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Effect of CuO doped TiO_2 on Morphology, Crystal Structure and Photocatalytic Activity

Siti Khalijah KAMARUDIN[1,a*],Nur Farhana M. YUNOS[1,b],Banjuraizah JOHAR[1,c], Suhaimi ILLIAS[2,d] and Muhammad Asri IDRIS[1,e]

[1]School of Materials Engineering, Universiti Malaysia Perlis (UniMAP) 02600 Jejawi, Perlis, Malaysia.

[2]School of Manufacturing Engineering, Universiti Malaysia Perlis (UniMAP)02600 Jejawi, Perlis, Malaysia.

[a]khalijah276@gmail.com, [b]farhanadiyana@unimap.edu.my, [c]banjuraizah@unimap.edu.my, [d]suhaimi@unimap.edu.my, [e]asri@unimap.edu.my

ABSTRACT. Copper oxide doped Titanium Dioxide (CuO= 0-1.0wt.%) powders were prepared using sol-gel method and all the powder were sintered at 500 °C. The samples were characterized using X-ray diffraction(XRD), scanning electron microscopy(SEM), Brunauer-Emmett-Teller (BET) and UV/Vis spectrophotometer. The doping concentration of CuO gave significant influenced on the structural properties of TiO_2. The lattice parameter, particles size and specific surface area of TiO_2 size were increased with increasing CuO concentration. The degradation rate of methylene blue (MB) was calculated to investigate the photocatalytic activity of CuO doped TiO_2. The degradation rate were increased when the concentrations of CuO increased.

Keywords: *Photodegradation, Photocatalytic activity, Anatase, Microstructural;*

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1. INTRODUCTION

TiO_2 had been recognized as one of the semiconductor metal oxide due to its unique properties like wide bandgap (3.20eV), strong ultraviolet absorptivity, good photocatalytic activity, non-toxicity and long term chemical stability [1-2]. It is desired for photocatalystto havehigh reaction for solar spectrum ranges. Thus, simultaneous catalytic process could be run naturally by sunlight. However, the wide band gap of anatase phase (3.2eV) became limited in order to get higher photocatalytic performance. The previous research had provided some promising methods to enhance the UV light photo activity such as metal and non-metal doping, dye sensitization, and semiconductor coupling method [3]. The properties of TiO_2 also reported to be influenced by the synthesize method like sol-gel, hydrothermal or reverse micelle method. Currently, the modification methods by metal ions was being considered where the process required the higher temperature of calcination temperature.

Previous study proposedthat the metal doping can effectively reduced the band gap of TiO_2 in order to increase the number of photogenerated electron-hole pairs separation [4-5]. It was reported by Sangpour et al. [6], the effect of photocatalytic activity on copper (Cu) and silver (Ag) doped TiO_2were performedin the following order Cu: TiO_2> Ag: TiO_2 > TiO_2. Accordingly, Cu-doped TiO_2 was found to be promising materials for high photocatalytic activity[7].It was well reportedthat mesoporous materials with larger surface area

with relatively regular channel structure are good materials for catalyst [8]. Therefore, morphological and surface analysis is vital tool in enhancing photocatalytic activity. While, Nakata et al. [9] revealed the significant role of polymeric template and calcination temperature on producing high crystallinity and large surface area of synthesized TiO_2.

In the present study, copper oxide doped TiO_2 powders was prepared using sol-gel method with different dopants concentration from 0-1.0wt.% and sintered at 500 °C. Different concentration of

CuO was doped to investigate the effect on structural, morphological and photocatalytic performance. The structural properties of powders were characterized using X-ray diffraction (XRD), Scanning electron microscopy (SEM) and Brunauer-Emmett-Teller (BET) while the photocatalytic performance was investigated using UV/vis spectrophotometer. The photocatalytic activities of CuO doped TiO_2 were evaluated by photo degradation of methylene blue (MB).

