Ag$_3$PO$_4$/CoFe$_2$O$_4$ magnetic nanocomposite: synthesis, characterization and applications in catalytic reduction of nitrophenols and sunlight-assisted photocatalytic degradation of organic dye pollutants

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A novel magnetically recyclable Ag$_3$PO$_4$/CoFe$_2$O$_4$ nanocomposite (containing 30 wt% CoFe$_2$O$_4$) was synthesized by a facile hydrothermal method. The composition and microstructure of the nanocomposite was fully characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), UV-visible spectroscopy (UV-vis), field emission scanning electron microscopy (FESEM)-energy dispersive X-ray (EDX) spectroscopy, transmission electron microscopy (TEM), and a vibrating sample magnetometer (VSM). Thereafter, the catalytic performance of the Ag$_3$PO$_4$/CoFe$_2$O$_4$ nanocomposite was investigated. The Ag$_3$PO$_4$/CoFe$_2$O$_4$ nanocomposite showed high efficiency for the degradation of methylene blue (MB) and Rhodamine B (RhB) dyes under direct sunlight irradiation. The photocatalytic activity of Ag$_3$PO$_4$/CoFe$_2$O$_4$ under sunlight irradiation was almost 1.5 and 4.7 times as high as those of the pure Ag$_3$PO$_4$ and CoFe$_2$O$_4$, respectively. The enhancement of sunlight photocatalytic activity in Ag$_3$PO$_4$/CoFe$_2$O$_4$ should be assigned to the effective separation and transfer of photogenerated charges originating from the well-matched overlapping band-structures. Trapping experiments indicated that superoxide anion ("O$_2^-$") radicals were the main reactive species for dye degradation in the present sonocatalytic system. A proposed mechanism for the enhanced photocatalytic activity is also discussed based on the experimental results. In addition, the catalytic activity of the nanocomposite in the reduction of nitrophenols by using NaBH$_4$ was evaluated. The results showed that Ag$_3$PO$_4$/CoFe$_2$O$_4$ exhibited the best performance in the reduction of 4-nitrophenol (4-NP) and 2-nitrophenol (2-NP) and revealed 100% conversion into the corresponding amino derivatives within 24–46 min with rate constant equal to 0.0714 min$^{-1}$ and 0.0329 min$^{-1}$, respectively. Moreover, due to the existence of the CoFe$_2$O$_4$, the Ag$_3$PO$_4$/CoFe$_2$O$_4$ nanocomposite could be magnetically separated from the reaction mixture and reused without any change in structure.

1. Introduction

Solar energy is the most clean, abundant and renewable energy source. The energy from the sun that hits the earth for one hour is much more than that needed by human beings for one year.\textsuperscript{5,6} It is well-known that the ultraviolet (UV) region occupies only approximately 4% of the entire solar spectrum, while 43% of the energy is that of visible light.\textsuperscript{3,4} Therefore, the development of novel efficient photocatalysts, particularly visible light responsive catalysts, is necessary for the efficient utilization of solar energy in photocatalysis.\textsuperscript{3,4} Developing a novel photocatalyst with efficient visible-light absorption and excellent stability remains a great challenge.

Among various photoactive materials, silver orthophosphate (Ag$_3$PO$_4$) has attracted considerable attention and found to be an excellent photocatalyst in visible light region because of its superior semiconductor property for directly splitting water, degrading organic contaminants and photodecomposition of organic dyes.\textsuperscript{7,8} Ag$_3$PO$_4$ has a relatively narrow band gap (2.36–2.43 eV) and is thus active under visible-light irradiation ($\lambda < 530$ nm).\textsuperscript{9} Unfortunately, Ag$_3$PO$_4$ suffers from the structural stability issues because the photocatalytic process is usually accompanied by the transformation of Ag$^+$ into Ag$^0$ in the absence of a sacrificial reagent. However, previous investigations have demonstrated that combining two or more semiconductors to fabricate an appropriate composite structure may be a good strategy.\textsuperscript{10,11}

To date, many efforts had been tried, and some Ag$_3$PO$_4$-based hybrid composite, such as Ag$_3$PO$_4$/WO$_3$,\textsuperscript{12} Ag$_3$PO$_4$/CeO$_2$,\textsuperscript{13} Ag$_3$PO$_4$/Cr-SrTiO$_3$,\textsuperscript{14,15} Ag$_3$PO$_4$/In(OH)$_3$,\textsuperscript{16} BiOCl/Ag$_3$PO$_4$,\textsuperscript{17}...
CoFe2O4 nanoparticles themselves have a strong magnetic property, and therefore, CoFe2O4 based composites can be magnetically separable in a suspension by virtue of their own magnetic properties without introduction of additional magnetic particles.

