

Research Article

Hydrothermal Preparation of Visible-Light-Driven N-Br-Codoped TiO₂ Photocatalysts

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Using a facile hydrothermal method, N-Br-codoped TiO₂ photocatalyst that had intense absorption in visible region was prepared at low temperature (100°C), through a direct reaction between nanocrystalline anatase TiO₂ solution and cetyltrimethylammonium bromide (CTAB). The results of X-ray photoelectron spectroscopy (XPS) showed the existence of N-Ti-N, O-Ti-N-R, Ti³⁺ (attribute to the doped Br atoms by charge compensation), and TiO_xN_y species, indicating the successful codoping of N and Br atoms, which were substituted for lattice oxygen without any influence on the crystalline phase of TiO₂. In contrast to the N-doped sample, the N-Br-codoped TiO₂ photocatalyst could more readily photodegrade methylene blue (MB) under visible-light irradiation. The visible-light catalytic activity of thus-prepared photocatalyst resulted from the synergetic effect of the doped nitrogen and bromine, which not only gave high absorbance in the visible-light range, but also reduced electron-hole recombination rate.

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1. INTRODUCTION

The development of photocatalysis has attracted much attention in the recent 30 years [1–3]. Of the materials being developed for photocatalytic applications, titanium dioxide (TiO₂) remains the most promising due to its high efficiency, low cost, chemical inertness, and photostability [4–6], and so forth. However, its wide-band gap (3.2 eV \equiv 380 nm for anatase) can only capture UV light, a small fraction (about 3–5%) of the solar irradiance at the earth surface, compared to the 45% of visible light [7]. Thus any red shift in the optical response of TiO₂ from the UV band to the visible band will have a profound positive effect on the photocatalytic efficiency of the materials [8, 9].

Doping TiO₂ with transition-metal elements was used as the initial approach to shift the optical response of TiO₂ from the UV band to the visible band [10–15]. However, these metal-doped TiO₂ materials suffered from thermal instability and low-quantum efficiency because of increased carrier trapping after doping, or require expensive facilities in the ion implantation case [8, 16, 17]. In contrast, better visible optical response of TiO₂ could be achieved by using nonmetal doping [8, 9, 18, 19]. Kinds of nonmetal elements, in-

cluding nitrogen [20–23], phosphor [24], carbon [25], sulfur [26, 27], boron [28], fluorine [18, 29], iodine [30], chlorine, and bromine [31], were found to be capable of making doped TiO₂ respond to visible light. In particular, the presence of substitutional N atoms in the TiO₂ matrix enhanced the absorption in the visible band and then led to a corresponding photocatalytic activity [32]. Moreover, doped halogen atoms into the oxygen sites should be accompanied by the formation of Ti³⁺ to maintain the overall electroneutrality of the crystal lattice, and a certain amount of Ti³⁺ reduced the electron-hole recombination rate and further enhanced the photocatalytic activity [18, 33]. Thus, one may want to know whether halogen atoms codoped in TiO₂ together with nitrogen have higher photocatalytic activity than that of N-doped TiO₂. To the best of our knowledge, there was no report on the visible-light-driven TiO₂ photocatalyst codoped by nitrogen and bromine.

Hereby, a simple process was utilized to prepare the N-Br-codoped TiO₂ nanocrystals via the direct reaction between nanocrystalline TiO₂ solution and cetyltrimethylammonium bromide (CTAB). Based upon the results of the present work, we found that the N-Br-codoped TiO₂ could be considered as an effective visible-light-driven photocatalyst.

2. EXPERIMENTAL

2.1. Materials preparation

All chemicals, including Titanium tetraisopropoxide (TTIP, Tianchang Chemical Co., Ltd., Tianchang, China), nitric acid (65–68%, Shanghai chemicals, Shanghai, China), CTAB (Tianjin Chemical International Trading Co., Ltd., Tianjin, China), and anhydrous ethanol (Tianjin Chemical International Trading Co., Ltd., China), were of reagent grade and were used without further purification. Water was doubly distilled and deionized.