2. MATERIALS AND METHODS

2.1 Sample Preparation. TiO_2 was synthesized through the sol-gel method by the hydrolysis of titanium isopropoxide ($Ti(OC_4H_9)_4$,12.8 mL). Titanium isopropoxide was added into the mixture solution of 18.6 mL of isoprophyl alcohol and 20.6 mL of acetic acid. Then, a mixed solution of 18.6 mL alcohol dissolved with copper nitrate trihydrate ($Cu(NO_3)_2{\cdot}3H_2O$) was added into the solution according to the anticipant Cu content (0.2%-1.0%, weight fraction). Finally, a few drops of deionized water was dropped in the solution while stirring. Stirring was held for the whole course and continued for 1 hour. After stewing for 24 hours, the solution became gel and was dried in an oven at 80 °C for 24 hours to form the powder. The powder was then put in a muffle furnace and sintered at 500 °C for 6 hours to acquire the Cu-doped TiO_2 powders with different CuO contents from 0.2wt.% to 1.0wt.%.

2.2 Characterization. XRD patterns were obtained with a diffractometer on Shidmadzu XRD 6000 2500 V using Cu Ka radiation. UV-vis adsorption spectra were recorded using a Genspec III (Hitachi, Japan) spectrometer. Scanning electron microscopy (SEM) images of the product were taken on a field with an accelerating voltage of 20 kV. Specific surface area was determined by BET.

2.3 Photocatalytic activity. The photocatalytic activity of TiO_2 and CuO doped TiO_2 was evaluated by the degradation of MB in solution under illumination of UV light (wavelength about 365nm). The UV lamp was placed horizontally hung. A 500ml beaker contain reaction solution were stirring using magnetic stirrer which irradiated under UV light. The distance from the beaker to the lamp was 30cm. In this experiment, the TiO_2 powder was added to aqueous of MB, and the initial concentration of MB and amount of TiO_2 and CuO/TiO_2 were set at 20ppm and 5mg per little, respectively. The reaction time were ranged from 0 to 180min. The degradation of MB was calculated using formula: Degradation = $(A_o- A)/A_o$, where A_o and A were the absorbance of the primal and remaining MB respectively. The absorbance then was measured with UV/vis spectrophotometer.

3. RESULTS AND DISCUSSION

3.1 Phase structure. The phase and structure analysis of the samples were investigated by X-ray diffraction pattern in Fig. 1 for different weight percent of CuO. All peaks observed were indicated to anatase structure of titanium dioxide. There was no Cu peak observed in this pattern observed indicated that Cu was doped into TiO_2 lattice. The average crystallite sizes of TiO_2 and 0.2 wt.%-1.0 wt.% CuO were calculated using Debye-Sherrer equation. The increased of crystallite size due to the presence of Cu species in the TiO_2 matrix. Pham et al. [1] reported that (101) plane of Cu doped materials was slightly shifted to higher diffraction angles when the Cu content increased. They also confirmed that Cu was incorporated into TiO_2 lattice. Other researchesfound that Cu^{2+} could be substituted in Ti^{4+} position due to similar ionic radii which is Ti = 0.68Å and Cu = 0.72Å. The diffraction peak decreased in intensity and became broadened as the Cu content was

increased shows that the average size of TiO_2 particles decreased [10]. In Table 1, the crystallite size increased with increasing copper oxide concentration from 102.2 up to 260.8. The rietveld

refinement were carried out using tetragonal structure with space group I41/amd (141). The lattice parameter (a,b, and c) and microstructural parameter including crystallite was refined.

