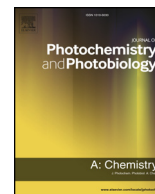




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# Molten salt assisted in-situ synthesis of TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> composites with enhanced visible-light-driven photocatalytic activity and adsorption ability

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## ABSTRACT

In this work, zero-dimensional (0D)/ two-dimensional (2D) TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> composite photocatalysts with homogeneous well-developed heterostructures were successfully prepared from LiCl-KCl flux using a facile molten salt assisted in-situ route. The phase composition, morphology, surface area, chemical structure, thermal stability as well as optical property of the heterostructured composites were systematically characterized. Benefiting from the exfoliation effect of molten salt flux, the flux-grown g-C<sub>3</sub>N<sub>4</sub> products exhibit a rough surface with porous structures and many co-existed secondary products including nanosheets, nanorods and nanotubes, which also lead to an obvious increase in the surface area of the flux-grown g-C<sub>3</sub>N<sub>4</sub> and composites. The photocatalytic performance of the TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> heterostructure composites was evaluated by photodegradation of methyl orange (MO) and rhodamine B (RhB) under the visible light irradiation ( $\lambda > 420$  nm), and proved to be greatly improved compared to individual TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub>. Moreover, the enhanced photocatalytic activity of TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> composites can be attributed to the higher surface area and the synergistic effects between TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> including the increased light harvesting ability and more efficient separation of the photogenerated charge carriers, which originates from the construction of TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> heterostructures at the interface between the two components. Furthermore, a possible mechanism responsible for the enhanced photocatalytic performance was also proposed. Additionally, the TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> composites showed a superior adsorption ability for the removal of cationic dye methylene blue (MB) from aqueous solutions, due to their high surface area and strong electrostatic interactions between catalysts and dye molecules.

## 1. Introduction

Nowadays, the treatment of dye wastewater has become an important aspect of environmental remediation because many synthetic organic dyes produce health hazards toward humans and aquatic ecosystems due to their toxicity, carcinogenicity and low degradability [1,2]. Thus, it is imperative to remove various hazardous dye pollutants from the industrial effluents before discharging into receiving water bodies. Currently, semiconductor photocatalysis, as an alternative and environmentally-friendly technology, has received more and more research interests due to its potential applications in solving the worldwide problems of environmental pollution and energy crisis [3–5]. Unfortunately, the existing photocatalysts usually suffer from the shortcomings including the wide energy band gap and low solar-energy utilization efficiency, etc., which hinder their large-scale applications in

a practical way. Therefore, it is still a great challenge to seek and design novel visible-light-active photocatalytic materials with high efficiency for practical environmental applications.

Recent years, a metal-free polymeric semiconductor, graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) with appropriate band gap ( $\sim 2.7$  eV) and good physicochemical stability, has received extensive attention in the field of photocatalysis once reported by Xinchun Wang et al. in 2009 [6]. Nevertheless, a small specific surface area ( $\sim 10$  m<sup>2</sup> g<sup>-1</sup>), low visible light utilization efficiency and the high recombination rate of photo-generated electron-hole pairs in pure g-C<sub>3</sub>N<sub>4</sub> greatly limit its photocatalytic properties [7]. Consequently, significant efforts have been devoted to improving the visible-light-driven photocatalytic performance through ion doping [8,9], noble metal modification [10,11], sensitizing with organic dyes [12,13], coupling with other semiconductor materials [14–17], and so on. Among these methods, the

