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Self-cleaning SiO_2/TiO_2/PMMA nanocomposite films fabricated by spin coating technique: Effect of different spin speed and film layers

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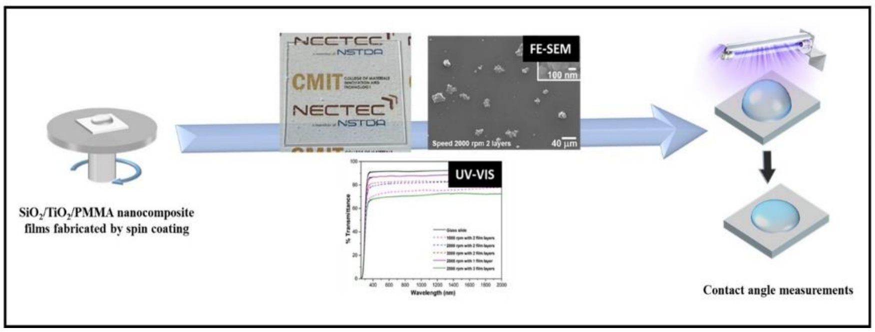
Abstract



This research aims to develop the self-cleaning efficiency of silicon dioxide/titanium dioxide/methyl methacrylate (SiO_2/TiO_2/PMMA) nanocomposite films proved by optical and structural properties. The SiO_2/TiO_2/PMMA nanocomposite films were prepared by spin coating technique with the crucial parameters of spin speed and film layers. The ratio of SiO_2:TiO_2 in SiO_2/TiO_2 nanocomposite was conducted at 1:1 by sonochemical process and loading at 1 wt.% in PMMA matrix. Spin speed of SiO_2/TiO_2/PMMA nanocomposite films in coating process was conducted at 1000, 2000, and 3000 rpm with film growth at 2 layers. Meanwhile, the different film layers of the nanocomposite film were selected as other crucial parameter in spin coating technique and studied at 1, 2, and 3 layers with spin speed 2000 rpm. Surface morphologies, cross-section and element contents of SiO_2/TiO_2/PMMA nanocomposite films with different spinning speed and film layers were monitored by the photographs, field emission scanning electron microscope (FE-SEM) and energy dispersive X-ray spectroscopy (EDS). Moreover, optical property in transmission mode of SiO_2/TiO_2/PMMA nanocomposite films was characterized by UV-VIS spectrophotometer. Furthermore, the contact angle measurement of SiO_2/TiO_2/PMMA nanocomposite films can identify to hydrophilic properties on the film surface. Therefore, the improvement of self-cleaning property on SiO_2/TiO_2/PMMA nanocomposite film was occurred by the optimized conditions of spinning speed at 2000 rpm and film growth at 2 layers by spin coat technique.

Keywords: Nanocomposite; PMMA; SiO_2/TiO_2 nanocomposite; Spin coating; Sonochemical

