TiO_2 thin films.

3.2 Optical properties

Figure 3a displays the band gap energy of TiO_2 and SiO_2-TiO_2 thin films. The calculated band gap of the SiO_2-TiO_2 thin film based on Tauc's relationship [15] displays a redshift corresponding to a reduced band gap from 3.13 eV to 2.63 eV due to the introduction of Si into TiO_2 structure to create energy levels related to the defects in the band gap [8, 16] (Fig. 3a). Also, as indicated in Fig. 3b, the absorption of TiO_2 thin film in the visible range (λ>~430 nm) with the addition of SiO_2 increases. This shows the higher photo-activity of SiO_2-TiO_2 rather than TiO_2 in the visible region.

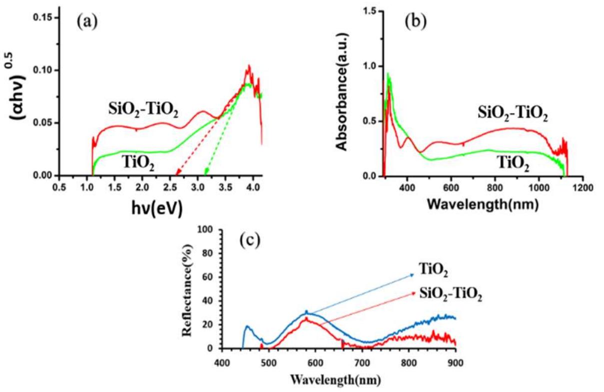


Figure 3. (a) Tauc plot, (b) absorption, (c) reflection spectra of the of TiO_2 and SiO_2-TiO_2 thin films coated on the glass substrates.

As shown in Fig. 3c, the reflectance is higher in the TiO_2 sample. Therefore, it is expected that the TiO_2 coated glass possesses lower transparency in the visible region. Decrease in the reflection of the TiO_2 coated glass surface with addition of SiO_2 is in accordance with another research [17]. Figure 4 shows that the transparency of SiO_2-TiO_2 thin films is improved compared to that of TiO_2. According to the FESEM images, large particles on the surface of TiO_2 scatter light and as a result, the transparency is reduced and the image under the pure TiO_2 thin film looks blurred.

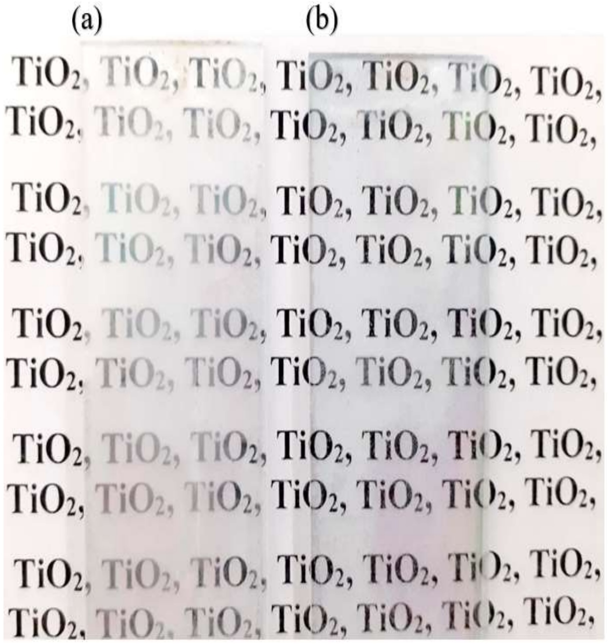


Figure 4. transparency of (a) pure TiO_2 and (b) SiO_2-TiO_2 thin film.

3.3 Photocatalytic activity and Super-hydrophilic properties

In the degradation process of pollutants with photocatalyst, active radical hydroxyl ($OH^{\cdot}$), and superoxide ($O_2^{\cdot -}$) species are formed upon reaction of photogenerated carriers with H_2O and O_2 molecules [18]. Figure 5 shows the photocatalytic degradation of MB solution by TiO_2 and SiO_2-TiO_2 samples under visible light irradiation. TiO_2 has the lower photocatalytic activity under visible light (25% decrease of MB after 210 min) because of its bandgap energy in the UV region, while SiO_2-TiO_2 sample shows a significant enhancement (100% decrease of MB after 210 min).

