High photocatalytic activity of mixed anatase-rutile phases on commercial TiO\textsubscript{2} nanoparticles

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Abstract. Titanium dioxide (TiO\textsubscript{2}) is well-known as an active photocatalyst for degradation of various organic pollutants. Over the years, a wide range of TiO\textsubscript{2} nanoparticles with different phase compositions, crystallinities, and surface areas have been developed. Due to the different methods and conditions used to synthesize these commercial TiO\textsubscript{2} nanoparticles, the properties and photocatalytic performance would also be different from each other. In this study, the photocatalytic removal of 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) was investigated on commercial Evonik P25, Evonik P90, Hombikat UV100 and Hombikat N100 TiO\textsubscript{2} nanoparticles. Upon photocatalytic tests, it was found that overall, the photocatalytic activities of the P25 and the P90 were higher than the N100 and the UV100 for the removal of both 2,4-D and 2,4,5-T. The high activities of the P25 and the P90 could be attributed to their phase compositions, which are made up of a mixture of anatase and rutile phases of TiO\textsubscript{2}. Whereas, the UV100 and the N100 are made up of 100\% anatase phase of TiO\textsubscript{2}. The synergistic effect of the anatase/rutile mixture was reported to slow down the recombination rate of photogenerated electron-hole pairs. Consequently, the photocatalytic activity was increased on these TiO\textsubscript{2} nanoparticles.

1. Introduction
Photocatalytic decomposition of organic pollutants is a promising solution for agricultural, industrial and domestic wastewater treatment. Titanium dioxide (TiO\textsubscript{2}) is widely used for the photodegradation of hazardous chemical wastes due to its high activity, stability and non-toxicity \cite{1, 2}. In particular, nanoparticulate TiO\textsubscript{2} is of great interest due to its higher surface area and photocatalytic activity than the bulk TiO\textsubscript{2}. Hence, various TiO\textsubscript{2} nanoparticles have been developed and supplied for large scale commercial applications. Different synthesis methods would result in different properties of TiO\textsubscript{2}, such as different phase compositions, crystallinities, and surface areas, which would affect the performance of the TiO\textsubscript{2} as a photocatalyst. In this context, it is of great interest to investigate the influence of various properties on the photocatalytic activity of the commercial TiO\textsubscript{2} nanoparticles. In preceding literatures, the photocatalytic activity of some commercial TiO\textsubscript{2} has been investigated for dye degradation and pollutant decomposition \cite{3, 4}, which can be considered as models for potential environmental wastewater treatment systems.
In this study, the photocatalytic activities of commercial Evonik P25, Evonik P90, Hombikat UV100 and Hombikat N100 TiO$_2$ nanoparticles for the removal of 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) were investigated. The P25 TiO$_2$ is a commercial nanoparticulate titania powder that is widely recognized as the benchmark material for photocatalytic degradation studies, while the P90 TiO$_2$ is a similar material synthesized by analogous preparation, comprised of smaller sized nanoparticles of mainly anatase phase [5]. Likewise, the UV100 and the N100 are commercially synthesized by an analogous method and used for a variety of applications [6]. While the test pollutants (2,4-D and 2,4,5-T) are widely used as herbicides, they have been categorized as drinking water contaminants as they are toxic, hardly biodegradable and difficult to remove from the environment [7]. This study showed that the commercial TiO$_2$ photocatalysts gave large variations in the photocatalytic activity and the highest activity was observed on the photocatalyst having mixture of anatase-rutile phases.

2. Materials and methods

2.1. Materials

Commercial P25 TiO$_2$ and P90 TiO$_2$ were obtained from Evonik Industries. Commercial Hombikat UV100 TiO$_2$ and Hombikat N100 TiO$_2$ were obtained from Sachtleben Chemie. The test pollutants 2,4-dichlorophenoxyacetic acid (2,4-D, C$_8$H$_6$Cl$_2$O$_3$, ≥ 98%) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T, C$_8$H$_5$Cl$_3$O$_3$, 95%) were purchased from Sigma.

