An in-situ anion exchange method synthesized of Ag₃PO₄ functionalized with Fe₃O₄ and AgI for photocatalytic degradation of methyl orange under visible light irradiation

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To cite this article:

Abstract: A novel of visible light induced photodegradation of methyl orange over Fe₃O₄-Ag₃PO₄@AgI photocatalyst has been observed. The nanoparticles have been synthesized by a facile and effective in-situ ion exchange method and characterized by scanning electron microscopy (SEM), X-ray diffraction meter (XRD) and UV−visible diffuse reflectance spectroscopy. The results show that the magnetic nanoparticles and AgI molecules are immobilized on surface of Ag₃PO₄ without the loss of photofunctionality and magnetic properties. The Fe₃O₄-Ag₃PO₄@AgI has exhibited higher photocatalytic activity better than Ag₃PO₄@AgI and Ag₃PO₄ respectively. The photocatalytic activity of Fe₃O₄-Ag₃PO₄@AgI was evaluated by degradation of the methyl orange nearly 100% after short irradiation time with a good recyclability.

Keywords: Fe₃O₄, Ag₃PO₄, AgI and Visible Light Photocatalytic

1. Introduction

Water pollution is one of the main threats and challenges that humanity faces today. Everyday human activities introduce contaminant substances and wastes into rivers, lakes, groundwater aquifers and oceans. This contamination changes the aquatic environmental quality producing large quantities of water pollutants unsuitable for various uses, including human consumption. Common water pollutants including organic dyes such as methyl orange (MO), methyl blue (MB), rhodamine and so on, which have wide-range potential applications, released into the aquatic environment [1-3]. These compounds are toxic, human carcinogens even at low concentrations, hardly biodegradable and difficult to remove from the environment [4, 5]. Therefore, it is very important to found an innovative and cost effective method for the complete destruction of organic pollutants, water quality and safety monitoring.

In recent years, Photocatalytic oxidation has attracted scientific and technological attention for treatment of wastewater due to the fact that they possess interesting optical, electrical, magnetic and heterogeneous catalytic properties [6-10]. An advanced oxidation process is one of the cost-effective technologies for the degradation of organic pollutants. As well as, heterogeneous photocatalysis has been extensively investigated as a promising candidate for water purification. However, the Photocatalytic materials available to date are generally limited by either poor photocatalytic efficiency in the visible light range or insufficient charge separation ability [11]. To develop the efficiency of the photocatalytic systems, the synthesis of high-performance photocatalysts with good recyclability remains a great challenge.

More recently, silver phosphate (Ag₃PO₄) has been employed forward as a novel photocatalyst that exhibits extremely high photooxidative capabilities for the photodecomposition of organic dyes under visible-light irradiation [13]. Additionally, AgX (X = Cl, Br and I) employs on the surface of Ag₃PO₄ could greatly enhance the chemical stability and activity of Ag₃PO₄ [14]. Fe₃O₄ which have been widely used in the biotechnology and catalysis has proven to
be a promising candidate for the fabrication of visible-light-responsive photocatalytic composites. As well as, Fe$_3$O$_4$ could act as an electron-transfer channel and acceptor, which would suppress the photogenerated carrier recombination [15-17].

In order to avoid tedious separation methods, in our study we describe a facile and effective in-situ ion exchange method of surface modification process that induces the magnetic nanoparticles and AgI to be functionalized with Ag$_3$PO$_4$ to obtain Fe$_3$O$_4$-Ag$_3$PO$_4$@AgI without the loss of photo functionality and magnetic properties for the treatment of methyl orange (MO) in aqueous solution under visible irradiation.

2. Experimental Section

2.1. Chemicals and Reagents

All materials have analytical grade and used as received without further purification. All of the solutions were prepared using deionized water (18.2 MΩ). The pH value of a model sample solutions was determined using a PHS-3D pH meter.

2.2. Preparation of Fe$_3$O$_4$-Ag$_3$PO$_4$@AgI

Fe$_3$O$_4$ was prepared by the modified co-precipitation method [18]. 0.02mol of FeCl$_3$:4H$_2$O and 0.03mol of FeCl$_3$:6H$_2$O were dissolved in 100mL of deionized water, and 2mL of oleic acid was added to the mixture and ultrasond for 20min, the temperature elevated to 60°C then 15mL of ammonium hydroxide was added drop by drop with stirring (600 revolutions/min) under nitrogen atmosphere. After 0.5h, 2.0mL of oleic acid was added again drop-by-drop to the mixture with stirring and reacted for 1h at 80°C. After that, the magnetic precipitate was isolated from the solvent by a permanent magnet, washed with water and ethanol in sequence, and then dried at 50°C under vacuum for 24h.

In dark condition at room temperature through an in-situ anion-exchange method, the as made Fe$_3$O$_4$ (50mg) was dispersed in to distilled water (50ml) and sonicated for 1h to give black aqueous suspension and then A (10mL, 0.6M) of AgNO$_3$ was added into the suspension solution and stirred for 0.5h. Subsequently, aqueous solution of (10mL, 0.2M) Na$_2$HPO$_4$ was added drop-by-drop with continues stirring for more 0.5h, and then sodium iodide was added drop-by-drop in to mixture above which the theoretical molar ratio of I/P was controlled to be 40%. Finally the precipitate was separated by a permanent magnet and washed with distilled water several time and dried under vacuum for 24h.

