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Article

Photodegradation of rhodamine B and methyl orange by Ag_3PO_4 catalyst under visible light irradiation

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ABSTRACT

A visible-light-driven Ag_3PO_4 catalyst was successfully synthesized by a facile ion-exchange route. The as-synthesized Ag_3PO_4 was characterized by X-Ray diffraction (XRD), field-emission scanning electron microscopy, N_2 adsorption-desorption, UV-Vis diffuse reflectance spectroscopy and Fourier transform infrared spectroscopy. Under visible light irradiation, the Ag_3PO_4 catalyst showed excellent photocatalytic activity for rhodamine (RhB) degradation, but was poor at degrading methyl orange (MO) because of lower adsorption of MO molecules onto the surface of the Ag_3PO_4 . The photodegradation of RhB and MO was achieved by holes and $\text{O}_2^{\cdot-}$ radical attack in the Ag_3PO_4 suspension. The photodegradation of MO over the Ag_3PO_4 catalyst was greatly enhanced in the presence of RhB owing to greater production of $\text{O}_2^{\cdot-}$ radicals.

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1. Introduction

Dyes are often lost in waste streams during manufacturing or processing operations, resulting in potential harm to the environment and human health [1]. It is usually difficult to remove such dyes completely with biological and physical treatments [2]. Heterogeneous photocatalysis is a common advanced oxidation approach to eliminate these dyes from wastewater [3–5].

In recent years the development of highly efficient visible light-driven photocatalysts has received increasing attention [6–8]. Among them, Ag_3PO_4 is an excellent and promising photocatalyst for the photodegradation of dyes under visible-light irradiation due to a high separation of photoinduced electron and hole pairs [9]. Many studies have reported that Ag_3PO_4 possessed excellent photocatalytic performance in the degradation of typical organic dyes under visible light irradiation

[10–17]. For example, Yan et al. [10] and Dong et al. [11] studied the morphology-dependent photocatalytic properties of Ag_3PO_4 for the degradation of dyes. Vu et al. [12] investigated the size-dependent photocatalytic activities of nano-sized Ag_3PO_4 . Bi et al. [17] revealed a facet effect of Ag_3PO_4 samples on their photocatalytic performances for RhB and MO degradation. Although these previous works reported that Ag_3PO_4 exhibited different photocatalytic ability towards RhB and MO degradation [10,17], the photodegradation mechanisms of RhB and MO in the Ag_3PO_4 system have not been shown in detail.

In this work, a Ag_3PO_4 catalyst was successfully synthesized at room temperature using a facile ion-exchange method. The photodegradation rates of RhB (a cationic dye) and MO (an anionic dye) under visible light by the Ag_3PO_4 catalyst were compared, and the possible photocatalytic mechanisms of RhB and MO degradation in Ag_3PO_4 suspension were proposed in detail. The photocatalytic performance of Ag_3PO_4 catalyst for

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MO degradation in the presence of RhB was also discussed.

2. Experimental

2.1. Materials

EDTA, benzoquinone, isopropyl alcohol and terephthalic acid were purchased from Acros Corp (Belgium). RhB and MO were obtained from Shanghai Aladdin Chemistry Corp (China). All other chemicals were purchased from Tianjin Chemical Company (China) and used as received.

2.2. Synthesis and characterization

In a typical process, 0.006 mol AgNO_3 was dissolved in 20 mL H_2O , and 40 mL of an aqueous Na_2HPO_4 (0.002 mol) solution was then added dropwise into the solution under vigorous stirring. After stirring for 30 min, the yellow precipitate was collected by centrifugation, washed with distilled water and absolute ethanol, and then dried in air.

The phase of the as-obtained product was characterized by X-ray diffraction (XRD) with a Rigaku D/Max-2500 X-ray diffractometer using $\text{Cu K}\alpha$ radiation, $\lambda = 0.154056$ nm. The morphology and size of the as-prepared product were characterized by field emission scanning electron microscopy (FESEM, JEOL JSM-6700). The Brunauer-Emmett-Teller (BET) surface area of the sample was measured on a Micromeritics Tristar 3000 analyzer. UV-Vis diffuse reflectance spectra (DRS) were recorded in the range of 200–800 nm with a UV-Vis spectrophotometer (Shimadzu, UV-3600) using BaSO_4 as the reference. Fourier transform infrared (FT-IR) spectra were recorded using a Nicolet AVATAR360 infrared Fourier spectrometer with the KBr wafer technique.

