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Development of Antibacterial Fabrics by CuO Doped TiO_2 Composites

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The study aimed to get the optimum antibacterial properties on fabric. CuO-doped TiO_2 composite was synthesized by photo assisted deposition method. The amount of CuO loading varied (1.5%, 3% and 6%) in the total weight of composite to obtain the optimum effect of CuO in photodisinfection *Escherichia coli.* The 3% CuO/TiO_2 possessed the optimum antibacterial activity with 92% of *E. coli* were disinfected within 2 h. This phenomenon was supported by the UV-Vis DRS results, which implied the addition of CuO could act as a dopant and an electron trapper in reducing the band-gap energy to 2.97 eV in 3% CuO/TiO_2. Fourier-transform infrared spectroscopy (FTIR) analysis showed the Ti-O-Ti and Ti-O-Si bands, which confirmed TiO_2 attach on fabric.

Keywords: Composite, Photocatalyst, Metal dopant, Disinfection.

INTRODUCTION

Cotton fabrics are used by people around the world, both as clothes and another supporting product. Nowadays, trend of using cotton fabrics is not only focused to cover or wear, but also become a media development for some multifunctional properties. However, cotton fabrics provide an excellent environment for microorganisms to grow and proliferate due to their ability to retain moisture [1]. In overcoming this problem, some technology had been developed in modifying fabrics to enhance the antibacterial properties, such as antimicrobial chemicals [1], herbal products [2] and enzyms [3]. But these methods are inefficient and can create another side-effect. An alternative method of photocatalysis has been developed, which can disinfect microbes by using catalysts and light sources [4-7]. The used catalyst is a semiconductor which can absorb light photons, so it can generate electrons and holes, followed by the production of hydroxyl groups. Hydroxyl groups will oxidize the cell wall of bacterial, followed by cell malfunction and cell death [8-10].

Titanium dioxide (TiO_2) is one of semiconductors which is recently being carried out in modified fabric. It has attracted since its low cost, highly photocatalytic activity, high stability, low level of toxicity and moderate operation condition [11,12]. Generally, TiO_2 has band gaps of 3.2 eV for anatase, 3.0 eV for rutile and 3.2 eV for brookie. In other words, TiO_2 absorbs optimum photons form UV light with wavelength shorter than 380 nm [13]. The oxidation of *Escherichia coli* has been demonstrated in the previous study [14]. The reactive oxygen species (ROS) generated by illuminated TiO_2 cause various damages to living organisms. TiO_2 photocatalytic activity has been intensively conducted on certain organisms, including bacteria, viruses, fungi, algae and cancer cells [14].

A common limitation in TiO_2 to achieve and maintain high photocatalytic efficiency is the fast recombination of photogenerated electron and holes [15]. Metal dopant has been primarily studied to improve the photocatalytic activitiy of TiO_2 [16]. Many dopants such as Cu, Ag, Fe and Mn have been used to chance the photoabsorption ability of TiO_2 [7,17-20]. Metal copper was considered as one of the promising doping elements to inhibit the recombination between electron and holes and also increase the surface hydroxyl groups, which contributed to the disinfection ability [15]. Slamet *et al.* [7] found that CuO exhibit better photoreduction ability of CO_2 rather than copper. Besides, copper oxide has been proved to decrease band-gap energy and widely used before [7]. Not only as a dopant, copper metal has been proven in disinfecting *Escherichia coli* and *Shigella* [21].

In this study, CuO doped TiO_2 will be impregnated on cotton fabric to obtain antibacterial fabric. This study will focus on the synthesis of CuO doped TiO_2 and get the optimum composition of loading CuO to disinfection ability. The structure and band-gap energy of CuO doped TiO_2 was analyzed by X-ray diffraction (XRD) and UV-Vis DRS techniques. The functional groups were attached on fabric was analyzed by FTIR. While the performance of composites material was examined by photodisinfection of *E. coli*.

EXPERIMENTAL

Sample preparation: Copper(II) chloride ($CuCl_2·2H_2O$) was used as metal precursor. TiO_2 P25 (2 g) were dispersed in 170 mL distilled water and the pH was adjusted using nitric acid (HNO_3 65%). The TiO_2 sol was sonicated for 15 min, while copper chloride solution (1.5%, 3% and 6% w/w of TiO_2 P25) was made by dispersing the certain among of copper chloride in 100 mL distilled water. The TiO_2 and copper chloride solution were mixed and added with 30 mL methanol, followed by irradiation under UV light for 6 h. The solution was washed several times until the pH reached about 5. After that solids of CuO/TiO_2 were dried and calcined at 300 ºC for 1 h.

