Construction Of 2D Porous Graphitic C\textsubscript{3}N\textsubscript{4} Nanosheets/SnS\textsubscript{2} Photocatalysts For Enhanced Degradation Of Pollution

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Abstract. The 2D porous graphitic C\textsubscript{3}N\textsubscript{4} nanosheets/SnS\textsubscript{2} was synthesized by the simple in situ hydrothermal method. In this work, the 2D porous graphitic C\textsubscript{3}N\textsubscript{4} nanosheets was prepared by pyrolysis method, and then SnS\textsubscript{2} was grown on porous g-C\textsubscript{3}N\textsubscript{4} sheets by the hydrothermal method. The visible light responsive characteristics were assessed by the degradation of methyl orange dye under visible light illumination and the results showed that the 2D porous g-C\textsubscript{3}N\textsubscript{4} nanosheets/SnS\textsubscript{2} heterostructure has a better photodegradation ability compared with the pure g-C\textsubscript{3}N\textsubscript{4} and SnS\textsubscript{2}. The superior performance was attributed to the narrow band gap, higher surface area, unique 3D structure and interfacial transportation of charge carriers.

1. Introduction

Since the dawn of the industrial age, the excessive development and utilization of the fossil fuels, such as coal, oil and natural gas resources, caused serious environmental pollution and energy shortage problem.\textsuperscript{[1]} Fortunately, the photocatalytic technology, with directly using the solar energy water decomposition hydrogen or degradation of pollutants and not producing secondary pollution, is regarded as an efficient way to solve the problem of environmental pollution and energy green cleaning method.\textsuperscript{[2,3]} Especially the g-C\textsubscript{3}N\textsubscript{4} due to its narrower band gap for remarkable wide spectrum absorption, has attracted wide attention.\textsuperscript{[4,5]} However, the highly recombination rate of photogenerated electrons-holes and smaller surface area in graphite phase carbon nitride would lead the lower efficiency of photocatalytic degradation of pollutants and decrease the utilization efficiency of visible light.\textsuperscript{[6-11]} Hence, how to increase such problems would be an important way to improve the photocatalysis.

Currently, the n-type semiconductor of SnS\textsubscript{2}, with the non-poisonous, relatively inexpensive, physical-chemically stability and a narrower band gap (2.2–2.35 eV), is considered as a suitable candidate for the effective utilization of solar energy.\textsuperscript{[12-14]} By calculation, the SnS\textsubscript{2} and g-C\textsubscript{3}N\textsubscript{4} have matching band potentials to extend the visible light response and photoinduced charge separation efficiency of heterostructure materials substantially.\textsuperscript{[15]} The 2D porous g-C\textsubscript{3}N\textsubscript{4} nanosheets/SnS\textsubscript{2} heterojunction nanosheets exhibit significant enhancement on the photocatalytic activities as compared to pure g-C\textsubscript{3}N\textsubscript{4} and SnS\textsubscript{2} due to the highly effective charge separation.

In this work, we synthesized the 2D porous graphitic C\textsubscript{3}N\textsubscript{4} nanosheets/SnS\textsubscript{2} heterostructures by hydrothermal method. Compared with the pure 2D porous graphitic C\textsubscript{3}N\textsubscript{4} nanosheets or SnS\textsubscript{2}, the SnS\textsubscript{2} modified g-C\textsubscript{3}N\textsubscript{4} heterojunction exhibit an obvious enhancement in photodegradation.
2. Experiment

2.1. Materials
All the chemicals are analytical grade and purchased from Aladdin Industrial Corporation (shanghai, China).

2.2. Synthesis of the 2D Porous Graphitic C3N4 nanosheets
The 2D porous g-C₃N₄ nanosheets were synthesized by typical pyrolysis method,⁴⁶ 5 g of urea was placed in a furnace, which was heated to 550 ºC at a rate of 2 ºC min⁻¹ and maintained at 550 ºC for 4 h. The resulting yellow powder was washed with deionized water and dried in a vacuum oven at 60 ºC.

2.3. Fabrication of the 2D Porous Graphitic C3N4 nanosheets/SnS2 heterostructures
The 2D porous graphitic C₃N₄ nanosheets/SnS₂ heterostructures was synthesized using a simple solvothermal method, in which g - C₃N₄ powder(180 mg) with ultrasonic 2h , and then a certain amount of SnCl₄ · 5 H₂O and thiourea (TAA) dissolved in the above suspension, the resulting suspension stirring 30 minutes, then transfer the mixture to 25 ml at 160 ºC for 12 h in the Teflon-lined autoclave. The pale yellow complex was resulted, and then was centrifuged and washed with distilled water and ethanol before being dried at 60 ºC in air overnight.

2.4. Characterization
The phase composition of the as-prepared samples were determined by X-ray diffraction (XRD, Bruker D8 Discover) using Cu Kα (λ = 1.5406 Å) radiation at 40 kV and 40 mA. The micromorphology of the samples were characterized by scanning electron microscopy (FESEM Hitachi S-4800) and transmission electron microscopy (TEM JEM-2100). The PL spectra were recorded by a Hitachi F-7000 spectrofluorimeter at the excitation wavelength of 330 nm. The UV-vis diffuse reflectance spectra were obtained by the UV-vis spectrophotometer (Hitachi-U3900).

