



# Construction of amorphous Ta<sub>2</sub>O<sub>5</sub>/g-C<sub>3</sub>N<sub>4</sub> nanosheet hybrids with superior visible-light photoactivities for organic dye degradation and mechanism insight



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## ABSTRACT

In this paper, amorphous Ta<sub>2</sub>O<sub>5</sub>/g-C<sub>3</sub>N<sub>4</sub> nanosheet (ATCN) hybrid was firstly constructed by a facile ultrasonic dispersion process. In this way, amorphous Ta<sub>2</sub>O<sub>5</sub> nanoparticles anchored evenly onto the surface of g-C<sub>3</sub>N<sub>4</sub> nanosheets, forming the intimate interfacial contacts. The as-prepared ATCN composites exhibited significantly enhanced photocatalytic activities for the degradation of RhB compared to pure g-C<sub>3</sub>N<sub>4</sub> and amorphous Ta<sub>2</sub>O<sub>5</sub> nanoparticles under visible light illumination ( $\lambda > 420$  nm). The optimal ATCN-3 photocatalyst possessed the highest visible-light photocatalytic activity (99.14%) and the degradation rate constant was 2.0055 h<sup>-1</sup>, which was almost 6.2 and 14.9 times as high as those of individual g-C<sub>3</sub>N<sub>4</sub> and amorphous Ta<sub>2</sub>O<sub>5</sub>, respectively. Particularly, ATCN sample had good reusability and stability even after four cycles. Interestingly, amorphous Ta<sub>2</sub>O<sub>5</sub>/g-C<sub>3</sub>N<sub>4</sub> nanosheet hybrid showed higher photocatalytic activity than crystalline Ta<sub>2</sub>O<sub>5</sub>/g-C<sub>3</sub>N<sub>4</sub>. The enhanced photocatalytic performance was assigned to the synergistic effects including high surface area, enhanced visible light harvesting, efficiently interfacial charge transfer and reduced charge recombination. The plausible mechanism for improved photocatalytic properties was elucidated.

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## 1. Introduction

In recent years, semiconductor photocatalysis technology offering a "green" method has been intensely researched in the environmental pollution control and renewable utilization of solar energy [1–5]. Various semiconductor photocatalysts such as TiO<sub>2</sub> [3], ZnO [4], Ta<sub>2</sub>O<sub>5</sub> [5], CdS [6], and g-C<sub>3</sub>N<sub>4</sub> [7] have been developed for the degradation of organic pollutants under ultraviolet light (UV) or visible light irradiation. Among these photocatalysts, Tantalum pentoxide (Ta<sub>2</sub>O<sub>5</sub>), as a promising and efficient photocatalyst, has been found to be almost comparable to the landmark photocatalyst of TiO<sub>2</sub> owing to its unique characteristics including good chemical and thermal stability, optical properties and large band gap. Ta<sub>2</sub>O<sub>5</sub> has been attracted a great deal of attentions in numerous areas such as hydrogen production, photosensitive solar cells, nonlinear optical applications and waste water recovery [8–11]. Unfortunately, the photocatalytic performance of Ta<sub>2</sub>O<sub>5</sub> is substantially restricted due to the high recombination probability of photoinduced electron-hole pairs and its wide band gaps (3.8 eV), only active in the UV region of the solar spectrum [5]. To address these

inherent drawbacks, many significant efforts have been focused on improving the photocatalytic activity of Ta<sub>2</sub>O<sub>5</sub>. The most common and effective method is incorporating Ta<sub>2</sub>O<sub>5</sub> with other semiconductors to form well combinative photocatalysts, which can efficiently retard the rapid photogenerated electron-hole recombination of single-component photocatalyst. Up to date, a variety of composite photocatalytic systems based on Ta<sub>2</sub>O<sub>5</sub>, such as Bi<sub>2</sub>O<sub>3</sub>/Ta<sub>2</sub>O<sub>5</sub> [11], nanocarbon/Ta<sub>2</sub>O<sub>5</sub> [5], NiO<sub>x</sub>/Ta<sub>2</sub>O<sub>5</sub> [12] and CdS/Ta<sub>2</sub>O<sub>5</sub> [13], have been investigated. Indeed, the considerable improvements in the photocatalytic performance of composites are obtained compared with their individual constituents. Nevertheless, only few studies have so far investigated the enhancements of the visible-light photocatalytic of Ta<sub>2</sub>O<sub>5</sub> hybrids [13,14]. Thus, the design and synthesis of hybridizing or modifying Ta<sub>2</sub>O<sub>5</sub> composite photocatalysts with highly efficient visible-light photocatalytic activity via a simple route under a mild condition are still very necessary.

