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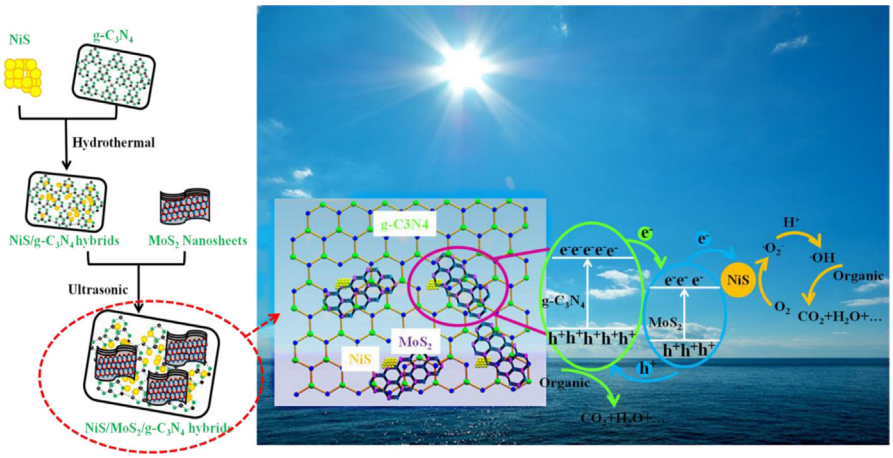
NiS and MoS_2 nanosheet co-modified graphitic C_3N_4 ternary heterostructure for high efficient visible light photodegradation of antibiotic

Xuejun Lu[a], Yu Wang[a], Xinyi Zhang[b], Guangqing Xu[a], Dongmei Wang[a], Jun Lv[a,*], Zhixiang Zheng[a], Yucheng Wu[a,c,**]

[a] Laboratory of Functional Nanomaterials and Devices, School of Materials Sciences and Engineering, Hefei University of Technology, Hefei 230009, China
[b] School of Chemistry, Monash University, Clayton, VIC3800, Australia
[c] Anhui Provincial Key Laboratory of Advanced Functional Materials and Devices, Hefei University of Technology, Hefei 230009, China

GRAPHICAL ABSTRACT



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ABSTRACT

The development of efficient solar driven catalytic system for the degradation of antibiotics has become increasingly important in environmental protection and remediation. Non-noble-metal NiS and MoS_2 nanosheet co-modified graphitic C_3N_4 ternary heterostructure has been synthesized via a facile combination of hydrothermal and ultrasound method, and the ternary heterostructure has been utilized for photocatalytic degradation of antibiotic agents. The antibiotics of ciprofloxacin (CIP) and tetracycline hydrochloride (TC) were photodegraded by the hybrid under the visible light. The optimal photodegradation rate of the ternary heterostructure reaches about 96% after 2 h irradiation, which is 2.1 times higher than that of pure g-C_3N_4 for TC degradation. The photocatalytic degradation rates of the ternary heterostructure for both CIP and TC obey the pseudo-first-order kinetic model. The enhanced visible

* Corresponding author.
** Corresponding author at: Laboratory of Functional Nanomaterials and Devices, School of Materials Sciences and Engineering, Hefei University of Technology, Hefei, 230009, China.
E-mail addresses: lvjun117@126.com (J. Lv), ycwu@hfut.edu.cn (Y. Wu).

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light adsorption and charge separation efficiency contribute to the photocatalytic performance of the ternary heterostructure. This work provides new insights and pathways by which efficient degradation of antibiotics can be achieved and will stimulate further studies in this important field.

1. Introduction

There has been an increasing demand for new environmental remediation technologies due to the greater awareness and concern about environmental pollution. In particular, a large amount of broad-spectrum antibiotics, such as ciprofloxacin (CIP) and tetracycline hydrochloride (TC) for therapeutic use, pollute increasingly lakes, rivers and seas, causing various adverse influence on ecosystem and great threats to the human health [1–3]. Therefore, it is urgent to find a green and sustainable way to tackle the antibiotic pollution in the aquatic environment. Among potential solutions, semiconductor-based photocatalysis using inexhaustible solar light as a driving force has emerged as one of the most fascinating technologies for degradation of organic pollutants [4,5], hydrogen production [6–8] and CO_2 reduction [9]. However, catalyst efficiency and cost are key challenges that have limited the practical development of photocatalysts. Antibiotics are relatively more difficult to be photodegraded in comparison with other water pollutants such as dyes [10–13]. Thus, to study new effective photocatalysis with higher antibiotic degradation efficiency is highly necesarry.

Metal-free Graphitic C_3N_4 (g-C_3N_4) with heptazine ring structure and high condensation degree possesses many advantages, such as easy preparation, good stability and suitable band gaps (2.7 eV) [14,15], which make it a promising photocatalyst. Nevertheless, low charge mobility, high recombination rate and low specific area lead to the low photocatalytic efficiency under visible light irradiation for this potential photocatalyst [16]. Consequently, applying a hybrid system (binary or ternary hybrids system) would be a better way to solve the problem. Meanwhile, g-C_3N_4-based heterostructures can be formed by hybridizing with other photocatalytic semiconductor materials due to its unique two-dimensional layered structure [17,18]. Furthermore, some approaches have been adopted to improve the photocatalytic efficiency of g-C_3N_4, such as the formation of surface coupling hybridization [7] and construction of mesoporous structure [19]. Among them, MoS_2 has been one of the most studied transition metal dichalcogenides (TMDs), owing to its changeable layered structures with variable band energies [20,21]. A few researches have reported the formation of MoS_2/g-C_3N_4 heterostructure [5,22,23], which can efficiently enhance the visible-light absorption and accelerate the separation of photogenerated electron-hole pairs due to their well matched band energy alignment and the increase of active sites [24,25]. In our previous work, we have synthesized MoS_2/g-C_3N_4 hybrids via a facile bathing and ultrasound way [26], which greatly improves the photocatalytic activity under visible light irradiation. However, it is believed that there are still opportunities to further promote its photocatalytic performance. Ni compound/g-C_3N_4 co-photocatalysts have received much attention because of their low cost and excellent photocatalytic activity [8,27,28]. Among Ni compound, Ni chalcogenides are considered as promising candidates. Non-noble-metal NiS/g-C_3N_4 co-catalyst has been chosen to replace noble-metal Pt co-catalyst to construct the co-catalysts [29–31]. After the addition of NiS co-catalyst, MoS_2/g-C_3N_4 hybrids can achieve a significant photocatalytic activity enhancement with great kinetics improvement resulted from the extended lifetime of photogenerated electrons [32,33]. However, to the best of our knowledge, there is no available report about photocatalytic degradation of organics by a g-C_3N_4 ternary hybrid co-modified with both NiS and MoS_2 nanosheets.

In this work, NiS was added through hydrothermal method to synthesize the NiS/g-C_3N_4 hybrids, and then NiS/MoS_2/g-C_3N_4 ternary hybrids were synthesized via a facile ultrasound and bathing method. Comparing to pure g-C_3N_4 and binary hybrids of NiS/g-C_3N_4 or MoS_2/g-C_3N_4, significantly enhanced visible light photocatalytic performance of ternary NiS/MoS_2/g-C_3N_4 hybrids was achieved. Furmore, the effect of NiS loading amount on the photocatalytic activity of the ternary hybrids for photodegradation of simulative pollutant methyl orange (MO) and practical antibiotic agents (CIP and TC) was investigated. Besides, a possible photocatalytic mechanism was proposed.

2. Experimentals

2.1. Synthesis of NiS/g-C_3N_4 hybrids

In a typical procedure of producing NiS/g-C_3N_4 hybrids: 150 mg as-prepared g-C_3N_4 and an appropriate amount of thiourea were dissolved into 30 mL and 10 mL distilled water respectively. After being ultrasonic treated for 30 min, a given volume of 0.5 M $Ni(NO_3)_2$ solution was dropped into g-C_3N_4 dispersion and kept stirring for 30 min. Then, the 10 mL thiourea solution was slowly added into the solution. The molar ratio of $Ni(NO_3)_2$/thiourea was fixed at 1:3. After that the mixed suspension was transferred into a Teflon-lined stainless autoclave and kept at 200 °C for 6 h in an oven before cooling down to the room temperature. Finally, the sample was collected, washed with ethanol and distilled water several times, dried at 60 °C for 10 h.

2.2. Synthesis of NiS/MoS_2/g-C_3N_4 hybrids

NiS/MoS_2/g-C_3N_4 hybrids were synthesized via the bathing and ultrasound method described in Fig. 1. The weight ratios (X) of both NiS to (NiS + g-C_3N_4) and NiS to (NiS + MoS_2 + g-C_3N_4) are 0.5, 1, 3, 5 and 7 (wt%), respectively. Obtained samples are denoted as X-NiS/C and X-NiS/MC, in which M and C represent for MoS_2 and g-C_3N_4 respectively.

3. Results and discussion

3.1. Phases and microstructure analysis

The crystalline structures of as-prepared samples were investigated with X-ray diffraction (XRD). The XRD patterns of pure g-C_3N_4 and NiS/g-C_3N_4 photocatalysts with different amount of NiS are shown in Fig. 2(a). Two distinct diffraction peaks are observed from all samples at approximately 12.9° and 27.6° which are indexed to the (100) and (002) planes of g-C_3N_4 (JCPDS file no. 87-1526). The results agree with that of our previous work and in the literature [26,32]. Besides, the strong peak at 27.6 °corresponds to an interlayer distance of 0.32 nm and is a characteristic interlayer stacking reflection of conjugated aromatic system, indicating that as-prepared g-C_3N_4 is well crystallized. Furthermore, it is also observed from Fig. 2(a) that the characteristic peaks at 30.1°, 34.4°,