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Synthesis and Evaluation of Novel TiO₂-based Self-cleaning Coating Layer for Buildings

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Abstract. This research was carried out in order to analyse the potential of novel nitrogen-doped TiO₂/SWCNT (N-doped TiO₂/SWCNT) photocatalyst nanocomposites for pollutant removal that deposits on surfaces of buildings. In the present work, the procedure to fabricate this nanocomposite follows a simple method which is sol-gel synthesis method using titanium tetraisopropoxide (TTIP) and ammonia as the precursor. Different composition of TiO₂ and SWCNT were used to achieve the optimum composition suitable for building surfaces as a self-cleaning coating. The fabricated dried sols were characterized by XRD to ensure TiO₂'s anatase nanocrystalline structure was maintained even after doping. The morphology of these novel coatings was observed by FESEM. FESEM showed that uniform dispersion between TiO₂ and SWCNT is present which exhibited a vine-like structure. Methylene blue degradation test was conducted to measure the photocatalytic efficiency of each coating. The highest degradation efficiency achieved was 72.43 %. Spin-coating method was used to deposit a thin layer of this coating on the glass substrate to inspect the water contact angle (WCA) of the as-prepared coatings. The coatings displayed a contact angle of 21.3 °proving that the wetting characteristic falls under hydrophilic category in which any sprinkled water is able to remove the dirt that deposits on the surface. Self-cleaning testing was carried out on glass substrates to further evaluate the coating layers. The coated substrates cleaned about 99 % of the dirt that deposited on its surface. These coatings could be utilized in various applications be it indoors or outdoors, for water remediation, energy saving panels and many potential fields.

1. Introduction

For decades, organic contaminants that deposits on the buildings owing to rough climates, microorganism growths, bird droppings, has been major concerns in our societies. To trigger this situation, huge water demand, cleaning chemicals, and higher manpower are necessary to clean the deposited dirt on the window surface, not to mention the areas with water scarcity. Numerous approaches have been presented to keep the window surface of the buildings clean by restraining the microalgal fouling. Among them, bioinspired surfaces like plants and insect's wings [1] that displays the lotus-leaf effect has been researched extensively because of its self-cleaning attribute.

Self-cleaning coating is one of the readily available and favourable technique that could be utilized to wash the building surfaces be it windows or any glasses and TiO₂, being the renowned photocatalyst has attracted enormous attention lately [2]. Studies prior to this field have emphasized TiO₂ based coating due to its self-cleaning property, inexpensiveness, higher photocatalytic activity (PCA), and chemical inertness [3].

Nonetheless, bare TiO₂ have one drawback due to its broad band-gap energy (BGE) which is 3.2 eV for anatase and 3.0 eV for rutile [4] that limits the visible light absorption ability. This condition



decreases the PCA performance and also causes TiO_2 unemployable for indoor applications. To suppress this BGE, TiO_2 has been doped with various materials like Ag^+ [5], SiO_2 [6], N_2 [7] lately to enhance the PCA property. Besides these materials, the techniques used are also essential in synthesizing hydrophilic self-cleaning coatings. Li et al. [8] fabricated self-cleaning silver-doped TiO_2 coating using a dip-and-dry technique but these coatings could not be used as self-cleaning layers as its potential in anti-microbial attribute is yet to be explored. Similar study was conducted by Powell et al. [9] using vanadium (IV) oxide and TiO_2 to fabricate a self-cleaning coating using chemical vapor deposition method. However, VO_2 is slightly pricey and are inclined to chemical attacks, possesses poor adherence on substrates and also, the coatings are translucent which refrains the sunlight from penetrating the film. Bergamonti et al. doped Nitrogen with TiO_2 coating using sol-gel synthesis which was 'brushed' on top of stone to evaluate its self-cleaning property [10]. This research is still under lab-scale as brushing a coating layer on a surface is not feasible for large-scale.

In spite of all these extensive studies, a low-cost synthesis route to fabricate a hydrophilic self-cleaning coating in large-scale is not mentioned clearly in the literature review. The synthesis method utilized seemed expensive and the coating methods are slightly complicated for larger applications. Therefore, the objective of this paper is focused on inducing self-cleaning property by doping TiO_2 with inexpensive materials using sol-gel synthesis method. This coating is expected to result in a better hydrophilicity with a higher water contact angle that could be coated on buildings to ease the self-cleaning process over an extensive period.

