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Visible light photocatalytic reduction of Cr(VI) on Ag_3PO_4 nanoparticles

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ABSTRACT

Ag_3PO_4 nanoparticles of ~300 nm were synthesized by an ion-exchange reaction between $AgNO_3$ and $(NH_4)_2HPO_4$ at ambient condition. X-ray powder diffraction, scanning electron microscopy, UV−Vis diffuse reflectance spectroscopy were employed to investigate the phase structure, morphology, and optical property of the Ag_3PO_4 nanoparticles. Nearly 80% of Cr (VI) ions was removed after visible-light irradiation in Ag_3PO_4 suspension, the excellent photocatalytic reduction performance due to the high separation efficiency of electron and hole pairs. In addition, the possible photoreduction mechanism of Cr(VI) in Ag_3PO_4 suspension was discussed. The system of Ag_3PO_4 may provide an alternative way for the efficient removal of Cr(VI) under visible-light irradiation.

Keywords: Ag_3PO_4 nanoparticles; Cr(VI); Photocatalytic reduction

1. Introduction

With the industrial development, a large number of various toxic pollutants are released into the environment that are hazardous to human health. Chromium (VI) is a common toxic pollutant in wastewaters originating from various industrial processes such as electroplating, pigment production, and leather tanning [1]. Therefore, the elimination of Cr (VI) is of great importance in the view of environmental security.

Recently, increasing attention has been paid to the TiO_2 photocatalytic reduction process, in which Cr(VI) is reduced to less harmful and immobile Cr(III), followed by the combination with other effective separation method to yield a practical technology for removing toxic metals from wastewaters [1–5]. However, TiO_2 with a relatively wide bandgap of 3.2 eV limits its efficient utilization of sunlight. Therefore, it is highly desirable to design new visible-light-induced photocatalysts from the viewpoint of using solar light.

In recent years, visible-light-driven photocatalysts such as $TiO_{2-x}N_x$ [6], $In_{1-x}Ni_xTaO_4$ [7], $CaBi_2O_4$ [8], and Ag@AgCl [9] have been developed. In this area, a breakthrough was made to find silver ortho-phosphate (Ag_3PO_4) as an active visible-light-induced photocatalyst [10,11]. Yi et al. reported that Ag_3PO_4 crystal possessed an excellent photocatalytic ability due to the high separation of photoexcited electrons and holes [10]. The work reported by Bi et al. revealed a facet effect of single-crystalline Ag_3PO_4 products on their

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photocatalytic performances [12]. Dinh et al. discussed the size-dependent photocatalytic activities of the Ag_3PO_4 product [13]. However, no study about photocatalytic activity for the reduction of aqueous Cr(VI) ions by Ag_3PO_4 was investigated.

In this contribution, a facile method was employed to synthesize Ag_3PO_4 product at room temperature. The photocatalytic ability of the as-obtained Ag_3PO_4 product was investigated by photoreduction of Cr(VI) ions. In addition, the different atmosphere, pH-dependent photoreduction experiments, and possible photoreduction mechanism in Ag_3PO_4 suspension were also discussed.

2. Methods and materials

2.1. Preparation of Ag_3PO_4

Ag_3PO_4 was synthesized by a simple ion-exchange method. In a typical process, 0.5100 g of $AgNO_3$ was dissolved in 20 mL of H_2O, then 30 mL of $(NH_4)_2HPO_4$ (0.1300 g) aqueous solution was added by drops into the above solution under vigorous stirring. After stirring for 30 min, the yellow precipitate was collected by filtration, washed with distilled water and absolute ethanol for several times, and then dried at a temperature of 105˚C for further use. TiO_2 was synthesized according to the previous report [14].

2.2. Characterizations

Ultraviolet–visible (UV–Vis) diffuse reflectance spectra of Ag_3PO_4 were performed using a VARIAN Cary-5000 UV/Vis/NIR spectrophotometer. $BaSO_4$ is used as a reference standard sample. X-ray diffraction (XRD) patterns for Ag_3PO_4 powder were obtained with a Rigaku (Tokyo, Japan) D/MAX-2500 diffractometer with a Cu–Kα radiation (1.54056 Å). The morphology and size of the as-prepared product were characterized by using a field emission scanning electron microscope (JEOL JSM-5610LV).

