PHOTOCATALYTIC ACTIVITY OF S\textsubscript{8}/G-C\textsubscript{3}N\textsubscript{4}/RGO NANOCOMPOSITE UNDER VISIBLE LIGHT IRRADIATION

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**Abstract** - In this work, we reported a heterojunction photocatalyst fabricated by wrapping reduced graphene oxide (RGO) and protonated g-C\textsubscript{3}N\textsubscript{4} (PCN) nanorods on crystals of cyclooctasulfur (α-S\textsubscript{8}). This structure exhibited photocatalytic degradation of Acid Blue 92 (AB92) under visible-light irradiation due to good electrical conductivity of RGO. In addition type II heterojunction formed by coupling PCN with α-S\textsubscript{8} improved photocatalytic activity.

1. Introduction

The growing concerns about energy and environmental remediation have drawn much attention to produce photocatalysts. Photocatalysis is a promising method for solar energy conversion, environmental purification, splitting of water into hydrogen and oxygen [1-5]. Among the photocatalysts, TiO\textsubscript{2} is the most extensively used due to its physical/chemical inertness, nontoxicity, and easy availability. However, the low quantum yields and the low solar energy conversion efficiency limit its practical application, therefore the fabrication of new and more efficient visible-light photocatalysts is still a big challenge [6,7].

Cyclooctasulfur (S\textsubscript{8}) could be a promising visible light driven elemental photocatalyst for photoelectrochemical water splitting and photodegradation of Rhodamine B (RhB). However, large particle size, poor hydrophilicity and fast recombination of photoinduced e\textsuperscript{-}h\textsuperscript{+} pairs have limited its application. In the case of α-sulfur, the energy level of the valence-band maximum (VBM) is more positive while the conduction-band minimum (CBM) is less negative than of g-C\textsubscript{3}N\textsubscript{4} (a metal-free photocatalyst), respectively. Therefore, the metal free heterojunction system of α-sulfur/g-C\textsubscript{3}N\textsubscript{4} could have a staggered gap (Type II) [8].

Graphitic carbon nitride (g-C\textsubscript{3}N\textsubscript{4}), is a semiconductor nanosheet that have applications in water splitting and contaminant degradation under visible light irradiation and coating on other compounds to improve their photocatalytic activity [9,10] due to very high thermal and chemical and photochemical stabilities, non-toxicity, being abundant and suitable electronic structure with band gap of 2.7 eV. However, g-C\textsubscript{3}N\textsubscript{4} always show rather low activity due to low quantum efficiency. To overcome this limitations several methods have been proposed to increase the photocatalytic efficiency such as adding impurities to the pure g-C\textsubscript{3}N\textsubscript{4} with dipping process, protonation, synthesizing of nano/porous g-C\textsubscript{3}N\textsubscript{4} and making of heterostructured photocatalysts by coupling g-C\textsubscript{3}N\textsubscript{4} with other semiconductors [11].

Graphene is single layer of carbon atoms with 2-dimensional properties because of its unique properties such as extra ordinary optical, mechanical, thermal, large specific surface area and good intrinsic carrier mobility, it have been used in many application, including nanoelectronics, biosensing, polymer composites, supercapacitors, Li-ion batteries and catalysis [12-15]. Graphene and its derivatives such as Graphene Oxide (GO) is combined with other materials (GO/g-C\textsubscript{3}N\textsubscript{4}, graphene/SnO\textsubscript{2}, graphene/CdS, Ag/AgX/GO) in order to improved photocatalytic activity [16-20].

In this study, by cowrapping α-S\textsubscript{8} with graphitic carbon nitride nanorods and graphene sheets, a metal-free heterojunction photocatalysts was successfully synthesized for photocatalytic degradation of Acid Blue 92 (AB92) under visible-light irradiation.

2. Materials and methods

In synthesis of GO, all of reagents were purchased from Sigma Aldrich and Triton X-100 (TX-100) (Merck, Germany) Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} (Fisher Scientific, Hong Kong) Hcl 37% (Merck, Germany) melamine (Aldrich, 99%). All materials were used without purification. GO was synthesized by oxidative treatment of graphite powder according to a modified Hummers’ method [21].

1.0 g of graphite powder and 0.5 g of sodium nitrate (NaNO\textsubscript{3}) was dispersed in 24 mL of concentrated sulfuric acid (H\textsubscript{2}SO\textsubscript{4}, 98%) and was put in an ice-bath under stirring for 30 min. 3.0 g of potassium permanganate (KMnO\textsubscript{4}) was added slowly into the above mixture to appear a brown color at room temperature. Then 30 mL of DI water was slowly added into the brown paste and then stirred for 24 h. Afterward, 3.5 mL of hydrogen dioxide (H\textsubscript{2}O\textsubscript{2}, 30 wt%) was added drop by drop to complete the oxidation process. The precipitate was washed with diluted HCl solution several times and dried at 80 °C for 12 h.

