



Preparation of Titania/Hollow Copper Oxide as Photocatalyst in the Photodegradation of Naphthalene

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Abstract

Due to the potential environmental applications, photocatalytic reactions occurring on the surface of titania (TiO_2) have garnered wide interest. However, the limited absorption from the solar spectrum, recombination of photogenerated electrons (e^-) and holes (h^+) pairs and direct modification on its surface restrict TiO_2 's performance. Therefore, structural modification of TiO_2 in defined microstructures is suggested to boost its photocatalytic activity as it possesses pore systems and higher surface areas. In this study, the synthesis of a novel core-shell composite photocatalyst that consists of commercially available TiO_2 particles encapsulated in a hollow copper oxide shell ($\text{CuO}/\text{void}/\text{TiO}_2$) is reported. The synthesis method was divided into three parts, which were the synthesis of C/TiO_2 using glucose solution as the carbon source, followed by a layer of CuO with different concentrations (0.5 – 1.5 mol), before removing the carbon through calcination to form $\text{CuO}/\text{void}/\text{TiO}_2$. The obtained photocatalysts were characterized by transmission electron microscopy (TEM) and ultraviolet-visible-near-infrared (UV-vis-NIR) spectroscopy. It was shown that the existence of TiO_2 particles as the core, where they were successfully coated with CuO shell. The optical properties of the $\text{CuO}/\text{void}/\text{TiO}_2$ photocatalysts showed a reduction in bandgap energy (E_g), where the light response was broadened from UV to visible light for more efficient solar energy use. In the photocatalytic activity testing, it was observed that $\text{CuO}(1.0)/\text{void}/\text{TiO}_2$, synthesized with 1.0 mol of CuO , showed a higher degradation percentage of naphthalene under UV (67.8%) and visible light (71.2%) irradiations as compared to other concentrations of CuO and the TiO_2 directly covered by CuO ($\text{dir-CuO}(1.0)/\text{TiO}_2$). It can be concluded that $\text{CuO}/\text{void}/\text{TiO}_2$ photocatalysts have been successfully obtained and the photocatalysts displayed a good photocatalytic ability under both UV and visible light irradiations.

Keywords: Titania (TiO_2) core - Copper oxide (CuO) shell; Hollow core-shell particle; Naphthalene

Introduction

The usage of photocatalysts is particularly important for the degradation of organic pollutants in wastewater systems [1-3]. Titania (TiO_2) is one of the most utilized photocatalysts due to its chemical and photo-corrosion resistance, non-toxicity and hydrophilicity. When compared to traditional remediation methods, photocatalysis and advanced oxidation using TiO_2 are two ideal methods for the photodegradation of pollutants due to their chemical stability and environmental friendliness [1].

However, due to its narrow photocatalytic region ($\lambda < 400$ nm) and ability to absorb only a small fraction (5%) of incident solar irradiation, the application of TiO_2 is limited [2]. A previous study has reported the usage of TiO_2 for the degradation of organic pollutants with direct modification of inorganic support to its surface [4] will cause the surface of TiO_2 to be covered and cannot effectively absorb light. Not only that, TiO_2 has a wide bandgap (anatase, 3.2 eV), which can only absorb UV light. It has also been reported that due to the high energy of UV-light input, an increase in the formation of by-products can be observed. Therefore, efforts should be made to broaden the light response of TiO_2 from UV to visible light to effectively utilize solar energy for significant positive impacts [3].

In order to boost the photocatalytic activity of TiO_2 , one approach for selective organic synthesis is structural modification of TiO_2 photocatalysts; usage of photocatalysts in defined microstructure [3]. The TiO_2 particles are distributed onto or into inorganic supports with pore structures and/or high surface areas. Many researchers are interested in utilizing TiO_2 for the formation of core-shell nanoparticles, which is said to be able to incorporate the properties of both the core and the shell, as well as the ability to have more efficient physical and chemical properties [5,6], the study of which has been done before using silica (SiO_2), shown in Figure 1 below.

