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Synthesis of $\text{TiO}_2\text{-SiO}_2\text{-CuO}$ Nanocomposite Material and Its Activities for Self-cleaning

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Abstract: Synthesis of $\text{TiO}_2\text{-SiO}_2\text{-CuO}$ nanocomposite material have been prepared by Photo Assisted Deposition (PAD) and Stober method to obtain self-cleaning material which is useful for life commodity. The self-cleaning ability were measured by its hydrophilicity, furthermore, the nanocomposite also have been evaluated for its performance in the decolorization of methylene blue. The order of PAD and Stober method in nanocomposite synthesis were adjusted for different nanocomposite morphology. The characteristic of $\text{TiO}_2\text{-SiO}_2\text{-CuO}$ nanocomposite consist the chemical bonding of Ti-O-Si which could enhance its hydrophilicity for self-cleaning purposes and the CuO dopant in the nanocomposite enhance the light responses to visible region. The SiO_2 addition affect the morphological structure, then enhance the nanocomposite surface area, adsorption of methylene blue, and its hydrophilicity. So the $\text{TiO}_2\text{-SiO}_2\text{-CuO}$ nanocomposite exhibit much higher performance in decolorization of methylene blue which could reach 80% for 5 minutes and has 60° contact angle compared with CuO-TiO_2 . The morphology 1 nanocomposite which most of the CuO were at TiO_2 lattice possess superior self-cleaning ability than the morphology 2 nanocomposite which most of the CuO inhibits SiO_2 .

Keywords: Hydrophilicity; Nanocomposite; Photodegradation; PAD; Self-cleaning

1. Introduction

There are many problems of fabric clothes that are a disturbance for daily life, one of them is that the clothes must be cleaned everytime it was used especially when it was made of pure cotton that is often exposed to dirt, so research lately about the development of self-cleaning fabric is an objective sought by the textile industry in the framework of new products classified as intelligents fabrics^{1),2)}. The cost saving using these fabrics, presenting a total or a partial self-cleaning properties, is one benefit. Such an innovation comprises TiO_2 deposited in the fabric surface, TiO_2 was shown in the last decade to be the best candidate for a photocatalytic applications²⁻¹³⁾. So in this paper, the material that will be reviewed about its self-cleaning activity is TiO_2 which is measured by its hydrophilicity and decolorization of organic compound such as methylene blue. Nano-sized TiO_2 exhibits self-cleaning activity under light irradiation due to the oxygen vacancies and ROS (Reactive Oxygen Species) formation because of the excited electron and hole⁵⁾. Generally, TiO_2 absorbs UV light with wavelength shorter than 380 nm, with the band gap energy of different forms of TiO_2 is 3.2 eV for anatase, 3.0 eV for rutile, and only make use of 3–4% of the solar energy^{14),15)}. The high recombination rate of photogenerated electron-hole pair and lack of utilization of sunlight that reduced the ROS formation has

to be improved and many reports focus on effective way to utilize the TiO_2 nanoparticle on visible light region. For instances, doping is one of the most effective way to reduce the electron-hole pair recombination, energy gap and thus shift the absorption spectrum to the visible region. Also in the recent years, doping with transition metal can increase the ROS formation from TiO_2 such as $\text{Ag}^{16),17)}$, Fe^{3+} ¹⁸⁾, $\text{Pt}^{19),20)}$ and $\text{Cu}^{21)}$, for owning a cheaper cost, Cu-doped in the form of CuO is more likely to be used.

In the recent studies, enhancing the hydrophilicity of TiO_2 is also an objective to increase its self-cleaning ability, that was done by compositing TiO_2 with other material that could contain water such as silica in the form of silica dioxide (SiO_2)^{11),22),23)}. SiO_2 is an optical transparency material that can help the heat stabilization of TiO_2 anatase and also can enhanced the the hydrophilicity on the surface by increasing its acidity, beside that, the chemical bond between TiO_2 and SiO_2 could maintain the hydrophilicity much longer even in the absence of light irradiation⁴⁾. The combination of Cu-doped TiO_2 and SiO_2 nanocomposite also have been studied to improve the ROS formation even in visible light because of its synergistic effect⁸⁾, but the hydrophilicity of the nanocomposite remains unexplored. However, the development from the nanocomposite perspective are still rarely been explored such as the effect of nanocomposite morphology to the self-cleaning activities. As far as its

known, different synthesis of the nanocomposite procedure could cause different morphology and with the same composition, the nanocomposite would have a different properties²⁴. Also, the metal doped in the TiO_2 lattice and metal in the surface of SiO_2 which act as an dispersal agent could have different antibacterial activities²⁵, which could be further explored the effect of the position of CuO in the nanocomposite to its self-cleaning activities.