2.3. Photocatalytic reduction of Cr(VI) under visible light

The reduction activity of the photocatalysts was evaluated by measuring the reduction ratio of Cr(VI). A 500 W halogen lamp equipped with circulating cold water was used as the visible light source. The distance was 20 cm between the light source and the reactor containing $K_2Cr_2O_7$ aqueous solution (20 mL, 0.4 mmol/L). The catalyst powder (20 mg) was added to the reactor and then stirred with a magnetic stirrer in the dark for 30 min to reach the adsorption/desorption equilibrium prior to irradiation. The reactor was kept at an ambient temperature either opened to the air or nitrogen. The reduction ratio was determined by the photometric method at 540 nm with diphenylcarbazide [15].

3. Results and discussion

3.1. Characterization

Fig. 1 shows the SEM image of the Ag_3PO_4 nanoparticle with an average size of ~300 nm. Fig. 2 shows the UV–Vis diffuse reflectance spectra of Ag_3PO_4. Obviously, the absorption band edge of the prepared Ag_3PO_4 is ~530 nm, which is consistent with the previous report [16]. Band gap of the Ag_3PO_4 was determined by optical absorption near the band edge by the following equation: $\alpha h\nu = A(h\nu - E_g)^{n/2}$, where, α, $h\nu$, A, and E_g are the optical absorption coefficient, photonic energy, proportionality constant, and band gap, respectively [17]. In this equation, n decides the type of the transition in a semiconductor ($n = 1$, direct absorption; $n = 4$, indirect absorption). By calculation, the E_g of the Ag_3PO_4 was estimated to be 2.44 eV, which is consistent with the reported value ($E_g = 2.45$ eV) [17]. It can be indicated that the Ag_3PO_4 nanoparticle exhibits significant broadening in both ultraviolet and visible absorption. Therefore, Ag_3PO_4 photocatalyst inherently possess the photocatalytic potential for reactions involved in both organic and inorganic pollutant degradation.

The XRD spectra patterns were obtained using an instrument (D/max-2500/PC) with Cu–Kα radiation. Fig. 3 shows the powder XRD patterns of Ag_3PO_4 nanoparticles. The sharp and intense XRD peaks

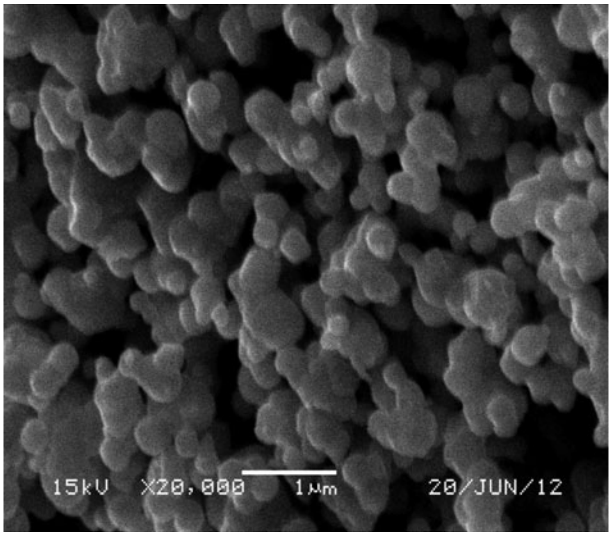

Fig. 1. SEM image of Ag_3PO_4 nanoparticle.

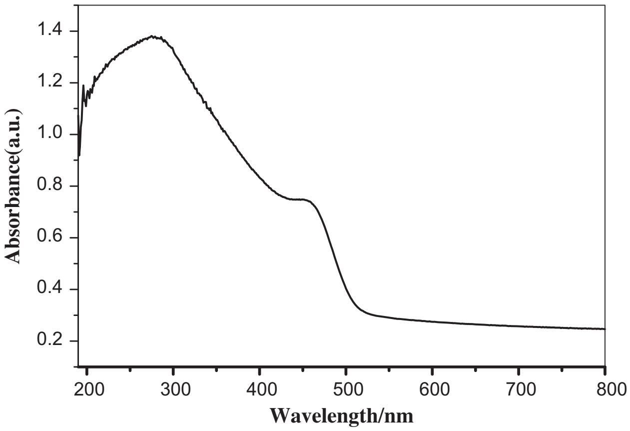

Fig. 2. UV–Vis diffuse reflectance spectra of Ag_3PO_4 nanoparticle.