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construction of g-C<sub>3</sub>N<sub>4</sub>-based semiconductor heterostructures has emerged one of the most effective strategies to improve the photocatalytic performance by widening the range of light adsorption and promoting the separation of photogenerated charge carriers at the interface of semiconductor-semiconductor heterostructures, including g-C<sub>3</sub>N<sub>4</sub>/ZnO [18], g-C<sub>3</sub>N<sub>4</sub>/TaON [19], g-C<sub>3</sub>N<sub>4</sub>/ZnWO<sub>4</sub> [20], g-C<sub>3</sub>N<sub>4</sub>/CoTiO<sub>3</sub> [21], g-C<sub>3</sub>N<sub>4</sub>/MoS<sub>2</sub> [22], g-C<sub>3</sub>N<sub>4</sub>/Ag<sub>3</sub>VO<sub>4</sub> [23], and other composite systems [7,24,25]. Based on the well-matched energy band structures between g-C<sub>3</sub>N<sub>4</sub> and TiO<sub>2</sub>, up to now, numerous studies have revealed the successful construction of organic-inorganic TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> composite heterostructures with enhanced photocatalytic activity for dye degradation [16,26], water splitting [27,28], CO<sub>2</sub> reduction [29,30], and bacterial inactivation [31], and so on. However, to the best of our knowledge, there is no report concerning molten salt assisted synthesis of TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> composite photocatalysts.

In our work, OD Degussa P25 TiO<sub>2</sub> nanoparticles (NPs) with the superior UV-light photocatalytic activity have been successfully coupled with the 2D g-C<sub>3</sub>N<sub>4</sub> sheets through a facile molten salt assisted in-situ growth route using the binary KCl-LiCl eutectic chloride salts with low melting point (353 °C) as a reaction medium and intercalated guest. In this way, TiO<sub>2</sub> NPs can be well dispersed and deposited on the surface of 2D g-C<sub>3</sub>N<sub>4</sub> sheets, resulting in the successful formation of well-developed TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> heterostructures, which can efficiently facilitate the transfer and separation of photogenerated charge carriers across the intimate interface between the both semiconductors. Moreover, the surface area of these flux-grown g-C<sub>3</sub>N<sub>4</sub>-based composites obviously increased. The as-prepared heterostructured composites also showed much higher photocatalytic activity for the degradation of anionic dye MO and cationic dye RhB in aqueous solution under visible light irradiation ( $\lambda > 420$  nm) compared to individual g-C<sub>3</sub>N<sub>4</sub> and TiO<sub>2</sub>. Meanwhile, a possible mechanism responsible for the enhanced photocatalytic performance was proposed and discussed. Furthermore, the composite photocatalysts exhibited excellent selective adsorption toward cationic dye MB in aqueous solution. Therefore, such a novel TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> composite can be qualified as a promising candidate for photocatalyst and adsorbent to efficiently remove dye pollutants from wastewater, which is significant for environmental remediation and solar energy utilization.

## 2. Experimental

### 2.1. Materials

All reagents used in this work were of analytical grade and without further purification. Melamine (C<sub>3</sub>H<sub>3</sub>N<sub>6</sub>), lithium chloride (LiCl), potassium chloride (KCl), methyl orange (C<sub>14</sub>H<sub>14</sub>N<sub>3</sub>SO<sub>3</sub>Na, MO), methylene blue (C<sub>16</sub>H<sub>18</sub>ClN<sub>3</sub>S, MB) and rhodamine B (C<sub>28</sub>H<sub>31</sub>ClN<sub>2</sub>O<sub>3</sub>, RhB) were provided by Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). P25 (TiO<sub>2</sub>, Degussa) was supplied by Evonik Degussa Corporation (Germany). Deionized water was utilized in whole process of experiments.

### 2.2. Preparation of TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> composites

TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> composite photocatalysts were prepared by a facile molten salt in situ method, as shown in Fig. 1. In a typical procedure, the mixture of P25 TiO<sub>2</sub> and melamine powders with the given mass ratio of TiO<sub>2</sub>: melamine = 1:4, 1:8, 1:15 and 1:30 was ground homogeneously in the presence of excessive KCl-LiCl eutectic salts (59.2 mol % LiCl + 40.8 mol% KCl) in an agate mortar for 30 min. The obtained powders were transferred into a 80 cm<sup>3</sup> corundum crucible sealed loosely with a lid and placed in an electric furnace. Then, the crucible was subjected to a heat treatment at 540 °C in air holding for 4 h and subsequently cooled down to room temperature naturally in the furnace. In order to remove the residual chloride salts, the products were repeatedly washed with warm deionized water and separated by a

paper filter (Wathman No. 42). Finally, the obtained powders were dried at 80 °C overnight. According to this method, a series of the TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> composite photocatalysts were obtained and denoted as TO/CN-4, TO/CN-8, TO/CN-15, and TO/CN-30, respectively.