2.3. Evaluation of photocatalytic performance

The photocatalytic activity of the as-obtained sample was evaluated using the degradation of RhB and MO under visible light. The photodegradation reactions were carried out in a simple photocatalytic reactor without a water circulation facility (Fig. 1). A 10 W LED lamp was employed as the visible light source. The distance between the lamp and solution was about

Fig. 1. Photocatalytic apparatus. (1) Magnetic stirrer; (2) Ag_3PO_4 photocatalyst; (3) Magnet; (4) Dye solution; (5) LED lamp; (6) Sampler.

6 cm. The Ag_3PO_4 photocatalyst (0.05 g) was added to aqueous RhB or MO solution (5 mg/L, 100 mL) and was magnetically stirred in the dark for 30 min. 3 mL of the suspension was taken at given time intervals and separated through centrifugation. The concentrations of RhB and MO in the supernatant were analyzed at 553 nm and 464 nm, respectively, on a UV-Vis spectrophotometer (Shimadzu, UV2550). The active species generated during the photocatalytic process were detected using *in situ* capture experiments.

2.4. Terephthalic acid fluorescence probe

The terephthalic acid fluorescence probe technique was employed to detect $\text{OH}\cdot$ radicals in the system. We added 0.05 g of the Ag_3PO_4 photocatalyst to 100 mL of an aqueous solution containing 2 mmol/L NaOH and 0.5 mmol/L terephthalic acid. Prior to irradiation, the suspension was stirred in the dark for 30 min. Three milliliters of the suspension was collected at predetermined time intervals and centrifuged. The fluorescence spectrum of the remaining clear supernatant was measured using a Hitachi F4500 spectrometer.

3. Results and discussion

3.1. Characterization results

The phase structure and purity of the product were characterized by XRD. Figure 2(a) shows the XRD pattern of the as-obtained product. All of the diffraction peaks can be indexed to the cubic structure of Ag_3PO_4 (JCPDS card No.06–0505). No peaks assignable to other phases were observed, indicating

Fig. 2. XRD pattern (a) and SEM image (b) of the Ag_3PO_4 sample.

Fig. 3. (a) UV-Vis diffuse reflectance spectrum of the Ag_3PO_4 product; (b) Plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ for the Ag_3PO_4 product.

that high-purity Ag_3PO_4 was obtained. The sharp and strong diffraction peaks indicated that the Ag_3PO_4 product was well crystallized. The shape and size of the as-prepared Ag_3PO_4 product were investigated by FESEM. The SEM image revealed that the as-obtained product was composed of quasi-spherical particles having diameters in the range of 150–500 nm (Fig. 2(b)). The BET surface area of the as-obtained Ag_3PO_4 product was $2.6 \text{ m}^2/\text{g}$.

The UV-Vis diffuse reflectance spectrum of the as-obtained Ag_3PO_4 is shown in Fig. 3(a), which shows that the product exhibited absorption in the visible range as well as the UV range. The band gap (E_g) of a semiconductor can be obtained from the following equation (Eq. 1):

$$\alpha h\nu = A(h\nu - E_g)^{n/2} \quad (1)$$

where α , ν , and A are absorption coefficient, light frequency, and proportionality constant, respectively. The band gap (E_g) of the Ag_3PO_4 was obtained from the plot of $(\alpha h\nu)^{1/2}$ versus $(h\nu)$ [15], as shown in Fig. 3(b), and was estimated to be 2.24 eV.

The FT-IR spectrum of the as-synthesized Ag_3PO_4 is shown in Fig. 4. The peaks at 1670 and 3200 cm^{-1} were attributable to the bending vibration and the bending vibration of O–H [11], respectively. In addition, two strong peaks observed at 560 and

Fig. 4. FT-IR spectra of the as-prepared Ag_3PO_4 product.

1014 cm^{-1} were assignable to the molecular vibrations of phosphate (PO_4^{3-}) [11].

