Fabrication of SWCNT/TiO_2 for Creating Self-Cleaning Property on the Glass

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Abstract- The significance of this research is to fabricate a Single Wall Carbon Nanotubes/ Titanium dioxide (SWCNT/TiO_2) composite to be coated on glass which has the self-cleaning property. It has been observed that the surface of the glass tends to get dirty and dusty with time. The objectives of this paper are to compare and analyze the transmittance and also the photocatalytic activity of the nanocomposite solutions prepared. The method used to fabricate this composite is sol-gel synthesis as it has a higher amount of dispersion and is the easiest way to use and the method used to coat the solution on substrate is spin coating method since it has a uniform coating compared to other methods. It is important to ensure that the solution prepared is transparent so as to ease the coating process. 20 different samples were fabricated using different amount of SWCNT and TiO_2 composition. In order to analyze transparency and photocatalytic activity, two different characterizations were conducted namely Fourier Transform Infrared Radiation spectroscopy (FTIR) for transmittance and Ultraviolet Visible absorption spectroscopy (UV-vis) for Methylene Blue (MB) concentration photodegradation. The highest transmittance obtained were (a) 10ml of TiO_2, 0.04g SWCNT which was 82.2% and (b) 10ml of TiO_2, 0.06g SWCNT which was 73.2% of transmittance. Also, the lowest concentrations achieved by MB are (a) 10ml of TiO_2, 0.06g SWCNT which was 2.48mg/L and (b) 7.5ml TiO_2, 0.02g SWCNT which was 3.1mg/L. By comparing the transmittance and photocatalytic activity, the highest efficiency obtained were (a) 10ml TiO_2, 0.06g SWCNT which was 64.6% and also (b) 7.5ml TiO_2, 0.04g SWCNT which was 56.3%.

Keywords Single Wall Carbon Nanotubes (SWCNT), Titanium dioxide (TiO_2), solar cell, self-cleaning coating layer.

1. Introduction

Photocatalytic activity is the capability to speed up the photoreaction when a photocatalyst is merged with sunlight. The photocatalyst here refer to all types of oxides namely ZnO, SnO_2, TiO_2 and many. The photocatalyst the author chose is TiO_2 as it has strong oxidizing property that could decompose the organic pollutants. Decomposition is only possible when there is sunlight available. TiO_2 is also known for its superhydrophilic property [1, 2]. These two properties alone are very significant for self-cleaning property. It is very easy to apply TiO_2-based coatings on any substrates for any purposes. Also, TiO_2 has the ability to decompose and kill organic contaminants and bacteria that are attaching to the surface but with the presence of UV-Visible light [3, 4].

Different semiconductors were used for the removal of pollutants which could also be used for photocatalysis. Yet, they do have major drawbacks. For instance, metal sulfides are not stable enough for catalysis in aqueous medium due to photo anodic corrosion and they are also toxic. Iron oxides (FeO) undergo photocathodic corrosion. Zinc oxide (ZnO) is unstable in water and forms Zn $(OH)_2$ on the particle's surface [3].

TiO_2 is very well known for its excellent photocatalytic property as it is vastly used in environmental issues. TiO_2 is the suitable oxide that could be used as it could react with water elements to produce organics which are useful for self-cleaning property [5-7]. This will only be possible under the illumination of ultra violet (UV) and visible rays. TiO_2 is being studied widely for the use of water and air decontamination for future applications. TiO_2 is used in solar cells for electrical energy production and it also plays a major role as gas sensor. TiO_2 is also used as white dye in conventional paints and many cosmetic products. It also act as corrosion free coating layer and as optical coating layer in electric devices and ceramics. Although anatase phase TiO_2 has a higher photocatalytic activity compared to brookite, rutile and mixed phase, titanium isopropoxide (TTIP) would be used in this paper so as to compare the results. TTIP would be hydrolysed and TiO_2 would be created by this hydrolysing process.

