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Copolymerization And Solvothermal Synthesis of S-Scheme CdS/g-C₃N₄ to Improve the Photocatalytic Degradation Activity of Rhb Under UV-Visible Light.

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Abstract.

The synthesis of photocatalysts with high charge separation and transfer efficiency are of immense significance in the process of using photocatalysis technology for wastewater treatment. In this study CdS/g-C₃N₄ photocatalyst presented an improved morphology in its characterization using techniques such as SEM, DRS, PL, MS, EIS, and XRD, and enhanced photodegradation of oxcarbazepine. Different composites were obtained as confirmed by the various characterization techniques studied, including CdS/g-C₃N₄ photocatalyst. The synthesized photocatalysts showed high visible light absorption efficiency within a range of ~655 to 420 nm. S-Scheme CdS/g-C₃N₄ photocatalyst demonstrated high photocatalytic activity ascribed to high load separation and transition as shown in PL, Photocurrent reaction and EIS. It is understandable that CdS/g-C₃N₄ photocatalyst have confirmed to be one of the ultimate promising entrants for ground-breaking photocatalyst scheming.

Keywords: CdS/g-C₃N₄ photocatalyst, Copolymerization method, Solvothermal method, and Rhodamine B

Introduction

Air and water pollution as result of intensive human activity is undoubtedly a major concern worldwide. This challenge urges the scientific community to look for sustainable and green solutions without imposing more strain on the environment. The use of materials which can be activated by renewable energy sources such as sunlight could be an ideal solution. Bismuth based photocatalysts are semiconductor materials which are capable of generating electron; hole pairs under UV light irradiation. These evolved charge carriers can then react with the surrounding water and oxygen molecules to generate reactive radicals which can thus induce photo-degradation of various pollutants, toxic substances and also, viruses and bacteria. Thus, Carbon based photocatalysts are suitable for the purification and detoxification of air and water, and in the purification of fuel.

Since the discovery of the photocatalytic properties of TiO_2 by Fujishima and Honda for the first time in 1972 (Fujishima and Honda, 1972), many researches have been conducted on improving the efficiency of semiconductor photocatalysts (Qi et al., 2017). A major challenge is to suppress the recombination of photogenerated electron-hole pairs, which are easily recombined due to the strong coulomb force (Wang et al., 2017; Ye et al., 2017). In addition, for single-component photocatalysts, the dilemma of their application is the lack of good compatibility between strong redox capability and light response range (Bi et al., 2015; Zhang et al., 2017; Fu et al., 2018). That is, in order to obtain a sufficient redox capability for a specific reaction to occur on a single photocatalyst, a larger band gap is required. However, the higher utilization of solar energy, the

smaller band gap is required to increase the ability of absorbing light (Fu et al., 2017; Zhao et al., 2015). Therefore, it is of great significance to modify the photocatalyst against these contradictions (Qi et al., 2017; Najafian et al., 2018; Mahdiani et al., 2018; Wu et al., 2019).

Nowadays, the researchers mainly focus on the development of visible-light-response photocatalysts for the decomposition of toxic dyes and organic pollutants, such as C-based (i.e., g-C₃N₄, CdS/g-C₃N₄, CdS) (Hu et al., 2013) and other semiconductors (Zhu et al., 2018). Among those materials, CdS/g-C₃N₄ has been reported to possess an excellent visible-light-driven photocatalytic activity, but the absorption capacity of solar energy is still limited (Zhu et al., 2018). The design of heterostructure photocatalysts has been considered to be an effective approach to extend the light responsive range and enhance the photo-generated carriers separation rate (Yu et al., 2009; Zhang et al., 2018). Carbon-based heterojunctions have been designed to improve the efficiency of the single phases. For instance, CdS/g-C₃N₄ nanocomposite exhibited higher photocatalytic activities for degradation of dye and phenol than CdS/g-C₃N₄ (Li et al., 2015; Chen et al., 2016).

