

Enhanced the hydrophobic surface and the photo-activity of TiO₂-SiO₂ composites

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Abstract. The aim of this research is to develop nanomaterials for coating applications. This research studied the effect of various TiO₂-SiO₂ composites in acrylic paint to enhance the hydrophobic properties of the substrate. Titanium dioxide containing silica in the range 20–35 mol% has been synthesized using sol–gel route. The XRD's spectra show that increasing SiO₂ content in the composite, decreasing its crystalline properties but increasing the surface area. TiO₂-SiO₂ composite was dispersed in acrylic paint in 2% composition by weight. The largest contact angle was 70, which produced by the substrate coated with TS-35-modified acrylic paint. This study also investigated the enhanced photo-activity of TiO₂-SiO₂ modified with poly-aniline. The XRD spectra show that the treatment does not change the crystal structure of TiO₂. The photo-activity of the composite was evaluated by degradation of Rhodamine-B with visible light. The best performance of the degradation process was handled by the composite treated with 0.1mL anilines per gram of TiO₂-SiO₂ composite (TSP-A). On the other side, the contact angle 70 has not shown an excellent hydrophobic activity. However, the AFM spectra showed that nanoroughness has started to form on the surface of acrylic paint modified with TiO₂-SiO₂ than acrylic alone.

1. Introduction

The photo-catalytic property of nano-crystalline TiO₂ has been explored by many researchers as high-technology applications [1–2]. Titanium dioxide (TiO₂), also known as titania, is well known for physical and chemical stability [3], non-toxicity, low cost and less photo-corrosion [4]. Thus, titania has become a perfect choice for self-cleaning surfaces that leads to a large scale commercialisation of such products [5]. A common and simple method for preparing TiO₂ is the sol-gel method. The Addition of another oxide as dopants such as SiO₂ [6-7], to titania matrix has been found to further modify the photo-catalytic property of this material. The Addition of silica also enhances the thermal stability of the anatase phase by delaying the transformation to rutile by inhibiting the growth of titania particles. Most of the earlier work reported on titania-silica are about the ones synthesized from alkoxide precursors.

The wet ability of solid surfaces is a very important property governed by both the chemical composition and the geometric features of the surfaces. A surface with water contact angle (CA) greater than 90° is usually referred to as hydrophobic, and one with water CA higher than 140° is qualified as ultra-hydrophobic. The surfaces with very high water contact angles, particularly greater than 150°, are usually called super-hydrophobic surfaces, which have been extended to more



applications. Current applications for self-cleaning paints involve two types of approaches: super-hydrophobicity and super-hydrophilicity [8]. In the former, liquid water forms spherical droplets that roll down the surface carrying dirt deposited on the surface. Both, hydrophilic and hydrophobic surfaces exhibit self-cleaning property through the nature of the interaction of water on the surface, the former by rolling droplets and the latter by sheeting water that carries away dirt. Hydrophobic self-cleaning has very interesting aspects. A self-cleaning surface requires high static contact angle, $\theta_s > 90^\circ$ and a minimum inclination angle for the drop to roll off the surface [9].

Here we report, a simple sol-gel method to synthesize high temperature stable photoactive $\text{TiO}_2\text{-SiO}_2$ system, useful in the preparation of coatings on various substrates. Titania sol and silica sol were prepared separately through sol-gel route which was then mixed for getting different $\text{TiO}_2\text{-SiO}_2$ compositions [10]. The Hydrophobic property of $\text{TiO}_2\text{-SiO}_2$ nanoparticles in the water-based acrylic coating was evaluated. $\text{TiO}_2\text{-SiO}_2$ nanoparticles were then modified with aniline to form $\text{TiO}_2\text{-SiO}_2\text{-Pani}$. The photo-catalytic activity of $\text{TiO}_2\text{-SiO}_2\text{-Pani}$ was evaluated by decomposing Rhodamine-B dye stuff as a model. The main application of photo-catalytic activity in organic coatings is in the decomposition of organic contaminants of water and air [11]. Illuminated anatase TiO_2 also exhibited super-hydrophilic properties, which were exploited for various applications such as self-cleaning, anti-fogging and antimicrobial effects in coatings [12-13].

