Copper oxide modification to improve the photocatalytic activity of titanium dioxide nanoparticles: P25 versus P90

I. Yuliati1, 2, N Hasan3 and H O Lintang1, 2

1Ma Chung Research Center for Photosynthetic Pigments, Universitas Ma Chung, Malang 65151, East Java, Indonesia
2Department of Chemistry, Faculty of Science and Technology, Universitas Ma Chung, Malang 65151, East Java, Indonesia
3Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, UTM Johor Bahru, Johor 81310, Malaysia

Corresponding author’s email: leny.yuliati@machung.ac.id

Abstract. Titanium dioxide (TiO2) has been recognized as one of the most active photocatalysts for organic pollutant degradation under ultraviolet (UV) light irradiation. In order to reduce the fast charge recombination in the TiO2, various methods have been investigated, including the addition of metal oxide co-catalysts. Owing to the characteristic of the nanoparticles, the modification of nanoparticles involving heat treatment is still a challenging task. In this work, two commercial TiO2 nanoparticles, namely P25 and P90 (Evonik), were modified by copper oxides (CuO) and the photocatalytic activity was evaluated for degradation of 2,4-dichlorophenoxyacetic acid (2,4-D) under UV light. The CuO/P25 and CuO/P90 samples with various loading amounts (0.1, 0.25, 0.5 and 1.0 wt %) were prepared by precipitation of copper(II) nitrate to the P25 or P90 nanoparticles at pH of 9, followed by calcination at 573 K. X-ray diffraction (XRD) patterns indicated that all samples have the characteristics of both anatase and rutile phases. While the addition of CuO did not much affect the structure, crystallite size, and anatase-rutile ratio of the P25 and P90 nanoparticles, the presence of the copper species was confirmed by the scanning electron microscopy (SEM) equipped with the energy-dispersive X-ray (EDX) spectroscopy. Moreover, fluorescence spectra also showed that the CuO quenched the emission intensity of both the P25 and P90 nanoparticles, suggesting the successful decrease of the charge recombination in the TiO2 nanoparticles. Photocatalytic activity tests showed that the P25 and P90 gave percentage degradation of 90 and 47 %, respectively, after a 1-hour reaction. Even though not much improvement was observed for P25 TiO2 nanoparticle after the CuO addition (92 %), the activity of P90 nanoparticle was enhanced from 47 % to 86 % with the CuO addition of 0.1–0.25 wt %. This study demonstrated that it is feasible to improve the photocatalytic activity of TiO2 commercial nanoparticles, in this case, the P90, by surface modification using the CuO.

Keywords: Copper oxide, P25, P90, photocatalyst, titanium dioxide

1. Introduction
Titanium dioxide (TiO2) is one of the most investigated photocatalysts so far since it shows an incredible high photocatalytic activity [1–4]. Although being an active photocatalyst, TiO2 suffers from recombination of charge carriers under UV illumination, which reduces its photocatalytic activity.
Photocatalytic activity of TiO\textsubscript{2} under UV light irradiation can be further enhanced by depositing co-catalyst such as copper oxide (CuO) on the surface of TiO\textsubscript{2} [5-8]. This modification is essential to achieve high efficiencies in environmental photocatalysis. It has been reported that the presence of CuO co-catalyst deposited on the surface of titania would reduce the electron transfer resistance and increase the photocurrent of the TiO\textsubscript{2} [5], which in turn would enhance the overall photocatalytic activity of TiO\textsubscript{2}.

The photocatalytic activity of TiO\textsubscript{2} has been reported to be dependable on the crystal phase of TiO\textsubscript{2}. However, there are different photocatalytic activities between the two phases of TiO\textsubscript{2}, which are anatase and rutile [9-11]. Previous study reported that anatase exhibited a higher photocatalytic activity compared to rutile because of several good properties such as the good crystallite size, large specific surface area and porosity, as well as low amount of defect formation. All these parameters would affect the charge recombination process. The anatase also possesses 0.1 eV higher Fermi level than the rutile, leading to the higher level of hydroxyl groups on the surface as well as the lower oxygen affinity. It was also stated in literature that the mixture of anatase to rutile, which was usually in the ratio of 70:30 (the Evonik P25 and P90) was found to have very high photocatalytic activity [9, 10].