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Introduction

Organic contamination, industrial pollutants and air pollution on building surface especially windowpanes are the main problems in big city [1]. The basic idea to removing the contaminations on their surfaces is the development of self-cleaning properties on material surface which is one of effective alternative for environmentally friendly and cost reduction. Dust, water, and other pollutants on the material surface with Self-cleaning hydrophilic surface can be easily removed by spreading water droplets entire the surface to cleaning these contaminations. Moreover, a thin film layer from covering water droplets on hydrophilic surface may be related to the possibility of photocatalytic mechanism by photocatalyst and self-cleaning material under UV and visible illumination. Therefore, the adhesion between the external dirt and the covered water film can be evidently created to remove the contamination on its surface [2]. The mechanism of self-cleaning property with photocatalytic reaction on material surface is occurred by the generation of electron-hole pairs under light activation to produce superoxide radicals and hydroxyl radicals for removing organic pollutants and the contaminations on the surface [3]. This is an effective method to enhance self-cleaning property by the influence of photocatalytic reaction that can be occurred in famous metal oxide materials such as titanium dioxide (TiO_2), zinc oxide (ZnO) and bismuth vanadate ($BiVO_4$). Among metal oxide-based materials, TiO_2 is one of potential materials with excellent self-cleaning and photocatalytic properties due to simultaneous superhydrophilic and superhydrophobic domains under light activation [3]. Meanwhile, the enhancement of self-cleaning property in TiO_2 material can be obtained by doping with metal, non-metal and composite formation relating to band gap narrowing, localized energy levels within the bandgap and the defects of oxygen vacancies. The improvement in optical property in TiO_2 material as transparent, anti-fogging and visibility after testing in rainy weather of SiO_2/TiO_2 nanocomposite films was obtained by sol-gel method for the nanocomposite and spin coating technique for film fabrication as reported by Boutamart and co-workers [4]. The enhancement of photocatalytic reaction and mechanical properties in the host polymeric composites was appeared by the modification of TiO_2 material with SiO_2 addition owing to good particles dispersion TiO_2/SiO_2 nanocomposite [1]. However, the disadvantage of sol-gel method strongly required thermal treatment in production. Meanwhile, sonochemical process is one of facile processes by using powerful ultrasound radiation in range of 20 kHz–10 MHz which created the molecules by acoustic cavitation in a chemical reaction. According to the powerful ultrasound energy, high temperature and pressure are occurred in the process relating to the efficient energy in the system to create the material product without the post thermal treatment [5]. Then, sonochemical technique is properly interested in the production of nanocomposite material with one-step process.

For the fabrication of composite film with powder-assisted, polymer solution is necessary required to attach the particles on the substrate. The unique distribution of TiO_2 nanoparticles in PMMA phase was successfully fabricated by miniemulsion polymerization as reported by L. Yang and research group [6]. Meanwhile, film fabrication processes on the substrates are proposed as dip coating, spray coating, sputtering and spin coating technique [7]. Most of all, spin coating method is properly suitable for the particulate suspension by spinning the particle adhesion on the surface with the influence of polymer matrix to create the homogenous and smooth films [8, 9]. For significant parameters in spin coating process, homogenous surface and film thickness were controlled by solution viscosity, spin speed and growth film layers [10]. Particle aggregation is evidently shown by the variation of layer-by-layer on the films according to the study of the number of silica layers in polymer matrix as reported by C.K. Söz and research group [9]. Meanwhile, the height of film thickness can be controlled by spin speed in the process. The improvement of residual stress on ZnO films was obtained by increasing spin speed corresponding to the decrease of film thickness [8].

This work focused on the fabrication of SiO_2/TiO_2/PMMA nanocomposite films prepared by spin coating method. The crucial parameters in spin coating technique were conducted on spin speed (1000, 2000, and 3000 rpm) and film growth layers (1, 2, and 3 layers). Structural, morphological and optical properties of SiO_2/TiO_2/PMMA nanocomposite films were extensively investigated included the self-cleaning properties by water contact angle measurement.

Materials and Methods

Firstly, SiO_2/TiO_2 nanocomposite powder was synthesized from the precursors of tetraethyl orthosilicate (TEOS) and titanium isopropoxide (TTIP) by sonochemical process [11]. The nanocomposite ratio of $SiO_2:TiO_2$ was conducted at 1:1. For poly (methyl methacrylate) (PMMA) matrix preparation, PMMA powder was dissolved in glacial acetic acid under magnetic stirring for 60 min. After that SiO_2/TiO_2 nanocomposite loading at 1 wt.% was dispersed in PMMA solution. Then SiO_2/TiO_2/PMMA nanocomposite films were fabricated by spin coating technique on glass slide and silicon substrate for the specific characterized techniques. The crucial parameters of SiO_2/TiO_2/PMMA nanocomposite films by spin coating process was conducted at spin speed at 1000, 2000, and 3000 rpm with 2 film layers and different film layers at 1, 2, and 3 layers under spin speed at 2000 rpm. The transparent SiO_2/TiO_2/PMMA nanocomposite films were obtained after film baking at 100 °C for 10 min. For characterization techniques, overall surface of the nanocomposite films on glass substrate was monitored by the photographs. Meanwhile, surface morphologies, cross-section and element contents of SiO_2/TiO_2/PMMA nanocomposite films on silicon substrate were investigated by field emission scanning electron microscope (FE-SEM; Hitachi S-8030). The optical transmittance of the nanocomposite films on glass surface in wavelength range of 200 – 2000 nm was monitored by a universal measurement spectrophotometer (Agilent; Cary

7000). For self-cleaning property, the water droplet angle on the nanocomposite films on glass surface was carried out by contact angle measurements (ramé-hart instrument co.) under UV irradiation for 120 min.

