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A new application of high-efficient silver salts-based photocatalyst under natural indoor weak light for wastewater cleaning

Xia Hua [a, b, c], Fei Teng [a, *], Yunxuan Zhao [a], Juan Xu [a], Chuangye Xu [a], Yang Yang [a], Qiqi Zhang [a], Shashi Paul [b], Yi Zhang [b], Mindong Chen [a], Xudong Zhao [c]

[a] Jiangsu Engineering and Technology Research Center of Environmental Cleaning Materials (ECM), Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control (AEMPC), Jiangsu Joint Laboratory of Atmospheric Pollution Control (APC), Collaborative Innovation Center of Atmospheric Environment and Equipment Technology (AEET), School of Environmental Science and Engineering, Nanjing University of Information Science & Technology, 219 Ningliu Road, Nanjing 210044, China

[b] Emerging Technologies Research Centre, De Montfort University, The Gateway, Leicester LE1 9BH, United Kingdom

[c] School of Engineering, University of Hull, Cottingham Road, Hull HU6 7RX, United Kingdom

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ABSTRACT

As a high-quantum-efficiency photocatalyst, the serious photo-corrosion of silver phosphate (Ag_3PO_4), limits the practical applications in water purification and challenges us. Herein, Ag_3PO_4 is found to have a high stability under natural indoor weak light irradiation, suggesting that we can employ it by adopting a new application strategy. In our studies, rhodamine B (RhB, cationic dye), methyl orange (MO, anionic dye) and RhB–MO mixture aqueous solutions are used as the probing reaction for the degradation of organic wastewater. It is found that RhB, MO and RhB–MO can be completely degraded after 28 h under natural indoor weak light irradiation, indicating that multi-component organic contaminants can be efficiently degraded by Ag_3PO_4 under natural indoor weak light irradiation. The density of natural indoor weak light is measured to be 72cd, which is merely one-thousandth of 300 W xenon lamp (68.2×10^3cd). Most importantly, Ag_3PO_4 shows a high stability under natural indoor weak light irradiation, demonstrated by the formation of fairly rare Ag. Furthermore, we also investigate the influence of inorganic ions on organic dyes degradation. It shows that the Cl^- and Cr^{6+} ions with high concentrations in wastewater have significantly decreased the degradation rate. From the viewpoint of energy saving and stability, this study shows us that we can utilize the Ag-containing photocatalysts under natural indoor weak light, which could be extended to indoor air cleaning process.

1. Introduction

One of the most pervasive problems afflicting people and environment is the wastewater discharge during industrial production. Up to now, various methods including filtration, adsorption and precipitation have been applied to purify the wastewater (Qu, 2008). However, industrial wastewater generally contains multiple organic contaminations and inorganic salts, conventional methods could only treat individual kind of pollutants, and some of the methods are significantly affected by inorganic salts in wastewater. Advanced oxidation processes (AOPs) have been put forward to solve the wastewater problems through oxidizing organic pollutants by strong oxidative radical species (Grcic and Li Puma, 2013). Among the AOPs, photocatalytic degradation has emerged as an environmentally friendly and sustainable strategy for the wastewater purification, since the photo induced redox power of TiO_2 was reported in 1972 (Fujishima, 1972). After that, TiO_2 has been widely investigated for environmental remediation purpose due to its strong oxidizing power, good stability and nontoxicity. However, the practical application of TiO_2 in industrial wastewater treatment is hindered by its small quantum efficiency and difficult recovery. Due to the small quantum efficiency of TiO_2, artificial light sources are always built to make up the low density of natural sunlight, implying high energy consumption. Great effort has been made to design novel photocatalyst, which can effectively utilize solar energy.

Silver phosphate (Ag_3PO_4) has been reported as an efficient photocatalyst for the decomposition of environmental pollutants

* Corresponding author.
E-mail address: tfwd@163.com (F. Teng).

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(Yi et al., 2010). Ag_3PO_4 has a narrow band gap (2.45 eV), it can be activated by visible light above 420 nm. The quantum efficiency of silver phosphate can reach as high as 90% (Bi et al., 2011), implying an excellent conversion efficiency of solar energy. Meanwhile, Ag_3PO_4 has a high specific weight (6.37 g cm^{-3}), thus the effective separation and recovery of the catalyst can be achievable, which is useful for industrial applications (Wang et al., 2012a, 2012b). Although Ag_3PO_4 is an efficient photocatalyst under visible light, it also presents an obvious shortage—photocorrosion. Ag_3PO_4 is relatively unstable during photocatalytic reaction, because the Ag(I) can be easily reduced into metal Ag when exposing to light. The activity of Ag_3PO_4 could be decreased during photocatalytic reaction due to generation of Ag and loss of Ag_3PO_4 substance. This can be the main obstacle to limit the long term utilization of Ag_3PO_4. Importantly, Ag_3PO_4 is slightly soluble in aqueous solution, the free Ag(I) can be easily reduced into Ag by the photon generated electron (Jiang et al., 2013). From practical application viewpoint, it is necessary to improve its stability and service life. Although several methods including semiconductor complex (Zhang et al., 2012; Yao et al., 2012), morphology control (Liang et al., 2012) and carbon-based composite (Yang et al., 2013) have been proposed by researchers to strengthen the stability of Ag_3PO_4, there is few report on the influence of light density to the service life of Ag_3PO_4. Thus, how to utilize the high-efficiency Ag_3PO_4 remains a big challenge.