2. Methodology

2.1 Catalyst preparation

All reagents were used directly without further purification. These novel nanocomposites were prepared using sol-gel synthesis method. Briefly, TTIP powder according to Table 1 was stirred with 50 mL ethanol and kept aside. 4 mL nitric acid, 10 mL of ethanol and 10 mL ammonia water (28 wt %) were mixed and kept aside. This then added drop-wise to the TTIP mixture under constant stirring for 10 hours at room temperature. After 10 hours, the liquid was then heated in an oven at 80 °C for 12 hours and calcined in the furnace at 350 °C for 6 hours. The samples were labelled as N_1 till N_4 .

Table 1. Compositions of TTIP and SWCNT.

Samples	TTIP (mL)	SWCNT (g)
N_1	2.5	0.1
N_2	5	0.01
N_3	10	0.05
N_4	2.5	0.01

Later, the functionalized SWCNT was mixed with 50 mL of 2-propanol and were sonicated for 20 minutes. 5 mL of ethanol was added drop by drop to TTIP and functionalized SWCNT according to Table 1. The obtained slurry stirred for 10 hours at 90 °C while adding 5 mL acetic acid dropwise. This stirred slurry then dried at 120 °C in the oven for 10 hours. 0.05 g of the obtained powder is diluted using 5 mL dimethylformamide (DMF) and spin coated on 2 cm by 2 cm glass substrates at 1800 rpm for 40 seconds. These substrates dried at 70 °C for 20 minutes.

2.2. Catalyst characterization

XRD analysis was done by Bruker D8B advanced X-ray diffractometer (XRD) in the $2\theta = 10-90^\circ$ range. The crystal size (D) of the particles were measured using the Scherrer's equation. Field Emission Scanning electron microscope (FESEM) analysis was utilized to obtain the morphological structure of the samples. Methylene blue (MB) degradation was carried out under visible light irradiation as stated in previous study [11]. The degradation efficiency of MB was calculated using:

$$\text{Degradation } \eta = \frac{C_i - C_f}{C_i} \times 100\% \quad (1)$$

where C_i is the initial concentration of MB and C_f is the concentration of the samples at each interval. Pendant drop method was used to obtain the water contact angle of the coating on the glass surface. Briefly, an automated syringe dispensed 5 μL water on 2 cm by 2 cm glass substrates. The angle between the glass substrate surface and the water droplet is measured after 15 seconds. 20 g of coal dust was dispersed in 20 mL of water and then deposit it on the substrates to test the self-cleaning performance. These deposited substrates later dried at ambient temperature for an hour.

3. Results and discussions

3.1 Characterization results

Figure 1a exhibits the XRD patterns of the prepared samples in the range of $2\theta = 10-90^\circ$. These powder samples of TTIP showed the diffraction peaks at $2\theta = 25.6^\circ, 38.1^\circ, 48.4^\circ, 54.2^\circ$, and 63.1° , which is proportional to that of anatase phase TiO_2 . This proves that doping of Nitrogen on to TiO_2 lattice did not show any other phases. Also, it is conceivable to conclude that doping of Nitrogen into TiO_2 restricted the anatase phase transformation to brookite. This is a crucial phase as anatase has better photocatalytic activity compared to brookite and rutile.

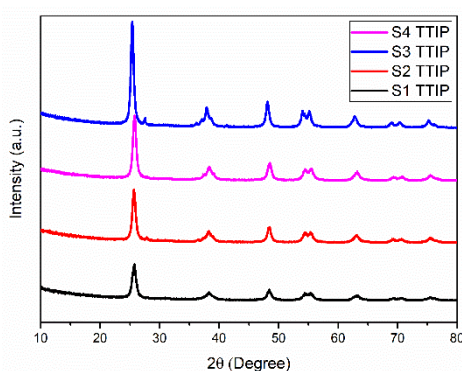
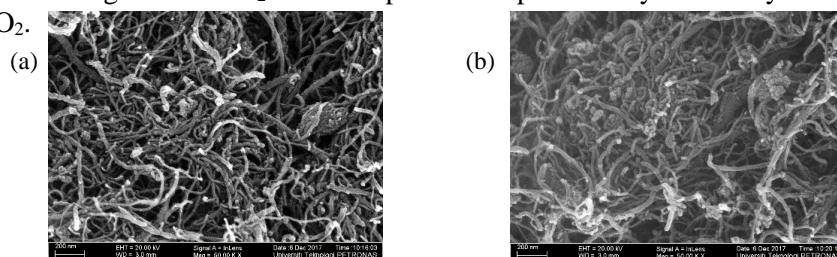