Therefore, the key objective of this study is to investigate the enhanced self-cleaning mechanism of different TiO_2 - SiO_2 -CuO nanocomposite. Synthesis of TiO_2 - SiO_2 -CuO nanocomposite were prepared by Photo Assisted Deposition (PAD) to added the CuO dopant in the nanocomposite and Stober method to added the SiO_2 in the nanocomposite. The order of PAD and Stober method in nanocomposite synthesis were adjusted for different nanocomposite morphology.

2. Experimentals

2.1 Materials

The material used in this study were Aquadest, Ethanol MERCK, Methanol MERCK, Ammonia water 25% MERCK, Nitric Acid (HNO_3) MERCK, Tetraethyl Orthosilicate (TEOS) MERCK, TiO_2 Evonik P25, Copper Chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) and Methylene Blue. While the tool used is a photocatalyst reactor, sonicator, UV lamp 15W, beaker, pH meter, pipette, volumetric pipette, magnetic stirrer, magnetic bar, stopwatch, Photoreactor, and UV-Vis Spectrophotometry.

2.2 Methods

The first step is to prepared the CuO- TiO_2 catalyst which were prepared by PAD method. 2 g of TiO_2 P25 were dissolved on 170 ml aquadest then add a droplet of HNO_3 to be sonicated for 30 minutes and 100 ml CuCl_2 solution with 3% weight Cu to TiO_2 were made. TiO_2 soles and CuCl_2 solution were mixed to be irradiated with UV light for 6 hours with the addition of 30 ml methanol. After that the solution were washed several times then dried in hot plate and grounded to obtain Cu doped TiO_2 catalyst. After that TiO_2 - SiO_2 -CuO were prepared by stober method. Solution contain of 24 ml of ammonia water and 20 ml of anhydrous ethanol were prepared, various amount of Tetraethyl orthosilicate (TEOS) and 2 ml of aquadest were put into the solution. 1 gr of Cu doped TiO_2 that has been washed and 8 ml of aquadest were put afterwards into the solution. The solution were stirred in ambient air for 3 hours then dried in hotplate and ground to be calcinated at 300°C in atmospheric furnace maintain 2 hours to obtain Cu doped TiO_2 - SiO_2 nanocomposite. The order of PAD and Stober method in synthesis were adjusted for different nanocomposite morphology. The morphology illustration can be seen in Figure 1a. The difference of both morphology in Figure 1a that based on the synthesis method are the distribution of the CuO in the

nanocomposite, where in morphology 1 (M1) nanocomposite, CuO mostly inhibits the TiO_2 lattice while for the morphology 2 (M2), CuO were mostly inhibits the pore of SiO_2 or/and the surface of TiO_2 .

The nanocomposite will be characterized with Fourier Transformed Infrared Spectroscopy (FTIR), UV-Vis Diffuse Reflectance Spectroscopy (DRS), Surface Area Analyzer and Field Emission Scanning Electron Microscopy (FE-SEM)/Energy Dispersive X-ray (EDX) then to be evaluated for its self-cleaning activities. The decolorization of methylene blue (MB) were done in a photoreactor which consist 4 UV lamps, 7 ppm of 300 ml methylene blue were put into a beaker and 0.3 g of TiO_2 - SiO_2 -CuO nanocomposite were also put in that beaker, the beaker were stirred in a magnetic stirrer for 2 hours, the methylene blue sample were taken to be measured in UV-Vis Spectrophotometry. The hydrophilicity of the nanocomposite were measured by the contact angle of water in a thin film after irradiated by a single UV lamp for 30 minutes with a Contact Angle Meter (CAM), the nanocomposite were diluted in a aquadest solution then coated to a thin glass to be sonicated and finally cured in an oven. The self-cleaning mechanism methods of the nanocomposite could be described in Figure 1b, the oxygen vacancies occurred by photocatalyst process (excitation of electron leaving a hole), which the hole oxidized the O_2 atom to leave its structure, that cause the TiO_2 possess hydrophilic properties which formed a thin layer of H_2O adsorbed. Thin layer prevent dirt from contacting directly to the surface of a film which could be easily washed off, and if is an organic compound, by photodegradation process, would be reduced to CO_2 and H_2O . The more hydrophilic properties of the nanocomposite, the better it could prevent dirt^{1),4)}.

