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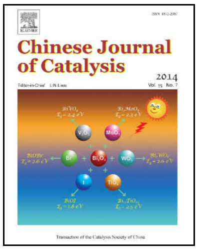

Article

Pr, N, and P tri-doped anatase TiO_2 nanosheets with enhanced photocatalytic activity under sunlight

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ABSTRACT

Pr, N, and P tri-doped anatase TiO_2 nanosheets (PrNPTO) were synthesized by a combined sol-gel solvothermal method and characterized by X-ray diffraction, transmission electron microscopy, N_2 adsorption-desorption, X-ray photoelectron spectroscopy, UV-vis absorbance spectroscopy, and photoluminescence spectroscopy. When the Pr-doping concentration was 1.75 wt% and calcination temperature employed was 550 °C, the resulting PrNPTO showed the highest photoactivity towards the degradation of methylene blue under visible and UV light irradiation. PrNPTO also displayed superior photoactivity towards the degradation of 4-chlorophenol under sunlight ($k_{app} = 3.90 \times 10^{-2}$ min^{-1}) over the non-doped, single-doped, and co-doped samples, and P25 TiO_2 ($k_{app} = 1.17 \times 10^{-2}$ min^{-1}). The high photoactivity of PrNPTO was attributed to the increased UV and visible light absorption properties, reduced recombination of photogenerated carriers, increased surface hydroxyl content, and improved surface textural properties. PrNPTO was highly efficient and stable under simulated sunlight irradiation, which are essential attributes for practical application in environment-related remediation schemes.

1. Introduction

Heterogeneous photocatalysis is an advanced oxidation process that has been extensively investigated in a wide range of energy and environmental applications [1,2]. Among various oxide semiconductor materials, TiO_2 remains to date the most frequently employed photocatalyst for water treatment, air purification, antibacterial, deodorization, and self-cleaning coating owing to its strong redox power, high photocorrosion resistance, chemical inertness, and commercial availability [3–5]. However, the relatively large energy band gap (3.2 eV for the anatase phase) and low quantum efficiency severely limit its practical application and commercial interest. Many strategies have been developed to overcome these drawbacks, including doping, loading, coupling, and dye sensitization [6,7].

Non-metal doping of TiO_2 has shown great promise in achieving visible light response. More specifically, nitrogen is the most promising dopant because of its comparable atomic size with oxygen and small ionization energy. In 2001, Asahi et al. [8] explored the visible light activity of N-doped TiO_2 prepared by sputter deposition of TiO_2 under a N_2/Ar atmosphere, followed by annealing under N_2. Since then, the scientific com-

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munity has devoted its interest to non-metal dopants such as N, P, B, C, S, F, Cl, and Br. Studies have primarily focused on N-doped TiO_2 systems. Significant efforts have been devoted to investigating the structural, electronic, and optical properties of N-doped TiO_2, understanding the underlying mechanisms, and improving the photocatalytic and self-cleaning performance under visible and solar light. However, some fundamental issues concerning the mechanism of visible light response, and the chemical nature and location of species that allow extension of the absorption to the visible light region, are still under debate. Moreover, visible light absorption does not always result in satisfactory visible light activity because of the increased recombination rate of charge carriers and reduced oxidation power under visible light irradiation [9].

Phosphorus (P) species have also generated increased interest because of their ability to stabilize mesoporous structures and enhance photoactivity [10–14]. Lin et al. [11] synthesized highly photoactive P-doped TiO_2 with visible light response. P-doping significantly increased the surface area of titania and provided a higher content of surface hydroxyl groups. Moreover, the thermal stability of titania was improved, and phase transformation from anatase to rutile was inhibited [15].

Furthermore, lanthanide ions with a 4*f* electron configuration can promote transition processes in the visible light region and act as an electron sink, thereby reducing the recombination of photogenerated electron-hole pairs and efficiently improving the photochemical or electrochemical properties of semiconductors [16]. Chiou et al. [17] synthesized Pr-doped TiO_2 nanoparticles by an acid-peptized sol-gel method; the resulting nanoparticles showed high photoactivity towards the degradation of phenol. The presence of Pr ions in TiO_2 generated a significant absorption shift towards the visible light region.

