Titania nanoparticles coated on polycarbonate car headlights for self-cleaning purpose

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Titania nanoparticles coated on polycarbonate car headlights for self-cleaning purpose

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Abstract. Due to the quick advancement of automotive headlights from glass to polycarbonate (PC) plastic, ultraviolet (UV) hard coating that offers excellent properties are ideal in meeting the requirements of modern designs. However, PC is known to deteriorate upon exposure to sunlight, moisture, dirt and other environmental conditions. In this work, TiO_2 in the form of suspensions were attached on the PC sheet's surface that had been modified by sodium hydroxide (NaOH) and 3-aminopropyltrimethoxysilane (APTMS). FESEM results showed that the TiO_2 are almost spherical in shape and agglomerated. Analysis using GI-XRD showed that the coated samples were of anatase phase with low crystallinity. Based on the results, it was found that TiO_2 prepared via method 3 coated on PC sheets managed to produce a more uniform coating, with the strongest adhesion, although with some reduction in transparency. The photocatalytic activity testing was carried out through the photodegradation of methyl orange (MO) under UV light irradiation and it was found that the prepared samples were able to decompose MO, although not at a lower percentage. It can also be observed that PC sheet coated with TiO_2 prepared by method 3 showed a higher photocatalytic activity as compared to the other method.

1. Introduction

With the rapid development of automotive headlights from glass to polycarbonate (PC) plastic that offers excellent properties in terms of impact resistance, transparency, weight reduction, low-cost, softer and the ability to be easily-shaped, are ideal in meeting the requirement of modern designs [1,2]. However, PC is known to deteriorate upon exposure to sunlight, moisture, dirt and other environmental conditions [3]. The deterioration of PC headlights can reduce the driver's vision and can well be the cause of accidents. Therefore, there is a need to improve the properties of the surface of PC polymers without changing their bulk properties [4]. In order to overcome this issue, the introduction of different strategies, such as the usage of toothpaste, to UV refinishing hard coats, has been carried out. Allnex USA Inc. had reported that the polishing technique and sealant can be very effective in resolving this issue [5]. The newest improvements in material science offer a wide range of new coatings that can solve this problem [6].

One of the most widely-used methods available to coat PC plastics to prevent deterioration are physical or chemical vapor deposition (PVD or CVD) [7]. However, these techniques are not only expensive, but also only a limited range of material can be coated. Furthermore, the adhesion between the substrate and the coating is also poor most of the time [7,8]. Wet coatings such as spin coating, dipcoating, spray-coating and drop-cast method can be used as an alternative to the techniques mentioned before, as they are simpler and cheaper [9].

Another method to prevent the deterioration of PC car headlights is by coating the PC with a layer of transparent photocatalyst, which is capable of undergoing self-cleaning [2]. Titania (TiO_2) photocatalyst can be effectively used for this purpose as it has excellent photocatalytic properties and is able to break down organic compounds under ultra-violet (UV) light irradiation [10]. The usage of TiO_2 is due to its strong oxidation power, non-toxicity, high photostability, chemical inertness, environmental-friendliness, and it is also readily available in the Earth's crust [1,11]. The coating of TiO_2 on the surface of PC headlights can keep the lens and reflectors clean [12]. When TiO_2 is irradiated by light, dirt, grease, moisture and organic contaminants can be decomposed. The decomposed components then can be easily removed by water [13].

Among the convincing technological products that have demonstrated the use of photocatalyst-coated on polymeric materials in the industry are building roofs and windows, car roofs and mirrors, automotive headlights, ophthalmic lenses and optical products [1]. As PC is also a type of polymer, it will be also feasible to coat a layer of TiO_2 on PC car headlights in order to utilize the self-cleaning properties of TiO_2. The possibility of coating PC's surface with TiO_2 for self-cleaning purposes has been elucidated by Yaghoubi *et al*. [9]. However, many careful steps will have to be taken in order to retain the photocatalytic ability of the TiO_2 without obstructing the visibility of the PC car headlights.

In order to coat TiO_2 on PC car headlights for self-cleaning purposes, the coating must be transparent and adherent, while maintaining high photocatalytic activity [6]. Optical transparency is one of the most significant conditions that need to be complied in order to retain the effectiveness of the car headlights [14]. The size of TiO_2 coated must be in the nano-range, the photocatalytic activity can be increased due to the large surface area of the material [15].

