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Research paper

Fabrication of ternary Mn doped ZnO nanoparticles grafted on reduced graphene oxide (RGO) sheet as an efficient solar light driven photocatalyst

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HIGHLIGHTS

- Uniform distribution of ZnO and Mn doped ZnO nanoparticles on graphene oxides sheets.
- Enhanced photocatalytic degradation of Congo red and Rhodamine B over ternary Mn doped ZnO photocatalyst.
- Excellent photochemical stability of prepared of photocatalyst.

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ABSTRACT

A simple hydrothermal method is adopted to prepare ternary Mn doped ZnO nanoparticles uniformly grafted on reduced graphene oxide (RGO) sheets. The effect of Mn doping on ZnO/RGO nanocomposite has been investigated using different characterization techniques. Field emission scanning electron microscope (FESEM) images clearly show the uniform distribution of nanoparticles on RGO sheets. The doping of Mn in ZnO/RGO composites have been confirmed by X-ray photoelectron spectroscopy (XPS). Photocatalytic activities of as-prepared samples were examined by the degradation of Rhodamine B (RhB) and Congo red (CR) under sun light. The prepared ternary heterojunction photocatalyst exhibit the excellent photocatalytic activity for degradation of RhB (degradation rate nearly 99% within 140 min) and CR (degradation rate nearly 100% within 160 min) under sunlight irradiation which is higher than that of binary ZnO/RGO heterojunction. The improved photocatalytic performance of the ternary nanocomposite can be ascribed to extend solar light absorption, enhanced adsorption of the composite catalyst surface and efficient charge separation of photo-induced electrons.

1. Introduction

ZnO has green properties, cheap price, appropriate redox potential, nontoxicity, high physico-chemical stability, great photo stability, so it is one of the most the popular and effective photocatalysts [1,2]. Many efforts were taken to improve photocatalytic activity of ZnO [3,4]. For instance, doping in ZnO to enhance light absorption along with coupling it with graphene to reduce recombination of photo-generated electron hole pairs [5–7]. Recently, Mn-doped ZnO system has achieved significant progress owing to its specific technological applications [8]. Lu et al [9] have reported that 5% Mn doped ZnO highest degradation efficiency amongst all other doped samples under visible light. However, Mn doped ZnO still have a high recombination rate of photo-induced electrons. We have reported in our previous study that the photocatalytic efficiency of such undoped and doped ZnO can be significantly improved by hybridizing it with graphene oxide [10,11].

Being a two-dimensional carbon sheet, graphene has become the subject of interest in the preparation of graphene-based metal oxides photocatalyst besides its unusual property of treating wastewater [12–16]. The easy transfer of photo-induced electrons from the semiconductor surface to the conjugated plane of graphene can be achieved by its exceptional conductivity properties [17–19]. Knowing that graphene has zero band gap and is low Fermi level material, it acts like an electronic ampule to collect electron from the photo excited semiconductor [20,21]. This significantly restricts electron–hole pair recombination, therefore, improving the photocatalytic performance of semiconductor. RGO sheets may act a good support material it has large surface-to-volume ratio [22]. Zhu et al [23] recently reported that the ZnO-graphene composites prolongs light-absorption range to visible light region and this is helpful for developing more excitons.

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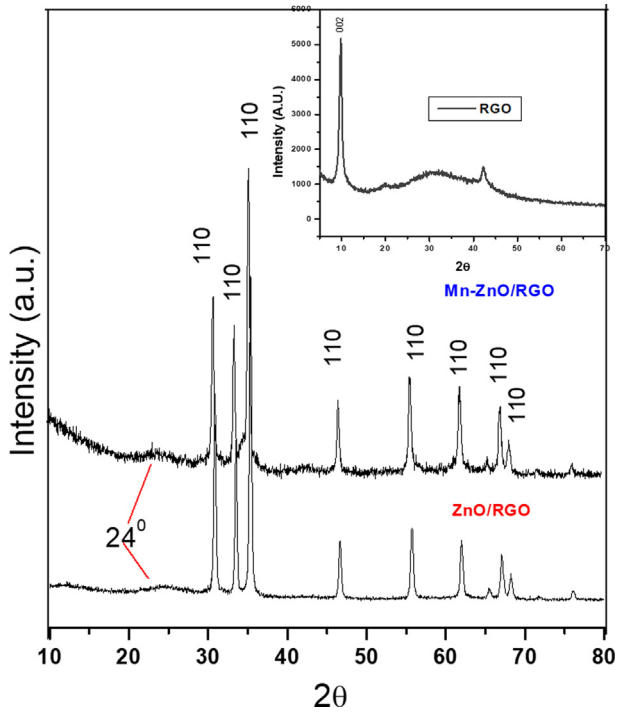

Fig. 1. XRD pattern of ZnO/GO and Mn-ZnO/GO (Inset shows the XRD pattern of GO).

Table 1
Structural properties of as-prepared catalyst.

