Effect of preparation methods on the activity of titanium dioxide-carbon nitride composites for photocatalytic degradation of salicylic acid

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Abstract. In this study, titanium dioxide-carbon nitride (TiO$_2$-CN) composites were prepared by three methods, which were one pot oxidation, impregnation, and physical mixing. Each series of the photocatalysts was prepared with different ratios of titanium to carbon (Ti/C), i.e., 1, 5, 10, 20, and 50 mol%. All samples were characterized by X-ray diffraction (XRD) and diffuse reflectance ultraviolet-visible (DR UV-Vis) spectrosopies. The characterization results confirmed the successful preparation of TiO$_2$, CN, and the TiO$_2$-CN composites. Photocatalytic activity tests were carried out for degradation of salicylic acid at room temperature for 6 h under UV and visible light irradiations. It was confirmed that all the prepared TiO$_2$-CN composites showed better photocatalytic activities than the bare TiO$_2$ and the bare CN. Under UV light irradiation, 90.6% of salicylic acid degradation was achieved on the best composite prepared by one pot oxidation with 5 mol% of titanium to carbon (Ti/C) ratio. On the other hand, the highest degradation under visible light irradiation was 94.3%, observed on the composite that was prepared also by one pot oxidation method with the Ti/C ratio of 10 mol%. Therefore, among the investigated methods, the best method to prepare the titanium dioxide-carbon nitride composites with high photocatalytic activity was one pot oxidation method.

1. Introduction

Photocatalysis by titanium dioxide (TiO$_2$) has been discovered more than 90 years ago [1]. During the last three decades, many researches have been explored to understand its possible applications in the remediation of air and water. Owing to its high stability and non-toxicity, TiO$_2$ has been the most used and researched photocatalyst [2]. In general, pure anatase TiO$_2$ showed better photocatalytic activity than the pure rutile TiO$_2$. However, the high charge recombination rate in the TiO$_2$ leads to the low efficiency in the photocatalytic reactions [1]. Moreover, due to their large band gap energy (3.0–3.2 eV), the TiO$_2$ in anatase form can be mainly activated by UV light while TiO$_2$ in rutile form can only extend its absorption near to visible light irradiation.
Since sunlight energy has a greater portion of visible light than the UV light, it is most beneficial to develop visible light-driven photocatalysts. In order to make TiO$_2$ become active in visible light irradiation, the material needs to be incorporated with other materials, which able to absorb visible light and also can act as active compounds, such as carbon nitride (CN). Such strategy was used in some semiconductors, such as zinc oxide [3] and gallium oxide [4]. CN itself has been recognized as a good photocatalyst for degradation of organic pollutants [5-7]. In the present study, the TiO$_2$-CN composites were prepared by three methods, namely one pot oxidation, impregnation, and physical mixing. Investigating the effect of these preparation methods is an important approach to develop highly active photocatalysts. The composites were evaluated for degradation of salicylic acid as one of the organic pollutants.

2. Experimental

2.1. Preparation of TiO$_2$ and CN
Titanium chloride (TiCl$_4$, > 97%, Merck) was used as a precursor to prepare TiO$_2$. The first step was the reaction between TiCl$_4$ precursor and water to form titanium hydroxide, Ti(OH)$_4$. The precipitate was then dried and calcined at 823 K for 4 h to obtain TiO$_2$. As for the preparation of CN, urea was used as the precursor [5]. The thermal polymerization of urea to CN was carried out by calcination process at 823 K for 4 h.

2.2. Preparation of TiO$_2$-CN composites

2.2.1. One pot oxidation. Certain amounts of urea and TiCl$_4$ with different mol ratios of titanium to carbon (Ti/C, $x = 1, 5, 10, 20,$ and $50 \text{ mol\%}$) were dissolved in ethanol. The mixture was then heated to dry by stirring it on a hot plate at 348–353 K. The obtained solid sample was then calcined at 823 K for 4 h. The final product was denoted as TiO$_2(x)$-CN OPO composite, with $x$ shows the mol ratio of Ti/C.

2.2.2. Impregnation Method. The TiO$_2(x)$-CN IM composites were synthesized by an impregnation method where a certain amount of TiCl$_4$ was impregnated onto the prepared CN with various mol ratios of Ti/C ($x = 1, 5, 10, 20,$ and $50 \text{ mol\%}$). The TiCl$_4$ was first dissolved in ethanol and the prepared CN was added to the solution. The mixture was stirred on a hot plate at 348–353 K to evaporate the solvent. The obtained solid was subjected to calcination process for 4 h at 823 K to produce the TiO$_2(x)$-CN IM composite.