In this work, a layer of size-controlled and transparent TiO_2 nanoparticles (NPs) was deposited on the surface of PC to be used for self-cleaning purposes. TiO_2 in the form of suspensions were attached on the PC sheet's surface that had been modified by NaOH and APTMS, by spray-coating and drop-casting methods. For the spray-coating method, the TiO_2 suspension was sprayed directly onto the surface the PC sheets followed by heating near to its melting point. As for the drop-casting method, the TiO_2 suspension was drop-casted directly onto the PC sheets followed by direct heating near to its melting point. Then, the melted PC sheets were cooled down drastically to room temperature. It is expected that the TiO_2 will be intertwined between the polymeric structures of the PC, hence allowing good attachment. The surface and optical properties of the synthesized materials were then determined, followed by the photocatalytic activity testing in the photodegradation of methyl orange (MO).

2. Methods

2.1. Chemicals

Analytical grade chemicals were used without purification as received. The substrate used was a PC roof sheet (Suntech) with 2 mm thickness, cut into 30 mm x 20 mm pieces.

2.2. Synthesis of TiO_2 colloidal suspension in solution form

In order to coat TiO_2 onto PC sheets, TiO_2 in the form of colloidal suspension was firstly prepared. The concentration of titanium used in the preparation of colloidal suspension was kept constant at 0.05 mol, for all 3 methods of TiO_2 preparation. In the first method (method 1 but without drying and calcination), 14.79 mL of titanium isopropoxide (TTIP, Aldrich 97%) was used as the precursor and was added drop wise into 150 mL of mixed ethanol (Merck 100%) water solution (4:1 volume ratio) [16]. The pH of the mixed ethanol water solution was achieved to 0.7 by means of nitric acid (QRëC 65%). A clear solution was formed after several hours of stirring. The TiO_2 colloidal suspension obtained was colourless. It is important to note that the TiO_2 colloidal suspension prepared by method 1 need to be prepared freshly during the coating process. This is due to the changes in physical appearances of the colourless colloidal suspension into cloudy suspension solution after being left for a few hours, which indicated the instability of colloidal suspension. In second method (method 2 but without drying and calcination), 0.05 mol TTIP was rapidly added into 3.125 g oxalic acid di-hydrate solution (Merck 99.5%) which has been dissolved in 30 mL ethanol, producing a thick white mass solution [17]. 180 mL of water was added into the homogeneous thick white mass produced and the aqueous slurry was heated in a water-bath at 65 ºC for 2 h. A transparent colloidal sol was formed after stirring vigorously for 2 h. Aliquots of the colloidal sol (~10 mL) were further heated in sealed vials at 95 ºC for 72 h. The TiO_2 colloidal suspension obtained was cloudy after the hydrothermal reaction. The TiO_2 colloidal suspension was then coated onto the PC substrate. In third method (method 3 but without drying and calcination), 0.05 mol of titanium-di-isopropoxide bis(acetylacetonate) (TTDB, Aldrich 75%) was dissolved in 100 mL ethanol by using an ultrasonic device [18]. After the solution was ultrasonicated, the TiO_2 colloidal suspension was obtained. The colloidal suspension obtained was yellowish in colour. This yellowish colloidal suspensions was then coated onto the PC substrate.

2.3. Surface modification of the PC sheets
PC sheets with 30 mm x 20 mm were first washed by distilled water, then with detergent and the PC sheets were again rinsed with distilled water. The substrate was further cleaned in 2-propanol (Emsure 99.8%), where the PC sheets were ultrasonicated for 5 min and then rinsed with distilled water, before drying at 60 ºC. Surface modification was done on the PC sheets by two methods, which were chemical-etching process and treatment with 3-aminopropyltrimethoxysilane (APTMS, Aldrich 97%)). In the chemical-etching process, the PC sheets were hydrolyzed in 2 M sodium hydroxide (NaOH, QRëC) for 2 h at 37 ºC [19,25]. The PC sheets were further rinsed with distilled water and dried in an oven at 60 ºC for 5 min. For the treatment of PC sheets with APTMS, 2.2 mmol of APTMS were dissolved in 100 mL of ethanol [21]. The PC sheet was immersed in 20 mL of 2.2 mmol of APTMS and was shaken steadily for 2 h at room temperature. The PC sheets were then removed from the APTMS solution, rinsed with distilled water and dried in an oven at 60 ºC for 5 min.

