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A novel Ni^{2+}-doped Ag_3PO_4 photocatalyst with high photocatalytic activity and enhancement mechanism

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HIGHLIGHTS

- Ni^{2+}-modified with higher photodegradation ability was synthesized.
- •OH radicals were the main active species in the oxidation of MO.
- The doping of Ni^{2+} in Ag_3PO_4 is responsible for the enhanced activity.

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ABSTRACT

Ni^{2+}-doped Ag_3PO_4 (Ni^{2+}-Ag_3PO_4) photocatalysts with superhigh activity for photodegradation of organic pollutants were prepared by a simple hydrothermal method. The photocatalysts were characterized with X-ray powder diffractometry, transmission electron microscopy, ultraviolet–visible absorption spectroscopy, X-ray photoelectron spectroscopy, measurement of total organic carbon, and electron paramagnetic resonance spectrometry. The photocatalysts were evaluated by methyl orange (MO) photodegradation experiments under visible light irradiation ($\lambda > 420$ nm). Comparative analysis showed the optimal doping dosage was 0.05 mol/L Ni^{2+}. The optimal Ni^{2+}-Ag_3PO_4 has an MO photodegradation rate constant four times larger than pure Ag_3PO_4. The photocatalytic ratio of 40 mg/L MO over the optimal Ni^{2+}-Ag_3PO_4 after 10 min is 89%, which indicates excellent photocatalytic ability in high-concentration MO solutions. The Ni^{2+} doping into Ag_3PO_4 can increase the level of band gap, and accelerate the utilization of photons and the separation of photo-generated charges. Therefore, the Ni^{2+} doping into Ag_3PO_4 is responsible for the enhancement of photocatalytic ability.

1. Introduction

Photocatalytic technology is an effective way to solve environmental pollution because of low cost, no secondary pollution, simple process, and energy saving [1,2]. Before the popularization of this technology, however, one major challenge is to develop new efficient and stable photocatalysts [3]. One such candidate is silver phosphate (Ag_3PO_4), which is a yellow cubic crystal solid powder. Ag_3PO_4 has a direct bandgap of 2.43 eV and an indirect band gap of 2.36 eV. Ag_3PO_4 can absorb ultraviolet–visible (UV–vis) light at wavelength (λ) less than 525 nm [4] and has strong photocatalytic ability under visible light irradiation. The photocatalytic oxidation experiment of Ag_3PO_4 was first reported in 2010 [5,6]. Ag_3PO_4 not only produces O_2 through water photolysis, but also degrades organic dyes under visible radiation, with quantum efficiency above 90%. These results prove that Ag_3PO_4 is a high-efficiency photocatalyst with great application potential [7–10]. So far, much work has been done to improve the photocatalytic ability of Ag_3PO_4 through modification.

Modification based on metal or non-metallic ions is an effective way to enhance the degradation ability of photocatalysts [11–16]. During cation doping, an impurity band formed in the band gap of materials can reduce the band gap and enhance the efficiency of low-energy high-wavelength visible light utilization [17,18]. Meanwhile, metal cations can act as an electron acceptor to capture

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photo-generated electrons, thereby greatly facilitating the formation of reactive species (e.g. hydroxyl radical) on the catalyst surfaces [19,20]. In addition, the recombination between photo-generated electrons and holes can be effectively prevented, thereby improving the photocatalytic properties.

In this study, we aimed to enhance the photocatalytic ability of Ag_3PO_4 by Ni^{2+} doping. There are reports about the modification of photocatalysts by using Ni^{2+}, such as $K_2Ni(VO_3)_4$ [21], Ni-$InVO_4$ [22], Ni-TiO_2 [23] and Ni-CdS [24]. Ni 3d orbits can form impurity energy band in a semiconductor. The empty Ni 3d orbits in impurity energy band help to migrate photo-generated electrons and separate photo-generated electron-hole pairs, thus greatly improving the photocatalytic oxidation. For example, the Ni^{2+} doing in $K_2Ni(VO_3)_4$ can reduce the band gap energy. Thus, the photo-generated electrons can be easily produced under visible light and migrate from O 2p to the empty Ni 3d. The electron separation could significantly improve the oxidation ability of photocatalysts [21]. In addition, the Ni^{2+} doping, such as Ni^{2+}-CdS, can improve the stability and service life. These studies help to investigate the Ni^{2+}-doped Ag_3PO_4 catalysts (Ni^{2+}-Ag_3PO_4). We explored in detail how the physiochemical properties of Ni^{2+}-Ag_3PO_4 impact the photocatalytic oxidation of methyl orange (MO), and analyzed the mechanism of oxidation ability enhancement. This study underlies the development of new efficient Ag_3PO_4 photocatalysts.

2. Experimental

2.1. Synthesis of samples

Ag_3PO_4 was prepared by a coprecipitation method. Specifically, appropriate amounts of $AgNO_3$ and $NaH_2PO_4 \cdot 2H_2O$ were dissolved in 50 mL of deionized water to form a yellow precipitate. The precipitate was collected, washed and dried to form pure Ag_3PO_4. Ni^{2+}-Ag_3PO_4 was synthesized by a hydrothermal method. Specifically, appropriate amounts of Ag_3PO_4 and $Ni(NO_3)_2 \cdot 6H_2O$ were added to 50 mL of deionized water under stirring. The mixed solution was transferred to a 100 mL stainless steel autoclave and allowed to react at 60 °C for 2 h. After the autoclave was cooled to room temperature, the products were collected, washed with anhydrous ethanol and deionized water several times, and dried in a vacuum oven at 80 °C for 6 h.

2.2. Characterization of samples

Crystal phases and sizes were measured by a Rigaku D/max 2500 powder X-ray diffractometer (XRD, CuKα, λ = 1.5406 Å, 40 kV, 40 mA). Optical performance and band gaps were measured by an HP8453 UV–vis spectrometer using $BaSO_4$ as the reference. Morphology and particle size were visualized by a JEM 2100 transmission electron microscope (TEM, JEOL, Japan; 200 kV) and a scanning electron microscope (ZEISS Gemin SEM 500). Specific surface areas of Brunauer-Emmett-Teller (BET) were determined on a Micromeritics ASAP 2020M apparatus at the liquid nitrogen temperature of −196 °C. Surface bond energy was measured by a Perkin-Elmer PHI5300 X-ray photoelectron spectroscope (XPS). Carbon (C_{1s}, 284.6 eV) was used to calibrate bond energy. Total organic carbon contents (TOCs) in the remaining solutions were measured by a Shimadzu-Toc-Vcph meter. Zeta potential at room temperature was measured with a Zetasizer nanoscale ZS90 instrument. Electron spin resonance (ESR) spectra were recorded by a JES FA200 electron paramagnetic resonance spectrometer.

2.3. Activity measurement

MO photodegradation experiments were conducted by adding 100 mg of a photocatalyst into 100 mL of 10–40 mg/L MO solutions. The home-made reactor was vertically irradiated by a 300 W xenon lamp (λ > 420 nm). Before exposure to light irradiation, each mixture solution was stirred in dark for 30 min to reach adsorption equilibrium. Then, 3 mL from each solution was taken out every 2 min and centrifuged for UV–vis absorption measurements.

3. Results and discussion

3.1. Characterization of photocatalysts

The XRD spectra of Ag_3PO_4 and Ni^{2+}-Ag_3PO_4 are presented in Fig. 1A. The XRD peak of Ag_3PO_4 reveals a pure crystalline and cubic phase (JCPDS 06-0505, space group: $P\bar{4}3n$[218], $a = b = c = 6.013$ Å). Similarly, the peaks of Ni^{2+}-Ag_3PO_4 all confirm the formation of a cubic crystalline phase. No other components including $Ni_3(PO_4)_2$ are found in Fig. 1A. To further investigate the doping of Ni^{2+}-Ag_3PO_4, we enlarged the XRD patterns of Ag_3PO_4 and Ni^{2+}-Ag_3PO_4 (Fig. 1B). Clearly, the main peaks of Ni^{2+}-Ag_3PO_4 shift to right, which indicates the addition of Ni^{2+} causes the lattice contraction of Ag_3PO_4. The reason is that Ni^{2+} has a smaller radius than Ag^+ and enters the crystal lattice of Ag_3PO_4 to substitute Ag^+, leading to the

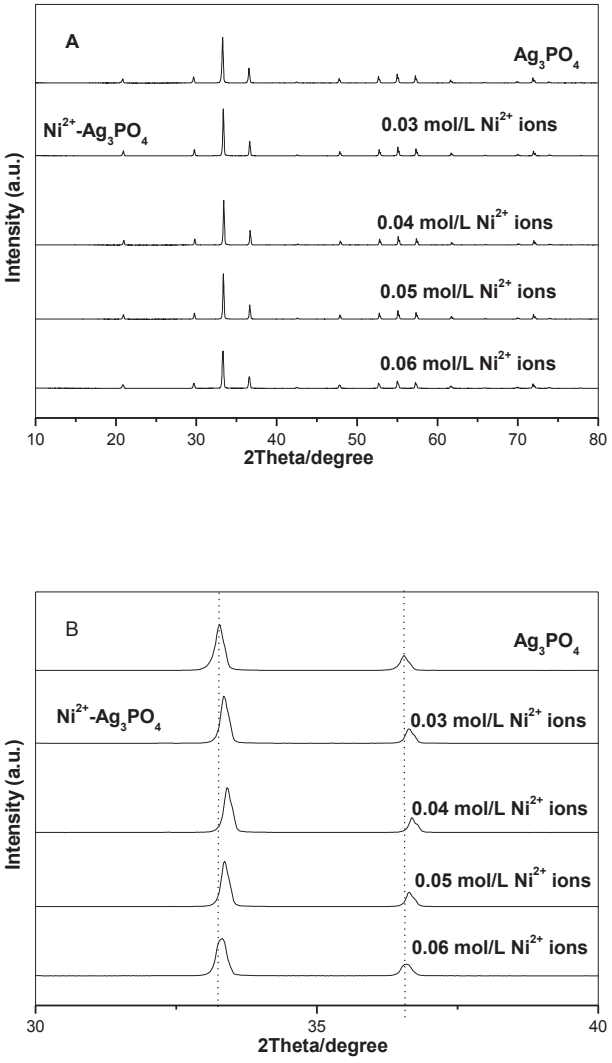

Fig. 1. (A) X-ray diffraction patterns of undoped and Ni^{2+}-doped Ag_3PO_4. (B) Partially enlarged XRD patterns of undoped and Ni^{2+}-doped Ag_3PO_4.