2.2.3. Physical Mixing. The prepared TiO$_2$ was mixed physically with the prepared CN by grinding process. Various mol ratios of Ti/C ($x = 1, 5, 10, 20,$ and $50 \text{ mol\%}$) were used and the obtained samples were labeled as TiO$_2(x)$-CN PM composites.

2.3. Characterizations of TiO$_2$, CN, and TiO$_2$-CN composites
In order to study the structural and optical properties of the prepared TiO$_2$, CN, and TiO$_2$-CN composites, all the samples were characterized by X-ray diffractometer and diffuse reflectance ultraviolet-visible spectrophotometer (DR UV-Vis), respectively. The XRD patterns were recorded on a D8 Advance (Bruker) at room temperature using radiation of Cu-Kα at 40 kV and 40 mA. The DR UV-Vis spectra were measured on a Lambda 900 (Perkin Elmer) by using barium sulfate as the reference.

2.4. Photocatalytic degradation of salicylic acid
In order to determine the required time for the sample to achieve adsorption equilibrium, the sample (0.05 g) was dispersed in a beaker containing 50 mL of salicylic acid (100 µM). The beaker was placed on the stirring plate in a closed box to ensure that there would be no activation by light. The dark
condition tests were conducted for 30 min, 1, 2, and 3 h. After each time, the photocatalyst was separated from the solution by centrifugation. The concentration of salicylic acid was then measured by using a UV-Vis spectrophotometer (Genesys 10S, Thermo Scientific). Since the required time to achieve the equilibrium was 1 h, such dark condition was conducted before the photocatalytic degradation tests were carried out. Similar to dark condition test, the sample (0.5 g) was dispersed in a beaker containing 50 mL of salicylic acid (100 µM). After 1 h adsorption process in the dark, the photocatalytic degradation of salicylic acid was carried out for 6 hours under 8 W UV lamp or 150 W halogen lamp as the visible light source. After the sample was separated from the solution, the concentration of remaining salicylic acid was determined by the UV-Vis spectrophotometer.

3. Results and Discussion

3.1. Properties of the prepared TiO$_2$, CN, and TiO$_2$-CN composites

The structural and optical properties of the prepared samples were investigated by XRD and DR UV-Vis spectroscopies. Figure 1 [A](a) shows the XRD pattern of the prepared TiO$_2$. As indicated in the figure, the prepared TiO$_2$ has the crystal planes of anatase crystal structure [8]. On the other hand, the successful formation of graphitic CN could be shown in Figure 1 [A](b), where one peak around 28° was observed due to the interlayer spacing of the CN [5-7]. The XRD patterns of the TiO$_2$(x)-CN OPO composites are displayed in Figure 1 [A](c)-(g). It was obvious that when the ratio of Ti/C was low, the composite samples only showed the main peak of CN. On the other hand, with the increase of the Ti/C ratio, the peak of CN decreased and the peak of anatase TiO$_2$ became the dominant diffraction peaks. The disappearance of the CN peak might suggest the possibility that the CN was oxidized easier in the presence of TiO$_2$ during the heating process in the synthesis part.

Figure 1 [B] shows the DR UV-Vis spectra of all samples. In Figure 1 [B](a) TiO$_2$ showed a significant increase in the absorption at a wavelength shorter than 400 nm, which could be assigned to the intrinsic band gap absorption of pure anatase TiO$_2$ (about 3.2 eV) [2]. On the other hand, the CN gave a strong absorption peak at around 370 nm, which was the characteristic of CN [5-7]. The DR UV-Vis spectra of TiO$_2$(x)-CN OPO composites are shown in Figure 1 [B](c)-(g). All samples prepared by one pot oxidation method showed absorption in the visible region above 400 nm, suggesting that they have good ability to absorb visible light and might show good activity under visible light irradiation.

![Figure 1. A] XRD patterns and [B] DR UV-Vis spectra of (a) TiO$_2$, (b) CN, (c) TiO$_2$(1)-CN OPO, (d) TiO$_2$(5)-CN OPO, (e) TiO$_2$(10)-CN OPO, (f) TiO$_2$(20)-CN OPO, and (g) TiO$_2$(50)-CN OPO.](image-url)

Figure 2 [A] shows the XRD patterns of TiO$_2$(x)-CN IM composites. Similar to the trend observed on the TiO$_2$(x)-CN OPO composites, the TiO$_2$(x)-CN IM composites with low Ti/C ratio (1-5%) were mainly characterized by the presence of CN, while high Ti/C ratio (> 10%) were dominated by the...
diffraction peaks of TiO$_2$. Again, the result suggested that the CN might be decomposed easier when heated in the presence of TiO$_2$. The DR UV-Vis spectra of the TiO$_2$(x)-CN IM composites are illustrated in Figure 2 [B]. Depicted in Figure 2 [B](b), only TiO$_2$(I)-CN IM composite showed absorption in the visible light region above 400 nm. On the other hand, with the increasing amount of Ti/C ratio, the absorption in the visible light region decreased and shifted to a lower wavelength. These DR UV-Vis spectra are in good agreement with their respective XRD patterns.