In this study, two types of commercial TiO\textsubscript{2}, which were Evonik P25 and P90, were modified with CuO. The Evonik P25 and P90 consists of both anatase and rutile phases, but with different ratio from each other [9, 10]. The photocatalytic activity of unmodified TiO\textsubscript{2} and CuO-modified TiO\textsubscript{2} were then examined for the degradation of 2,4-dichlorophenoxyacetic acid (2,4-D). The 2,4-D is a low biodegradable herbicide and hazardous to human health and environment [12, 13]. This work demonstrated that the activity of TiO\textsubscript{2} P90 could be more improved than the TiO\textsubscript{2} P25 by the addition of CuO.

2. Experimental

P25 TiO\textsubscript{2} or P90 TiO\textsubscript{2} (1 g) and double distilled water (20 mL) were added into a glass beaker. After the beaker was sealed with parafilm and put onto the stirring plate, the beaker was stirred for 2–3 min, followed by ultrasonication for 5 min. In another glass beaker, a certain amount of copper(II) nitrate, Cu(NO\textsubscript{3})\textsubscript{2}, was taken and diluted in the double distilled water (5 mL) to give 0.1, 0.25, 0.5, and 1.0 wt % as compared to the amount of the TiO\textsubscript{2}. The solution was then added into the beaker consisting of TiO\textsubscript{2} and double distilled water. While stirring the mixture, ammonium hydroxide, NH\textsubscript{4}OH, was dropwisely added until the mixture reached pH 9. The pH value was measured in all stages and the stirring was kept for one hour. In order to eliminate the solvent, the mixture was slowly heated at 55 °C. The obtained powder was further dried in an oven before it was calcined at 300 °C for 4 h. The prepared photocatalysts were labelled as CuO(x)/P25 and CuO(x)/P90, where x represents the amount of loaded Cu(NO\textsubscript{3})\textsubscript{2} (in wt %). The resulting solids were in white and light blue color, depending on the amount of added CuO. For the treated TiO\textsubscript{2} samples, the P25 and P90 were prepared under the similar conditions, but without the addition of CuO.

The properties of the prepared photocatalysts were examined by several instruments. X-ray diffraction (XRD, Bruker, AXS Diffrac plus release 2000) was used to record the diffraction patterns of TiO\textsubscript{2} and the CuO/TiO\textsubscript{2} photocatalysts. A spectrofluorometer (JASCO, FP-8500) was employed to study the excitation and emission sites of the prepared catalysts. Field emission scanning electron microscopy energy dispersive X-ray (FESEM-EDX, JSM-6710) spectrometer was applied to determine the surface morphology, particle size, and elements present in the photocatalyst.

Prior to the photocatalytic degradation of 2,4-D, adsorption test was performed at room temperature. Typically, 2,4-D (28 mL, 5 × 10^{-4} M) was transferred into a beaker glass containing photocatalyst (0.028 g). The mixture was then sonicated for 5 min and followed by stirring process under dark condition for 1 h. About 3 mL of the mixture was taken by a syringe, filtered, and the obtained solution was measured for its absorbance by using UV-Vis spectroscopy (Thermo Scientific, Genesys 10S) at the monitoring wavelength of 283 nm. The suspension (25 mL) was then irradiated for 1 h under UV light irradiation in a closed box on a stirring plate. After the reaction finished, another 3 mL of the mixture was taken and filtered, prior to the 2,4-D absorbance measurement using the UV-Vis.
spectrometer. The reaction steps were repeated by using the different types of photocatalyst under the similar conditions. The amount of the degraded 2,4-D was compared to the initial 2,4-D to give the photocatalytic activity as shown in the equation 1.

\[
\frac{A_0 - A_1}{A_0} \times 100 \%
\]

where \(A_0\) showed the concentration of the 2,4-D at the initial state and \(A_1\) referred to the concentration of the 2,4-D after the photocatalytic reaction.

3. Results and discussion

3.1. Characterizations and activity of P25 and CuO(x)/P25 photocatalysts

The P25 and prepared CuO(x)/P25 series were characterized using XRD in order to study the structure and crystallinity. As shown in figure 1, all samples exhibited clear diffraction peaks, which could be observed at \(2\theta\) of 25.35° (101), 27.45° (110), 37.80° (101), 48° (200), 55.10° (211), 62.65° (204) and 68.85° (112) due to the presence of both anatase and rutile phases of TiO\(_2\) (PDF-00.021-1272, PDF-00-021-1276). After either calcination at 300 °C or addition of CuO, the intensities of the diffraction peaks were mostly unchanged, suggesting that the crystallinity and/or crystallite size for all samples were similar to each other. The crystallite size could be calculated using the anatase peak at (101) plane by the Scherrer equation [6] and the calculated results are shown in table 1. There was no diffraction peak of CuO that was detected by XRD. This result suggested that the low amount of added CuO or the well dispersion of CuO on the P25 could be the reason why the CuO could not be detected by the XRD [5-8].