Recently, a polymeric mental-free photocatalyst graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) has attracted considerable attention for the potential applications in photocatalysis owing to its good chemical stability, appropriate electronic structure and inexpensive preparation [7,15]. In addition, the  $\pi$ -conjugated structure of g-C<sub>3</sub>N<sub>4</sub> facilitates charge transfer, and the narrow band gap of 2.7 eV makes it

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respond to visible light with the wavelength shorter than 460 nm [7,15,16]. Nevertheless, the photocatalytic activity of individual  $g\text{-C}_3\text{N}_4$  is limited, in which the photoaction suffers from low conversion efficiency due to the fast recombination of photogenerated  $h^+e^-$  pairs [15,16]. Fortunately,  $g\text{-C}_3\text{N}_4$  hybridized with others semiconductors such as  $\text{TiO}_2$  [16],  $\text{MoS}_2$  [17],  $\text{In}_2\text{S}_3$  [18],  $\text{Zn}_2\text{SnO}_4$  [19] and  $\text{Ag}_2\text{CO}_3$  [20], is an effectively method to reduce the charges recombination rate for enhancing photocatalytic performance. These hybrids have exhibited enhanced performance owing to their unique properties and potential applications that cannot be achieved solely by single-component catalyst.

Inspired from the aforementioned superiorities of  $\text{Ta}_2\text{O}_5$  and  $g\text{-C}_3\text{N}_4$ , our study initially intends to the development of coupling  $\text{Ta}_2\text{O}_5$  with  $g\text{-C}_3\text{N}_4$  as a high-performance visible-light photocatalyst. Concretely, the band gap of  $g\text{-C}_3\text{N}_4$  ( $E_{\text{CB}} = -1.12$  eV,  $E_{\text{VB}} = 1.58$  eV) [21] makes it a good candidate for well matching with that of  $\text{Ta}_2\text{O}_5$  ( $E_{\text{CB}} = -0.17$  eV,  $E_{\text{VB}} = 3.63$  eV) [11]. The well-aligned straddling band structures in hybrids can restrain the photoinduced charge recombination and enhance the transfer of electron-hole pairs, which improves photocatalytic activity of photodegrading organic pollutants. Moreover, in the view of the superior photocatalytic performance of amorphous  $\text{Ta}_2\text{O}_5$  to that of crystalline  $\text{Ta}_2\text{O}_5$  [13,14], if amorphous  $\text{Ta}_2\text{O}_5$  sol with good dispersion is used to modify  $g\text{-C}_3\text{N}_4$  nanosheet to form amorphous  $\text{Ta}_2\text{O}_5/g\text{-C}_3\text{N}_4$  nanosheet composites, amorphous  $\text{Ta}_2\text{O}_5$  may act as a recipient of the photoexcited electrons from  $g\text{-C}_3\text{N}_4$  to greatly improve visible-light photocatalytic performance of hybrid photocatalyst. However, amorphous  $\text{Ta}_2\text{O}_5$  sol integrated with  $g\text{-C}_3\text{N}_4$  for the application in environmental purification has been scarcely reported. In the present research, the novel inorganic-organic amorphous  $\text{Ta}_2\text{O}_5/g\text{-C}_3\text{N}_4$  nanosheet composites with different proportions of amorphous  $\text{Ta}_2\text{O}_5$  sols to  $g\text{-C}_3\text{N}_4$  nanosheet were firstly prepared by a facile ultrasonic dispersion process. The morphologies, structures and properties of as-prepared samples were characterized in detail. The optimization of experimental conditions over amorphous  $\text{Ta}_2\text{O}_5$  modifying  $g\text{-C}_3\text{N}_4$  nanosheet was also investigated. And the feasible mechanism of amorphous  $\text{Ta}_2\text{O}_5/g\text{-C}_3\text{N}_4$  nanosheet hybrid photocatalysts in reaction system was proposed according to the energy band position and the active species trapping, photoluminescence and photocurrent experiments.

## 2. Experimental

### 2.1. Materials

Tantalum (V) chloride ( $\text{TaCl}_5$ , 99%) was purchased from Sino-pharm Chemical Reagent Co., Ltd. Melamine (99%), triethanolamine (TEOA), 1, 4-benzoquinone (BQ), isopropanol (IPA), and Rhodamine B (RhB) ( $\text{C}_{28}\text{H}_{31}\text{ClN}_2\text{O}_3$ ,  $\geq 95\%$ ) and ethanol were obtained from Sahn chemical technology (Shanghai) Co., Ltd. All chemicals were of analytical grade and used without any further purification. Deionized water was used throughout this research.

### 2.2. Fabrication of amorphous $g\text{-C}_3\text{N}_4/\text{Ta}_2\text{O}_5$ nanosheet hybrid photocatalysts

The graphitic carbon nitride ( $g\text{-C}_3\text{N}_4$ ) powder was synthesized by a traditional pyrolysis of melamine [22]. Typically, 5 g of melamine was put into a semi-closed quartz boats, and further heat-treated to 550 °C for 4 h in a muffle furnace using a heating rate of 2.3 °C  $\text{min}^{-1}$ . When the muffle furnace was cooled to the room temperature after the reaction, the as-prepared yellow solid product was collected and ground into fine powder for further use.