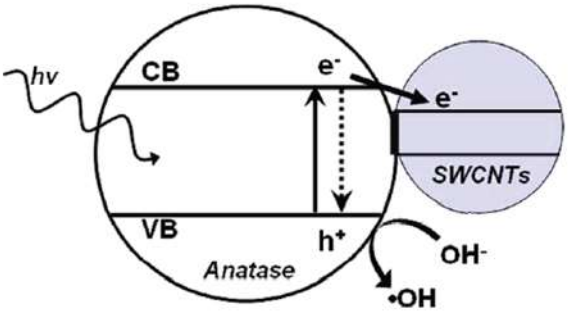

Fig. 1. Mechanism of photocatalytic activity.

From figure 1, electrons will be excited to Conduction Band (CB) from Valence Band (VB) which would create a hole (h+) in the VB. In order for this electron to excite, UV illumination is very necessary. Mostly all of these excited charges will recombine quickly if there is no presence of the SWCNTs. The excited state of both CB and VB electrons will recombine and evaporate in heat form. Yet, only small amount of electrons and holes will take part in photocatalytic reactions (less than 1%) which directly results in lower photocatalytic activity [5]. If the energy of a photon, hv equals or exceeds the energy of the band gap of the semiconductor, an electron will excite from VB to CB leaving a hole at VB. SWCNT's conduction band edge position allows the electrons to transfer from anatase surface whenever SWCNT is in close contact with the surface of anatase. This proximity will permit the charge separation, hindered recombination and also stabilization of the electrons shuttling independently along SWCNT's conducting arrangement. Thus, as the lifespan of the holes increases, the photocatalytic activity of the nanocomposite will increase.

SWCNT was chosen to incorporate with TiO_2 because this composite will create more reactive photocatalyst than the other Carbon Nanotubes (CNTs) such as Multi Wall Carbon Nanotube (MWCNTs) [6]. It possesses a very large surface area which is greater than $1315 m^2g^{-1}$ [8, 9]. Also, it could conduct electrons and has an excellent adsorption capacity for various organic and inorganic pollutants [10]. SWCNT is fully utilized to intensify the photocatalytic activity of TiO_2 since it could conduct electrons and also it has a higher adsorption capacity for particular organic substrates.

There are four major methods used to manufacture SWCNTs which are laser ablation, electric-arc discharge, Chemical Vapor Deposition (CVD) and plasma torch [11]. Langmuir–Hinshelwood mechanism explains well the photocatalytic degradation in which the atoms would be adsorbed onto the surface diffusing across the surface. This is where the atoms would start to degrade. A molecule would be formed, causing desorption to occur [12, 13].

Activated carbon has a very large specific surface area and also, it were used in researches related to photodegradation. Langmuir–Hinshelwood mechanism in figure 1 explains well the photocatalytic degradation. Thus, by increasing the specific surface area, the adsorption of pollutants amount would increase as well, which directly leads to an increase in photocatalytic activity. Yet, a higher concentration of SWCNT (5-10% weight) reduces the light intensity particles on the titanium dioxide surface which in return lowers the photocatalytic activity of this composite [14]. To assess the photocatalytic activity, the most common method vastly used is by evaluating MB concentration degradation with the help of UV-vis spectroscopy under UV illumination. Normally, MB will be mixed with the samples and kept in a dark place before irradiating it. Irradiation is done using appropriate ultra-violet lamp according to the preferences of one project. Although MB concentration is one of the easiest way to assess the photocatalytic activity, [8, 15] has used phenol oxidation method for over a 90 minutes reaction time. In it, SWCNT/TiO_2 with ratio of 20:1 indexed the highest degradation rate which is about 2.0mg/L. Also, when SWCNT ratio was added from 20:1 to 10:1, the phenol degradation did not increase because SWCNT tend to block the intensity of light that transmit on the surface of TiO_2. This research aims at investigating the efficient method to fabricate the SWCNT/TiO_2 nanocomposite. The project was analyzed based on [3, 16] studies. The self-cleaning characteristics of these solutions are to be assessed through FTIR and UV-vis. To achieve the goal, the following objectives are formulated:

1. To fabricate SWCNT/TiO_2 nanocomposite coating and coat it on top of a glass.

2. To compare and analyze the photocatalytic activity of SWCNT/TiO_2 nanocomposite.

3. To compare and analyze the transmittance of SWCNT/TiO_2 nanocomposite layer for cover glass.

2. Experimental Setup

The SWCNT/TiO_2 solution is fabricated using sol-gel synthesis. One advantage of this method is that it could be sintered under a very low temperature which is about 200-600˚C. Besides, films sintered in this temperature range seemingly very hard and is also impossible to scratch this layer off from the substrate [17]. This method could give a uniform and small sized powder and it is easy to do coating for films. Later, this solution would be coated onto glass substrate using spin coating method. This spin coating method is capable of reducing excessive waste of SWCNT/TiO_2 solution and the thickness of film could be controlled according to the preferred requirement. The coating of $SWCNT/TiO_2$ composites using this spin coating method involves deposition of little $SWCNT/TiO_2$ nanocomposite splash at the center of the glass substrate. After depositing, the substrate were spun at high speed to allow uniform dispersion throughout the substrate including the edge. This coating will look like a thin film. The configuration of this coating coated as in figure 2.

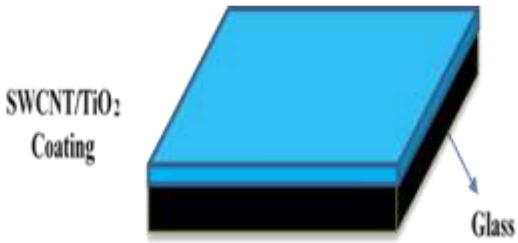

Fig. 2. The configuration of coating layer

2.1. Fabrication of transparent SWCNT-TiO_2 coatings

Various composition of SWCNT (0.02g, 0.04g, 0.06g, 0.08g and 0.1g) were prepared. 40ml of 2-propanol is added to each SWCNT composition and sonicated for 3 hours. TTIP (2.5ml, 5ml, 7.5ml and 10ml) were mixed with 10ml of ethanol and 1ml of acetic acid. Later, each composition were mixed according to Table 1 which was obtained by the Design of Experiment software. Keep each solution in stirrer for 8 hours with 80˚C heat. Later, the solution was kept in oven at 100 ˚C for 12 hours. Powder composite of 20 different samples were obtained. From each sample obtained, about 0.05g is measured individually and added with acetone. Lastly, the solutions were spin coated on glass substrate. This spin coating method must be done under the condition of 150 ˚C for 30 minutes. Procedures are shown in figure 3 in simplified manner.

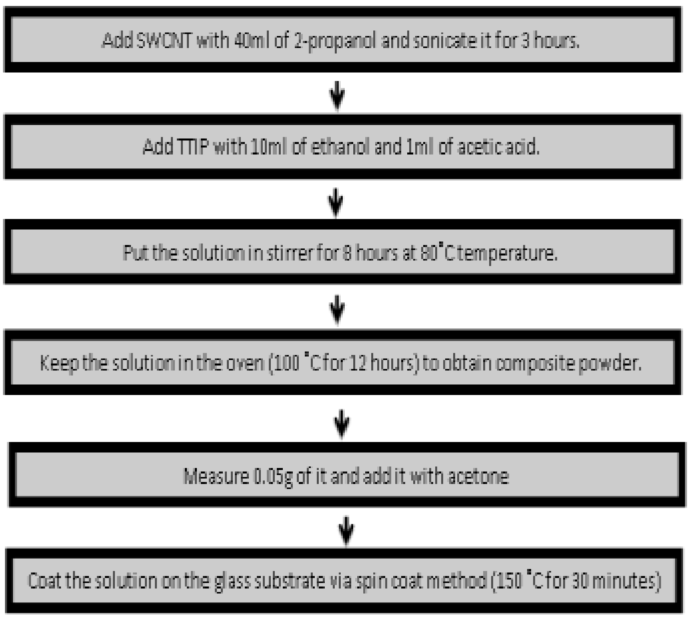

Fig. 3. Flowchart for $SWCNT/TiO_2$ solution fabrication

2.2. Spin coating

The coating layer of $SWCNT/TiO_2$ composites was applied using spin coating method. Small amount of $SWCNT/TiO_2$ solution deposited at the centre of the glass substrate inside the spin coater. Figure 4 shows how the spin coater look like in which the solution would be deposited on the glass substrate. After depositing, spin coater spun at very high speed (2500rpm) to allow uniform dispersion throughout the glass substrate. The acceleration will permit the solution to spread evenly throughout the substrate including its edge. A thin film on the surface of the glass substrate was obtained. To attain a uniform thickness and well-spread coating, the viscosity of dispersion, spin time and the angular speed plays a major role.