Results and Discussions

The photographs of overall surface on SiO_2/TiO_2/PMMA nanocomposite films with different spin speed and film layers coating on the glass substrates are depicted in Fig. 1. The clusters of SiO_2/TiO_2 nanocomposite powders were obviously covered on PMMA matrix. For the different spin speed, the aggregation of SiO_2/TiO_2 clusters was distinctly appeared at spin speed for 1000 rpm because of low centripetal force at lower speed relating to high particle accumulation on film surface, as shown in Fig. 1(a). Meanwhile, the increase of spin speed at 2000 and 3000 rpm showed good particles dispersion and less aggregation on film surface owning to higher centripetal force, as illustrated in Fig. 1(b) – 1(c). However, the amount of the composite clusters on PMMA film was reduced after spin operation at 3000 rpm, according to the excessive high centrifugal force. Therefore, the optimized spin speed for SiO_2/TiO_2/PMMA nanocomposite film was at 2000 rpm with the appearance of good particle dispersion compared with 1000 rpm and

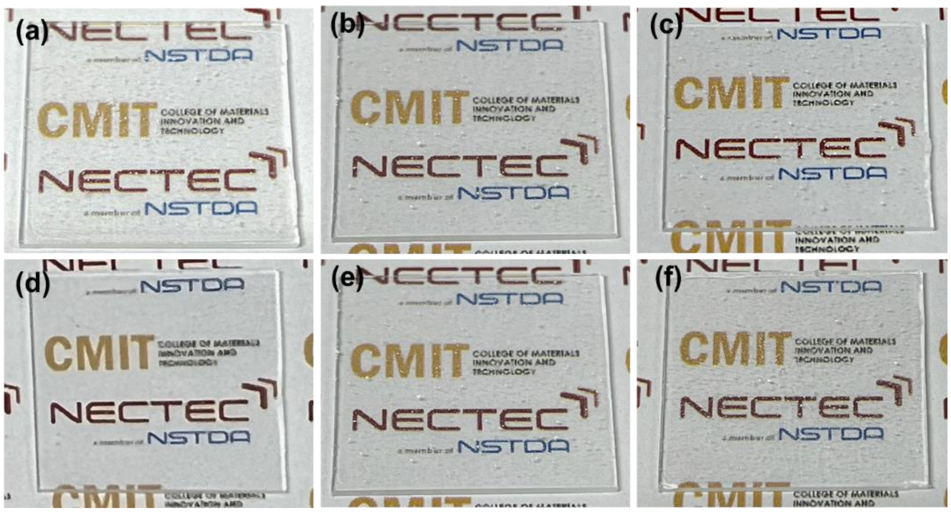

Fig. 1 The photographs of SiO_2/TiO_2/PMMA nanocomposite films by spin coating technique with the different spin speed at (a) 1000 rpm, (b) 2000 rpm, and (c) 3000 rpm with 2 film layers and various film layers at (d) 1 layer, (e) 2 layers, and (f) 3 layers with spin speed 2000 rpm.

