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Combination Mechanism and Enhanced Visible-Light Photocatalytic Activity and Stability of CdS/g-C_3N_4 Heterojunctions

Huanyan Xu *, Licheng Wu, Liguo Jin, Kejia Wu

School of Materials Science and Engineering, Harbin University of Science and Technology, Harbin 150040, China

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In this study, CdS/g-C_3N_4 (CSCN) heterojunctions were *in situ* fabricated with a large amount of CdS nanoparticles anchored on g-C_3N_4 nanosheets. A wet chemical method was developed for the first time to determine the actual content of CdS in CSCN composites. X-ray diffraction (XRD), Fourier transform infrared spectra (FTIR), high-resolution transmission electron microscopy (HRTEM) and UV-vis diffuse reflectance spectra (DRS) were employed to characterize the composition, structure and optical property of CSCN composites. Based on the isoelectric point (IEP) analysis of g-C_3N_4, a conclusion was obtained on the combination mechanism between CdS nanoparticles and g-C_3N_4 nanosheets. The photocatalytic activity of CSCN composites was much better than those of individual CdS and g-C_3N_4 for the degradation of azo dye Methyl Orange (MO) by 40 min adsorption in the dark followed by 15 min photocatalysis under visible light irradiation. After 5 cycles, CSCN composites still maintained high reactive activity with the MO degradation efficiency of 93.8%, exhibiting good photocatalytic stability. The Cd^{2+} concentration dissolved in the supernatant detected by atomic absorption spectroscopy (AAS) of CSCN composites was lower than that of pure CdS, implying that the photocorrosion of CdS could be suppressed via the combination with g-C_3N_4. Photoluminescence emission spectra (PL) results clearly revealed that the recombination of photogenerated electron-hole pairs in CSCN composites was effectively inhibited due to the formation of heterojunctions. Based on the band alignments of g-C_3N_4 and CdS, the possible photocatalytic mechnism was discussed.

1. Introduction

Solar energy is inexhaustible and widely utilized in many forms such as photo-thermal conversion, solar photovoltaic generation and photochemical reaction. In recent years, due to ongoing energy shortages and environmental crisis, the development of environmentally-friendly photocatalytic semiconductors has become a hot topic[1,2]; thus, the photochemical utilization for solar energy has emerged and continues to attract more and more attention. This mainly includes three aspects: photocatalytic reduction of CO_2[3], photocatalytic splitting of water into H_2[4], and photocatalytic degradation of organic pollutants[5]. Among these, the photocatalytic degradation of organic pollutants holds great significance as a solution to the problems of environmental pollution. As a well-known photocatalytic semiconductor material, titanium dioxide (TiO_2), with a wide band gap (3.2 eV) can only use ultraviolet light which occupies only about 4% of the whole solar spectrum[6]. Therefore the performance of TiO_2 does not meet the needs of industrial applications for solar energy utilization and, as a result, the development of new efficient photocatalytic systems is still in progress[7].

Recently carbon nitride material with graphite-like structure (g-C_3N_4) has been developed and considered as a novel metal-free semiconductor material, on the basis of its excellent semiconductor properties and appropriate band gap (2.69 eV). g-C_3N_4 exhibited superior photocatalytic performance in the fields of photocatalytic water splitting for H_2 evolution[8,9] and photocatalytic degradation of organic pollutants under visible-light irradiation[10,11]. The most common method used for preparation of g-C_3N_4 was thermal polycondensation by directly heating different organic precursors, which was easy to operate and suitable for mass production[12–14]. Meanwhile, the precursors for g-C_3N_4 preparation mainly included dicyandiamide[15], melamine[16], urea[17] and thiourea[18], which were much cheaper than the raw materials for the preparation of other photocatalysts. Nevertheless, the photocatalytic efficiency of bare g-C_3N_4 is still limited due to the high recombination rate of photogenerated electron-hole pairs[19], and many attempts have been made by researchers to enhance photocatalytic activity and inhibit the electron-hole recombination of bare g-C_3N_4. Xu et al.[20] synthesized g-C_3N_4/Ag_2O composite photocatalyst that presented better photocatalytic activity than that of pure

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* Corresponding author. Ph.D.; Tel.: +86 451 86392501; Fax: +86 451 86392555.
E-mail address: xhy7587@aliyun.com (H. Xu).

