Titania with Alkaline Treated Graphitic Carbon Nitride (g-C$_3$N$_4$) to Improve Photocatalysis Properties

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Abstract. The graphitic carbon nitride (g-C$_3$N$_4$) was treated via alkaline hydrothermal treatment to change the porous structure of g-C$_3$N$_4$ to “tube-like” structure. The developed alkaline treated g-C$_3$N$_4$ (A-g-C$_3$N$_4$) was combined with P25 Degussa TiO$_2$ for the competent removal of methylene blue (MB). The morphological changes increased the crystallite size and pore size of g-C$_3$N$_4$, causing a decrease in the specific surface area of A-g-C$_3$N$_4$. The pure g-C$_3$N$_4$ demonstrated the best degradation efficiency among the all samples due to its high specific surface area, low band gap energy and small pore size. The combination of both A-g-C$_3$N$_4$ and g-C$_3$N$_4$ with TiO$_2$ did not exert significant effect on the degradation efficiency of MB owing to the low specific surface area, high band gap and large pore size. Thus concluding the degradation efficiency of organic dye is attributed predominantly to the factors of energy band gap, specific surface area and pore sizes.

1. Introduction

TiO$_2$ is commonly used as photocatalyst for reductive and oxidative reactions on its surface among the semiconductors. To boost the photocatalytic efficiency of TiO$_2$, the mass transfer limitation has to be minimized since photocatalytic reaction mainly occurs on the surface of TiO$_2$. The adsorption of organic pollutants on TiO$_2$ surface is restricted by its poor affinity towards the pollutants. Therefore, how to concentrate the target pollutants around the TiO$_2$ nanoparticles to enhance photocatalytic efficiency requires consideration. The TiO$_2$ nanoparticles may undergo aggregation due to the instability of the nanosized particle during the photocatalytic degradation process which may hamper the light incidence on the active centers and consequently reduce its catalytic activity [1,2]. TiO$_2$ has been highly employed for commercial purposes, due to its better photoactivity and stability under ultraviolet (UV) radiation i.e., $\lambda < 400$ nm. Though it has above mentioned advantages the major limitations are: a) It is active only under UV light and can only absorb about 5% of sunlight in the UV region [3] and b) high recombination rate of photoinduced charge carriers cause TiO$_2$ unable to apply efficiently [4]. Graphitic carbon nitride material (g-C$_3$N$_4$) has recently emerged as a novel photocatalyst attributed to its visible-light driven band gap (2.69 eV), high thermal and chemical stability, and facile synthesis method. However, the surface area of g-C$_3$N$_4$ is relatively small (14.3 m$^2$/g) [5]. It is considered that the small specific surface area of g-C$_3$N$_4$ could contribute to the slow photocatalytic reaction rate [6]. The specific surface area of g-C$_3$N$_4$ need to be increased to make g-C$_3$N$_4$ become a promising and versatile semiconductor for sunlight harvesting [7,8].
2. Preparation of g-C_{3}N_{4} and A-g-C_{3}N_{4}

20 g of urea (R & M Marketing Essex, U.K) was dried in an oven at 80 °C for 1 day and then put in a muffle for 3 h at 500 °C. The yellowish product was washed with nitric acid (0.1 M) several times and distilled water to remove any residual alkaline species. The g-C_{3}N_{4} and 90 cm^{3} of NaOH (0.10 mol dm^{3}) solutions were mixed in Teflon-lined autoclave and subjected to hydrothermal treatment at 150 °C for 18 h. The solid product was then dried at 80 °C for 24 h and the as-obtained sample was denoted as A-g-C_{3}N_{4}.

2.1. Synthesis of g-C_{3}N_{4}/A-g-C_{3}N_{4} hybridized TiO_{2}

0.15 g prepared g-C_{3}N_{4}/A-g-C_{3}N_{4} sheet was well dispersed in distilled water ultrasonically. 4.8 g of freshly prepared P25 Degussa TiO_{2} was then added into the solution and subjected to 70 °C for 1 h. The resulting suspension was then centrifuged and washed repeatedly with distilled water for few times and dried overnight at 60 °C. The sample obtained by synthesized was denoted as g-C_{3}N_{4}/TiO_{2} and A-g-C_{3}N_{4}/TiO_{2}, respectively.