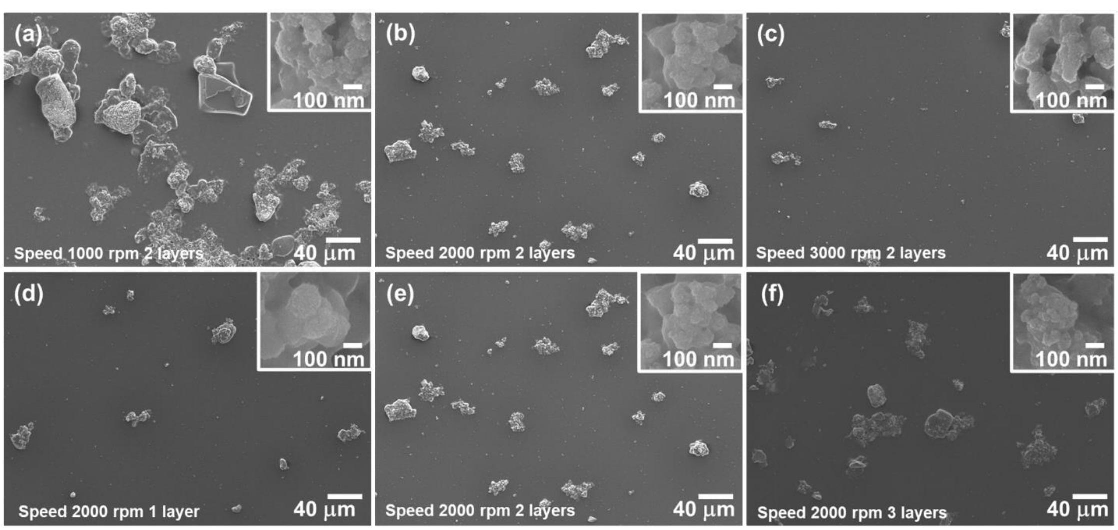

Fig. 2 Surface morphology by FE-SEM images of SiO_2/TiO_2/PMMA nanocomposite films with the difference of (a) – (c) spin speed and (d) – (f) film layers (inset: composite cluster area).

3000 rpm. This optimized condition was used as the constant spin speed to further study the addition of film layers on SiO_2/TiO_2/PMMA nanocomposite film. Meanwhile, the amount of SiO_2/TiO_2 clusters on the film tends to increase as the number of film layer increases, as shown in Fig. 1(d)-1(f). Less particulate clusters, transparent film and abundant voids were obtained at 1 film growth layer of SiO_2/TiO_2/PMMA nanocomposite film. After adding growth film layers on the first layer, some particulate in colloidal precursor solution was facilely attached on the original particle pattern. Therefore, the optimized layer of SiO_2/TiO_2/PMMA nanocomposite film was obtained at 2 or 3 layers due to the increase of particulate materials on the film.

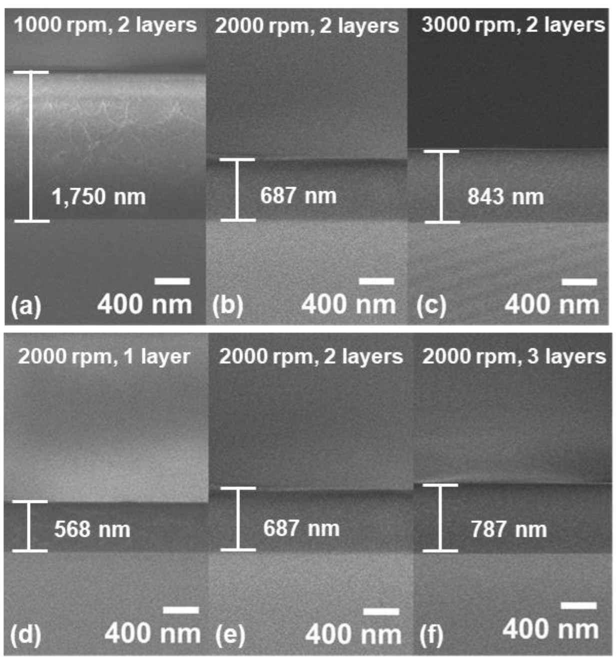

Fig. 3 Cross-section images of SiO_2/TiO_2/PMMA nanocomposite films with the difference of (a) – (c) spin speed and (d) – (f) film layers.

