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Anchoring of ZnO nanoparticles on exfoliated MoS_2 nanosheets for enhanced photocatalytic decolorization of methyl red dye

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ABSTRACT

In this work, a facile method has been employed for the decoration of ultrafine ZnO nanoparticles over the exfoliated MoS_2 nanosheets (ZnO-MoS_2 composite) for the decolorization of methyl red dye under solar light irradiation. Further, the exfoliation of MoS_2 nanosheets from bulk MoS_2 powder and synthesis of pure ZnO nanoparticles was also demonstrated. Then, the prepared different photocatalyst materials have been characterized using various analytical techniques. The formation of ZnO and exfoliation of MoS_2 in the composite has been evidently confirmed by XRD, FT-IR and Raman spectroscopic analysis. HR-TEM analysis clearly revealed the formation of ultrafine ZnO nanoparticles that are anchored on the exfoliated MoS_2 nanosheets. In addition, the size of ZnO nanoparticles in the composite was significantly reduced compared to bare ZnO nanoparticles since the presence of MoS_2 nanosheets which hinders the growth of ZnO nanoparticles. Due to the synergistic interaction between ZnO nanoparticles and exfoliated MoS_2 nanosheets, the prepared composite exhibits superior photocatalytic activity towards the decolorization of methyl red dye up to 89% after 60 min irradiation time compared to pure ZnO nanoparticles (69%) and exfoliated MoS_2 nanosheets (55%).

1. Introduction

In recent years, significant attention has been arousing in the synthesis of semiconductor nanomaterials owing to their unique physico-chemical properties. The outstanding size dependent optical and electronic properties of nanomaterials can be utilized to various promising applications such as electrochemical energy storage and conversion, electro/photochromism, sensors and photocatalytic applications [1–4]. Among them, photocatalytic hydrogen/oxygen evolution reactions and decolorization of organic dyes using solar energy irradiation have been received great attention recently. Particularly, the removal of organic dyes from contaminated water using photocatalysts with the help of sun light irradiation has been considered as the promising route to purify the water [5–7]. An enormous amount of waste/used dyes from various industries are directly discarded into soil and water body systems that are mainly responsible for environmental pollutions. Thus, it is very important to find the cheap, earth abundant and visible-light photocatalyst for large scale dye removal applications. Recently, numerous efforts were made to synthesize the semiconductor metal oxides/sulfides/nitrides/phosphides and their composites for photocatalytic applications [8–11]. Among the different metal oxides, zinc oxide (ZnO), n-type semiconductor, has been identified as the promising material and it can be effectively used for diverse applications such as solar cells, sensors, photo detectors and field emission devices due to its distinctive properties such as high electron mobility, low-cost, non-toxicity, large surface area and good chemical stability [12–16]. Recently, ZnO based nanocomposite has attracted for light harvesting efficiency and fast electron transport in dye sensitized solar cell application [17]. Moreover, ZnO is a well-known photocatalyst for the decolorization of various organic dyes in the presence of sun light because its bandgap energy is similar as TiO_2 [18]. However, large scale practical photocatalytic applications using ZnO nanostructures are limited owing to its wide bandgap, fast recombination of electron-hole pairs and its absorption is limited to ultraviolet (UV) light region [19–21]. To enhance the photocatalytic activities by utilizing the visible light source, it is important to reduce the recombination of photogenerated electron-hole pairs [22,23]. In addition, the formation of the composite with ZnO using narrow band gap semiconducting nanomaterials and doping of noble metals (Au, Ag and Pt) as co-catalysts in ZnO has been suggested.

Besides, molybdenum disulfide (MoS_2), a transition metal chalcogenide, has attracted much attention owing to its unique layered

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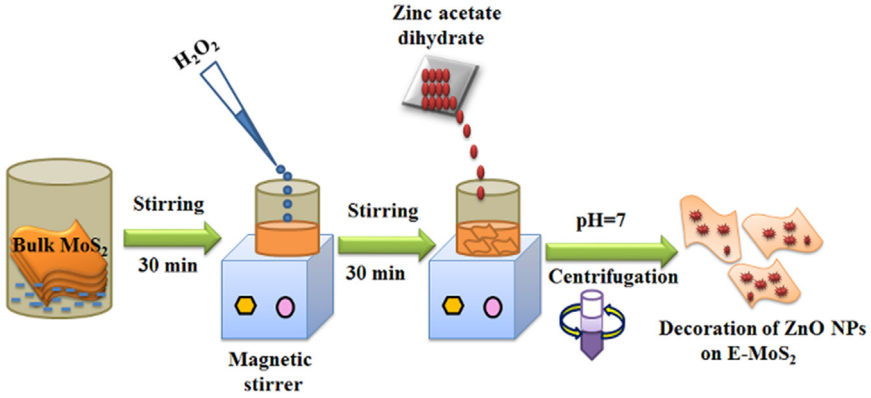

Fig. 1. Schematic representation for the synthesis of ZnO-MoS_2 composite.

