

SYNTHESIS AND CHARACTERIZATION OF SUPERHYDROPHILIC SELF-CLEANING FILM BASED ON $\text{TiO}_2/\text{SiO}_2$ COMPOSITE FOR PHOTOVOLTAIC APPLICATIONS

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ARTICLE INFO	ABSTRACT
Received: 17/9/2022	Transparent, superhydrophilic materials in photovoltaic (PV) applications are indispensable for their self-cleaning function, which can protect the solar cell and raise the efficiency of solar modules. This study presented the synthesis and fabrication of $\text{TiO}_2/\text{SiO}_2$ films by the dip-coating method of sol-gel solutions on glass. The $\text{TiO}_2/\text{SiO}_2$ composites containing different SiO_2 contents were characterized by XRD and FTIR. The transparency and hydrophilic properties of the films were investigated by UV-vis and WCA. TiO_2 sol was mixed with SiO_2 sol by differing $\text{TiO}_2/\text{SiO}_2$ ratios of 1/3, 1/1, and 3/1. The best $\text{TiO}_2/\text{SiO}_2$ coating with the ratio of 1/3 was attained on the glass surface after calcining the template at 400 °C. The maximum transmittance of this film reached ~93.0%, and the film surface showed an excellent super-hydrophilicity with WCA $\approx 4.7^\circ$. The results revealed that this composite material would be a promising candidate for the self-cleaning applications of solar module surfaces.
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TỔNG HỢP VÀ ĐÁNH GIÁ MÀNG VẬT LIỆU $\text{TiO}_2/\text{SiO}_2$ TỰ LÀM SẠCH, SIÊU THẤM NƯỚC ỨNG DỤNG TRONG LĨNH VỰC ĐIỆN MẶT TRỜI

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THÔNG TIN BÀI BÁO	TÓM TẮT
Ngày nhận bài: 17/9/2022	Việc nghiên cứu vật liệu có độ truyền qua cao và có tính siêu ưa nước ứng dụng cho lĩnh vực điện mặt trời là nhằm mục đích bảo vệ bề mặt của tấm pin, duy trì hiệu suất quang điện và giảm chi phí bảo dưỡng cho hệ thống. Bài báo này trình bày quá trình tổng hợp vật liệu kết hợp $\text{TiO}_2/\text{SiO}_2$ bằng phương pháp sol-gel và chế tạo màng vật liệu kết hợp này trên nền kính bằng phương pháp phủ nhúng. Phương pháp XRD, FTIR, UV-vis và WCA được sử dụng để đánh giá ảnh hưởng của hàm lượng SiO_2 trong vật liệu kết hợp $\text{TiO}_2/\text{SiO}_2$ lên tính chất trong suốt và tính ưa nước của tấm kính được phủ màng vật liệu kết hợp. Tỷ lệ $\text{TiO}_2/\text{SiO}_2$ trong nghiên cứu này là 1/3, 1/1 và 3/1. Kết quả phân tích cho thấy tấm kính được phủ bởi vật liệu kết hợp $\text{TiO}_2/\text{SiO}_2$ tỷ lệ 1/3 tại nhiệt độ thiêu kết 400°C cho kết quả tốt nhất với độ truyền qua đạt tới ~93,0%, đồng thời bề mặt có tính chất siêu ưa nước với WCA $\approx 4,7^\circ$. Với tính chất siêu ưa nước tốt và độ truyền qua cao, vật liệu kết hợp $\text{TiO}_2/\text{SiO}_2$ có tiềm năng lớn trong các ứng dụng tự làm sạch cho bề mặt tấm pin năng lượng mặt trời.
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TỪ KHÓA	
Siêu ưa nước	
Tự làm sạch	
Xúc tác quang	
Phương pháp sol-gel	
Pin mặt trời	

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1. Introduction

Solar energy is currently one of the most important renewable energy sources because of its unlimited source of energy, carbon-free energy source, and easy conversion of solar energy into electricity. A huge amount of energy per day from the sun sends to the earth, equivalent to more than 4000 trillion kWh [1]. The development of solar energy-converting technologies is needed to investigate points within the creation of photovoltaic (PV) devices and makes them more cost-competitive with conventional energy sources [2] – [4]. Efficiency in solar panels is a measure of the amount of sunlight irradiation that falls on a solar panel's surface and is converted into electricity. Owing to the many advances in solar panel technology in recent years, the average panel conversion efficiency has expanded from about 15% to 20% [5].

