



Preparation, characterization, and photocatalytic activity of CdV₂O₆ nanorods decorated g-C₃N₄ composite



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ABSTRACT

Novel CdV₂O₆/g-C₃N₄ hybrid system was synthesized by a facile mixing-calcination method. The photocatalytic test indicated that the decoration of CdV₂O₆ nanorods on g-C₃N₄ can significantly promote the photocatalytic activity in RhB degradation under visible light. The optimal CdV₂O₆/g-C₃N₄ sample exhibited a degradation rate of 0.041 min⁻¹, which is 4.5 times higher than that of pure g-C₃N₄. Various techniques including N₂ 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 CdV₂O₆/g-C₃N₄. The results indicated that the enhanced activities were mainly attributed to the interfacial transfer of photogenerated electrons and holes between CdV₂O₆ and g-C₃N₄, 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, CO₂ 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 Ag₃VO₄ [1], CdS [2], BiOBr [3], g-C₃N₄ [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-C₃N₄ 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-C₃N₄ 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-C₃N₄ [7,8]; (2) Doping metal or nonmetal element to extend the light absorption range of g-C₃N₄ [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-C₃N₄ based heterojunctions have been developed [10–20], for instance, MVO₄ (M = Sm, Fe)/g-C₃N₄ [15,16], W₁₈O₄₉/g-C₃N₄ [17], Ag₃PO₄/g-C₃N₄ [18], BiOBr/g-C₃N₄ [19], AgX (X = Br, I)/g-C₃N₄ [20], S-TiO₂/g-C₃N₄ [21] and WO₃/g-

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C₃N₄ [22]. They all show significantly higher photoactivity than pure g-C₃N₄. 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-C₃N₄.

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 BiVO₄ [24], Ag₃VO₄ [1] and Zn₃V₂O₈ [25] have been reported to exhibit good photocatalytic activity in dye degradation, water splitting or CO₂ reduction. Meanwhile, they can act as co-catalysts to promote the catalytic activity of a photocatalyst. For example, Hong et al. reported that the WO₃ film modified by BiVO₄ showed enhanced photocatalytic activity by 74% relative to bare WO₃ [26]. Wang et al. found that the doping of Ag₃VO₄ could significantly promote the activity of TiO₂ in photocatalytic oxidation of gaseous benzene [27]. Especially, the metal vanadate shows great promotion effect on g-C₃N₄ [9,15,16]. A possible reason is that the chemical reaction between g-C₃N₄ 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. CdV₂O₆ 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 CdV₂O₆ with g-C₃N₄ might generate an efficient photocatalyst. However, to the best of our knowledge, no research focused on the photocatalytic activity of CdV₂O₆/g-C₃N₄ composite has been reported. Therefore, in this paper, a novel CdV₂O₆/g-C₃N₄ 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-C₃N₄ was prepared by directly heating melamine at 520 °C for 4 h. The CdV₂O₆ nanorods were prepared via a hydrothermal method. Typically, 0.9358 g NH₄VO₃ were dissolved in deionized water (30 mL) to obtain solution A. 0.9132 g CdCl₂·2.5H₂O 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 NH₃·H₂O (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 CdV₂O₆/g-C₃N₄ composites were prepared as follows. CdV₂O₆ nanorods and g-C₃N₄ 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 CdV₂O₆/g-C₃N₄ hybrids with various CdV₂O₆ contents.

2.2. Photocatalytic test

Photocatalytic oxidation of RhB was used as a model reaction to evaluate the photocatalytic activities of CdV₂O₆/g-C₃N₄ 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 CdV₂O₆/g-C₃N₄ 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 N₂ 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 CdV₂O₆/g-C₃N₄ composites

Although pure g-C₃N₄ has high stability, the previous literatures have proven that chemical reaction between g-C₃N₄ and coupled oxide semiconductors usually occurs at a low temperature [11,15,31,32], which fastens the decomposition of g-C₃N₄ and results in the loss of g-C₃N₄. Hence, TG analysis is necessary to investigate the real concentration of g-C₃N₄ in the CdV₂O₆/g-C₃N₄ composites. Fig. 1 shows the TG profiles of CdV₂O₆/g-C₃N₄ composites with different CdV₂O₆ content. It can be observed that all samples except CdV₂O₆ have a sharp weight decrease, which can be assigned to the loss of g-C₃N₄. The weight loss temperature of CdV₂O₆/g-C₃N₄ composites is much lower than that of pure g-C₃N₄, indicating the contribution of CdV₂O₆ and the interaction between CdV₂O₆ and g-C₃N₄. This result is consistent with the previous results [11,15,31,32]. Based on the weight of residual the CdV₂O₆ 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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