2.2.1. Synthesis of Ag$_3$PO$_4$ and Ag$_3$PO$_4$@AgI

In a typical synthesis, AgNO$_3$ (10mL, 0.6M) aqueous solution was prepared and then (10mL, 0.2M) Na$_2$HPO$_4$ aqueous solution was added drop-by-drop under sonication to form yellow milk solution. Ag$_3$PO$_4$@AgI hybrid photocatalyst was prepared according to pervious report [19]. In which the theoretical molar ratio of I/P was controlled to be 40%.

2.3. Evaluation of Photocatalytic Activities

A photocatalytic degradation experiment of MO was carried out under visible light irradiation at room temperature. A mixture of (100mL, 0.02mg/ml) MO solution and 50mg of Fe$_3$O$_4$-Ag$_3$PO$_4$@AgI were put in a sealed glass beaker and first ultrasonicated for 0.5h then kept in a dark condition for 0.5h to achieve an equilibrium adsorption of the MO on the surface of the particles before irradiation visible light. After visible light irradiation, 3mL of the mixture were taken out at regular time interval of 3mins, and separated by applying permanent magnet. The supernatants were analyzed by recording variations of the absorption band maximum in the UV–visible spectrophotometer. In addition, the photocatalytic activities of Ag$_3$PO$_4$@AgI, Ag$_3$PO$_4$, pure Fe$_3$O$_4$ nanospheres and photolysis were also evaluated by decomposing MO dye under visible light irradiation.

2.4. Characterization

The morphologies of the as-synthesized samples were investigated by field-emission scanning electron microscopy (FESEM, JEOL, JSM-7001F). The phases of the obtained products were collected on a Bruker D8 Advance X-ray diffractometer in a 2θ range from 20° to 80° at room temperature. UV–visible diffuse reflectance spectra were recorded within the 355–800nm wavelength range using a Shimadzu UV2450 spectrometer.

3. Result and Discussion

3.1. Morphology and Structure

The morphology and structures of as-prepared samples were first investigated by field-emission scanning electron microscopy (SEM). It can be seen in “Fig 1A”, “1B”, that as-prepared Fe$_3$O$_4$-Ag$_3$PO$_4$@AgI through an in-situ anion-exchange method in a dark condition at room temperature in different magnifications were obtained with ununiformed in size and shape and an average diameter of 420 nm, because Ag$_3$PO$_4$ possess an irregular polyhedral morphology [20]. Furthermore, “Fig 1A”, and 1B were clearly reveals that the magnetic nanoparticles and AgI were successfully immobilized on the surface of Ag$_3$PO$_4$. As shown in “Fig 1C”, the polyhedral hybrid Ag$_3$PO$_4$@AgI was observed when an aqueous solution of AgNO$_3$ (10mL, 0.6M) was dropped in to (10mL, 0.2M) Na$_2$HPO$_4$ aqueous solution and then 20 ml of NaI was added drop wise in which the theoretical molar ratio of I/P was controlled to be 40% possessing an irregular polyhedral morphology. As shown in “Fig. 1D”, pure Ag$_3$PO$_4$ possesses an irregular cubic polyhedral morphology.

X-Ray diffraction (XRD) patterns were used to investigate the different crystalline structures of Fe$_3$O$_4$-Ag$_3$PO$_4$@AgI, Ag$_3$PO$_4$@AgI, Ag$_3$PO$_4$, and Fe$_3$O$_4$ as shows in “Fig 2A”, clearly revels that Ag$_3$PO$_4$ is cubic structure, while Fe$_3$O$_4$-Ag$_3$PO$_4$@AgI and Fe$_3$O$_4$ both possesses roughly nanospherical structure confirms that the magnetic
nanoparticle are successfully immobilized on the surface of \( \text{Ag}_3\text{PO}_4 \). However, all of the diffraction peaks of the nanospherical and cubic samples could be indexed to the body-centered cubic structure of \( \text{Ag}_3\text{PO}_4 \) phase-centered cubic structure [12].

Moreover, the UV–visible diffuse reflectance spectra of the three samples were displayed in “Fig. 2B”, the absorption of \( \text{Fe}_2\text{O}_3-\text{Ag}_3\text{PO}_4@\text{AgI} \) has exhibited two absorption edges at about 463 - 512 generates red shift, also exhibited higher absorption in the visible region than the pure \( \text{Ag}_3\text{PO}_4 @ \text{AgI} \) and \( \text{Ag}_3\text{PO}_4 \), while \( \text{Ag}_3\text{PO}_4@\text{AgI} \) exhibited one absorption edge at about 467 nm, implying a combination of the optical absorption property of AgI with that of \( \text{Ag}_3\text{PO}_4 \) [21]. Pure \( \text{Ag}_3\text{PO}_4 \) has exhibited one absorption edge at about 466nm.