2. Experiment

2.1. Material and Methods:

The chemicals used in this study were titanium tetra-isopropoxide (TTIP, 97%, Sigma-Aldrich) as a titanium precursor, tetra-ethyl ortho-silicate (TEOS, 98%, E-Merck) as silica source, NH_3 (25 wt%, E-Merck), and anhydrous ethanol ($\text{C}_2\text{H}_5\text{OH}$, E-Merck), Aniline (E-Merck), acrylic paint.

2.2. General Procedure

2.2.1 Synthesis of $\text{TiO}_2\text{-SiO}_2$ (TS) composite. The $\text{TiO}_2\text{-SiO}_2$ (TS) composite was prepared by the following method. In the synthesis of Sol A, TTIP was used as a precursor and was mixed with ethanol, aqueous of 0.1 M HCl solution and deionized water in the volume ratio 1:2:2:2, respectively. The mixture was stirred for an hour and maintained in the pH range from 1 to 2. In Sol B, TEOS was mixed with 40 mL ethanol under a nitrogen atmosphere and stirred for an hour. Sol A was then added into Sol B, and the mixture was stirred for 3 h at 60°C [14]. The aqueous solution of PVA (1 %) was added to the above mixture at the rate of 0.5 mL/min and was stirred for 2 h. The gel was dried at room temperature. Finally, the mixture was heated at 120°C for an hour. The powder was calcined at 500°C for 3 hours. The composite produced was denoted as TS.

2.2.2 Preparation of $\text{TiO}_2\text{-SiO}_2$ (TS) mixed with acrylic. 0.5 g of $\text{TiO}_2\text{-SiO}_2$ nanoparticles (1 mol %) were directly added to the 25 ml distilled water and dispersed using ultrasonic irradiating for 20 min. The dispersions were then added to the 25 g emulsion resins and 0.5 g coalescing agent, mixed for further 60 min at a constant rate [15]. Coating samples with a wet thickness of $200 \pm 5 \mu\text{m}$ were applied on the acrylic substrate using a film applicator. The applied films were then allowed to dry at $23 \pm 2^\circ\text{C}$ for about a week. These films were further used to investigate the structural, morphological, and wetting properties by contact angle measurement [16].

2.2.3 Preparation of $\text{TiO}_2\text{-SiO}_2\text{-Polianiline}$. $\text{TiO}_2\text{-SiO}_2$ nanoparticles (1 g) were dispersed in 190 ml of HCl aqueous solution (1.21 M) containing 0.3 ml aniline under ultrasonic vibration to reduce the aggregation of $\text{TiO}_2\text{-SiO}_2$ nanoparticles. APS (0.863 g) was dissolved in 15 ml of HCl aqueous solution (1.21 M) and added drop-wise to the solution containing aniline monomer under constant stirring [17]. The mixture was allowed to polymerize under stirring for 5 h at room temperature. The Reaction mixture was filtered under vacuum and washed with ethanol and water and then dried at 60°C for 24 h to obtain PANI emeraldine salt (ES) as a green powder.

2.2.4 Evaluation of Photo-catalysis. The photo-catalytic activity of TiO_2 and $\text{TiO}_2\text{-SiO}_2\text{-Pani}$ nanocomposite was evaluated by determining the Rhodamine-B photo-degradation. The aqueous solutions of Rh-B were used as a model pollutant for investigation of the photo-catalytic activity of samples. 50 mg of TiO_2 or $\text{TiO}_2\text{-SiO}_2\text{-Pani}$ photo-catalysts was added to 50 ml of Rh-B aqueous solution ($10 \text{ mg}\cdot\text{L}^{-1}$) under magnetic stirring. The suspension was stirred in dark condition at room temperature (25°C) for 30 min to achieve adsorption equilibrium for Rh-B[18]. Afterward, the suspension was illuminated by a 100 W linear Xenon lamp for 80 min. Samples are collected once every 20 min, and the concentration of the Rh-B was determined using UV–Vis spectrometer. To quantify the concentration of rhodamine B, the UV–vis spectrometer was calibrated to a concentration range between 2 mg/L – 10 mg/L at a wavelength of 554 nm, which corresponds to the absorption maximum of RB.