Fig. 1: Illustration of (a) Nanocomposite Morphology and (b) Self-Cleaning Mechanism

3. Results and discussion

3.1 Characteristic of The Nanocomposite

The FTIR spectrum of several $\text{TiO}_2\text{-SiO}_2\text{-CuO}$ nanocomposite (% SiO_2 based on mole) is shown in Figure 2. It contain bands at $3400\text{-}3600\text{ cm}^{-1}$, 1630 cm^{-1} , $1060\text{-}1220\text{ cm}^{-1}$, 941 cm^{-1} , and $590\text{-}647\text{ cm}^{-1}$. Basically, all the $\text{TiO}_2\text{-SiO}_2\text{-CuO}$ has the same wavenumber spectrum but the intensity were different according to the mole percentage of the SiO_2 in the nanocomposite and its clearly that the Cu-doped TiO_2 doesn't contain functional group of SiO_2 spectrum in the FTIR analysis. The bands at $3400\text{-}3600\text{ cm}^{-1}$ and 1630 cm^{-1} are assigned to OH bending and stretching vibrations respectively. It can be defined as a Ti-OH, Si-OH, and O-H bending related to physically absorbed moisture (interaction of hydrogen bonds with water molecule)²⁶⁾, the bands at $1060\text{-}1220\text{ cm}^{-1}$ is the characteristic bonds of Si-O-Si asymmetric stretching and at 941 cm^{-1} refers to Ti-O-Si asymmetric stretching, thus the Ti-O-Si bond were developed when the calcination process occurred, The effect of Ti-O-Si bond can increase the surface hydrophilicity of the nanocomposite, so it could adsorbed more H_2O at the surface of the nanocomposite. The peak at $590\text{-}647\text{ cm}^{-1}$ were the characteristic of Ti-O-Ti bonding which

attributed to TiO_2 . New absorption peak were detected at wavenumber 2335 cm^{-1} , it may be attributed to lattice defect cause by heat treatment²⁾, so it was predicted that dopants of Cu has been incorporated into the TiO_2 to substitute Ti^{4+} . Beside that, it can be seen in both morphology, there were no specific peaks of Si-O-Cu which indicated that Cu were uniformly dispersed in the TiO_2 lattice or SiO_2 as CuO, the form of Cu as CuO can be predicted from the synthesis method⁷⁻¹⁰⁾.

The DRS response in Figure 3 showed that the Cu doped in TiO_2 lattice could enhance the visible light respons of the photocatalyst showed by the increase of absorbance in wavelength between $400\text{-}800\text{ nm}$ and lowered its bandgap, the bandgap were calculated by Kulbelka-Munk equation⁹⁾. The addition of SiO_2 to CuO- TiO_2 catalyst slightly affect the visible light response and bandgap of the photocatalyst that can be seen in Table 1, SiO_2 is known to have optical properties so it doesn't block the light at the surface of TiO_2 when SiO_2 act as a shell in the nanocomposite. There were no significant difference between the bandgap of CuO- $\text{TiO}_2\text{-}33\%\text{SiO}_2$ M1 and M2 nanocomposite, even if the CuO doesn't inhibits the TiO_2 lattice which doesn't play the role as electron trapper, it could still lower the bandgap because the effect of surface plasmon resonance⁷⁾.

Fig 2. FTIR Spectrums of the Nanocomposite

Fig 3. DRS patterns of the Nanocomposite

FE-SEM analysis of the nanocomposite indicated that addition of SiO₂ on Cu doped TiO₂ can affect the surface morphology of the catalyst, however there was no significant effect on the aggregate sizes. The granular shape on the TiO₂-SiO₂-CuO nanocomposite is the silica that shaped as a shell in the TiO₂ surface. As the silica

content increased, the agglomeration of silica particle also increased as can be seen in the FE-SEM images based on Figure 4. The elemental weight of Cu, Ti, Si can be seen in Table 1 which is measured by EDX analysis. The Cu and Ti content decrease by the increase of the silica content in the nanocomposite.

