

## **SYNTHESIS AND PHOTOCATALYTIC ACTIVITIES OF CuO-TiO<sub>2</sub> NANOCOMPOSITES**

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### **ABSTRACT**

TiO<sub>2</sub> nanotubes were prepared by hydrothermal method and then modified by CuO by two different methods: adsorption – calcination (A-C) method and photo-reduction method. The obtained solid product (CuO-TNTs) was investigated of: morphology, crystal structure and absorbance spectroscopy by transmission electron microscopy (SEM), X-ray diffractometry (XRD), UV-vis spectroscopy; respectively. The photocatalytic ability of CuO-TNTs was determined by absorbance spectroscopy of methylene blue (MB) solution under various irradiation conditions. Results showed that the photocatalytic activity of CuO-TNTs is lower than that of the original TNTs in UV irradiation. In contrast, it shows the better performance in visible light and sunlight than that of the TNTs.

*Keywords:* CuO-TiO<sub>2</sub>, TiO<sub>2</sub> nanotubes, hydrothermal synthesis, photo-reduction, A-C, photocatalysis.

### **1. INTRODUCTION**

Among the photocatalytic material such as TiO<sub>2</sub> [1], ZnO [2], SnO<sub>2</sub> [3]. TiO<sub>2</sub> has attracted an excellent attention due to its chemical stability, high catalytic efficiency, low cost and environmentally friendly impact [4]. The photocatalytic performance of these materials is enhanced by the effect of quantum confinement of charge carriers [5]. Previous studies reported that CuO-TiO<sub>2</sub> shows higher photocatalytic activity than that of TiO<sub>2</sub> [4, 6]. In addition, CuO-TiO<sub>2</sub> shows the ability to create hydrogen gas by photocatalytic water splitting [4,7]. CuO is one of the promising materials due to its low cost and high-performance applications [8]. However, the valence band edge of CuO is more negative than the oxidation potential necessary to generate \*OH radicals (Figure 1a). Therefore, CuO cannot generate \*OH free radicals under sunlight, causing its low photocatalytic performance [9]. Miyauchi et al. [12] indicated that the photocatalytic activity of CuO is not effective for water treatment because CuO cannot create a significant amount of high oxidative potential \*OH radicals and cause the oxidation reaction of

organic pollutants. The charge transport mechanism of CuO-TiO<sub>2</sub> and the difference between the conduction band (CB) and valence band (VB) edges are shown in Figure 1b.

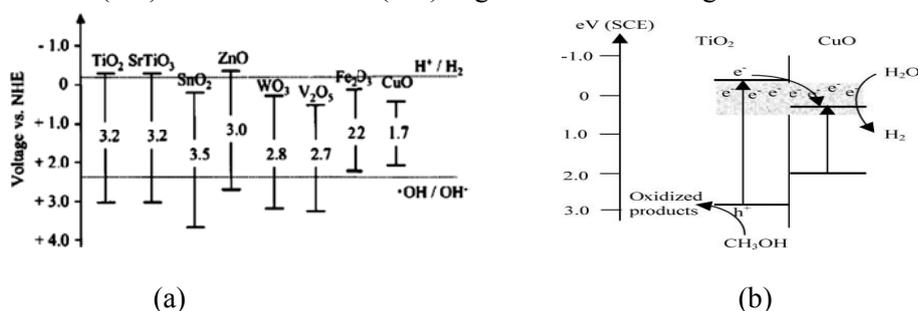


Figure 1. (a) Band gap (eV) and redox potentials of several semiconductors [10,11] and (b) the energy band positions of TiO<sub>2</sub>, CuO and the electron transfer direction [4].

In this paper, TiO<sub>2</sub> nanotube structures were fabricated by the hydrothermal method, reported in our previous studies [15,16]. The modified CuO-TiO<sub>2</sub> was synthesized by two methods: A-C method [13] and photo-reduction method [14]. The structural characterization and the photocatalytic activity of CuO-TNTs through the absorption of an aqueous solution of methylene blue (MB) under different irradiation conditions are presented.

## 2. EXPERIMENTS

### 2.1. Materials

The commercial TiO<sub>2</sub> powder (TiO<sub>2</sub>-Merck, 99,9 %), 10M NaOH, 2M HNO<sub>3</sub>, distilled water and Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O were used.

### 2.2. Synthesis of CuO-TNTs

TNTs are fabricated by the hydrothermal method from commercial TiO<sub>2</sub> powder in 10M NaOH aqueous solution. The detail of the parameter of the hydrothermal process is shown in our previous studies [16]. The modified CuO-TiO<sub>2</sub> (white powder) is fabricated by two methods: A-C method and photo-reduction method (Figure 2).