3.2. Photocatalytic activity and mechanism

The photodegradation of RhB (a cationic dye) and MO (an anionic dye) by a suspension of the Ag_3PO_4 under irradiation with visible light was investigated. In the absence of Ag_3PO_4 catalyst, removal of the dyes was almost negligible (data not shown). Figure 5(a) shows the photodegradation of RhB and MO in Ag_3PO_4 suspensions as a function of irradiation time. After 30 min exposure to visible light, 98.8% of the RhB was degraded, but only 42.8% of the MO was removed. The zero point charge (pHzpc) for Ag_3PO_4 is about 5.4 [18]. At ranges lower or higher than the pHzpc, Ag_3PO_4 is positively charged or negatively charged, respectively. Therefore, in the neutral solution used (photodegradation of the dyes in water without pH adjustment), negatively charged Ag_3PO_4 surfaces were available for the adsorption of positively charged RhB (a cationic dye), which promoted degradation reaction. This was further confirmed with an adsorption experiment. Figure 5(b) displays the time-resolved adsorption of the dyes by the Ag_3PO_4 catalyst in the dark. After 60 min, the amount of RhB adsorbed by the Ag_3PO_4 catalyst in the dark was 24.5%, compared with only 3.1% adsorption of MO.

The photodegradation efficiency for MO was still low when the Ag_3PO_4 loading was increased (from 0.5 g/L to 1.0 g/L) while keeping all the other conditions unchanged; only 58.8% of the MO was degraded (Fig. 6). This result further indicated that the as-synthesized Ag_3PO_4 catalyst was not good at degrading MO dye using visible light. However, the rate of MO photodegradation was greatly enhanced in the presence of RhB; about 81.0% of the MO in the aqueous suspension was decomposed by the Ag_3PO_4 catalyst under visible light irradiation.

Fig. 5. (a) Photocatalytic degradation of RhB and MO in Ag_3PO_4 suspension under visible light without pH adjustment; (b) Time-resolved adsorption of dye by Ag_3PO_4 catalyst in the dark. Ag_3PO_4 dose, 0.5 g/L ; initial concentration of dye, 5 mg/L .

Fig. 6. Photodegradation of MO in Ag₃PO₄ suspension under visible light (initial concentration of MO, 5 mg/L).

tion after 30 min (Fig. 6). The reason for this phenomenon will be given in the following section.

To investigate the photocatalytic mechanism of dye degradation in the Ag₃PO₄ system, we measured the reactive oxygen species present during the photocatalytic processes. It is well known that terephthalic acid reacts with OH• radicals to form 2-hydroxy terephthalic acid, which emits fluorescence at 426 nm ($\lambda_{\text{ex}} = 315$ nm) [19,20]. As shown in Fig. 7, no obvious fluorescence peak at 426 nm was observed, and the fluorescence intensity at 426 nm was not significantly changed with extended irradiation time, indicating that OH• is not the main reactive oxygen species in the Ag₃PO₄ system [20]. From a theoretical viewpoint, the valence band edge potential of Ag₃PO₄ catalyst (2.45 eV) [16] is less positive than $E^{\ominus}(\text{OH}^{\bullet}/\text{H}_2\text{O})$ (2.68 eV) [21], which indicates that Ag₃PO₄ holes cannot oxidize adsorbed H₂O molecules to OH• radicals. Next, reactive species trapping experiments were conducted to investigate the reactive oxygen species in the photocatalytic process of the Ag₃PO₄ system. Isopropyl alcohol, EDTA, and benzoquinone were introduced into the photocatalytic system as scavengers for OH•, h⁺, and O₂^{•−} [22–24], respectively. As shown in Fig. 8, the addition of isopropyl alcohol had little effect on the photocatalytic performance of the Ag₃PO₄ catalyst, which further indicates that OH• does not play a key role in the degradation of dyes in

Fig. 7. OH• trapping PL spectra for a terephthalic acid solution of the Ag₃PO₄ catalyst under visible light irradiation.