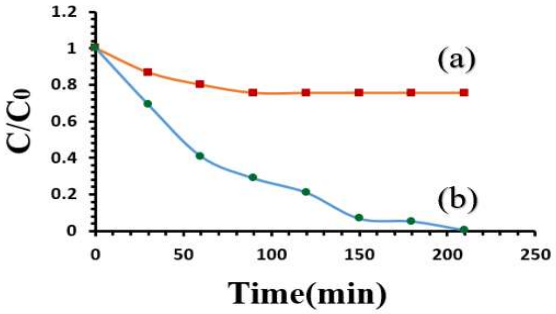


Figure 5. the photocatalytic degradation of MB solution by (a) TiO_2 and (b) SiO_2-TiO_2 samples upon visible light illumination.

Under visible irradiation, electrons in the valance band jump to the conduction band to reduce Ti^{+4} to Ti^{+3}. After the reaction of Ti^{+3} ions with oxygen molecules in the atmosphere, O_2^- and Ti^{+4} ions are prepared. Surface holes oxidize O_2^- species and form oxygen molecules which desorb from the surface. Water molecules in the atmosphere adsorb on the oxygen vacancies and decompose to OH groups on the surface to make the surface hydrophilic. Upon exposure to water droplets, these OH groups physically bond with water molecules and spread them on the surface, as described schematically in Fig. 6 [19,20]. In darkness, water contact angle increases. This results in accumulation of organic contaminants and other molecules on the surface. The SiO_2-TiO_2 structure due to the extra positive charges on the surface possesses higher acidity. Therefore, adsorbed OH groups on the surface may be retained hydrophilic state for a long time without light [21].

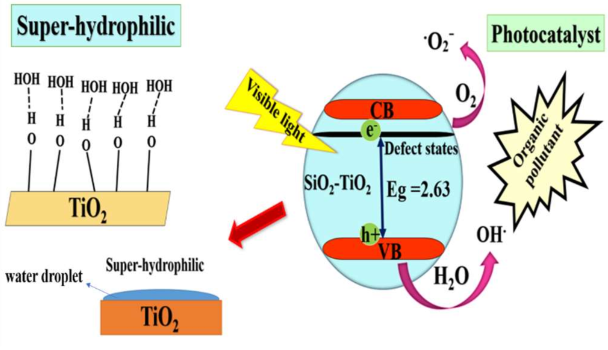


Figure 6. The photocatalytic and super-hydrophilic mechanism of SiO_2-TiO_2.

According to Table.1, with light illumination, WCA quickly approaches to zero degree and this super-hydrophilic property is remained to a large extent even after turning light off.

The super-hydrophilic property of the surface can increase attraction of the liquid solution for removing dirt and degradation of dye pollutants effectively. The self-cleaning property was measured by wetting bare and SiO_2-TiO_2 coated glass slides covered by ash particles, as seen in Fig. 7. The strong adhesion between water droplets and the SiO_2-TiO_2 coated sample caused the droplets to spread on the surface and make a slippery surface under the ash. In this way, ash particles are lifted and removed from the surface effectively compared to the uncoated sample.

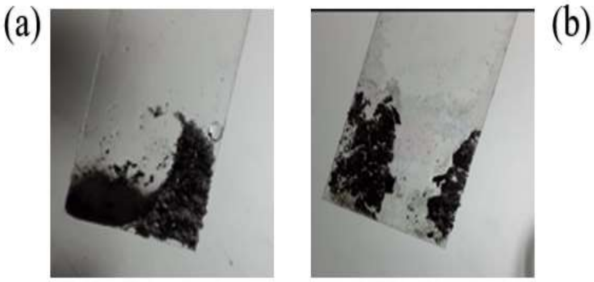


Figure 7. Self-cleaning of (a) bare glass and (b) SiO_2-TiO_2 coated glass.

Table 1. water contact angle measurement.