2.3. Characterization

The roughness of the films (coating) was characterized using atomic force microscope (Park System XE-70 Non-contact). The tapping mode was selected during analysis at an analytical range of 5mm. Transmission electron microscopy (TEM) study was carried out using a JEOL JEM-1400. The samples of TEM were prepared by dispersing the final nanoparticles in ethanol; the suspension was then dropped on carbon-copper grids. Fourier-transform infrared spectra (FT-IR) of the samples were recorded on a spectrometer (SHIMADZU) in the range of $400\text{--}4000 \text{ cm}^{-1}$. Measurements were performed in the transmission mode in spectroscopic grade KBr pellets for all the powders. The composites X-ray diffraction (XRD) patterns were performed in the range of $2\theta = 10\text{--}90^\circ$ on a SHIMADZU diffractometer, using Cu Ka radiation ($\lambda = 0.15406 \text{ nm}$) as an X-ray source, operated at 40 kV and 30mA. Crystallite size of anatase TiO_2 can be calculated from the line broadening by Scherer's formula.

3. Results and Discussion

3.1. X-Ray Diffraction (XRD)

Figure 1 shows the XRD patterns of SiO_2 , TiO_2 , nanosized $\text{TiO}_2\text{-SiO}_2$ (with varying weight percentage of SiO_2), and $\text{TiO}_2\text{-SiO}_2\text{-Pani}$ (TSP) samples. All were calcined under the same condition in air at 500°C for 3 h. TiO_2 and nanosized $\text{TiO}_2\text{-SiO}_2$ showed a clear anatase-type crystal structure. The sharp peak and strong intensities indicated that crystallization was present, and the higher the percentage of TiO_2 gave the higher intensity of peaks. The peak associated with SiO_2 show that it is an amorphous form of silica. There is no difference between the XRD pattern of $\text{TiO}_2\text{-SiO}_2\text{-Pani}$ and XRD pattern of pristine TiO_2 nanoparticles, which reveals deposition of PANI on the surface of $\text{TiO}_2\text{-SiO}_2$ nanocomposites which has no effect on the crystallinity of TiO_2 nanoparticles. Therefore, the polymorph of TiO_2 in the $\text{TiO}_2\text{-SiO}_2\text{-Pani}$ nanocomposite is still anatase [18]. The crystallite sizes of Titania, TS, and TSP are listed in table 1.

Table 1. The crystallite size and BET surface area of TiO_2 , TS, and TSP

Composite/nanoparticle	Crystallite size (nm)	Surface area (BET) m^2/g
TiO_2	19.57	98.0
TS-20	16.17	113.2
TS-25	15.53	184.4
TS-30	13.90	194.4
TS-35	11.90	214.8
TSP	21.13	-

