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Article

Pr, N, and P tri-doped anatase TiO₂ nanosheets with enhanced photocatalytic activity under sunlight

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ABSTRACT

Pr, N, and P tri-doped anatase TiO₂ nanosheets (PrNPtO) were synthesized by a combined sol-gel solvothermal method and characterized by X-ray diffraction, transmission electron microscopy, N₂ 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 ($k_{\text{app}} = 3.90 \times 10^{-2} \text{ min}^{-1}$) over the non-doped, single-doped, and co-doped samples, and P25 TiO₂ ($k_{\text{app}} = 1.17 \times 10^{-2} \text{ min}^{-1}$). 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.

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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, TiO₂ 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 TiO₂ 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 TiO₂ prepared by sputter deposition of TiO₂ under a N₂/Ar atmosphere, followed by annealing under N₂. 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 TiO₂ systems. Significant efforts have been devoted to investigating the structural, electronic, and optical properties of N-doped TiO₂, 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 TiO₂ 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 4f 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 TiO₂ 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 TiO₂ 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 TiO₂ 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 TiO₂ 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 TiO₂ [23,24]. To our knowledge, a systematic study on Pr, N, and P tri-doped TiO₂ has never been reported.

In the present study, Pr, N, and P tri-doped anatase TiO₂ 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(NO₃)₃·6H₂O was high pure, and other chemicals were analytical pure, which were used without further purification..

Pr, N, and P tri-doped anatase TiO₂ 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(NO₃)₃·6H₂O, and 0.5 mL phosphoric acid (2.92 mol/L; the mass percentage of PO₄³⁻ in the theoretical TiO₂ 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 TiO₂ 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 TiO₂ 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 TiO₂ 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 TiO₂ 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 (λ = 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 $\varepsilon = \beta/4\tg\theta$, where ε is the lattice distortion. The morphology was observed on a FEI Tecnai G²TF20 (USA) transmission electron micro-

scope (TEM), operating at an accelerating voltage of 200 kV.

Brunauer-Emmett-Teller (BET) surface area (S_{BET}), pore volume, and average pore size of the samples were determined from N_2 adsorption isotherms at -196°C using a Quantachrome NOVA2000E (USA) specific surface area analyzer after samples degassed in a flow of N_2 at 180°C for 3 h.

X-ray photoelectron spectroscopy (XPS) measurements of the samples were performed on a PHI-5700 ESCA System (Perkin Elmer, USA) with $\text{Al } K\alpha$ radiation ($h\nu = 1486.6 \text{ eV}$). The binding energies of all investigated elements were calibrated with the $\text{C } 1s$ peak at 284.6 eV . The target power was run at 280 W , and the accelerating voltage was maintained at 13.5 kV .

UV-vis absorbance spectra of the samples were recorded on a Shimadzu UV-2550 (Japan) spectrophotometer equipped with an integrating sphere using BaSO_4 as the reference standard at room temperature.

Photoluminescence (PL) spectra of the samples were measured on a Hitachi F-4500 (Japan) fluorescence spectrophotometer at room temperature using He-Cd laser as an excitation light source. The excitation wavelength was 325 nm .

2.3. Photoactivity measurements

Optimization of the experimental conditions was carried out by monitoring the degradation of MB in aqueous solution under visible light and UV irradiation. The method employed for the photocatalytic study is similar to that provided in previous reports [23,25].

The photoactivities of the samples towards the degradation of 4-CP in aqueous solution under simulated sunlight irradiation were also investigated and compared. The method adopted for the photocatalytic study is similar to that described in a previous report [24]. In a typical photocatalytic experiment, 80 mg of the photocatalyst was dispersed in 100 mL 4-CP solution (20 mg/L) using an ultrasonic bath for 15 min in the dark. The remaining experimental steps were similar to those in the reported process.

To investigate the mineralization of 4-CP by PrNPTO, the total organic carbon (TOC) content was analyzed using a Shimadzu total organic carbon analyzer (TOC-VCPN).