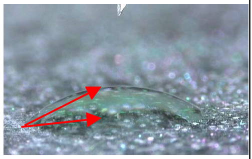
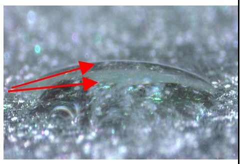
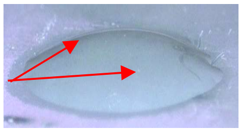
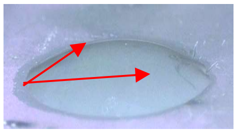
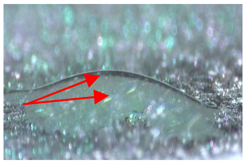
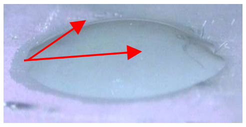
	t=0	t=2 h visible light
SiO_2-TiO_2	 4°	 1°
TiO_2	 8°	 7°
	t=2 h dark	
SiO_2-TiO_2	 2°	
TiO_2	 7°	

Figure 8 displays rainproof performance for glass substrate and SiO_2-TiO_2 thin films. In Fig. 8a large droplets on the bare glass substrate create the blurry view due to light scattering. However, water droplets on the surface of the super-hydrophilic SiO_2-TiO_2 coated sample come together and form a transparent thin layer. This is due to this phenomenon that water droplets on a hydrophilic surface can spread easily. Therefore, this water thin layer does not affect largely the transparency of the SiO_2-TiO_2 coated glass sample (Fig. 8b). In some researches, this experiment has been conducted under dangerous UV light for long periods of time [1].

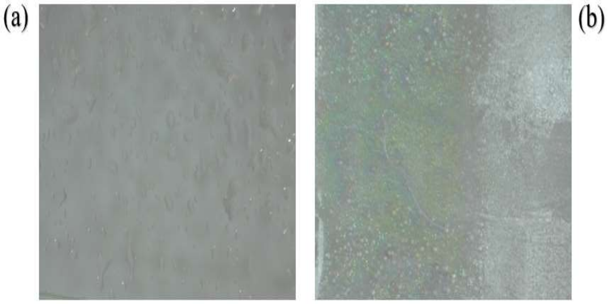


Figure 8. rainproof property of (a) the bare glass and (b) SiO_2-TiO_2 coated glass.

Figure 9 shows the formation of fog on the bare glass and coated glass. The large droplets appear on the bare glass in Fig. 9a which scatter the incident light and decrease the transparency of the glass substrate. The super-hydrophilic surface of SiO_2-TiO_2 thin films spreads the fog droplets like a thin layer (Fig. 9b).

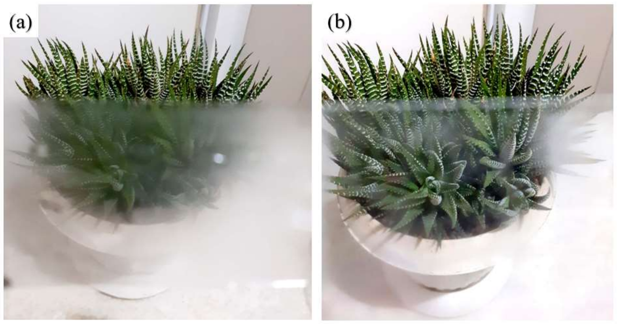


Figure 9. anti-fog property of (a) the bare glass and (b) SiO_2-TiO_2 coated glass.

4 Conclusions

A self-cleaning, anti-fog and rainproof coating was prepared through deposition of SiO_2-TiO_2 thin film on the glass substrates by a dip-coating method. According to the XRD patterns, with addition of SiO_2 to TiO_2 the crystallite size was reduced from 51.0 nm to 22.7 nm and active anatase phase of TiO_2 became dominant. Also, the band gap reduces from 3.13 eV to 2.63 eV and shifts it toward the visible spectrum. The degradation of MB dye pollutant solved in water by SiO_2-TiO_2 samples was investigated under visible light and compared to TiO_2 samples. In addition to the higher photocatalytic efficiency (100% degradation of 10 mg/L MB after 210 min), super- hydrophilicity, self-cleaning, anti-fog and rainproof properties were achieved for the deposited SiO_2-TiO_2 thin films.

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