Table 1. Composition and Bandgap of Several Nanocomposite

Sample	% weight				Bandgap (eV)	Surface Area (m ² /g)
	Cu	O	Ti	Si		
CuO-TiO ₂	3.41	35.98	60.61	0	2.92	73.99
CuO-TiO ₂ -16%SiO ₂	3.23	14.83	79.02	2.92	2.93	-
CuO-TiO ₂ -33%SiO ₂ M1	1.66	44.79	43.24	10.31	2.99	128.15
CuO-TiO ₂ -33%SiO ₂ M2	1.92	42.65	43.73	11.70	3.02	99.13

Fig 4 Nanocomposite Morphology at 20000x magnitude (a) CuO-TiO₂, (b) CuO-TiO₂-16%SiO₂, (c) CuO-TiO₂-33%SiO₂ M1, and (d) CuO-TiO₂-33%SiO₂ M2

3.2 Decolorization of Methylene Blue

Decolorization of MB consisted 2 process, which were adsorption and photodegradation of MB, the adsorption depends on the surface area or hydrophilicity of the nanocomposite to adsorbed more MB in the solution and the photodegradation depends on the OH radicals formation to photo oxidized the MB to CO₂ and H₂O. Figure 5 (a) showed that the addition of SiO₂ will increase the efficiency of MB decolorization until 80% in 5 minutes, the effect of SiO₂ in the nanocomposite was increasing the surface hydrophilicity of the photocatalyst (by Ti-O-Si bond), so it can adsorb more H₂O and with the

charge separation rate is higher because of the CuO dopant, the hole can easily meet another OH⁻ from the adsorbed H₂O in the surface so it could produce more OH radicals. On the contrary when the SiO₂ content increase, TiO₂ content is decrease, so the photogenerated holes also decrease and when it comes to the point that the decrease of holes becomes more dominant than the holes oxidized the hydroxyl group, the total OH radicals produced will be lower to degradate the MB and would reduce its decolorization efficiency. So the synergis effect of SiO₂ addition with the TiO₂ to produce more OH radicals would occurred until 33% SiO₂ mole composition which higher than 33% could reduce the MB decolorization efficiency.

Fig 5. MB Decolorization (a) $\text{TiO}_2\text{-SiO}_2\text{-CuO}$ Nanocomposite (b) in the absence and presence of UV light

Based on Figure 5 (b) the decolorization process were caused by the adsorption of the catalyst/nanocomposite surface which depends on its surface area in the absence of photon energy. There was a time span where there was no significant decrease in absorbance, this was believed because methylene blue has covered the entire surface of the catalyst/nanocomposite and because of the absence of photon energy there was no photodegradation process occurred. The addition of SiO_2 to nanocomposite could increase the methylene blue adsorption ability because it increases the nanocomposite surface area especially if SiO_2 was amorphous, there are significant differences between M1 and M2 nanocomposites in adsorbing methylene blue where M1 nanocomposite is superior. This occurred because the surface area of M1 nanocomposite is larger than M2 nanocomposite based on Table 1, a decrease in surface area was happened because referring to the morphological illustrations in M2 nanocomposite, CuO mostly inhibits at amorphous SiO_2 which would likely covered its pore. When the UV lamp was turned on, the photodegradation process of methylene blue begins to occur, so that the methylene blue absorbance will begin to decrease. Catalysts/nanocomposites has different photodegradation performance and because of the different adsorption effects causes the initial absorbance in the beginning of photodegradation were dissimilar, so to compare the photodegradation ability, it used the kinetics reaction rate approach with 2nd order reaction. The value of the reaction rate constant for TiO_2 catalyst in photodegradation of methylene blue is 0.2571 L/mg.min and the catalyst 3% CuO-TiO_2 has a greater reaction rate constant of 0.4282 L/mg.min. $\text{CuO-TiO}_2\text{-33\%SiO}_2$ M1 nanocomposite has a reaction rate constant of 0.8968 L/mg.min, this can be achieved because of the synergistic effect between the dopant of CuO and SiO_2 composites in increasing OH radical production. But M2 nanocomposite has a reaction rate constant lower than half of $\text{CuO-TiO}_2\text{-33\%SiO}_2$ M1 nanocomposite which is equal to 0.4004