3. Results and discussion

3.1. Structural properties

The phase structure of TiO_2 greatly affects its photoactivity. Figure 1 shows the XRD patterns of the as-prepared samples. Only diffraction peaks corresponding to the anatase phase of TiO_2 are observed in all samples. However, doping influences the crystallization of the samples. For instance, broadening of the (101) plane diffraction peak at 25.3° is observed in the spectra of the single-doped samples. Also, the relative peak intensities decrease in the order of $\text{TO} > \text{NTO} > \text{PTO} > \text{PrTO}$, indicating that crystal growth is inhibited by the dopants to different extents. Pr and P single-doping significantly inhibit the crystal growth of TiO_2 , with Pr-doping exhibiting the strongest inhibiting effect (Table 1). This reduction in crystal-

Fig. 1. XRD patterns of TO, PrTO, NTO, PTO, and PrNPTO.

lite size may be due to the segregation of the doping ions at the crystal boundary that limits direct contact between crystallites, consequently inhibiting crystal growth.

The average crystallite size and lattice distortion degree of the samples are given in Table 1. PrNPTO features an average crystallite size of 10.46 nm , which is larger than that of PrTO and PTO but significantly smaller than that of NTO. This indicates that dopants Pr and P play a key role in inhibiting crystallite growth. When aqueous ammonia was employed as a nitrogen source, its addition was expected to increase the pH of the solution that correlates to an increase in the concentration of hydroxyl groups in the solution. This would subsequently promote hydrolysis of the precursor alkoxide under acid conditions. Accordingly, the amount of non-hydrolyzed alkyl groups remaining in the precursor solution decreased and instigated particles to be at closer proximity to each other, subsequently leading to agglomeration of particles. The lower the content of non-hydrolyzed alkyl groups remaining in the precursor, the better the crystallization of TiO_2 and the larger the crystallite size [26]. The degree of lattice distortion in all doped samples is higher than that in TO, indicating the incorporation of the doping atoms in the lattice structure of TiO_2 .

The morphology of PrNPTO was characterized by TEM (Fig. 2). PrNPTO exhibits irregular nanosheets with a diameter of $\sim 9\text{--}12 \text{ nm}$ (Fig. 2(a)). The corresponding selected area electron diffraction (SAED) pattern of the PrNPTO nanosheet (Fig. 2(a), inset) indicates that the sample exists as anatase polycrystals with high crystallinity. This is further confirmed by the high-resolution TEM (HRTEM) image of the lattice fringes in Fig. 2(b). The spacing between the lattice fringes was measured as 0.352 nm , corresponding to (101) planes of anatase TiO_2 . These results are consistent with the results of XRD analysis.

Table 1
Physicochemical properties of TO, PrTO, NTO, PTO, and PrNPTO.

Sample	Crystallite size (nm)	(101) interplanar distance (nm)	Lattice distortion, ϵ	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
TO	20.95	0.3520	0.0222	11	0.030	3.80
PrTO	8.59	0.3517	0.0478	116	0.365	9.72
NTO	18.58	0.3520	0.0251	33	0.087	5.61
PTO	10.13	0.3534	0.1432	126	0.210	4.91
PrNPTO	10.46	0.3520	0.0445	112	0.268	6.60

Fig. 2. (a) TEM image (inset, SAED pattern) and (b) HRTEM image of PrNPTO.

Figure 3 presents the N_2 adsorption-desorption isotherms and pore size distribution curves of the as-prepared samples. As shown in Fig. 3(a), all samples exhibit type IV isotherms with type H2 hysteresis loops (based on IUPAC classification) in the relative pressure range of 0.45–0.95, indicating that the samples contain mesopores with narrow pores (ink-bottle pores) [26,27]. These mesopores mainly correspond to voids formed as a result of the primary aggregation of nanosheets [28]. As observed in Fig. 3(a), the adsorption curves of the doped samples shift upward, and the associated hysteresis loops shift to higher relative pressures, suggesting that doping leads to an increase in both the specific surface areas and average pore sizes. The pore size distribution of the samples determined by the BJH method is shown in Fig. 3(b). All samples feature a narrow unimodal pore size distribution. As deduced, doping leads to an increase in the average pore diameters in the order of $TO < NTO < PTO < PrNPTO < PrTO$, confirming that dopant Pr plays a primary role in increasing the average pore diameter.

