



# Preparation, characterization, and photocatalytic activity of CdV<sub>2</sub>O<sub>6</sub> nanorods decorated g-C<sub>3</sub>N<sub>4</sub> composite



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## ABSTRACT

Novel CdV<sub>2</sub>O<sub>6</sub>/g-C<sub>3</sub>N<sub>4</sub> hybrid system was synthesized by a facile mixing-calcination method. The photocatalytic test indicated that the decoration of CdV<sub>2</sub>O<sub>6</sub> nanorods on g-C<sub>3</sub>N<sub>4</sub> can significantly promote the photocatalytic activity in RhB degradation under visible light. The optimal CdV<sub>2</sub>O<sub>6</sub>/g-C<sub>3</sub>N<sub>4</sub> sample exhibited a degradation rate of 0.041 min<sup>-1</sup>, which is 4.5 times higher than that of pure g-C<sub>3</sub>N<sub>4</sub>. Various techniques including N<sub>2</sub> adsorption, X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), UV-vis diffuse reflectance spectroscopy (DRS), and photoluminescence (PL) spectroscopy were applied to investigate the origin of the enhanced photoactivity of CdV<sub>2</sub>O<sub>6</sub>/g-C<sub>3</sub>N<sub>4</sub>. The results indicated that the enhanced activities were mainly attributed to the interfacial transfer of photogenerated electrons and holes between CdV<sub>2</sub>O<sub>6</sub> and g-C<sub>3</sub>N<sub>4</sub>, leading to the effective charge separation in the composite, which were evidenced by photoluminescence spectroscopy and photocurrent analysis. This work may provide some useful information for the future design and practical application of multifunctional hybrids photocatalysts in water purification.

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## 1. Introduction

Since 1972, semiconductor photocatalysis has shown its great potential in water splitting, CO<sub>2</sub> reduction, and organic pollutant removal, and thus attracts considerable research interests. The development of visible-light driven photocatalyst with high efficiency is currently of great interest in view of the practical application of photocatalysis [1–6]. Till to now, various metal vanadate, sulfide, bismuth oxyhalide, and polymer semiconductor photocatalysts, such as Ag<sub>3</sub>VO<sub>4</sub> [1], CdS [2], BiOBr [3], g-C<sub>3</sub>N<sub>4</sub> [4] etc., have been applied for organic pollutants degradation or water splitting. However, the fast recombination of electron and hole pairs still limit their photocatalytic activities, indicating that the modification of these semiconductor photocatalysts is desirable in order to obtain higher photocatalytic efficiency.

Polymeric g-C<sub>3</sub>N<sub>4</sub> is the most stable allotrope of carbon nitride. It has a moderate band gap of 2.70 eV and can be used as visible-light

driven photocatalyst. Since Wang et al. first reported its photocatalytic activity in water splitting in 2009 [4], this polymeric material attracts many scientists' interests due to its good stability, visible-light response and low cost. However, just like other pristine semiconductors, the photocatalytic efficiency of g-C<sub>3</sub>N<sub>4</sub> is seriously limited by the fast recombination of photogenerated charge carriers and low surface area. Hence, in order to improve its catalytic efficiency, many methods have been developed, which can be divided into three categories. (1) Introduction of nano/mesoporous structure to improve the specific surface area of g-C<sub>3</sub>N<sub>4</sub> [7,8]; (2) Doping metal or nonmetal element to extend the light absorption range of g-C<sub>3</sub>N<sub>4</sub> [9,10]; (3) Fabrication of heterostructured composite to retard the recombination of charge carriers [11–14]. Particularly, considering that the separation efficiency of photogenerated electron-hole pairs is recognized as the key factor influencing the catalytic activity of a photocatalyst, the last approach is seen as the most efficient way and attracts more attentions than the others. Up to now, a great variety of g-C<sub>3</sub>N<sub>4</sub> based heterojunctions have been developed [10–20], for instance, MVO<sub>4</sub> (M = Sm, Fe)/g-C<sub>3</sub>N<sub>4</sub> [15,16], W<sub>18</sub>O<sub>49</sub>/g-C<sub>3</sub>N<sub>4</sub> [17], Ag<sub>3</sub>PO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub> [18], BiOBr/g-C<sub>3</sub>N<sub>4</sub> [19], AgX (X = Br, I)/g-C<sub>3</sub>N<sub>4</sub> [20], S-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> [21] and WO<sub>3</sub>/g-

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C<sub>3</sub>N<sub>4</sub> [22]. They all show significantly higher photoactivity than pure g-C<sub>3</sub>N<sub>4</sub>. However, due to the high standard of practical application, it is still necessary to find suitable compounds to further improve the photocatalytic performance of g-C<sub>3</sub>N<sub>4</sub>.