However, this study spotlights on the capacity and efficacy of reformation schemes to upsurge visible light responsive photocatalytic degradation of the Rhodamine B by CdS/g-C₃N₄ photocatalyst nanocrystals for wastewater management and environmental treatment in directive to scheme potential operations for solving environmental problems. Consequently, this material is well-known as eye-catching candidates for environmental applications such as water purification, purified fuel production and treatment of waste water. In this systematic study, CdS/g-C₃N₄ photocatalyst nanocrystals with their high photocatalytic activity are agreeably offered with their

distinctive structure and innovative preparation procedures, and the enlightened concepts are then emphasized on extending CdS/g-C₃N₄ photocatalyst preparation and synthesis.

Materials and methods

Chemicals

Cadmium chloride (CdCl₂·2.5H₂O), thiourea (NH₂CSNH₂), ethylenediamine, barbituric acid, dicyandiamide, nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O), sodium hydroxide (NaOH), sodium hypophosphite (NaH₂PO₂·H₂O), sodium sulfide (Na₂S), sodium sulfite (Na₂SO₃) and ethanol were all analytic reagents and used without further purification.

Preparation of CdS nanorods

CdS nanorods were prepared through a solvothermal method (Jang et al., 2007, Wu et al., 2017). In general, 9.26 g of CdCl₂·2.5H₂O and 9.26 g of NH₂CSNH₂ were added into the Teflon-lined autoclave with a total capacity of 200 mL. Then, after 120 mL ethylenediamine was added, the autoclave was heated to 160 °C and maintained for 36 hours. The yellow products were collected and washed several times with deionized water and ethanol respectively.

Preparation of bulk g-C₃N₄

The g-C₃N₄ was prepared by copolymerization method (Zhang et al., 2010, Wu et al., 2017). 4 g of dicyandiamide and 0.2 g of barbituric acid were added in the 20 mL of distilled water to form a homogeneous suspension with vigorously stirring for 15 min. After that, the suspension was transferred to oil bath with constant stirring under 90 °C until all the water was evaporated. Then the white solid was calcined at 550 °C for 4 h in the atmosphere. Finally, the obtained yellowish bulk was grinded and collected.

Preparation of CdS/g-C₃N₄ Nanorods

The CdS/g-C₃N₄ core/shell nanorods were fabricated through a chemisorption and self-assembly method (Zhang et al., 2013, Wu et al., 2017). Accurately weighting 0.06 g g-C₃N₄ was mixed with 20 mL methanol. Then, the above suspension was ultrasonicated for 1 h to reach a homogeneous suspension. 1.5 g CdS was then added in the suspension and continuous stirred for 24 h. Finally, the methanol was removed by rotary evaporator and dried in vacuum oven at 60°C. The g-C₃N₄ first adsorbs on the surface of CdS nanorods and then undergoes a rolling mechanism and a regrowth process during the reaction. Hence, the g-C₃N₄ could curl up and wrap around the CdS nanorods to form the CdS/g-C₃N₄ composites (Pan, et al., 2012). Similar synthesis procedure was used to prepare the CdS/g-C₃N₄-0 mg, CdS/g-C₃N₄-87 mg and CdS/g-C₃N₄-173 mg composites, respectively. To a portion of the sample, there was calcination of 550°C.

Characterization

X - ray diffractograms (XRD, Rigaku, SmartLab) were used in the range of 10-80° 2θ to analyze the phase purity and crystallite size of the as-synthesized photocatalysts. The morphologies and microstructures were carried out using electron microscopy and electron microscopy (TEM) with high resolution transmission. Use of high - resolution electron microscope (HR - TEM) JEOL JEM 2100 with an accelerating voltage of 200 KV, XRD, and TEM imagery was performed. XRD patterns for centrifuged and dried samples were also documented using X - ray Bruker D8 Advance X - ray diffractometer with source Cu Kα ($\lambda = 1.5406 \text{ \AA}$). A spectrophotometer (Thermo fisher Evolution 220) has documented UV -Vis diffuse reflectance spectra (DRS). The carbon contaminant as reference contact was used to standardize all binding energies (C 1s= 284.6 eV).

Transient photocurrent response measurements were performed on an electrochemical system CHI-660E (Chenhua, China) with a standard three - Na_2SO_4 solution electrode system (0.2 mol / L) to evaluate the electrical properties of the sample. The platinum electrode and the Ag / AgCl saturated electrode were respectively used as counter electrode and reference electrode. 0.020 g of photocatalyst was spread in 3 mL of ethanol with ultrasonic treatment to prepare the working electrode, and the mixture solution was then dip-coated onto an ITO glass working electrode.