Considering the above, in the present work we have synthesized magnetically recyclable Ag3PO4/CoFe2O4 nanocomposite by a simple hydrothermal route. The visible light photocatalytic activity of the as-synthesized Ag3PO4/CoFe2O4 nanocomposite was evaluated for the degradation methylene blue (MB) and Rhodamine B (RhB) dyes under natural sunlight irradiation. In addition, the catalytic activity of this magnetic nanocomposite for the reduction of nitrophenols was investigated. The recycle experiments and possible photodegradation mechanism in Ag3PO4/CoFe2O4 system were also proposed.

2. Experimental

2.1. Materials

Cobalt(II) nitrate hexahydrate (Co(NO3)2·6H2O, 98%), iron(II) nitrate nanohydrate (Fe(NO3)2·9H2O, 98%), silver nitrate (AgNO3, 98%), disodium hydrogen phosphate (Na2HPO4, 98.5%), sodium borohydride (NaBH4, 98.5%), 2-nitrophenol (98%), 4-nitrophenol (98%), methylene blue (99%) and Rhodamine B (99%) were obtained from Merck chemical company (99%), 4-nitrophenol (98%) and disodium hydrogen phosphate (Na2HPO4, 98%) were dissolved in 25 mL of water by magnetic stirring for 30 min. A 0.15 mol L−1 Na2HPO4 (0.15 mol L−1) aqueous solution were added into the suspension and sonicated for 3 h. The dispersed mixture was added to a Teflon-lined stainless steel autoclave for hydrothermal treatment at 160 °C for 3 h. Then, the reaction mixture was allowed to cool to room temperature and the precipitate was filtered, washed with distilled water three times, and dried in an oven at 80 °C for 2 h.

2.3. Synthesis of Ag3PO4/CoFe2O4 nanocomposite

The preparation of Ag3PO4/CoFe2O4 (30 wt%) nanocomposite was carried out as follows: in a typical experiment, 26 mg CoFe2O4 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 sonicated for 3 h. The dispersed mixture was added to a Teflon-lined stainless steel autoclave for hydrothermal treatment at 160 °C for 3 h. Then, the reaction mixture was allowed to cool to room temperature and the precipitate was filtered, washed with distilled water three times, and dried in an oven at 80 °C for 6 h. The exact content of CoFe2O4 in the nanocomposite was also confirmed by using ICP-AES. The CoFe2O4 content measured was 29.45 wt% which is in agreement with the theoretical amount (30 wt%). For comparison, pure Ag3PO4 was also prepared under the same conditions without adding CoFe2O4.

2.4. Characterization techniques

The XRD patterns of the samples were obtained on an X-ray diffractometer (PANalytical/X’Pert Pro MPD) using Ni-filtered Cu Kα radiation (λ = 1.54059 Å) radiation FT-IR spectra were recorded on a Schimadzu system FT-IR 160 spectrophotometer in transmission mode from 4000 to 400 cm−1 using KBr pellets. UV-vis spectra of samples (photocatalysts, nitrophenols and dyes) were analyzed at room temperature using a CARY 100 double beam spectrophotometer operated at a resolution of 2 nm with quartz cells with path length of 1 cm in the wavelength range of 200 to 750 nm. UV-visible DRS of the photocatalysts samples were recorded with a Shimadzu UV-2450 spectrophotometer over the spectral range 200–700 nm. The shape and morphology of samples were observed by a MIRA3 TESCAN scanning electron microscope (SEM) equipped with a link energy-dispersive X-ray (EDX) analyzer. The particle size was determined by a LEO-912AB transmission electron microscope (TEM) at an accelerating voltage of 80 kV. TEM samples were prepared by dropping the ethanol dispersion on a carbon coated copper grid. Magnetic measurements were carried out at room temperature using a vibrating sample magnetometer (VSM, Magnetic Daneshpajoh Kashan Co., Iran) with a maximum magnetic field of 10 kOe. The content of CoFe2O4 in the nanocomposite was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, model OEC-730).

2.5. Catalytic reduction tests

In order to study the catalytic performance of the as-synthesized Ag3PO4/CoFe2O4 nanocomposite in reduce processes, the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) by excess NaBH4 in aqueous solution was used as the model reaction. For the catalytic reduction tests, freshly prepared