Amorphous  $\text{Ta}_2\text{O}_5$  sol was prepared by a hydrothermal method. Briefly, a certain amount of  $\text{TaCl}_5$  was dissolved in 15 mL ethanol,

and then transferred into a 30 mL Teflon-lined autoclave. The autoclave was sealed in a stainless steel tank and calcined at 200 °C for 4 h to achieve amorphous  $\text{Ta}_2\text{O}_5$  sol. The synthesized  $\text{Ta}_2\text{O}_5$  sol was then dispersed into ethanol to get 80 mL sol solution, which was sonicated for 30 min to get light-blue transparent homogeneous  $\text{Ta}_2\text{O}_5$  sol solution.

The amorphous  $\text{Ta}_2\text{O}_5/g\text{-C}_3\text{N}_4$  nanosheet composites (ATCN) were synthesized via a facile ultrasonic dispersion method and illustrated in Scheme 1. In detail, 0.1410 g  $g\text{-C}_3\text{N}_4$  powder was added into 150 mL ethanol and ultrasonically stirred for 1 h to completely disperse pure  $g\text{-C}_3\text{N}_4$ . Subsequently, different volumes of  $\text{Ta}_2\text{O}_5$  sol solution were dropwise added into  $g\text{-C}_3\text{N}_4$  ethanol solution under continuous ultrasonic processing and then sealed and stirred for 24 h. After the suspension was evaporated, the residue was dried overnight under vacuum at 50 °C before further characterizations. The samples were labeled as ATCN-1, ATCN-2, ATCN-3 and ATCN-4 according to  $\text{Ta}_2\text{O}_5$  sol solution volume of 40, 20, 10, 5 mL respectively. The thermogravimetric analysis (TG) was used to analyze the weight contents of  $\text{Ta}_2\text{O}_5$  in composites. As shown in Fig. S1, the weight content of  $\text{Ta}_2\text{O}_5$  in ATCN-1 is about 41.4%. Similarly, the weight content of  $\text{Ta}_2\text{O}_5$  in ATCN-2, ATCN-3 and ATCN-4 can be estimated as 26.1%, 15.0% and 8.1%, respectively. As comparison, crystalline  $\text{Ta}_2\text{O}_5/g\text{-C}_3\text{N}_4$  nanosheet composite (CTCN-3) with the weight amount of 15.0%  $\text{Ta}_2\text{O}_5$  was also prepared. Firstly, the amorphous  $\text{Ta}_2\text{O}_5$  sol was dried at 80 °C and ground to fine powder. Then, a certain amount amorphous  $\text{Ta}_2\text{O}_5$  powder (AT) was crystallized by a calcination at 650 °C to form crystalline  $\text{Ta}_2\text{O}_5$  (CT). After that, a measured amount of crystalline  $\text{Ta}_2\text{O}_5$  was added to 10 mL ethanol and sonicated for 30 min. The other procedures for preparing CTCN-3 were similar to that of sample ATCN-3.

### 2.3. Characterization

X-ray powder diffraction (XRD) analysis were performed on a D/MAX-2500 diffractometer using  $\text{Cu K}\alpha$  radiation over the range of  $2\theta = 5\text{--}80^\circ$  at the scan rate of  $5^\circ \text{min}^{-1}$  to examine the phase compositions and crystal structures of all photocatalysts. Fourier transform infrared spectroscopy (FTIR) was recorded in the range of  $400\text{--}4000 \text{ cm}^{-1}$  on a Nicolet-560 FT-IR Spectrometric Analyzer using KBr pellet at room temperature. Chemical compositions of hybrid photocatalysts were examined by the X-ray photoelectron spectroscopy (XPS) with a Thermo ESCALAB 250X (America) electron spectrometer using 150 W Al  $\text{K}\alpha$  X-ray sources. The surface morphologies of samples were characterized by transmission electron microscopy (TEM: JEM-2010, Japan) and scanning electronic microscopy (SEM) on an S-4800 field emission SEM (SEM, Hitachi, Japan) equipped with an energy-dispersive X-ray spectroscopy (EDS) operated at an acceleration voltage of 10 kV. The Brunauer-Emmett-Teller (BET) specific surface areas ( $S_{\text{BET}}$ ) and pore size distribution of the samples were measured by A ASAP2000 surface area and pore size analyzer (Micromeritics, USA). The thermogravimetry and differential thermal analysis were carried out using a Shimadzu TGA-60H thermal analyzer. UV-vis diffuse reflection spectroscopy (DRS) was conducted on a UV-2450 spectrophotometer (Shimadzu Corporation, Japan), using  $\text{BaSO}_4$  as the reference. Photoluminescence (PL) spectra were measured on a Perkin-Elmer LS 55 at room temperature. The excitation wavelength was 350 nm with the widths of excitation and emission slit both 5 nm. Photocurrent was measured on electrochemical workstation (CHI 660B Chenhua Instrument Company).

### 2.4. Photocatalytic activity tests and determination of reactive species

The photocatalytic activities of as-prepared photocatalysts were evaluated by the photocatalytic degradation of RhB under visible

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