We measured all binding energies as their indication point using the carbon contaminant (C 1s= 284.6 eV). Electron spin resonance measurements (ESR) were analyzed on the X - band of a

The Mott-Schottky curves were performed on an electrochemical workstation using a regular three - electrode device (CHI-660E, China). An aqueous solution containing 0.1 M of Na_2SO_4 was utilized as the electrolyte. The counter-and reference electrodes were platinum wire, and Ag / AgCl (saturated KCl), respectively. The working electrode was photocatalyst film electrodes mounted on fluoride-tin oxide (FTO) glass which was washed 1.5 cm x 1.0 cm.

In order to assess the electrical properties of the samples, electrochemical impedance spectroscopy (EIS) and transient photocurrent response measurements were performed on an electrochemical system CHI-660E (Chenhua, China), with a standard three - electrode system in solution Na_2SO_4 (0.2 mol / L). The platinum electrode and the Ag / AgCl saturated electrode were respectively used as counter - electrode and reference electrode.

To prepare the working electrode, 0.020 g of the photocatalyst was distributed with ultrasonic treatment in 3 mL of ethanol, and the mixture solution was then dip-coated onto an electrode working in ITO glass. The catalyst's photoluminescence spectroscopy (PL) was measured using the FLS1000 transient fluorescence spectrometer from Edinburgh-state/. A 450 W ozone-free xenon lamp with an excitation wavelength of 425 nm was the source of the excitement.

Photocatalytic activity evaluation

In short, 0.025 g of photocatalysts were suspended in aqueous solutions of Rhodamine B (RhB), (50 mL, 10 mg L⁻¹) for the degradation of Rhodamine B (RhB). The suspension was stirred in the dark for 30 min before light irradiation to complete the photocatalyst's surface adsorption – the organic contaminant desorption equilibrium and dissolved oxygen. A 300 W Xe lamp with a 420 nm filter under magnetic stirring was then irradiated to the suspension. The current for work had been set at 15 A. The suspension was removed from the reaction vessel at a given time interval, and the photocatalyst was removed by centrifugation. Finally, a UV vis-spectrophotometer was used to screen the concentrations of Rhodamine B (RhB), in a solution.

The measured absorbance intensities were converted into the reduction ratio calculated using the following expression at different illumination times;

Reduction ratio =

$$\frac{C}{C_0} = \left(\frac{A_0 - A_t}{A_0} \right) \times 100 \quad \text{Equation 1}$$

where A_0 and A_t are the absorbance intensities when illuminated and t min, respectively.

Recycling experiments were conducted under the same scenario. 1 mM of ammonium oxalate as the scavenger holes, 1 mM of tert - butanol (TBA) was used in the trapping experiments as the radical hydroxyl scavenger, and 1 mM of p-benzoquinone (BQ) as the radical superoxide scavenger (He et al., 2018; Xiang et al., 2013; Hu et al., 2014).

Results And Discussions

Figure. 1. XRD pattern of g-C₃N₄, CdS, 87 mg CdS/C₃N₄ and 173 mg CdS/C₃N₄ composites.

The peaks at 24.88°C, 28.17°C, 43.84°C, 47.83°C and 51.79°C corresponds to (100), (101), (110), (103) and (112) plane of the hexagonal CdS (PDF#: 77-23-06). The peak at 26.56°C corresponds to (002) plane of hexagonal g-C₃N₄ (PDF#: 87-1526). This proves the existence of both g-C₃N₄ and CdS compounds in the synthesized catalyst semiconductor.

X - Ray Diffraction (XRD) was done to study the nanoparticles. Illustration in this. Figure 1 presents XRD patterns of the various composites. From the XRD result, diffraction peaks of $2\theta = 24.88^\circ$, 28.17° , 43.84° , 47.83° and 51.79° corresponds to (100), (101), (110), (103) and (112) plane of the hexagonal CdS were detected. The peak at 26.56° corresponds to (002) plane of hexagonal g-C₃N₄ (PDF#: 87-1526). This proves the existence of both g-C₃N₄ and CdS compounds in the synthesized catalyst semiconductor. Samples with distinctive composites (e.g. 173 mg CdS/C₃N₄) were shown to be distinctly amorphous as small diffraction peaks of g-C₃N₄ were spotted.

The XRD analysis also verified that the samples obtained are pure g-C₃N₄, CdS and CdS/C₃N₄ composites without further impurity phases since no peaks were observed referring to other phase / structure. Because CdS/C₃N₄ gives better crystallinity at 173 mg, it was selected for the CdS process in further experiments.

Figure 2: Survey XPS spectra of C_3N_4/CdS , Cd3d, O1s, N1s, C1s and S2s (a) and high resolution XPS spectra of (b) C1s (c) S2p (d) Cd3d

The XPS spectra agrees with the XRD spectra that confirms the successful phase transformation of cadmium sulphate from CdS/C_3N_4 photocatalyst up to CdS- d as the calcination temperature increases with increasing concentration of the schemed photocatalyst.

Figure 3. EDX images of (a) 0mg CdS/g- C_3N_4 (b) 87mg CdS/g- C_3N_4 (c) 173mg CdS/g- C_3N_4 (d) g- C_3N_4

The chemical analysis of the prepared sample showed that the Cd: S: C: Cl: N, k -ratio is 0.44979: 0.06337: 0.01732: 0.00820: 0.00079 $\pm$ 0.022, which is close to the theoretical relation. The picture of the prepared CdS/ C_3N_4 is shown in Figure 3, the CdS/ C_3N_4 granules are cylindrical, with a diameter of approximately 2.0 μm and a length of 1.0–2.5 μm (SEM and EDX observed CdS/ C_3N_4

surface morphology). As shown in Figures 2 and 3, CdS/C₃N₄ granules are made up of small particles that form a highly porous composition.

Figure 4. The low and high magnified SEM images of (a) 0mg CdS/g- C₃N₄ (b) 87mg CdS/g- C₃N₄ (c) 173mg CdS/g- C₃N₄ (d) g- C₃N₄ composites.

The CdS with a very good contact point with C₃N₄ (as can be seen in the TEM analysis) acts as a load sink for collecting electron from C₃N₄ and a faster transfer of charge compared to C₃N₄ due to high mobility of electrons, thus reducing the probability of recombination. The low magnified

TEM (Figure 4a) and high magnified TEM (Figure 4b) of Bare CdS/C₃N₄ revealed the presence and aggregation of large quantities of nanorods with an average diameter of 20 nm and 50 nm, respectively.

Figure 5: Transient photocurrent response (a) and EIS Nyquist plots of 0mg C_3N_4 , 0mg CdS/ C_3N_4 , 87mg CdS/ C_3N_4 and 173mg CdS/ C_3N_4

NB: 21-EIS-1; C_3N_4 , 21-EIS-2; 0mg CdS/ C_3N_4 ; 23-EIS-1; 87mg CdS/ C_3N_4 ; 23-EIS-2; 173mg CdS/ C_3N_4

In addition, photocatalytic activity is determined specifically by the proficiency of isolated photogenerated electrons and holes. The density of photoelectrode-generated photocurrent could be used as an indicator for assessing separation of electrons and holes (Low et al., 2019; Meng et al., 2017; Khan et al., 2013). Illustration in figure 5 exhibits instantaneous photocurrent density of the, CdS/g- C_3N_4 -87 mg and CdS/g- C_3N_4 -173 mg composites electrodes. The photocurrent density of the photoelectrode constituted of CdS/g- C_3N_4 composite (173 mg) has increased notably paralleled with the other CdS/g- C_3N_4 combinations, advocating that the composite material comprising CdS/g- C_3N_4 is more promising to the photogenerated electrons.

Furthermore, the EIS of C_3N_4 , CdS/g- C_3N_4 -0 mg, CdS/g- C_3N_4 -87 mg and CdS/g- C_3N_4 -173 mg composites semiconductors were also studied to confirm the interfacial charge carrier transfer. Figure 7(a), shows the EIS Nyquist plots of C_3N_4 , CdS/g- C_3N_4 -0 mg, CdS/g- C_3N_4 -87 mg and CdS/g- C_3N_4 -173 mg photocatalysts. The small arc radius exhibited by C_3N_4 reveals a low resistance of the interfacial charge carrier transfer in the electrode-electrolyte interphase region.