2.1.1. Preparation of nanocrystalline TiO_2 solution

The preparation proceeded as follows: 15 mL of TTIP and 3 mL of ethanol were mixed and then added dropwise into 100 mL of water in a 200 mL beaker under continuous stirring. After 15 minutes ultrasonication, 2 mL of nitric acid were added to the mixture, and then the hydrothermal crystallization was carried out at 100°C for 5 hours to obtain a nanocrystalline TiO_2 blurry solution (denoted as TOS for convenience, the original solution for the following preparation).

2.1.2. Preparation of photocatalysts

For N-Br-codoped TiO_2 , 18.6 g of CTAB was added into TOS and was refluxed at 80°C for 3 hours under vigorous stirring, leading to a yellow milky solution. The product was then evaporated under low pressure (20-mmHg) to a yellow xerogel. Finally, the unreacted CTAB and other organic by-products were washed out with ethanol in a Soxhlet extractor and then the N-Br-codoped TiO_2 photocatalyst was obtained (denoted as TNB).

For comparison, N-doped TiO_2 photocatalyst (accordingly designed as TDN) was prepared by a direct reaction between TOS and triethylamine as the above process, and another undoped TiO_2 photocatalyst (denoted as TOX derived from TOS by a low-pressure evaporation) was also prepared.

2.2. Photocatalysts characterization

Several techniques were used to characterize the structure and properties of the above materials TDN and TNB. The X-ray diffraction (XRD) patterns were obtained on a D8 Advance diffractometer (Bruker AXS, GmbH, Karlsruhe, Germany) using Cu K α radiation. Line traces were collected over 2θ values ranging from 20° to 70°. The lattice spacing was observed by transmission electron microscopy (TEM, JEOL JEM-2010). Diffuse reflection absorption spectra (DRAS) of the samples were recorded using a UV-Vis-NIR spectrometer (UV-3150 spectrometer Shimadzu, Japan), and BaSO_4 was used as the reference sample. The DRAS spectra were used to evaluate the optical absorption properties of the samples [34]. The states of the charges were investigated by XPS (Mg k α as radiation source, PHI-5300X, Perkin-Elmer physics electronics), and all the bonding energies were calibrated to that of the adventitious C 1s peak fixed at 284.8 eV. In order to investigate the depth profile of N and Br atoms in

the lattice of TiO_2 particles, XPS analysis of sample TNB using Ar etching was performed.

For the undoped TiO_2 sample, TOX, XRD, and DRAS spectra were used to characterize the structure and properties.

2.3. Measurement of photocatalytic activity

2.3.1. Photoreactor

For UV-activity determination, the photocatalytic experiments were carried out on a photochemical reactor (SGY-1, Jiangsu Provincial Academy of Environmental Sciences) with a 300-W high-pressure mercury lamp as the light source, which provides a main irradiation wavelength about 365 nm.

For vis-activity determination, the light source was a 250 W metal halide lamp (Philips), which was positioned inside a cylindrical Pyrex vessel surrounded by a circulating water jacket to cool the lamp. A cutoff filter was also placed between lamp and the Pyrex jacket to remove the radiation below 420 nm, ensuring the reaction system to be irradiated only by visible light.

2.3.2. MB, photocatalytic activity determination

The photocatalytic experiments were carried out by adding 250 mg of samples into 250 mL of methylene blue (MB) solution (50 ppm). The suspension was stirred in dark for 30 minutes to obtain the saturated adsorption of MB before UV/visible light illumination. The concentration of MB at this point was used as the initial value for the further kinetic treatment of the photodecomposition process. At given irradiation time intervals, the dispersion was sampled (4 mL), centrifuged, and subsequently filtered through a millipore filter (pore size, 0.22 μm) to separate the catalyst particles. The concentration of MB was measured at 665 nm wavelength using UV-Visible spectrophotometer. Firstly, a series of standard MB solutions (2.5, 5, 10, 15, and 20 ppm) were prepared and measured using UV-Vis spectrophotometer. Then, a standard curve could be obtained. The concentration of MB during the degradation process could be obtained from the standard curve. Absorption spectra were recorded after 4-fold dilution.