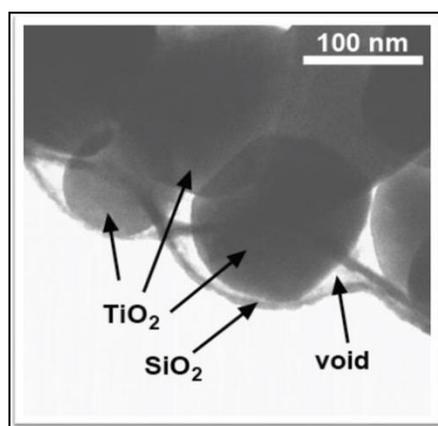


Figure 1 $\text{SiO}_2/\text{void}/\text{TiO}_2$ photocatalyst synthesized using silica as the shell and TiO_2 as the core [4]

In this study, TiO_2 photocatalysts were encapsulated in a hollow CuO shell. CuO is a semiconductor with a small bandgap ($E_g = 1.2 - 1.5$ eV) that has applications in a variety of fields such as photovoltaic and optoelectronic devices, catalysts, sensors and antibacterial performances [7]. Due to the photocatalyst's modified optical property in this study, where the synthesized $\text{CuO}/\text{void}/\text{TiO}_2$ photocatalyst will be able to tap into the visible light spectrum of solar irradiation, it is predicted that the photocatalyst will display enhanced activity in the photodegradation of organic pollutant, namely naphthalene, under both UV light and visible light irradiations. Naphthalene is a polycyclic aromatic hydrocarbon that can cause liver and neurological damage if it is inhaled or ingested [8]. Furthermore, it has been classified as a possible human carcinogen, which can cause cancer in humans. Naphthalene is used as a household fumigant and it is the main ingredient in the production of mothballs, resins, and dyes, which increase the spread of highly toxic compounds into our water sources and efficient techniques for its removal are very much needed [9].

Materials and methods

Synthesis of $\text{CuO}(x)/\text{void}/\text{TiO}_2$

$\text{CuO}/\text{void}/\text{TiO}_2$ was prepared by coating TiO_2 particles with a layer of carbon, followed by a layer of CuO layer. Heat treatment was then carried out to remove the carbon layer through calcination. In a typical synthesis process, 0.2 g of TiO_2 powder was suspended in a methanolic solution (10 mL) of 3-aminopropyltriethoxysilane (APS) (1.1 mmol). After vigorous stirring of the suspension for 2 h at room temperature, the sample was washed with ethanol and dried overnight at 80 °C. The APS-modified TiO_2 was then stirred in aqueous glucose (65 mL) with the concentration of 0.5 mol dm^{-3} before being transferred into a Teflon-sealed autoclave at 180 °C for 6 h. The resulting polysaccharide (PS)-covered particles were centrifuged, and washed several times with water and ethanol, before drying overnight at 80 °C. This procedure resulted in the coating of the particle aggregates with a thick uniform layer of amorphous carbon (C/TiO_2).

In the next step, 0.2 g of the obtained C/TiO₂ was stirred in a methanolic solution (10 mL) of 1.1 mmol 3-(2-aminoethylamino)propyltrimethoxysilane (AEAPS) for 2 h at ambient temperature. Then, the resulting AEAPS-treated sample was dispersed in copper(II) nitrate trihydrate (Cu(NO₃)₂·3H₂O) solution of different concentrations. The required amount of Cu(NO₃)₂·3H₂O was dissolved in distilled water. Under vigorous stirring, the resultant mixture was heated at 80 °C until the solvent evaporated. The sample was then washed with ethanol and dried overnight at 80 °C. TiO₂ particles covered with carbon and CuO layers (CuO/C/TiO₂) were obtained in this stage. Finally, the carbon layer was removed by calcination at 600 °C for 2 h in air, thus successfully yielding TiO₂ encapsulated in a hollow CuO shell (CuO/void/TiO₂). The resultant powder was stored under ambient conditions. The samples were labelled as CuO(x)/void/TiO₂, with x showing the concentration of CuO used in mol and varied in the range of 0.5 – 1.5 mol (e.g., CuO (0.5)/void/ TiO₂ for a sample obtained using 0.5 mol of CuO).

Synthesis of *dir*-CuO/TiO₂

For comparison purposes and to show the efficiency of the hollow core-shell structure, TiO₂ directly coated with CuO (*dir*-CuO/TiO₂) was also prepared. 0.2 g portion of TiO₂ powder was stirred in a methanolic solution (10 mL) of 1.1 mmol AEAPS for 2 h at ambient temperature. Then, the resulting AEAPS-treated sample was dispersed in Cu(NO₃)₂·3H₂O. The required amount of Cu(NO₃)₂·3H₂O was chosen based on the concentration of CuO that showed the highest photocatalytic activity among void samples. Under vigorous stirring, the resultant mixture was heated at 80 °C until the solvent evaporated. The sample then was washed with ethanol and dried overnight at 80 °C. Finally, samples were calcined at 600 °C for 2 h in air, thus successfully yielding TiO₂ directly coated with CuO (*dir*-CuO/TiO₂). The resultant powder was stored under ambient conditions. The samples were labelled as CuO(x)/TiO₂, with x showing the concentration of CuO used in mol.