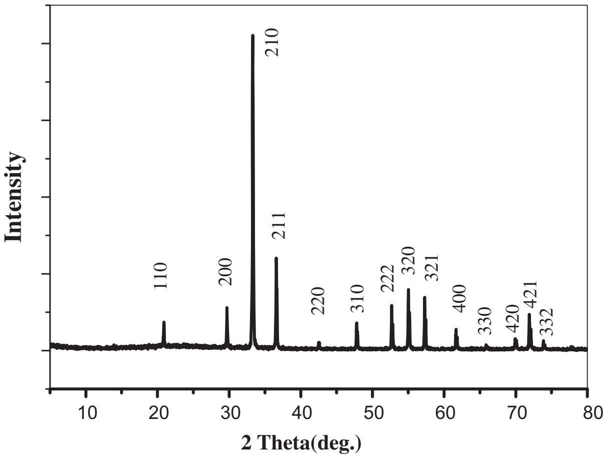

Fig. 3. XRD pattern of Ag_3PO_4 nanoparticle.

indicate the highly crystallized structure of Ag_3PO_4, and all the peaks in the XRD pattern can be indexed to the body-centered cubic phase Ag_3PO_4 (JCPDS No.06-0505).

3.2. *Photocatalytic activity*

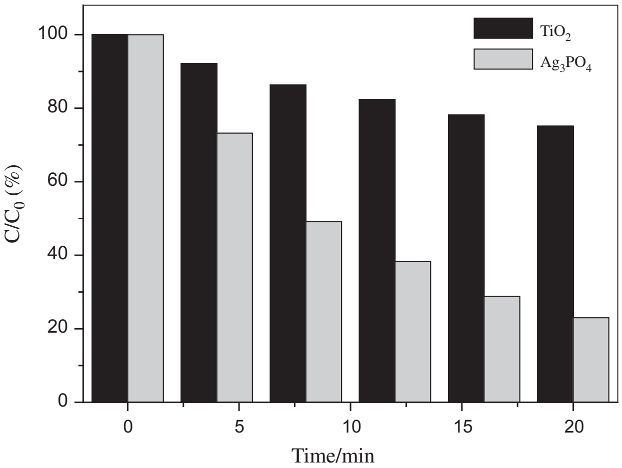

Fig. 4. Photocatalytic reduction of Cr(VI) by Ag_3PO_4 or TiO_2.

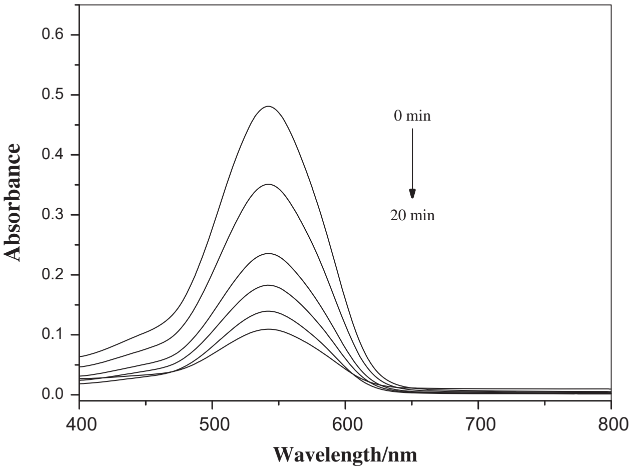

Fig. 5. The process of photocatalytic reduction of Cr(VI).

The photocatalytic activities of Ag_3PO_4 in photoreduction Cr(VI) were evaluated under a visible-light irradiation. As shown in Figs. 4 and 5, photocatalytic activities of the TiO_2 were very low, whereas the Ag_3PO_4 showed remarkably photocatalytic activity. This can be explained by the weak absorption in the visible region for TiO_2. Nearly 80% of Cr(VI) was reduced over Ag_3PO_4 after 20 min under visible-light irradiation. The result demonstrates that the concentration of Cr(VI) decreased rapidly in the case of the Ag_3PO_4 particles (Fig. 5). It can be concluded that Ag_3PO_4 exhibits much higher photocatalytic activity than TiO_2. The result demonstrates that the recombination of photoexcited electrons and holes of Ag_3PO_4 is very weak [18].

Fig. 6 shows the relationship between the irradiation time and photocatalytic reduction efficiency of Cr (VI) ions in different atmosphere. In N_2 atmosphere, the Ag_3PO_4 photocatalysts exhibit higher photocatalytic activity than in the conditions of air atmosphere. This phenomenon implies that the reduced photocatalytic activity of the Ag_3PO_4 in air is probably due to the effect of dissolved oxygen on the electron migration between Cr(VI) ions and Ag_3PO_4. On the one hand, some electrons shuttled freely along the Ag_3PO_4 reacting with the O_2 to yield active oxygen species (O_2^{-}, $^{\cdot}OOH$ and $^{\cdot}OH$ radicals) [19], which means that the adsorbed O_2 will compete electrons with Cr(VI)

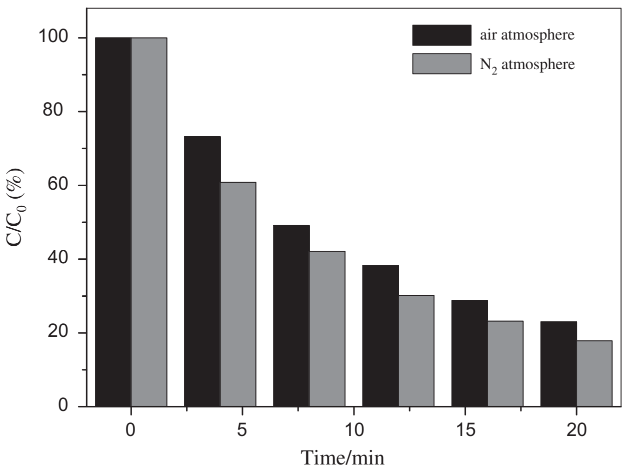

Fig. 6. Photocatalytic reduction of Cr(VI) under air or N_2 atmosphere.

ions in water. Therefore, a lower reduction efficiency of Cr(VI) ions in aqueous solution is ineluctable under air atmosphere.

The effect of pH on the Ag_3PO_4 photocatalytic reduction of Cr(VI) was examined under visible-light irradiation. Fig. 7 shows the removal of Cr(VI) at three different pH values, the removal of Cr(VI) increased with decreasing pH. The pH effect on the Cr(VI) conversion is mainly ascribed to the following reasons. Firstly, the increased potential difference between the conduction band of Ag_3PO_4 and Cr(VI)/Cr(III) as well as the anionic-type adsorption of Cr(VI) onto the Ag_3PO_4 surface. As discussed previously, thermodynamic driving force for the reduction of Cr(VI) is related with the potential difference between the conduction band of Ag_3PO_4 and the metal ions [20]. Secondly, the pH at zero point charge (pH_{zpc}) of Ag_3PO_4 is 6.55 [21]. Therefore, it is reasonable that anionic species of Cr(VI), such as CrO_4^{2-} and $HCrO_4^-$, can easily be adsorbed onto the Ag_3PO_4 surface below the pH_{zpc}.

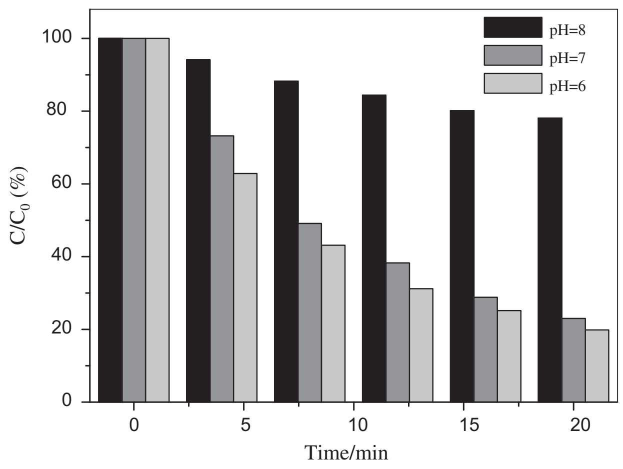

Fig. 7. Photocatalytic reduction of Cr(VI) under different pH values.

4. Conclusions

The photocatalytic reduction based on Ag_3PO_4 nanoparticles is a promising technique for the removal of toxic Cr(VI). As an extension to the catalytic process of Ag_3PO_4 under visible light, the present work investigated the photoreduction of Cr(VI) over neat Ag_3PO_4 under visible-light irradiation. The removal of Cr(VI) was greatly enhanced under the neutral solution in N_2 atmosphere. The results suggested that Ag_3PO_4 is a promising photocatalyst in efficient utilization of solar energy for the treatment of Cr(VI)-containing wastewater.

Acknowledgments

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