2.2. Methods

2.2.1. Characterizations. Diffraction patterns of the samples were collected in the 2θ range of 20 to 60° by an X-Ray diffraction (XRD; Bruker D8 Advance diffractometer) at room temperature, using Cu-K$_\alpha$ radiation (λ = 1.5406 Å) at 40 kV and 40 mA. The diffuse reflectance ultraviolet-visible (DR UV-Vis) spectra of the samples were measured on a Shimadzu, UV-2600 under ambient conditions using barium sulphate as the reference. The morphology of the catalysts was studied by a transmission electron microscopy (TEM, JEM-2100) at an accelerating voltage of 200 kV. The sample was dispersed in ethanol and a drop of the suspension was placed on a carbon-coated copper grid.

2.2.2. Photocatalytic activity tests. Model pollutants used for photocatalytic tests were 2,4-D and 2,4,5-T herbicides. The commercial TiO$_2$ sample (50 mg) was first dispersed in 50 ml of the pollutant solution (0.5 mM). The mixture was then stirred in the dark for 1 hour to achieve adsorption-desorption equilibrium. While under constant stirring, the mixture was then exposed for 1 hour to a Xe-Hg UV lamp (200 W, $\Phi_i = 4$ mW cm$^{-2}$) with an optical filter cutting off wavelength above 400 nm. All reactions were made open to air in order to provide sufficient oxygen for the oxidative degradation of the pollutants. The amount of pollutant removed during the adsorption process and after UV lamp exposure was determined by a high performance liquid chromatography (HPLC; Shimadzu Prominence LC-20A). The adsorption capacity of the catalysts was determined from the measurement of pollutant concentration before and after the adsorption process. The percentage of pollutant adsorbed on the catalyst surface was determined from the equation (1).

\[
\text{Adsorption of pollutant (\%) } = \frac{C_0 - C_A}{C_0} \times 100
\]  

where $C_0$ is the initial concentration of pollutant and $C_A$ is the concentration of pollutant after 1-hour adsorption under dark condition. Likewise, the photocatalytic activity of the catalysts was determined from the measurement of pollutant concentration before and after UV light irradiation. The removal of pollutant was determined from the equation (2).

\[
\text{Removal of pollutant (\%) } = \frac{C_A - C_R}{C_A} \times 100
\]  


where $C_A$ is the concentration of pollutant after adsorption and $C_R$ is the concentration of pollutant after reaction for 1 hour under UV light irradiation.

3. Results and discussion

3.1. Crystalline structure and optical properties

Figure 1(a) shows the XRD patterns of the P25, P90, UV100 and N100 commercial TiO$_2$, indexed to anatase and rutile phases. It can be seen that while the P25 and the P90 are made up of a mixture of anatase and rutile phases, the UV100 and the N100 are made up of TiO$_2$ anatase phase only. The ratio of anatase to rutile was calculated and shown in table 1. The anatase: rutile ratio of the P25 and the P90 was determined to be 80:20 and 92:8, respectively. The crystallite size of the commercial TiO$_2$ samples was estimated by the Scherrer equation and the results are also shown in table 1. As for the anatase phase, the P25 and the N100 commercial TiO$_2$ have a similar crystallite size of about 17-18 nm. On the other hand, the P90 has smaller crystallite size of 10.4 nm, followed by the UV100 that has the smallest crystallite size of 9.2 nm. As for the rutile phase, the crystallite sizes were 61.8 and 53.4 nm for the P25 and the P90 TiO$_2$, respectively. Based on the diffraction intensity, the P25 was more crystalline than the P90, while the N100 has better crystallinity than the UV100.

Figure 1. (a) XRD patterns, (b) DR UV-Vis spectra, and (c) Tauc plots of the commercial P25, P90, UV100 and N100 TiO$_2$ photocatalysts.
Figure 1(b) shows the DR UV-vis spectra of the commercial TiO$_2$ samples, representing the optical absorption of the samples. It was observed that the absorption edge of the P25, the P90, the UV100 and the N100 samples was similar to each other at around 390 nm, which is typical for absorption edge of TiO$_2$ [8]. The bandgap energy values of the samples were estimated by a Tauc plot ($\alpha$hv$^{1/2}$ versus hv), whereby the extrapolation of the linear part of the curve gives direct values of bandgap [9]. The results are shown in figure 1(c) and table 1. It was confirmed that the bandgap values of the commercial TiO$_2$ samples were similar to each other and in the range of 3.30 to 3.40 eV. The specific surface areas are also shown in table 1. The P25 has the lowest surface area while the UV100 has the largest surface area of the samples.