Characterizations of the photocatalysts

The physicochemical properties of the synthesized CuO/void/TiO₂ were determined by a JEOL JEM-ARM 200F 200kV TEM. The samples were carefully prepared by dispersing powder samples with the aid of ultrasound in an ethanol suspension before pipetting a few drops of suspension on the carbon-coated copper grid, which were left to dry for 24 h in a desiccator before analysis. A Shimadzu UV-vis-NIR spectrophotometer model UV-3600 Plus at the wavelength of 200 to 800 nm was used to identify the bandgap energy of the photocatalyst.

Photocatalytic activity under UV and visible light irradiation

The photocatalytic activities of the prepared TiO₂ based materials were tested out in the degradation of naphthalene using a 6 W lamp from Vilber Lourmat as the UV light source. 0.05 g of photocatalyst (CuO/void/TiO₂ or *dir*-CuO/TiO₂) was added to the naphthalene solution (100 ppm, 100 mL), and the beaker was sealed with parafilm to avoid the evaporation of naphthalene. The naphthalene solution with the presence of photocatalyst was placed inside the box containing the UV light source and stirred using a magnetic stirrer. It was left in the dark for 1 h to reach adsorption equilibrium. After that, the UV light was switched on and the photocatalytic reaction was performed for 2.5 h. 5 mL of naphthalene solution was taken out at the end of the reaction and its concentration was analyzed using a UV-vis spectrophotometer. For reaction under the radiation of visible light, a Philips 18W LED bulb was used instead of UV light and the same procedures stated above were repeated. The degradation percentage for each sample was calculated using the equation below.

$$\text{Degradation percentage (\%)} = \frac{C_0 - C}{C_0} \times 100\% \quad (1)$$

Where C₀ is the concentration of naphthalene after 1 h dark reaction and C is the concentration of naphthalene after being treated with UV and visible light radiation in ppm.

Results and discussion

Preparation of CuO/void/TiO₂

In this study, the CuO/void/TiO₂ nanoparticles were synthesized by coating the TiO₂ particles with different concentrations of CuO, which were 0.5, 1.0 and 1.5 mol. Figure 2 shows the observation of the samples synthesized with different concentrations of CuO. With different amounts of CuO, the colour of the resulting product also differed. Hence, the amount of CuO used most likely plays a significant role, as the amount of TiO₂ used in the synthesis procedure was kept constant at 1.0 mol. The intensity of colour increased proportionately with the higher concentration of CuO (1.5 mol) used. Since CuO is black and TiO₂ is white, the samples' brown-blackish colour indicated the formation of a CuO layer on the TiO₂ surface [10].

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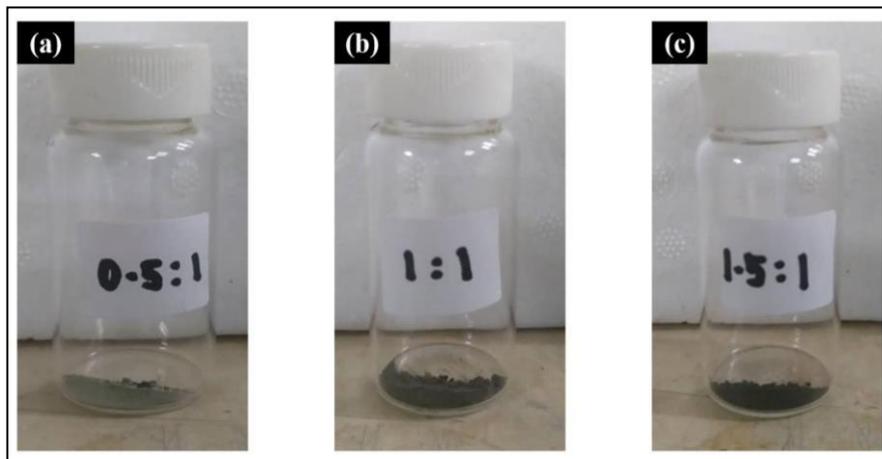


Figure 2 CuO/void/TiO₂ synthesized using different concentrations of CuO: (a) 0.5 mol (light grey), (b) 1.0 mol (dark grey) and (c) 1.5 mol (black).