3. RESULTS AND DISCUSSION

3.1. Crystal phase identification

Figure 1 shows the XRD patterns of samples, TOX, TDN, and TNB. The diffraction lines at $2\theta = 25.3^\circ, 37.8^\circ, 48.1^\circ, 53.9^\circ, 55.2^\circ,$ and 62.7° demonstrate that all the three samples are of the anatase phase. The average crystallite size, D_A , determined from the diffraction peak of the anatase (101) planes, is about 6.5 nm estimated from the Debye-Scherrer equation [35]. TEM (see Figure 2) of sample TDN and TNB clearly revealed the fringes of (101) planes of anatase with a lattice spacing of about 0.352 nm [36], which corresponds to the XRD patterns. Among the three main polymorphs, anatase TiO_2 is believed to exhibit the highest photocatalytic activity

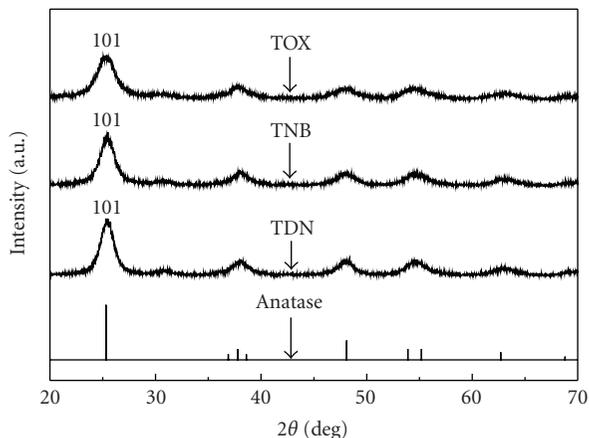


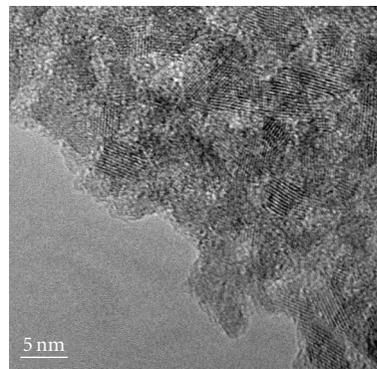
FIGURE 1: XRD patterns of samples, TOX, TDN, and TNB. Sample TOX was undoped TiO_2 , sample TDN was N-doped TiO_2 , and sample TNB was N, Br-codoped TiO_2 .

[31]. The anatase phase of the photocatalysts will contribute to a good photocatalytic activity.

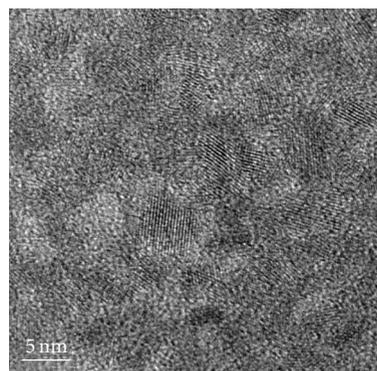
3.2. Optical properties and XPS analysis

The samples, TOX, TDN, and TNB show different color. TOX looks white, TDN yellow while TNB tan. From Figure 3 (DRAS of the samples), TOX have no absorption in the visible band; while the other two samples both have distinctly great absorption in the visible band. Compared to sample TDN, sample TNB showed obvious enhanced absorption in the visible range of 400–600 nm. The broad absorption below 500 nm is because the N 2p orbitals are localized above the top of the O 2p valence bands, whereas the absorption above 500 nm is mainly caused by oxygen vacancies [37]. The band gap energy of the synthesized samples was estimated to be about 3.12 eV for TOX, 2.03 eV for TDN, and 1.88 eV for TNB by the absorption edge. The band gap narrowing will result in the obvious red-shift in the optical response, which is helpful for visible photocatalytic activity.