Samples	Lattice parameter (Å)		Volume (Å)^3	c/a ratio	Crystallite size (D) nm
	a	c			
ZnO-GO	3.2861	5.3420	49.9555	1.6256	31.6361
Mn/ZnO-GO	3.2864	5.3374	49.9216	1.6241	30.9608

Furthermore, fast transfer and migration of photo-generated electrons takes place as a result of the intimate electronic contact at the interface of graphene and ZnO. Additionally, the photo-corrosion of semiconductor during photocatalytic reaction can be effectively prevented by combining it with graphene oxide [24]. When coupled with graphene oxide, unexpectedly the semiconductors like metal sulphides also behave as stable photocatalysts and do not suffer from photo-corrosion [25]. Recently, Hsieh et al [26] prepared ternary Cu-ZnO/RGO (reduced graphene oxide) nanocomposite photocatalyst by microwave-assisted hydrothermal method. They reported that the copper doping reduced band gaps as well as increased the O-H/Zn-O ratios and more O^{2-} vacancies in the samples, which led to enhanced visible light absorption. Besides, the superior degradation activity of such a ternary photocatalyst may be due to the enhanced adsorption of pollutant on catalyst surface, efficient charge separation and improved generation of potential oxidizing species [27].

In our previous work, we followed the wet impregnation method to decorate ZnO on graphene oxide sheets. However, it was difficult to control the morphology and distribution of nanoparticles on the graphene oxide sheets [11]. The exploitation of optimum surface area and electron mobility of graphene may restrict to certain level by agglomeration and non-uniform distribution of ZnO nanoparticles on graphene oxide sheets. Xue and Zou reported that the uniform distribution of ZnO nanoparticles on the surface of RGO plane favours the interfacial charge transfer and restricts the electron–hole recombination. Consequently, the emitted photoelectrons can be effectively accepted by RGO and thereby, results in high degradation efficiency of the strongly coupled composites [28].

Herein, inspired by our previous work and to overcome the difficulty of controlling the morphology and distribution of nanoparticles on the RGO sheets, the hydrothermal method was adopted to prepare highly efficient solar light assisted Mn doped ZnO grafted on RGO sheets. The effect of Mn doping on the structural, morphological, optical and photocatalytic properties of ZnO/RGO nanocomposites were systematically investigated. The photocatalytic performance of the resultant Mn-ZnO/RGO and ZnO/RGO composites was studied in detail. The prepared ternary nanocomposites can be a potential photocatalyst in industrial waste water treatment for commercial purpose.

2. Materials and methods

2.1. Materials

For the synthesis of Mn doped ZnO nanoparticles grafted on RGO sheets, analytical grade zinc nitrate ($Zn(NO_3)_2{\cdot}6H_2O$, > 98% pure) and magnesium nitrate hexahydrate ($Mn(NO_3)_2{\cdot}6H_2O$, > 98% pure) was purchased from Merck, India. Graphite powder has been procured from MDB Chemicals Pvt. Ltd. Jalgaon, MS India. All the chemicals were used as they were received from the supplier without further purification.

2.2. Synthesis of Mn doped ZnO nanostructures grafted on RGO sheets (Mn-ZnO/RGO)

RGO was prepared by using modified Hummer's method as reported in our previous study [10]. In a typical synthesis procedure, zinc nitrate hexahydrate and manganese (II) nitrate tetrahydrate were mixed in 80 mL deionised water with continuous stirring (Mn/Zn being 0.5%

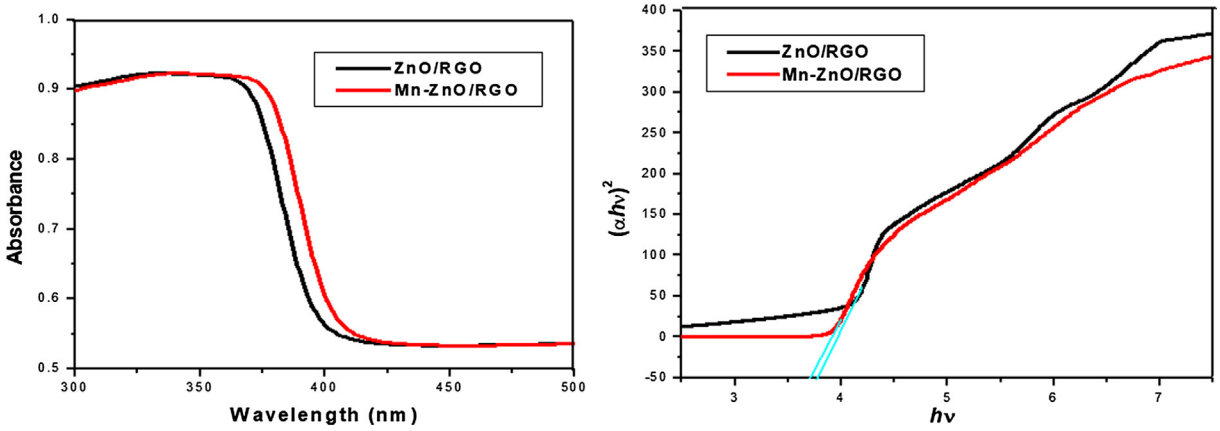

Fig. 2. FESEM and EDX images of ZnO/GO and Mn-ZnO/GO.