Transition-metal vanadates (M-V-O) have been reported as active materials in the fields of lithium batteries, sensors, and catalysts. The valence band (VB) of the ternary system consists of hybridized V3d, O2p and transition-metal orbitals (such as Bi 6s, Ag4d, Gd4f), which results in an increase of the VB level and the narrowing of the band gap [23]. Hence, transition-metal vanadates usually have moderate band gaps and show great potential in the field of photocatalysis. Till now, a great deal of metal vanadates including BiVO<sub>4</sub> [24], Ag<sub>3</sub>VO<sub>4</sub> [1] and Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub> [25] have been reported to exhibit good photocatalytic activity in dye degradation, water splitting or CO<sub>2</sub> reduction. Meanwhile, they can act as co-catalysts to promote the catalytic activity of a photocatalyst. For example, Hong et al. reported that the WO<sub>3</sub> film modified by BiVO<sub>4</sub> showed enhanced photocatalytic activity by 74% relative to bare WO<sub>3</sub> [26]. Wang et al. found that the doping of Ag<sub>3</sub>VO<sub>4</sub> could significantly promote the activity of TiO<sub>2</sub> in photocatalytic oxidation of gaseous benzene [27]. Especially, the metal vanadate shows great promotion effect on g-C<sub>3</sub>N<sub>4</sub> [9,15,16]. A possible reason is that the chemical reaction between g-C<sub>3</sub>N<sub>4</sub> and metal vanadate easily occurs due to the strong redox property of vanadates, which promotes the formation of chemical bonds between the two semiconductors, favors the charge transfer on the interface, and finally retards the recombination of charge carriers. CdV<sub>2</sub>O<sub>6</sub> is one of the big family of metal vanadates. Recently, Li et al. reported that the complex exhibited moderate photocatalytic activity in methylene blue degradation, indicating its potential in photocatalysis [28]. Combing with the previous analysis, it can be inferred that the coupling of CdV<sub>2</sub>O<sub>6</sub> with g-C<sub>3</sub>N<sub>4</sub> might generate an efficient photocatalyst. However, to the best of our knowledge, no research focused on the photocatalytic activity of CdV<sub>2</sub>O<sub>6</sub>/g-C<sub>3</sub>N<sub>4</sub> composite has been reported. Therefore, in this paper, a novel CdV<sub>2</sub>O<sub>6</sub>/g-C<sub>3</sub>N<sub>4</sub> heterojunction was prepared via a simple mixing and calcination method. The photocatalytic test indicates that the prepared composite exhibits excellent activity for rhodamine B (RhB) degradation under visible light irradiation.

## 2. Experimental section

### 2.1. Catalysts preparation

All these reagents are analytical pure grade and used without further purification. g-C<sub>3</sub>N<sub>4</sub> was prepared by directly heating melamine at 520 °C for 4 h. The CdV<sub>2</sub>O<sub>6</sub> nanorods were prepared via a hydrothermal method. Typically, 0.9358 g NH<sub>4</sub>VO<sub>3</sub> were dissolved in deionized water (30 mL) to obtain solution A. 0.9132 g CdCl<sub>2</sub>·2.5H<sub>2</sub>O were dissolved in 30 mL deionized water to obtain solution B. Then, solution A was added to solution B under vigorous agitation. The pH value of the mixture was adjusted to 5.5 with NH<sub>3</sub>·H<sub>2</sub>O (25%) solution. The mixture was then transferred into a 100 mL Teflon-lined steel autoclave and heated at 160 °C for 24 h. After the autoclave was cooled to room temperature, the resulting products were separated by centrifugation, washed with absolute ethanol for 4 times and dried at 60 °C.

The CdV<sub>2</sub>O<sub>6</sub>/g-C<sub>3</sub>N<sub>4</sub> composites were prepared as follows. CdV<sub>2</sub>O<sub>6</sub> nanorods and g-C<sub>3</sub>N<sub>4</sub> with different ratios were added into a mortar and then ground for 30 min. The resultant mixed powders were put into a crucible with a cover and then heated at 400 °C for 2 h to obtain CdV<sub>2</sub>O<sub>6</sub>/g-C<sub>3</sub>N<sub>4</sub> hybrids with various CdV<sub>2</sub>O<sub>6</sub> contents.