The chemical composition of surface was determined by XPS (see Figure 4). The C 1s, O 1s, Ti 2p, and N 1s peaks components are discernible in the wide scan spectrum of the two samples, but obvious peaks of Br 3d can be found only for TNB. The N 1s core-level spectra of the two samples are showed in Figure 5. For TDN sample (Figure 5(a)), the feature at 396.7 eV is generally known as the “nitride” peak and can be assigned to the N^{2-} anions that replace oxygen atoms in the TiO_2 lattice to form N-Ti-N [38, 39]. N 1s peak of 399.3 eV can be attributed to the binding energy of the N atom in special environment of O-Ti-N-R (R: alkyl) [38–40]. The weak N 1s peak at 401.7 eV indicates the trace amount of nitrogen in the form of Ti-N-O [39]. For TNB sample, No N 1s peaks from N^+ of CTAB (at 402.3 eV) can be found in Figure 5(b) [38, 41], indicating that residual CTAB has been completely removed by the Soxhlet extracting method or at least the residual CTAB was too little to be detected. The two main N 1s peaks at 396.5 eV and 399.3 eV can be attributed to the binding energy of the N atom in special environment of N-Ti-N and O-Ti-N-R (R: alkyl) [38–40].



(a)



(b)

FIGURE 2: TEM images of samples, TDN (a) and TNB (b).

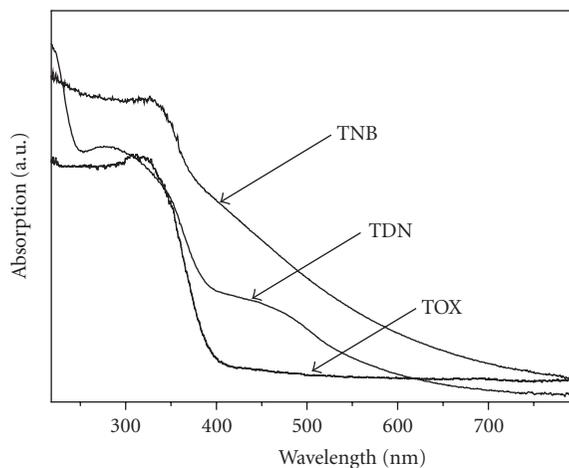


FIGURE 3: UV-Vis diffuse reflection absorption spectra of samples, TOX, TDN, and TNB.

Figure 6 showed Ti 2p core-level spectra of TDN and TNB. For TDN sample (Figure 6(a)), the deconvolution of Ti 2p bands yields two major doublets ($2p_{3/2}$ and $2p_{1/2}$) encompassing the set of two $2p_{3/2}$ peaks. The main Ti $2p_{3/2}$ peak at 458.6 eV is typical for pure TiO_2 [38, 42] and can be attributed to those unreacted TiO_2 , the other Ti $2p_{3/2}$ peak at 457.2 eV for TiO_xN_y [38, 42]. For TNB sample (Figure 6(b)), the deconvolution of the complex Ti 2p bands yields three major

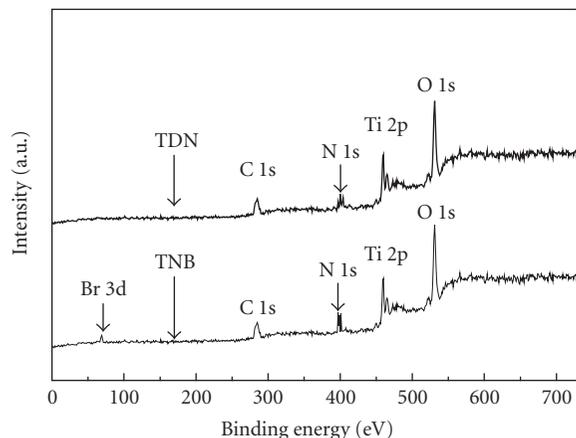


FIGURE 4: XPS wide scan spectra of samples, TDN and TNB.

TABLE 1: Results of XPS analysis using Ar etching, sample TNB.

