

Regular Article

Titanium dioxide and cadmium sulfide co-sensitized graphitic carbon nitride nanosheets composite photocatalysts with superior performance in phenol degradation under visible-light irradiation

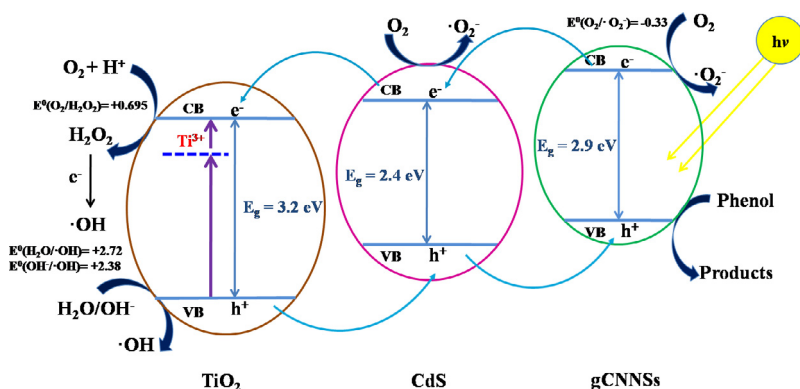


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GRAPHICAL ABSTRACT

The excellent visible light photocatalytic activity of TiO₂-CdS-gCNNSs heterojunction photocatalysts of phenol degradation was mainly ascribed to more effective separation rate of electron-hole.



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ABSTRACT

In this work, TiO₂-CdS-gCNNSs heterojunction photocatalysts were successfully synthesized. CdS was deposited on the surface of gCNNSs via electrostatic attraction; Ti—O—C, Ti—O—C=O and Ti—O—N bonds were produced in TiO₂-CdS-gCNNSs, strengthening the interaction between TiO₂ and gCNNSs. The TiO₂-CdS-gCNNSs photocatalyst showed excellent photocatalytic activity for phenol degradation under visible-light irradiation, which was higher than that of CdS-gCNNSs, CdS-TiO₂ and TiO₂-gCNNSs. The improved photocatalytic performance of TiO₂-CdS-gCNNSs was ascribed to more adsorption sites, enhanced light harvesting ability and effective separation rate of electron-hole pairs. Furthermore, the results of photocatalytic mechanism indicated that h⁺ and ·O₂⁻ played a more significant role on the phenol degradation.

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1. Introduction

Photocatalytic degradation is one of the most expected methods to solve the environmental problems, especially the removal of

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organic pollutants, due to its convenient operation and low toxicity [1–4]. Among semiconductor photocatalysts, TiO_2 is considered as one of the most potential candidates due to its appealing properties such as low cost, nontoxicity and high photo-stability [5,6]. However, TiO_2 has a large band gap (3.2 eV); this drawback makes TiO_2 can only use <5% solar energy for photodegradation, which restricts the rational use of solar energy resources [7]. In order to make more use of solar energy, visible-light responsive semiconductor photocatalysts have attracted intensive attention in recent years.

Graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) with a band gap of 2.7 eV is considered as a promising visible light photocatalyst [8–10]. However, limited visible light harvesting ability and high recombination rate of charge carriers suppressed its application in photocatalysis [11,12]. Many efforts have been carried out to modify its band gap to broaden the optical absorption edge and inhibit the recombination of photogenerated electron-hole pairs [13–16]. Combining $g\text{-C}_3\text{N}_4$ with other appropriate semiconductors [17–20] to form semiconductor heterostructure was considered as an effective method to enhance photocatalytic activity. Modification of the morphology of $g\text{-C}_3\text{N}_4$, such as mesoporous $g\text{-C}_3\text{N}_4$ and $g\text{-C}_3\text{N}_4$ nanosheets, was also found to be beneficial to improve photocatalytic activity.

CdS is considered as a fascinating catalyst for photocatalytic degradation of pollutants under visible light irradiation since it has a narrow band gap (2.4 eV) and suitable band-edge positions. However, there are two main shortcomings of CdS semiconductor which limited its applications: the fast recombination of photoexcited electron-hole pairs and self-photo-corrosion [21,22]. Combining $g\text{-C}_3\text{N}_4$ with CdS can improve the separation of photoinduced electron-hole pairs due to the formation of $g\text{-C}_3\text{N}_4\text{-CdS}$ heterostructures. For example, Fu et al. [23] fabricated $\text{C}_3\text{N}_4\text{-CdS}$ composite photocatalysts which exhibited improved photocatalytic activities and stability on organic compounds degradation under visible light irradiation. In our previous work, $g\text{-C}_3\text{N}_4\text{-CdS}$ composite catalysts were prepared via the precipitation method and this catalyst showed much higher photocatalytic activity and photostability as compared to CdS or $g\text{-C}_3\text{N}_4$ toward the MB degradation under visible-light irradiation. Besides of binary photocatalysts, many ternary photocatalysts were investigated in recent years. Yuan et al. [24] prepared ternary $g\text{-C}_3\text{N}_4\text{-CdS-NiS}$ materials which exhibited enhanced visible-light photocatalytic activity compared to binary composite photocatalysts based on $g\text{-C}_3\text{N}_4$. Ternary composite photocatalysts could improve the interfacial charge transfer and reduce the recombination of electron-hole pairs. However, to our knowledge, $\text{TiO}_2\text{-CdS}$ composite semiconductors co-sensitized $g\text{-C}_3\text{N}_4$ photocatalysts have not been studied. It is speculated that the addition of TiO_2 , especially the existence of Ti^{3+} could further enhance the light harvesting and electron transfer.