The surface morphologies of SiO_2/TiO_2/PMMA nanocomposite films with different spin speeds and film layers are shown in Fig. 2. The surface morphology of SiO_2/TiO_2/PMMA nanocomposite films was related to the optical images exhibiting some composite clusters on PMMA film. For lower spin speed at speed 1000 rpm in Fig. 2(a), dense particle aggregation form SiO_2/TiO_2 nanocomposite was observed. This occurrence could be resulted from insufficient centripetal force for particle separation on the film surface during spin coating process. Meanwhile, the improvement of SiO_2/TiO_2 particle dispersion in PMMA matrix can be achieved by increasing spin speed at 2000 and 3000 rpm, as shown in Fig. 2(b) – 2(c). Significant reduction in dense areas of SiO_2/TiO_2 nanocomposite powder is noticed regarding the influence of high centripetal force during spin coating process reflecting good particle dispersion on the film surface. However, the film fabrication with spin speed at 3000 rpm is still immoderate to form the composite cohesion on the polymer film. In case of film layer parameter, the amount of SiO_2/TiO_2 nanocomposite powder considerably increased by the addition of SiO_2/TiO_2/PMMA film layers from 1 – 3 layers, as depicted in Fig. 2(d) – 2(f). Hence, particle accumulation on the film surface at each layer could be resulted from the increase of growth layer, as shown at the nanocomposite film with 3 layers [9]. Moreover, the cross-section of SiO_2/TiO_2/PMMA nanocomposite films with different spin speed and film layers are illustrated in Fig. 3. The effect of film layers parameter is related to the film thickness on the substrate. For spin speed consideration in Fig. 3(a) – 3(c), the thickness of SiO_2/TiO_2/PMMA nanocomposite films was approximately 1.75, 0.69, and 0.84 μm, followed by spin speed at 1000, 2000, and 3000 rpm, respectively. The highest film thickness obtained from low spin speed at 1000 rpm was originated from less centripetal force in spin coating process. As observed, the film thickness possessed the same value range of 600 – 900 nm, indicating insignificant variation with the number of film layers. Therefore, the crucial parameter of SiO_2/TiO_2/PMMA nanocomposite film fabrication must be focused on spin speed because of the evident height in film thickness and particulate dispersion on the film surface. Moreover, the optimized spin speed is mostly required to spreading the colloidal precursor solution on substrate for the production of homogenous and uniform film surface. Furthermore, EDS analysis of the SiO_2/TiO_2/PMMA nanocomposite film at spin speed 2000 rpm and 2 layers analyzed in cluster area and matrix area (flat area) are revealed in Fig. 4. The element contents of cluster area in Table 1 showed the elemental of C, O, Si and Ti from the aggregation of SiO_2/TiO_2 nanocomposite [12]. The detection of carbon element in this area may be originated from PMMA covering on SiO_2/TiO_2 nanocomposite during the blending precursor solution. Meanwhile, the analysis of matrix area in Table 2 also showed the elemental of C, O, Si and Ti. High Si content is due to silicon substrate. However, the major element in matrix area is from PMMA polymer as the matrix in film fabrication because of C weight content at 6.22%. Some elements of Si and Ti can be detected by the insertion of small particles from SiO_2/TiO_2 nanocomposite.

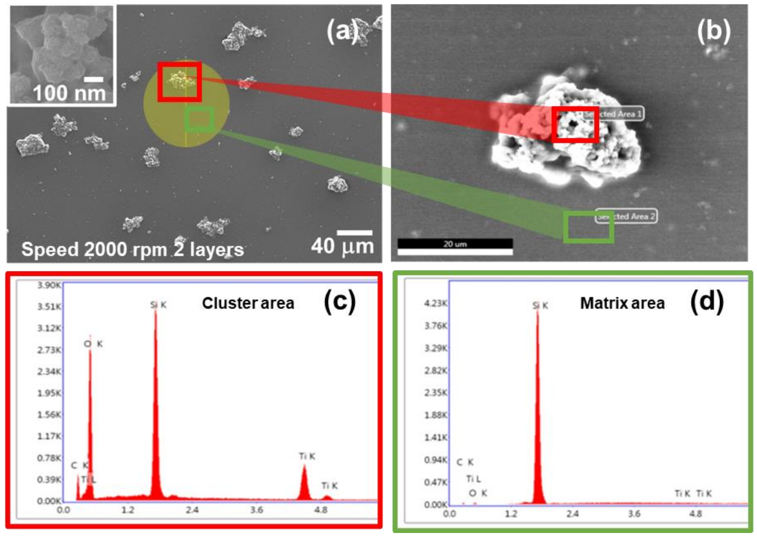

Fig. 4 EDS analysis of the SiO_2/TiO_2/PMMA nanocomposite film at spin speed 2000 rpm and 2 layers (a) surface morphology, (b) high magnification, (c) EDS spectra of cluster area and (d) EDS spectra of matrix area.