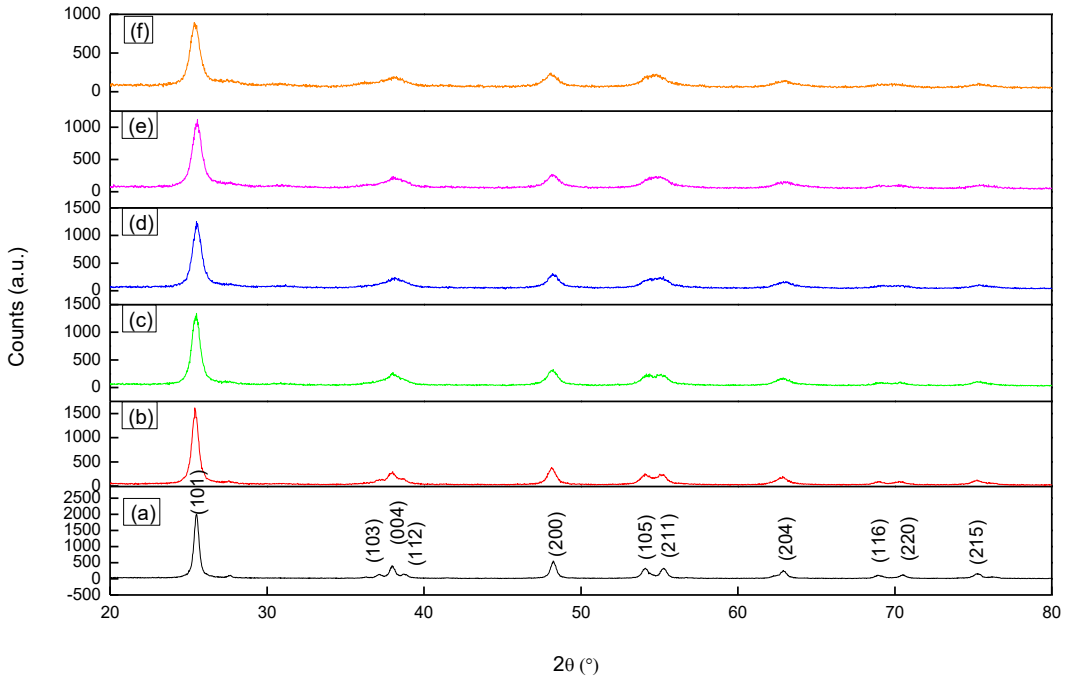

Fig. 1XRD pattern different weight percent of CuO (a)0wt.%, (b)0.2wt.%, (c)0.4wt.%,(d)0.6wt.%, (e)0.8wt.%, and (f)1.0wt.%

Table 1 Lattice parameter and crystallite size of doped and undoped TiO_2

Doping concentration (wt.%)	Lattice parameter, a (Å)	Lattice parameter, b (Å)	Lattice parameter, c (Å)	Crystallize size (Å)	Reliability
0	3.78686	3.78686	9.51762	102.2	12.1314
0.2	3.78847	3.78847	9.50429	105.8	11.3611
0.4	3.79087	3.79087	9.49885	119.4	11.4029
0.6	3.79093	3.79093	9.48808	138.6	12.4353
0.8	3.79057	3.79057	9.48510	195.3	12.6082
1.0	3.79204	3.79204	9.47465	260.8	12.8860

3.2 Morphological analysis. Fig. 2 shows SEM images of TiO_2 and CuO doped TiO_2 samples sintered at 500°C for 6 hours. From SEM micrographs (Fig.2(a)-(f)), the particles sizes were increase with increasing CuO concentration and the changes were clearly seen for sample 1.0wt.%CuO. Colon et al. reported that BET surface area values of powders increased with increasing Cu-doping concentration [11]. As shown in Table 2, the specific surface area increased with increasing CuO concentration. It was increased from 18.245 m^2/g for 0wt.%CuO up to 47.1855 m^2/g for 1.0wt.%CuO.