### 2.3. Characterization methods

The crystal structure, morphology and absorbance spectroscopy of CuO-TNTs were characterized by X-ray diffraction (Bruker D8-ADVANCE), transmission electron microscopy (TEM, JEM-1400), and UV-vis spectrophotometer (JASCO – V670), respectively.

The photocatalytic activities of TNTs were evaluated by the photo-degradation of methylene blue (MB) under different irradiation conditions: UVA (Philips, 25W), visible light (Compact Lamp- CFL 3UT4 30W H8) and sunlight (between 11h30 ÷ 13h30 noon). A UV-Vis spectrophotometer (JASCO-V670) was then used for monitoring the absorption of MB solutions at a wavelength of 664.6 nm.

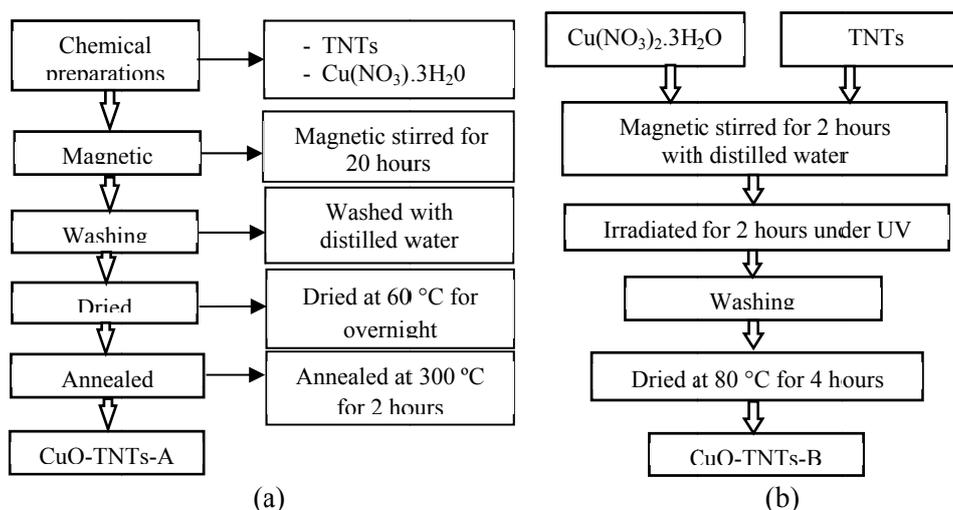


Figure 2. The preparation process of CuO-TNTs: (a) A-C method (CuO-TNTs-A) and photo-reduction method (CuO-TNTs-B).

### 3. RESULTS AND DISCUSSION

#### 3.1. The morphological and crystal structure characteristics of CuO-TNTs

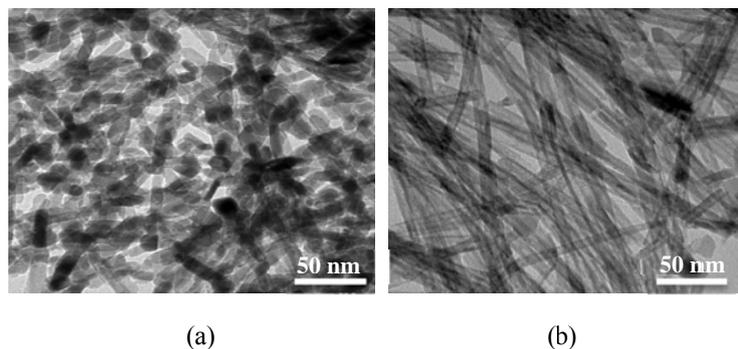


Figure 3. TEM images of (a) CuO-TNTs-A and (b) CuO-TNTs-B.

Figure 3a and b shows the TEM image of CuO-TNTs-A and CuO-TNTs-B, respectively. Results showed that CuO-TNTs-A and CuO-TNTs-B remained the tubular structure. However, the length of the CuO-TNTs-A (Figure 3a) was not retaining initial length. The majority of the tube was broken. It can be explained by the thermal shock during the heating. The tubular structure of CuO-TNTs-B (Figure 3b) is not broken. The length and diameter of CuO-TNTs-B tubes are similar to the initial tubular structure. This indicates that magnetic stirring and UV light irradiation in photo-reduction method increased the thermal motion of atoms and  $\text{Cu}^{2+}$  ions could easily deposit on the surface TNTs without making TNTs broken.