Fig. 8. Photodegradation of RhB (a) and MO (b) by Ag₃PO₄ catalyst under different conditions. (1) No scavengers; (2) 1 mmol/L isopropyl alcohol; (3) 1 mmol/L benzoquinone; (4) 1 mmol/L EDTA. Ag₃PO₄ loading, 0.5 g/L; initial concentration of dye, 5 mg/L.

the Ag₃PO₄ system. The addition of 1 mM EDTA strongly inhibited the photocatalytic activity of the Ag₃PO₄ catalyst for the degradation of both RhB and MO. Inhibition of RhB and MO degradation was also observed when 1 mmol/L benzoquinone was added to the photocatalytic reaction systems, suggesting that O₂^{•−} radicals contribute to the photocatalytic performance of Ag₃PO₄ suspensions under visible light irradiation (Fig. 8). To confirm this result, the photocatalytic activities of Ag₃PO₄ for RhB and MO degradation were investigated with continuous N₂ sparging. Under anoxic conditions, both RhB and MO photodegradation were strongly inhibited (Fig. 9). Thus, it can be concluded that h⁺ and O₂^{•−} are the main reactive species in the Ag₃PO₄ system for RhB and MO degradation under visible light irradiation (Figs. 8 and 9).

On the basis of the above results, we propose a possible photocatalytic mechanism for RhB or MO degradation in Ag₃PO₄ suspension using visible light. Under irradiation, the electron-hole pairs of the Ag₃PO₄ semiconductor are separated, and the electrons at the valence band are excited to the conduction band, resulting in the formation of holes in the valence band. The valence band edge potential of Ag₃PO₄ is 2.45 eV [16], which indicates that holes formed in the valence band of the Ag₃PO₄ catalyst could directly oxidize RhB or MO adsorbed on its surface [25]. Much more RhB than MO could be adsorbed by the Ag₃PO₄ catalyst (Fig. 5(b)), resulting in a much higher rate of RhB photodegradation than that of MO by the as-synthesized Ag₃PO₄ catalyst. O₂ molecules adsorbed on the Ag₃PO₄ catalyst surface can be reduced by the photogenerated electrons to form O₂^{•−} radicals, which contribute to the photodegradation of dyes in the Ag₃PO₄ system [22]. Meanwhile, the dye molecules can be excited by the visible light, and the resulting photoelectrons are immediately injected into the con-

Fig. 9. Photodegradation of RhB (a) and MO (b) by Ag_3PO_4 with and without N_2 . (1) No N_2 ; (2) With continuous N_2 -sparging. Ag_3PO_4 loading, 0.5 g/L; initial concentration of dye, 5 mg/L.

duction band of Ag_3PO_4 catalyst, further facilitating the removal of the dye [26,27]. The photocatalytic mechanism of RhB or MO degradation in the present Ag_3PO_4 system under visible light irradiation is thus as follows:

According to the experimental results, the photodegradation of MO over the as-obtained Ag_3PO_4 catalyst under visible light irradiation was greatly enhanced with the assistance of RhB (Fig. 6). However, the rate of RhB photodegradation by the Ag_3PO_4 catalyst was decreased in the presence of MO (Fig. 5(a) and Fig. 10). As shown, RhB is easily adsorbed onto the surface of the Ag_3PO_4 catalyst. Under visible light irradiation, the adsorbed RhB molecules were excited by the visible light and the excited-state electrons are injected into the conduction band of Ag_3PO_4 catalyst. The injected electrons and the photoinduced

Fig. 10. Photodegradation of a mixture of RhB and MO solution by Ag_3PO_4 . Ag_3PO_4 loading, 0.5 g/L; initial concentration of dye, 5 mg/L.

electrons (Eq. 4) reacted with O_2 to generate $O_2^{\cdot-}$ radicals, which may have contributed to the degradation of MO via the photoreduction process [25], and thereby decreasing the efficiency of RhB photodegradation in the presence of MO. Hence, we deduced that the photodegradation of MO by Ag_3PO_4 was enhanced by a greater number of $O_2^{\cdot-}$ radicals produced with the assistance of RhB.

4. Conclusions

A facile ion-exchange method was used to synthesize a visible-light-driven Ag_3PO_4 catalyst. The as-prepared Ag_3PO_4 catalyst showed much higher photocatalytic activity for RhB degradation than for MO degradation under visible light irradiation. The photodegradation of RhB and MO in the Ag_3PO_4 suspension was achieved by the action of holes and attack by $O_2^{\cdot-}$ radicals. The efficiency of MO photodegradation over the Ag_3PO_4 catalyst was greatly enhanced in the presence of RhB.

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Graphical Abstract

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Photodegradation of rhodamine B and methyl orange by Ag_3PO_4 catalyst under visible light irradiation

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As-obtained Ag_3PO_4 catalyst exhibited excellent photocatalytic ability for rhodamine B (RhB) degradation under visible light irradiation. The photodegradation of RhB and methyl orange in the Ag_3PO_4 suspension was achieved by the action of holes and $O_2^{\cdot-}$ radical attack.