Figure 6: Photoluminescence (PL) spectra of CdS/g-C₃N₄-87 mg and CdS/g-C₃N₄-173 mg at $\lambda=510\text{nm}$ excitation wavelength

In studying the separation capacity for the generated electrons and holes pairs of the synthesized CdS/g-C₃N₄-87 mg and CdS/g-C₃N₄-173 mg photocatalysts, the photoluminescence (PL) spectroscopy study was carried out on the fluorescence spectrophotometer (F-7000 Hitachi-Japan) with an excitation wavelength at 510nm. The maximum PL spectra peaks of CdS/g-C₃N₄-87 mg, and CdS/g-C₃N₄-173 mg were recorded at ~515nm and 650nm wavelength (figure 6) which is close to the one reported in literatures (He et al., 2019). The low PL intensity of CdS/g-C₃N₄-87 mg reflects the low recombination of charge carriers followed by CdS/g-C₃N₄-87 mg at 650nm while CdS/g-C₃N₄-87 mg showing to have higher electron holes recombination at 515nm which is ascribed to low band gap energy.

Figure 7. Photocatalytic activities of the as prepared (a) CdS/C₃N₄ catalysts prepared via calcination and non-calcination (b) CdS/C₃N₄ composites in the decolourisation of RhB under visible light irradiation.

RhB degradation has been used to investigate the photoactivity under visible light of different samples. Several experiments took place under the same conditions. Just like shown on Fig. 7a, the addition of a calcined and 87mg CdS/C₃N₄ photocatalyst for RhB photodegradation is very negligible and confirms its durability under light irradiation. As seen, after 30 minutes in the existence of 0mg CdS/C₃N₄, only 50 per cent of RhB was eliminated. Additionally, RhB degradation on the CdS/C₃N₄ samples is very premiere than that of the pristine non-calcined and calcined CdS/C₃N₄ weight percentage has a remarkable effect on removal efficiency. Accordingly, the results indicated that with the increased weight percentage of 173mg and CdS/C₃N₄ up to 98.9 percent, the photodegradation of RhB was rapidly boosted and about 98 percent of RhB was removed within 300min over the non-calcined CdS/C₃N₄ photocatalyst and then reduced with the

addition of additional CdS/C₃N₄. Adding extra CdS content might demolish the heterojunction among complements owing to agglomeration and modest distribution of nanoparticles, leading to reduced photocatalytic capacity.

In addition, the calculated photocatalytic activity of this pollutant's UV - vis spectral concentration variations were displayed in Fig 7(a)(b) to monitor the RhB's photodegradation response at different timescales; As can be detected, the solution concentration has been gently decreased in the position of maximum absorption with irradiation time, without any movements. Thus, the removals of nanocomposite RhB are deduced to follow aromatic ring - opening pathways (Huang et al., 2016). Based on the results, the absorption spectrum disappeared in the presence of the photocatalyst CdS/C₃N₄ about 30 min after light illumination, while nearly 100 percent of the contaminant was degraded in the presence of CdS/C₃N₄.

Figure 8. Trapping experiments of CdS/g-C₃N₄ catalyst with/without scavengers in the degradation of RhB.

The radical scavenger experiment (trapping experiment) was piloted to appreciate the role of the active species in the degradation of residues. The photocatalytic activity of any catalyst is credited to photogenerated species such as holes (h^+), hydroxyl ($\cdot OH$) and superoxide ($\cdot O_2^-$) radicals. The trapping experiment was carried out with the addition of various organic trapping agents such as ammonium oxalate (h^+ scavenger), tert-butanol ($\cdot OH$ scavenger percentage), and p-benzoquinone ($\cdot O_2^-$ scavenger percentage) (Ong et al., 2016; Brindha et al., 2017; Nosaka et al., 2017). Fig.8 confirms how radical scavengers affect degradation of the photocatalytic pigments. All of these scavengers decreased the activity of CdS/g-C₃N₄, but p-benzoquinone among them decreased the activity to the utmost degree, exposing the primary responsibility of $\cdot O_2^-$ radical in the photocatalytic reaction to decay.

