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Controlling the synergistic effect of oxygen vacancies and N dopants to enhance photocatalytic activity of N-doped TiO_2 by H_2 reduction

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ABSTRACT

This paper focuses on improving photocatalytic activity of N-doped TiO_2 photocatalyst for efficiently utilizing solar energy. A simple H_2 reduction is found to remarkably enhance the photocatalytic activity of N-doped TiO_2 for ethylene oxidation under visible light or simulated solar light irradiation. Ultraviolet/visible diffuse reflectance spectra (UV/vis DRS), X-ray photoelectron spectra (XPS) and electron paramagnetic resonance (EPR) spectra were employed to characterize the surface properties and chemical states of nitrogen dopants in H_2-reduced N-doped TiO_2. The results reveal that H_2 reduction facilitates the creation of oxygen vacancies and Ti^{3+} species in N-doped TiO_2 but without removal of nitrogen species from catalyst surface. The formed oxygen vacancies and Ti^{3+} species seriously influence electron excitation from doped nitrogen species and subsequently tune the generation of active oxygen species $O_2^{\bullet-}$ radicals on N-doped TiO_2. The synergistic effect of oxygen vacancies and doped nitrogen species contributes to the enhancement of photocatalytic activity of N-doped TiO_2 samples, but the formed Ti^{3+} ions largely suppress the photocatalytic activity.

1. Introduction

One of the major challenges in heterogeneous photocatalysis is the development of photo-functional materials that work under visible light irradiation in order to improve the utilization of solar energy. Recently, nitrogen-doped TiO_2 has received considerable attentions as a promising visible-light-driven photocatalyst [1–6], since Asahi et al. reported that N-doping shifts the absorption edge of TiO_2 to lower energy and reveals photocatalytic activity for the degradation of methylene blue and gaseous acetaldehyde under visible-light irradiation [7]. Although there have been intense debates in photoactive centers and electronic structure of N-doped TiO_2, various synthesis methods have been conducted on N-doped TiO_2 with the goal of developing practical application system [8–12]. However, the visible-light photocatalytic activity of N-doped TiO_2 is still too low for practical use and N-doping also leads to greatly impair the UV activity of TiO_2 [13,14].

In order to improve the photocatalytic efficiency of N-doped TiO_2 catalysts, many approaches have been made to modify N-doped TiO_2. For example, Chen et al. [15] showed that post-nitridation annealing of N-doped TiO_2 catalyst can improve both its activity and stability for the photocatalytic oxidation of ethylene under visible light. Higashimoto et al. [16] used various metal ions to modify nitrogen-doped TiO_2 and found that photocatalytic activity of N-doped TiO_2 is greatly increased by adding vanadium species for the decomposition of various volatile organic compounds (VOCs) under both visible light and UV-light irradiation. Sakthivel et al. [17] used Au to load on $TiO_{2-x}N_x$ and found the enhancements on the photocatalytic oxidation of CO under visible light illumination. Li et al. [18] reported that the N–F-co-doped TiO_2 exhibits higher photocatalytic activity under both ultraviolet and visible light irradiations.

Here, we report an effective method to enhance both visible light and simulated solar light photocatalytic activities of N-doped TiO_2 by a simple H_2 reduction of N-doped TiO_2. H_2 reduction is a novel approach for the creation of defect sites on metal oxide surfaces [19,20]. Defects including oxygen vacancies and Ti^{3+} states are always produced concomitantly during nitrogen doping of TiO_2 and thus influence the visible-light photocatalytic activity of N-doped TiO_2 [21–23]. However, the role of defects in the photocatalytic performance of N-doped TiO_2 still remains unclear. Belver et al. [24] suggested that a oxygen vacancy-N impurity interaction give a plausible way to explain photocatalytic activity of various N-doped TiO_2 prepared by several methods. Chen et al. [15] indicated that oxygen vacancies and associated Ti^{3+} species act as the recombination centers for the photoinduced electrons and holes to reduce the photocatalytic activity of N-doped TiO_2. Therefore, a systematic

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Table 1
BET specific surface area and particle size of the TN samples reduced at different temperature and time.

Sample	TN	TN-450-3	TN-450-5	TN-450-10	TN-550-3	TN-550-5	TN-550-10
BET ($m^2 g^{-1}$)	81.7	82.3	81.6	80.3	75.2	74.9	74.0
Particle size (nm)	17.6	17.7	17.6	17.6	18.3	18.4	18.6

knowledge about the effect of defects on N-doped TiO_2 is required. Accordingly, we employed H_2 reduction of N-doped TiO_2 at various temperature and time to tune defects on catalyst surface and investigated their role in photocatalytic activity. Photocatalytic decomposition of ethylene was used as a model reaction to examine the photocatalytic behavior of the reduced N-doped TiO_2. The effect of H_2 reduction temperature and time on optical properties, chemical states of doped nitrogen species and formation of defect sites (oxygen vacancies and Ti^{3+} ions) was characterized in detail by ultraviolet–visible diffuse reflectance (UV–vis DRS), X-ray photoelectron spectra (XPS) and electron paramagnetic resonance (EPR) spectroscopies. The characterization results clearly reveal that the interaction between the formed oxygen vacancies with doped nitrogen species accounts for the enhanced photocatalytic activity, but Ti^{3+} ions seriously suppress the photocatalytic activity of N-doped TiO_2.