Table 1 EDS analysis of cluster area of the SiO_2/TiO_2/PMMA nanocomposite film with the condition of spin speed at 2000 rpm and 2 layers.

Element	Weight (%)	Atomic (%)	Error (%)
C K	13.19	20.69	11.82
O K	49.69	58.55	9.51
Si K	22.15	14.87	3.66
Ti K	14.97	5.89	3.60

Table 2 EDS analysis of matrix area of the SiO_2/TiO_2/PMMA nanocomposite film with the condition of spin speed at 2000 rpm and 2 layers.

Element	Weight (%)	Atomic (%)	Error (%)
C K	6.22	13.50	31.88
O K	0.56	0.91	78.16
Si K	90.89	84.33	2.02
Ti K	2.32	1.26	32.54

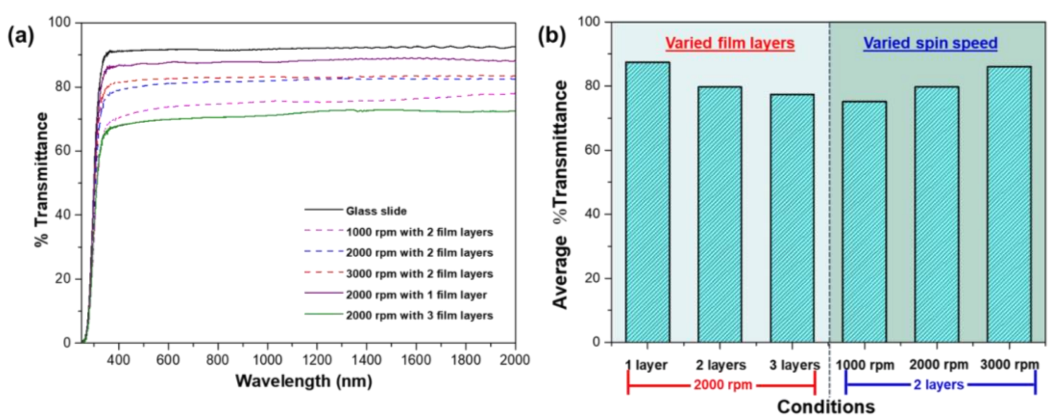

Fig. 5 (a) Transmittance spectra and (b) the average transmittance percentage of SiO_2/TiO_2/PMMA nanocomposite films with different spin speed and film layers.