The CuO/TiO_2 composite (0.2 g) was dissolved in 100 mL distilled water and the pH of the solution should be adjusted using nitric acid until reached pH 3. The suspension of CuO/TiO_2 was then added by 2 mL of TEOS and continued with gentle mixing for 15 min. The solution was also sonicated for 30 min. A clean cotton fabric with dimension of 10 cm × 10 cm was used for coating. The fabric was immersed in the mixed solution and mixed for 5 min. Afterward, the fabric was removed and dried in an oven at 110 ºC for 10 min.

Characterization: Optical absorbance spectra and band-gap energy of CuO/TiO_2 composites were obtained from UV-vis diffuse reflectance spectrophotometry (Cary 60 UV-Vis). The composites crystallinity were examined by X-ray powder diffraction (XRD). The function groups that represent the interaction of any compound on fabric was obtained from Fourier-transform infrared spectroscopy (NicoletTM iSTM 5 FTIR spectrometer).

Antibacterial activity test: *E. coli* (1 mL) was added on a beaker glass filled with 20 mL distilled water and 20 mg composite. The solution was mixed and irradiated with UV light for 2 h inside a photoreactor. The samples were taken 1 mL every 0.5 h to be dilluted in a 10 mL buffered Pepton water solution. The number of dillutions were 5 times. Then, 1 mL of diluted samples were put into petri dishes and followed by filling with place count agar (PCA) solution. After the PCA solidified, the petri dishes were incubated at 37 ºC for 24 h. The number of viable *E. coli* in each petri dishes were observed and counted, thus the percentage of disinfection of nanocomposites can be calculated using eqn. 1:

$$\text{Disinfection (\%)} = \frac{C_o - C}{C_o} \times 100 \quad (1)$$

where C_o and C are the concentration of *E. coli* in CFU/mL which can be calculated in eqn. 2:

$$C = \frac{d \times N}{V} \quad (2)$$

where N is the total *E. coli* colonies in the plate count agar, d is the dillution factor and V is the volume of sample added into the agar plate.

RESULTS AND DISCUSSION

UV-visible studies: The UV-visible spectra of bare TiO_2, 1.5% CuO/TiO_2, 3% CuO/TiO_2 and 6% CuO/TiO_2 are shown in Fig. 1. The Kubelka-Munk function is used to analyze the band-gap energy of each samples. On this basis, the calculated band-gap energy can be derived from the spectra by plotting $[F(R)h\nu]^{1/2}$ against hν [22]. The results indicate that the absorption edges of CuO/TiO_2 samples are shifted compare to bare TiO_2. The presence of CuO on TiO_2 enhance the light absorption toward the visible region.

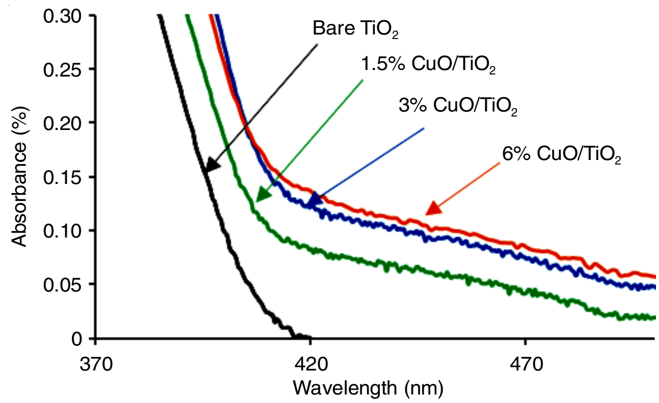

Fig. 1. Light absorption spectra of each samples

The bang-gap energy can be obtained by extrapolating the rising region of UV spectrum to the *x*-axis at zero absorption [4]. The measured band gap values were also in line with that of typical band-gap of titania-based materials, revealing the values of 3.05, 2.99, 2.97 and 2.95 eV for undoped TiO_2, 1.5% CuO/TiO_2, 3% CuO/TiO_2 and 6% CuO/TiO_2, respectively. The band-gap of CuO/TiO_2 samples decreased as the copper loading is increasing (Table-1). On TiO_2, CuO also performs as an impurity which hybridized Ti. The hybridization generates new level in intra-band of TiO_2, which is more positive than the valence band [13,23]. This phenomenon could decrease the required energy to excitate electrons.

TABLE-1
CALCULATED BAND-GAP ENERGY

Sample	Band-gap energy (eV)	Wavelength (nm)
Undoped TiO_2	3.05	407
1,5% CuO/TiO_2	2.99	415
3% CuO/TiO_2	2.97	418
6% CuO/TiO_2	2.95	421

XRD studies: Typical XRD patterns of bare TiO_2 and 6% CuO/TiO_2 are shown in Fig. 2. The 2θ values of 25.3º, 37.8º and 48.0º correspond to anatase phase. Similarly, peaks at 2θ values of 27.4º, 36.0º and 41.2º rutile phase of TiO_2. However, no diffractions peaks in the patterns of Cu-doped samples were observed. This is probably attributed to the low CuO loading or may be caused of very small CuO particle size, thus results in high dispersion of dopant species [4,24]. The crystalline size and TiO_2 phase percentage in each composite are shown in Table-2.