According to the XRD analysis of TNTs and CuO-TNTs (Figure 4), the diffraction peaks appear at the  $2\theta = 25.08^\circ$ ,  $37^\circ$ ,  $48.05^\circ$  and  $64^\circ$  corresponding to A (101), A (004), A (200) and A (204) of  $\text{TiO}_2$ , respectively. In addition, the reflections appeared at the  $2\theta$  of  $35.3^\circ$  and  $53.3^\circ$ ,

representing the C (001) and C (020) planes of CuO in both CuO-TNTs-A and CuO-TNTs-B samples. On the other hand, the impurity peaks of Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>, NaCl, NaNO<sub>3</sub> and H<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> crystals are not detected in synthesized products, contrasting to the report of the previous work [17]. Furthermore, the phase transition is not observed in CuO-TNTs samples whilst the peak of Cu<sub>2</sub>O and Cu have not appeared in the XRD pattern which was consistent with another report [18]. CuO peaks appeared in these two synthetic methods, but the intensity of the characteristic TiO<sub>2</sub> and CuO peaks of CuO-TNTs-A (Figure 4.a) was higher than those of CuO-TNTs-B (figure 4.b).

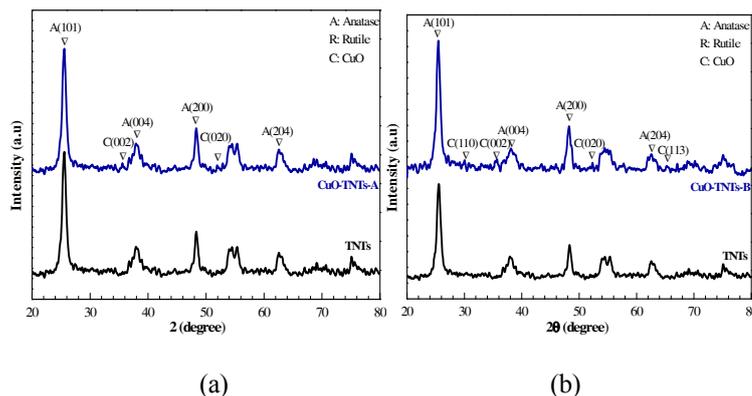


Figure 4. XRD patterns of (a) CuO-TNTs-A and (b) CuO-TNTs-B.

From the results presented above, the photo-reduction method was chosen to synthesize the CuO-TNTs in different experimental parameters. The fabrication conditions are shown in Table 1.

Table 1. The fabricated conditions of CuO-TNTs with with different Cu(NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O:TiO<sub>2</sub> ratio.

Samples	Materials	Cu(NO <sub>3</sub> ) <sub>2</sub> .3H <sub>2</sub> O: TNTs (wt%)	Magnetic stirring time (hour)	Hydrothermal temperature and time (°C, hour)
CuO-TNTs-B1	TNTs, Cu(NO <sub>3</sub> ) <sub>2</sub> .3H <sub>2</sub> O	10:1	3	130, 22
CuO-TNTs-B2	TNTs, Cu(NO <sub>3</sub> ) <sub>2</sub> .3H <sub>2</sub> O	30:1	3	130, 22
CuO-TNTs-B3	TNTs, Cu(NO <sub>3</sub> ) <sub>2</sub> .3H <sub>2</sub> O	40:1	3	130, 22

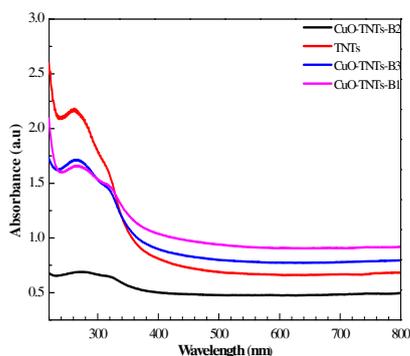


Figure 5. UV-vis absorption spectra of (a) TNTs and CuO-TNTs with different Cu(NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O:TiO<sub>2</sub>.

The UV–vis absorption spectra of TNTs, and CuO-TNTs with different  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}:\text{TiO}_2$  ratio is displayed in Figure 5. Results show that the absorbance of CuO-TNTs-B samples are significantly shifted from the UV light to the longer wavelength of, indicating that the band gap energy ( $E_g$ ) of CuO-TNTs-B samples decrease. The absorbance of CuO-TNTs-B3 shifts from the UV light to the visible range with a wavelength of about 443 nm whilst the absorbance of CuO-TNTs-B2 had a wider shift to the light visible with a wavelength of about 517 nm. For the CuO-TNTs-B1, its absorbance shifts to the light visible with a wavelength of about 591 nm. It revealed that the CuO concentration was a significant effective on the  $E_g$  and absorbance of CuO-TNTs samples. This result was entirely consistent with the report of Yu et al. [19].