Name	Content/%	
	Br	N
Before etching	0.31	3.68
First etching	0.11	1.81
Second etching	0	1.79
Third etching	0	1.17

doublets ($2p_{3/2}$ and $2p_{1/2}$) encompassing the set of three Ti $2p_{3/2}$ peaks. The strongest Ti $2p_{3/2}$ peak at 458.7 eV is typical for pure TiO_2 [38] and can be attributed to those unreacted TiO_2 , other peaks, at 455.7 eV typical for Ti^{3+} [38], and at 457.2 eV for TiO_xN_y [38, 42]. Doped nitrogen atoms result in the formation of TiO_xN_y [42], meanwhile, the formation of Ti^{3+} might attribute to the substitution of bromine atoms for oxygen just like the case of fluorine doping [33, 43].

From the results of the depth profile of N and Br atoms of sample TNB (see Table 1), we found that N and Br atoms were mainly at the surface of TiO_2 particles. Besides, the results of XPS indicate that N and Br atoms were actually existed in the lattice of the titania crystal.

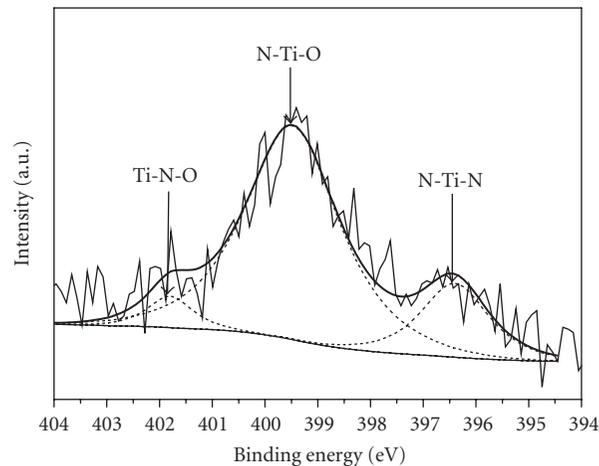
3.3. Photocatalytic activity

3.3.1. UV-activity

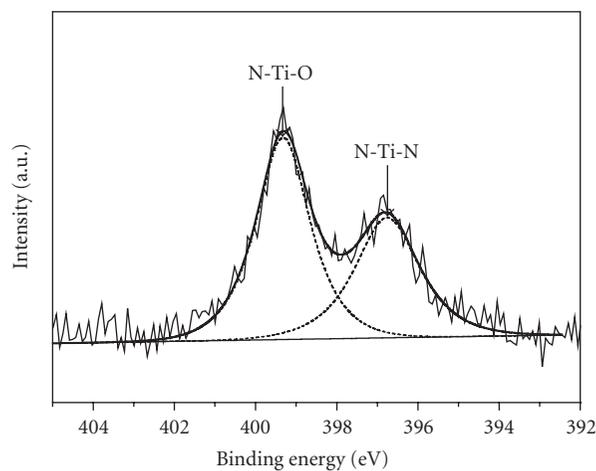
The photodecomposition of the MB in aqueous solution was carried out under UV light. The time-dependent concentration of MB is shown in Figure 7(a). With high crystallization, P25 can more readily photodegrade MB. The photocatalysts, TOX, TDN, and TNB, exhibit similar and good photocatalytic activity, which due to their similar crystallization and microstructure. Because the doping process was performed under low temperature, then there is little change of crystallization and microstructure.

3.3.2. Vis-activity

The photodecomposition of the MB in aqueous solution was carried out under visible light. The time-dependent concen-



(a)



(b)

FIGURE 5: (a) N 1s core-level spectrum (deconvolution of N 1s bands) of TDN. (b) N 1s core-level spectrum (deconvolution of N 1s bands) of TNB.

tration of MB in solution is shown in Figure 7(b). Compared with the visible-inactive P25 and TOX, both of TDN and TNB exhibit excellent photocatalytic activity, and obviously TNB can more readily photodegrade MB than TDN. One may raise the doubt of whether it is the photocatalyst that plays the key role in decomposing MB because MB can absorb visible light itself. This doubt, however, is not necessary considering the case using P25, TOX, TDN, or TNB as photocatalyst. If the decomposition of MB is due to the light absorbance itself, then the efficiency of the decomposition using a different photocatalyst may not vary so much as is shown in Figure 7(b). Also, one may consider such dyes degradation on photocatalysts surface under visible light to be a sensitization mechanism. If the decomposition of MB is due to a sensitization mechanism, then the efficiency of the decomposition using TOX may be similar to that of TDN and TNB due to their similar crystallization and microstructure.

