Solar Energy Materials and Solar Cells 178 (2018) 154–163

Contents lists available at ScienceDirect

Solar Energy Materials and Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Novel magnetically separable $Ag_3PO_4/MnFe_2O_4$ nanocomposite and its high photocatalytic degradation performance for organic dyes under solar-light irradiation

Eslam Abroshan, Saeed Farhadi*, Abedin Zabardasti

Department of Chemistry, Lorestan University, Khoramabad 68151-44316, Iran

ARTICLE INFO

Keywords:
$Ag_3PO_4/MnFe_2O_4$
Magnetic nanocomposite
Photocatalytic degradation
Solar light irradiation
Organic dye pollutants

ABSTRACT

Novel magnetically separable $Ag_3PO_4/MnFe_2O_4$ nanocomposite with 30wt% $MnFe_2O_4$ was synthesized for the first time by a facile hydrothermal route and the composition and microstructure of the nanocomposite was fully characterized. The photocatalytic activity of $Ag_3PO_4/MnFe_2O_4$ nanocomposite was evaluated in the degradation of methylene blue (MB) and Rhodamine B (RhB) dyes under natural solar-light irradiation with an average light intensity of $\sim$ 185 mW cm^{-2}. The results displayed that the degradation efficiency of the $Ag_3PO_4/MnFe_2O_4$ nanocomposite was 98% for methylene blue (MB) and 100% for Rhodamine B (RhB) in 82 min. The photocatalytic activity of $Ag_3PO_4/CoFe_2O_4$ was almost 1.5 and 3 times as high as those of the pure Ag_3PO_4 and $CoFe_2O_4$, respectively. The remarkably enhanced photocatalytic performance of $Ag_3PO_4/MnFe_2O_4$ nanocomposite compared with the individual Ag_3PO_4 and $MnFe_2O_4$ was ascribed to its higher specific surface area and the existence of a synergic effect between Ag_3PO_4 and $MnFe_2O_4$ that resulted in efficient separation of electron–hole pairs. Trapping experiments indicated that the photodegradation of dyes was mainly achieved by superoxide radicals ($\bullet O_2^-$) attack in $Ag_3PO_4/MnFe_2O_4$ suspension. Furthermore, the possible mechanism of excellent solar-light photoactivity activity of the $Ag_3PO_4/MnFe_2O_4$ nanocomposite was proposed based on the experimental results. Due to the existence of the magnetic $MnFe_2O_4$ nanoparticles, the $Ag_3PO_4/MnFe_2O_4$ nanocomposite could be magnetically separated from the reaction mixture by a usual magnet with an intensity of 0.1 T (= 1 kOe) and reused without any change in structure.

1. Introduction

Over the past few decades, many kinds of new organic pollutants have been found in water with the development of industry. These organic pollutants cannot be effectively treated by traditional treatment methods. Fortunately, the semiconductor-based photocatalysis as a technology for the treatment of polluted water can degrade most organic pollutants. As a result, the photocatalytic degradation of organic pollutants in the presence of semiconductors has attracted increasing interest because it is a promising, green, and cost-effective technology for the treatment of contaminated groundwater and wastewater [1–4]. Many studies have reported that various organic pollutants can be degraded completely through photocatalysis using metal oxide semiconductor nanostructures under UV light irradiation [5–7]. However, the need for ultraviolet radiation in photodegradation processes has limited both the practicality and environmental benefits on industrially relevant scales. This is because the UV region occupies only around 4% of the solar energy as a renewable resource, while 43% of the energy belongs to visible light. Therefore, the development of novel photocatalysts, particularly visible light responsive catalysts is necessary for the efficient utilization of solar energy in the photocatalysis [8–17].

Owing to relatively narrow band gap (2.35–2.45 eV) and its excellent photocatalytic activity for the degradation of organic pollutants under visible light irradiation, silver orthophosphate (Ag_3PO_4) captured tremendous attention in the last few years [18,19]. In order to improve photocatalytic activity of Ag_3PO_4, various synthetic strategies have been developed to fabricate Ag_3PO_4 nano-structures with different morphologies [20,21]. However, Ag_3PO_4 has itself drawbacks such as low photostability, large particle size with smaller surface area, unstability in aqueous solution, under visible light irradiation silver ions delivered from Ag_3PO_4 in aqueous solution can be reduced to metallic Ag, which would decrease the visible light absorption and the reuse of Ag_3PO_4 catalyst [22]. To overcome to these problems many efforts had been tried, and some Ag_3PO_4-based hybrid composite such as $Ag_3PO_4/In(OH)_3$ [23], CdS/Ag_3PO_4 [24], Ag_3PO_4/CeO_2 [25], Fe_3O_4/Ag_3PO_4 [26], g-C_3N_4/Ag_3PO_4 [27,28], Ag_3PO_4/BiOI [29], Ag_3PO_4-Bentonite