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$g\text{-}C_3N_4$. The photocatalytic activity of $g\text{-}C_3N_4/Ag_2O$ was about 6 times as large as pure $g\text{-}C_3N_4$ for photodegradation of Methyl Orange (MO) under visible light irradiation. Liu et al.[21] modified graphitic carbon nitride using ZnO by a facile ball milling method, and the obtained $g\text{-}C_3N_4/ZnO$ composite exhibited higher photocatalytic activity for the degradation of rhodamine B (RhB) under visible light irradiation than that of pure $g\text{-}C_3N_4$. Li et al.[22] reported that under visible light irradiation, the photocatalytic degradation capacity for RhB by $g\text{-}C_3N_4/SmVO_4$ was 2.4 times higher than that of pure $g\text{-}C_3N_4$, and the composite photocatalyst exhibited excellent photostability in the photocatalytic process. Moreover, many studies on the modification of $g\text{-}C_3N_4$ were investigated such as the doping of metal elements (Au, Ag, Co, etc.)[23–25] and non-metal elements (B, C, S, P, etc.)[26–29], which were intended to improve the electron transfer, reduce the electron-hole recombination rate and expand the range of visible light response.

Among these approaches, fabricating heterojunctions between two semiconductor materials appear as a fascinating mean of improving the photocatalytic activity of $g\text{-}C_3N_4$. Therefore, it is a crucial issue to find a suitable semiconductor material which can be well matched with $g\text{-}C_3N_4$. Cadmium sulfide (CdS) is a semiconductor photocatalyst with visible light response, attributed to its narrow band gap (2.14 eV). However, CdS alone would suffer from photocorrosion via the oxidation of S^{2-} by photogenerated holes during the photocatalytic reaction[30]. Due to the narrow band gap, CdS has been widely used as a sensitizer to realize the visible light response of wide band gap semiconductors. The conduction band (CB) and valence band (VB) potentials of CdS are –0.39 and 1.75 eV, while the CB and VB potentials of $g\text{-}C_3N_4$ are –1.12 and 1.57 eV, suggesting that CdS and $g\text{-}C_3N_4$ fit the requirements to form heterostructures with well-matched band energies[31]. On the one hand, the heterojunctions would prompt an effective separation and transfer of photogenerated electron-hole pairs; on the other hand, the emigration of photogenerated holes from the valence band of CdS would avoid the photocorrosion of CdS by self-oxidation. Hence, two birds can be killed with one stone: coupling CdS and $g\text{-}C_3N_4$ could not only enhance photocatalytic activity, but also improve the photo-stability of CdS under visible light irradiation. Although the photocatalytic degradation of organic dyes over $CdS/g\text{-}C_3N_4$ composite has been investigated by other researchers[30–33], there still exist many unresolved problems. For instance, the combination mechanism between CdS and $g\text{-}C_3N_4$ has not been clarified; the determination method of actual content of CdS in the composite has not been developed; the enhanced photocatalytic activity and improved photo-stability are still under discussion.

Herein, we designed a facile route to anchoring CdS nanoparticles onto $g\text{-}C_3N_4$ nanosheets, *in situ* fabricating $CdS/g\text{-}C_3N_4$ (CSCN) heterojunctions with enhanced photocatalytic activity and improved photo-stability. A wet chemical method was developed to determine the actual content of CdS in CSCN composites. The obtained CSCN heterostructured photocatalysts were characterized by X-ray diffraction (XRD), Fourier transform infrared spectra (FTIR), transmission electron microscopy (TEM), UV-vis diffuse reflectance spectra (UV-vis DRS), photoluminescence emission spectra (PL) and Brunauer–Emmett–Teller (BET) surface area analyzer. Subsequently, based on the measurement of surface Zeta potential (ξ) of $g\text{-}C_3N_4$, the combination mechanism between CdS and $g\text{-}C_3N_4$ was proposed. The photocatalytic activity of CSCN heterojunctions was evaluated using a typical anionic dye, Methyl Orange (MO) as the target pollutant. Atomic absorption spectroscopy (AAS) was employed to detect the dissolved amount of Cadmium ion into MO solution after photocatalytic reaction, indicating the improved photostability of CdS by combination with $g\text{-}C_3N_4$ nanosheets. Then, the possible photocatalytic mechanism of CSCN heterojunctions was expounded.