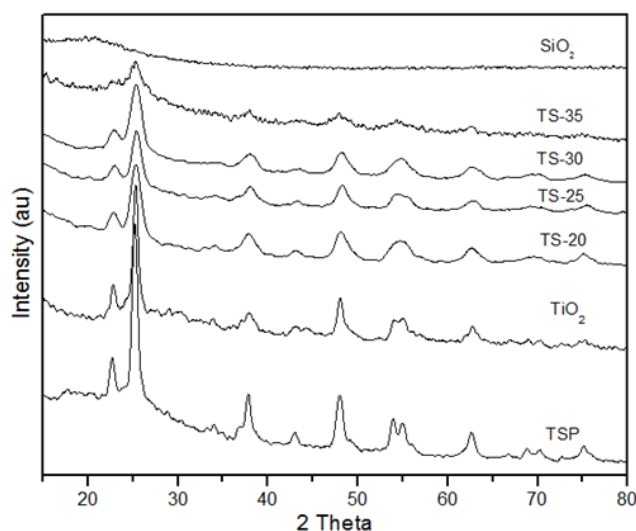


Figure 1. The XRD patterns of TiO_2 , TS, and TSP

3.2. Infrared Spectra

The FT-IR spectra of pure titania and all the titania-silica samples calcined at 500 °C in the wavenumber range 4000–400 cm^{-1} is presented in figure 2. IR of pure silica was also taken for comparison. The absorption bands at around 3,440 and 1,635 cm^{-1} observed in all spectra are attributed to the stretching mode of water and hydroxyl group [6]. The peak around 1,080 cm^{-1} and 455 cm^{-1} in the case of silica added sample correspond to the asymmetric stretching vibration of Si–O–Si [19]. The peak at 950 cm^{-1} corresponding to the vibration of Si–O–Ti confirmed the formation of Si–O–Ti inorganic network between SiO_2 and TiO_2 [10, 19] in TS-30 sample. After TS composites mixed with acrylic paint, the general structure of the paint did not change sharply. This can be seen in figure 3.

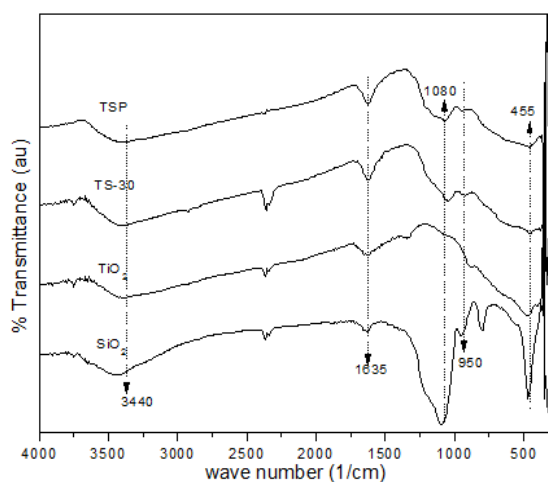


Figure 2. Spectra of TiO_2 , SiO_2 , TS, and TSP.

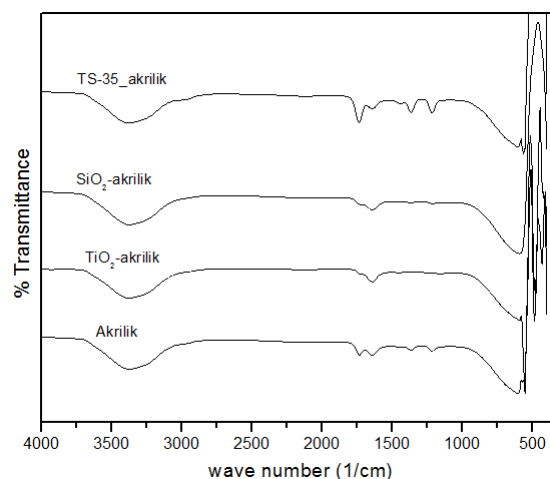


Figure 3. Spectra of acrylic, TiO_2 -acrylic, SiO_2 -acrylic, and TS-35-acrylic

3.3. Contact Angle Measurement

Static Contact Angle measurements performed on a solid surface without irradiation. Results of static contact angle measurements are shown in table 2 below. For the measurement of static water contact angle, acrylic paint- TiO_2 - SiO_2 particles dispersed in the acrylic solvent and distributed on an acrylic

substrate with a lateral size of $2\text{ cm} \times 2\text{ cm}$. A droplet of distilled water with a volume of $3\text{ }\mu\text{L}$ was deposited on the sample surface. For each sample, the water contact angle was measured twice after dropping and the average value was recorded [20].