---

* Corresponding author.
E-mail address: sfarhadi1348@yahoo.com (S. Farhadi).

https://doi.org/10.1016/j.solmat.2018.01.026
Received 26 August 2017; Received in revised form 29 December 2017; Accepted 17 January 2018

[30], Ag_3PO_4-graphene [31], Ag_3PO_4/TiO_2 [32], Ag@(Ag_2S/Ag_3PO_4) [33], Ag_3PO_4/SnO_2 [34], AgX/Ag_3PO_4 (X = Cl, Br, I) [35,36], Ag_3PO_4/HAP [37], $Ag_3PO_4/BiVO_4$ [38,39], Ag_3PO_4/Nb_2O_5 [40] and had been successfully synthesized, which showed enhanced photocatalytic stability and activity than pure Ag_3PO_4. Through these approaches, the quantum efficiencies or stability of the materials have been improved to some degree. In spite of these hybrids improved the photocatalytic activity and stability but separating and recycling of most these catalysts from a mixed suspension limited the expansion of applications.

One effective pathway to solve the above difficult is the coupling Ag_3PO_4 with magnetic materials. Recovery and reuse of suspended nanocatalysts after degradation are of great importance for sustainable process management [41]. Magnetic separation provides a convenient technique for removing and recycling magnetized catalysts under an external magnetic field. Adding magnetic species to a variety of solid matrixes allows for the combination of well-known procedures for catalyst heterogenization with techniques for magnetic separation. Manganese ferrite ($MnFe_2O_4$) nanoparticles have been of great interest, because they have proven to be useful in many magnetic applications [42–45]. $MnFe_2O_4$-based nanocomposites especially provide a potential advantage for repeated magnetic separation purposes [46]. Furthermore, $MnFe_2O_4$ is a visible-light-driven semiconductor with a relatively narrow band gap (1.50–2.10 eV) which shows high photochemical stability. Thus, it is possible to improve the efficiency of photoinduced charge separation in $MnFe_2O_4$ by coupling it with another semiconductor, resulting in high photocatalytic performance [47].

In the present work, we report on the synthesis, characterization and photocatalytic activity of a new magnetically recyclable $Ag_3PO_4/MnFe_2O_4$ nanocomposite. The magnetic $Ag_3PO_4/MnFe_2O_4$ nanocomposite was prepared by a simple hydrothermal route. Among the various methods, the hydrothermal method is an important one-step technology for synthesizing inorganic nanocomposites without phase-separation at low temperature and under air atmosphere. This method uses water as a green solvent under the pressure and temperature above its critical point to increase the solubility of a solid as well as speed of reactions. The composition, microstructure and optical properties of the hydrothermally synthesized nanocomposite were fully characterized by various physical techniques. The solar-light driven photocatalytic activity of $Ag_3PO_4/MnFe_2O_4$ nanocomposite was evaluated based on the degradation of MB and RhB organic dyes. The results showed that the photodegradation rate of organic dyes over the $Ag_3PO_4/MnFe_2O_4$ nanocomposite was almost 1.5 and 3 times as high as those of the pure Ag_3PO_4 and $MnFe_2O_4$, respectively. Furthermore, a possible mechanism for solar-light photoactivity of the nanocomposite was proposed. To the best of our knowledge, there is no report on the combination of Ag_3PO_4 and $MnFe_2O_4$ as a composite photocatalyst until now.

2. Experimental

2.1. Materials

Manganese(II) Chloride dihydrate ($MnCl_2 \cdot 6H_2O$, 98%), iron(III) Chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, 98%), silver nitrate ($AgNO_3$, 98%), disodium hydrogen phosphate (Na_2HPO_4, 98.5%), sodium borohydride ($NaBH_4$, 98.5%), MB (99%) and RhB (99%) were obtained from Merck Chemical Company and used as received without further purification.

