Novel magnetically separable Ag₃PO₄/MnFe₂O₄ nanocomposite and its high photocatalytic degradation performance for organic dyes under solar-light irradiation

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ABSTRACT
Novel magnetically separable Ag₃PO₄/MnFe₂O₄ nanocomposite with 30wt% MnFe₂O₄ 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 Ag₃PO₄/MnFe₂O₄ 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 ~ 185 mW cm⁻². The results displayed that the degradation efficiency of the Ag₃PO₄/MnFe₂O₄ nanocomposite was 98% for methylene blue (MB) and 100% for Rhodamine B (RhB) in 82 min. The photocatalytic activity of Ag₃PO₄/MnFe₂O₄ was almost 1.5 and 3 times as high as those of the pure Ag₃PO₄ and MnFe₂O₄, respectively. The remarkably enhanced photocatalytic performance of Ag₃PO₄/MnFe₂O₄ nanocomposite compared with the individual Ag₃PO₄ and MnFe₂O₄ was ascribed to its higher specific surface area and the existence of a synergic effect between Ag₃PO₄ and MnFe₂O₄ that resulted in efficient separation of electron–hole pairs. Trapping experiments indicated that the photodegradation of dyes was mainly achieved by superoxide radicals (O₂⁻) attack in Ag₃PO₄/MnFe₂O₄ suspension. Furthermore, the possible mechanism of excellent solar-light photoactivity activity of the Ag₃PO₄/MnFe₂O₄ nanocomposite was proposed based on the experimental results. Due to the existence of the magnetic MnFe₂O₄ nanoparticles, the Ag₃PO₄/MnFe₂O₄ 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 (Ag₃PO₄) captured tremendous attention in the last few years [18,19]. In order to improve photocatalytic activity of Ag₃PO₄, various synthetic strategies have been developed to fabricate Ag₃PO₄ nano-structures with different morphologies [20,21]. However, Ag₃PO₄ has itself drawbacks such as low photostability, large particle size with smaller surface area, instability in aqueous solution, under visible light irradiation silver ions delivered from Ag₃PO₄ in aqueous solution can be reduced to metallic Ag, which would decrease the visible light absorption and the reuse of Ag₃PO₄ catalyst [22]. To overcome to these problems many efforts had been tried, and some Ag₃PO₄-based hybrid composite such as Ag₃PO₄/In(OH)₃ [23], CdS/Ag₃PO₄ [24], Ag₃PO₄/CeO₂ [25], Fe₃O₄/Ag₃PO₄ [26], g-C₃N₄/Ag₃PO₄ [27,28], Ag₃PO₄/BiOI [29], Ag₃PO₄-Bentonite...
A g3PO4-graphene [31], Ag3PO4/TiO2 [32], Ag@>(Ag2S@Ag3PO4) [33], Ag3PO4/SnO2 [34], AgX@Ag3PO4 (X = Cl, Br, I) [35,36], Ag3PO4/HAP [37], Ag3PO4/BiVO4 [38,39], Ag3PO4/Nb2O5 [40] and had been successfully synthesized, which showed enhanced photocatalytic stability and activity than pure Ag3PO4. 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 Ag3PO4 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 matrices allows for the combination of well-known procedures for catalyst heterogenization with techniques for magnetic separation. Manganese ferrite (MnFe2O4) nanoparticles have been of great interest, because they have proven to be useful in many magnetic applications [42–45]. MnFe2O4-based nanocomposites especially provide a potential advantage for repeated magnetic separation purposes [46]. Furthermore, MnFe2O4 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 MnFe2O4 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 Ag3PO4/MnFe2O4 nanocomposite. The magnetic Ag3PO4/MnFe2O4 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 Ag3PO4/MnFe2O4 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 Ag3PO4/MnFe2O4 nanocomposite was almost 1.5 and 3 times as high as those of the pure Ag3PO4 and MnFe2O4, 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 Ag3PO4 and MnFe2O4 as a composite photocatalyst until now.

2. Experimental

2.1. Materials

Manganese(II) Chloride dihydrate (MnCl2·6H2O, 98%), iron(III) Chloride hexahydrate (FeCl3·6H2O, 98%), silver nitrate (AgNO3, 98%), disodium hydrogen phosphate (Na2HPO4, 98.5%), sodium borohydride (NaBH4, 98.5%), MB (99%) and RhB (99%) were obtained from Merck Chemical Company and used as received without further purification.

2.2. Synthesis of MnFe2O4 nanoparticles [48]

1.082 g of iron(III) Chloride hexahydrate (FeCl3·9H2O) and 0.3238 g Manganese(II) chloride dihydrate (MnCl2·2H2O) 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 homogenous 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.

2.3. Synthesis of Ag3PO4/MnFe2O4 nanocomposite

The preparation of Ag3PO4-MnFe2O4 (30 wt%) nanocomposite was carried out as follows: 26 mg MnFe2O4 powder was added into 20 mL deionized water and sonicated for 10 min to get uniform dispersion. Then, 1.0 mL Na2HPO4 (0.15 mol L−1) and 3.0 mL AgNO3 (0.15 mol L−1) aqueous solutions were added into the suspension and

Fig. 1. XRD patterns of (a) Ag3PO4, (b) MnFe2O4 and (c) Ag3PO4/MnFe2O4 nanocomposite.

Fig. 2. FT-IR spectra of (a) Ag3PO4, (b) MnFe2O4 and (c) Ag3PO4/MnFe2O4 nanocomposite.