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可见光驱动 Ag_3PO_4 催化降解罗丹明B和甲基橙

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摘要: 采用简易离子交换法制备可见光驱动 Ag_3PO_4 光催化剂. 通过X射线衍射、场发射扫描电子显微镜、 N_2 吸附-脱附、紫外-可见漫反射光谱及傅里叶变换红外光谱对所制备的 Ag_3PO_4 催化剂进行表征. 结果表明, 在可见光照射下, Ag_3PO_4 催化剂对罗丹明B降解表现出优越的光催化活性, 但对甲基橙的降解活性低, 这归因于 Ag_3PO_4 催化剂对甲基橙分子吸附量低. 可见光照 Ag_3PO_4 反应体系中, 空穴和超氧自由基共同发挥作用导致罗丹明B和甲基橙光催化降解. 在罗丹明B的协助作用下, Ag_3PO_4 催化剂对甲基橙的可见光催化降解活性大大增强, 这是由于罗丹明B的存在可产生更多的超氧自由基, 从而使甲基橙进一步降解.

关键词: 可见光; 磷酸银; 罗丹明B; 甲基橙; 机理

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1. 前言

染料工业制造和加工过程中, 有机染料往往会进入水环境中, 对生态环境和人类健康具有潜在的危害^[1]. 实际上, 传统的生物和物理处理技术很难将水体中的有机染料彻底地去除^[2]. 作为一种高级氧化技术, 非均相光催化技术能够有效消除废水中的有机染料^[3-5].

近年来, 高效可见光驱动光催化材料的发展逐渐引起广泛的关注^[6-8]. 其中, 具有较高光生电子和空穴分离效率的磷酸银(Ag_3PO_4)是一种前景良好的利用可见光降解有机染料的光催化剂^[9]. 对于水体中典型的有机染料, Ag_3PO_4 呈现出优良的可见光催化降解活性^[10-17]. Yan等^[10]和Dong等^[11]研究了不同形貌的 Ag_3PO_4 对有机

染料的光催化活性; Vu等^[12]探讨了具有不同尺寸的纳米 Ag_3PO_4 光催化剂的催化性能; Bi等^[17]揭示了具有不同暴露晶面的 Ag_3PO_4 光催化剂对有机染料罗丹明B和甲基橙的可见光催化降解活性. 结果表明^[10,17], Ag_3PO_4 对罗丹明B和甲基橙具有不同的光催化降解活性, 然而, 相关光催化机理未见详细阐述.

本文采用一步简易离子交换法在室温条件下制备了 Ag_3PO_4 催化剂样品. 在可见光照射下, 对比研究了 Ag_3PO_4 样品光催化降解水体中的罗丹明B(阳离子染料)和甲基橙(阴离子染料)的速率, 分别详细阐述了 Ag_3PO_4 可见光催化降解罗丹明B和甲基橙的机理, 考察了在罗丹明B存在的条件下 Ag_3PO_4 可见光催化降解甲基橙的活性.

2. 实验部分

2.1. 实验试剂

乙二醇四乙酸、苯醌、异丙醇和对苯二甲酸购于Acros化学试剂. 罗丹明B和甲基橙购于上海阿拉丁化学试剂. 其它试剂均购于天津化学试剂.

2.2. 催化剂的制备与表征

将0.006 mol AgNO_3 和0.002 mol Na_2HPO_4 分别溶于20和40 mL水中, 在强烈磁搅下将 Na_2HPO_4 溶液逐滴加入到 AgNO_3 溶液中, 滴加完后继续磁力搅拌30 min, 离心, 用蒸馏水和无水乙醇洗涤多次, 于空气中干燥备用.

采用X射线衍射仪(XRD, 日本理学, D/Max-2500型, $\text{Cu K}\alpha$, $\lambda = 0.154056 \text{ nm}$)分析制备样品的晶相. 通过场发射扫描电镜(FESEM, JEOL, JSM-6700型)观察样品的形貌和尺寸. 采用氮吸附仪(Micromeritics, Tristar 3000)测定样品的BET比表面积. 通过紫外-可见(UV-Vis)分光光度计(Shimadzu, UV-3600)对样品进行紫外-可见漫反射光谱分析, 以 BaSO_4 为参比, 扫描范围为200–700 nm. 采用傅里叶变换红外光谱仪(Nicolet, AVATAR360)测定样品的红外光谱(FT-IR).