2. Experimental

2.1. Catalyst preparation

N-doped TiO_2 samples (TN) were synthesized by annealing anatase TiO_2 powder (Alfa Chemical Co.) under NH_3 gas stream at 450 °C for 20 h. Thus obtained TN samples were reduced in a flowing pure H_2 at 450 or 550 °C for 3, 5 or 10 h to produce reduced TN samples (designated as TN-*x*-*y*, $x = 450$ or 550 °C, $y = 3$, 5 or 10 h).

2.2. Catalyst characterizations

The X-ray diffraction (XRD) measurements were performed on a Bruker D8 Advance X-ray diffractometer using Cu $K\alpha_1$ radiation ($\lambda = 1.5406$ Å). Transmission electron microscopy (TEM) images were obtained by a JEOL model JEM 2010 EX instrument at the accelerating voltage of 200 kV. UV–vis DRS spectra were obtained on a Varian Cary 500 Scan UV–VIS–NIR spectrophotometer using $BaSO_4$ as a reference. The N_2 absorption–desorption isotherms were determined at 77 K with a Micromeritics ASAP 2010 instrument. EPR spectra were recorded by a Bruker A-300-EPR X-band spectrometer. XPS spectra were carried out on a VG ESCALAB 250 XPS system with a monochromatized Al Ka X-ray source (15 kV 200 W 500 μm pass energy = 20 eV). All binding energies were referenced to the C 1s peak at 284.6 eV of surface adventitious carbon.

2.3. Photocatalytic measurements

All photocatalytic reactions were carried out in a fixed-bed reactor operated in a continuous flow mode. A 300 W Xe-arc lamp with a 420 nm cut-off filter ($\lambda \geq 420$ nm) and a cut-off filter (300 nm < λ < 400 nm) was used as the visible light source and UV light, respectively. The weight of catalyst (50–70 mesh) was kept at 0.40 g. Ethylene diluted with humid zero air (79% nitrogen, 21% oxygen; total hydrocarbons <1 ppm) was used to afford a reactant stream. The flow rate of reactant stream was maintained at 20 mL min^{-1}. The initial concentrations of ethylene and carbon dioxide in the stream were 340 and 0 ppm, respectively. Simultaneous determination of the concentrations of acetone and carbon dioxide was performed with an online gas chromatograph (HP6890) equipped with a flame ionization detector, a thermal conductivity detector, and a Porapak R column. Ethylene was found to be stable in the catalyst-loaded reactor without visible light illumination. No degradation of ethylene was observed when it was illuminated in the absence of catalyst.

3. Results and discussion

3.1. Structural characteristics and optical properties of the reduced N-doped TiO_2 samples

Fig. 1 shows the crystalline structure of the parent TN and the reduced TN samples characterized by XRD. It can be seen no remarkable change in the crystalline phase but a slight increase in the diffraction peak intensity after H_2 reduction at 450 and 550 °C, indicating enhanced crystallinity of the TiO_2 powder which is attributed to the agglomeration of particles at higher temperature [25]. The average crystallize sizes of TiO_2 in reduced N-doped TiO_2 samples calculated from XRD pattern by using the Scherrer formula [26] are given in Table 1. After nitridation at 450 °C for 20 h, the crystallize size of anatase is 17.6 nm. H_2 reduction at 450 °C does not alter the particle size. However, as the reduction temperature reaches 550 °C, the crystallize size of anatase increases slightly to 18.6 nm with prolonged reaction time. BET specific surface areas data are also listed in Table 1. It is obvious that the tendency of surface area is well consistent with that of crystallize size with increasing reduction temperature and time. The TEM images of pure TiO_2 and TN samples are presented in Fig. 2. TiO_2 has uniform particle size of about 20 nm. After nitrodation and H_2 reduction, it can be seen clearly that these nanoparticles maintain their original shape and size. Obviously, these TEM results are in good agreement with the XRD results.

Fig. 3 shows the light absorption properties of the reduced TN samples. Compared to pure TiO_2, TN sample displays a broad absorption shoulder centered at about 430 nm in the visible light region, which is the typical absorption feature reported for N-doped TiO_2 materials [23,27]. The visible-light absorption below 500 nm for TN samples arises from the contributions of doped nitrogen

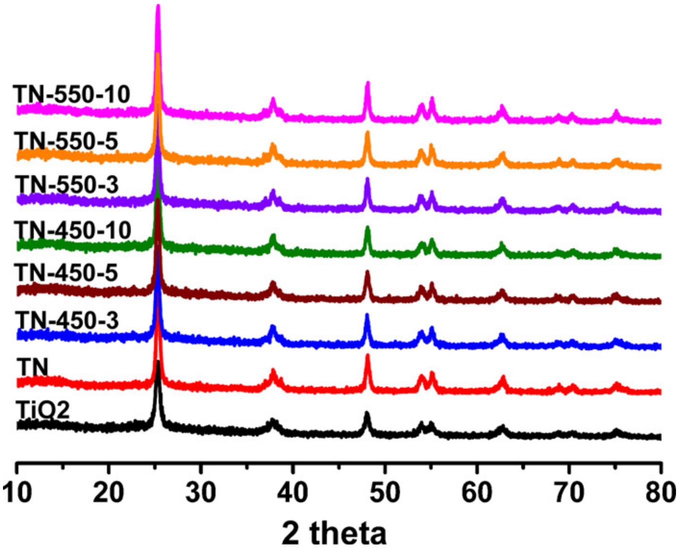

Fig. 1. XRD patterns of the parent TN and the reduced TN samples.