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Highly efficient solar-driven photocatalytic degradation on environmental pollutants over a novel C fibers@$MoSe_2$ nanoplates core-shell composite

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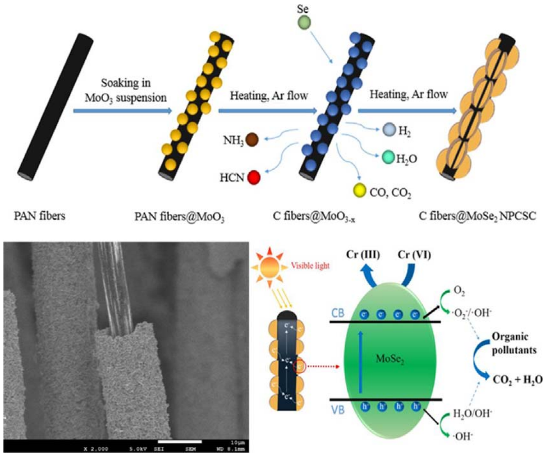
GRAPHICAL ABSTRACT



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ABSTRACT

As an important member of two-dimensional transition metal dichalcogenides, $MoSe_2$ has a wide range of photoelectrochemical properties. However, $MoSe_2$ alone can not directly be used as photocatalyst for its poor performance owing to the strong recombination of photogenerated electron-hole pairs. Here, we propose a novel C fibers@$MoSe_2$ nanoplates core-shell composite, which was prepared by a facile, one-step thermal evaporation method. The composite has a remarkable feature of numerous $MoSe_2$ thin nanoplates grown in-situ, densely and even vertically on the surface of the C fibers. Due to the effective separation of photogenerated electron-hole pairs promoted by the prompt transfer of photogenerated electrons through C fibers, compared with commercially available pure $MoSe_2$ powder, such composite exhibits greatly improved solar-driven photocatalytic activity and high stability for the degradation of various organic/inorganic environmental pollutants including methylene blue, rhodamine B, *p*-chlorophenol and $K_2Cr_2O_7$ aqueous solutions, showing the great potential for environmental remediation by degrading toxic industrial chemicals in waste water using sunlight. Moreover, this

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one-step thermal evaporation is an easy-handling, eco-friendly and low-cost synthesis method, which is suitable for large-scale production.

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1. Introduction

With the development of human society, the increasingly uncontrolled exploitation and use of fossil fuels have caused enormous environmental pollution, seriously threatening the survival of human beings. To date, it has become the focus of current researches to find efficient methods for environmental remediation. Among them, semiconductor-based photocatalysis is an effective way to degrade various pollutants together with the generation of new clean and renewable energy sources [1,2].

As an important member of two-dimensional graphene-like transition metal dichalcogenides, $MoSe_2$ has been widely applied. Because $MoSe_2$ possesses a low coefficient of friction, high chemical stability, large surface area, high surface activity and excellent catalytic activity, traditionally, it has been used for solid lubricants, high temperature and high pressure lubricants, and catalysts in oil processing industry for hydrogenation, desulfurization, and so on [3–5]. Recently, $MoSe_2$ has gained greater attention for various applications in energy storage, electrocatalysis, photocatalysis, photoelectronics, biosensors, and so on, due to its novel photoelectrochemical properties [6]. In particular, although the narrow band-gap (1.33–1.72 eV) and good resistance against photocorrosion of $MoSe_2$ offer it the possibility for high photocatalytic performance within the range of the solar spectrum, to the best of our knowledge, there are only a few reports on $MoSe_2$-based photocatalysts [7–12], possibly because of the low efficiency of light absorption, slow charge transfer, and strong recombination of photogenerated electron-hole pairs, among which the latter two phenomena are generally existed in semiconductor photocatalysts [6,13].

In order to reduce the recombination of photogenerated electron-hole pairs of semiconductor photocatalysts and promote the charge transfer, thus improving their photocatalytic efficiency, constructing composites of nanoscaled semiconductor photocatalysts with other catalysts or materials of good conductivity is an efficient way [14–16]. In particular, because carbon materials are highly conductive, non-toxic and generally low-cost, they are favorites to provide a channel for electron transfer to reduce the recombination of photogenerated electron-hole pairs in semiconductor photocatalysts and thus improve their activities [17–19]. Similarly, the composites of $MoSe_2$ nanostructures with carbon materials might also be desirable for photocatalytic applications.