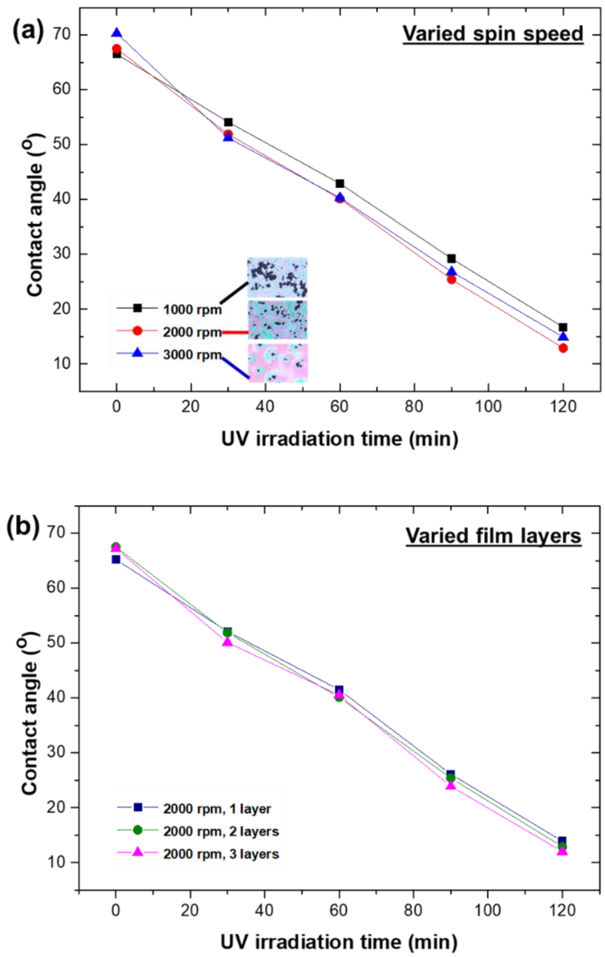

Fig. 6 Water contact angles measurement of SiO_2/TiO_2/PMMA nanocomposite films with the difference of (a) spin speed and (b) film layers under UV irradiation.

The analysis of optical property in transmission mode in SiO_2/TiO_2/PMMA nanocomposite films with the influences of different spin speed and film layers is illustrated in Fig. 5. Transmittance spectra of SiO_2/TiO_2/PMMA nanocomposite films with different spin speed and film layers in Fig. 5(a) were approximately 75 – 80%. The prepared SiO_2/TiO_2/PMMA nanocomposite films are highly transparent with good homogeneity since their corresponding transmittance spectra is close to the transmission value of bare glass substrate [13]. The average transmittance values of all samples with different spin speeds and film growth layers are shown in the Fig. 5(b). The average %T of the specimens with different growth layers tends to decrease as number of growth layer increases owing to the addition of particulate accumulation on each film layer. Meanwhile, increasing spin speed in film fabrication showed the improvement of the average %T to high transparent due to the decrease of thickness height and less particulate aggregation on the film surface.

Therefore, the optimized condition for the spin coating fabrication of SiO_2/TiO_2/PMMA nanocomposite films with high transparency and less particle aggregation on film surface was achieved as deposition was conducted with spin speed of 2000 rpm for 2 layers.

Self-cleaning property of SiO_2/TiO_2/PMMA nanocomposite films can be proved by water contact angles measurement under UV irradiation as depicted in Fig. 6. As observed in Fig. 6(a), the least contact angle value of approximately 12º after UV irradiation for 120 min was reached as the composite film was prepared at 2000 rpm. This feature could be associated to good SiO_2/TiO_2 particle dispersion and homogeneity of the film surface. The decrease of water contact angle value on SiO_2/TiO_2/PMMA nanocomposite films could be induced by the existence of Si⁻O⁻Ti bonding in SiO_2/TiO_2 nanocomposite [14]. Meanwhile, the self-cleaning properties can be improved by the generation of hydroxyl groups and oxygen vacancies induced by electron-hole pair generation in TiO_2 under UV irradiation, leading to increasing interaction of these radicals with water molecules on the film surface [15]. For high contact angle value obtained from the film deposited with spin speed of 1000 rpm, the particle agglomeration on the film could retard of water flatness on the surface. Whilst the specimen fabricated with spin speed of 3000 rpm exhibited inconsiderable change in contact angle value when compared with the sample prepared at spin speed of 2000 rpm that could be due to homogeneity of the film surface and less particle aggregation. As noticed in Fig. 6(b), the deposited films with different growth layers indicates the same contact angle value in the vicinity of 12º – 13º. Therefore, good hydrophilic property of SiO_2/TiO_2/PMMA nanocomposite films can be attained by the increase of growth film layer.

Conclusion

The fabrication of SiO_2/TiO_2/PMMA nanocomposite films was successfully obtained by spin coating technique with the incorporation of ultrafine SiO_2/TiO_2 nanocomposite in PMMA polymer matrix. From experimental results, it can be deduced that the optimized condition for the fabrication of SiO_2/TiO_2/ nanocomposite on PMMA matrix was achieved as the deposition was conducted at 2000 rpm with 2 repeating layers, showing least contact angle at 12º as a result from the homogeneity of film and uniform particle distribution with less particle dispersion. The results additionally suggest that spin speed is a crucial process parameter for the spin coating fabrication of SiO_2/TiO_2/PMMA nanocomposite film. However, the variation of growth film layer exhibits insignificant influence on neither physical structure nor self-cleaning property due to the appearance of good particle dispersion on the first layer.