The BET surface area, pore volume, and pore size of the samples are listed in Table 1. Generally, the smaller the crystallite size, the larger the specific surface area. Although PrTO has a smaller crystallite size (8.59 nm) than PTO (10.13 nm), PTO features a larger specific surface area ($126 \text{ m}^2/\text{g}$) than PrTO ($116 \text{ m}^2/\text{g}$), probably because of the superior dispersion of PTO. All single-doped samples displayed larger specific surface areas, pore volumes, and average pore diameters than TO. Among the single-doped samples, PTO exhibits the largest specific surface area, and PrTO shows the largest pore volume. As a result, PrNPTO exhibits a specific surface area of $112 \text{ m}^2/\text{g}$, a pore volume of $0.268 \text{ cm}^3/\text{g}$, and an average pore size of 6.6 nm, which can be attributed to a cooperative effect of Pr, N, and P tri-doping.

Fig. 3. (a) N_2 adsorption-desorption isotherms and (b) pore size distribution curves of TO, PrTO, NTO, PTO, and PrNPTO.

3.2. Chemical composition

XPS analysis was carried out to investigate the electronic environment, oxidation states, and concentrations of the surface elements. The N 1s XPS spectrum of PrNPTO is shown in Fig. 4(a). The characteristic peaks of nitrogen are weak owing to the low N-doping concentration. However, a broad peak within a range of 398–402 eV, which is a characteristic peak of N 1s species, can be observed. PrNPTO displays two distinct peaks around 399.5 and 401.5 eV, corresponding to substitutional N in the form of N–Ti–O [29,30] and interstitial N in the form of Ti–O–N [29,31], respectively. Because of the higher electronegativity of oxygen relative to that of nitrogen, the electron density on N in N–Ti–O is smaller, resulting in an increased binding energy when compared with that associated with the N 1s peak in a Ti–N bond (396 eV) [32]. The electron density of the oxidized N in Ti–O–N is increasingly smaller, and thus the binding energy of the oxidized N 1s shifts to a higher energy.

Figure 4(b) displays the P 2p XPS spectrum of PrNPTO. The XPS peak in the P $2p_{3/2}$ region appears at 133.6 eV, suggesting that P exists as P^{5+} [33]. It is generally believed that the P 2p peak at a relatively high binding energy (133.4–133.8 eV) corresponds to the partial substitution of Ti^{4+} in the TiO_2 lattice by P^{5+} that results in the preferential formation of Ti–O–P linkages over phosphate anions (PO_4^{3-}) [11,28]. No peaks are observed at $\sim 128.6 \text{ eV}$ that are associated with Ti–P bonds [11].

Fig. 4. XPS spectra of (a) N 1s, (b) P 2p, (c) Pr 3d, and (d) Ti 2p of PrNPTO.

Figure 4(c) shows the Pr 3d XPS spectrum of PrNPTO. Peaks observed at 934.3 and 952.9 eV correspond to Pr $3d_{3/2}$ and Pr $3d_{5/2}$, respectively, that are assigned to Pr^{3+} [19]. Compared with the Pr $3d_{3/2}$ peak in Pr_2O_3 observed at a binding energy of 933.3 eV [18], the Pr $3d_{3/2}$ peak in PrNPTO is observed at a higher binding energy (by 1 eV). This shift indicates that the chemical environment of the Pr atoms in PrNPTO has been changed, possibly because of the formation of Pr–O–Ti linkages. Substitution of Ti^{4+} by Pr^{3+} is expected to be difficult as the ionic radius of Pr^{3+} (0.101 nm) is larger than that of Ti^{4+} (0.068 nm). However, Ti^{4+} ions may easily integrate the lattice of Pr_2O_3 , which can subsequently alter the electron field of Pr^{3+} (i.e., decrease its electron density), and hence increase the binding energy of Pr^{3+} . The presence of other oxidation states of praseodymium was not observed.

The Ti 2p XPS spectrum of PrNPTO is shown in Fig. 4(d). Peaks are observed at 458.725 and 464.85 eV that correspond to Ti $2p_{3/2}$ and Ti $2p_{1/2}$, respectively, and are assigned to Ti^{4+} . When compared with the Ti $2p_{3/2}$ peak of TO that was observed at 458.4 eV, the Ti $2p_{3/2}$ of PrNPTO was observed at a higher binding energy (positive shift of 0.325 eV) as a result of the bridging structure between PO_4^{3-} and Ti^{4+} . The latter structure is due to the substitution of Ti^{4+} in the TiO_2 lattice by P^{5+} , generating Ti–O–P linkages that subsequently decrease the electron density of Ti, thereby increasing the binding energy.