### 2.2. Photocatalytic test

Photocatalytic oxidation of RhB was used as a model reaction to evaluate the photocatalytic activities of CdV<sub>2</sub>O<sub>6</sub>/g-C<sub>3</sub>N<sub>4</sub> heterojunction under visible light irradiation. The visible light source is a 350 W xenon lamp with two cut-off filters (800 nm > λ > 420 nm). Before light irradiation, a suspension containing 100 mL RhB solution (10 mg/L) and 0.2 g of catalyst were stirred 1 h in the dark. At a given time of intervals, about 8 mL of suspension was withdrawn and centrifuged to remove catalyst for analysis. The concentration of RhB was determined by measuring the maximum absorbance at about 554 nm using a UV-vis spectrophotometer. Besides RhB, methyl orange (MO) and phenol were also used as the simulated pollutants to investigate the photocatalytic activity of CdV<sub>2</sub>O<sub>6</sub>/g-C<sub>3</sub>N<sub>4</sub> composite. The degradation procedures were as same as that of RhB. Trapping experiments were performed to determine the reactive species during the photodegradation of RhB. The detailed process was described elsewhere [29].

### 2.3. Characterizations

Thermo-gravimetric (TG) analysis (Netzsch STA449) was performed in a thermal analyzer (Netzsch STA449) in air flow (10 mL/min) with a heating rate of 10 °C/min. The powder X-ray diffraction (XRD) patterns of the samples were recorded on a Philips PW3040/60 X-ray diffractometer with Cu Kα radiation (40 kV/40 mA). The N<sub>2</sub> physical absorption measurements were carried out at 77 K with an Autosorb-1 apparatus (Quantachrome Instruments). The specific surface area was calculated by Brunauer-Emmett-Teller (BET) method. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) were performed on a Field emission scanning electron microscope (Hitachi S-4800). UV-vis diffuse reflection spectroscopy was performed on a UV-vis spectrophotometer (PerkinElmer Lambda900). X-ray photoelectron spectroscopy (XPS) measurements were performed by a Quantum 2000 Scanning ESCA Microprobe instrument using AlKα. The C 1s signal was set to a position of 284.6 eV. The photoluminescence (PL) spectra of the samples were collected on FLS-920 spectrometer (Edinburgh Instrument), using a Xe lamp (excitation at 365 nm) as light source. The transient photocurrent measurements were performed by using a CHI 660B electrochemical workstation with a standard three-electrode cell at room temperature [30].

## 3. Results and discussion

### 3.1. Characterizations of CdV<sub>2</sub>O<sub>6</sub>/g-C<sub>3</sub>N<sub>4</sub> composites

Although pure g-C<sub>3</sub>N<sub>4</sub> has high stability, the previous literatures have proven that chemical reaction between g-C<sub>3</sub>N<sub>4</sub> and coupled oxide semiconductors usually occurs at a low temperature [11,15,31,32], which fastens the decomposition of g-C<sub>3</sub>N<sub>4</sub> and results in the loss of g-C<sub>3</sub>N<sub>4</sub>. Hence, TG analysis is necessary to investigate the real concentration of g-C<sub>3</sub>N<sub>4</sub> in the CdV<sub>2</sub>O<sub>6</sub>/g-C<sub>3</sub>N<sub>4</sub> composites. Fig. 1 shows the TG profiles of CdV<sub>2</sub>O<sub>6</sub>/g-C<sub>3</sub>N<sub>4</sub> composites with different CdV<sub>2</sub>O<sub>6</sub> content. It can be observed that all samples except CdV<sub>2</sub>O<sub>6</sub> have a sharp weight decrease, which can be assigned to the loss of g-C<sub>3</sub>N<sub>4</sub>. The weight loss temperature of CdV<sub>2</sub>O<sub>6</sub>/g-C<sub>3</sub>N<sub>4</sub> composites is much lower than that of pure g-C<sub>3</sub>N<sub>4</sub>, indicating the contribution of CdV<sub>2</sub>O<sub>6</sub> and the interaction between CdV<sub>2</sub>O<sub>6</sub> and g-C<sub>3</sub>N<sub>4</sub>. This result is consistent with the previous results [11,15,31,32]. Based on the weight of residual the CdV<sub>2</sub>O<sub>6</sub> concentration in the composites are calculated to be 14.1 wt.%, 18.0 wt.%, 22.6 wt.%, and 30.3 wt.%, respectively.

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