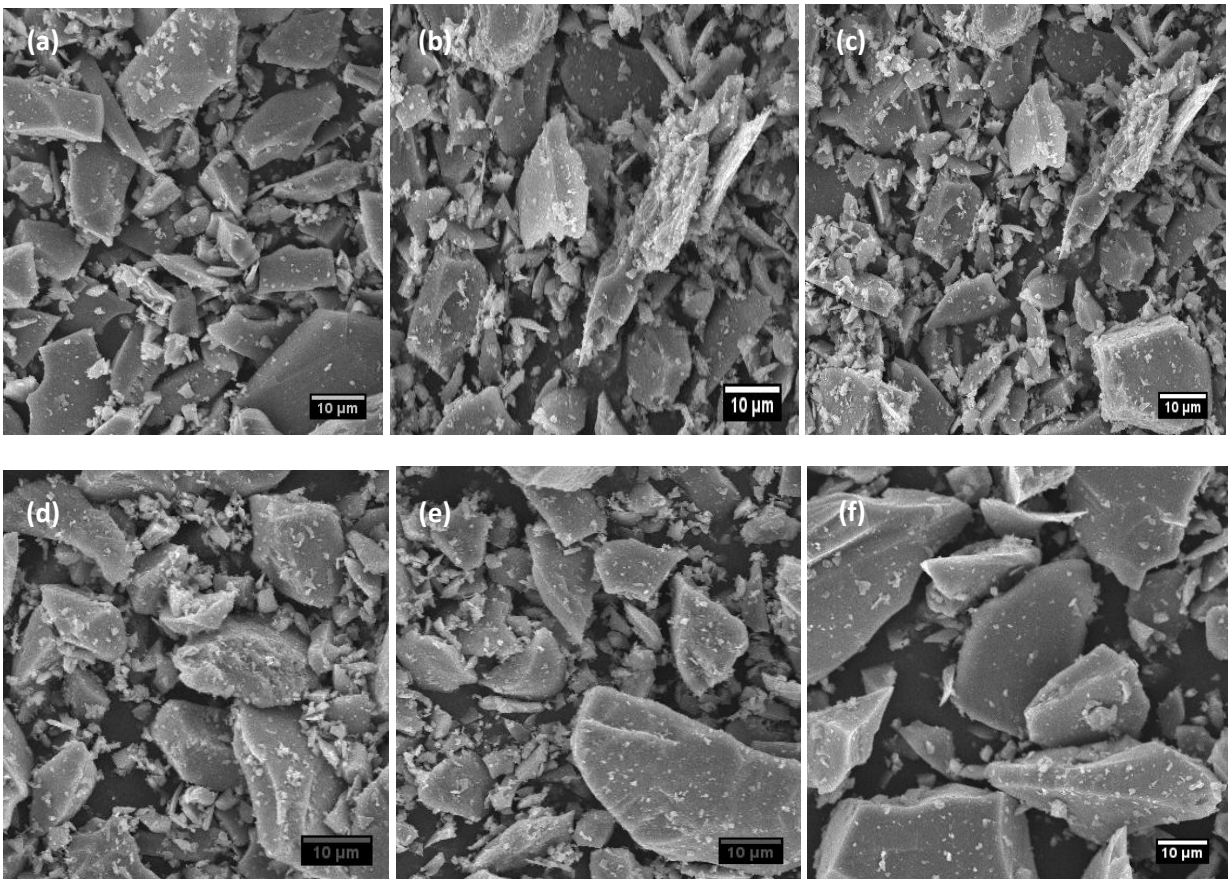

Fig. 2 SEM micrographs of (a) TiO_2, (b)0.2wt.%CuO, (c)0.4wt.%CuO, (d)0.6wt.%CuO,(e)0.8wt.%CuO, and (f)1.0wt.%CuO

Table 2 Specific surface area of 0-1.0 wt.%CuO/TiO_2

CuO concentration (wt.%)	0	0.2	0.4	0.6	0.8	1.0
Specific surface area(m^2/g)	18.245	23.0288	31.5431	41.7041	42.9819	47.1855

3.3 Photocatalytic activity. The photocatalytic activity of TiO_2 and CuO doped TiO_2 was study by observing degradation of MB under UV light irradiation. Fig. 3 shows the photocatalytic activity of CuO-doped TiO_2 with different CuO weight percent and undoped TiO_2 on the degradation of 20mg/L MB. From the graph, the degradation rate of MB increased with increasing the weight percent of CuO content from 0.2 to 1.0 wt.%.