2.4. Coating
The concentration of titanium used in the coating process was kept constant at 0.05 mol. The first coating technique applied was the spray coating method. The TiO_2 suspension was sprayed directly by using a commercial mist spray bottle (50 mL) onto the PC sheets before it was heated. First, the TiO_2 suspension was also sprayed onto the PC sheets before the PC sheets were heated until 190 ºC. Before being inserted into the muffle furnace for heating, the PC sheets were sprayed with the TiO2 suspension prepared. This was followed by heating until 190 ºC, where afterwards, the melted PC sheets were left to cool at room temperature. The second coating technique employed was the drop-casting technique. 0.2 mL of the TiO_2 suspension was drop-casted directly by a 1 mL micropipette onto the treated PC sheets, followed by heating at 190 ºC [22]. The residual solvent was removed at this temperature and it was anticipated that the adherence between the TiO_2 NPs and the PC sheets will become stronger [23].

2.5. Characterizations
The crystalline structure of the coated PC sheets were performed by Rigaku Smart Lab, Germany with Cu Kα radiation (λ=1.5418 Å) operated at 40 kV and 30 mA. The diffraction pattern was scanned in the 2θ range of 5º to 90º. The morphological features and surface characteristics of the photocatalyst were characterized using FESEM (JEOL JSM 6710F) at an accelerating voltage of 15 kV. The chemical element content of the photocatalysts was observed by FESEM. The adhesion of the coatings was assessed by the tape test according to ISO9211 on the coated area [26]. A black cellophane tape was pressed firmly on the surface and pulled out as fast as possible from the sample [27]. This procedure was repeated until there is no attached coating can be found on the tape.

2.6. *Photocatalytic testing*

The photocatalytic activity of the coated PC sheet was tested out in the degradation of methyl orange (MO, Aldrich 85%) using a 1200 W lamp UV light source. Prior to that, the coated PC sheet was immersed into MO solution (20 ppm, 20 mL) and the solution was stirred using magnetic stirrer in the dark condition for 2 h in order to reach the adsorption equilibrium. After reaching adsorption equilibrium by magnetically stirring the solution in the dark, the UV light was switched on. 3 mL of the treated MO was collected after 5 h of reaction. The concentration of the MO from the withdrawn aliquot was analyzed using a UV-Vis spectrophotometer. The same procedure was used for all the coated PC sheets.

3. Results and Discussion

In this research, TiO_2 has been successfully coated on the surface of PC sheets by drop-casting and spray-coating method. First, the preparation of TiO_2 suspension by three different methods was carried out. Following that, surface modification of the PC sheets was carried out by the usage of NaOH and APTMS solution in order to obtain a good adhesion of TiO_2 on the PC surface. The TiO_2 suspension was drop-casted and sprayed directly onto the treated PC sheets. The coated PC was then heated at 190 ºC in order to remove any residual solvent and to enhance the adhesion of TiO_2 suspension onto the PC surface.

3.1. *Effect of coating method*

In order to determine which method is better to coat the PC sheets with TiO_2, comparison were made based on their physical appearance. The PC sheet that was coated by the spray coating method showed an uneven layer of TiO_2 and some agglomeration. In fact, some parts of the PC sheet did not exhibit any coating at all (Fig. 1 (a, c and e)). As shown in Figure 1, the drop-casting method (Figure 1 (b, d and f)) was able to produce a more uniform layer than the spray-coating method (Figure 1 (a)). As reported by Lee *et al*. [28], thin film deposited by spraying-coating is commonly non uniform due to the formation of isolated droplets and pinholes. However, the transparency of the PC sheets was slightly affected using the drop-casting method. Since uniformity is crucial for the photocatalytic activity, the drop-casting method was chosen for further experiments.