For comparison, molten salt synthesis of g-C<sub>3</sub>N<sub>4</sub> and P25 nanomaterials (named as CN-MS and P25-MS, respectively) in absence of TiO<sub>2</sub> or melamine were also carried out under the same experiment condition. Moreover, pure g-C<sub>3</sub>N<sub>4</sub> was prepared by direct thermal condensation of melamine at 540 °C for 4 h, as described in our previous report [21].

### 2.3. Characterization

The crystalline phase composition and crystallinity of the as-prepared samples were measured by a X-ray diffraction (XRD) diffractometer (Rigaku D/MAX-2550 VB/PC) with Cu-K $\alpha$  radiation at a scan rate of 0.02°/s in the range of  $2\theta = 10$ –80°. The chemical composition of the composite sample was determined by an energy dispersive X-ray spectroscope (EDS, EDAX, Genesis XM2). The Hitachi S-3400N scanning electron microscopy (SEM) and JEOL JEM-2100 transmission electron microscopy (TEM) were employed to characterize the surface morphology and structure of the samples, and simultaneously high resolution transmission electron microscopy (HRTEM) images were also obtained on the JEM-2100 instrument at an accelerating voltage of 200 kV. Nitrogen adsorption-desorption measurements used to determine the Brunauer-Emmett-Teller (BET) surface area and pore size distribution of the samples were obtained on a Micromeritics ASAP 2010 instrument. Thermogravimetric (TG) analysis was performed on PerkinElmer (Pyris Diamond) at a heating rate of 10 °C/min in air atmosphere. The intermediates generated at given time intervals by the photodegradation of MO were measured by using an ESI-TOF mass spectrometer (Xevo G2 TOF, Waters). Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 6700 spectrometer using KBr pellets for the samples. UV-vis diffuse reflectance spectra (DRS) were carried out on a Perkin-Elmer Lambda 950 UV-vis-NIR spectrophotometer equipped with an integrating sphere attachment. Photoluminescence (PL) emission spectra were recorded on a Perkin-Elmer LS-55 fluorescence spectrofluorometer with an excitation wavelength of 325 nm. Zeta potentials of the samples dispersing in water were analyzed by a Malvern Zeta Analyzer (Nano-ZS, Malvern Instrument, UK).

### 2.4. Photocatalytic evaluation

The photocatalytic activity of the as-prepared samples was evaluated by photodegradation of organic dye pollutants in aqueous solutions under visible light irradiation ( $\lambda > 420$  nm). A 300 W Xe lamp (PLS-SXE300, Beijing Perfect Light Co., Ltd.) equipped with a UV cutoff filter was served as the visible light source. Anionic MO and cationic RhB dyes were selected as the degradation objects. In a typical run, 60 mg catalyst samples were evenly dispersed in 60 ml aqueous dye solutions with an initial concentration of 10 mg L<sup>-1</sup> in a self-designed quartz reactor and then stirring the aqueous dye solutions in the dark for 60 min to achieve an adsorption-desorption equilibrium between the photocatalysts and the substrates. Subsequently, the light source was switched on, and the reactor was cooled by circulating water throughout the experiment. Then, the suspensions were sampled at the given irradiation time intervals and centrifuged to remove the photocatalysts at 10,000 rpm for 5 min. The decay of absorbance of the collected dye solutions (about 4 mL) was monitored on the Lambda 950 spectrophotometer to calculate the dye removal efficiency. The concentrations of the irradiated dye solutions were determined by using a calibration curve (concentration vs. absorbance) plotted by the known concentrations of dye solutions.

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