In this study, we mainly explore the photocatalytic performances of Ag_3PO_4 for wastewater purification under natural indoor weak light, without any artificial light source. Cationic rhodamine B (RhB) dye, anionic methyl orange (MO) dye and their mixture are chosen as the degradation targets to simulate industrial wastewater purification. It is found that the RhB—MO mixture dye can be completely degraded by Ag_3PO_4 within 28 h. Absolutely under natural indoor weak light, the stability of Ag_3PO_4 is substantially enhanced, compared with that under artificial light source. This discovery reveals that Ag_3PO_4 is efficient and with long service life under natural indoor weak light irradiation, which contributes to practical applications of Ag_3PO_4. Also, the influences of K^+, Ba^{2+}, Cl^-, SO_4^{2-} and Cr^{6+} have been investigated to simulate real polluted water. The results show that the presences of Cr^{6+} and high concentration of Cl^- significantly decrease the degradation rate of dyes, but the others do not. This work develops a weak light irradiation strategy for the efficient wastewater purification, which could be extended to air purification programme in future.

2. Materials and methods

2.1. Chemicals

All chemicals used were analytic grade reagents without further purification; polyethylene glycol 200 (PEG200), silver acetate, silver nitrate, 85% phosphoric acid, hexamethylenetetramine, tetramethylene oxide and sodium hydroxide were purchased from Shanghai Reagents Company (Shanghai, China).

The preparation procedures of Ag_3PO_4 dendrites (Li et al., 2014), tetrapods (Wang et al., 2012a, 2012b), porous microtubes (Hua et al., 2014) and dodecahedrons (Bi et al., 2011) are provided in Electronic Supporting Information (ESI).

2.2. Characterization

The crystal structures of the samples were determined by X-ray powder polycrystalline diffractometer (Rigaku D/max-2550VB), using graphite monochromatized CuK radiation ($\lambda = 0.154$ nm), operating at 40 kV and 50 mA. The XRD patterns were scanned in the range of 20–80° (2θ) at a scanning rate of 5° min^{-1}. The samples were characterized on a scanning electron microscope (SEM, Hitachi SU-1510) with an acceleration voltage of 15 keV. The samples were coated with 5-nm-thick gold layer before observations. The texture properties of the samples were measured by nitrogen sorption isotherms. The surface areas and pore size distribution of the samples were calculated by the Brunauer—Emmett—Teller (BET) and Barret—Joyner—Halender (BJH) methods, respectively. UV—Vis diffused reflectance spectra (UV-DRS) of the samples were obtained using a UV—vis spectrophotometer (UV-3600, Shimadzu, Japan). Light density was measured by irradiatometer (FZ-A type, Handy, China).

2.3. Degradation under natural indoor dim light

Activities of the samples were evaluated by using RhB, MO and RhB—MO mixture wastewater as the probing molecules. Typically, 0.05 g of powder was added into the dye solution (200 mL, 10 mg/L RhB or MO). The suspension was stirred for 30 min to reach an adsorption—desorption equilibrium of dye molecules on the surface of photocatalyst; then the dye solution was degraded under natural indoor dim light (72cd) in our laboratory room (Nanjing, in China), without any artificial light source. During degradation, 4 mL of suspension was collected at a given interval time and centrifuged to remove the particles. The concentration of dye remained in the solution was determined by using UV—Vis spectrophotometer. For RhB—MO mixture wastewater, 200 mL of 10 mg/L RhB and 10 mg/L MO are employed. The pH values of all the solutions are tested to be approximately 6.

2.4. Degradation under artificial visible light irradiation

The procedure of pollutant degradation under visible light irradiation is the same as those above, except that a 300 W Xe arc lamp is used to replace the natural indoor weak light.

3. Results and discussion

The photocatalytic activities of the samples, including Ag_3PO_4 dendrites (X1), microtubes (X2), tetrapods (X3) and dodecahedrons (X4) (Fig. S1, ESI), are evaluated by degrading individual RhB, individual MO and RhB—MO mixture under both natural indoor weak light and artificial visible light, respectively. The influences of inorganic ions on photocatalytic degradation are investigated by adding proper amount of K^+, Ba^{2+}, Cl^-, SO_4^{2-} and Cr^{6+} ions into the aqueous solution system, respectively. The degradation mechanism and stability of Ag_3PO_4 are also investigated through analyzing active species, scanning electron microscope (SEM), X-ray diffraction and cycling experiment. The results have demonstrated the good activity and stability of Ag_3PO_4 for wastewater purification under natural indoor weak light.

3.1. Degradation of individual dye solution

3.1.1. Under artificial visible light irradiation ($\lambda \geq 420$ nm)

The photocatalytic activity of silver phosphate is evaluated by degrading organic dyes under visible light. A 300 W xenon lamp is used to simulate the sunlight above 420 nm. The light density of the xenon lamp is measured to be approximately 68.2×10^3cd.

Fig. 1a shows the degradation curves of individual cationic RhB over samples X1, X2, X3, X4 under visible light irradiation (≥420 nm). The results illustrate individual RhB aqueous solution can be degraded to a very low concentration level by X1, X2, X3 and X4 within 9, 9, 18 and 33 min, respectively. The X1 show the highest activity for the RhB degradation, followed by the X2, X3 and X4. The reaction kinetic curves for the samples are presented in Fig. 1b. The apparent reaction kinetic constants are calculated to be as follows: