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New synthesis of excellent visible-light TiO$_{2-x}$N$_x$ photocatalyst using a very simple method

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Abstract

An excellent visible-light-responsive (from 400 to 550 nm) TiO$_{2-x}$N$_x$ photocatalyst was prepared by a simple wet method. Hydrazine was used as a new nitrogen resource in this paper. Self-made amorphous titanium dioxide precursor powders were dipped into hydrazine hydrate, and calcined at low temperature (110 °C) in the air. The TiO$_{2-x}$N$_x$ was successfully synthesized, following by spontaneous combustion. The photocatalyst was characterized by X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET), transmission electron microscope (TEM), UV–Vis diffuse reflectance spectrometer (DRS), and X-ray photoelectron spectroscopy (XPS). Analysis of XPS indicated that N atoms were incorporated into the lattice of the titania crystal during the combustion of hydrazine on the surface of TiO$_2$. Ethylene was selected as a target pollutant under visible-light excitation to evaluate the activity of this photocatalyst. The newly prepared TiO$_{2-x}$N$_x$ photocatalyst with strong photocatalytic activity and high photochemical stability under visible-light irradiation was firstly demonstrated in the experiment.
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1. Introduction

TiO$_2$-based semiconductor photocatalysis technology has been proved to be potentially advantageous for photoinduced water splitting, or for the removal of organic pollutions in water and air [1]. However, for the wide band-gap of TiO$_2$ (3.2 eV for anatase), the large-scale application of titanium dioxide as an efficient photocatalyst is hampered by the fact that it absorbs only a very small ultraviolet part (3–4%) of the solar light. In order to use an abundant amount of visible light (about 45%) from the solar light, the development of photocatalysts effectively working under visible-light irradiation is a very hot topic in the area of photocatalysis research.

Many researches have showed that doping nitrogen into TiO$_2$ to form TiO$_{2-x}$N$_x$ can efficiently shift the optical response to the visible spectral range [2–5]. At present, it has been used in visible-light degradation of pollutants. The main synthesis methods of TiO$_{2-x}$N$_x$ were shown as

below: heat treatment of TiO$_2$ in NH$_3$ (67%)–Ar atmosphere [2], sputtering TiO$_2$ target in N$_2$–O$_2$ gas [3], nitrogen ion implantation on the TiO$_2$ [4], mechanochemical method [5], and so on. But these methods usually have a complicated process or need expensive apparatus, and seldom consider the effect of nitrogen source. And most researches also have not demonstrated the photochemical stability of TiO$_{2-x}$N$_x$ under visible light. Traditional wet synthesis methods of TiO$_{2-x}$N$_x$ were followed by the calcination of resulting materials at high temperature [6–8]. Gole et al. [9] have reported "nitridation" of TiO$_2$ nanoparticles using alkylammonium salt at room temperature, but it has been found unstable after irradiation under ultraviolet light [10].

Now, we report a new, simple, and effective method to prepare nitrogen-doped TiO$_2$ with photochemical stability under both ultraviolet light and visible-light irradiation, which has not been reported in the visible-photocatalytic field up to now.

Hydrazine is an active chemical and it can be burned in air at a relatively low temperature with a strong heat release (621.74 kJ/mol). In this paper, we firstly

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demonstrate a wet method to prepare nitrogen-doped TiO_2 using hydrazine as the nitrogen source by utilizing its ignitability. Ethylene was selected as a target pollutant under visible-light excitation. The process of this nitrogen-doped method is very simple and does not need calcination at high temperature. The newly prepared photocatalyst had a small crystalline size, large specific surface area, and exhibited a strong photocatalytic activity for decomposition of ethylene with high photochemical stability under both ultraviolet light and visible-light irradiation.