2. Experimental

2.1. In situ *fabrication of CSCN heterojunctions*

$g\text{-}C_3N_4$ was firstly prepared via a facile pyrolytic method according to our previous report[34]. In the typical procedure, 6 g of melamine was put into the crucible with a cover and heated at 500 °C for 2 h in a muffle furnace. After cooling, the resultant product was ground in a mortar, and then the yellow $g\text{-}C_3N_4$ powder was exfoliated in 100 mL deionized water under ultrasonication for 3 h in order to obtain $g\text{-}C_3N_4$ nanosheets for further use.

In situ fabrication of CSCN heterojunctions was implemented by a one-step soft chemistry method, using Cadmium nitrate tetrahydrate [CNT, $Cd(NO_3)_2{\cdot}4H_2O$] and thiourea [TU, $(NH_2)_2CS$] as Cd and S sources, respectively. Generally, a certain number of $g\text{-}C_3N_4$ nanosheets were re-dispersed in 50 mL deionized water and cleaned ultrasonically again for 1 h. After that, a 50 mL mixed solution of CNT and TU with a molar ratio of 1:1 was added to the above suspension of $g\text{-}C_3N_4$ nanosheets and mechanically stirred for another 2 h. Then, the suspension was carefully adjusted toward $pH = 10$ with a 0.5 mol/L NaOH solution and continuously stirred for 20 h to reach complete reaction. Thereafter, the final suspension was centrifuged and the obtained precipitate was repeatedly washed with deionized water. After being dried at 80 °C for 12 h, the product underwent heat treatment at 250 °C for 1 h. According to the above-described method, CSCN heterojunctions with different mass ratios of CdS and $g\text{-}C_3N_4$ were obtained. As comparison, the pure CdS sample was also prepared using the same procedure except for the addition of $g\text{-}C_3N_4$.

2.2. *Characterization techniques*

XRD was employed to identify the phase composition of the as-prepared samples. The patterns were recorded on a Rigaku D/max-3B X-ray diffractometer using Cu-K_α radiation ($\lambda = 0.15418$ nm) at 40 kV and 30 mA over the 2θ range of 10°–60°. FTIR was used to confirm the chemical groups in CSCN heterostructured photocatalysts. Measurements were made on a Nicolet Nexus infrared spectrometer after the sample was mixed with 300 mg of spectroscopic grade KBr and pressed into thin slices. The crystal morphology and structure of CSCN heterojunctions were observed by TEM. The TEM observations were realized on a JEOL JEM-2010 transmission electron microscope at an accelerating voltage of 200 kV. UV-vis DRS spectra in the range of 400–800 nm were recorded on an USB4000 UV-vis spectrometer (Ocean Optics) equipped with an integral sphere using a standard template provided by South Africa Optics as the reference. PL spectra were detected by a RF-5301PC Fluorescence spectrophotometer at room temperature using a 150-W Xenon lamp as the excitation source at the wavelength of 304 nm. The BET specific surface area of samples was obtained from nitrogen adsorption–desorption data and measured using a Sibata SA-1100 surface area analyzer at liquid nitrogen temperature. Surface Zeta potential of $g\text{-}C_3N_4$ nanosheets was examined by Zeta potential analyzer (Nano-ZS90) at different medium pHs.

2.3. *Photocatalytic performance*

All the adsorption and photocatalysis experiments were performed at room temperature, and the pH value of MO solution was adjusted to 7 by NaOH and HCl provided that there was no special instruction during the experiment process. The light source used in this study was simulated solar light, emitted by a HSX-F300 device equipped with a 300 W Xe lamp, which can output a stable continuous spectrum from ultraviolet to near infrared (300–2500 nm), similar to natural sunlight. The light intensity was adjusted to

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