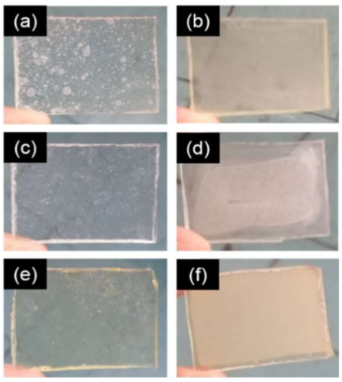

Figure 1. Thin films of TiO_2 coated on PC sheets; (a) TiO_2 suspension prepared by method 1 was spray-coated onto PC sheets, (b) TiO_2 suspension prepared by method 1 was drop-casted onto PC sheets, (c) TiO_2 suspension prepared by method 2 was sprayed-coated onto PC sheets, (d) TiO_2 suspension prepared by method 2 was drop-casted onto PC sheets, (e) TiO_2 suspension prepared by method 3 was sprayed-coated onto PC sheets and (f) TiO_2 suspension prepared by method 3 was drop-casted onto PC sheets.

3.2. *Effect of surface modification*

Figure 2 shows the differences between TiO_2 coated on PC's surface after modification with NaOH and APTMS. The TiO_2 suspension was prepared by method 1, 2 and 3 and coated using drop-casting method. Based on Figure 2, it can be seen that the surface modification with NaOH (Figure 2 (a, c and e)) produced a non-uniform layer of coating. In fact, some parts of the PC sheet did not exhibit any coating at all. While, surface modification with APTMS produced a uniform layer of coating (Figure 2 (b, d and f)).

3.3. Effect of TiO_2 suspension's preparation method

Figure 3 shows photographs of the PC sheets that have been coated by TiO_2 suspension prepared by the three different methods. Initially, the PC sheets were transparent with no colour. As shown in Figure 3 (a), the PC sheets coated by method 1 changed from colourless to yellow in colour due to the presence of nitric acid in the TiO_2 colloidal suspension [29]. This is because the PC sheets are vulnerable to acid attack. The yellowing of PC sheets was not favourable for the application purposes. Meanwhile, PC sheets coated by method 2 remained transparent. However, a formation of crystal layer can be seen on the surface (Figure 3 (b)). The TiO_2 suspension prepared by method 3 managed to produce a uniform layer of coating on the surface of the PC sheets. But the PC sheets coated by method 3 show less transparency compared to those of method 2, with an almost opaque appearance (Figure 3 (c)).

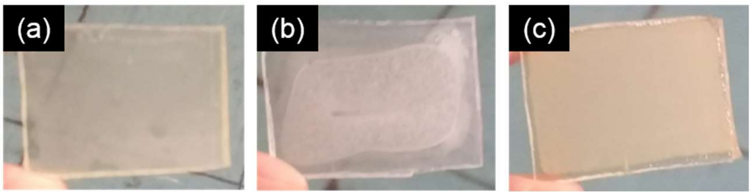

Figure 3. Photographs of coated PC sheets by using drop-casting method with TiO_2 suspensions prepared by (a) method 1, (b) method 2 and (c) method 3.

In this study, the attachment of TiO_2 coating onto PC sheets was further studied using peel adhesion test by Rouw [30] but with slight modifications. Figure 4 (a-c) shows the coating material before peel test whereby TiO_2-coated on PC by (a) method 1, (b) method 2 and (c) method 3. The black cellophane tape was pressed firmly on the surface and pulled out as fast as possible from the sample [27]. This procedure was repeated until no attached coating can be found on the tape. Figure 4 (d-f) show the pictures of the cellophane tape after being peeled off from the samples.

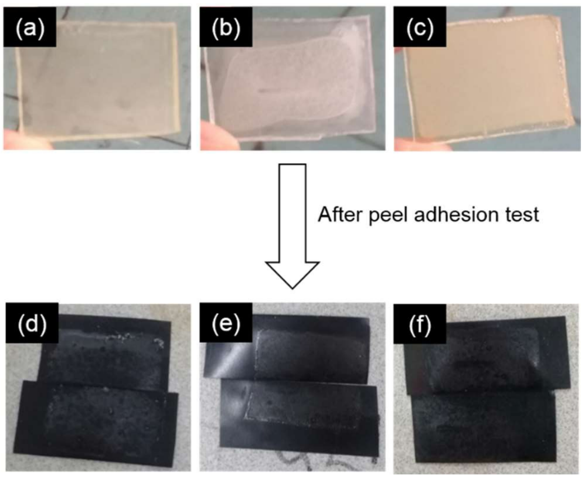

Figure 4. Images of TiO_2 coated by drop-casting method on PC sheets before (a-c) and after (d-f) peel adhesion test.