Table 1. Crystallite size, anatase: rutile ratio, bandgap and surface area of the commercial TiO$_2$ samples.

| Commercial TiO$_2$ | Crystallite size$^a$ (nm) | Anatase: rutile ratio$^b$ | Bandgap energy$^c$ (eV) | Specific surface area$^d$ (m$^2$/g) |
|-------------------|-------------------------|--------------------------|-------------------------|--------------------------|
| P25               | 17.9                    | 61.8                     | 80:20                   | 3.37                     | 50 [5, 8, 10] |
| P90               | 10.4                    | 53.4                     | 92:8                    | 3.40                     | 91 [5, 11]   |
| UV100             | 9.2                     | -                        | 100:0                   | 3.36                     | 290 [8]     |
| N100              | 17.1                    | -                        | 100:0                   | 3.30                     | 104 [12]    |

$^a$Estimated from FWHM of XRD anatase (101) or rutile (110) reflection by a Scherrer equation.

$^b$Estimated from XRD by the formula A(%) = (100 × IA)/(IA + 1.265 × IR), whereby A(%) is the percentage of anatase, IA and IR correspond to the intensity of the anatase (101) and rutile (110) reflections.

$^c$Estimated from Tauc plot of DR UV-Vis data.

$^d$Obtained from the previously reported works.

3.2. Morphology and particle size

The commercial P25 and P90 TiO$_2$ were supplied by Evonik Industries, which have been reported to have similar morphology to each other [8, 11]. Likewise, the UV100 and the N100 both supplied by Sachtleben Chemie were also expected to have similar morphology. Hence, the P25 and the UV100 were selected as the representative samples to study morphology and particle size by TEM. Figure 2(a) shows the TEM image of the P25 TiO$_2$. The P25 has irregular polyhedra shape, and most of the particles fall within the size range of about 15-25 nm, which would be the anatase phase of the P25 sample. The larger particles in the range of 50-60 nm were also observed due to the rutile phase of the P25. On the other hand, the TEM image of the UV100 sample is shown in figure 2(b). Comparison to the P25, the UV100 has aggregates with a smaller primary particle size of about 7 nm. The particle size observed from the TEM for both the P25 and the UV100 agreed well with the crystallite size results obtained from the XRD mentioned above.

Figure 2. TEM images of commercial (a) P25 TiO$_2$ and (b) UV100 TiO$_2$. 
3.3. Photocatalytic activity

The photocatalytic activities of the commercial TiO$_2$ samples for the removal of 2,4-D and 2,4,5-T herbicides are shown in figure 3. It can be clearly seen that after 1-hour exposure to the UV irradiation, regardless of the type of commercial TiO$_2$ used for the reactions, the amount of the 2,4,5-T removed was higher than that of the 2,4-D. The higher removal of the 2,4,5-T compared to the 2,4-D could be rationalized by considering its adsorption to the commercial TiO$_2$ samples.

![Figure 3. Photocatalytic removal of the 2,4-D and the 2,4,5-T model pollutants in the presence of commercial P25, P90, UV100 and N100 TiO$_2$ photocatalysts.](image)

Figure 4 shows the percentage of 2,4-D and 2,4,5-T adsorbed onto the surface of the commercial TiO$_2$ samples when adsorption-desorption equilibrium was achieved. It was shown that for all types of commercial TiO$_2$ used, a greater amount of 2,4,5-T was adsorbed compared to the 2,4-D. It has been widely accepted that there is a corresponding relation between the surface adsorption of the pollutants with their photocatalytic degradation activity in the presence of TiO$_2$ [10]. Higher adsorption of the pollutant molecules implies that more of the pollutants are at close proximity to the TiO$_2$ surface, where active species are generated. Hence, the higher adsorption of the 2,4,5-T led to a higher photocatalytic removal activity compared to the 2,4-D.