Figure 5 shows the O 1s XPS spectra of TO, PrTO, NTO, PTO, and PrNPTO. The obtained asymmetric broad peak was fitted with two peaks. The stronger fitted peak at about 530.23 eV corresponds to bulk oxygen in Ti–O bonds. The minor fitted peak at ~532.18 eV is attributed to the presence of hydroxyl oxygen [34]. The contents of surface hydroxyl groups in TO,

PrTO, NTO, PTO, and PrNPTO evaluated by XPS are 9.98%, 16.57%, 12.08%, 18.75%, and 17.66%, respectively. As observed, Pr, N, and P single-doping increased the surface hydroxyl group's content relative to that of the non-doped TiO_2 . Surface hydroxyl groups content increased in the order of TO < NTO < PrTO < PTO. However, no further increase in the surface hydroxyl group's content is observed in PrNPTO, which is slightly lower than that of PTO. This indicates that P-doping plays the most significant role in increasing the surface hydroxyl group's content.

The atomic ratio of Ti:O:Pr:N:P in PrNPTO calculated by an elemental sensitive factor method is 1:2.62:0.008:0.77:0.034. The atomic ratio of O:Ti is larger than 2, suggesting the presence of numerous oxygen-containing surface states.

3.3. Optical properties

The optical absorption properties of the samples were studied by recording the UV-vis absorption spectra of the samples, as shown in Fig. 6(a). All samples feature a broad intense absorption below ~390 nm, which is the characteristic absorption corresponding to the excitation of electrons from the valence band to the conduction band in anatase TiO_2 . It is worth noting that PrNPTO exhibits the highest absorption of UV light, indicating that the Pr, N, and P tri-doping enhances the UV light absorption ability of TiO_2 . Also, Pr-doping leads to a red shift of the absorption edge of TiO_2 . Regarding the Pr-doping system, $4f$ spin-down states located nearby the conduction band of TiO_2 and a narrow band gap are expected. Moreover, to achieve electron neutrality in the entire system, the generation of oxygen vacancies upon substitution of Ti^{4+} by Pr^{3+} ions is inevitable.

Fig. 5. O 1s XPS spectra of TO, PrTO, NTO, PTO, and PrNPTO.

Fig. 6. (a) UV-vis absorbance spectra and (b) plot of $(\alpha hv)^{1/2}$ as a function of light energy ($h\nu$) of TO, PrTO, NTO, PTO, and PrNPTO.

ble. Oxygen vacancies also play an important role in reducing the band gap [16]. The extent of red shift in the absorption edge of NTO and PTO is comparable to and larger than that of PrTO. Both substitutional N and interstitial N induce the generation of localized states in the gap, accounting for the visible light absorption capabilities of N-doped TiO_2 [35,36]. Dopant P in the TiO_2 lattice can reduce the energy gap by mixing the P 3p states with the O 2p states [10]. However, PrNPTO exhibits a reduced red shift when compared with that of NTO and PTO, and a larger red shift than that of PrTO.

The Kubelka-Munk function was used to estimate the band gap energies of the samples by plotting $(\alpha hv)^{1/2}$ as a function of energy of light ($h\nu$), as shown in Fig. 6(b). The band gap energies for TO, PrTO, NTO, PTO, and PrNPTO are 3.01, 2.98, 2.91, 2.89, and 2.95 eV, respectively. The band structure of PrNPTO is mainly influenced by two opposing effects. On one hand, the

decrease in the crystallite size (10.46 nm) produces a quantum size effect that can lead to a blue shift of the absorption edge. On the other hand, the presence of nitrogen and phosphorus in the TiO_2 lattice can alter the electronic band structure and result in a red shift of the absorption edge.

Figure 7 shows the photoluminescence (PL) spectra of TO, PrTO, NTO, PTO, and PrNPTO at an excitation wavelength of 325 nm. All samples exhibit similar PL curve shapes except for PrTO and PrNPTO, implying that Pr-doping gives rise to new PL phenomena owing to its unique $4f^2$ electron configuration. The new peaks in the visible region of the PL spectra are associated with Pr^{3+} internal transitions [37]. Compared with TO, NTO shows a higher PL signal intensity owing to the increased oxygen vacancies introduced by N^{3-} substitution of O^{2-} in the TiO_2 lattice. The stronger the PL peaks, the higher the content of surface oxygen vacancies and defects [38].