Morphology and Elemental Composition by TEM and EDX Analyses

The TEM images in Figure 3 show the morphology of CuO/void/TiO₂ synthesized with different concentrations of CuO. The images show that the TiO₂ particles as aggregates successfully encapsulated in hollow CuO shells. The thickness of the lateral CuO shell varies with the different concentration of CuO used. A higher concentration of CuO resulted in a thicker CuO layer and vice versa. However, the size of the void space was difficult to control as the aqueous glucose was not coated uniformly around the TiO₂ particles. Stirring TiO₂ in aqueous glucose before hydrothermal treatment may not have the same effect as same as when rotating a Teflon-sealed autoclave was used in a previous study [4]. PS formation proceeds spontaneously and without proper rotation, which led to carbon layers that were not uniform around TiO₂.

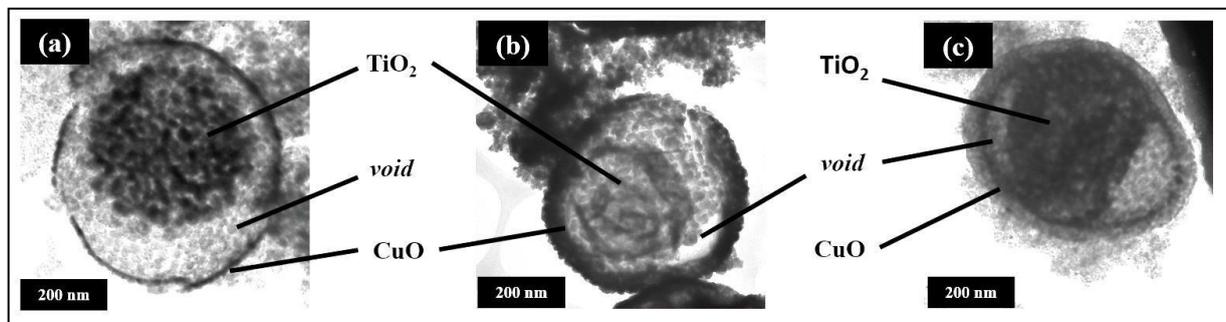


Figure 3 TEM images of (a) CuO(0.5)/void/TiO₂, (b) CuO(1.0)/void/TiO₂ and (c) CuO(1.5)/void/TiO₂.

Bandgap determination by Ultraviolet-visible-Near-Infrared (UV-vis-NIR) Spectroscopy

The bandgap energy of commercial TiO_2 (Fig. 4 (a)) determined by the Tauc plot was 3.40 eV, which is slightly higher than the bandgap of anatase TiO_2 (3.2 eV) and mixed anatase-rutile (3.18 eV) as shown in Figure 4 [11]. This might be due to the different arrangement of TiO_6 (octahedral) units to make up the crystalline structure of TiO_2 . Such different arrangements will affect the optical properties of TiO_2 [11].

