Fullerene-modified magnetic silver phosphate (Ag$_3$PO$_4$/Fe$_3$O$_4$/C$_{60}$) nanocomposites: hydrothermal synthesis, characterization and study of photocatalytic, catalytic and antibacterial activities

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In this work, fullerene-modified magnetic silver phosphate (Ag$_3$PO$_4$/Fe$_3$O$_4$/C$_{60}$) nanocomposites with efficient visible light photocatalytic and catalytic activity were fabricated by a simple hydrothermal approach. The composition and structure of the obtained new magnetically recyclable ternary nanocomposites were completely characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy, Brunauer–Emmett–Teller (BET) specific surface area analysis, vibrating sample magnetometry (VSM), diffuse reflectance spectroscopy (DRS), field emission scanning electron microscopy (FE-SEM), energy dispersive X-ray (EDX) spectroscopy and transmission electron microscopy (TEM). This novel magnetically recyclable heterogeneous fullerene-modified catalyst was tested for the H$_2$O$_2$-assisted photocatalytic degradation of MB dye under visible light. The results show that about 95% of the MB (25 mg L$^{-1}$, 50 ml) was degraded by the Ag$_3$PO$_4$/Fe$_3$O$_4$/C$_{60}$ nanocomposite within 5 h under visible light irradiation. The catalytic performance of the Ag$_3$PO$_4$/Fe$_3$O$_4$/C$_{60}$ nanocomposite was then examined for 4-nitrophenol (4-NP) reduction using NaBH$_4$. This new nanocomposite showed that 4-NP was reduced to 4-aminophenol (4-AP) in 98% yield with an aqueous solution of NaBH$_4$. In both photocatalytic and catalytic reactions, the Ag$_3$PO$_4$/Fe$_3$O$_4$/C$_{60}$ nanocomposite could be magnetically separated from the reaction mixture and reused without any change in structure. The antibacterial activity of the nanocomposites was also investigated and they showed good antibacterial activity against a few human pathogenic bacteria.

1. Introduction

Today, water pollution is one of the main problems that human beings encounter. Every day, human activities lead to the release of contaminant substances and waste into the rivers, lakes, groundwater aquifers and oceans. This contamination affects the aquatic environmental quality for various uses and human consumption. Water pollutants, including organic material such as methyl orange, methylene blue and rhodamine B dyes, are hazardous, toxic and carcinogenic for humans even at low concentrations, and they are hardly biodegradable and difficult to remove from the environment. The ingestion of liquid products containing concentrated nitrophenol can cause serious gastrointestinal damage and even death. In animals, longer-term exposure to high levels of nitrophenol cause damages to the heart, kidneys, liver and lungs. It is therefore very important to find innovative and cost-effective ways for the complete removal of organic pollutants and for monitoring water safety. One way is the production of catalysts to eliminate water contamination, either in the dark or in visible light. Certainly, due to their high efficiency and promising economy, semiconductor-based catalytic and photocatalytic technologies have opened up new opportunities to control pollutants and deal with their effects. To date, various metal oxides, sulfides, carbon compounds and composite materials have been investigated for the development of effective photocatalysts.

In recent years, considerable attention has been paid to silver orthophosphate (Ag$_3$PO$_4$), a new photocatalyst with an extremely high photooxidative capability for O$_2$ generation from water splitting. This is due to its highly positive VB position, low toxicity and superior photodegradation rate of organic dyes, which is dozens of times faster than the surface level of commercial TiO$_2$ under visible light irradiation. Unfortunately, because of its low structural stability, it is possible for Ag$_3$PO$_4$ to be photochemically decomposed to Ag if no sacrificial reagent is involved. Increasing both the stability and the catalytic activity of pure Ag$_3$PO$_4$ by coupling Ag$_3$PO$_4$ with other
materials has been proven to be an effective strategy.26 Many Ag₃PO₄-based composites, such as Ag₃PO₄/CeO₂,27 Ag₃PO₄/Fe₃O₄/GO,28 AgX/Ag₃PO₄ (X = Cl, Br, I),29 Ag₃PO₄/TiO₂,30 Cds/Ag₃PO₄,31 Ag₃PO₄/MoS₂/GR,32 Ag₃PO₄/Bi₂WO₆,33 Ag₃PO₄/BiVO₄,34 Ag₃PO₄/LaFeO₃,35 Ag₃PO₄/CleO₃,36 Ag₃PO₄/CoFe₂O₄,37 Ag₃PO₄/Ag/MWCNTs,38 TiO₂/Ag₃PO₄,39 P₂S/Ag₃PO₄/GO,40 g-C₃N₄ nanorod/Ag₃PO₄ (ref. 41) and GO/Ag₃PO₄,42 display enhanced stability and photocatalytic activity.

Carbon materials have potential applications in many fields of environmental pollution control due to their special properties, such as their higher specific surface area, superior electronic characteristics, confinement effects and strong physical/chemical stability.51-54 Among the large family of carbon-based nanomaterials, fullerene (C₆₀) is known as an excellent electron acceptor with an appropriate band gap of 1.7-1.9 eV, and thus can lead to rapid photoinduced charge separation and relatively slow charge recombination.47-48 A C₆₀ molecule has a closed shell configuration consisting of 30 bonding molecular orbitals with 60 p electrons, which is advantageous for shuttling and transporting electrons.49,50 Moreover, this unique structure endows C₆₀ with many other intriguing characteristics, which mainly include its excellent exciton mobility, high thermal stability, low density, strain-tunable semiconducting characteristics, moderate elastic modulus and high bending flexibility.51,52 From the perspective of the excellent properties of C₆₀, hybridizing C₆₀ with Ag₃PO₄ should be beneficial for improving the photocatalytic performance of Ag₃PO₄. However, separation and recycling of the binary Ag₃PO₄/C₆₀ composite is difficult and severely limits its potential applications. To overcome this problem, coupling with magnetic materials e.g. Fe₃O₄ is highly desirable. Such magnetic composite catalysts can be easily recovered by a magnet and reused for catalytic reactions several times without any considerable reduction in catalytic efficiency.