2.2. Characterization

The powder X-ray diffraction (XRD, PANalytical-Empyrean) patterns were acquired with Cu Kα radiation at a scanning speed of 0.02s^{-1}. High resolution transmission electron microscope (HRTEM, JEM-2100F, Jeol) images were obtained at 200 kV. The EDX analysis of the A-g-C_{3}N_{4}/TiO_{2} was observed on a field emission scanning electron microscope (FESEM JEOL 6701-F). The Brunauer–Emmett–Teller specific surface area and pore volume of samples was determined at liquid nitrogen temperature (77 K) based on nitrogen adsorption-desorption isotherms with TriStar II 3020 (Micrometrics®, USA).

2.3. Photocatalytic degradation of organic pollutants

0.02 g of photocatalysts were immersed in a glass beaker containing 250 mL aqueous solutions for MB (5 ppm). Prior to photodegradation and to establish an adsorption-desorption equilibrium, the solutions were magnetically stirred in a dark for 1 h. A 500 W tungsten-halogen lamp was used as visible light source with filter glass to filter UV light (λ < 420nm). The dye samples were collected at regular interval, then analyzed for residual MB concentration with visible spectrophotometer (DR 6000 ™ UV-Vis spectrophotometer (Hach)) to measure the intensity of light passing through MB (λ_{max}= 664 nm).

3. HRTEM and EDX

In figure 1, it is clearly seen that TiO_{2} nanoparticles were well distributed on the surface of g-C_{3}N_{4}. The surface of A-g-C_{3}N_{4} was aggregated with nanoclusters of TiO_{2} due to the nanometer effect [9]. The EDX spectrum for elemental compositions of the g-C_{3}N_{4}/TiO_{2} is illustrated in figure 1b, confirming the prepared sample was a constituent of C, Ti, O and N.

![Figure 1](attachment:figure1.png)

**Figure 1.** (a) HRTEM and (b) EDX spectrum for elemental compositions of the A-g-C_{3}N_{4}/TiO_{2}
4. Crystallite size and BET surface

The average crystallite sizes of TiO$_2$ anatase and g-C$_3$N$_4$ were calculated using Scherrer equation:

$$D = \frac{K\lambda}{\beta\cos\theta}$$  \hspace{1cm} (1)

where K is the shape factor taken as 0.89 for calculations, $\lambda$ is the wavelength of X-ray (0.154 nm), $\beta$ is the full width half maximum (FWHM) for the 2θ peak, and $\theta$ is the diffraction angle. The crystallite size of TiO$_2$ anatase and g-C$_3$N$_4$ is listed in table 1. After incorporating both g-C$_3$N$_4$ and A-g-C$_3$N$_4$ in binary composites, it is observed that the crystallite size of TiO$_2$ decreased while the crystallite size of g-C$_3$N$_4$ increased. The size of TiO$_2$ was inhibited by the g-C$_3$N$_4$ nanosheet since TiO$_2$ nucleated and grew on the g-C$_3$N$_4$ surface [8]. The alkaline hydrothermal treatment of g-C$_3$N$_4$ significantly increased the crystallite size of A-g-C$_3$N$_4$ to 43.17 nm and thus, a decreasing specific surface area could occur in this sample.

Table 1: Average crystallite size for P25, A-g-C$_3$N$_4$/TiO$_2$, g-C$_3$N$_4$, A-g-C$_3$N$_4$ and g-C$_3$N$_4$/TiO$_2$

| Sample              | Crystallite size(nm)$^a$ | Crystallite size(nm)$^b$ |
|---------------------|-------------------------|-------------------------|
| P25                 | 32.35                   | -                       |
| A-g-C$_3$N$_4$/TiO$_2$ | 24.7                   | 43.17                   |
| g-C$_3$N$_4$        | -                       | 5.27                    |
| A-g-C$_3$N$_4$      | -                       | 18.68                   |
| g-C$_3$N$_4$/TiO$_2$ | 25.26                   | 35.04                   |

$^a$: TiO$_2$  
$^b$: g-C$_3$N$_4$

According to the International Union of Pure and Applied Chemistry (IUPAC) classification, all of the samples in figure 2 demonstrated adsorption-desorption isotherms of type III which indicating the existence of mesopores. Characteristic of type III was the heat of adsorption less than the adsorbate heat of liquefication, adsorption and the interaction with the adsorbent surface is lower than the adsorbate interaction with an adsorbed layer [10]. The shape of the hysteresis loop is Type H2 when the low P/P$_0$ range from 0.5 to 0.8, indicating the existence of ink-bottle pores with broad bodies and narrow necks [5].