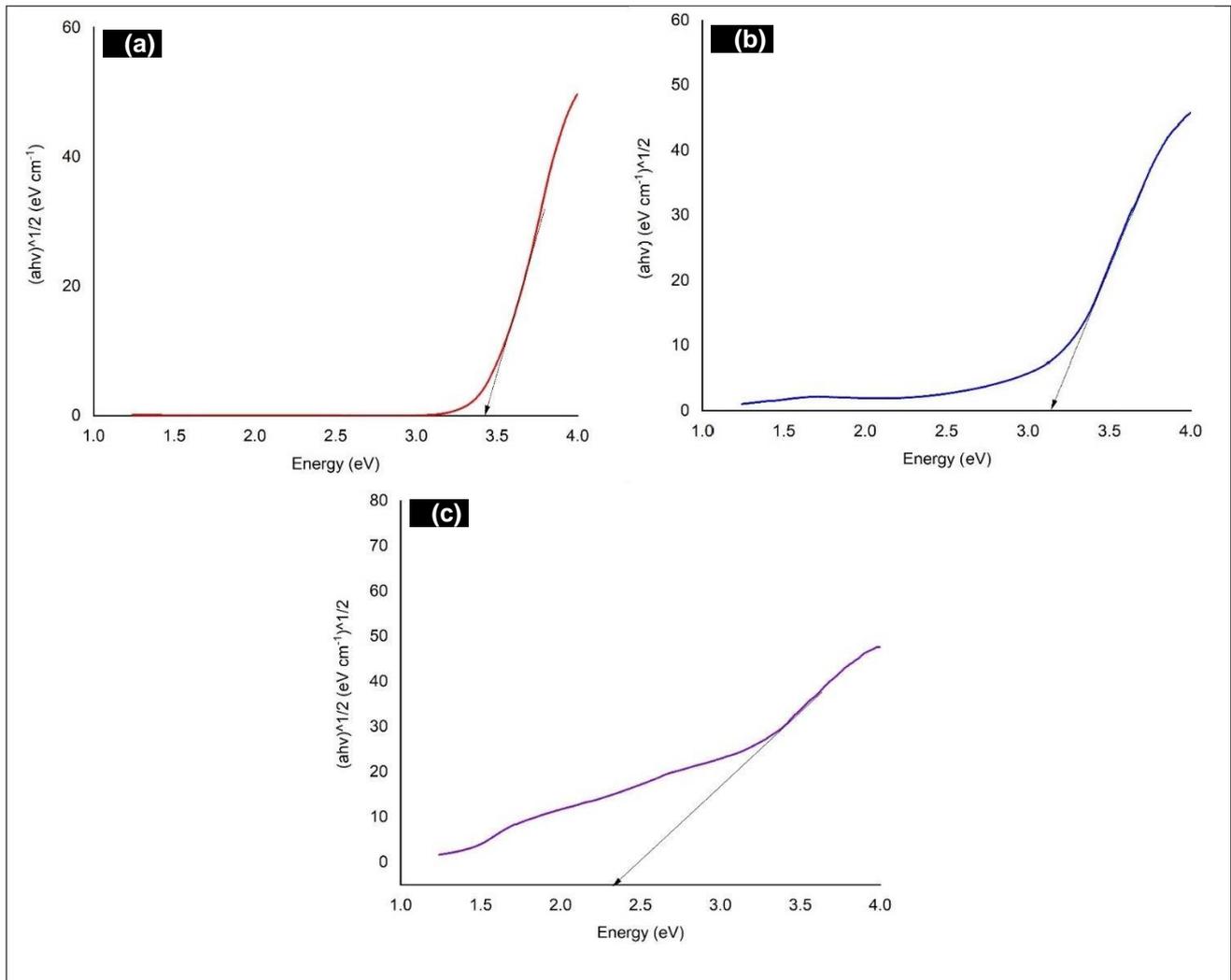


Figure 4 Tauc model plot of (a) TiO_2 , (b) $\text{CuO}(0.5)/\text{void}/\text{TiO}_2$, and (c) $\text{CuO}(1.0)/\text{void}/\text{TiO}_2$ photocatalysts.

On the other hand, $\text{CuO}(1.0)/\text{void}/\text{TiO}_2$ and $\text{CuO}(0.5)/\text{void}/\text{TiO}_2$ samples indicated a red shift extending up to 400 and 600 nm, respectively. The addition of CuO nanoparticles distinctively alters the adsorption spectrum of the system, with a new adsorption feature appearing at 400 – 800 nm. The shifted adsorption band at 410 – 510 nm is in accordance with the charge transfer from the valence to the conduction bands of CuO. The adsorption band at 520 – 800 nm is associated with the d-d transition of Cu^{2+} [12,13]. The successful synthesis of $\text{CuO}/\text{void}/\text{TiO}_2$ is also evident from the change in the colour observed in the samples, shifting from pure white commercial TiO_2 to blackish, as shown in Figure 2 [14]. The bandgap energy of $\text{CuO}(0.5)/\text{void}/\text{TiO}_2$ (Fig. 4 (b)) was reported to be 3.18 eV and $\text{CuO}(1.0)/\text{void}/\text{TiO}_2$ (Fig. 4 (c)) was observed to be 2.47 eV.

The presence of CuO as the core layer in $\text{CuO}/\text{void}/\text{TiO}_2$ reduced the bandgap energy (E_g), which can be explained by the movement of photogenerated electrons from the CuO to the conduction band of TiO_2 by overcoming Schottky barriers formed at $\text{CuO}/\text{void}/\text{TiO}_2$ interface [15]. This process subsequently reduced the E_g of the TiO_2 and suppressed the recombination rate. $\text{CuO}(1.0)/\text{void}/\text{TiO}_2$ showed the highest

reduction of E_g among all the photocatalysts. As the concentration of CuO increases, the reduction in E_g became more evident. There is possibly a greater amount of photogenerated electrons from the CuO core that migrated to the conduction band of TiO_2 than to its surface. The increased concentration of Cu brings in higher numbers of hydroxyl radicals and oxygen species, increasing the availability of active sites for photocatalytic performances [16].