In the present work, we explored the role of C₆₀ towards the photochemical performance of hybridized Ag₃PO₄/Fe₃O₄/C₆₀ composites. The structural characteristics of Ag₃PO₄/Fe₃O₄/C₆₀ with a varied C₆₀ content were first studied, then their performances were evaluated by the visible light photocatalytic degradation of MB dye and the catalytic reduction of 4-nitrophenol (4-NP). Based on the characterization and photocatalytic/catalytic results, possible mechanisms were proposed. The results of this work demonstrate that hybridizing C₆₀ with Ag₃PO₄ could improve the separating efficiency of photoinduced electrons and holes, which resulted in the enhanced photocatalytic activity of Ag₃PO₄/Fe₃O₄/C₆₀ composites. The antibacterial activity of the nanocomposites was also investigated.

2. Experimental

2.1. Materials

All chemicals were reagent grade and were used without further purification, such as iron(II) diammonium sulfate hexahydrate ([NH₄]₂FeSO₄·6H₂O), iron(m) ammonium bisulfate dodecahydrate (NH₄Fe(SO₄)₂·12H₂O), sodium borohydride (NaBH₄), absolute ethanol, disodium hydrogen phosphate (Na₂HPO₄), silver nitrate (AgNO₃), 4-nitrophenol, 2-nitrophenol, 4-nitroaniline, 2-nitroaniline, hydrogen peroxide (H₂O₂, 30%) and methylene blue (MB, C₁₅H₁₁Cl₃N₃S). The reagents were purchased from Merck and used as received. Fullerene (C₆₀, 99.9%) was purchased from Sigma-Aldrich. Double distilled deionized water was used for the experiments. All glassware was properly washed with distilled water and dried in an oven.

2.2. Synthesis of the Ag₃PO₄/Fe₃O₄/C₆₀ (m-APO/C₆₀) nanocomposites

The Fe₃O₄ nanoparticles were prepared through a hydrothermal process. 1 mmol Fe²⁺ and 2 mmol Fe³⁺ were dissolved in 30 ml deionized water and an appropriate amount of NaOH was added, and the pH was set to be 11 at 50 °C for 10 min with continuous stirring, yielding a uniform black suspension. It was then transferred to an autoclave (50 ml) at 180 °C for 20 h. Subsequently, the autoclave was cooled to room temperature naturally. The as-obtained black samples were centrifuged, washed with deionized water and ethanol three times, and dried at 70 °C for 3 h. To prepare the Ag₃PO₄/Fe₃O₄/C₆₀ (wt 5%) nanocomposite, a mixture of 0.2 g of the Fe₃O₄ nanoparticles dispersed in 5 ml deionization water, 1 mmol of Na₂HPO₄·12H₂O, 3 mmol of AgNO₃ and 10 ml of C₆₀ toluene solution (1 g L⁻¹) were stirred for 30 min. After sonication for 30 min, the homogenized suspension was transferred into a 50 ml Teflon-lined stainless steel autoclave, sealed and maintained at 180 °C for 20 h. The autoclave was then naturally cooled to room temperature and the resulting precipitate was separated by a magnet, washed with deionized water several times, dried at 60 °C and used for further characterization. It was then transferred to a 50 ml autoclave and heated at 180 °C for 20 h. Subsequently, the autoclave was cooled to room temperature naturally. The product was collected by applying an external magnetic field, washed several times with absolute ethanol and distilled water, and finally dried at 70 °C for 3 h. The samples with 10 and 20 wt% of C₆₀ were prepared in a similar manner. For comparison, the pure Ag₃PO₄ nanostructure was synthesized according to the typical synthesis described above with Fe₃O₄ and C₆₀ being absent. The obtained samples with 5, 10 and 20 wt% of C₆₀ and pure Ag₃PO₄ are denoted as m-APO/C₆₀(5), m-APO/C₆₀(10), m-APO/C₆₀(20) and APO, respectively.

2.3. Photocatalytic dye degradation tests

Photocatalytic degradation of the aqueous solution of methylene blue (MB) was carried out in the presence of the m-APO/C₆₀ photocatalyst using a 400 W high pressure mercury lamp as an irradiation source, with a cool water circulating filter to absorb the near IR and a UV light cut-off filter to avoid direct photolysis of the organic dyes (λ ≥ 420 nm). In a typical experiment, 0.05 g of the m-APO/C₆₀ photocatalyst was added to 50 ml of MB (25 mg L⁻¹) to perform the photocatalytic degradation. Before irradiation, the solution was stirred for 30 min to achieve an adsorption–desorption equilibrium of the dye on the photocatalyst surface. It was then subjected to visible light irradiation in the presence of H₂O₂. At given time intervals, 2 ml aliquots of the reaction solution were sampled, and the catalyst was...