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Two-dimensional mesoporous g-C_3N_4 nanosheet-supported $MgIn_2S_4$ nanoplates as visible-light-active heterostructures for enhanced photocatalytic activity

Wei Chen [a], Yu-Xiang Hua [a], Ying Wang [b], Ting Huang [a], Tian-Yu Liu [a], Xiao-Heng Liu [a,*]

[a] Key Laboratory of Education Ministry for Soft Chemistry and Functional Materials, Nanjing University of Science and Technology, Nanjing 210094, China
[b] School of Metallurgy and Environment, Central South University, Changsha, Hunan 410083, China

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ABSTRACT

A series of novel visible-light-driven $MgIn_2S_4$/g-C_3N_4 (MISCN) heterostructures were fabricated in situ by a simple one-pot hydrothermal method. The synthesis of the $MgIn_2S_4$ (MIS) nanoplates and the construction of intimate interfacial contacts by loading MIS nanoplates onto mesoporous g-C_3N_4 (CN) nanosheets were achieved simultaneously in a hydrothermal environment. Systematic characterization, including powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), UV–vis diffuse reflection spectroscopy (UV–vis DRS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), Brunauer–Emmett–Teller (BET), X-ray photoelectron spectroscopy (XPS), and photoelectrochemical measurements were employed to analyze the phase structure, chemical composition, absorption properties, microstructure, and photocatalytic mechanism. The as-prepared MISCN photocatalysts exhibit improved photocatalytic activity for 4-nitroaniline (4-NA) reduction and methyl orange (MO) degradation as compared with pure MIS nanoplates and pristine CN nanosheets under visible light irradiation. The enhancement of photocatalytic performance can be attributed to faster charge separation and transport benefitting from the construction of tight heterogeneous interfaces and band offset structure between MIS nanoplates and mesoporous CN nanosheets. This investigation may be extended to explore and fabricate the novel and highly efficient visible-light-driven g-C_3N_4-based heterostructures for organic transformations and pollutant removal.

1. Introduction

Solar light harvesting by semiconductors to convert solar energy into chemical energy is considered a promising way to solve the crisis that mankind has faced as a result of environmental pollution and energy shortage since the pioneer work done by Fujishima and Honda, who first reported photoelectrochemical water splitting for hydrogen evolution on a titanium dioxide (TiO_2) electrode under ultraviolet light irradiation [1]. It is well known that pure TiO_2 is not able to make the best use of solar energy because it is endowed with a broad band gap only corresponding to ultraviolet absorption and thus it is unlikely that pure TiO_2 will meet the requirements of practical application [2,3]. To enhance the efficiency of solar light utilization, the design and creation of simple yet stable photocatalysts with highly efficient visible light response is highly desired in the photocatalytic field. Recent years have witnessed ever-increasing interest in the construction of ternary chalcogenide AB_2X_4 (A = Zn, Cd, Ca, Cu; B = In, Ga, Al; X = S, Se, Te) semiconductors as visible-light-active photocatalysts for potential application in photocatalytic fields due to their unique electronic structure, tunable optical properties, and appropriate band gaps and band edges, such as photocatalytic pollutant degradation [4–7], photocatalytic hydrogen production from H_2S or water splitting [8–10], photocatalytic carbon dioxide reduction [11,12], and photochemical organic syntheses [13]. Although great efforts have been devoted to synthesizing different types of AB_2X_4 semiconductors, the isolated AB_2X_4 photocatalysts still exhibit unsatisfactory photocatalytic activity because of the relatively high recombination rate of photoexcited hole and electron pairs as compared with other highly efficient semiconductors, such as cadmium sulfide. In addition, the sulfide-based AB_2X_4 photocatalysts suffer the critical drawback of remarkable photocorro-

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* Corresponding author. Fax: +86 25 84315054.
E-mail address: xhliu@mail.njust.edu.cn (X.-H. Liu).

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sion with light irradiation, leading to short lifetimes for recycling reusability.

Thus, to overcome these obstacles, diverse strategies, including morphology regulation [14,15], element doping [16,17], metal loading [18,19], and heterogeneous coupling [20,21], have been developed to raise their photocatalytic activity and meanwhile reinforce their stability for photocorrosion resistance. Among these modification strategies, heterogeneous coupling is becoming a research focus because of its contribution to fabricating efficient and stable photocatalysts with nanosized interfacial contacts. This interfacial design not only facilitates the faster transfer of charge carriers, but also is conducive to strengthening the photostability of as-obtained photocatalysts. Jo et al. [22] fabricated hierarchically structured $ZnIn_2S_4$ marigold flower/Bi_2WO_6 flowerlike nanoarchitectures by a combination of the hydrothermal route and the wet impregnation method, which exhibit highly efficient visible light-responsive photocatalytic activity for degradation of metronidazole and still maintain highly efficient photocatalytic performance even after successive irradiation for 1000 min. Yu et al. [23] reported the improvement of photocatalytic activity and photocorrosion resistance for hydrogen evolution from water splitting under visible light irradiation using hydrothermally prepared $ZnIn_2S_4$/$CdIn_2S_4$ nanocomposites. This researches reveals that it is feasible to optimize AB_2X_4 by the fabrication of AB_2X_4-based nanostructures.