Table 1 also shows the percentage composition of anatase to rutile phases on the P25 and the CuO/P25 samples, calculated using the equation 2, where \(A\) is the percentage (%), \(I_A\) is the intensity of anatase phase and \(I_R\) is the intensity of rutile phase.

\[
A (\%) = \frac{1}{1 + 1.265 \left( \frac{I_R}{I_A} \right)}
\]

Figure 1. XRD patterns of (a) unmodified P25, (b) treated P25, (c) CuO (0.1)/P25, (d) CuO (0.25)/P25, (e) CuO (0.5)/P25, and (f) CuO (1.0)/P25 samples.
After calcined at 300 °C, the percentage of anatase phase in P25 was slightly increased from 71.7 to 74.4 %. On the other hand, addition of CuO did not much change the percentage of anatase. All CuO/P25 samples showed similar percentage of anatase to each other, which was in the range of 75–76 %. The ratio of anatase to rutile on CuO/P25 samples (3:1) was remained unchanged, might be due to the high stability of crystallite structure of P25 itself.

In order to study the morphology of the CuO/P25 series, FESEM image of the CuO(0.1)/P25 was recorded and shown in figure 2. The CuO(0.1)/P25 has spherical shape and particle size of 30 to 60 nm. The particle size of the CuO(0.1)/P25 was very close to the reported particle size of the P25 [14, 15]. As revealed by SEM, the P25 was reported to have particle size of 19–24 nm [14], while another study by transmission electron microscopy (TEM) gave particle size distribution in the range of 9–53 nm with the average diameter of 23 nm [15]. EDX analysis confirmed the presence of elements, which were Cu, O, and Ti on the surface of the CuO(0.1)/P25. This result suggested the clear evidence for the successful loading of CuO on the P25.

The fluorescence spectra for the P25 and CuO/P25 series are shown in figure 3. The P25 and CuO/P25 samples have excitation at 218 nm and emission at 276 nm. From the spectra, the unmodified P25 showed the highest intensity followed by the treated P25. It can be suggested that after calcination process, the electron-hole recombination was suppressed. For the modified sample, CuO(0.5)/P25 showed the highest intensity followed by CuO(1.0)/P25, CuO(0.1)/P25 and CuO(0.25)/P25. It can be proposed that addition of CuO on P25 might decrease the electron-hole recombination.

| Table 1. Crystallite size, percentages of anatase and rutile phases of P25 and CuO/P25 samples. |
| Sample | Crystallite size (nm) | Percentage of anatase (%) | Percentage of rutile (%) | Degradation of 2,4-D (%) |
|--------|----------------------|---------------------------|--------------------------|-------------------------|
| Unmodified P25 | 13.2 | 71.7 | 28.3 | 89 |
| Treated P25 | 14.4 | 74.4 | 25.6 | 90 |
| CuO(0.1)/P25 | 14.3 | 76.2 | 23.8 | 92 |
| CuO(0.25)/P25 | 15.8 | 76.6 | 23.4 | 86 |
| CuO(0.5)/P25 | 15.8 | 76.5 | 23.5 | 84 |
| CuO(1.0)/P25 | 14.3 | 75.1 | 24.9 | 90 |

Figure 2. (a) FESEM image and (b) EDX analysis of CuO(0.1)/P25 sample.
The P25 and CuO/P25 samples were tested for photocatalytic degradation of 2,4-D in order to investigate the photocatalytic performance. Table 1 shows the percentage degradation of 2,4-D over the P25 and CuO/P25 photocatalysts after UV light irradiation for 1 h. The unmodified P25 showed high activity toward 2,4-D degradation with percentage of 89%. The treated P25 that was calcined at 300 °C showed almost similar photocatalytic activity to that of unmodified P25, while the addition of 0.1 wt % of CuO to P25 slightly increased the photocatalytic activity to 92% degradation of 2,4-D. Addition of CuO to the P25 from 0.25 to 1.0 wt % did not increase the activity, even slightly reduced the activity to 84-90%. It can be proposed that since the P25 is already an active photocatalyst, further modification did not give much improvement in the photocatalytic activity. The highest photocatalytic activity was obtained with the optimum loading amount of CuO, which was 0.1 wt %.