Photocatalytic Activity of the Photocatalysts

In the photocatalytic activity testing of organic pollutant, namely naphthalene, $CuO(1.0)/void/TiO_2$ showed the highest percentage of naphthalene degradation under both UV and visible light irradiation, which were 67.8% and 71.2%, respectively, followed by $CuO(1.5)/void/TiO_2$ (UV – 63.7% and visible – 65.3%) and the lowest degradation percentage (UV – 53.9% and visible – 53.8%) were recorded by $CuO(0.5)/void/TiO_2$, as shown in Figure 5. It can be clearly shown the presence of CuO nanoparticles extends the absorption to the visible region. This was possible due to the localized surface plasmon resonance effect contributed by the hollow CuO, which facilitated extra movements of electrons [11].

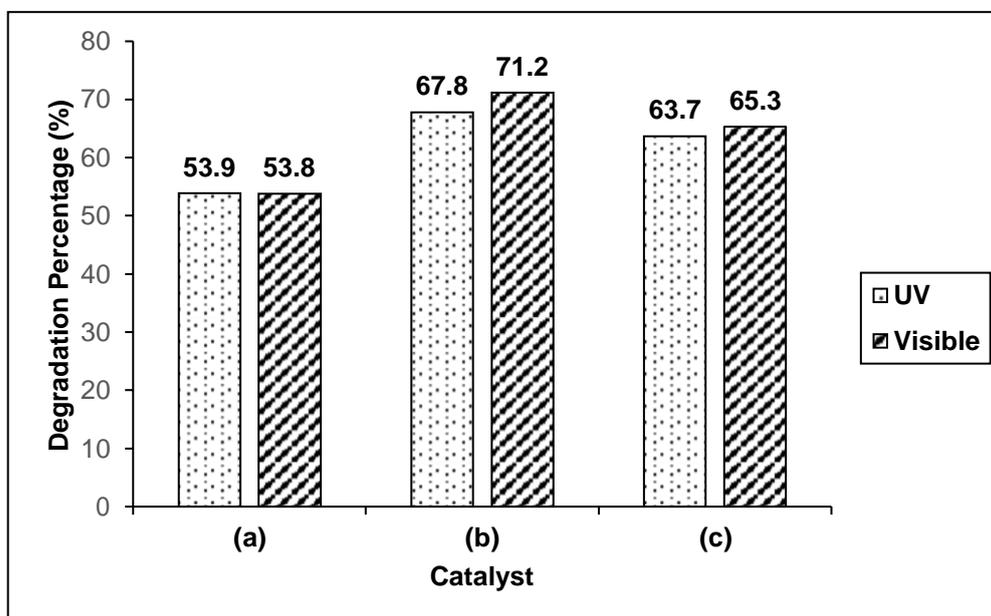


Figure 5 Degradation percentage of naphthalene under UV and visible light irradiations in the presence of catalysts: (a) $CuO(0.5)/void/TiO_2$, (b) $CuO(1.0)/void/TiO_2$ and (c) $CuO(1.5)/void/TiO_2$

The photocatalytic activity of $CuO/void/TiO_2$ also increased under both light sources, with the increase of CuO up to 1.0 mol. Unfortunately, the higher concentration of CuO (1.5 mol) resulted in a lower photocatalytic activity compared to when 1.0 mol of CuO was used. This result clearly suggested that the proper amount of CuO, which was 1.0 mol, is the optimum amount in this study, to give the highest photocatalytic activity for the $CuO/void/TiO_2$ photocatalysts. On the other hand, the high amount of CuO might reduce the electrons in the conduction band of TiO_2 or may give a masking effect on TiO_2 , which prevents the UV or visible light source from reaching the active sites of TiO_2 [17]. Therefore, the optimum amount of CuO can result in the optimum activity with no blocking of active sites of the TiO_2 .