2.5. Photocatalytic activity
Photocatalytic activity of the 2D porous graphitic C₃N₄ nanosheets/SnS₂ heterostructures was evaluated by monitoring the photodegradation of methyl orange aqueous solution under UV light irradiation. In the photodegradation experiments, 25 mg the 2D porous graphitic C₃N₄ nanosheets/SnS₂ heterostructures was put in MO aqueous solution(50 ml,5 mg/L). The solution was stirred in the dark for 30 min to reach adsorption–desorption equilibrium between the organic dye and the catalyst surface. Then under magnetic stirring, the mixed solution was irradiated UV light. The relative concentration of methyl orange in the solution was determined by comparing the UV–vis absorption intensity with that of the initial methyl orange solution.

3. Results and discussions
Fig. 1. The XRD spectra of the porous g-C3N4 nanosheets modified with different ratio of SnS2.

X-ray diffraction patterns of the 2D porous graphitic C3N4 nanosheets/SnS2 heterostructures are shown in figure 1. The obvious diffraction peaks at 28 ° peak corresponds to the (002) crystal plane of g-C3N4, compared with the pure porous carbon nitride. 2D porous graphitic C3N4 nanosheets/SnS2, this suggests that the layer porous carbon nitride basically is not affected by the introduction of SnS2 material. Two characteristic peaks on the XRD pattern of SnS2 is ascribed to the 2T-type hexagonal berndtite SnS2(JCPDS, no. 23-677).

Fig.2. The SEM of (a) porous g-C3N4 nanosheets, (b) SnS2, (c) Porous Graphitic C3N4 nanosheets/10%SnS2.

The morphology of photocatalyst was observed in Fig.2. The porous carbon nitride in fig.2 is composed of a number of curved nanomaterials with laminar morphology. It is produced by amino bubbles during the pyrolysis of urea. The gases released contribute to the expansion of the stack, leading to the formation of several layers and porous structures. As shown in figure 2, the prepared SnS2 is a typical nanobar structure. With the loading of SnS2, the porous nitride carbon sheet layer is rough. This indicates that SnS2 is loaded on the porous nitride carbon nanosheets.
Fig. 3. The UV-vis absorption spectra of porous g-C\textsubscript{3}N\textsubscript{4} nanosheets modified with different ratio of SnS\textsubscript{2} and pure porous g-C\textsubscript{3}N\textsubscript{4} nanosheets

The UV-vis diffuse reflectance spectra of the synthesized porous carbon nitride and 2D porous graphitic C\textsubscript{3}N\textsubscript{4} nanosheets/SnS\textsubscript{2} heterostructures are shown in fig. 3. As shown in figure 3, the absorption of the composite material has a significant red shift, which may lead to enhanced photocatalytic performance in the visible light region. Compared with porous carbon nitride, the absorption peak value of the porous graphitic C\textsubscript{3}N\textsubscript{4} nanosheets/SnS\textsubscript{2} heterostructures was increased significantly. In addition, porous graphitic C\textsubscript{3}N\textsubscript{4} nanosheets/SnS\textsubscript{2} heterostructures absorption edge shifted to the long wavelength region, which can produce more electron hole pair under visible light irradiation, and thus lead to the higher photocatalytic activity.

Fig. 4. The PL of (a) pure porous g-C\textsubscript{3}N\textsubscript{4} and (b) the porous graphitic C\textsubscript{3}N\textsubscript{4} nanosheets/10wt\%SnS\textsubscript{2} heterostructures

Fig. 4 displays The PL of the porous graphitic C\textsubscript{3}N\textsubscript{4} nanosheets/10wt\%SnS\textsubscript{2} heterostructures and pure porous g-C\textsubscript{3}N\textsubscript{4}. It can be seen from figure 5 that the peak value of between the porous graphitic C\textsubscript{3}N\textsubscript{4} nanosheets/10wt\%SnS\textsubscript{2} is lower than that pure porous g-C\textsubscript{3}N\textsubscript{4}, which indicates that the separation efficiency of photoelectron and hole is improved.
Fig. 5. Photocatalytic degradation curves of MO over the as-fabricated products under visible light irradiation ($C_0=5\text{mg L}^{-1}$; photocatalyst:25 mg; MO:50ml).

Fig. 5 shows the photocatalytic degradation curves of as-fabricated products under visible light irradiation. These photodegradation ratios are much higher than the corresponding degradation ratios of above pollutants when using pure porous g-C$_3$N$_4$ nanosheets and SnS$_2$. It can be seen from the figure 5 that the degradation rate of the porous graphitic C$_3$N$_4$ nanosheets/10wt%SnS$_2$ heterostructures to MO is higher than of pure porous g-C$_3$N$_4$ nanosheets and SnS$_2$. When the loading capacity of SnS$_2$ is 10wt%, the degradation rate is the highest. The photocatalytic performance is improved due to increasing the migration rate of photogenic carriers when loading SnS$_2$ on porous g-C$_3$N$_4$ nanosheets. It matches the results of the PL.

4. Conclusions
In our work, we have successfully prepared the porous graphitic C$_3$N$_4$ nanosheets/SnS$_2$ heterostructures by the hydrothermal method. The degradation efficiency of the porous graphitic C$_3$N$_4$ nanosheets/SnS$_2$ heterostructures for MO is greater than pure porous g-C$_3$N$_4$ nanosheets and SnS$_2$ due to the porous structure and the rapid generation, separation and transportation of photogenic carriers. Therefore, the porous graphitic C$_3$N$_4$ nanosheets/SnS$_2$ heterostructures is a promising photocatalyst.

Acknowledgment
This work was supported by Natural Science Foundation of China(Nos. 51672249), Zhejiang Provincial Natural Science Foundation of China (Nos. LQ17F040004).

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