Based on Figure 4, for all 3 methods, samples can be seen on the cellophane tape. Out of all 3 methods, method 1 shows the most samples attached on the cellophane tape after being peeled off. For method 2, some of the sample was observed on the cellophane tape after the peel adhesion test due to the formation of a crystal layer on the PC sheets surface. The crystal layer can be easily peeled off from the PC sheets. Meanwhile, for method 3, after the peel adhesion test, it can be observed that there is still more sample remained coated on the PC sheets compared to the cellophane tape. TiO_2 suspension prepared by method 3 was able to attach strongly on the PC sheets compared to the other methods. A higher durability could not be achieved most probably due to the usage of low temperature during deposition steps, which was 190 ºC. A further calcination process is needed in order for the coating to adhere strongly on the PC sheets. However, due to the physical limitations of PC, which is a thermoplastic polymer, higher temperature could not be used [31]. Based on the appearance of the coating, PC sheets coated with TiO_2 prepared by method 2 was able to produce a slightly transparent coating. However, the attachment is not as strong on the PC sheet's surface. Meanwhile, for the adherent of TiO_2 coated on PC sheets, PC sheets coated with TiO_2 prepared by method 3 was able to adhere strongly onto the PC surface, although with reduced transparency. Based on these results, only PC sheets coated with TiO_2 prepared by method 2 and method 3 were further characterized and used for photocatalytic activity testing.

3.4. Physicochemical properties of TiO_2 coated on PC sheets

The main purpose of this study is to coat TiO_2 on PC, which can be extended to application in car headlights. Several properties of the coating need to be considered before such application, especially the optical transparency and uniformity of the coating. Therefore, only PC sheets modified with APTMS and deposition of TiO_2 colloidal suspension via drop-cast was further characterized due to the formation of a more uniform layer coated on the PC sheets. These TiO_2 coated on PC sheets were then characterized using FESEM-EDX and GI-XRD.

The FESEM images shown in Figure 5 reveal the morphology of TiO_2 coated by method 1, 2 and 3 on PC sheets. The magnification for Figure 5 (a) was 50 000 times, while the magnifications for Figure 5 (b) and (c) were 70 000 times. TiO_2 particles that are almost spherical and agglomerated can be seen on all three samples. However, the TiO_2 coating seem more uniform and smaller in size for method 1 (Figure 5 (a)) and method 3 (Figure 5 (c)). More agglomeration can be seen on Figure 5 (b) prepared by method 2.

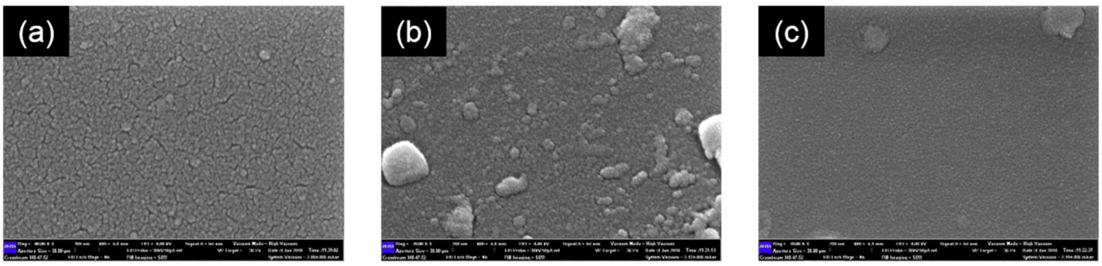

Figure 5. FESEM images PC sheets modified by APTMS followed by coating via drop-casting method with TiO_2 suspension prepared by (a) method 1 with magnification of 50000 times, (b) method 2 with magnification of 70000 times and (c) method 3 with magnification of 70000 times, all with accelerating voltage of 5.0 kV.

In order to confirm the observation above, the particle sizes were measured and listed in Table 1. The measurements confirmed that method 1 and method 3 are more capable of producing TiO_2 with a smaller size, for coating onto PC sheets. Meanwhile, method 2 was not able to produce TiO_2 within the desired size to be coated onto PC sheets. Therefore, method 1 and 3 have shown the ability to produce TiO_2 coated onto PC sheets within the desired size range, which was in between 7 – 20 nm.