The stability of the catalysts has been tested by using the photocatalysts repeatedly three times. No visible change of the photoactivity has been observed throughout these three

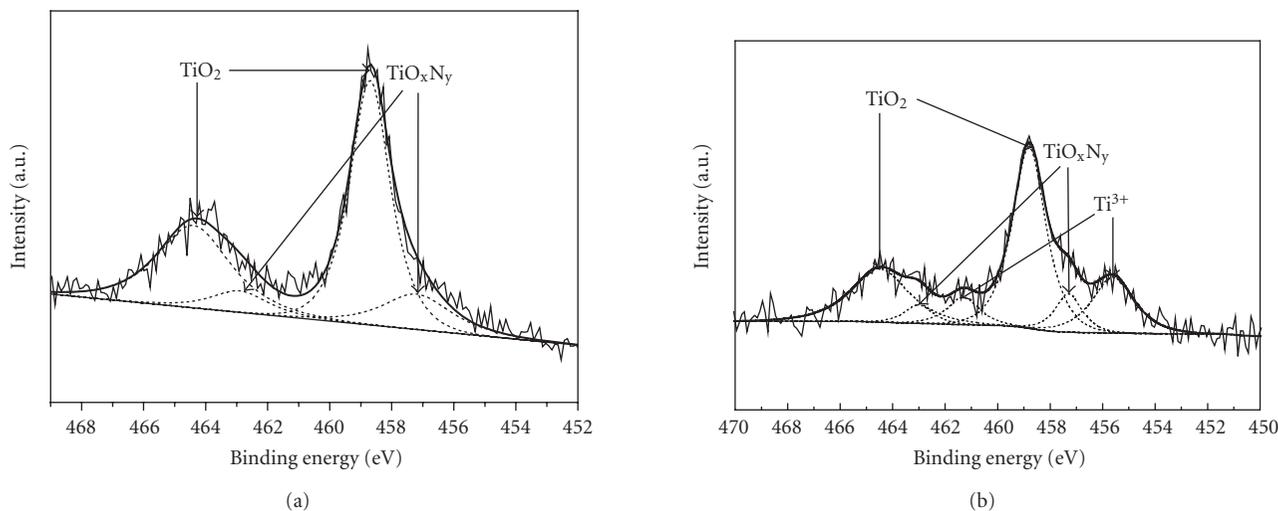


FIGURE 6: (a) Ti 2p core-level spectrum (deconvolution of Ti 2p bands) of TDN. (b) Ti 2p core-level spectrum (deconvolution of Ti 2p bands) of TNB.