Fig. 7. PL spectra of TO, PrTO, NTO, PTO, and PrNPTO.

In contrast, Pr and P single-doping lowers the PL signal intensities. As PL emissions give a measure of the recombination of free carriers, a lower PL peak intensity indicates a lower recombination rate of the electron-hole pairs and hence a higher charge separation efficiency [39]. It can thus be deduced that Pr and P single-doping can inhibit indirect recombination of the photogenerated electrons and holes. Pr^{3+} ions with unique $4f^2$ electron configuration serve as shallow traps that can temporarily capture photogenerated electrons before reacting with acceptors such as O_2 adsorbed on the surface to form $\cdot\text{O}_2^-$. In regards to P-doping, charge imbalance caused by P^{5+} substitution of Ti^{4+} is compensated by the increased production of surface hydroxyl groups or the reduction of oxygen vacancies, thereby efficiently delaying the recombination of the photogenerated electrons and holes. As observed, PrNPTO features a lower PL signal intensity than that of PrTO but a higher signal than that of PTO, indicating that the presence of P in the TiO_2 lattice is mainly responsible for inhibiting the recombination of photogenerated electrons and holes.

3.4. Effect and mechanism of doping on the photoactivity of TiO_2

3.4.1. Optimization of Pr-doping concentration and calcination temperature

The photocatalytic degradation of MB in aqueous solution

under visible and UV light irradiation was carried out to optimize the Pr-doping concentration and calcination of Pr, N, and P tri-doped TiO_2 . The kinetic curves for the photocatalytic degradation of MB over the tri-doped sample correspond to first-order kinetics. The apparent rate constants (k_{app}) of the samples were calculated according to the equation $\ln(C_t/C_0) = -k_{\text{app}}t$, where C_0 and C_t are the initial equilibrium concentration and reaction concentration after t minutes of irradiation, respectively. The effects of Pr-doping concentration and calcination temperature on the apparent first-order rate constant (k_{app}) of the tri-doped samples under visible and UV light irradiation are depicted in Fig. 8. As observed in Fig. 8(a), the photocatalytic degradation rate of MB over the tri-doped sample increases and then decreases after achieving a maximum degradation rate at a Pr-doping concentration of 1.75 wt%. At concentrations below the optimal value, the photoactivity increases with increasing Pr-doping concentrations because there are increasingly higher amounts of available trapping sites in the $4f^2$ states of Pr^{3+} , located near the conduction band of TiO_2 [16]. However, at excessively higher Pr-doping concentrations, the tri-doped sample exhibits a decreased photoactivity owing to the exponential increase of the recombination rate of the charge carriers. The increased recombination rate is due to the reduced average distance between trap sites that becomes significant with increasing amounts of dopant confined within a given particle [40]. As shown in Fig. 8(b), the calcination temperature also influences the photoactivity of the tri-doped sample. A calcination temperature of 550 °C appears to be optimal for generating high photoactivity. Higher or lower calcination temperatures lead to a decrease in the photoactivity. High calcination temperatures can improve the anatase crystallinity and reduce the residual carbonate species content, and subsequently enhance the photoactivity. However, at temperatures above the optimal calcination temperature, the photoactivity of the sample decreases because the resulting larger-sized semiconductor particles promote fast recombination of the photogenerated holes and electrons [41].

3.4.2. Comparison of photocatalysts and possible mechanisms

To eliminate the contribution of inferring photosensitized processes in MB, 4-CP was also chosen as a model target pollu-

Fig. 8. Effect of (a) Pr-doping concentration and (b) calcination temperature on the photoactivity of the tri-doped samples under visible and UV light irradiation.

Fig. 9. (a) Kinetic curves for the photocatalytic degradation of 4-CP over different samples under simulated sunlight irradiation and (b) absorption spectra of 20 mg/L 4-CP solution in the presence of 0.8 g/L PrNPTO photocatalyst after different irradiation times.