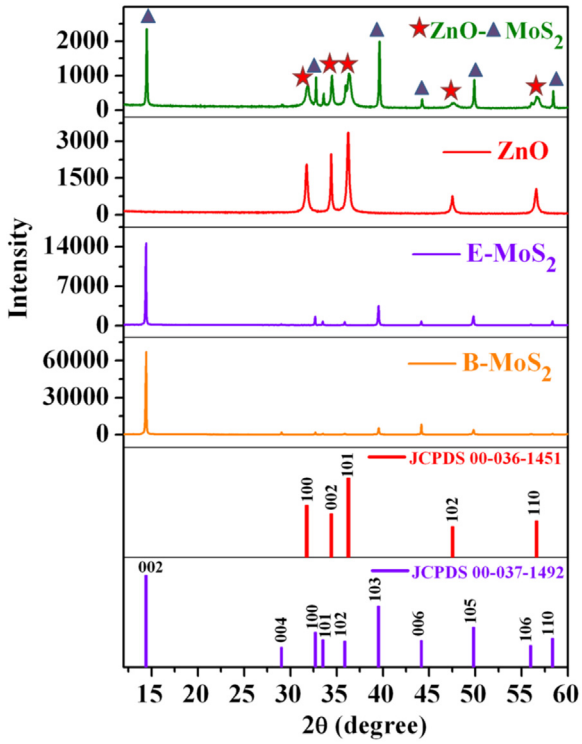

Fig. 2. XRD patterns of B-MoS_2, E-MoS_2, pure ZnO and ZnO-MoS_2 composite (★ indicates ZnO and ▲ indicates MoS_2 diffraction lines in the composite).

structure [24]. A single layer of MoS_2 comprises three sublayers (S-Mo-S) where molybdenum sublayer sandwiched between two sulphur sublayers in a trigonal prismatic arrangement that are connected by covalent bonds and van der Waals forces exist between the layers of MoS_2. The main drawbacks of MoS_2 are a lesser amount of active sites and low electronic conductivity [25]. It is worthy to mention here that the surface dependent catalytic properties are observed for the exfoliated MoS_2 (E-MoS_2) nanosheets. Thus, significant attention has been paid for the exfoliation of MoS_2 nanosheets from bulk MoS_2 (B-MoS_2) using various exfoliation methods [26]. However, a facile, rapid and green exfoliation method is still needed for the isolation of MoS_2 nanosheets from B-MoS_2 with defect free and high yield. The band gap energy of MoS_2 can be varied from 1.2 eV to 1.9 eV when reducing the thickness and lateral size of MoS_2 [27–29]. Recently, it has been successfully utilized for photocatalytic applications because MoS_2 nanosheets can absorb visible light efficiently from natural sun light due to its narrow band gap and unique exfoliated layered structure with large exposed active sites. By the combination of ZnO and MoS_2 nanostructures, the fast recombination of electron-hole pairs was suppressed and thereby an increase in charge transfer function was observed which resulted in the enhanced photocatalytic activity. Thus, researchers are seeking to develop the ZnO-MoS_2 composite by facile synthesis route for electro/photocatalytic applications. Recently, Tan et al., demonstrated the synthesis of MoS_2 @ZnO nano-heterojunctions by three step synthetic process where they have used polyethyleneimine as a binding agent. Then, they evaluated the synthesized nanostructures for photocatalytic degradation of methylene blue (MB) dye and found that only 7.3% MB dye was presented in the solution after 100 min solar light irradiation time [30]. Similarly, Liu et al., synthesized the highly efficient photocatalyst which is composed of P-doped ZnO nanosheets with atomic MoS_2 layers for the degradation of MB dye up to 95% under natural sunlight irradiation [31]. To the best of our knowledge, there is no much research has been carried out on the fabrication of ZnO-MoS_2 composite using facile method for the decolorization of various organic dyes applications.

In this work, the decoration of ZnO nanoparticles (ZnO NPs) on the E-MoS_2 nanosheets, pure ZnO NPs and E-MoS_2 nanosheets from B-MoS_2 powder have been synthesized for the decolorization of methyl red (MR) dye. Interestingly, the synthesized composite exhibits superior photocatalytic activity towards the decolorization of MR dye compared to bare ZnO NPs and E-MoS_2 nanosheets due to the strong synergistic effect of combined materials.

2. Experimental section

2.1. Exfoliation of MoS_2 nanosheets

For the exfoliation of MoS_2 nanosheets, ~180 mg of B-MoS_2 powder was added in 20 mL of deionized water and stirred for 30 min using a magnetic stirrer. Then, 20 mL of H_2O_2 solution, an oxidizing agent, was added drop wisely to the above solution and stirred for 30 min. Subsequently, the pH of the solution was adjusted to pH = 7 using sodium hydroxide (NaOH) solution and stirred for 30 min. The exfoliated MoS_2 nanosheets were collected by washing with ethanol-water mixture using the repeated centrifugation and dried in a vacuum oven at 60 °C for 12 h. The added H_2O_2 and NaOH molecules are initially intercalated to all the interlayers of B-MoS_2 and are the responsible for the formation of molybdenum oxides on the surface of MoS_2 nanosheets followed by the exfoliation using continuous stirring. The formed molybdenum oxides are well suspended in the supernatant solution that is completely removed by the repeated centrifugation.

2.2. Synthesis of pure ZnO NPs

For the synthesis of pure ZnO NPs, ~400 mg of zinc acetate dihydrate powder was added in 20 mL of deionized water solution. The white color precipitate of ZnO NPs was formed while the pH of the