Among all the coating types such as dip coating, film coating and so on, this spin coating produces a better and efficient result in achieving uniform thin layer on glass substrate. By using spin coating method, the thickness of coating layer could be controlled and excess waste of the $SWCNT/TiO_2$ composite could be avoided.

Fig. 4. Spin coater

2.3. Preparation of Methylene blue (MB) for degradation test.

7mg of MB powder was measured and mixed with 1L of water in a flask. Initial concentration of MB is 7mg/L. 25ml of the solution were poured into 8 different test tubes. 0.12g of each $SWCNT/TiO_2$ powder composite were measured and kept in each of the tubes. The solution was mixed well. Solutions were kept in dark atmosphere for at least 2 hours. Later, the solutions were irradiated with one 60w UV-lamp, which was kept 10 cm away from the surface of the solution. Each sample were withdrawn for every 1 hour, 3 hours, 5 hours and 7 hours and immediately centrifuged to disperse any agglomerated suspension. Altogether, there will be 32 different samples. The photocatalytic activity of each of the solution were analyzed using UV-vis absorption spectroscopy. The higher the degradation of MB, the higher the photocatalytic activity of the solution. The results were recorded for each sample and the MB concentration degradation at the characteristic wavelength of 630nm was indexed.

2.4. Design of Experiment (DOE)

Since DOE is a systematic and reliable method to investigate various relationship between various parameter and shows the precise output that would result in optimum photocatalytic activity, this method is made use for this project. Table 1 shows the data obtained from DOE. DOE is conducted for this project in order to identify the mass of SWCNT and amount of titanium isopropoxide to be used for 20 test runs. The data is collected for the experiment using DOE. 20 samples are suggested for testing.

Table 1. Data obtained from DOE

Runs	SWCNT (mg)	TiO_2 (ml)
1	0.1	2.5
2	0.06	5
3	0.08	7.5
4	0.06	10
5	0.04	10
6	0.08	2.5
7	0.1	7.5
8	0.04	7.5
9	0.04	2.5
10	0.02	7.5
11	0.02	5
12	0.08	5
13	0.02	10
14	0.06	7.5
15	0.08	10
16	0.1	5
17	0.04	5
18	0.1	10
19	0.06	2.5
20	0.02	2.5

3. Results and Discussion

3.1. Effect of SWCNT and TiO_2 on Transmittance

Fourier Transform Infrared Radiation Spectroscopy (FTIR) characterization is used for testing on all the 20 samples that have been prepared in order to obtain the percentage of transmittance for each solution. Transmittance is directly related to the transparency of the solution. Thus, the higher percentage of transmittance, the higher the transparency of the solution would be. Besides, this characterization requires only one gram of each samples. This testing is conducted for the wavelength range from 300nm till 1000nm and the transmittance value starts from 0% till 100% as maximum. Accordingly, the transmittance of the plain water is 100%. There are 4 graphs present namely 2.5ml, 5ml, 7.5ml and 10ml of TiO_2 plotted in order to identify the relationship between 0.02g SWCNT, 0.04g SWCNT, 0.06g SWCNT, 0.08g SWCNT and 0.1g SWCNT in accordance with the transparency of the solution. The results of the FTIR are discussed as follows:

From figure 5, the highest transmittance is achieved by 0.04g of SWCNT which approximately shows 59% transmittance. The second highest transmittance is achieved by 0.06g SWCNT, 51%. It is very conspicuous that the amount of SWCNT affects the percentage of transmittance. Both these lines show a huge absorbance at 350nm wavelength. This is mainly because the ultraviolet wavelength range is from 100nm till 350nm and after this wavelength, the spectrum enters the visible light range. This clearly exhibits the property of TiO_2, which is having an excellent scattering and absorption properties at optical and ultraviolet wavelengths. The lowest transmittance is achieved by SWCNT of 0.1g which is about 10%.