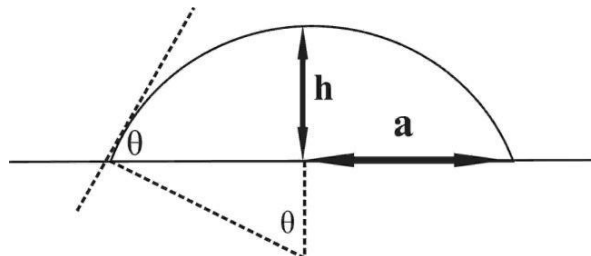
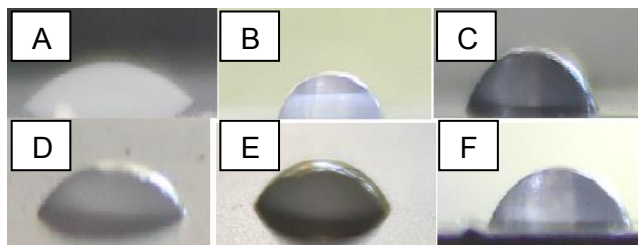


Figure 4. Water droplets photo

The amount of nanoparticle or nanocomposite (TiO_2 , SiO_2 , and $\text{TiO}_2\text{-SiO}_2$) in the acrylic paint is 2% by weight. The influence of the amount of composites in the acrylic paint has not been presented in this paper. The results of water contact angle measurements showed that the surface paint had not shown the hydrophobic nature because the contact angle is smaller than 90° . The variation of mixed $\text{TiO}_2\text{-SiO}_2$ also influence to the contact angle magnification. Coating the surface with a $\text{TiO}_2\text{-SiO}_2$ modified acrylic paint has not given satisfactory results as the coating by PDMS reported by Kim, *et al.*, [20]. Kim, *et al.*, [20] report that PDMS-coating was resistant toward photo-catalytic decomposition: the very high water contact angle of the PDMS-coated TiO_2 was sustained with time, and no CO_2 evolution occurred in the presence of UV light.

Table 2. Static Water Contact Angle of the composite

sample	Contact angle
Acrylic (A)	46.65
Acrylic- SiO_2 (B)	67.65
Acrylic- TiO_2 (C)	72.94
Acrylic-TS-35 (F)	70.02
Acrylic-TS-25 (E)	64.43
Acrylic-TS-15 (D)	60.68

3.4. Atomic Force Microscope

The roughness of the coating surface was characterized using atomic force microscope (Park system XE-70 Non-contact). Hydrophobic surfaces with static contact angle $\theta_s > 150^\circ$ are usually developed by the combination of surface roughing and lowering of surface energy [21]. Figure 5 shows the coating surface with the widest nanoroughness is figure 5b, and followed by figure 5c and 5a.