Metal-free graphitic carbon nitride (g-C_3N_4) has attracted great attention because of abundant availability of precursors, simple synthesis, suitable band positions, and excellent stability in different chemical environments [24–27]. Usually, several precursors, such as melamine, cyanamide, dicyandiamide, and urea, were used to synthesize bulk g-C_3N_4 (BCN) by polycondensation. As-prepared BCN is in the form of a graphitic stacking structure, which assembles from a two-dimensional nanosheet plane mainly constructed from tri-s-triazine units by weak van der Waals forces. According to previous reports, BCN possesses a narrow band gap with a value of 2.7 eV, and its conduction band (CB) is located at −1.13 eV [28,29]. The narrow band gap and negative CB make it a competent candidate to act as a sensitizer. Until now, many papers about the sensitization of BCN have been reported via the careful design and construction of BCN-based nanocomposites. Qiu et al. [30] designed a mixed solvent route to prepare flower-on-sheet $ZnIn_2S_4$/g-C_3N_4 nanocomposites for improved photocatalytic decomposition of 2,4-dichlorophenoxyacetic acid. Chen's group [31] reported the interfacial engineering of $CaIn_2S_4$/g-C_3N_4 nanocomposites with enhanced photocatalytic performance for hydrogen generation and MO degradation. In these hybrid frameworks, the electrons generated in CB of BCN tend to transfer to that of counterpart semiconductors, and then the electron-rich CB on the counterpart will attend to the photocatalytic reaction. However, the photocatalytic performance of this hybrid system would be largely limited by the BCN. On one hand, the BCN exhibits poor photocatalytic quantum efficiency, only 0.1% at irradiation wavelengths from 420 to 460 nm as a result of the formation of interior defects during the high-temperature preparation process, which would promote the recombination of photogenerated holes and electrons during their migration from the bulk to the surface of BCN [32]. Obviously, the presence of interior defects decreases the concentration of effective photoinduced electrons, which indicates that the BCN is not ideal to serve as a sensitizer for coupling with other semiconductors. On the other hand, considering that the CB of BCN is more negative in the heterostructure, its main role is to transfer photogenerated electron to its partner, rather than to provide catalytic sites for the photocatalytic reduction process. Based on these investigations, we hold the view that prepared nanocomposites would be expected to exhibit highly efficient photocatalytic activity if the transfer path of photogenerated electrons could be modulated to accumulate on the CB of g-C_3N_4. Therefore, the following points should be taken into account for successful regulation: (1) to prepare ultrathin CN nanosheets with more exposed surfaces to provide more surface-active sites; (2) to decrease the CB potential of CN to accept photo-generated electrons from a coupled other semiconductor; (3) to have more effective electrons generated by counterpart semiconductors.

Here, we design a feasible template-free route, involving frozen expansion pretreatment followed by thermal post-exfoliation, to synthesize ultrathin CN nanosheets with mesoporous structures. The results from Mott–Schottky curves reveal that the CB of mesoporous CN ultrathin nanosheets presents a significant downward shift compared with BCN, and its CB is determined to be −0.33 V vs. a normal hydrogen electrode (NHE). There is no doubt that the decreased CB position would make it easier for CN to accept photogenerated electrons from its partner than using BCN. What is more, the mesoporous CN ultrathin nanosheets are able to function as a supporting platform to immobilize AB_2X_4 to generate a tight heterogeneous interface. After assessment of the band gap and band potential of AB_2X_4, we select $MgIn_2S_4$(MIS) as a counterpart semiconductor to construct a well-matched band structure between CN and AB_2X_4, which would induce efficient photogenerated electron separation from MIS to CN. A simple one-step hydrothermal route was adopted to fabricate the MISCN nanocomposites for the first time with different addition of mesoporous CN nanosheets. The as-obtained MISCN nanocomposites were systematically characterized by analyzing their phase structure, chemical composition, microstructure, etc. The photocatalytic activity of prepared MISCN nanocomposites was evaluated by selective reduction for 4-NA transformation and photocatalytic degradation for MO removal.

2. Experimental

2.1. Materials

Melamine ($C_6H_6N_6$, AR), magnesium nitrate hexahydrate ($Mg(NO_3)_2{\cdot}6H_2O$, AR), indium nitrate hydrate ($In(NO_3)_3{\cdot}4.5H_2O$, AR), thioacetamide (TAA, AR), and 4-nitroaniline (4-NA) were bought from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Ammonium formate (CH_5NO_2, AR) was obtained from Aladdin Industrial Corporation. All reagents were used as provided without further purification.

2.2. Catalyst preparation

The mesoporous g-C_3N_4 (CN) ultrathin nanosheets were prepared by exfoliation from a corresponding bulk CN (BCN) sample. In detail, the bulk CN was dispersed into hot water to guarantee sufficient water absorption for swelling. Subsequent low-temperature freezing was performed to expand the interlamellar spacing of layered CN. After unfreezing, the collected products were heated at 550 °C for 4 h to obtain mesoporous g-C_3N_4 ultrathin nanosheets. Here, the bulk CN was synthesized by thermal polycondensation of melamine at a heating rate of 2.3 $K{\cdot}min^{-1}$ to reach 550 °C and kept at this temperature for another 4 h in air. The $MgIn_2S_4$/g-C_3N_4 (MISCN) nanocomposite with different addition of mesoporous CN ultrathin nanosheets was synthesized by a simple hydrothermal route. The typical experimental procedure for fabricating these heteroarchitectures can be described as follows: A settled number of mesoporous CN ultrathin nanosheets were homogeneously dispersed into 70 mL of aqueous solution including magnesium nitrate hexahydrate (1 mmol, 0.256 g) and indium nitrate hydrate (2 mmol, 0.764 g) by sonication in an ultrasonic apparatus for 1 h. Then 8 mmol of thioacetamide was added