In another part of the experiment, under both UV and visible light irradiations, it was observed that only 50.0% and 44.6% of naphthalene was degraded, respectively, when *dir*-CuO(1.0)/TiO₂ was used, which were lower than those displayed by CuO(1.0)/*void*/TiO₂, as shown in Figure 6. From these results, it can be concluded that direct modification of metal oxide on the surface of TiO₂ somehow has the tendency to reduce its photocatalytic activity as it cannot effectively absorb light [4]. Apart from that, it is observed in this study that the large bandgap of TiO₂ has been reduced, which enables CuO/*void*/TiO₂ to tap into the visible light range of the solar irradiation to show enhanced degradation of naphthalene owing to their modified optical property.

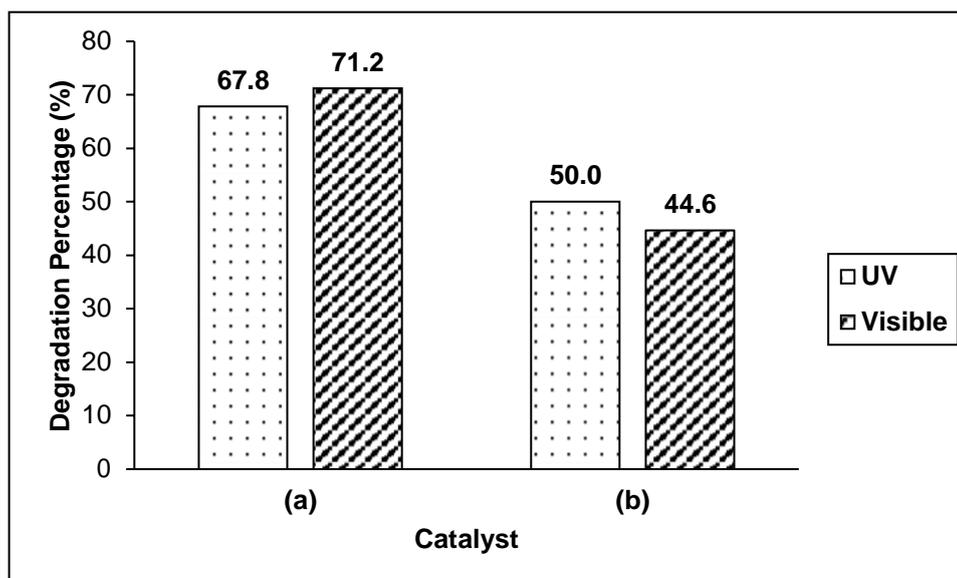


Figure 6 Degradation percentage of naphthalene under UV and visible light irradiation in the presence of catalyst: (a) CuO(1.0)/*void*/TiO₂ and (b) *dir*-CuO(1.0)/TiO₂

Conclusion

In this study, it has been proven that CuO/*void*/TiO₂ has been successfully synthesized and the morphology was confirmed by the TEM images. It was revealed that the thickness of the lateral CuO shell varies with the different concentrations of CuO used. The optical properties of the CuO/*void*/TiO₂ photocatalysts showed a reduction in E_g of the photocatalysts. Among all of the photocatalysts prepared, CuO(1.0)/*void*/TiO₂ exhibited the highest photocatalytic activity in both UV and visible light irradiations. It was also observed that direct modification of metal oxide on the surface of TiO₂ somehow cannot effectively absorb light and has the tendency to reduce its photocatalytic activity. Future works relating to this research should be continued due to the potential of this work, such as studying the effect of different concentrations of aqueous glucose on the size of the void space in CuO/*void*/TiO₂ and its reusability. In conclusion, the synthesized CuO/*void*/TiO₂ photocatalysts displayed the ability to be a good UV and visible light active photocatalyst, which proved the effectiveness of the hollow core-shell structure.

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References

- [1] Dong, H., Zeng, G., Tang, L., Fan, C., Zhang, C., He, X., & He, Y. (2015). An overview on limitations of TiO₂-based particles for photocatalytic degradation of organic pollutants and the corresponding countermeasures. *Water research*, 79, pp. 128-146.