In literature, there have been several reports working on $MoSe_2$/C composite nanomaterials. In 2013, Li et al. [3] successfully prepared the composites of $MoSe_2$ and reduced graphene oxide (rGO) by hydrothermal synthesis of $MoSe_2$ nanoflowers on rGO sheets. In 2015, Yang et al. [20] synthesized a $MoSe_2$/C nanofibers hybrid via chemical vapor deposition. Later, Liu et al. [21] successfully synthesized a sheet-like $MoSe_2$/C composite by using $Na_2MoO_4{\cdot}2H_2O$, Se powder and glucose as the source materials through a hydrothermal method and subsequent annealing treatment. In 2016, Wu et al. reported a hydrothermal synthesis method to prepare novel ultrathin $MoSe_2$ nanosheets perpendicular to graphene for the adsorption and photodegradation of organic dyes under visible light [7]. More recently, also via a solvothermal method, Ren et al. prepared a carbon quantum dots decorated $MoSe_2$ photocatalyst for Cr(VI) reduction in the whole spectrum of solar light [9]. On one hand, however, there exist some limitations in these reported preparation methods for $MoSe_2$/C composite materials. The products prepared by hydrothermal synthesis are usually of low purity, in which the by-products and impurities are difficult to remove. And the deposition of $MoSe_2$ onto C materials by vapor deposition is generally of low yield and difficult to control. On the other hand, there are continuing enthusiasm and efforts to prepare various morphologies of $MoSe_2$ nanostructures to improve their optoelectrical performance [14–16].

In this work, we reported a novel C fibers@$MoSe_2$ nanoplates core-shell composite (NPCSC). The composite was prepared by simultaneously graphitizing pre-oxidized polyacrylonitrile (PAN) fiber together with selenidizing MoO_3 at high temperature through using a PAN fibers@MoO_3 powder composite as the precursor and selenium powder as the evaporation source. The composite has a remarkable feature of numerous $MoSe_2$ thin nanoplates grown in-situ, densely and even vertically on the surface of the C fibers. And the photocatalytic activity of the composite was evaluated by decomposing organic model dyes methylene blue (MB) and rhodamine B (RhB), and actual organic environmental pollutant *p*-chlorophenol (4-CP) and inorganic one potassium dichromate ($K_2Cr_2O_7$) in aqueous solution under simulated sunlight irradiation (SSI), respectively. Due to the effective separation of photogenerated electron-hole pairs promoted by the prompt transfer of photogenerated electrons through C fibers, compared with commercially available $MoSe_2$ powder (*c*-$MoSe_2$), such composite exhibits greatly improved solar-driven photocatalytic activity and high stability, showing the great potential for environmental remediation by degrading toxic industrial chemicals in waste water using sunlight. Moreover, this one-step thermal evaporation is an easy-handling, eco-friendly and low-cost synthesis method, which is suitable for large-scale production, resulting in products of high density, high purity and controllable morphology that can be used without post-treatment.

2. Experimental section

2.1. Samples preparation

The reported C fibers@$MoSe_2$ NPCSC was synthesized in a horizontal quartz tube furnace. In the optimized process (see details in Figs. 1–5 in Ref. [22]), 1.0 g of commercially bought reagent grade MoO_3 nano-powder was first mixed within 5 mL of absolute ethanol, resulting in a white MoO_3 suspension. Then, 0.15 g of commercially available PAN fibers was soaked in the suspension for 10 min. After soaking, the PAN fibers were taken out from the suspension and dried quickly, obtaining a PAN@MoO_3 composite. Subsequently, 0.30 g of the obtained PAN@MoO_3 composite was laid on an alumina ceramic plate at the center of the vacuum furnace, and 3 g of reagent grade Se powder was loaded in an alumina ceramic crucible at approximately 37 cm away from the PAN@MoO_3 composite on the upstream.

Before heating, the quartz tube was pumped out to -0.01 Pa or less, and flushed repeatedly with 99.99 vol.% Ar gas for several times. After that, the furnace was firstly heated up to 400 °C at a rate of 20 °C/min and held at 400 °C for 10 min. Then, the temperature was raised up to 1100 °C at a rate of 20 °C/min, and soaked at 1100 °C for 3 h. After heating, the furnace was cooled naturally to room temperature. Throughout the whole heating process, the Ar gas flow inside the quartz tube was maintained at 200 sccm, while the vacuum system was continuously operated. Finally, a large amount of black-purple fiber-like products was collected on the alumina ceramic plate. Through a rough evaluation, the $MoSe_2$/C molar ratio in the composite is approximately 1:2.9.

2.2. Materials characterization

The morphology and microstructure of the as-synthesized products were examined by optical microscopy (OM, Sony A580, Japan), field