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Simultaneous nanostructure and heterojunction engineering of graphitic carbon nitride *via in situ* Ag doping for enhanced photoelectrochemical activity

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ABSTRACT

A novel mesoporous ternary photocatalyst consisting of g-C_3N_4 nanosheets, metallic silver and MoS_2 nanosheets is prepared using $AgNO_3$ as a multifunctional modifier during thermal polymerization of melamine and few-layer MoS_2 in a simple one-pot process. The gas bubbles from $AgNO_3$ form an extra soft templates to *in situ* alter the polymerization behavior of melamine, creating thin g-C_3N_4 nanosheets and large porous structure that exhibit enhanced light absorption. The solution-based, soft-chemical synthesis enables homogeneous inclusion of metallic silver in the g-C_3N_4 nanosheets and high dispersibility of ultrathin MoS_2 nanosheets in the obtained nanocomposite. *In situ* coupling between metallic silver and g-C_3N_4 nanosheets produces nanoscale Mott–Schottky effect, provides an effective channel for charge separation and transfer, and tunes energy band of the latter. More importantly, modulated energy band of g-C_3N_4 nanosheets synergistically expedites the separation and transfer of photogenerated electron–hole pairs at the interface of two-dimensional g-C_3N_4/MoS_2 heterojunction. As a result, the ternary nanocomposite exhibits improved photoelectrochemical performance and photocatalytic activity under simulated sunlight irradiation compared with other reference materials. Our results provide new insights into the design and large-scale production of semiconductor photocatalyst.

1. Introduction

High-performance semiconductor photocatalysis is important to solar cells, water splitting, and environmental control [1–4]. Among various semiconductors, layered graphitic carbon nitride (g-C_3N_4, denoted as CN) analogous to graphite is especially attractive to conversion of solar energy to electrical or chemical energy because of its abundance, appropriate bandgap (~2.7 eV) and excellent chemical stability [5–12]. However, broader application of pristine CN is seriously hampered due to various factors including high recombination rate of photogenerated electron–hole pairs, low absorption coefficients, or poor catalytic activities [6,7]. Hence, extensive effort has been devoted to improve pristine CN with high activity and good working stability. Doping with metal [13–15] or nonmetal elements [11,16–19] has been proposed to resolve low photocatalytic efficiency of pristine CN, and binary heterojunction nanocomposite has recently emerged to be effective in high-performance CN-based photocatalysis [3,4,20,21]. In particular, two main types of CN-based heterojunction photocatalysis have been explored. One is nanocomposite prepared by physical mixing or *in situ* growth of another semiconductor with pristine CN [7,22–25]. For example, layered MoS_2 is considered one of the ideal candidates for the construction of semiconductor heterojunction with pristine CN due to suitable bandgap of about 1.8 eV [9,26,27]. The other is nanocomposite of pristine CN modified by highly conductive carbon materials such as carbon nanotubes as well as graphene and its derivatives [28–32]. Novel CN nanostructures such as mesoporous derivatives [9–11,33–36], nanotubes [37], nanorods [38] and nanosheets [12] endowing the materials with desired surface properties and morphologies, provide shortened pathway to promote charge migration and separation as well as mass diffusion/transfer during photoredox

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reactions. The coupled mediator of graphene or its derivatives acts as an electron transport “highway” or electron sink to facilitate the separation of photogenerated electron–hole pairs [2], whereas *p*–*n* heterojunction between pristine CN and another semiconductor functions as an electron separator to suppress the recombination of the photogenerated electron–hole pairs efficiently [3,4,39]. In addition, the coupled semiconductor with a smaller bandgap can extend light absorption range to improve light absorption performance. As expected, these CN-based nanocomposites exhibit better photocatalytic performance in splitting water and degrading pollutants than pristine counterparts. Despite recent progresses on many types of nanostructured CN-based binary heterojunction photocatalysis, practical application is still not satisfactory. In particular, the study of structural and electronic compatibility between pristine CN and co-catalysts has been limited so far. It is thus highly desirable, albeit challenging to develop new strategies of constructing novel CN-based nanocomposites to further enhance photocatalytic efficiency.

Coupling pristine CN with few-layer MoS_2 to form two-dimensional (2D) semiconductor heterojunction is an effective structure and electronic compatibility strategy to improve photoconversion efficiency [9,10,40,41]. The 2D CN/MoS_2 heterojunction not only increases contact area for efficient charge transfer across the interface compared to zero-dimensional nanoparticles with only point contact, but also promote the separation of photogenerated electron–hole pairs due to shortened charge transport time and distance, thereby leading to the enhancement of overall photoconversion efficiency. Hou et al. reported that photocatalytic hydrogen evolution activity under visible-light irradiation was enhanced notably by producing thin layers of MoS_2 on mesoporous CN to form a 2D heterojunction [9]. Very recently, Chen et al. designed a 2D ternary nanojunction consisting of porous CN nanosheets, nitrogen-doped graphene, and layered MoS_2 [10]. This 2D ternary nanostructure exhibited a higher photocurrent density and photocatalytic activity than other reference materials under simulated sunlight irradiation since the introduced nitrogen-doped graphene interlayers worked as electron mediator for shuttling electrons and hole between the CN nanosheet and layered MoS_2 so that the separation of photogenerated electron–hole pairs was more effective. According to electrochemical analysis, the conduction-band and valence-band edge potentials of pristine CN have been determined at −1.13 and +1.57 eV, respectively [6,7,42]. The work functions of most noble metals are in between these two values, implying that the introduction of noble metal into pristine CN can produce a rectifying Mott–Schottky effect [42,43]. The formed Mott–Schottky effect extends the lifetime of charge carriers by enhancing the rate of electron–hole separation at noble metal–semiconductor interface. As a result, the catalytic performance of resulting hybrid catalyst is improved [44–48]. Hence, integrating 2D semiconductor heterojunction with Mott–Schottky effect is expected to be useful to construct high-performance CN-based photocatalysis.