**Figure 1.** FESEM images of (A, B) \( \text{Fe}_2\text{O}_3-\text{Ag}_3\text{PO}_4@\text{AgI} \) in different magnifications, (C) \( \text{Ag}_3\text{PO}_4 @ \text{AgI} \) hybrid and (D) bar \( \text{Ag}_3\text{PO}_4 \).

**Figure 2.** (A) XRD pattern of four samples as insert in image. (B) UV–visible diffuses reflectance spectra of \( \text{Fe}_2\text{O}_3-\text{Ag}_3\text{PO}_4 @ \text{AgI} \), \( \text{Ag}_3\text{PO}_4 @ \text{AgI} \) and \( \text{Ag}_3\text{PO}_4 \).
3.2. Photocatalytic Degradation Results and Analysis

In order to investigate the application possibility for water purification, the photocatalytic performance of the samples fabricated in this study was measured using the degradation of MO in an aqueous solution at pH 10 under visible light irradiation as a model reaction “Fig. 3”, the results were indicated that the photodegradation rate of MO as a function of irradiation time in the presence of the different photocatalysts Fe₃O₄-Ag₃PO₄@AgI, Ag₃PO₄@AgI and Ag₃PO₄, nearby 100%, 80% and 60% respectively, while the degradation of MO in the presence of light and magnetic nanoparticles without one of these Fe₃O₄-Ag₃PO₄@AgI, Ag₃PO₄@Ag and Ag₃PO₄ were not observed. “Fig. 4A”, shown that Fe₃O₄-Ag₃PO₄@AgI materials exhibited excellent photocatalytic activities in the degradation of MO under the visible light irradiation for 6 min nearly 100%, exhibited the highest photocatalytic activity. “Fig. 4B”, display that Ag₃PO₄@AgI was needed 12 min to show degradation nearly 80%. The probable reason for this decrease in “Fig. 4A” is that magnetic nanoparticles and AgI were successfully functionalized on the surface of Ag₃PO₄ which led to improve the photocatalytic activity of the photocatalyst; it also could be due to more AgI particles have formed on the surface and adjustment the pH of the MO solution.

Figure 3. The photodegradation rate of MO solution by visible light as a function of irradiation time in the presence of Fe₃O₄-Ag₃PO₄@AgI, Ag₃PO₄@AgI, Ag₃PO₄, photolysis and magnetic nanoparticles. C/C₀, relative concentration of MO solution, where C₀ is an initial concentration and C the concentration as a function of irradiation time.

Figure 4. UV-visible absorption spectral changes of MO in aqueous solution of pH 10 (A) over Fe₃O₄-Ag₃PO₄@AgI and (B) over Ag₃PO₄@AgI irradiation by visible light at different times. The inset composite as a function of irradiation time shows the color changes of the MO solutions corresponding to the degradation times.

In order to investigate the stability and recyclability for the reuse of Fe₃O₄-Ag₃PO₄@AgI in the photocatalytic reaction, the recycling efficiency of the degradation of MO solutions by using the same catalyst after successfully separated by permanent magnet was investigated “Fig. 5”, the results shown similar photocatalytic activity nearly 100%. Subsequently, by this way we can also avoid the probability of the secondary contamination.

Figure 5. (A, B) Recycling photodegradation experiment for MO solution in the presence of reusedFe₃O₄-Ag₃PO₄@AgI under visible light irradiation.
3.3. Probable Mechanism

As illustrated in Scheme 1: FeO₃₋₄–Ag₃PO₄@AgI under visible light irradiation, the electron at the valence band (VB) of AgI are excited to the conduction band (CB) of AgI and then transmission to the surface of Ag₃PO₄ due to the CB of AgI is more negative than that of Ag₃PO₄. Further migrate to the surface of FeO₃₋₄ to react with adsorbed molecular oxygen to form O₂− which oxidized the MO. At the same time, the holes in the VB of Ag₃PO₄ move to that of AgI which direct oxidized the MO.

Scheme 1. Proposed photocatalytic mechanism scheme of FeO₃₋₄–Ag₃PO₄@AgI.

4. Conclusion

In summary, we have successfully synthesized the magnetic nanoparticles functionalized with Ag₃PO₄ and AgI by using a facile and effective in-situ anion-exchange method at room temperature. The magnetic nanoparticles and AgI were successfully immobilized on the surface of Ag₃PO₄ to improve the photocatalytic activity under the visible light irradiation. The photocatalytic degradation has been suggested to be efficient for the degradation of organic dyes in water in the presence of photocatalysis under visible light. Furthermore, the FeO₃₋₄–Ag₃PO₄@AgI has provides good efficiency and recyclability of photocatalyst make this product suitable for many applications in this field.

Acknowledgments

This work was supported by the Natural Science Foundation of China (Grant Nos. 21327005, 21175108); the Program for Chang Jiang Scholars and Innovative Research Team, Ministry of Education, China. (Grant No. IRT1283); the Program for Innovative Research Group of Gansu Province, China (Grant No. 1210RJIJA001).

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