2.3. 光催化活性评价

通过降解水体中的罗丹明B和甲基橙评价样品的可见光催化性能. 光催化实验在自制无需循环水的反应装置中进行(见图1). 以10 W LED灯作为可见光光源, 灯和液面的垂直距离为6 cm. 将一定量的光催化剂(0.05 mg)加入到100 mL浓度为5 mg/L的罗丹明B溶液(甲基橙溶液)中, 光照前在黑暗条件下磁力搅拌30 min. 光照条件下, 每隔一定时间取样3 mL, 高速离心分离后采用紫外-可见分光光度计(Shimadzu, UV2550)测定罗丹明B(甲基橙)的浓度. 采用原位捕获实验检测光催化过程产生的反应活性物种.

2.4. 对苯二甲酸荧光探针

对苯二甲酸(Acros)荧光探针技术用来检测光催化反应过程中产生的羟基自由基. 将0.05 g Ag_3PO_4 催化剂加入到100 mL含有NaOH (2 mmol/L)和对苯二甲酸(0.5 mmol/L)的水溶液中. 光照射之前在黑暗条件下磁力搅拌30 min. 光照后每隔一定时间取样3 mL, 离心后取上层清液, 通过荧光分光光度计(Hitachi, F4500)获取上层清液的荧光光谱.

3. 结果与讨论

3.1. 样品表征结果

图2(a)为所制备样品的XRD谱. 由图可见, 该样品

的衍射峰与立方相 Ag_3PO_4 一致(JCPDS 06-0505), 没有发现其它晶相衍射峰, 证实所制备样品为高纯立方相 Ag_3PO_4 , 且所有衍射峰峰形尖锐、强度高, 表明样品晶型完整、结晶度高. 如图2(b)所示, Ag_3PO_4 样品呈现类球形颗粒状, 尺寸大小在150–500 nm范围内, 其比表面积为 $2.6 \text{ m}^2/\text{g}$.

Ag_3PO_4 样品的UV-Vis谱见图3(a). 可以看出, Ag_3PO_4 样品对紫外光和可见光均有明显的吸收. 半导体的带隙能(E_g)可由公式(1)求得:

$$\alpha h\nu = A(h\nu - E_g)^{n/2} \quad (1)$$

式中 α , ν 和 A 分别为吸收系数、光频率以及比例常数. 如图3(b)所示, 通过以 $(\alpha h\nu)^{1/2}$ 对 $h\nu$ 作图获取 Ag_3PO_4 的 E_g 为2.24 eV.

图4是 Ag_3PO_4 样品的FT-IR谱. 可以看出, 1670和 3200 cm^{-1} 处出现的吸收峰分别为O–H的伸缩振动峰和弯曲振动峰^[11], 而560和 1014 cm^{-1} 处吸收峰为 PO_4^{3-} 的分子振动峰^[11].

3.2. 光催化活性及机理

在没有 Ag_3PO_4 催化剂存在的条件下, 罗丹明B和甲基橙不降解(数据未给出). 图5(a)是在可见光催化系统中 Ag_3PO_4 催化降解罗丹明B和甲基橙的曲线图. 可以看出, 可见光照30 min后, 罗丹明B降解了98.8%, 而甲基橙仅降解了42.8%, 可见 Ag_3PO_4 催化剂对阳离子染料罗丹明B具有显著的可见光催化去除效果. Ag_3PO_4 的零电荷点(pHzpc)为5.4左右^[18], 当pH值低于(高于) pHzpc时, Ag_3PO_4 表面带正电(负电). 在本文中性条件下, Ag_3PO_4 表面带负电, 容易吸附带正电的罗丹明B分子, 从而有利于降解反应的进行, 吸附实验也证实上述结论. 在黑暗条件下 Ag_3PO_4 催化剂吸附罗丹明B和甲基橙的曲线如图5(b)所示. 可以看出, 吸附60 min后, Ag_3PO_4 催化剂对罗丹明B的吸附为24.5%, 而对甲基橙仅为3.1%.