2. Experimental

2.1. Preparation and characterization of samples

Nitrogen-doped TiO_2 powders were prepared using a simple method by treating amorphous TiO_2 with hydrazine hydrate at 110 °C. Then, 10 ml titanium(IV) tetraisopropoxide was added dropwise to 200 ml demonized water without any other reagent under vigorous stirring. The obtained products were filtered and rinsed with deionized water several times, then dried at 60 °C to form white powders (denoted as T60). These white powders were dipped in hydrazine hydrate (80%) for 12 h, then filtered and dried at 110 °C for 3 h in air. Finally, the yellow nitrogen-doped TiO_2 powders were formed (denoted as NTH). In the drying process, we could find that, after evaporating a few solutions on the surface, the powders were still white. But after several minutes, there was a glow which was detected on the surface of the powders for a moment, and then the catalysts turned to yellow. In contrast, if we use N_2 instead of air in the same condition, we could not find these phenomena. The color of the catalysts was still white after calcining in nitrogen atmosphere, and remained so even after increasing the temperature to 150 °C. Therefore, we can conclude that this glow came from the combustion of hydrazine that adsorbed on the surface of TiO_2 powders because of its ignitability in air. The reaction to form nitrogen-doped TiO_2 is seen to take place in seconds, coincidental with that of heat release. Pure TiO_2 powders were produced by the same method without dipping in hydrazine hydrate (denoted as TH), and the P25 powders were annealed under NH_3 flow at 550 °C by traditional nitrogen-doped method [2,11] (denoted as NP25) as for reference samples.

The phase constitution of the products was determined by X-ray diffraction (XRD) analysis (Philips D8 Advanced) using $CuK\alpha$ radiation ($\lambda = 0.15406$ nm), and the crystallite size was calculated from the peak half-width with corrections for instrumental line broadening by using the Scherrer equation, $D = 0.89\lambda/\beta\cos\theta$, where D is the crystallite size, 2θ is the peak position, and β is the half-width of the peak. The specific surface area measurement was performed by Brunauer–Emmett–Teller analyzer (Coulter Ominisor 100 CX). Microstructures of photocatalysts were observed by a transmission electron microscope (Philips Tecnai F30). The optical properties were analyzed by a UV–visible diffuse reflectance spectrometer (Varian Cary 500). The binding energy of N1s was measured using an X-ray photoelectron spectroscopy (PHI Quantum 2000 System).

2.2. Photocatalytic activity measurements

The photoactivities of the samples were evaluated by the photocatalytic oxidation of ethylene (C_2H_4) into carbon dioxide (CO_2) in gas phase. The catalyst particles (0.9 g, 50–70 mesh) were packed into a $5 \times 2 \times 0.1$ cm^3 fixed bed plane reactor, which was operated in a single pass mode. A 500 W Xe-lamp with a cut-off filter ($\lambda < 420$ nm) was used as the light source to test its stability under ultraviolet light, while with two cut-off filters (420 nm $< \lambda <$ 800 nm) was used as a visible-light source. Other cut-off filters (such as 450–800, 500–800, and 550–800 nm) were also used to test its optical response range of photocatalytic activity. Ethylene was used as a reactant stream (flow rate: 20 ml/min), which was diluted in water-saturated zero air. The adsorption/desorption equilibrium of ethylene gas on the photocatalyst was obtained after 3 h in the dark before carrying out an activity measurement. The respective initial concentrations of ethylene and carbon dioxide in the stream were 700 and 0 ppm. Ethylene was found to be thermally stable in the reactor in the dark. Analysis of the reactor effluent was conducted by a gas chromatograph (HP6890). All experiments were thermostated at 27 °C.

3. Result and discussion

3.1. Characterization of prepared nitrogen-doped TiO_2

Fig. 1 shows the XRD patterns of the starting white powder (T60), TH, and NTH. No obvious peak can be found in Fig. 1(a). It demonstrates that the white precursor
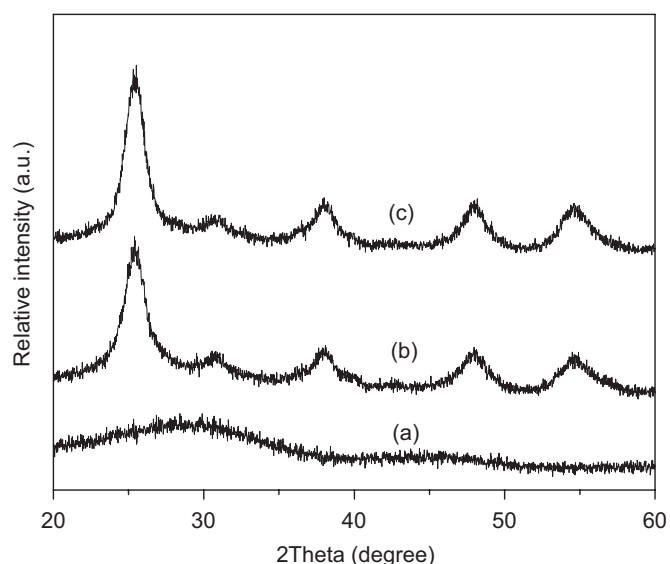

Fig. 1. XRD patterns of T60 (a), TH (b), and NTH (c).

powder (T60) was amorphous. The main peak of $2\theta = 25.4°$ observed in Fig. 1(b) and (c) matches the (1 0 1) crystallographic planes of anatase TiO_2 nanoparticles, indicating that both TH and NTH nanoparticle structures dominantly correspond to anatase crystalline. The main peak of NTH is a little sharper than TH. The average crystalline size of NTH and TH is 5.2 and 5.0 nm, respectively. It demonstrated that the degree of crystallization of NTH is a little better than TH. This may be affected by the spontaneous combustion of hydrazine on the surface of TiO_2. The process of crystallization might be accelerated by the transient high temperature. Fig. 2 shows the TEM observation of NTH. Fig. 2(a) indicates that the sample is composed of a large quantity of agglomerated nanoparticles with a size of about 5 nm, which is in good agreement with the results calculated by XRD patterns. The high-magnification TEM in Fig. 2(b) shows the fringes of $d = 0.35$ nm which corresponds to the (1 0 1) crystallographic planes of anatase TiO_2 nanoparticles. It also matches the XRD patterns. From the BET measurement, the specific surface areas are $152.24 \, m^2/g$ on NTH, while $179.06 \, m^2/g$ on TH. The decreased surface area may be due to the increased crystalline size and the enhanced agglomeration of NTH which is caused by the effect of the combustion process. From these results, we can find that on comparing with the pure TiO_2 prepared in the same temperature, the doped nitrogen by the combustion of hydrazine has a slight effect on the formation of TiO_2 structure. The nitrogen-doped TiO_2 prepared by this method showed anatase phase, small crystalline size, and large specific surface areas.

Fig. 3 compares the UV–visible diffuse reflectance spectrum of NTH and TH. The results indicated that doped nitrogen by the combustion of hydrazine can give rise to a clear red-shift in the optical response of TiO_2. High visible absorbance (400–550 nm) was observed for N-doped TiO_2 powder prepared by this method.

X-ray photoelectron spectroscopy analysis was employed as an important characteristic method to detect the chemical states of nitrogen of the $TiO_{2-x}N_x$ catalyst. It was considered that substitutional nitrogen in the lattice of
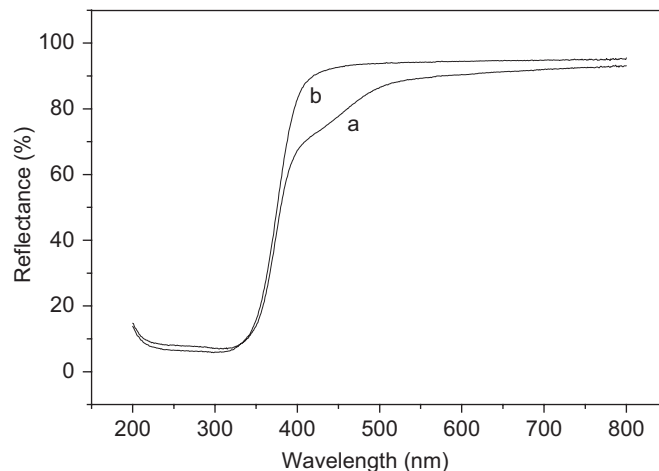

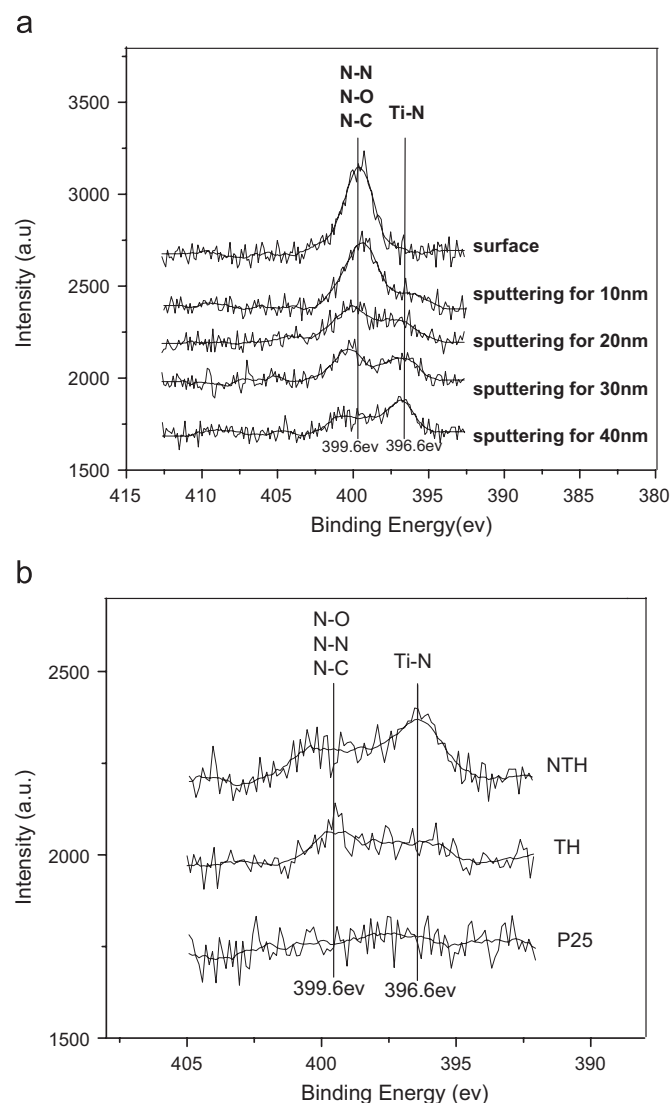Fig. 3. The diffuse reflectance spectra of NTH (a) and TH (b).

Fig. 4. N1s XPS spectra of NTH after Ar^+ ion etching at 40 nm.

the titania crystal to form Ti–N bond was responsible for the enhanced visible activity both from calculation and experiments [2]. Fig. 4(a) shows the XPS spectra of the N1s
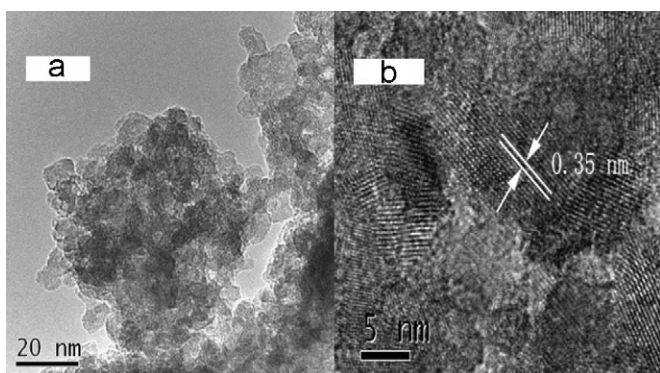

Fig. 2. TEM image of NTH (a) TEM image and (b) high magnification TEM image.

profile of NTH at different Ar$^+$ sputter depths. We could find the peak intensity at 399.6 eV (attributed to N–O, N–N or N–C bond [12]) decreasing with an increase in the depth of Ar$^+$ ion sputtering step by step. On the other hand, the peak intensity at 396.6 eV (attributed to N–Ti bond [2,13]) increased with the enhanced depth of Ar$^+$ ion sputtering. This may be due to the molecular-chemisorbed γ-N$_2$ or some other nitrogen compounds on the surface, which hid the existence of Ti–N binding before Ar$^+$ ion sputtering [2,13,14]. Fig. 4(b) shows the N1s XPS spectra of NTH, TH, and P25 after Ar$^+$ sputtering for 40 nm. The peak at 396.6 eV that was associated with the Ti–N bond was only found in NTH. The results of XPS indicate that Ti–N binding was actually formed in the lattice of the titania crystal during the process of hydrazine combustion on the surface of TiO$_2$ powders.

3.2. Photocatalytic activity and stability

Fig. 5 shows the visible-light-driven photocatalytic conversion of ethylene on NTH, NP25, TH, and P25. The result demonstrates the high photocatalytic performance on NTH in the photocatalytic process. The conversion of ethylene is about 9%, compared to NP25 (about 2%), TH ($<0.5\%$), and P25 ($<0.5\%$). In another experiment, it showed the same results when we used methyl chloride as the target pollutant under the same condition. Fig. 6 shows the photocatalytic activity of the conversion of ethylene on NTH of the different cut-off wavelengths of the optical high-path filters under irradiated Xe-lamp. In all activity tests, the conversion of ethylene was steady after visible-light irradiation for 5 h. The data in Fig. 6 shows the conve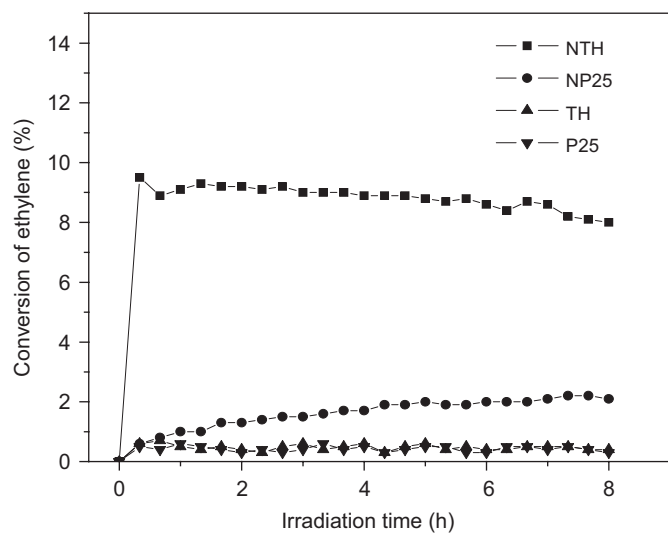rsion of ethylene when it was steady. From the results we can find that the photocatalytic activity of NTH corresponds well with the visible-light
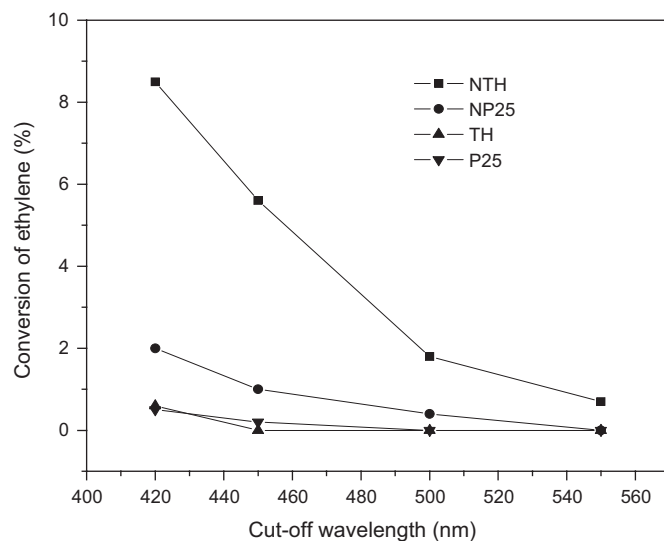

Fig. 6. Photodegradation of ethylene under different cut-off wavelengths for NTH, TH, and P25.
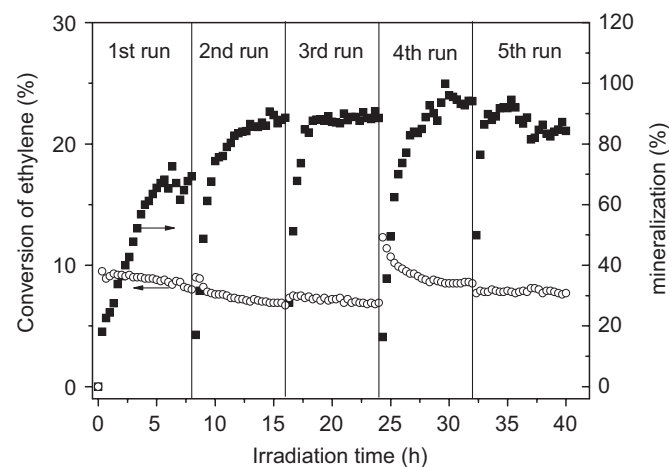

Fig. 7. Cyclic photodegradation of ethylene under visible light by reusing NTH five times (—○— conversion and —■— mineralization).

adsorption in UV–Vis diffuse reflectance spectrum. Fig. 7 shows the chemical stability test of photocatalytic performance of NTH towards ethylene decomposition. The result demonstrates the high photocatalytic stability of NTH for the ethylene oxidation after 40 h of testing, by the repeated use of the same catalyst five times. We also found that the mineralization of ethylene increased to more than 90% from the second run when it was steady. Furthermore, in another experiment (Fig. 8), we could also find that the activity of visible-light-induced catalytic conversion of ethylene on NTH was almost unchanged under ultraviolet light irradiation for 8 h. From these results we can conclude that NTH exhibited a strong photocatalytic activity for decomposition of ethylene under visible-light irradiation with high photochemical stability.
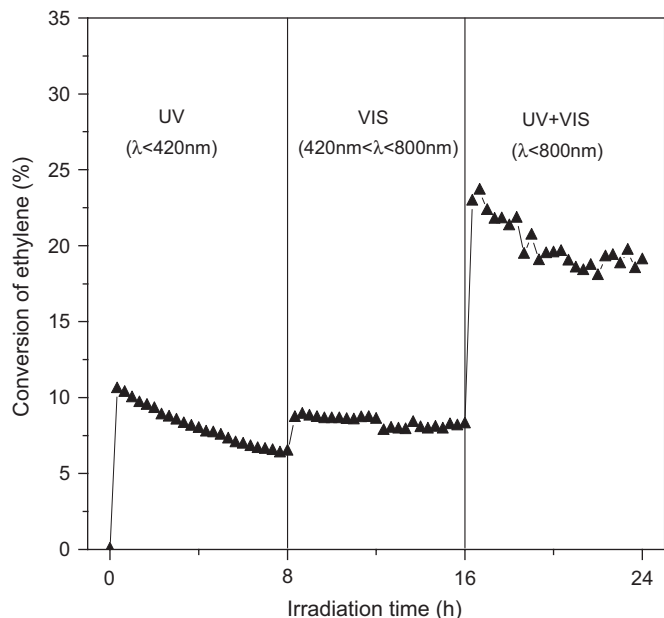

Fig. 5. Visible-light-induced catalytic conversion of ethylene on NTH, NP25, TH, and P25.

Fig. 8. The tests of photochemical stability of NTH under different light wavelength range irradiations for photodegrading ethylene.

4. Conclusions

A new nitrogen-doped TiO_2 was successfully prepared by a simple wet method at low temperature. It has been made by treating self-made amorphous TiO_2 powders with hydrazine hydrate (80%) in 110 °C. From the experiment, we can conclude that the introduction of nitrogen element into titanium dioxide was due to the combustion of hydrazine on the surface of TiO_2. Ti–N binding was actually formed in the lattice of the titania crystal from XPS result. The results showed that the new prepared $TiO_{2-x}N_x$ was of anatase phase with small crystalline size and large specific surface area. It exhibited a strong photocatalytic activity for decomposition of ethylene under visible-light irradiation with high photochemical stability.

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