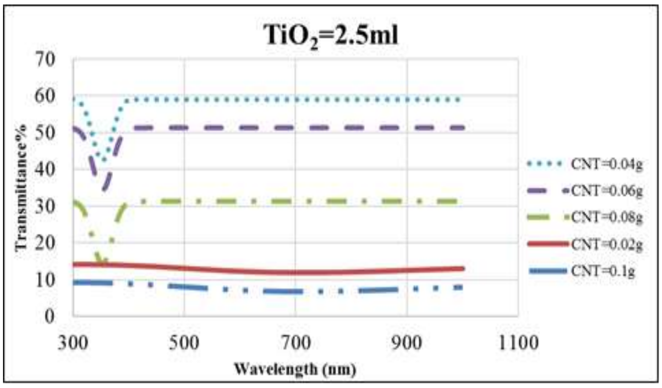

Fig. 5. Transparency of SWCNT in 5ml of TiO_2.

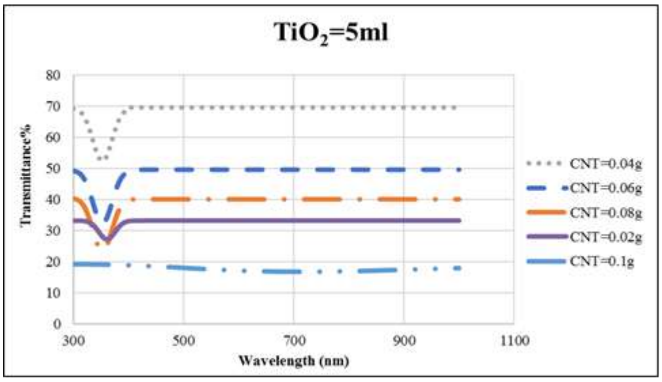

Fig. 6. Transparency of SWCNT in 5ml of TiO_2.

From figure 6, the highest transmittance is achieved by SWCNT of 0.04g which is approximately 70%. From previous graph, the highest transmittance was also indexed by 0.04g of SWCNT. And secondly, the transmittance percentage is about 50% as per 0.06g of SWCNT which is slightly lower compared to 0.04g SWCNT. The pattern here is, SWCNT of 0.04g shows an optimal increase in transmittance, which directly tells us that the transparency is at higher level compared to all other masses used for SWCNT.

According to figure 7, the highest transmittance is shown by 0.04g of SWCNT which is 64.13% and the second highest is recorded by the sample that has 0.06g of SWCNT. Lowest transmittance is indexed by SWCNT of 0.1g which is 24%.

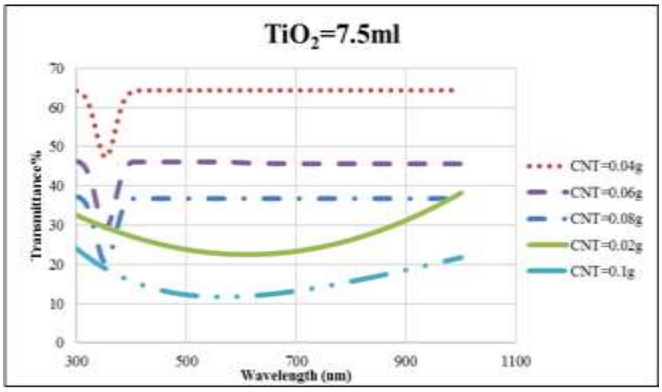

Fig. 7. Transparency of SWCNT in 7.5ml of TiO_2.

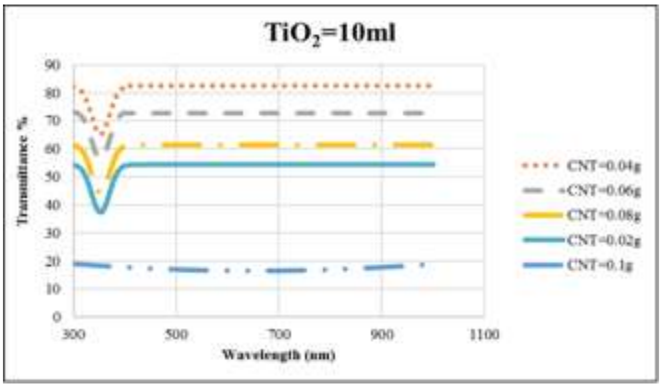

Fig. 8. Transparency of SWCNT in 10ml of TiO_2.