Figure 2. [A] XRD patterns and [B] DR UV-Vis spectra of (a) TiO$_2$, (b) CN, (c) TiO$_2$(I)-CN IM, (d) TiO$_2$(5)-CN IM, (e) TiO$_2$(10)-CN IM, (f) TiO$_2$(20)-CN IM, and (g) TiO$_2$(50)-CN IM.

The XRD patterns of the TiO$_2$(x)-CN PM composites are shown in Figure 3 [A]. Similar to the composites prepared by one pot oxidation and impregnation methods, the composite with low Ti/C ratio, i.e., TiO$_2$(I)-CN PM only exhibited the CN peak. However, the diffraction peak of CN was not disappeared even when the Ti/C ratio was increased to 50%. Even though the diffraction peaks of TiO$_2$ increased with the increase of the Ti/C ratio, all composites with the Ti/C ratio of more than 5% showed the diffraction peaks of both TiO$_2$ and CN, suggesting that both TiO$_2$ and CN existed in these samples. This is reasonable since physical mixing only included grinding process at room temperature. Shown in Figure 3 [B] is the DR UV-Vis spectra of the TiO$_2$(x)-CN PM composites. In contrast to the composites prepared by one pot oxidation and impregnation methods, all composites exhibited a similar absorption spectrum to each other regardless the difference in the Ti/C ratio. All composites showed the characteristics of light absorption for both TiO$_2$ and CN, and thus, able to absorb both UV and visible light.

3.2. Photocatalytic activity of the prepared TiO$_2$-CN composites

The photocatalytic performance of the TiO$_2$(x)-CN OPO composites prepared by the one pot oxidation method was evaluated for degradation of salicylic acid under UV or visible light irradiation. As shown in Table 1, under UV light irradiation, CN only gave degradation of 33.7%. The addition of TiO$_2$ up to 5 mol% increased the photocatalytic activity to 90.6%. The activity decreased with further increase of the Ti/C ratio and the TiO$_2$(50)-CN OPO showed the lowest degradation percentage among other composites, which was 79.6%. Compared to the bare TiO$_2$, all composites still gave better photocatalytic activity. Under visible light irradiation, CN only showed 43% degradation. On the other hand, the composite with a Ti/C ratio of 10 mol% gave an optimum enhanced photocatalytic activity of 94.3%. When the Ti/C ratio increased to 50%, the degradation percentage decreased to 77.7%, but this activity was still much higher than the bare TiO$_2$. Since all the TiO$_2$(x)-CN OPO composites gave higher photocatalytic activity than the bare TiO$_2$ and bare CN both under UV and visible light, it was suggested that there was a synergic effect between TiO$_2$ and CN to give high activity for the degradation of salicylic acid regardless the type of light source used in the reaction.
Figure 3. [A] XRD patterns and [B] DR UV-Vis spectra of (a) TiO$_2$, (b) CN, (c) TiO$_2$(1)-CN PM, (d) TiO$_2$(5)-CN PM, (e) TiO$_2$(10)-CN PM, (f) TiO$_2$(20)-CN PM, and (g) TiO$_2$(50)-CN PM.

Table 1. Photocatalytic degradation of salicylic acid on the TiO$_2$-CN composites prepared by one pot oxidation, impregnation, and physical mixing methods under UV or visible light irradiation

| Preparation Method | Sample          | Percentage of Degradation (%) | Under UV light | Under visible light |
|--------------------|----------------|------------------------------|---------------|-------------------|
| One Pot Oxidation  | CN             | 33.7                         | 43.0          |
|                    | TiO$_2$(1)-CN OPO | 67.3                         | 60.6          |
|                    | TiO$_2$(5)-CN OPO | 90.6                         | 91.6          |
|                    | TiO$_2$(10)-CN OPO | 77.4                        | 94.3          |
|                    | TiO$_2$(20)-CN OPO | 82.6                        | 84.1          |
|                    | TiO$_2$(50)-CN OPO | 79.6                        | 77.7          |
|                    | TiO$_2$         | 60.9                         | 21.4          |
| Impregnation       | CN             | 33.7                         | 43.0          |
|                    | TiO$_2$(1)-CN IM | 70.7                         | 65.1          |
|                    | TiO$_2$(5)-CN IM | 89.7                         | 82.6          |
|                    | TiO$_2$(10)-CN IM | 77.0                        | 86.7          |
|                    | TiO$_2$(20)-CN IM | 67.3                        | 81.0          |
|                    | TiO$_2$(50)-CN IM | 66.4                        | 78.0          |
|                    | TiO$_2$         | 60.9                         | 21.4          |
| Physical Mixing    | CN             | 33.7                         | 43.0          |
|                    | TiO$_2$(1)-CN PM | 80.0                         | 71.4          |
|                    | TiO$_2$(5)-CN PM | 79.7                         | 56.7          |
|                    | TiO$_2$(10)-CN PM | 78.1                        | 56.3          |
|                    | TiO$_2$(20)-CN PM | 76.1                        | 46.3          |
|                    | TiO$_2$(50)-CN PM | 81.0                        | 62.4          |
|                    | TiO$_2$         | 60.9                         | 21.4          |