Unfortunately, solar panels ended up messy over time as dust, grime, bird droppings, and other contaminants. It depends on where the PV system is installed and built, which is a factor causing the decrease in the efficiency of PV modules in systems on-site. Cleaning solar panels of contaminants to maintain optimum solar harvesting capabilities is time-consuming and expensive. Self-cleaning applications remove soil from the glass surface (as a glass cover) for the PV panels and make them become a cost-effective solution [6]. Another factor causing the decrease in the efficiency of PV panels is reflection. The low-iron glass is utilized as a cover plate in solar panels. The cover glasses can be 2.0 mm, 3.2 mm, and 4.0 mm in thickness, and the thicker glass provides reduced light transmittance strength. Moreover, the reflection of cover glass results in an optical loss of electrical power. So reducing the optical losses is a factor that increases the efficiency of the panel. Antireflective coating (ARC) is applied onto the cover glass to reduce optical losses. Therefore there are two reasons for decreasing the efficiency of a PV panel: dust and reflection [7]. The self-cleaning phenomena observed in nature have been quickly imitated in creating glass surfaces, inorganic and organic films.

Coating the glass surface with titanium dioxide (TiO_2) has drawn great attention due to its photocatalytic and self-cleaning properties to remove dirt in the presence of ultraviolet light. Under UV irradiation, the electrons in the valence band of TiO_2 are excited to the conduction band, while the holes remain in the valence band. Once the excited electrons migrate back to the interface, the holes in the valence bands will initiate, respectively, the reductive and oxidative reactions. In an aqueous medium, for instance, the negative electrons will combine with the oxygen into O^{2-} , while the positive holes oxidize with H_2O and hydroxyl to generate hydroxyl radicals (OH): these highly charged species are photocatalytically active in oxidizing organic pollutants. There is, however, one problem: the photogenerated electron-hole pairs have a flash recombination time of the order of 10^{-9} s, while the time scales for the chemical interactions of TiO_2 with the adsorbed dirt or chemicals is in the range from 10^{-8} to 10^{-3} s [8]. That is, this discrepancy between two times scales is much more favorable for the unintended recombination of electron-hole pairs than for the TiO_2 -dirt absorption, resulting in a decreased efficiency in the photocatalytic activity of TiO_2 . On the other hand, TiO_2 has a relatively wide band gap energy (3.2 eV), only able to absorb the UV region of the solar spectrum, representing only 5%. $\text{TiO}_2/\text{SiO}_2$ composite films can overcome both limitations. $\text{TiO}_2/\text{SiO}_2$ films present high transmittance, enhanced photocatalytic activity, and persistent hydrophilicity in dark environments. The nobility of SiO_2 allows its union with different materials, such as TiO_2 , where the SiO_2 is a support for the TiO_2 particles with chemical, electronic and hydrophilic properties. The synergistic effect of photocatalysis and hydrophilicity will result in long-term self-cleaning activity. Moreover, the high surface acidity due to the presence of Si cations makes adsorbing the hydroxyl groups, which is the main reason for the reduced contact angle.

In the present study, pure TiO_2 and $\text{TiO}_2/\text{SiO}_2$ composite films containing different SiO_2 content have been deposited over glass substrates by the dip-coating method in order to obtain superhydrophilic and transparent composite films. The influence of the calcination temperature

and the SiO₂ content has been emphatically discussed. The composite films have been compared and characterized regarding their transmittance and hydrophilic properties.

2. Experimental procedure

2.1. Materials

Tetraisopropylorthotitanat (TPOT) was purchased from Sigma-Aldrich and tetraethyl orthosilicate (TEOS) was from Macklin. Isopropyl alcohol/2-propanol (IPA) was purchased from Prolabo. Ethanol (EtOH) and Hydrochloric acid (HCl) 37% (HCl) were from Merck. All the chemicals were of analytical grade.

2.2. Mixed solution preparation and thin film deposition

Tetraisopropylorthotitanat (TPOT) was used as a metal resource and IPA as the solvent to prepare the TiO₂ solution. Firstly, ethanol and HCl (37%) were mixed and vigorously stirred well for 30 mins at 600 rpm. Then a quantity of 0.6 ml TPOT was added dropwise into the reaction mixture under stirring magnetic speed at 600 rpm for 2 h. The obtained homogeneous TiO₂ solution was sealed and aged for about 24 h at room temperature. The SiO₂ solution was then prepared from mixed solutions of EtOH, TEO, and HCl (37%) for 30 mins at 450 rpm and continued stirring for 2 h at 600 rpm and finally aged for 24 h.

