Synthesis and characterization of nitrogen-doped TiO$_2$ and its photocatalytic activity enhancement under visible light

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Abstract

Nitrogen-doped TiO$_2$ nanopowders were synthesized by homogenization and conventional mechanically stirred technique in DI water media. Different amount of nitrogen was loaded in TiO$_2$ matrix. As-obtained intermediate products were annealed at 100°C for 30, 60 and 120 min. The structural properties of samples were characterized by X-ray diffraction. The absorption spectrum of N-doped TiO$_2$ photocatalyst was analyzed via UV-Vis spectrophotometry. When doping TiO$_2$ with nitrogen, its absorption spectrum is shifted to visible region resulting in the enhancement of photocatalyst properties in dye photodegradation. The photocatalytic activity of TiO$_2$ and N-doped TiO$_2$ was investigated by the degradation of Rhodamine B dye under visible light.

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Keywords: N-doped TiO$_2$; photocatalyst; photodegradation; visible light.

1. INTRODUCTION

Photocatalysts have been widely researched and obtained great attraction since the past decades. Titanium dioxide (TiO$_2$) is one of functional metal oxide semiconductor that performs high efficiency in photocatalytic activities because of non-toxicity, excellent energy conversion efficiency and long-term chemical stability [1]-[3]. Several studies have been reported on the usage of TiO$_2$ photocatalyst in various environmental applications such as photodegradation of organic and inorganic pollutants, decolorization of dyes, water purification and hydrogen production from water-splitting reaction [4]-[8].

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However, TiO₂ can be activated in UV illumination due to its wide band gap energy. Thus, only 3-5% of UV in solar spectrum is less absorbed by itself. This is the main drawback of TiO₂ photocatalyst that is hardly activated in visible light. High recombination rate of photoelectron-hole is also one of its hindrances that still retarded the photocatalytic mechanism. Many efforts have been made to conquer these problems by doping with non-metal in TiO₂ such as Carbon (C), Sulfur (S) and Nitrogen (N) [9]-[11]. Among the non-metal dopant, N is one of material that was acknowledged for enhancing the photoresponding range into visible light. Horst Kisch and co-workers reported that band gap energy of TiO₂ can be reduced from 3.18 to 2.20 eV by nitrogen incorporation [12]. Jing Li and co-workers proved that the significant visible light response and strong increase of photocurrent under UV and visible range were obtained by N-doped TiO₂ [13]. S. Bangkedphol and colleague reported on the improvement of photocatalytic degradation of tributyltin under natural light by using N-doped TiO₂ [14].

The main objective of this work is to investigate the effect of the different content of N doping in commercial TiO₂ powder and baking time on its structure and response in visible range. The efficiency of N-doped TiO₂ photocatalysts were proved by the photocatalytic degradation of Rhodamine B (RhB) under visible illumination.

2. EXPERIMENT

N-doped TiO₂ was prepared by mechanical mixing through homogenization and magnetic stirring. Commercially available TiO₂ (Aeroxide® TiO₂ P25, Nippon Aerosil Co. Ltd.) was used as precursor-TiO₂ nanopowders. Ammonium hydrogen carbonate (NH₄HCO₃) was chosen as nitrogen source for doping in TiO₂. NH₄HCO₃ was dispersed in 100 ml of deionized water and stirred for 30 min at room temperature. The ratio of doping N in 6.0 g of TiO₂ P25 is designated at 10, 30 and 50 %wt. The suspension was mixed via homogenizer at 6000 rpm for 1h followed by stirring at 120°C until the evaporation of DI water was obtained. After that the precursor was kept as 100°C for 24 h. Finally, the white powder of N-doped TiO₂ was obtained by baking at 100°C for 30, 60 and 120 min. These samples were assigned as NT_30m, NT_60m, and NT_120m. The structural properties of N-doped TiO₂ were characterized by X-ray diffraction (XRD, Panalytical x’Pert Pro MPD).

The photocatalyst of N-doped TiO₂ was carried out by dye photodegradation of Rhodamine B (RhB) under visible light via halogen lamp (450 W). 50 g of N-doped TiO₂ was dispersed in 3 mM RhB and stirred for 20 min in the dark to obtain absorption/desorption equilibrium between RhB and the catalyst surfaces. The solution was irradiated in visible light at room temperature until color of dye completely disappeared. RhB degradation was investigated by the decrease of its absorbance at maximum wavelength (λ_max) via Helios UV-Vis spectrometer. The kinetic rate was calculated following the expression [15] by

\[ \ln \left( \frac{C}{C_0} \right) = k t \]  

(1)

where \( k \) is the rate constant, \( C_0 \) and \( C \) are the concentration of RhB at initial and after illumination for time; \( t \).

3. RESULTS AND DISCUSSION

The XRD patterns of raw TiO₂ P25 and 30%wt. N-doped TiO₂ baked at 100 °C for different baking time are illustrated in Fig. 1. For TiO₂ P25, the anatase phase located at 2θ = 25.4°, 37.8°, 38.6°, 48.1° and 55.2° correspond to (101), (004), (112), (200) and (211) planes whereas the peak at 2θ = 27.5°, 36.2°, 39.3°, 41.3° and 54.4° relates to the rutile phase in (110), (101), (200), (111) and (211) planes, respectively. For N-doped TiO₂, the XRD patterns have identical peaks pattern to raw TiO₂ P25 patterns.
As baking time increases, its phase is still retained without significant change. This result implies that doping N in TiO$_2$ does not change the basis crystalline of TiO$_2$ but it may be intermingle on TiO$_2$ surface. The crystalline size of N-doped TiO$_2$ which was calculated using Scherrer equation is in the range of 13 to 15 nm [16]. The decrease of crystalline size of N-doped TiO$_2$ may be caused by the less movement of hydroxyl carbonate from precursor [17].