The photocatalytic performance increase from 0.2wt.%CuO until 1.0wt.%CuO and best photocatalytic performance shows by sample with 1.0 wt.% CuO. The absorbance spectra of CuO-doped TiO_2 enhanced light harvest in both UV and visible light regions that enable much more light energy to be utilized for photocatalysisthus, increased the photocatalytic performance. Besides that, Cu species such as CuO, Cu_2O, and metallic Cu have smaller band gap and higher work function than bare TiO_2, where the electron can transfer from the conduction band of TiO_2 to metallic copper ion. This phenomenon results in the formation of Schottky barrier in the metal-semiconductor contact region, which then facilitated the charge separation, and hence enhances the photocatalytic performance of TiO_2 [12].

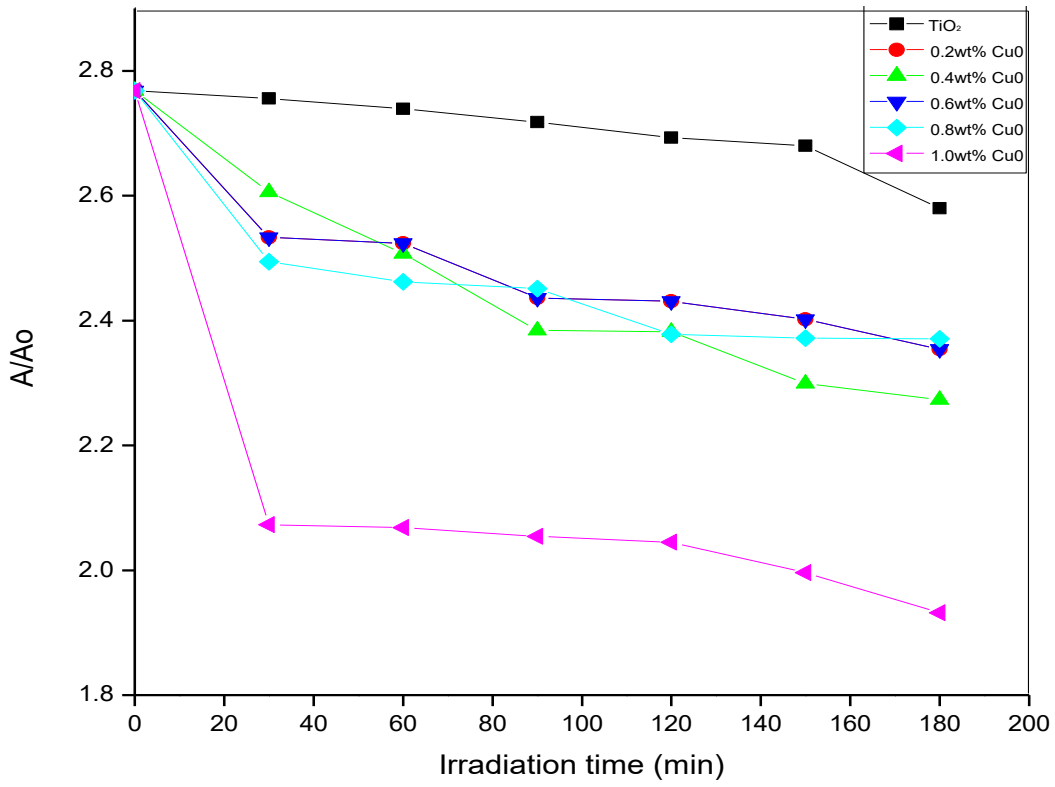

Fig. 3 Photodegradation of methylene blue (MB) using CuO doped TiO_2 with different CuO contents and undoped TiO_2 as catalyst

4. SUMMARY

The CuO doped TiO_2 samples were successfully prepared by sol-gel method and sintered at 500 °C. The synthesized samples were confirmed inanatase phase of $TiO_2$for doping range 0 -1.0wt.% of CuO. The largest crystallite size was recorded by sample 1.0wt.%CuO with 260.8 Å. The highest specific area was 47.1855m^2/grecorded by 1.0 wt.%CuO. The increasing of CuO content in TiO_2 obviously increased the photocatalytic performance of TiO_2. The highest photocatalytic performance was presented by 1.0 wt.%CuO doped TiO_2 which degraded more MB compared to others.Higher photocatalytic activity can increase water splitting performance for gas production.

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