Herein, we present the fabrication and characterization of mesoporous ternary nanocomposite consisting of CN nanosheets, metallic silver and MoS_2 nanosheets (denoted as CN–M–A). This ternary nanocomposite provides a broadening optical window for light harvesting and large contact area for fast interfacial charge separation and photoelectrochemical reactions. *In situ* coupling between metallic silver and CN nanosheets produces nanoscale Mott–Schottky effect, provides an effective channel for charge separation and transfer, and tunes energy band of the latter. More importantly, modulated energy band of CN nanosheets is helpful to the separation and transfer of photogenerated electron–hole pairs at the interface of 2D CN/MoS_2 heterojunction. As a result, the ternary nanocomposite is anticipated to exhibit good photoelectrochemical and photocatalytic activities under visible light irradiation.

2. Experimental

2.1. Materials synthesis

The typical synthesis procedure for CN is *via* thermal condensation of melamine powder. In details, melamine powder (5 g) was put into an alumina crucible with a cover. Then it was heated with a rate of 5 °C min^{-1} to 550 °C and kept this temperature for 4 h in air. The final yellow product was collected and ground with an agate mortar into powder. The ultrathin MoS_2 nanosheets with thickness about 5 nm (see Fig. S1) were prepared by hydrothermal intercalation and exfoliation method [49]. The procedure to prepare the CN–M–A ternary photocatalysis was as follows: 151 mg of $AgNO_3$ and 10 mg of MoS_2 ultrathin nanosheets were firstly dissolved in 5 mL deionized water with stirring. After being ultrasonicated for 30 min, melamine powder (5000 mg) was added to above suspension with stirring to make slurry. Finally, the slurry was thermally condensed with similar heating procedure and reaction time. With this method, CN–M–A ternary photocatalyst was obtained and ground with an agate mortar into powder for next characterization and testing. For comparison, binary photocatalysts of CN/Ag (denoted as CN–A) and CN/MoS_2 nanosheets (denoted as CN–M) were prepared using similar method without the presence of MoS_2 and $AgNO_3$, respectively.

2.2. Material characterization

The crystal structures of the synthesized samples were determined by powder X-ray diffraction (XRD, Rigaku, D/MAX 2500) using a copper Kα radiation source ($\lambda = 0.154$ nm). X-ray photoelectron spectroscopy (XPS) measurements were performed by Axis Ultra instrument using an Al Kα source (Kratos Analytical Ltd., UK). A binding energy of 284.8 eV for C 1s level was used as an internal. The morphology and microstructure of the samples were characterized using a field emission scanning electron microscopy (FESEM, Hitachi, S4800) with an energy dispersive spectroscope (EDS) and transmission electron microscopy (TEM, JEOL 2100) equipped with selected area electron diffraction (SAED). N_2 adsorption–desorption measurements were conducted on a Nove 2200e analyzer. Raman spectra were recorded on a Renishaw InVia system with a laser operating at $\lambda = 785$ nm as excitation source. Fourier transform infrared (FTIR) spectra measurements were carried out on a FTS-3000 Fourier transform infrared spectrophotometer with KBr as the reference sample. Diffuse-reflectance UV–vis absorbance spectra of the samples were obtained using a UV–vis spectrophotometer (Shimadzu, UV-2550) with $BaSO_4$ as a reflectance standard. Photoluminescence (PL) spectra of the samples were obtained using a fluorescence spectrometer (Perkin Elmer, LS55) with an excitation wavelength of 350 nm. All measurements were performed at room temperature.

2.3. Photocatalytic tests

The photocatalytic activities of the samples were evaluated by the degradation of Rhodamine B (RhB) using a Xe lamp with AM 1.5G filter as simulated sunlight. A UV-cutoff filter ($\lambda > 400$ nm) was added to allow only visible light to pass through. The incident visible-light intensity was measured using a Radiometer (Model FZ-A, Photoelectric Instrument Factory, Beijing Normal University). The illumination intensity was kept at 100 mW cm^{-2}. The photocatalytic experiments were conducted at ambient temperature as follows: 40 mg of photocatalyst were added to 80 mL aqueous solution of 10 mg L^{-1} RhB. Before irradiation, the suspensions