Proposed mechanisms

A probable mechanism for photoactivity over the CdS/g-C₃N₄ photocatalyst samples was proposed (Fig. 9). In the subsequent heterojunction device CdS acts as a sensitizer between band edge locations, while g-C₃N₄ acts as a substratum. The g-C₃N₄ ECB is less negative than the CdS ECB; thus, CdS can act as a sink for the produced electrons. So, during photocatalytic removal of RB, we thought that the electrons provided in the g-C₃N₄ CB could transfer to the CdS CB to form a Type II photocatalyst for heterojunction. In addition, CdS's CB position is negative than O₂ / percent O₂⁻'s redox potential (Asadzadeh-Khaneghah et al., 2018; Mousavi et al., 2018), meaning O₂ could be captivated and reduced to a O₂⁻ percentage. The remaining holes in the g-C₃N₄ VB are also capable of directly oxidizing RhB to the affected degradation products. As a result, the separation of carriers from charging is impressively increasing. Thus, the likelihood of recombination charging carriers is reduced, which results in significantly increased photoactivity.

Figure 9. Schematic diagram of photocatalytic reaction over the CdS/g-C₃N₄ nanocomposite /PS system.

In addition, PS is fragmented by coupling PS with a photocatalyst to harvest some per cent of SO₄⁻ ions. Meanwhile, in the CdS/g-C₃N₄ / PS system, PS can not only be excited to produce a percentage of SO₄⁻ ions by produced electrons on the photocatalyst surface, but it can also react with Cd²⁺ to produce Cd³⁺ and a percentage of SO₄⁻, resulting in a more produced percentage of SO₄⁻ being able to react with H₂O to produce a percentage of OH (Mousavi et al., 2018). The synergistic effect of PS and the formation of heterojunctions in the CdS/g-C₃N₄ nanocomposite

thus have a significant influence on the separation of charges and also a considerable role in improving the photocatalytic performance of the photocatalyst CdS.

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Author Contribution statement

Conceptualization- WKD, GKT, KL, HJ, and YL; Data curation and analysis - WKD, GKT, KL, HJ, and YL; writing—original draft preparation, WKD, GKT, KL, HJ, and YL; writing—review and editing: WKD, GKT, KL, HJ, and YL; supervision- YL; funding acquisition- LK, YL, and HJ. All authors have read and agreed to the published version of the manuscript.

Figures

Figure 1

XRD pattern of g-C₃N₄, CdS, 87 mg CdS/C₃N₄ and 173 mg CdS/C₃N₄composites.

Figure 2

Survey XPS spectra of C₃N₄/CdS, Cd3d, O1s, N1s, C1s and S2s (a) and high resolution XPS spectra of (b) C1s (c) S2p (d) Cd3d

Figure 3

EDX images of (a) 0mg CdS/g- C3N4 (b) 87mg CdS/g- C3N4 (c) 173mg CdS/g- C3N4 (d) g- C3N4

Figure 4

The low and high magnified SEM images of (a) 0mg CdS/g- C₃N₄ (b) 87mg CdS/g-C₃N₄ (c) 173mg CdS/g- C₃N₄ (d) g- C₃N₄ composites.

Figure 5

Transient photocurrent response (a) and EIS Nyquist plots of 0mg C₃N₄, 0mg CdS/C₃N₄, 87mg CdS/C₃N₄ and 173mg CdS/C₃N₄ NB: 21-EIS-1; C₃N₄, 21-EIS-2; 0mg CdS/C₃N₄; 23-EIS-1; 87mg CdS/C₃N₄; 23-EIS-2; 173mg CdS/C₃N₄

Figure 6

Photoluminescence (PL) spectra of CdS/g-C₃N₄-87 mg and CdS/g-C₃N₄-173 mg at $\lambda=510\text{nm}$ excitation wavelength

Figure 7

Photocatalytic activities of the as prepared (a) CdS/C₃N₄ catalysts prepared via calcination and non-calcination (b) CdS/C₃N₄ composites in the decolourisation of RhB under visible light irradiation.

Figure 8

Trapping experiments of CdS/g-C3N4 catalyst with/without scavengers in the degradation of RhB.