- [2] Gopinath, K. P., Madhav, N. V., Krishnan, A., Malolan, R., & Rangarajan, G. (2020). Present applications of titanium dioxide for the photocatalytic removal of pollutants from water: A review. *Journal of Environmental Management*, 270, pp. 110906-110915.
- [3] Wahyuni, E. T., Yulikayani, P. Y., & Aprilita, N. A. (2020). Enhancement of visible-light photocatalytic activity of Cu-doped TiO₂ for photodegradation of amoxicillin in water. *J. Mater. Environmental Science*, 11(4), pp. 670-683.
- [4] Chandren, S., & Ohtani, B. (2012). Preparation, characterization and photocatalytic performance of titania particles encapsulated in hollow silica shells as an efficient photocatalyst for redox-combined stereoselective synthesis of L- pipercolinic acid from L-lysine. *Journal of Photochemistry and Photobiology A: Chemistry*, 246, pp. 50-59.
- [5] Kitsou, I., Panagopoulos, P., Maggos, T., Arkas, M., & Tsetsekou, A. (2018). Development of SiO₂@TiO₂ core-shell nanospheres for catalytic applications. *Applied Surface Science*, 441, pp. 223-231.
- [6] Eskandarloo, H., Zaferani, M., Kierulf, A., & Abbaspourrad, A. (2018). Shape-controlled fabrication of TiO₂ hollow shells toward photocatalytic application. *Applied Catalysis B: Environmental*, 227, pp. 519-529.
- [7] Li, X., Guo, W., Huang, H., Chen, T., Zhang, M., & Wang, Y. (2014). Synthesis and photocatalytic properties of CuO nanostructures. *Journal of nanoscience and nanotechnology*, 14(5), 3428-3432.
- [8] Barman, S. R., Banerjee, P., Mukhopadhyay, A., & Das, P. (2017). Biodegradation of acenaphthene and naphthalene by *Pseudomonas mendocina*: Process optimization, and toxicity evaluation. *Journal of Environmental Chemical Engineering*, 5, pp. 4803-4812.
- [9] White, A. J., Bradshaw, P. T., Herring, A. H., Teitelbaum, S. L., Beyea, J., Stellman, S. D., & Conway, K. (2016). Exposure to multiple sources of polycyclic aromatic hydrocarbons and breast cancer incidence. *Environment International*, 89, pp. 185-192.
- [10] Wu, J., Li, C., Zhao, X., Wu, Q., Qi, X., Chen, X., & Cao, Y. (2015). Photocatalytic oxidation of gas-phase Hg⁰ by CuO/TiO₂. *Applied Catalysis B: Environmental*, 176, pp. 559-569.
- [11] Ribao, P., Rivero, M. J., & Ortiz, I. (2017). TiO₂ structures doped with noble metals and/or graphene oxide to improve the photocatalytic degradation of dichloroacetic acid. *Environmental Science and Pollution Research International*, 24, pp. 12628- 12637. 10.1007/s11356-016-7714
- [12] Shi, Q., Ping, G., Wang, X., Xu, H., Li, J., Cui, J., & Li, G. (2019). CuO/TiO₂ heterojunction composites: an efficient photocatalyst for selective oxidation of methanol to methyl formate. *Journal of Materials Chemistry A*, 7(5), 2253-2260.
- [13] Liu, J., Han, C., Yang, X., Gao, G., Shi, Q., Tong, M., & Li, C. (2016). Methyl formate synthesis from methanol on titania supported copper catalyst under UV irradiation at ambient condition: Performance and mechanism. *Journal of Catalysis*, 333, 162-170.
- [14] Dalapati, G. K., Masudy-Panah, S., Kakran, M., Lim, Y. F., Chua, C. S. & Tan, H. R., (2016). Graphene nanoparticle incorporated CuO thin film for solar cell application. *Journal of Renewable and Sustainable Energy*, 8, pp. 435-440.
- [15] Jiang, Z., Jiang, D., Yan, Z., Liu, D., Qian, K., & Xie, J. (2015). A new visible light active multifunctional ternary composite based on TiO₂-In₂O₃ nanocrystals heterojunction decorated porous graphitic carbon nitride for photocatalytic treatment of hazardous pollutant and H₂ evolution. *Applied Catalysis B: Environmental*, 170, pp. 195-205.
- [16] Zhang, J., Schneider, J., Matsuoka, M., Takeuchi, M., Horiuchi, Y., Anpo, M., & Bahnemann, D. W. (2014). Understanding TiO₂ photocatalysis: mechanisms and materials. *Chemical Reviews*, 114, pp. 9919-9986.
- [17] Yuliaty, L., Siah, W. R., Roslan, N. A., Shamsuddin, M., & Lintang, H. O. (2016). Modification of titanium dioxide nanoparticles with copper oxide co-catalyst for photocatalytic degradation of 2, 4-dichlorophenoxyacetic acid. *Malaysian Journal of Analytical Sciences*, 20, pp. 171-178.