Table 1: Average size of TiO_2 coated on PC sheets.

TiO_2 coated on PC sheets	TiO_2 particle size (nm)
Method 1	12-43
Method 2	86-260
Method 3	10-36

The crystallinity of the TiO_2 coated on PC sheets was determined by GI-XRD. Figure 6 shows the XRD patterns of the samples PC sheets by drop-casting coating with TiO_2 prepared by (a) method 1, (b) method 2 and (c) method 3. Based on the patterns, all 3 samples show mostly amorphous nature, which was proven by the broad halo peak at $2\theta = 17.6^{o}$ [32]. However, a small anatase peak can also be detected at around $2\theta = 25^{o}$ (PDF-00-021-1272), indicating low crystallinity in the sample.

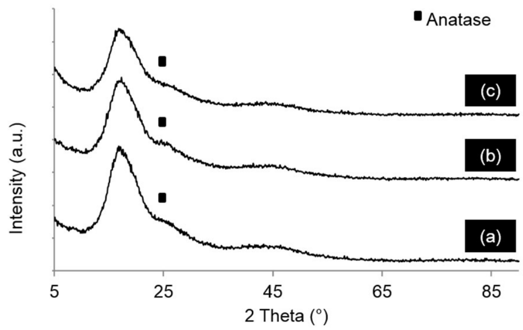

Figure 6. XRD patterns of PC sheets modified with APTMS followed by coating with TiO_2 prepared by: (a) method 1, (b) method 2 and (c) method 3 via drop-casting method.

3.5. Photocatalytic activity

The photocatalytic activity of the coated PC was tested out in the photodegradation of an aqueous solution of MO under UV light irradiation (1200W). Based on the characterization results, only TiO_2 coated by method 2 and method 3 were used for this testing. MO was chosen as the model of organic pollutant to evaluate the degradation activities of the coated samples and the degradation was monitored by UV-Vis spectrophotometer. Table 2 shows the degradation percentage of MO in the presence of PC sheets modified with APTMS followed by coating with TiO_2 prepared by method 2 and method 3 under UV light irradiation after 5 h.

Table 2: The degradation percentage of MO by TiO_2 coated PC sheets after 5 h of exposure to UV light irradiation.

TiO_2 coated on PC sheets	Degradation percentage (%)
Method 2	13.9
Method 3	19.9

For both coated PC sheets, it was found that TiO_2 coated on PC sheets (via method 2 and 3) are able to decompose MO under UV light irradiation, although not at high percentage. It can also be observed that PC sheet coated with TiO_2 prepared method 3 shows a higher photocatalytic activity as compared to that of PC sheet coated with TiO_2 prepared method 2. This could be explained by the difference of the TiO_2 particle sizes and the amount of coating attached on the PC's surface (Table 1). In the FESEM images (Figure 5), it was shown that the particle size of TiO_2 from method 3 was smaller compared to that of method 2. Smaller particle size not only increase transparency [33], it will also increase the surface area, hence increasing the catalytic activity [15]. The same trend can also be observed for the peel adhesion test, where less sample was peeled off from method 3 as compared to method 2. Based on the photocatalytic activity, it was shown that PC sheets modified by APTMS followed by coating with TiO_2 via drop-cast method is an effective photocatalyst for the degradation of MO dye under UV light irradiation. However, modifications and improvements would have to be made in order to apply this to PC car headlights.

4. Conclusion

The study present some initial results of coating PC sheets with TiO_2 for self-cleaning purpose. It was found that TiO_2 colloidal suspension prepared via method 3 coated on PC sheets modified with APTMS via drop-casting method managed to produce a more uniform coating, with the strongest adhesion, as proven by the peel adhesion test. However, some reduction in transparency can also be seen. The coating using TiO_2 suspension from method 1 and method 2 were less uniform and most of the samples were not strongly attached to the PC. On the basis of the characterizations and photocatalytic activity testing, it was shown that PC sheets modified by APTMS followed by coating with TiO_2 via drop-cast method is an effective photocatalyst for the degradation of MO dye under visible light irradiation. However, modifications and improvements would have to be made in order to apply this to PC car headlights.