Absorption spectra of TiO$_2$ P25 and N-doped TiO$_2$ at 100 °C with different baking time are illustrated in Fig. 2. It can be seen that the enhancement in optical absorption was clearly seen in NT$_{60m}$ photocatalyst. This result suggests that NH$_4$HCO$_3$ can be used as proper nitrogen source for doping in TiO$_2$ powder. The spectrum patterns of NT$_{30m}$ and NT$_{120m}$ were similar to TiO$_2$ P25 because of low nitrogen content when compared to pure TiO$_2$ [18]. It can be deduced that shift of absorption in visible range could be remarkably influenced by the presence of N in the powder and baking time. The amount of nitrogen content is also crucial factor that can further affect the absorption attribute as seen in Fig. 3. The spectrum patterns of N-doped powders performed good absorption in UV region but visible region. For the sample with 10 %wt N doping, this small amount of N loading may produce insufficient nitrogen atoms for modification. On the other hand, the large doping nitrogen content (50%wt.) could not completely decompose precursor for combining in TiO$_2$ matrix. Therefore, it can be deduced that optimized conditions providing the best photoreponse performance in visible light from this experiment was obtained by 30 %wt. N-doped TiO$_2$ baked at 100°C for 60 min accompanying the excellent efficiency in photocatalytic degradation.

![XRD patterns](image1)

**Fig. 1.** XRD patterns of (a) raw TiO$_2$ P25 and 30 %wt of N-doped TiO$_2$ at 100°C with different baking time (b) 30, (c) 60 and (d) 120 min.

**Table 1.** Structural characteristics of TiO$_2$ P-25 and N-doped TiO$_2$ with different baking time.

<table>
<thead>
<tr>
<th>Sample</th>
<th>β</th>
<th>cos θ</th>
<th>Crystalline size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$ P-25</td>
<td>0.43</td>
<td>0.22</td>
<td>14.56</td>
</tr>
<tr>
<td>NT$_{30m}$</td>
<td>0.45</td>
<td>0.22</td>
<td>13.83</td>
</tr>
<tr>
<td>NT$_{60m}$</td>
<td>0.43</td>
<td>0.22</td>
<td>14.70</td>
</tr>
<tr>
<td>NT$_{120m}$</td>
<td>0.46</td>
<td>0.22</td>
<td>13.45</td>
</tr>
</tbody>
</table>
The photodegradation of RhB in aqueous solution under visible light for 1 hour was conducted in order to make the comparison of photocatalyst efficiency of TiO$_2$ itself and N-doped TiO$_2$ and the corresponding results are shown in Fig. 4(a) and 4(b). Both N-doped TiO$_2$ and TiO$_2$ P25 can effectively degrade and decolorize RhB. The absorption spectrum of RhB degraded by N-doped TiO$_2$ photocatalyst exhibits that the decreased absorbance was initially higher than TiO$_2$ P25. The decolorization of dye was completely reached as the irradiation time up to 30 min for N-doped TiO$_2$ and 40 min for TiO$_2$ P25. The loss in absorption is associated to the destruction of dye chromogen. A noticeable shift of absorption spectra to higher energy was obviously observed by N-doped TiO$_2$ photocatalyst. This phenomenon is related to the generation of N-de-ethylation that is the last product of RhB [19].
The change of RhB absorbance versus irradiation time of N-doped TiO$_2$ and TiO$_2$ P25 is shown in Fig. 5. The constant rate of RhB degradation with TiO$_2$ P25 is 0.051 min$^{-1}$ whereas N-doped TiO$_2$ photocatalyst shows the constant rate of the activity of about 0.105 min$^{-1}$. These results imply that nitrogen additive doped in TiO$_2$ can significantly improve the photocatalytic degradation comparing to pure TiO$_2$ due to nitrogen-induced band gap energy contraction leading to the enhancement of optical absorption of photocatalyst under visible illumination [20].

4. CONCLUSION

In summary, doping nitrogen in TiO$_2$ were successfully carried out by homogenization and magnetic stirring without any binders or high temperature heat treatment. XRD pattern suggests that TiO$_2$ P25 is not changed its structure by either N doping or varied baking time. The optimized condition for the best photoresponse of TiO$_2$ in visible light is obtained by doping TiO$_2$ with nitrogen in the ratio 30 %wt. and baked at 100°C for 60 min. The photocatalytic degradation of RhB solution by N-doped TiO$_2$
photocatalysts was experimentally investigated via its absorption spectra. TiO$_2$ itself shows less degradation rate than N-doped TiO$_2$ when the irradiation time is up to 60 min. These results imply that doping nitrogen in TiO$_2$ can improve the photocatalytic activity due to narrowed band gap energy that relates to the enhancement of photocatalytic degradation under visible light.

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References