2.2. Synthesis of $MnFe_2O_4$ nanoparticles [48]

1.082 g of iron(III) Chloride hexahydrate ($FeCl_3 \cdot 9H_2O$) and 0.3238 g Manganese(II) chloride dihydrate ($MnCl_2 \cdot 2H_2O$) were dissolved in 25 mL of water by magnetic stirring for 30 min. After that, the mixture was adjusted to a pH = 12.0 with 6 M NaOH solution and stirred for 60 min, yielding a homogeneous emulsion. The resulting mixture was transferred into a 50 mL Teflon-lined stainless steel autoclave and heated to 200 °C for 12 h. The reaction mixture was allowed to cool to room temperature and the precipitate was filtered, washed with distilled water five times, and dried in a vacuum oven at 60 °C for 12 h.

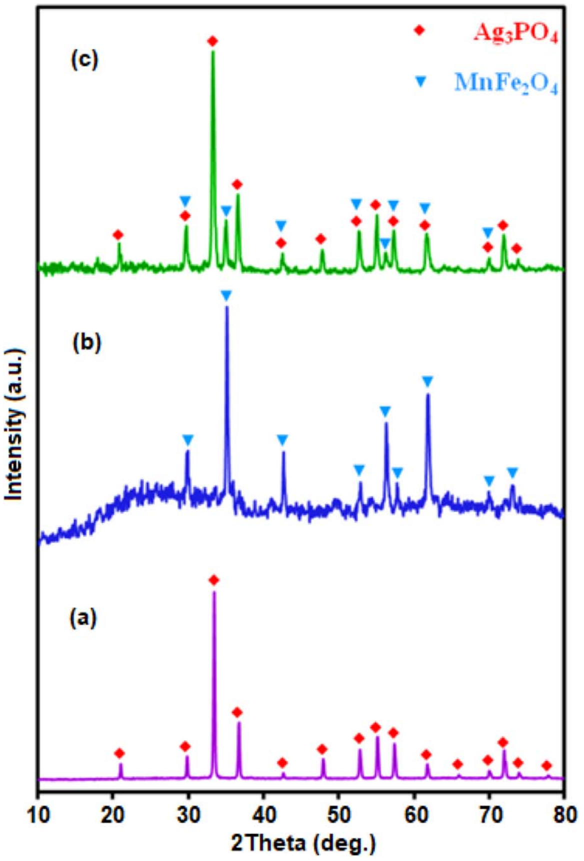

Fig. 1. XRD patterns of (a) Ag_3PO_4, (b) $MnFe_2O_4$ and (c) $Ag_3PO_4/MnFe_2O_4$ nanocomposite.

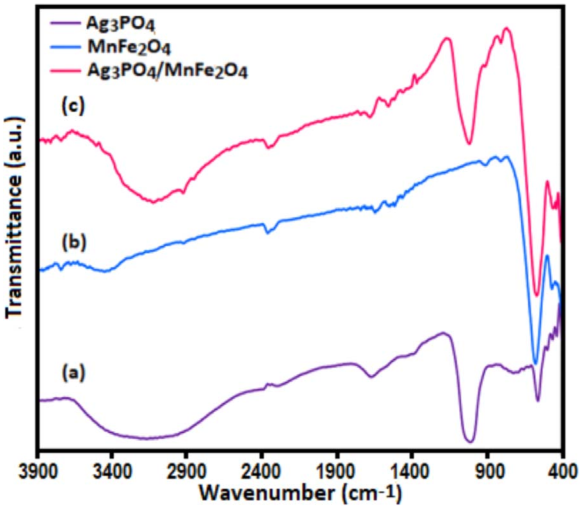

Fig. 2. FT-IR spectra of (a) Ag_3PO_4, (b) $MnFe_2O_4$ and (c) $Ag_3PO_4/MnFe_2O_4$ nanocomposite.

2.3. Synthesis of $Ag_3PO_4/MnFe_2O_4$ nanocomposite

The preparation of Ag_3PO_4-$MnFe_2O_4$ (30 wt%) nanocomposite was carried out as follows: 26 mg $MnFe_2O_4$ powder was added into 20 mL deionized water and sonicated for 10 min to get uniform dispersion. Then, 1.0 mL Na_2HPO_4 (0.15 mol L^{-1}) and 3.0 mL $AgNO_3$ (0.15 mol L^{-1}) aqueous solutions were added into the suspension and