tant to compare the photoactivities of the different prepared samples under simulated sunlight irradiation. The kinetic curves for the photodegradation of 4-CP over different samples under simulated sunlight irradiation are shown in Fig. 9(a). As observed, Pr, N, and P single-doping enhance the photoactivity of TiO_2 , which increases in the order of $\text{NTO} < \text{PrTO} < \text{PTO}$. The co-doped samples PrNTO and NPTO display higher photoactivities than the corresponding single-doped samples, indicating that Pr and N co-doping, and N and P co-doping produce a synergistic effect. However, the tri-doped sample PrNPTO exhibits the highest photoactivity among all samples, with an activity ($k_{\text{app}} = 3.90 \times 10^{-2} \text{ min}^{-1}$) that is 3.93 times higher than that of TO ($k_{\text{app}} = 9.93 \times 10^{-3} \text{ min}^{-1}$). This indicates that Pr, N, and P tri-doping produces a synergistic effect to further increase the photoactivity of TiO_2 when compared with the effect of the co-doping systems. Additionally, when compared with Degussa P25 TiO_2 , a commercially available titania with good photoactivity [29], PrNPTO achieves a superior photocatalytic performance, which is 3.33 times higher than that of P25 TiO_2 ($k_{\text{app}} = 1.17 \times 10^{-2} \text{ min}^{-1}$).

Figure 9(b) shows the absorption spectra of 4-CP solution (20 mg/L) in the presence of PrNPTO (0.8 g/L) after different irradiation times. As observed, the concentration of 4-CP significantly decreases with increasing irradiation times to ~ 0 mg/L after irradiation for 120 min, indicating the complete decomposition of 4-CP. The decomposition of organic pollutants can be used as a measure of the overall degradation process that ultimately involves mineralization of both the parent substance and its intermediates. Thus, TOC measurements were performed to evaluate the mineralization degree of 4-CP by PrNPTO. The result shows that the removal content of TOC amounts to 63.47% after irradiation for 120 min. The discrepancy between the TOC content and the extent (complete) of decomposition of 4-CP suggests the formation of organic intermediates by photocatalytic oxidation. It is expected that complete mineralization will be achieved at longer irradiation times.

A possible mechanism of the improved photocatalytic degradation of 4-CP over PrNPTO under simulated sunlight irradiation is described in Scheme 1. First, light absorption ability of the photocatalyst is a prerequisite for photoactivity. PrNPTO

exhibits an enhanced UV and visible light absorption property owing to its narrow band gap that is mainly ascribed to the presence of nitrogen and phosphorus in the TiO_2 lattice. Narrow band gaps are beneficial to increasing the production of photogenerated carriers required for the photocatalytic process. Second, the separation efficiency of the photogenerated carriers is also an important factor that influences light quantum efficiency. Efficient charge separation can prolong the lifetime of charge carriers and enhance the performance of interfacial charge transfer to adsorbed substrates, subsequently improving the photoactivity [42]. The lower the recombination rate, the higher the photoactivity. The presence of P in the TiO_2 lattice plays a significant role in inhibiting recombination processes. Charge imbalance, owing to P^{5+} substitution of Ti^{4+} , is compensated by the increased generation of surface hydroxyl groups or the reduction of oxygen vacancies, which effectively retards the recombination of photogenerated electrons and holes. Third, in the Pr, N, and P tri-doping TiO_2 system, P-doping plays the most significant role in increasing the production of surface hydroxyl groups that are beneficial to the photocatalytic process. Hydroxyl groups can react with the photogenerated holes to produce strong oxidant hydroxyl free radicals ($\cdot\text{OH}$). The generated hydroxyl free radicals in the solution attack 4-CP molecules in the suspension, instigating hydroxylation, oxidation, and finally mineralization of the 4-CP molecules into CO_2 , H_2O , and inorganic ions. The surface hy-

Scheme 1. Proposed mechanism of the enhanced photocatalytic degradation of 4-CP over PrNPTO photocatalyst under simulated sunlight irradiation.

Fig. 10. Repeated photocatalytic degradation of 4-CP over PrNPTO under simulated sunlight irradiation.

droxyl groups can also act as adsorption sites for O_2 , CO, and organic molecules. The adsorbed O_2 can trap photogenerated electrons to form superoxide species ($\cdot O_2^-$). Fourth, the Pr, N, and P tri-doping improves the surface textural properties of TiO_2 , resulting in a decreased crystalline size, an increased specific surface area, and an enlarged pore size. The volume recombination of photogenerated e^-h^+ , which is a dominant process in well-crystallized large TiO_2 particles, can be reduced by decreasing the particle size. Lower recombination rates promote high photocatalytic activity. Moreover, reduction in particle size leads to a larger surface area, which increases the available number of surface active sites. The dopant Pr plays a key role in increasing the pore diameter and pore volume. The larger mesopores allow rapid diffusion of various reactants and products during the photocatalytic reaction and enhance the photocatalytic reaction rate. The enhanced photoactivity is ascribed to the cooperation of all the above aspects.