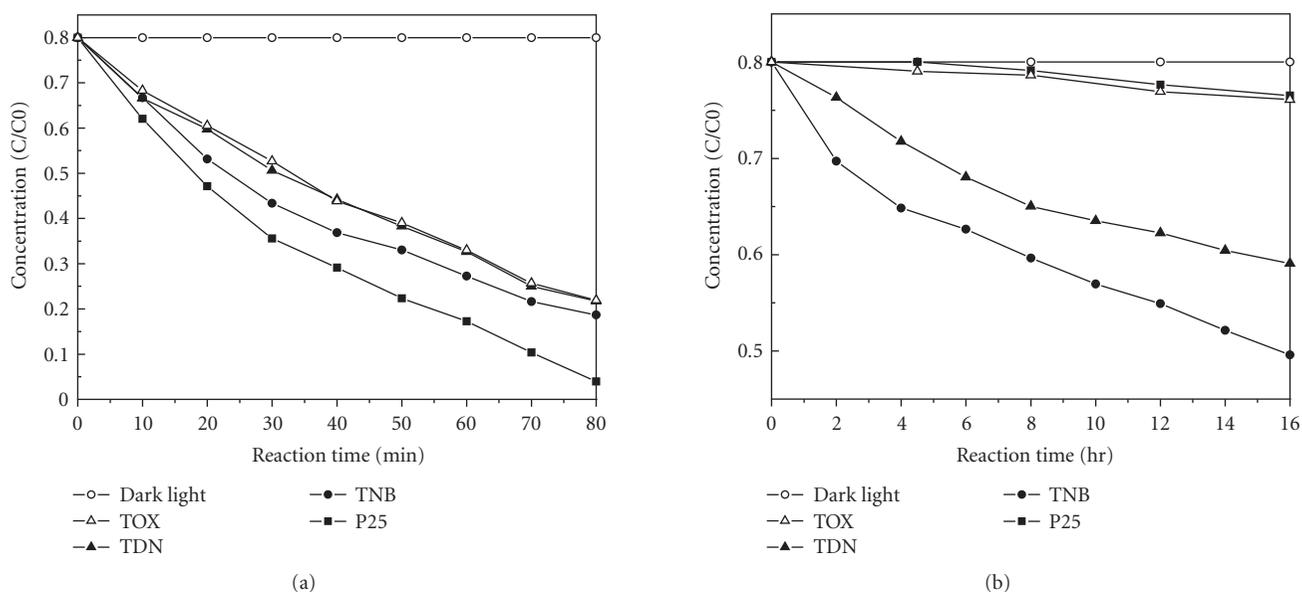


FIGURE 7: (a) Comparison of the UV photocatalytic activities of P25, TOX, TDN, and TNB on MB photodecomposition. Time-dependent concentration of MB in solution under UV light. (b) Comparison of the visible photocatalytic activities of P25, TOX, TDN, and TNB on MB photodecomposition. Time-dependent concentration of MB in solution under visible light.

runs. To ascertain the role of light radiation in the decomposition process, we have tested the effect of TNB without light radiation and the result is not unexpected (see Figures 7(a) and 7(b)). Without light, the decomposition process could hardly proceed.

Altogether, the excellent visible-light photoactivity of TDN and TNB can be explained by the doped microstructure. Because the N 2p orbitals are localized above the top of the O 2p valence bands, the doped N atoms will result in band gap narrowing and improve the visible light absorption of anatase TiO₂. The improved visible light absorption can increase the number of photoinduced electron. Undoubt-

edly, this can enhance the photocatalytic activity. Moreover, the N-doping is considered to have a contribution in the formation of oxygen vacancies [44–47]. Incorporation of two N atoms into the oxygen sites should be accompanied by the formation of one oxygen vacancy to maintain the overall electroneutrality of the crystal lattice. Many studies have confirmed that the formation of the superoxide ($O_2^{\cdot-}$) and hydroxyl radicals (OH^{\cdot}), two important active species for initiating a photocatalytic reaction [48–52], required oxygen vacancy sites [35, 53, 54]. For sample TNB, The contribution of the doped Br atoms to the visible photocatalytic activity is achieved mainly by the improvement of the quantum

efficiency. The doped Br atoms can convert Ti^{4+} to Ti^{3+} by charge compensation, and the existence of a certain amount of Ti^{3+} reduces the electron hole recombination rate and further enhanced the quantum efficiency and photocatalytic activity [43]. Moreover, halogen element, such as Br, Cl, F, doping for oxygen in TiO_2 can also cause the absorption edge of TiO_2 to shift to the lower energy region [31], though the red-shift is weak, which can enhance the photocatalytic activity too. Thus, the synergetic effect of doped N and Br atoms contributes to a higher visible photocatalytic activity of TNB.

4. CONCLUSIONS

In this paper, N-Br-codoped TiO_2 photocatalyst was prepared via a facile two-step homogeneous hydrothermal route at low temperature. As expected, the prepared photocatalyst showed a high-photocatalytic activity under visible irradiation, which was attributed to its anatase crystalline framework, low-electron hole recombination rate and high absorbance in the visible light range. A synergetic effect of both doped N atoms and Br atoms should be responsible for the enhanced visible photoactivity.

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