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ARTICLE

Synthesis, Characterization, and Nitrogen Concentration Depended Visible-Light Photoactivity of Nitrogen-Doped TiO_2 Nanosheets with Dominant (001) Facets

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Abstract: Anatase TiO_2 nanosheets with dominant (001) facets were prepared by a simple hydrothermal method. Nitrogen-doped TiO_2 nanosheets (TiO_2-N) with different nitrogen concentration were successfully synthesized by annealing TiO_2 nanosheets in NH_3 atmosphere with different NH_3 flow rate at 400 °C for 3 h. The morphology, nanostructures, and properties of TiO_2-N were characterized by X-ray diffraction, field emission scanning electron microscopy, high resolution transmission electron microscopy, ultraviolet-visible diffuse reflection spectroscopy, X-ray photoelectron spectroscopy, and photoluminescence. The effects of NH_3 flow rate on the nanostructures, properties, and visible-light photoactivity in the degradation of rhodamine B (RhB) aqueous solution under visible light ($\lambda > 400$ nm) irradiation of the prepared photocatalysts were investigated. Among all the prepared photocatalysts including nitrogen modified P25 (Degussa), TiO_2-N prepared with a NH_3 flow rate of 40 ml/min gave the highest visible-light photoactivity because of the dominant (001) facets, visible light responsibility, the slowest photogenerated electron (e^-) and hole (h^+) pairs recombination rate, and the highest hydroxyl radicle ($\cdot OH$) generation ability. Based on these experiments and analysis, the mechanisms of how the nitrogen concentration affects the visible-light photoactivity of TiO_2-N were proposed.

Key words: nitrogen doping; titanium dioxide nanosheet; nitrogen concentration; photoactivity; (001) facets

Titanium dioxide (TiO_2) is one of the most commonly available semiconductors with intrinsic properties, and has been widely studied by a lot of researchers since 1972 [1–3]. However, the large band gap (3.2 eV) causes anatase TiO_2 can only absorb the light with wavelength below 385 nm in the ultraviolet region, which is about 5% of the solar light irradiated on the earth [4]. Therefore, many methods such as metal and nonmetal doping have been used to extend the light absorption edge of anatase TiO_2 to the visible range in order to expand the practical application fields [5–7]. Nonmetal doping seems to be a promising way to improve the photocatalytic activity of TiO_2 under visible light irradiation. Nonmetals such as boron [8], carbon [9], nitrogen [2,8,12], fluorine [10], and sulfur [11] have been investigated and nitrogen is considered as the most effective one to enhance the visible-light photoactivity of TiO_2. Another important factor that affects the photocatalytic activity is the photogenerated h^+ and e^- pair separation ability. The photogenerated h^+ and e^- are able to form super power radicles on the surface of the photocatalysts to degradate organic contaminants and harmful gases [13]. What is the relationship between N doped concentration and the photogenerated h^+ and e^- recombination effect and how it affects the visible-light photoactivity are very promising topics to be discussed.

Recently, anatase TiO_2 nanosheets with a high percentage of (001) facets have attracted much attention due to their higher reactive properties than the traditional TiO_2 nanoparticles dominated by the (101) facets [14]. Experimental and theoretical studies indicate that TiO_2 nanosheets single crystals with fewer defects could reduce the photogenerated h^+ and e^- re-

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combination rate, and that will be favorable to the improvement of photoactivity [15]. The density of surface undercoordinated atoms is another factor affecting the photocatalytic activity of the crystal facets [16]. The more of the undercoordinated atoms exist, the higher of the photoactivity. As reported, the unsaturated Ti_{5c} atoms at the (001) facets is 100%, while the unsaturated Ti_{5c} atoms at the (101) facets is 50% [17]. Till now, TiO_2 nanosheets with dominant (001) facets have been used in a lot of fields, such as water slipping for hydrogen, contaminants decomposition, solar cells, and so on [18–20]. However, TiO_2 nanosheets also suffer from the problem of the large band gap. What's more, the condition for the crystal growth of TiO_2 nanosheets is very critical and thus limits the modification of TiO_2 nanosheets electronic structure in a certain degree [21]. Some researchers have proposed several methods to improve the visible-light photoactivity of TiO_2 nanosheets. Liu et al. [22] and Xiang et al. [23] synthesized N self-doped intersectional TiO_2 sheets from TiN, which extended the light response edge to about 550 nm. They found that the photocatalytic activity depended much on the size of TiO_2 sheets. Liu and his coworkers [24] synthesized intersectional anatase TiO_2 sheets with oxygen-deficiency from TiB, which also improved the photocatalytic activity. Xiang et al. [25] proposed a simple mixing-calcination method to dope the prepared TiO_2 nanosheets with sulfur and nitrogen. Still, noble metal was also used to improve the visible-light photoactivity of TiO_2 nanosheets [20].

In this study, N-doped TiO_2 nanosheets with a high percentage of (001) facets were obtained by a simple thermal treatment under NH_3 atmosphere. The effect of the N concentration on the structures and properties of as-prepared photocatalysts was analyzed. Modern characterization methods such as X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), and X-ray photoelectron spectroscopy (XPS) were applied to detect the crystal form and nanostructures of the prepared samples. Ultraviolet-visible (UV-Vis) diffuse reflection spectra (DRS) technique was used to detect the change of the band gap and light adsorption. Photogenerated h^+ and e^- recombination condition of the prepared photocatalysts was studied by the photoluminescence (PL) technique. Further, PL analysis was used to study the •OH generated on the surface of the photocatalysts in the aqueous solution containing terephthalic acid. The photocatalytic activities in the visible range of the prepared photocatalysts were measured by rhodamine B (RhB) degradation under xenon lamp irradiation with UV light filtered. At last, the visible-light photocatalytic mechanism of TiO_2-N was proposed.

1 Experiment

1.1 Preparation of the photocatalysts

1.1.1 Preparation of TiO_2 nanosheets

All the reagents were of analytical grade and were used without future purification. Distilled water was used in the whole experiment. TiO_2 nanosheets with a large percentage of exposed (001) facets were prepared via the hydrothermal method in the light of the procedure reported by Han and his coworkers [19].

In a typical synthesis, 25 ml of $Ti(OC_4H_9)_4$ and 15 ml of hydrofluoric acid solution (with a concentration 24 wt%) were mixed in a dry Teflon-lined autoclave (60 ml) at room temperature, followed by magnetic stirring for 30 min and hydrothermal treatment at 180 °C for 24 h. After the hydrothermal reaction, the white precipitates were collected by centrifuge and were washed with ethanol and distilled water for three times, respectively. At last, they were dried in a vacuum oven at 80 °C for 12 h before further N doping.

1.1.2 Synthesis of N-doped TiO_2 nanosheets and N-doped P25

The as-prepared TiO_2 nanosheets (0.2 g) were annealed under NH_3 atmosphere at 400 °C for 3 h in a tube furnace, and then the samples were cooled down to room temperature naturally. The flow rate of NH_3 was selected to be 20, 40, 70, and 100 ml/min, and the resulting samples were labeled as TiO_2-N20, TiO_2-N40, TiO_2-N70, and TiO_2-N100, respectively. N-doped P25 with different N concentration were prepared in the same way and were generally named P25-N.

1.2 Characterization of the photocatalysts

The structure characterization of samples was performed on a diffractometer (ARL X'TRA, American Thermo Elemental Company) employing Cu K_α radiation ($\lambda = 0.15406$ nm), with a scanning rate of 5°/min in the 2θ angle ranged from 20° to 80°. The morphology and size of TiO_2 nanosheets were measured by FESEM. TEM and HRTEM analysis were conducted on a JEM-2010 electron microscope (JEOL, Japan) at an accelerating voltage of 200 kV. UV-Vis DRS were obtained for the dry-pressed disk samples using an ultraviolet-visible-near infrared (UV-Vis-Nir) 3101 spectrophotometer (Shimadzu) with $BaSO_4$ as the reflectance sample in the wavelength ranged from 200 to 700 nm. The surface chemical environment and composition were analyzed by XPS on a PHI5000 VersaProbe system (ULVAD-PHI) with monochromatic Al K_α X-rays. PL emission spectra were conducted on a FL3-221 fluorescence spectrophotometer (Jobinyvon France) equipped with a 450 W xenon lamp as the excitation source at room temperature.

1.3 Visible-light photoactivity and ·OH generation analysis

The visible-light photocatalytic activity measurements of the