As for the TiO$_2$(x)-CN IM composites, the photocatalytic activity under UV light irradiation increased first to 89.7% when the ratio of Ti/C increased up to 5 mol%, then the activity decreased to 66.4% with a further increase of the Ti/C ratio. However, it was obvious that even though the activity decreased, compared to the bare TiO$_2$ and CN, all the TiO$_2$(x)-CN IM composites showed much higher activities. Similar to the case of reactions under UV light irradiation, the reactions under visible light irradiation also gave the same trend. The activity increased to 86.7% when the ratio of Ti/C increased up to 10 mol%, but then the activity decreased with further increase of the Ti/C ratio. Again, all the TiO$_2$(x)-CN IM showed much higher activities than the bare TiO$_2$ and bare CN.
The photocatalytic activities of the TiO$_2$(x)-CN PM composites were also tested under both UV and visible light irradiation. Under UV light irradiation, it was obtained that the photocatalytic activities of the samples were not much influenced by the amount of Ti/C ratio. All samples showed a similar level of activity with salicylic acid degradation was ca. 80%. It is worthy noted here that all samples prepared by physical mixing showed much higher activity than the bare TiO$_2$ and the bare CN. As for the reactions under visible light irradiation, the highest activity was obtained on the TiO$_2$(1)-CN PM that gave the salicylic acid degradation of 71.4%. While there was no clear relationship between the Ti/C ratio to the photocatalytic activity, all composites showed the percentage removals of 40–60%. Even though the activity of the composite was less enhanced compared to when it was prepared by impregnation or one pot oxidation method, the activity of TiO$_2$(1)-CN PM was much higher than the activity of bare TiO$_2$ or bare CN. This result again showed the synergic effect between TiO$_2$ and CN.

Among all composites prepared by three methods above, the TiO$_2$(5)-CN OPO and the TiO$_2$(10)-CN OPO showed the highest photocatalytic activity towards degradation of salicylic acid under UV and visible light, respectively. These results suggested that one pot oxidation method was the best approach to obtain TiO$_2$-CN composites with high activity. Under light irradiation with enough energy, the electrons in the valence bands of both TiO$_2$ and CN in the composite will be excited to the conduction bands. Since the conduction band of TiO$_2$ is higher than the conduction band of CN, the excited electrons will be transferred from the conduction band of TiO$_2$ to the conduction band of CN. Thus, the electron recombination rate of photoexcited TiO$_2$ will be reduced, giving the increased activity under UV light irradiation. The excited electrons would react with the dissolved oxygen to produce superoxide radical that could oxidize salicylic acid. In this study, the formation of hydroxyl and hydroperoxyl radicals could be excluded since water was not used as the solvent. Holes that were photogenerated in the valence band of both TiO$_2$ and CN would also react with the salicylic acid to finally produce water and carbon dioxide.

4. Conclusions
TiO$_2$-CN composites could be prepared by one pot oxidation, impregnation, and physical mixing. Among the three methods, the composites prepared by one pot oxidation method showed the highest photocatalytic activity for degradation of salicylic acid both under UV and visible light irradiation. The synergic effect between TiO$_2$ and CN in the composite was proposed to reduce the electron-hole recombination in the TiO$_2$, resulting in the better photocatalytic activity of the composite than the bare TiO$_2$ and the bare CN.

Acknowledgements
The academy of sciences for the developing world (TWAS) via COMSTECH-TWAS joint research grants programme for young scientists (RGA No: 10-231 RG/MSN/AS_C-UNESCO FR: 3240246318) and Directorate General of Strengthening Research and Development, Ministry of Research, Technology and Higher Education of the Republic of Indonesia via the Higher Education Excellent Applied Research Grant (PTUPT 2018) are greatly acknowledged.

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