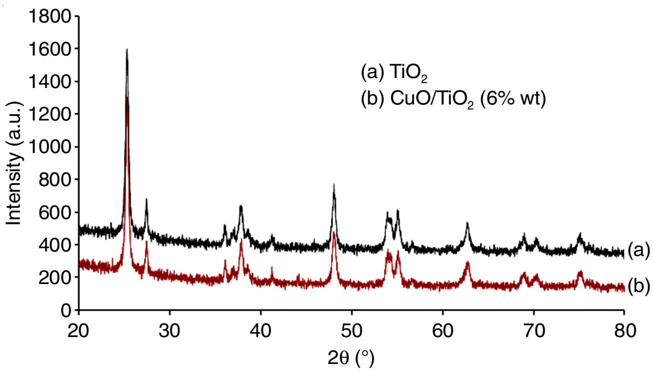

Fig. 2. XRD patterns of composites

TABLE-2
CRYSTALLINE SIZE AND PHASE

Sample	Crystalline size (nm)		Crystalline phase	
	Anatase	Rutile	Anatase	Rutile
Bare TiO_2	21	29	70.0	30.0
6% CuO/TiO_2	22	34	28.9	71.1

The crystalline size of anatase and rutile were relatively similar, ranging from 20-22 nm and 29-34 nm, respectively. The results indicated that there were an increase in crystalline size of TiO_2 after being doped by CuO dopant due to the thermal treatment in the synthesis [24,25].

FTIR analysis: The FTIR spectra of modified fabrics (CuO/TiO_2 fabric) as well as that which is unmodified are shown in Fig. 3. The unmodified fabric reveals, peaks signals in 3334-3204 cm^{-1} (O-H *str.*) and 2925 cm^{-1} (C-H *str.*), indicating the characteristic of celullose as one of the main constituents in cotton fabric. These findings agreed well with that reported in previous study [26]. A peak signal at 592 cm^{-1} represents Ti-O-Ti bond in modified fabric (CuO/TiO_2 fabric), while it is also observed in the case of unmodified fabric with much lower intensity. This finding is also in agreement with the previous study where Ti-O-Ti signal was found within the wavenumber range of 600-450 cm^{-1} [27]. Moreover, peak signal at 1100 cm^{-1} is attributed to the symetric vibration of Si-O-Si and a relatively weak signal related to Ti-O-Si is also found at 960 cm^{-1}, which is indicative of interaction between Ti and Si [28]. The formation of Si-O-Si and Ti-O-Si signified that TEOS was hydrolized forming SiO_2. The bond between SiO_2 and TiO_2 can occur both

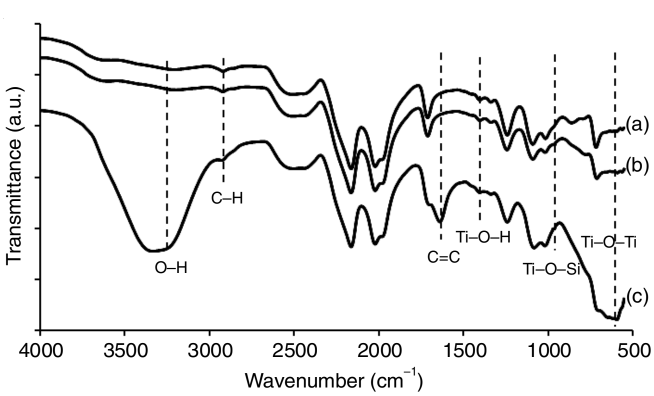

Fig. 3. FTIR patterns of (a) blank fabric, (b) CuO/TiO_2 fabric, (c) CLO-encap-CuO/TiO_2 fabric

chemically and physically, resulting in an increase of the surface acidity of the composites. This is particularly beneficial for photocatalytic redox reactions in terms of capturing hydroxyl radicals as well as increase in hydrophilicity and self-cleaning properties of the fabric [17].