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References

[1] F. Mohammadi, S. M. Mirabedini, K. khodabakhshi, S. Pazokifard, Degradation of pollutants in solid and gas states using waterborne acrylic nanocomposite paints, Build. Environ. 221 (2022) 109327.

[2] S. Nundy, A. Ghosh, T. K. Mallick, Hydrophilic and superhydrophilic self-cleaning coatings by morphologically varying ZnO microstructures for photovoltaic and glazing applications, ACS. Omega. 5 (2020) 1033 – 1039.

[3] S. Banerjee, D. D. Dionysiou, S. C. Pillai, Self-cleaning applications of TiO_2 by photo-induced hydrophilicity and photocatalysis, Appl. Catal. B. 176-177 (2015) 396 – 428.

[4] M. Boutamart, S. Briche, K. Nouneh, S. Rafqah, Y. Agzenai, Transparent and self-cleaning surfaces based on nanocomposite sol-gel coatings, Chemistry Select. 5 (2020) 8522 – 853.

[5] S.Z. Qiao, J. Liu, G.Q.M. Lu, Chapter 21 Synthetic Chemistry of Nanomaterials, Modern Inorganic Synthetic Chemistry. (2017) 613 – 640.

[6] L. Yang, S. Zhou, L. Wu, Preparation of waterborne self-cleaning nanocomposite coatings based on TiO_2/PMMA latex, Prog. Org. Coat. 85 (2015) 208 – 215.

[7] A. S. Sarkın, N. Ekren, Ş. Sağlam, A review of anti-reflection and self-cleaning coatings on photovoltaic panels, Solar. Energy. 199 (2020) 63 – 73.

[8] G. Demircan, E. F. Gurses, A. Acikgoz, S. Yalcin, B. Aktas, Effects of spin coating parameters on stress, electrical and optical properties of multilayer ZnO thin film prepared by sol–gel, Mol. Cryst. Liq. Cryst. 709(1) (2020) 61 – 69.

[9] C. K. Söz, E. Yilgör, I. Yilgör, Influence of the average surface roughness on the formation of superhydrophobic polymer surfaces through spin-coating with hydrophobic fumed silica, Polymer. 62 (2015) 118 – 128.

[10] S. K. Samal, S. Mohanty, S. K. Nayak, Superhydrophobic polymer coatings, First ed., Elsevier, Cambridge 2019.

[11] A. Rosales, L. O. Frade, I. E. M. Ramirez, L. A. Godínez, K. Esquivel, Self-cleaning of SiO_2-TiO_2 coating: effect of sonochemical synthetic parameters on the morphological, mechanical, and photocatalytic properties of the films, Ultrason. Sonochem. 73 (2021) 105483.

[12] M. Ranjbar, M. A. Taher, A. Sam, Single-step synthesis of SiO_2–TiO_2 hydrophobic core–shell nanocomposite by hydrothermal method, J. Clust. Sci. 27 (2016) 583 – 592.

[13] S. W. Heo, Ultra-flexible organic photovoltaics with nanograting patterns based on CYTOP/Ag nanowires substrate, Nanomaterials 10 (2020) 2185.

[14] Y. Y. Liu, L. Q. Qian, C. Guo, X. Jia, J. W. Wang, W.H. Tang, Natural superhydrophilic TiO_2/SiO_2 composite thin films deposited by radio frequency magnetron sputtering, J. Alloys Compd. 479(1-2) (2009) 532 – 535.

[15] E. Pakdel, W. A. Daoud, X. Wang, Self-cleaning and superhydrophilic wool by TiO_2/SiO_2 nanocomposite, Appl. Surf. Sci. 275 (2013) 397 – 402.