Figure 1. XRD pattern of the samples

Figure 2 below displays the FESEM images after the nanoparticles were doped with functionalized SWCNT. These images show that the SWCNT particles have vine-like structure intertwining with TiO_2 particles for all the samples. In Figure 2a and 2b, the mass of SWCNT used was 0.1 g and 0.01 g with 2.5 mL and 5 mL TiO_2 respectively and it shows a uniform distribution between SWCNT and TiO_2 particles. The SWCNT vines have covered almost all the TiO_2 particles evenly. As for Figure 2c, not all the TiO_2 particles are interweaved uniformly with SWCNT. Some TiO_2 particles were not meshed at all. Since the ratio of TiO_2 to SWCNT for N_3 is bigger than all the other samples, this may be the reason for the TiO_2 particles to not being meshed with SWCNT. Although XRD and FESEM contributes prominent data, a highly quantitative method is necessary to evaluate the degradation rate of these samples. MB degradation test was conducted to assess the photocatalytic activity of the coatings.

The results of these degradation rate efficiencies are exhibited in Figure 3. N_1 indexed the highest degradation rate of 72.43 % followed by N_2 which showed 67 % photocatalytic rate. These readings were compared with bare Degussa P25 and the value obtained was 50 % degradation rate. This value is way lesser compared to N_1 , N_2 and N_3 which showed 72.43 %, 67 % and 56.14 % respectively. Thus, N_1 , N_2 and N_3 have a better photocatalytic activity compared to bare TiO_2 . This means that incorporating SWCNT and Nitrogen into TiO_2 lattice improves the photocatalytic activity of the coatings compared to bare TiO_2 .



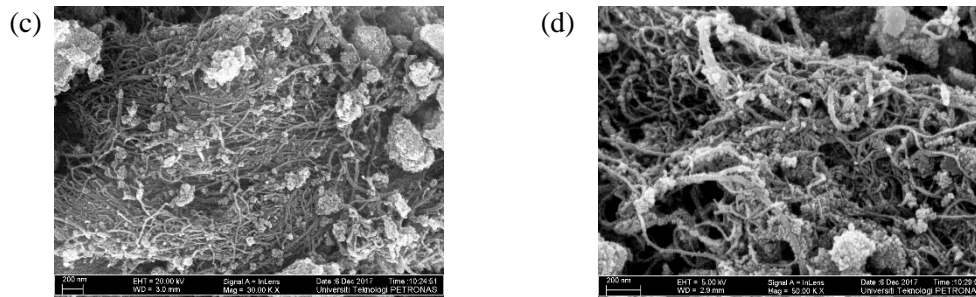


Figure 2. FESEM images of N-doped TiO₂ incorporated with SWCNT a) N₁TTIP, b) N₂ TTIP, c) N₃ TTIP, and d) N₄ TTIP at 50 X magnification.

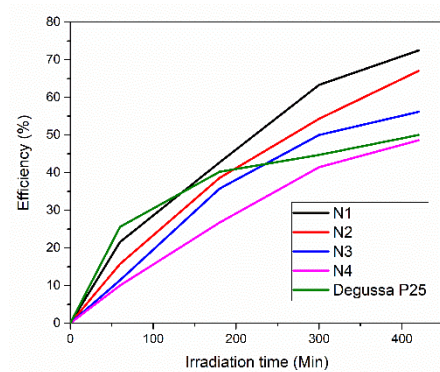


Figure 3. Photocatalytic degradation efficiency of the samples.

Table 2 shows the obtained degradation rate and photocatalytic activity of the samples. A previously done similar study on CNT-TiO₂ and reported 57 % as the highest degradation efficiency [12]. Thus, doping of Nitrogen enhances the PCA as nitrogen could prevent phase transformation of anatase to brookite and also narrows the wide band gap energy of TiO₂.

Table 2. Summary of the degradation rate and photocatalytic performance of the samples.

Samples	C/C ₀ (mg/L) after irradiation	Photocatalytic performance (%)
N ₁	1.93	72.43
N ₂	2.31	67.00
N ₃	3.07	56.14
N ₄	3.60	48.57

3.2. Wettability of the coating

In order to know the hydrophilic property of the coating, water pendant tests were conducted on the samples. The results of the different coatings namely a) N₁ and b) N₂ are demonstrated in Figure 4 below.

Figure 4a has a water contact angle (WCA) of 21.3° with a 2.5 mL TiO_2 and 0.1 g CNT which falls under the hydrophilic category. This dispensed water droplet spread throughout the glass substrate instantly. As for Figure 4b, the WCA is not very satisfying, as the angle obtained was 85.4° which is almost reaching hydrophobic property. The WCA remained the same even after 120 seconds indicating that sample N_1 possesses a strong hydrophilic property than sample N_2 .

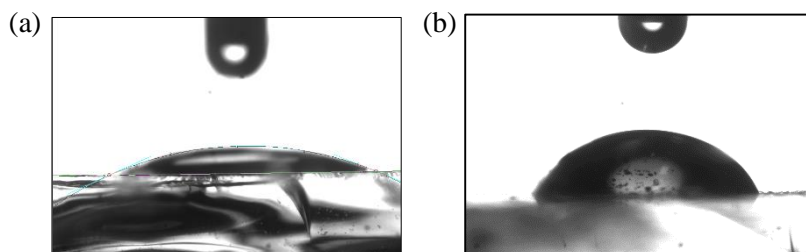


Figure 4. Contact angle of a) N_1 and b) N_2 .

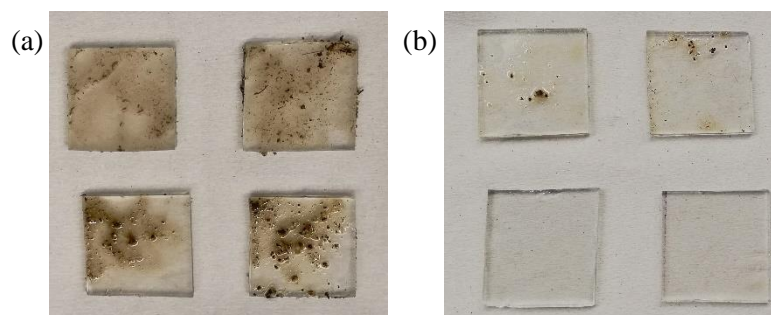


Figure 5. The glass substrates (a) after dipped in coal dust and (b) after spraying water.

Thus, the most suitable sample is N_1 as the self-cleaning property is massively influenced by the hydrophilic property. Whenever dirt is deposited on the surface, the water will wash away all the dirt effortlessly without the need to scrub it off ensuring that the self-cleaning performance is at an ideal level. These glass substrates later deposited with coal dust to test the self-cleaning performance as shown in Figure 5. The upper row indicates the uncoated glass and the lower row indicates the coated glass. After dipped in coal dust and sprayed with 5 mL of water, the uncoated glasses still had residue on it compared to the coated glasses, which is very clean without any dirt deposition. Therefore, the fabricated coating is indeed a success.

4. Conclusion

This paper presents the potential hydrophilic self-cleaning property of TiO_2 -based coating on the glass surface using sol-gel synthesis method. The developed coatings indexed a higher photocatalytic activity of 72.43 % which is slightly higher than Degussa P25 bare TiO_2 that has a 50 % efficiency. Besides, the WCA of N_1 sample is as low as 21.3° which is under hydrophilic property. This property could be utilized on buildings to wash away the dirt that deposits on it like bird droppings, dust and other pollutants by rolling the dirt away from the surface with the aid of water. Also, the contact angle increased as the amount of SWCNT reduces indicating that the coating acquires a very good hydrophilic property. Thus, the coatings demonstrated an excellent hydrophilic property on the glass. The developed invention is employable for large-scale outdoor applications, especially on buildings. It could be concluded that N-doped TTIP/SWCNT nanocomposite coating is suitable to be applied on the glass surfaces on the building as a self-cleaning agent.

5. References

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