3.2. Characterizations and activity of P90 and CuO(x)/P90 photocatalysts

The P90 and the prepared CuO/P90 series were characterized using XRD and their XRD patterns are shown in figure 4. All the P90 and modified photocatalysts showed the diffraction peaks at angle of 25.32° (101), 27.34° (110), 37.90° (004), 48.04° (200), 53.82° (211), 62.62° (002) and 68.86° (116), according to the PDF-00-021-1272 and PDF-00-021-1276. The presence of these diffraction peaks showed that all samples have both anatase and rutile phases. The calcination process did not much influence the diffraction peaks intensity, but the intensity was increased with the addition of high loading of CuO (1 wt %). It can be proposed that the addition of CuO with high amount might possibly contribute to the crystal growth. Similar to the CuO/P25 samples, there was no diffraction peak of CuO observed. The absence of CuO peaks might be due to the low amount of metal precursor added to be detected by XRD and well dispersion of CuO on the surface of P90 [5-8].

Table 2 shows the crystallite sizes for the P90 and CuO/P90 samples, calculated by using the Scherrer equation [6]. It can be observed that the calcination process did not have any impact to the crystallite size of the P90, which was calculated to be 9.6 nm when using the anatase peak at (101) plane. When considering all anatase and rutile peaks in the calculation, the average crystallite size of the P90 was calculated to be around 26 nm, which was in good agreement with the SEM measurement that gave 26–33 nm [14]. Addition of CuO up to 0.5 wt % also did not give much influence to the crystallite size. Only when the amount of CuO was 1.0 wt %, the crystallite size of P90 increased from 9.6 to 15.8 nm. This result showed that the addition of high loading of CuO might promote the growth of P90, which was not observed on the P25 TiO2 series.

![Excitation and emission spectra](image)

**Figure 3.** Excitation and emission spectra of unmodified P25, treated P25, and CuO/P25 samples.
Table 2 also displays the percentage of anatase and rutile in P90 and CuO/P90 samples. The percentage ratio of anatase to rutile was calculated using equation 2 as stated previously. From the table, it can be observed that the percentage of rutile was increased from 19.6 to 22.2 % when the P90 was calcined at 300 °C. There was no clear trend on the change of the anatase-rutile composition with the addition of CuO. However, it is clear that when the CuO amount was 1 wt %, the rutile phase increased from 19.6 to 24.9 %. As compared to P25, P90 was shown to be less stable since the anatase-rutile composition could be affected even with low calcination temperature and addition of CuO.

Figure 5 shows the fluorescence spectra for the P90 and CuO/P90 series. From the figure, it was observed that all samples showed similar excitation and emission spectra to each other, which excitation and emission wavelengths were at 218 and 276 nm, respectively. Different from the treated P25, the treated P90 was observed to have a higher intensity than the unmodified P90. This might be due to the different crystal phase composition induced by the calcination process. For the modified samples, CuO(0.25)/P90 showed the highest intensity followed by CuO(1.0)/P90, CuO(0.5)/P90 and CuO(0.1)/P90. It is noted that all the CuO/P90 series showed less intensity compared to the treated P90, suggesting the less electron-hole recombination on these CuO/P90 series.

The photocatalytic degradation of 2,4-D was evaluated using the P90 and CuO/P90 series under UV light irradiation. Table 2 shows the percentage degradation of 2,4-D over the P90 and CuO/P90 series. From the table, it can be observed that the unmodified P90 showed high photocatalytic activity with 68% degradation of 2,4-D but the P90 calcined at 300 °C showed a lower photocatalytic activity than

![Figure 4. XRD patterns](image)

**Table 2.** Crystallite size, percentages of anatase and rutile phases of P90 and CuO/P90 samples.

| Sample         | Crystallite size (nm) | Percentage of Anatase (%) | Percentage of Rutile (%) | Degradation of 2,4-D (%) |
|----------------|-----------------------|----------------------------|--------------------------|--------------------------|
| Unmodified P90 | 9.6                   | 80.4                       | 19.6                     | 68                       |
| Treated P90    | 8.3                   | 77.8                       | 22.2                     | 47                       |
| CuO(0.1)/P90   | 8.7                   | 78.4                       | 21.6                     | 86                       |
| CuO(0.25)/P90  | 9.9                   | 79.8                       | 20.2                     | 87                       |
| CuO(0.5)/P90   | 8.7                   | 76.9                       | 23.1                     | 70                       |
| CuO(1.0)/P90   | 15.8                  | 75.1                       | 24.9                     | 62                       |
Figure 5. Excitation and emission spectra of unmodified P90, treated P90 and CuO/P90 samples.

unmodified P90, which was 47% degradation of 2,4-D. The addition of CuO was found to give positive effect to the photocatalytic activity as Cu(0.1)/P90 and Cu(0.25)/P90 gave 86 and 87% degradation of 2,4-D, respectively. Increasing the amount of CuO from 0.5 to 1.0 wt% decreased the photocatalytic activity of P90 from 70 and 62%. This result proposed that the highest photocatalytic activity could be achieved when the amount of CuO was optimum, which was 0.25 wt%. This study demonstrated that when the P90 was modified with such a low amount of CuO, it would act as good co-catalyst to trap the photogenerated electron that would catalyze the reduction process, thus promoted the photocatalytic activity of P90. However, the high amount of CuO loading would block the active site of P90, thus decreased the degradation of 2,4-D.