Afterward, the SiO₂/TiO₂ solution was mixed respectively with the ratio of 1:3, 1:1, and 3:1 for 2 h from TiO₂ and SiO₂ solutions to prepare the coating solutions. Before the coating process, glass slides were sonicated in an ethanol bath for 30 minutes and dried. The coating solutions were prepared by the sol-gel method. However, the SiO₂/TiO₂ coating on glass substrates was done by the dip-coating method. Each film was pre-baked at 50 °C for 12 h and then followed by post-baked at 400 °C for 1 h in the atmosphere. SiO₂/TiO₂ powder samples from mixtures with a molar ratio of 1:3, 1:1, and 3:1 were heat-treated at 400°C and 700°C for characterizing by X-ray diffraction.

2.3. Characterization

Light transmittance (T) of the samples was measured by JASCO V-670 spectrophotometer in the range of 300–800 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%). The crystallite phases of CuNPs were determined by X-ray diffraction (XRD) using the D8 Advance-Bruker with Cu K α radiation.

3. Results and discussion

3.1. Formation of anatase (TiO₂)/silica (SiO₂) composite nanoparticles

The XRD diagrams of the pure TiO₂, 3T1S, 1T1S, 1T3S, and pure SiO₂ powders are shown in Figures 1 (a) and (b). The abbreviation 3T1S, 1T1S, and 1T3S are used to express the SiO₂/TiO₂ mixed solution with the molar rate of 1:3, 1:1, and 3:1. The composites composed by the mixture of SiO₂ and TiO₂ were obtained by treating in a muffle furnace at 400°C and 700°C.

XRD analysis of TiO₂/SiO₂ composites was carried out to determine the characteristics of the TiO₂ formed.

The XRD spectra of pure TiO₂ indicated the formation of anatase crystallite that corresponded to the featured peaks of the planes (101) at $2\theta = 25.5^\circ$, (004) at 38° , and (200) at 48° after sintering at 400°C for 1hr. There was also the appearance of rutile and brookite phases at this temperature. The rutile phase was determined with two diffraction peaks of (110) and (101) planes at $2\theta = 27.5^\circ$ and 36° respectively, and brookite phase with the peak at $2\theta = 31^\circ$ for (211) plane (JCPDS card #860148). Meanwhile, the XRD patterns of pure TiO₂ treated at 700°C only presented the rutile phase.

For the XRD spectra of $\text{TiO}_2/\text{SiO}_2$ nanocomposites (3T1S, 1T1S, 1T3S) calcined at 400°C and 700°C , as shown in this Figure, the crystal structure with anatase phase was obtained after sintering with three significant peaks at 25.5° , 38° and 48° , corresponding to (101), (004) and (200) crystal planes, respectively.

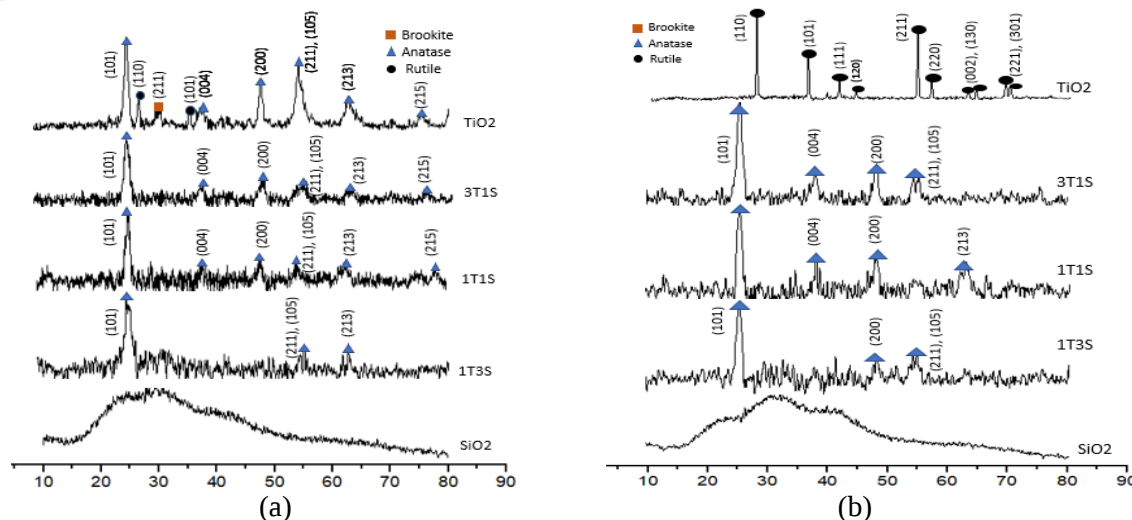


Figure 1. XRD patterns of different $\text{SiO}_2/\text{TiO}_2$ ratio composite powders being heated at various temperatures for 1 h (a) 400°C and (b) 700°C