Photocatalytic activities: Fig. 4 displays the temporal profiles of photocatalytic disinfection of *E. coli* by TiO_2 and CuO doped TiO_2 and without any photocatalyst under UV irradiation. The conditions without catalyst and UV irradiation are also shown as the control samples. Without catalyst and UV irradiation, the amount of *E. coli* proliferates with time. While UV irradiation could disinfect the bacteria even the decreasing is not significant than TiO_2 and nanocomposites. The CuO-doped can reduce the recombination of photogenerated charges in TiO_2 due to CuO conduction band is more positive than TiO_2, resulting more $OH^{\bullet}$ and more effective in disinfecting *E. coli* rather than undoped TiO_2 [8,17,29-32]. Another advantage of copper oxide is its natural properties as an antibacterial agent. Metallic copper could disinfect microbes (bacteria, yeasts and virus) even without any irradiation, so this property could enhance the disinfecting ability of CuO-doped TiO_2 [17,33]. The reaction mechanism of TiO_2 in producing $OH^{\bullet}$ and its oxidation are occurred in eqns. 4-10 [9].

$$TiO_2 + h\nu \longrightarrow h^+ + e^- \quad (4)$$

$$H_2O + h^+ \longrightarrow {}^{\bullet}OH + H^+ \quad (5)$$

$$O_2 + e^- \longrightarrow O_2^- \quad (6)$$

$$O_2^- + H^+ \longrightarrow HO_2^{\bullet} \quad (7)$$

$$2HO_2^{\bullet} \longrightarrow H_2O_2 + O_2 \quad (8)$$

$$H_2O_2 + e^- \longrightarrow {}^{\bullet}OH + OH^- \quad (9)$$

$${}^{\bullet}OH + \text{Organic compound} \longrightarrow CO_2 + H_2O \quad (10)$$

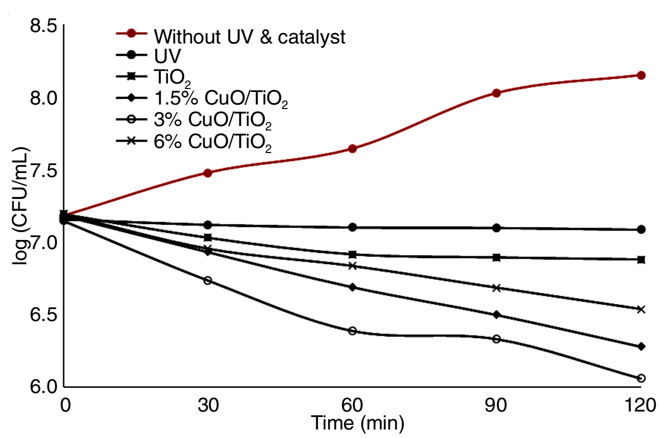

Fig. 4. Temporal profile of *E. coli* disinfection

The $OH^{\bullet}$ will first damage the cell wall of *E. coli*; this leads to the attack of peptidoglycan layer, peroxidation of the lipid membrane, which affects to the cell viability, resulting the loss of crucial cell function and cell death [9,10].

Fig. 5 shows that 3% CuO/TiO_2 has performed the best performance on *E. coli* disinfection with 92% within 2 h under UV irradiation followed by 1.5% CuO/TiO_2 and 6% CuO/TiO_2. The increase in CuO loading on TiO_2 is not always followed by an increase in disinfection ability. The 6% CuO/TiO_2 comp-

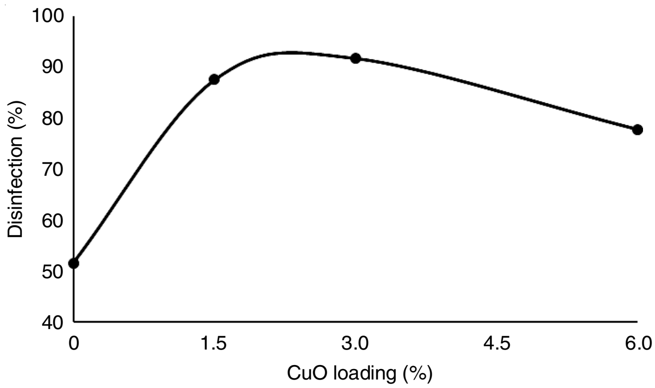

Fig. 5. Disinfection percentage to CuO loading after 2 h irradiation

osites exhibit the lowest percentage of disinfection among the other CuO-doped samples. This phenomenon might occur due to an excess of deposited CuO on TiO_2 so cover the active site of TiO_2, affects to poor photon absorption [34]. Therefore, 3% CuO/TiO_2 possesses the optimum loading CuO in *E. coli* disinfection.

Conclusion

In this work, the effect of CuO-doped TiO_2 on its antibacterial activity on modified fabrics were proposed. According to the disinfection of *E. coli*, the synergistic effect of CuO dopant both as an electron trapper and antibacterial agent, increase the disinfection percentage of CuO-doped TiO_2. The 3% CuO/TiO_2 has the optimum antibacterial activity that could disinfect 92% of *E. coli* colonies in 2 h of UV irradiation. This UV-Vis DRS characterization found that the deposited CuO decreased the band-gap energy of TiO_2 of 2.97 eV for 3% CuO/TiO_2. While the impregnation CuO doped TiO_2 was successful as the Ti-O-Ti and Ti-O-Si bands in FTIR characterization.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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