4. Conclusion

The CuO/TiO2 photocatalysts in various amounts of CuO loading from 0.1 to 1.0 wt % were prepared by deposition-precipitation method using different types of TiO2, which were Evonik P25 and P90. Based on the XRD result, all the modified photocatalysts clearly showed diffraction peaks of anatase and rutile phases. There was no CuO peak to be observed after the addition of CuO into the TiO2. The diffraction peaks intensity increased after calcination at 300 °C for CuO/P90 series. However, the peak intensity for CuO/P25 samples was remained unchanged. Accordingly, the crystallite size for CuO/P90 series increased with the calcination process at 300 °C, while no much difference was observed for the CuO/P25. After calcined at 300 °C, the percentage of anatase phase in P25 increased from 71.7 to 74.4 %, while the addition of CuO did not much change the percentage of anatase. On the other hand, the percentage of rutile phase in P90 increased from 19.62 to 24.87 % after addition of CuO. For the fluorescence study, all the series showed similar excitation and emission spectrum to each other. As compared to the treated ones, the addition of optimum amount of CuO on the P25 and the P90 decreased the spectra intensity. It was suggested that the presence CuO might suppress the electron-hole recombination process.

The P25 showed higher activity than the P90. CuO modification gave the highest activity for P25 when the amount was 0.1 wt %, while 0.25 wt % gave the highest activity for P90 series. Even though the CuO(0.1)/P25 gave the highest percentage degradation for 2,4-D (92 %), the CuO(0.25)/P90 showed the highest enhancement (87 %) as compared to the unmodified P90 (68 %).
Acknowledgments
The authors thank for the financial support from Directorate General of Strengthening Research and Development, Ministry of Research, Technology and Higher Education of the Republic of Indonesia via the World Class Research scheme (WCR 2019, No. 041/SP2H/LT/MULTI/L7/2019 and No. 014/MACHUNG/LPPM/SP2H-LIT-MULTI/III/2019).

References
[1] Schneider J et al. 2014 Chem. Rev. 114 9919-86
[2] Reza K M, Kurny ASW and Gulshan F 2017 Appl. Water Sci. 7 1569-78
[3] Shayegan Z, Lee CS and Haghighat F 2018 Chem. Eng. J. 334 2408-39
[4] Moma J and Baloyi J 2018 Modified titanium dioxide for photocatalytic applications Photocatalysis-Applications and Attributes pp 37-56
[5] Siah W R, Lintang H O, Shamsuddin M, Yoshida H and Yuliati L 2016 Catal. Sci. Technol. 6 5079-87
[6] Lee S C, Hasan N, Lintang H O, Shamsuddin M and Yuliati L 2016 IOP Conf. Ser.: Mater. Sci. Eng. 107 012012
[7] Yuliati L, Siah W R, Roslan N A, Shamsuddin M and Lintang H O 2016 J. Analytical Sci. 20 171-8
[8] Roslan N A, Lintang H O and Yuliati L 2015 Adv. Mater. Res. 1112 180-3
[9] Siah W R, Lintang H O, Shamsuddin M and Yuliati L 2016 IOP Conf. Ser.: Mater. Sci. Eng. 107 012005
[10] Siah W R, Lintang H O, Shamsuddin M and Yuliati L 2015 Malay. J. Fund. Appl. Sci. 11 106-10
[11] Sun Q and Xu Y 2010 J. Phys. Chem. 114 18911-8
[12] Majzik E S, Tóth F, Benke L and Kiss Z 2006 Chroma. 63 S105-9
[13] Barbash J E, Thelin G P, Kolpin D W and Gilliom R J 2001 J. Environ. Qual. 30 831-45
[14] Moro P, Stampachiacchiere S, Donzello M P, Fierro G and Moretti G 2015 Appl. Surf. Sci. 359 293-305
[15] Motzkus C, Macé T, Vaslin-Reimann S, Ausset P and Maillé M 2013 J. Phys.: Conf. Ser. 429 012012