Figure 1 shows that the composition of $\text{TiO}_2/\text{SiO}_2$ affects the peak intensity and the sharpness of the peak produced. For a higher SiO_2 content in nanocomposites, the sharpness of the peak intensity of TiO_2 is lower. Whether being calcined at 400°C or 700°C , the TiO_2 rutile phase was not seen in the XRD patterns. This can be explained by the fact that adding SiO_2 to the compounds helps prevent the formation of the rutile phase, which is significant in self-cleaning applications because the photocatalytic reaction efficiency in the anatase phase is much better than in the rutile phase.

Table 1. Crystal size of the TiO_2 , 3T1S, 1T1S, 1T3S samples calculated based on the Scherrer formula [9]

Samples	TiO_2	3T1S	1T1S	1T3S
The crystal size of the materials calcined at 400°C (nm)	10.35	4.6	8.17	9.7
The crystal size of the materials calcined at 700°C (nm)	24.3	6.84	8.55	9.45

Table 1 describes the crystal sizes of the nanomaterials formed at a temperature of 400°C and 700°C for TiO_2 , 3T1S, 1T1S, and 1T3S samples. The crystal sizes were estimated according to the Scherrer formula [9]. As shown in Table 1, adding SiO_2 to the composite leads to a considerable decline in crystal size in the 3T1S sample compared to the pure TiO_2 sample. Moreover, the average particle size gradually decreases with increasing SiO_2 , which is explained that an increased number of SiO_2 causes a decrease in the agglomeration and therefore reduces the particle size.

FTIR spectroscopy was used to characterize the bonds in $\text{TiO}_2/\text{SiO}_2$ nanocomposites. This analysis was carried out to classify functional groups in the composites at wave numbers $500 - 4000 \text{ cm}^{-1}$. The spectra in Figure 2 show $\text{TiO}_2/\text{SiO}_2$ composite formation characterized by Ti-O-Si bond appearance at 930 cm^{-1} wavelength. This bond helps improve thermal stability and prevent the phase transition of TiO_2 from anatase to rutile.

The absorption spectrum of pure TiO_2 in the wave number region from 930 cm^{-1} up to 500 cm^{-1} is referred to as the absorption region of the Ti-O-Ti bond. The strong and dominant absorption peak found on wave number 1060 cm^{-1} is the Si-O-Si bond called asymmetrical extension one. The peak presence at wave 800 cm^{-1} indicates Si-O-Si vibrations in the amorphous SiO_2 .

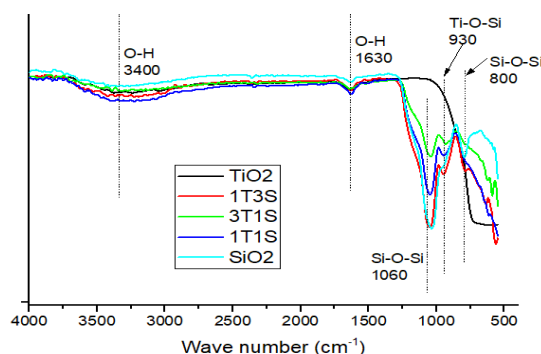


Figure 2. FTIR spectra of the $\text{TiO}_2/\text{SiO}_2$ nanocomposite calcined at 400°C with changing SiO_2 contents

The oscillation of the O-H bond appears at 1630 cm^{-1} and 3400 cm^{-1} . When increasing the SiO_2 content gradually, the O-H absorption peak intensity also increases. Therefore, the role of SiO_2 in the nanocomposite coating becomes important as the OH- radical can absorb water to increase hydrophilicity. Besides, SiO_2 also expresses an oxidant for polluting organic radicals. However, the O-H vibrational intensity in the absorption spectrum for pure SiO_2 is lower than that of the $\text{TiO}_2/\text{SiO}_2$ nanocomposites.

3.2. The effect of SiO_2 content of film surface on hydrophilic and transmittance properties

To investigate the optical behavior of the film coatings, we undertook spectrophotometry measurements. Fig. 3 shows the transmission curves of different $\text{TiO}_2/\text{SiO}_2$ films with ratios of 1:3, 1:1, 3:1, pure SiO_2 , and pure TiO_2 . On coating glass substrates with pure SiO_2 , the maximum transmittance of bare glass increases from 85% to 96% at wavelength 550 nm. The glass substrate with pure TiO_2 coating shows the lowest transmittance at the value of 75%.