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References

[1] Carneiro J O, Teixeira V, Portinha A, Magalhães A, Coutinho P, Tavares C J and Newton R 2007 *Mater. Sci. Eng.,* B **138**(2) 144
[2] Fateh R, Ismail A A, Dillert R and Bahnemann D W 2011 *J. Phys. Chem.* C **115** (21) 10405
[3] Howell S J 2009 *U.S. Patent Application* **12** (511) 561
[4] Subedi D P, Zajickova L, Bursikova V, and Janca J 2003 *Himal. J. Sci.* **1**(2) 115
[5] Dvorchak M J 2014 *RadTech 2014: Radyech UV & EB Technology and Conference 2014* Chicago USA
[6] Fateh R, Dillert R and Bahnemann D 2013 *Langmuir* **29**(11) 3730
[7] Hwang D K, Moon J H and Shul Y G 2003 *J Solgel Sci Technol.* **26** 783
[8] Mackenzie J D and Bescher E P 2007 *Acc. Chem. Res.* **40**(9) 810
[9] Yaghoubi H, Taghavinia N and Alamdari E K 2010 *Surf Coat Technol.* **204**(9-10) 1562
[10] Fujishima A, Rao T N, and Tryk D A 2000 *J Photoch Photobio* C **1** 1
[11] Daghrir R, Drogui P and Robert D 2013 *Ind Eng Chem Res.* **52**(10) 3581
[12] Hu F, O'Connor P and Chiao Y H 2000 *U.S. Patent Application No.* **09/729** 490
[13] Benedix R, Dehn F, Quaas J and Orgass M 2000 *LACER* **5** 157
[14] Latthe S, Liu S, Terashima C, Nakata K and Fujishima A 2014 *Coatings* **4** (3) 497
[15] Daghrir R, Drogui P, Ka I and El Khakani M A 2012 *J Hazard Mater.* **199** 15
[16] Chae S Y, Park M K, Lee S K, Kim T Y, Kim S K and Lee W I 2003 *Chem. Mater.* **15** (17) 3326
[17] Kemmitt T, Al-Salim N I, Lian J, Golovko V B and Ruzicka,J Y 2013 *Curr. Appl. Phys.* **13**(1) 142
[18] Chandren S, Ismail K, Nur H and Ohtani B. 2017 *Appl. Sci.* **7**(7) 698
[19] Lam S W, Soetanto A and Amal R 2009 *J. Nanoparticle Res.* **11**(8) 1971
[20] Rudolph A, Teske M, Illner S, Kiefel V, Sternberg K, Grabow N, Wree A and Hovakimyan M 2015 *PloS One* **10**(12) 0142075
[21] Chandren S and Ohtani B 2012 *Chem. Lett.* **41**(7) 677
[22] Lim H S, Kwak D, Lee D Y, Lee S G and Cho K 2007 *J Am Chem Soc* **129**(14) 4128
[23] Zhang Q, Chou T P, Russo B, Jenekhe S A and Cao G 2008 *Angew. Chem.* **120**(13) 2436
[24] Hidalgo M C, Aguilar M, Maicu M, Navío J A and Colón G 2007 *Catal Today.* **129**(1-2) 50

[25] Yang J, Wan Y, Tu C, Cai Q, Bei J and Wang S. 2003 *Polym Int.* **52**(12) 1892
[26] Schulz U, Lau K and Kaiser N 2008 *Appl Opt.* **47**(13) C83
[27] Kemell M, Färm E, Ritala M, and Leskelä M 2008 *Eur. Polym. J.* **44**(11) 3564
[28] Lee J H, Sagawa T and Yoshikawa S 2011 *Org Electron.* **12** 12 2165
[29] Xing R, Latthe S S, Bhosale A K, Li R, Kumar A M, and Liu S 2017 *J Mol Liq.* **247** 366
[30] Rouw A C 1998 *Prog Org Coat.* **34(**1) 181
[31] Ashby M F 2012 *Materials and the Environment: Eco-informed Material Choice* 2nd ed. Elsevier
[32] Sain P K, Goyal R K, Bhargava A K and Prasad Y V S S 2013 *J. Phys.* D **46**(45) 455501
[33] Winkler J 2013 *Titanium dioxide: Production, Properties and Effective Usage* 2nd ed (Vincentz Network)