In order to effectively synthesize TiO_2 and CdS co-sensitized $g\text{-C}_3\text{N}_4$ catalyst, $g\text{-C}_3\text{N}_4$ nanosheets (gCNNSs) were used as the based material since gCNNSs possessed high surface area and surface functional groups (such as -COOH). Cheng et al. [25] has found that the surface functional groups in $g\text{-C}_3\text{N}_4$ could be ionized into -COO^- in alkaline condition that favored the adsorption of bivalent cadmium to the surface of gCNNSs. It is speculated that the heterogeneous structure could be formed in $x\text{TiO}_2\text{-CdS-gCNNSs}$, and the electrons in conduction band (CB) of gCNNSs could transfer to CB of CdS, and then move to CB of TiO_2 . Meanwhile, the holes in valence band (VB) of TiO_2 could transfer to VB of CdS and then further migrate to VB of gCNNSs. The migration path could contribute to the effective separation of electron-hole pairs, leading to the improvement of catalytic activity. Meanwhile, CdS-gCNNSs, $\text{TiO}_2\text{-gCNNSs}$, $\text{TiO}_2\text{-CdS}$ catalysts were also fabricated.

All the catalytic activities of samples were investigated on phenol degradation under visible light irradiation.

2. Experimental

2.1. Preparation of catalysts

All reagents used in this paper were analytical purity and utilized without further purification. Graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) was obtained by polymerization of melamine at 550°C for 4 h with a heating rate of $2.0^\circ\text{C min}^{-1}$. The $g\text{-C}_3\text{N}_4$ nanosheets (gCNNSs) were synthesized by a chemical exfoliation method. In detail, 3 g as-prepared $g\text{-C}_3\text{N}_4$ was mixed with 30 mL H_2SO_4 (98 wt%) in a 100 mL beaker and vigorously stirred for 6 h at room temperature. Then, the viscous mixture was diluted by 400 mL distilled water, stirred for 30 min and then sonicated for exfoliation. The color of the materials changed from yellow to nearly white. After that, the suspension was centrifuged at 5000 rpm and washed with plenty of distilled water. During the process, unexfoliated $g\text{-C}_3\text{N}_4$ materials were removed, and the $g\text{-C}_3\text{N}_4$ nanosheets were collected by suction filter and dried at 60°C overnight.

The CdS-gCNNSs composite catalyst was fabricated by an electrostatic attraction process [25,26]. Firstly, 3 g gCNNSs was dispersed into 100 mL distilled water, stirred for 1 h, and then the pH of the mixture was adjusted to 10.0 using 5 M ammonia solution. Secondly, 1.92 g $\text{Cd}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ was dissolved in 50 mL deionized water, and the solution of $[\text{Cd}(\text{NH}_3)_4]^{2+}$ was obtained by adding 5 M ammonia solution into $\text{Cd}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ solution until the $\text{Cd}(\text{OH})_2$ precipitation disappeared. Thirdly, the solution of $[\text{Cd}(\text{NH}_3)_4]^{2+}$ was added drop by drop into the gCNNSs suspension, stirred for another 2 h, filtered, washed by distilled water and dried at 60°C . The as-obtained $[\text{Cd}(\text{NH}_3)_4]^{2+}/\text{gCNNSs}$ powder was dispersed in 23.4 g/L thioacetamide (TAA) solution, then stirred for 30 min at room temperature, kept another 30 min for stirring at 70°C . After cooling down the temperature, the material was washed with amounts of distilled water, dried at 60°C and the final products were marked as CdS-gCNNSs.

$x\text{TiO}_2\text{-CdS-gCNNSs}$ photocatalysts were synthesized through a hydrothermal method. Typically, tetrabutyl titanate (TBOT) with different quantity was added into CdS-gCNNSs powders under milling before 50 mL distilled water was dropwise added to hydrolyze TBOT and the hydrolysates were deposited on the surface of CdS-gCNNSs. After stirring for 1 h, the mixture was transferred into a 100 mL Teflon reaction kettle for hydrothermal treatment at 180°C for 6 h, followed by centrifugation, water-washing, and dry. The final products were denoted as $x\text{TiO}_2\text{-CdS-gCNNSs}$, where x stood for the weight ratio of TiO_2 and CdS-gCNNSs. For comparison, $\text{TiO}_2\text{-CdS}$ and $\text{TiO}_2\text{-gCNNSs}$ were also prepared using the same method.

2.2. Characterization

X-ray diffraction (XRD) was measured on a Bruker D8 Advanced diffraction-meter with Cu $K\alpha$ radiation. Atomic force microscopy (AFM) was conducted on Thermo microscope auto probe CP research system. Fourier transform infrared spectrometry (FT-IR) was performed by a Nexus 870 spectrometer. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM2100 microscopy at 200 kV acceleration voltage. X-ray photoelectron spectrum (XPS) were taken on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) accompanied with Mg $K\alpha$ radiation ($h\nu = 1253.6\text{ eV}$). The Brunauer-Emmett-Teller (BET) surface area was analyzed by N_2 adsorption and desorption on Micromeritics TriStarII 3020. UV-vis diffuse reflection spectroscopy (DRS) was

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