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In the second step, 100 mg of the GO powder was dispersed in 100 ml of water by sonicating it for 2 hours and then refluxed for 2 hours at 70 °C with 20 ml of hydrazine hydrate to facilitate the reduction [22]. The solution then changed its color to black, indicating the complete reduction of the GO sheets. Bulk g-C₃N₄ sheets were fabricated by pyrolysis of melamine in a crucible with a cover in air [22]. Typically, 20 g of melamine powder was put into an alumina crucible with a cover then the crucible was heated to 550°C at a rate of 2.3 °C/min in a muffle furnace and maintained at this temperature for another 4h. After, cooling to room temperature, the light yellow product was collected and milled to powder. The fabrication procedure of the g-C₃N₄ nanorods was as follows: 3 g of the as-prepared g-C₃N₄ nanoplates was placed a round-bottom, then ultrasound for about 1 hour. Then, 100 mL of methanol was added and refluxed for 3h, after cooling and washing, it was dried at 80 °C [23].

Synthesis of PCNRGOS₈: 3 mL 1% Triton X-100 (TX-100) aqueous solution was added in 250 mL water at about 50 °C and then 1.5 g Na₂S₂O₃ was added to the above solution. The solution was heated to 70 °C in an oil bath. After that 12 mL of HCl 37% was added to the Na₂S₂O₃ solution, and the system was at this temperature for 5 min under magnetic stirring. After 15 min, 10 mL PCN nanorods [24] solution (1 mg/mL) was added for further coating on RGO-wrapped sulfur particles. After 15 min, the reaction was allowed to cool to room temperature. The products was filtered and washed with DI water until pH=7, Then was dried under vacuum [1].

3. Results and discussion

The pure α-S₈ without RGO or PCN wrapping indicated negligible photocatalytic activity. wrapping α-S₈ with RGO sheets and PCN nanorods would improve
the photocatalitic activity efficiency because of the forming type II heterojunction by coupling PCN with α-Ss and excellent electron conductivity by wrapping RGO on α-Ss [fig. 1], all the photocatalytic experiments, no degradation was observed in light control (light irradiation without catalysts) and dark control (catalysts without light irradiation) experiments [fig. 2]. As shown in fig. 1 the photoinduced e− in the CB of PCN nanorods could shift to the CB of α-Ss by RGO sheets, while the photoinduced h+ in the VB of α-Ss could displace to the VB of CN by RGO sheets. Electrons generated in eq. 1 were trapped by O2 to make ‘O2−’ [eq. 2] and the reduction potential of CB electrons in α-Ss was negative enough to reduce O2 to ‘O2−’, and then ‘O2−’ radicals combined with H2O to be further transformed to ‘OH [eqs. 3, 5]. Moreover, the oxidation potential of VB holes in α-Ss was positive enough to oxidize H2O to ‘OH [eq. 6]. These reactive species (h+, ‘OH, ‘O2−, etc.) could degrade AB92 [eq. 7].

1) CNRGO8 + hv → e− + h+
2) O2 + e− → O2−
3) ‘O2− + H+ → OOH
4) ‘OOH + H+ → H2O2
5) H2O2 → ‘OH + OH
6) h+ + H2O → ‘OH + H
7) h+, ‘O2−, ‘OH + AB92 → degradation product

We investigated the effect of these reactive species on the photodegradation of AB92 in degradation process by different scavengers (iodide ion, AgNO3). When KI was used to trap both h+ and ‘OH, the degradation rate significantly decreased. As shown in Fig. 4, when AgNO3 was used as electron scavengers, the degradation of AB92 significantly increased.

So that the degradation efficiency was 53.16% in 90 min−1. The results indicated that h+ and then ‘OH are the main reactive species in the photocatalytic degradation of AB92 under visible light irradiation [fig. 3]. The removal percentage of AB92 was 22.78% by PCNRGO8 (without scavenger) after 120 min under visible-light irradiation [fig. 2]. To quantitatively determine the reaction kinetics of AB92 photodegradation by the as-prepared samples, the experimental data were fitted with the pseudo-first-order model, ln(Ct/C0) = kt, where k was the apparent first-order rate constant. All plots of ln(Ct/C0) against t exhibited linear trends [fig. 4].

The FT-IR spectra of the synthesized nanocomposite was shown in Fig. 4. Several strong bands in the 1200–1650 cm−1 region and the peaks at about 1245, 1320, 1405, 1571, and 1634 cm−1 related to the typical stretching modes of PCN heterocycles. In addition, peak at about 810 cm−1 corresponded to breathing mode of triazine units. There are the peaks of C=S and C=S stretching vibrations at about 1211 cm−1 and 470 cm−1 respectively. In PCNRGO8 nanocomposite the bands for PCN sheets still seen, and also the peaks at about 1557 cm−1 and at 3460 cm−1 demonstrating the presence of RGO sheets in the nanocomposite [Fig. 5] [1].

4. Conclusions

PCNRGO8 successfully fabricated and its photocatalytic activity was investigated under visible-light irradiation. These results significantly exhibited good photocatalytic activity in the present of AgNO3. Using of PCN nanorods in nanocomposite were improved the photocatalytic activity of PCNRGO8 nanocomposite because of its high surface area and enhanced quantum efficiency due to type II heterojunction via coupling PCN with α-Ss.
5. References