![Figure 2](image)

Figure 2. (a) Adsorption and (b) desorption isotherms of P25, A-g-C$_3$N$_4$/TiO$_2$, g-C$_3$N$_4$, A-g-C$_3$N$_4$ and g-C$_3$N$_4$/TiO$_2$ measured at 77 K

5. Photocatalytic Experiment

Figure 3 depicts visible-light-induced photocatalytic activity with the aid of prepared photocatalysts. The photocatalytic performance followed an order of g-C$_3$N$_4$ (62.67%) > P25 (49.47%) > A-g-C$_3$N$_4$ (47.33%) > A-g-C$_3$N$_4$/TiO$_2$ (46.87%) > g-C$_3$N$_4$/TiO$_2$ (45.79%). The g-C$_3$N$_4$ showed higher photodegradation efficiency which was 62.67% compared to that of other samples, while g-C$_3$N$_4$/TiO$_2$ exhibited the lowest photodegradation efficiency which was 45.79% (table 2). In addition, the large specific surface area of g-C$_3$N$_4$ (71.8 m$^2$g$^{-1}$) could provide more active adsorption sites for the reactant, and thus leading to superior degradation efficiency. The photodegradation efficiency of g-C$_3$N$_4$/TiO$_2$
was slightly lower than that of A-g-C$_3$N$_4$/TiO$_2$ and A-g-C$_3$N$_4$ due to its specific area was smaller than A-g-C$_3$N$_4$/TiO$_2$ and its band gap was higher than A-g-C$_3$N$_4$. Due to the large band gap and fast recombination rate of photo-generated electron-hole pairs, the other sample showed lower photodegradation efficiency than g-C$_3$N$_4$ [11]. The narrowest band gap in pure A-g-C$_3$N$_4$ did not lead to the enhancement of photocatalytic performance due to its small specific surface area, which was 6.3 m$^2$ g$^{-1}$. The photocatalytic activity performance was related to the specific area of the photocatalyst, the higher the specific surface area of the photocatalyst, the higher the photocatalytic activity [12]. The samples of A-g-C$_3$N$_4$/TiO$_2$, A-g-C$_3$N$_4$ and g-C$_3$N$_4$/TiO$_2$ showed an outstanding visible light harvesting properties, but their large pore sizes ranging from 230 to 270 nm and low specific surface area large contributed to the poorer photocatalytic activity compared to that of P25 TiO$_2$. The observed degradation data were fitted to the simple kinetic model and tabulated in Table 2. The first-order reaction kinetics is expressed by equation:

$$\ln\left(\frac{C}{C_0}\right) = -kt$$  \hspace{1cm} (2)

where $k$ is the first-order reaction constant, $C_0$ and $C$ are the MB concentrations in solution at times 0 and $t$, respectively.

![Figure 3. Photocatalytic degradation of MB as a function of reaction time](image)

**Table 2:** Degradation rate of MB by P25, A-g-C$_3$N$_4$/TiO$_2$, g-C$_3$N$_4$, A-g-C$_3$N$_4$ and g-C$_3$N$_4$/TiO$_2$

| Sample                | Degradation Rate$^a$ (%) | $K^b$ (min$^{-1}$) |
|-----------------------|--------------------------|--------------------|
| Blank(control)        | 32.78                    | 0.001              |
| P25                   | 49.47                    | 0.002              |
| A-g-C$_3$N$_4$/TiO$_2$| 46.87                    | 0.002              |
| g-C$_3$N$_4$          | 62.67                    | 0.003              |
| A-g-C$_3$N$_4$        | 47.33                    | 0.002              |
| g-C$_3$N$_4$/TiO$_2$  | 45.79                    | 0.002              |

$^a$ after reaction for 6 h  
$^b$ apparent rate constant deduced from linear fitting of ln($C/C_0$) versus reaction time

### 6. Conclusion

In summary, the binary composites namely A-g-C$_3$N$_4$/TiO$_2$ and g-C$_3$N$_4$/TiO$_2$ was successfully synthesized via a simple and facile method. The prepared binary composites displayed non appreciable changes in the photocatalytic performance compared to that of pure g-C$_3$N$_4$. This is mainly due to the decreasing specific surface area in binary nanocomposites when the titania agglomerated on the surface of both g-C$_3$N$_4$ and A-g-C$_3$N$_4$. The overetching effect caused by the non-optimized conditions of alkaline hydrothermal treatment also contributed to a trivial photocatalytic activity of A-g-C$_3$N$_4$. 
Hence, the specific surface area and crystallite size played a crucial role in boosting the photocatalytic performance of photocatalysts.

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