The chemical structures of the 2,4-D and the 2,4,5-T are shown in figure 5. It can be seen that the main difference between the 2,4-D and the 2,4,5-T is the extra chlorine substituent at the 5$^{th}$ carbon of 2,4,5-T. The larger and more highly substituted 2,4,5-T is less soluble in water than the 2,4-D. Consequently, it interacts more strongly with the TiO$_2$ surfaces. The increased absorption of the 2,4,5-T on the surface of TiO$_2$ could also be explained by considering the electron donor-acceptor (EDA) complex mechanism as has been proposed for adsorption of chlorophenol on mesoporous SBA-15 [13]. The aromatic ring of the 2,4-D and the 2,4,5-T acts as an electron acceptor and the oxygen atoms on TiO$_2$ surface serves as a donor. Since the chloro group is an electron-withdrawing group, increasing the number of chlorine substituents leads to a decrease of $\pi$-electron density in the aromatic ring. As a result,
the affinity of the 2,4,5-T for the non-binding electrons at TiO$_2$ surface oxygen also increased and this, in turn, leads to the increased adsorption of the 2,4,5-T as compared to the 2,4-D.

![Graph](image)

**Figure 4.** Adsorption of the 2,4-D and the 2,4,5-T model pollutants on the commercial P25, P90, UV100 and N100 TiO$_2$ photocatalysts.

![Chemical Structures](image)

**Figure 5.** The chemical structures of (a) 2,4-D and (b) 2,4,5-T.

While the removal of the pollutants was affected by the type of the pollutants due to the different adsorption, it was also strongly depended on the types of commercial TiO$_2$. Among the investigated samples, it was obvious that the P25 and the P90 gave similar photocatalytic activity to each other, and the activity was higher than the UV100 and the N100. However, it appeared that the specific surface area did not play a significant role in the adsorption and photocatalytic reactions. As shown in table 1, the specific surface area was in the order of P25 < P90 < N100 < UV100. On the other hand, the adsorption of pollutants was in the order of N100 < P25 < P90 < UV100. Moreover, the higher adsorption towards the pollutants did not necessarily lead to higher catalytic activity. For example, while having the highest adsorption of the 2,4-D and the 2,4,5-T, UV100 TiO$_2$ was not the most active catalyst for the removal of the 2,4-D and the 2,4,5-T. Instead, the P25 and the P90 were more active catalysts for the photocatalytic removal of these herbicides. These results suggested that there are other factors influencing the photocatalytic reactions apart from the surface adsorption.

As previously shown, the P25 and the P90 have a mixture of anatase-rutile phase, while the UV100 and the N100 only have anatase phase. This main difference caused the P25 and the P90 have higher photocatalytic activity than the UV100 and the N100. The mixture of anatase and rutile phase would lead to a synergistic electron transfer that improved the charge separation of the photogenerated electron-
hole pairs [14-17]. One of the widely accepted mechanism proposed that when anatase and rutile are in direct interfacial contact, the resultant band alignment leads to a favorable electron transfer pathway from rutile to anatase that stabilizes charge separation and prevents rapid recombination [14, 15]. This, in turn, caused the improved photocatalytic activity of the P25 and the P90 TiO$_2$. Even though the properties of the P25 and the P90 were slightly different, it was demonstrated that for TiO$_2$ anatase-rutile photocatalysts, the crystallinity, crystallite size, anatase-rutile ratio, and the specific surface area did not much affect the photocatalytic reactions.

Comparing the activity of the N100 and the UV100, the N100 displayed a higher photocatalytic activity for the removal of the 2,4-D and the 2,4,5-T than the UV100 TiO$_2$. As shown in figure 1(a), the N100 was more crystalline than the UV100. By having higher crystallinity, the N100 also have fewer defect sites, and consequently longer lifetime of photogenerated electron-hole pairs [4]. Therefore, for TiO$_2$ anatase photocatalyst, one factor that is important in the photocatalytic removal of the 2,4-D and the 2,4,5-T would be the crystallinity of the photocatalyst.

4. Conclusions
In conclusion, the photocatalytic activity of commercial P25, P90, UV100 and N100 TiO$_2$ was studied using 2,4-D and 2,4,5-T as the model pollutants. The higher photocatalytic removal of the 2,4,5-T than the 2,4-D on all four commercial TiO$_2$ samples could be associated with the higher adsorption between the 2,4,5-T and TiO$_2$, which in turn led to the improved pollutant-catalyst interaction. In addition, the higher photocatalytic activity of the P25 and the P90 compared to the UV100 and the N100 TiO$_2$ could be attributed to the synergistic effect of anatase and rutile phase mixture of the P25 and the P90, which led to the improved separation of photogenerated charge carriers.

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