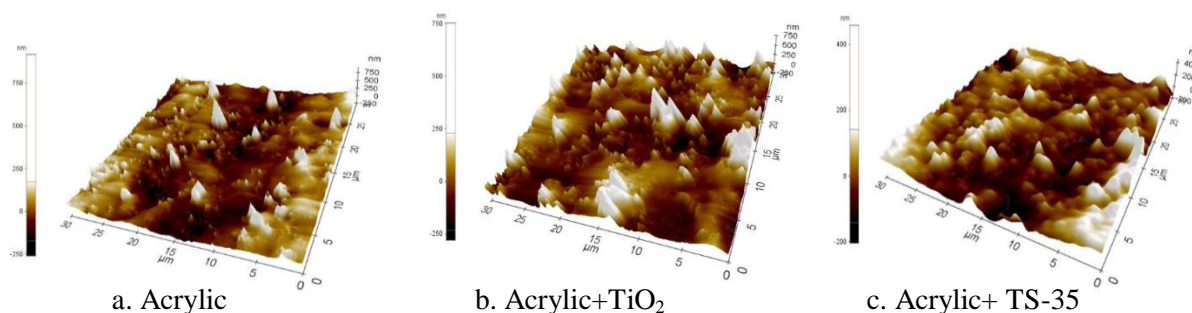


Figure 5. AFM spectra of acrylic, acrylic+ TiO_2 , acrylic+TS-35

3.5. Photo-degradation of Rhodamine-B

In addition to developing nanocomposite polymers to obtain material that has good hydrophobic properties, this study also developed a nanocomposite polymer having qualified photo-catalytic properties. The material that absorbed light of a broad wavelength becomes more effective and efficient. A mixed oxide $\text{TiO}_2/\text{SiO}_2$ is a more efficient photo-catalyst for the degradation of methylene blue than TiO_2 alone [18]. The PANI/ TiO_2 core-shell nanocomposite showed better photo-catalytic activity for Me-O photo-degradation in aqueous solution compared to the pristine TiO_2 nanoparticles under both UV and visible light illuminations [17]. This research studies the possibility of enhancement in the photo-catalytic performance of TiO_2 - SiO_2 composite if modified with PANI. One of the possible reasons for the improvement of PANI/ TiO_2 photo-catalytic activity under both UV and visible light illuminations is the reduced aggregation state of TiO_2 nanoparticles in PANI/ TiO_2 nanocomposite [17]. Therefore, adsorption of dye molecules on the nanocomposite is higher than pristine TiO_2 nanoparticles. Both PANI and TiO_2 nanoparticles absorb photons at their interface under irradiation. Since the CB (conduction band) of TiO_2 and lowest unoccupied molecular orbital (LUMO) of PANI are well matched for the charge transfer, the electrons generated by PANI $\pi \rightarrow \pi^*$ transition under visible light illumination can be injected into the CB of TiO_2 and the electrons in the VB of TiO_2 are delivered to PANI layer [22]. Under UV light illumination, photo-generated holes in the VB of TiO_2 can be transferred directly to highest unoccupied molecular orbital (HOMO) of PANI, as the Valence Band of TiO_2 matches well with the HOMO of PANI [17].

Figure 6 shows the photo-catalytic performance of TiO_2 - SiO_2 -Pani (TSP) for decomposing Rhodamine-B in aqueous solution.

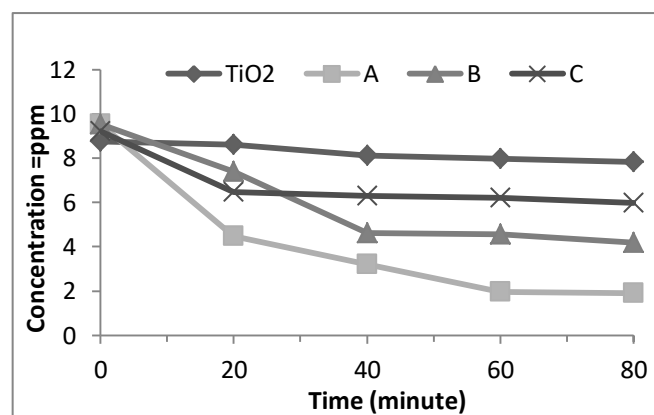


Figure 6. The photocatalytic performance of TiO_2 and TSP composites

Table 3. Percent degradation of Rh-B vs. Time

Time (minute)	TiO_2 (%)	TSP-A(%)	TSP-B(%)	TSP-C(%)
0	9.23	2.25	2.19	5.39
20	10.89	54.25	24.26	33.60
40	15.96	67.05	52.51	35.42
60	17.52	79.89	53.33	36.16
80	18.86	80.41	56.97	38.76

4. Conclusions

SiO₂-TiO₂ mixed sols of different compositions was prepared through sonication technique route which was further used for coating with acrylic paint as a matrix binder. The crystallite size obtained showed that addition of silica had prevented the grain growth of TiO₂ considerably. The hydrophobic activity studies showed that the optimum composition for getting the largest contact angle is around 30 mol% SiO₂ added TiO₂. This optimum composition with acrylic paint as a matrix binder only produces a contact angle of about 70. The contact angle of this magnitude has not been enough for the hydrophobic criteria. In this study revealed that the modified acrylic paint with SiO₂-TiO₂ nanocomposite 2% by weight is not enough to produce a hydrophobic surface with a contact angle greater than 90. The poor results may be caused by the poor nanoscale roughness at the surface paint and by the improper composition of TiO₂-SiO₂ nanocomposite with acrylic paint. In the application as a photo-catalyst, TiO₂-SiO₂ nanocomposite modified by PANI showed photo-catalytic performance in the visible light region. The optimum photo-catalytic performance obtained at the addition of aniline 0.1mL for each gram of TiO₂-SiO₂ (TSP-A) which decompose Rhodamine-B by 80.41%.

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