L/mg.min. This shows that the dopant of CuO plays a major role in producing OH radicals as an electron trapper and in accordance with M2 morphological, most CuO dispersed in SiO_2 so that the role of CuO as an electron trapper is very small resulting in much lower hole and electron separations even from 3% CuO-TiO_2 catalysts, hence the hydroxyl ions that were at the surface of the nanocomposite only a few meet holes which results in a lower OH radical/ROS production that lower its photodegradation of methylene blue ability.

3.3 Hydrophilicity in a Thin Film

Figure 6a showed that all nanocomposites have a contact angle below 30° (blank thin film has a contact angle of 45°) that meets the hydrophilic standard even the $\text{CuO-TiO}_2\text{-33\% SiO}_2$ M1 nanocomposite has a contact angle near 5° which indicates a superhydrophilic properties²³. The hydrophilic properties of $\text{TiO}_2\text{-SiO}_2\text{-CuO}$ nanocomposites are due to the presence of oxygen vacancies and physisorption or chemisorption of H_2O produced in the photocatalyst process. The addition of SiO_2 to the nanocomposite can increase the hydrophilicity because the presence of Ti-O-Si bonds that causes the surface acidity to increase so that more water could be adsorbed at the surface of the nanocomposite which cause the increase of physisorption and chemisorption of hydroxyl group to produce more thin layers⁴.

Fig 6. (a) Contact Angle of Water Droplets and (b) Viable Dirt at the Surfaces (20x magnitude) of Thin Glass Coated with Each TiO₂-SiO₂-CuO Nanocomposite

The enhanced hydrophilic properties of the nanocomposite could increase the thin film self-cleaning ability, which based on Figure 6b, the thin film coated with the more hydrophilic nanocomposite has fewer amount of dirt, since the more hydrophilic properties of a thin film causes the higher amount of H₂O or hydroxyl group that could be adsorbed, resulting in a more thicker layer of water at the surface of the thin film^(4),23) that could prevent more dirt and could be washed easily. Those were the benefits of having a self-cleaning material which reduce the consumption of detergent used to clean or wash the material.

The results in Figure 6 implies that when the SiO₂ composition is higher than 33%, the contact angle will decrease meaning that it has less hydrophilic properties. The increase of SiO₂ content will reduce the photogenerated hole and electron so that the oxygen vacancies would be less occurred, but due to the presence of Ti-O-Si bond that increase the surface acidity, the chemisorption or physisorption of H₂O would still be increased even with the decrease of oxygen vacancies, so the synergis between the oxygen vacancies and surface acidity to improve the hydrophilic properties of the nanocomposite will occurred until 33% SiO₂ composition and when the composition of SiO₂ is higher than 33%, the less oxygen vacancies would be more dominant than the increase of surface acidity that would overall lower the hydrophilic properties.

There was a significant difference in the hydrophilic characteristics between CuO-TiO₂-33% SiO₂ M1 and M2 nanocomposite, where the hydrophilicity of M2 nanocomposite is lower than M1 even though the two nanocomposites have the same composition of TiO₂-SiO₂. Thus, different morphologies can affect the hydrophilic properties of the nanocomposite, where based on the morphology illustration, it was believed that in M2 nanocomposite, most of CuO does not inhibits TiO₂ lattice but are dispersed on SiO₂ so that it does not function as an electron trapper that caused more recombination holes and electrons than M1 nanocomposite, therefore less oxygen vacancies produced in M2 nanocomposite.

4. Conclusion

From the experimental data, it can be concluded that TiO₂-SiO₂-CuO M1 and M2 nanocomposite possess self-cleaning properties that could decolorize methylene blue and has hydrophilic properties, which 33% SiO₂ mole composition in TiO₂-SiO₂-CuO nanocomposite has the best self-cleaning activities that has 80% efficiency at decolorization of methylene blue in 5 minutes and possess superhydrophilic properties. In the scope of self-cleaning activities, the TiO₂-SiO₂-CuO M1 nanocomposite which most of the CuO were at TiO₂ is superior than M2 nanocomposite which most of the CuO inhibits SiO₂.

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