### 3.2. Photocatalytic activity of CuO-TNTs

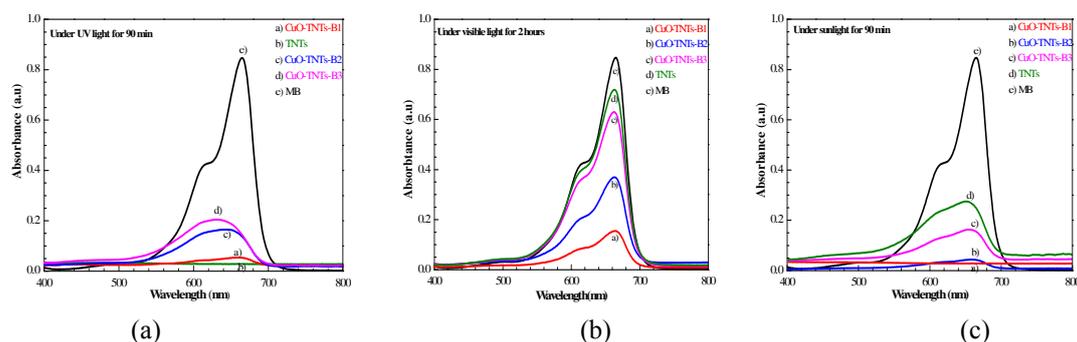


Figure 6. Absorption spectra of MB under (a) UV irradiation, (b) visible light and (c) sunlight in the presence of different catalysts, respectively.

The photocatalytic ability of TNTs and CuO-TNTs-B samples are evaluated by the absorption of MB in the presence of samples under the UV light, visible light and sunlight irradiation are presented in Figure 6. The peak absorption of MB appeared at 664.6 nm wavelength whilst the MB absorption efficiency varied with the structural properties of the catalysts. Figure 6a shows the absorption spectra of MB solution of TNTs and CuO-TNTs-B with various  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}:\text{TiO}_2$  ratio under UVB irradiation for 90 min. The absorption spectra of TNTs sample showed the largest change under UVB irradiation condition. Calculating from the absorption spectra in Figure 6a, the degradation efficiency of MB solution of CuO-TNTs-B1, CuO-TNTs-B2, CuO-TNTs-B3 and TNTs is 92 %, 85 %, 77 % and 99.92 % within 90 min. Results indicate that TNTs showed better photocatalytic activity than that of CuO-TNTs-B samples under UV irradiation. In contrast, under visible light and sunlight condition, CuO-TNTs-B samples exhibit better photocatalytic activity than that of TNTs (Figure. 6b, 6c). Calculating from the absorption spectra in Figure 6b, the degradation efficiency of MB solutions in CuO-TNTs-B1 is 85 % whilst Cu-TNTs-B2, CuO-TNTs-B3, and TNTs turn in 62 %, 38 %, and 30 % within 2 hours. Similarly, under sunlight irradiation, the degradation efficiency of the MB solution in CuO-TNTs-B1 is 98 % whilst Cu-TNTs-B2, CuO-TNTs-B3 and TNTs are 96 %, 84 %, 74 % within 90 min. It indicated that CuO concentration was effective on the photocatalytic ability of CuO-TNTs-B, and 10 wt.% CuO (CuO-TNTs-B1) was the optimized value to achieve the highest degradation efficiency of MB solution. According to the Figure 6b, 6c under the visible light and sunlight irradiation conditions, the CuO deposition on TNTs showed the better photocatalytic activity than that of TNTs. This can be explained by following hypothesis: CuO molecules exist on TNTs surface, forming the Ti-O-Cu bonds on the surface of TNTs.  $\text{Cu}^{2+}$  ions acted as an electron acceptor and play the role of electron trap in CB of TNTs. The recombination rate of

electron-hole pairs is limited, thus enhancing the photocatalytic activity. However, when the amount of CuO increased 30 wt.% and 40 wt.%, the light absorption of TNTs is prevented because all active sites on the TNTs would be covered by CuO deposition, reducing the efficiency of charge separation [14,20]. Moreover, results also showed that the absorption efficiency of MB in visible light (2 hours) was slower than in sunlight condition (90 min). This can be explained according to the sunlight region was largely an optical radiation source (mostly visible light and only 5 % of UV light the light absorption of TiO<sub>2</sub>) and led to the rate of photocatalytic degradation of MB in sunlight was faster than the rate photocatalytic degradation of MB in visible light region.

#### 4. CONCLUSION

CuO has been successfully deposited to TNTs by two different methods (A-C and photo-reduction). Compared to the A-C method, the photo-reduction method was more suitable because it remains the stability of morphology and the initial structure of TNTs. The appearance of CuO results in the gradually shifted absorption spectrum of TNTs to the longer wavelengths, in other words, contributing to narrowing the  $E_g$  of CuO-TNTs. Photocatalytic property of the synthesized CuO-TiO<sub>2</sub> nanocomposite is significantly improved under visible light and sunlight. Composite with 10 wt.% CuO (CuO-TNTs-B1) possessed the highest photocatalytic performance. The results of the efficient photocatalytic activity of CuO-TNTs under visible light and sunlight in this study indicate that CuO-TNTs nanocomposite has great promising applications in clean energy production.

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