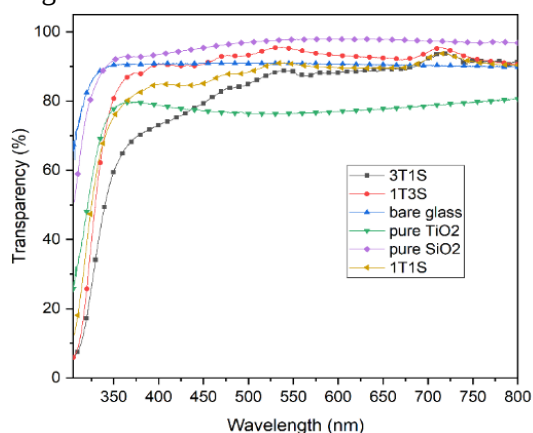


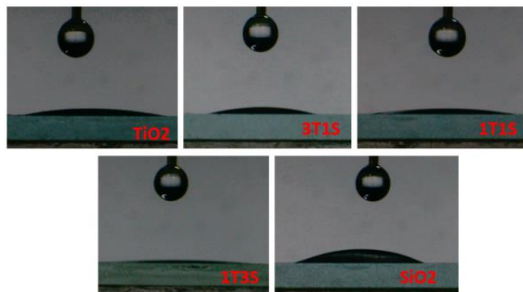
Figure 3. Transmission spectra of the different prepared nanocomposite coatings at a wavelength ranging from 300 to 800 nm

Additionally, increasing the SiO_2 content in the $\text{SiO}_2/\text{TiO}_2$ composite coatings, the transmission gradually increases, which can be attributed to the low refractive index of SiO_2 as compared with TiO_2 coating component. Low TiO_2 content can affect the photocatalytic efficiency of obtained coating films, which is essential to achieve self-cleaning surfaces. Coating samples with high transmittance are 1T1S and SiO_2 ; meanwhile the highest transmittance is for the 1T3S film with a value of about 93%, which ensures the good transmittance of glass for the application of solar panels.

As the results of the optical bandgap energy are displayed in Table 2, it is shown that the $\text{TiO}_2/\text{SiO}_2$ material with the ratio of 3:1 has the lowest value. The bandgap energy increases from 3.44 to 3.66 eV when gradually increasing the SiO_2 content in the composite coating materials.

Table 2. Optical bandgap of $\text{TiO}_2/\text{SiO}_2$ composite coatings with the different SiO_2 contents

Samples	pure TiO_2	3T1S	1T1S	1T3S	pure SiO_2
Optical bandgap energy (eV)	3.34	3.31	3.44	3.48	3.66

**Figure 4.** Water droplets on superhydrophilic surfaces with the different coating materials**Table 3.** Water contact angle values of $\text{TiO}_2/\text{SiO}_2$ composite coating samples with changing the SiO_2 contents

Samples	pure TiO_2	3T1S	1T1S	1T3S	pure SiO_2
WCA ($^\circ$)	11.2	10.5	9.8	4.7	25.8

Figure 4 shows the images of water contact angles (WCA) of the $\text{TiO}_2/\text{SiO}_2$ composite coating surfaces. And the results are summarized in Table 3. The values of WCA decrease from 10.5° to 4.7° after adding SiO_2 content. The WCA value of the $\text{TiO}_2/\text{SiO}_2$ coating film at the ratio of 1:3 gives the smallest value of 4.7° . In other studies, the type of $\text{TiO}_2/\text{SiO}_2$ composite material added more different substances to improve surface wettability. The fluorocarbon/ TiO_2 - SiO_2 composites revealed a WCA of 4.5° [10]. While the organization of SiO_2 and TiO_2 nanoparticles into fractal patterns on the glass surface with WCA is 6° - 8° [11], and around 5° [12] for the composite with TiO_2 added Vanadium catalyst. This can be explained that SiO_2 content increases the acidity of the coating film surface to absorb more OH^- radicals. The absorption of these many free radicals not only makes the surface enhance the hydrophilicity property but also actively contributes to the photocatalysis process in decomposing the organic pollutants.

4. Conclusions

$\text{TiO}_2/\text{SiO}_2$ composites were successfully synthesized by a simple sol-gel route. $\text{TiO}_2/\text{SiO}_2$ coating films with the ratio of 1:3 presented the highest transmittance of about 93% and the lowest water contact angle of 4.7° . These properties are essential for application in self-cleaning surfaces of solar energy areas, which require high transparency and low water contact angles.

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