3.4.3. Photocatalytic stability

To investigate the photocatalytic stability of PrNPTO, successive photocatalytic degradation of 4-CP over PrNPTO under simulated sunlight irradiation was carried out five times. After each run, the photocatalyst was retrieved by simple filtration and dried in the oven at 110 °C for 2 h before use in the following run. As shown in Fig. 10, no distinct decrease in the photocatalytic degradation performance is observed after five cycles, indicating that PrNPTO photocatalyst is very effective and stable, and hence is promising for practical application in environmental purification schemes.

4. Conclusions

Pr, N, and P tri-doped TiO_2 (PrNPTO) nanosheets were synthesized by a combined sol-gel solvothermal method. At a Pr-doping amount of 1.75 wt% and calcination of 550 °C, the resulting PrNPTO exhibited the highest photoactivity towards the degradation of methylene blue (MB) under visible and UV light irradiation. PrNPTO exhibited superior photoactivity for 4-chlorophenol (4-CP) degradation under sunlight irradiation over commercial P25 TiO_2 . The improved photoactivity was

attributed to a synergistic effect of the Pr, N, and P tri-doping and a good photocatalytic stability that are highly beneficial in environment-related purification schemes under sunlight irradiation. The doped Pr played a key role in increasing the pore diameter and pore volume, as well as inhibiting phase transformation from anatase to rutile. Also, P-doping inhibited the recombination of photogenerated carriers and increased the surface hydroxyl's content. The enhanced UV and visible light absorption properties of the tri-doped photocatalyst were mainly attributed to band gap narrowing by the nitrogen and phosphorus dopants in the TiO_2 lattice. Overall, the enhanced photoactivity of PrNPTO was attributed to the increased UV and visible light absorption properties, reduced recombination of the photogenerated electrons and holes, increased surface hydroxyl content, and improved surface textural properties.

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Graphical Abstract

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Pr, N, and P tri-doped anatase TiO₂ nanosheets with enhanced photocatalytic activity under sunlightHongquan Jiang*, Qiaofeng Wang, Shiyang Li, Jingshen Li, Qingyuan Wang
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Enhanced photoactivity of PrNPTO is attributed to increased UV and visible light absorption, reduced recombination of photogenerated e⁻-h⁺, increased surface hydroxyl content, and improved surface textural properties.

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太阳光下高光催化活性Pr-N-P三元掺杂锐钛矿TiO₂纳米片姜洪泉^{a,*}, 王巧凤^a, 李世洋^b, 李井申^a, 王庆元^a^a哈尔滨师范大学功能材料设计合成与绿色催化黑龙江省高校重点实验室, 黑龙江哈尔滨150025^b黑龙江中医药大学附属第二医院, 黑龙江哈尔滨150001

摘要: 利用溶胶-凝胶和溶剂热联合技术制备了Pr-N-P三元掺杂锐钛矿TiO₂ (PrNPTO)纳米片, 并采用X射线衍射、透射电镜、N₂吸附、X射线光电子能谱、UV-vis吸收谱和光致荧光光谱分析技术对其进行了表征。当Pr掺杂量为1.75 wt%, 焙烧温度为550 °C时, 制得的PrNPTO在可见和紫外光下光催化降解亚甲基蓝(MB)活性最佳。在模拟太阳光照射下, PrNPTO也表现出优越的光催化降解4-氯酚性能($k_{app} = 3.90 \times 10^{-2} \text{ min}^{-1}$), 优于未掺杂、单掺杂和双掺杂TiO₂样品, 其光活性是P25 TiO₂的3.33倍($k_{app} = 1.17 \times 10^{-2} \text{ min}^{-1}$)。PrNPTO光活性的提高归因于Pr-N-P三元掺杂增强了紫外和可见光吸收, 降低了光生载流子复合, 增加了表面羟基以及改善了表面织构特性。在模拟太阳光照射下, PrNPTO光催化效率高且光催化性能稳定, 适合于环境净化领域的实际应用。

关键词: 氧化钛; Pr-N-P三元掺杂; 溶胶-凝胶; 溶剂热; 太阳光; 光催化

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