当 Ag_3PO_4 催化剂的投入量由0.5 g/L增至1.0 g/L时, 甲基橙降解率仅为58.8% (图6), 进一步证实 Ag_3PO_4 催化剂不易降解甲基橙. 然而, 在上述反应体系中加入罗丹明B时, Ag_3PO_4 可见光催化降解甲基橙的速率大大提高, 其降解率可达81.0%.

为阐述 Ag_3PO_4 系统可见光催化降解有机染料的机理, 对光催化反应过程中产生的活性物种进行了检测. 众所周知, 对苯二甲酸可与羟基自由基反应生成2-羟基对苯二甲酸, 当激发波长为315 nm时, 在波长426 nm处会产生荧光^[19,20]. 由图7可见, 在 Ag_3PO_4 光催化反应系统中, 在426 nm处没有出现明显的荧光峰, 且随着光照时

间的延长,也未有明显的变化,表明该反应系统中羟基自由基并不是主要的活性氧物种^[20],这进一步在理论上证实了上述结论。 Ag_3PO_4 光催化剂的价带边电势为2.45 eV^[16],低于使水转化成羟基自由基的标准电极电势(2.68 eV)^[21],表明光生空穴不能氧化 Ag_3PO_4 表面吸附的水分子成羟基自由基。此外,活性物种捕获实验用来间接检测 Ag_3PO_4 光催化反应系统中产生的活性氧物种。异丙醇、乙二胺四乙酸和苯醌分别作为羟基自由基、空穴和超氧自由基的捕获剂,加入到光催化体系中以检测这三种活性物种的存在^[22–24]。由图8可知,加入异丙醇对 Ag_3PO_4 催化剂的光催化活性影响不大,证实羟基自由基对染料的降解贡献不大。乙二胺四乙酸和苯醌(1 mmol/L)的加入均明显抑制了 Ag_3PO_4 催化剂对罗丹明B和甲基橙的降解,表明空穴和超氧自由基在 Ag_3PO_4 可见光催化过程中起降解作用(图8)。正如图9所示,在连续充氮厌氧条件下,罗丹明B和甲基橙的降解均受到明显地抑制。综上所述,空穴和超氧自由基是 Ag_3PO_4 可见光催化系统中主要的反应活性物种。

基于以上分析,我们提出 Ag_3PO_4 可见光催化降解罗丹明B和甲基橙的反应机理。在光照条件下, Ag_3PO_4 催化剂产生光生电子和空穴,价带电子跃迁到导带上,同时在价带上生成空穴。 Ag_3PO_4 价带边电势为2.45 eV^[16],表明价带空穴能够直接氧化降解罗丹明B和甲基橙^[25]。相比于甲基橙,罗丹明B分子更易吸附到 Ag_3PO_4 催化剂表面,其降解速率也更高。 Ag_3PO_4 催化剂表面吸附的溶解性氧气分子可被导带上的光生电子还原,生成超氧自

由基,有利于染料分子的降解。同时,染料分子本身可被可见光激发,产生的光生电子能够注入到 Ag_3PO_4 催化剂导带上,从而促进了光催化降解反应的进行^[17,26]。 Ag_3PO_4 可见光催化降解罗丹明B和甲基橙的反应机理如下所示:

如图6所示,在罗丹明B协助下, Ag_3PO_4 可见光催化降解甲基橙的活性明显增加,但此时罗丹明B的降解速率下降(图5(a)和图10)。由于罗丹明B很容易吸附到 Ag_3PO_4 表面,当受可见光激发而产生光生电子注入到 Ag_3PO_4 导带上,可与 Ag_3PO_4 本身激发产生的光生电子一起吸附溶解氧,反应生成超氧自由基,通过还原反应从而促进了甲基橙的降解^[25]。正是由于部分超氧自由基参与降解甲基橙,从而抑制了罗丹明B的降解。可见在罗丹明B的协助下可产生更多的超氧自由基,从而促进甲基橙的降解。

4. 结论

采用简易离子交换法制备 Ag_3PO_4 可见光催化剂。相对于甲基橙,该催化剂对罗丹明B的可见光催化降解活性更高。可见光驱动 Ag_3PO_4 催化系统中产生的空穴和超氧自由基导致罗丹明B和甲基橙的降解。罗丹明B的存在可增加 Ag_3PO_4 可见光催化降解甲基橙的效率。