In recent years, much attention has been directed to co-doped titania systems consisting of cations and anions. For example, Pr and N co-doping produced a synergistic effect that consequently markedly improved the visible light activity of the resulting material [18,19]. The improved photoactivity of TiO_2 as a result of co-doping with P and N was further confirmed in these studies [20,21]. Umare et al. [22] reported an enhanced visible light activity of Ga, N, and S co-doped TiO_2 towards the decomposition of azo dyes. Also, our recent studies confirmed that RE, N, and P tri-doping (RE = Yb, Sm) produced a synergetic effect, leading to considerable increases in the visible light activity of TiO_2 [23,24]. To our knowledge, a systematic study on Pr, N, and P tri-doped TiO_2 has never been reported.

In the present study, Pr, N, and P tri-doped anatase TiO_2 was successfully synthesized via a combined sol-gel solvothermal process. The effects of Pr-doping concentration and calcination temperature on the photoactivities of the tri-doped samples towards the degradation of methylene blue (MB) in aqueous solution under visible and UV light irradiation were investigated. The performance of the different prepared photocatalysts was further assessed by evaluating the photocatalytic degradation of 4-chlorophenol (4-CP) under simulated sunlight irradiation. A possible synergetic mechanism of Pr, N, and P tri-doping was discussed in accordance with the corresponding characterizations.

2. Experimental

2.1. Preparation of photocatalysts

All chemicals used in this study were purchased from Fuhua Chemicals Co.(Tianjin, PRC). $Pr(NO_3)_3\cdot6H_2O$ was high pure, and other chemicals were analytical pure, which were used without further purification..

Pr, N, and P tri-doped anatase TiO_2 was prepared by a combined sol-gel solvothermal method similar to that described in previous reports [23,24]. In a typical procedure, 12 mL tetrabutyl titanate was dissolved in 24 mL absolute ethanol at room temperature to obtain solution A. Then, 24 mL absolute ethanol was mixed with 10 mL distilled water, 0.5 mL nitric acid (15.4 mol/L), a desired amount of $Pr(NO_3)_3\cdot6H_2O$, and 0.5 mL phosphoric acid (2.92 mol/L; the mass percentage of PO_4^{3-} in the theoretical TiO_2 powder was 5 wt%) to obtain solution B. Subsequently, solution B was added dropwise to solution A under vigorous stirring for 2 h at room temperature to form a light yellow transparent sol. The obtained sol was transferred to a 100 mL Teflon-lined stainless steel autoclave that contained a small tubule with 1 mL aqueous ammonia (25%, the mass percentage of N in the theoretical TiO_2 powder was 6.64 wt%). The sealed autoclave was then heated at 160 °C for 3 h for the solvothermal treatment, followed by natural cooling to room temperature. The obtained solid was thoroughly washed with distilled water, dried in an oven at 110 °C for 12 h, and calcined at different temperatures for 0.5 h. The Pr, N, and P tri-doped sample is denoted as PrNPTO.

Co-doped, single-doped, and non-doped TiO_2 samples were also prepared using a similar procedure under the same conditions and with slight variations with respect to the dopants involved. The Pr-doping concentration (the mass percentage of Pr in the theoretical TiO_2 powder) was 1.75 wt%, and the calcination temperature employed was 550 °C. The Pr and N co-doped, N and P co-doped, Pr-doped, N-doped, P-doped, and non-doped TiO_2 samples are denoted as PrNTO, NPTO, PrTO, NTO, PTO, and TO, respectively.

2.2. Characterization of photocatalysts

X-ray diffraction (XRD) patterns of the samples were obtained in the range of 10°–90° (2θ) on a Shimadzu XRD-6000 (Japan) X-ray diffractometer with Cu K_α radiation ($\lambda = 0.15418$ nm). The accelerating voltage and applied current were 50 kV and 40 mA, respectively. The crystallite size was calculated using the Scherrer equation $D = K\lambda/\beta\cos\theta$, where D is the crystalline size, K is the constant (i.e., 0.89), λ is the wavelength of X-ray radiation (0.15418 nm), β is the full width at half-maximum (FWHM) after subtraction of equipment broadening, and θ is the diffraction angle. Lattice distortion was also estimated from the XRD patterns using the formula $\varepsilon = \beta/4tg\theta$, where ε is the lattice distortion. The morphology was observed on a FEI Tecnai G^{2}TF20 (USA) transmission electron micro-