From figure 8, transmittance percentage of 82.2% is achieved by SWCNT of 0.04g. This is the highest percentage compared to all other amount of TiO_2 used. The second highest transmittance is 73.17% as recorded by 0.06g. This clearly shows that 10ml of TiO_2 solution is the most optimal amount of all other amounts used.

Therefore, higher SWCNT concentration seemingly reduces the light intensity on the TiO_2 surface which makes it unable to transmit the UV light [10]. This directly results in a lower transparency. In other words, only low percentage of UV light could penetrate into a sample that has higher SWCNT composition. Besides, TiO_2 shows its property of scattering the ultraviolet wavelength when there is a minimal absorbance at the wavelength of 350nm. This 350nm falls under the ultraviolet light range which tells us that blending of SWCNT with TiO_2 improves the composites' scattering and absorption of ultraviolet rays. Table 2 summarizes the highest transmittance achieved by top 10 samples. Since self-cleaning property requires higher transparency and higher photocatalytic activity, the samples that attained less transmittance would be ignored.

Table 2. Data obtained from DOE

	Composition of the sample	**Transmittance (%)**
1	10ml of TiO_2, 0.04g SWCNT	82.2
2	10ml of TiO_2 ,0.06g SWCNT	73.2
3	5ml of TiO_2, 0.04g SWCNT	70.0
4	7.5ml of TiO_2, 0.04g SWCNT	65.0
5	10ml of TiO_2, 0.08g SWCNT	61.2
6	2.5ml of TiO_2, 0.04g SWCNT	59.2
7	10ml of TiO_2, 0.02g SWCNT	54.2
8	2.5ml of TiO_2, 0.06g SWCNT	51.2
9	7.5ml of TiO_2, 0.06g SWCNT	45.6
10	2.5ml of TiO_2, 0.02g SWCNT	12.1

3.2. Effect of SWCNT and TiO_2 on Photocatalytic activity

As the concentration of the MB reduces, the photocatalytic activity will increase significantly. 8 different samples were tested for the photodegradation purpose. Distilled water is poured into one of the cuvette as a control variable. Samples of MB are poured into another one cuvette to measure the concentration degradation. The results of this UV-Vis liquid are discussed as follows:

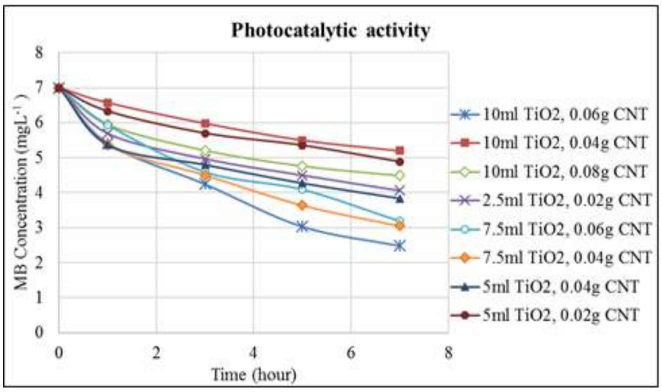

Fig. 9. Photodegradation of MB concentration with time

Figure 9 shows the concentration degradation of MB in aqueous solution relative to time of UV irradiation for the SWCNT/TiO_2 solution prepared. According to figure 9, after 7 hours of UV irradiation, 10ml of TiO_2, 0.06g SWCNT achieved a concentration degradation of 2.48mg/L. 7.5ml TiO_2, 0.02g SWCNT achieved 3.1mg/L and 7.5ml TiO_2, 0.06g SWCNT achieved 3.2mg/L concentration degradation.

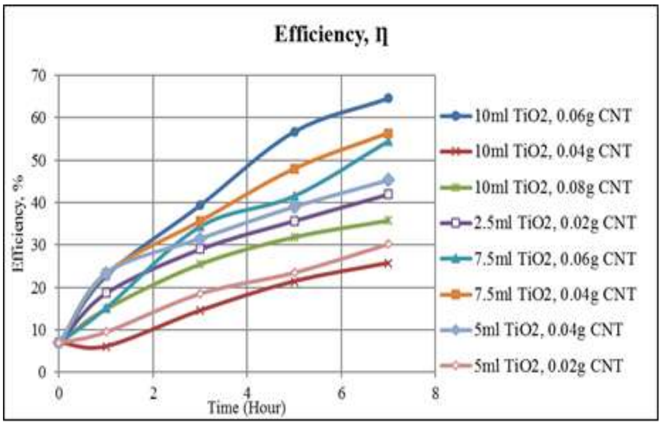

Fig. 10. Efficiency of each sample

Efficiency of the photodegradation of MB was calculated using the formula:

$$\eta = \frac{c_o - c_e}{c_o} \times 100 \qquad (1)$$

Where Co is the initial concentration of MB = 7mg/L. Ce = Concentration of samples at each hour. From figure 10, it is visible that the highest efficiency is achieved by 10ml TiO_2, 0.06g SWCNT which is 64%. This is followed by 7.5ml TiO_2, 0.04g SWCNT as in 56%. 54.4% efficiency is achieved by 7.5ml TiO_2, 0.06g SWCNT.

Table1. Comparison of highest efficiency with transmittance

	Samples	Efficiency (%)	Transmittance (%)
1	10ml TiO_2, 0.06g SWCNT	64.6	73.2
2	7.5ml TiO_2, 0.04gSWCNT	56.3	65
3	7.5ml TiO_2, 0.06gSWCNT	54.4	45.6
4	5ml TiO_2, 0.04g SWCNT	45.3	70
5	2.5ml TiO_2, 0.02gSWCNT	42.0	12.1

As shown in table 3, the highest efficiency of photocatalytic activity has a transmittance of 73.2% which is as per composition, 10ml TiO_2 solution with 0.06g of SWCNT. Since this sample has the highest photocatalytic activity and also a higher percentage of transmittance, this is the optimal composition required for self-cleaning property. To attain a better self-cleaning, one needs higher transparency which could be gained from higher transmittance, and also higher photocatalytic, which could be obtained from lowest MB concentration degradation.

However, Zhang and collaborators [18] obtained MWCNT/TiO_2 composites from titanium butoxide as TiO_2 precursor using a modified sol–gel technique. The results showed that a load higher MWCNT improved the methylene blue degradation in solution. In this research the transparency is one of the important factor and higher concentration of CNT will decreases the transmittance. So, we optimize the optimal concentration with high optical and photocatalytic properties. Other researchers [19, 20] have found that TiO_2/MWCNT composites show improved photocatalysis for light trapping in Dye solar cell application. In their works absorption is main factor, but our research has taken this work a number of important steps forward with SWCNT and for Silicon solar cells cover glass.

4. Conclusion

To achieve the best self-cleaning property, two factors are utmost necessary which are higher transparency that could be attained from higher transmittance, and also higher photocatalytic activity, which could be taken from the lowest MB photodegradation. In order to assess the transmittance of a sample, FTIR was used as it could show the percentage of transmittance. Also, to evaluate the photocatalytic activity of each sample, photodegradation of methylene blue was conducted using UV-vis spectra. Since self-cleaning property requires both higher transparency and higher photocatalytic activity, the optimal sample would be 0.06g SWCNT, 10ml TiO_2. Therefore, self-cleaning property could be achieved by incorporating SWCNT with TiO_2 as SWCNT has excellent mechanical, optical and electrical properties. Most importantly, SWCNT is very good in adsorbing organic reactants. The only disadvantage of SWCNT is that, its incapability to be transparent in colour. To achieve that, acetic acid is used. Lastly, all the objectives have been achieved.

Besides, the disadvantage of TiO_2 which is its incapability of achieving photocatalytic activity without the presence UV light could be overcome by coupling it with light absorbing semiconductor materials [21, 22]. By incorporating TiO_2 with visible light trapping semiconductors such as Tungsten Sulfide or even Cadmium Sulfide could enhance the photocatalytic activity and also the superhydrophilicity of TiO_2.

Acknowledgements

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