Enhanced the hydrophobic surface and the photo-activity of TiO$_2$-SiO$_2$ 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 TiO$_2$-SiO$_2$ 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 SiO$_2$ content in the composite, decreasing its crystalline properties but increasing the surface area. TiO$_2$–SiO$_2$ 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 TiO$_2$-SiO$_2$ modified with poly-aniline. The XRD spectra show that the treatment does not change the crystal structure of TiO$_2$. 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 TiO$_2$-SiO$_2$ 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 TiO$_2$-SiO$_2$ than acrylic alone.

1. Introduction

The photo-catalytic property of nano-crystalline TiO$_2$ has been explored by many researchers as high-technology applications [1–2]. Titanium dioxide (TiO$_2$), 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 TiO$_2$ is the sol-gel method. The Addition of another oxide as dopants such as SiO$_2$ [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, $\theta > 90^\circ$ 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 TiO$_2$-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 TiO$_2$-SiO$_2$ compositions [10]. The Hydrophobic property of TiO$_2$-SiO$_2$ nanoparticles in the water-based acrylic coating was evaluated. TiO$_2$-SiO$_2$ nanoparticles were then modified with aniline to form TiO$_2$-SiO$_2$-Pani. The photo-catalytic activity of TiO$_2$-SiO$_2$-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 (C$_2$H$_5$OH, E-Merck), Aniline (E-Merck), and acrylic paint.

2.2. General Procedure

2.2.1 Synthesis of TiO$_2$-SiO$_2$ (TS) composite. The TiO$_2$-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 TiO$_2$-SiO$_2$ (TS) mixed with acrylic. 0.5 g of TiO$_2$-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 ± 5 μm were applied on the acrylic substrate using a film applicator. The applied films were then allowed to dry at 23 ± 2 °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 TiO$_2$-SiO$_2$-Polianiline. TiO$_2$-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 TiO$_2$-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 TiO$_2$-SiO$_2$-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 TiO$_2$-SiO$_2$-Pani photo-catalysts was added to 50 ml of Rh-B aqueous solution (10 mg·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 400–4000 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 20 = 10–90° on a SHIMADZU diffractometer, using Cu Ka radiation (l = 0.15406 nm) as an X-ray source, operated at 40 kV and 30 mA. 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 TiO$_2$-SiO$_2$, and TiO$_2$-SiO$_2$-Pani (TSP) samples. All were calcined under the same condition in air at 500°C for 3 h. TiO$_2$ and nanosized TiO$_2$-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 TiO$_2$-SiO$_2$-Pani and XRD pattern of pristine TiO$_2$ nanoparticles, which reveals deposition of PANI on the surface of TiO$_2$-SiO$_2$ nanocomposites which has no effect on the crystallinity of TiO$_2$ nanoparticles. Therefore, the polymorph of TiO$_2$ in the TiO$_2$-SiO$_2$-Pani nanocomposite is still anatase [18]. The crystallite sizes of Titania, TS, and TSP are listed in table 1.

| 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                 | -                         |

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.

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 cm × 2 cm. A droplet of distilled water with a volume of 3 μL 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].

![Water droplets photo](image)

**Figure 4.** Water droplets photo

The amount of nanoparticle or nanocomposite (TiO$_2$, SiO$_2$, and TiO$_2$-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 TiO$_2$-SiO$_2$ also influence to the contact angle magnification. Coating the surface with a TiO$_2$-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.

| 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         |

**Table 2.** Static Water Contact Angle of the composite

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 roughening 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.

![AFM spectra](image)

**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 TiO$_2$/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.

![Graph showing photo-catalytic performance of TiO$_2$ and TSP composites](image)

**Figure 6.** The photocatalytic performance of TiO$_2$ and TSP composites

| 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

SiO$_2$-TiO$_2$ 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 TiO$_2$ considerably. The hydrophobic activity studies showed that the optimum composition for getting the largest contact angle is around 30 mol% SiO$_2$ added TiO$_2$. 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 SiO$_2$-TiO$_2$ 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 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 TiO$_2$-SiO$_2$ (TSP-A) which decompose Rhodamine-B by 80.41%.

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