Photocatalytic Removal of NO_x over Visible Light Responsive Oxygen-Deficient TiO₂

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S Supporting Information

ABSTRACT: Oxygen-deficient TiO₂ was prepared with a low-temperature method and utilized in photocatalytic removal of gaseous NO at the 400 ppbv level in air under visible light (420 nm < λ < 700 nm) irradiation. Catalysts synthesized at 200 °C (TiO₂-200) exhibited the highest ability to remove the NO gas in air under visible light irradiation. A higher oxidation ability for NO₂ to NO₃[−] leads to a higher conversion of NO_x on TiO₂-200. The relationship between the physicochemical properties and the photocatalytic performance of the as-prepared catalyst is discussed. The large surface area of TiO₂-200 can provide more active sites for the reaction. The oxygen vacancies of TiO₂-200 can effectively expand the absorption of visible light and accelerate the separation of photogenerated electrons and holes. The first-principles density functional theory (DFT) calculation further confirms the role of oxygen vacancies on the narrowing of the band gap and separating of photogenerated electron–hole pairs.

1. INTRODUCTION

Nitric oxide (NO), mainly produced from combustion of fossil fuels and vehicle exhaust, is considered as a common gaseous pollutant, since it is responsible for atmospheric environmental problems such as haze, photochemical smog, acid rain, and so on. Thermal catalysis methods can remove NO from emission sources; however, they are not economically feasible for the removal of NO at parts per billion (ppb) levels in urban environments.^{1,2} Semiconductor photocatalysis, as a “green” technology, has been used to remove NO at ppb levels.^{3–9}

During the photocatalytic process, electron (e[−])–hole (h⁺) carrier pairs are generated under the irradiation of light. These charge carriers can migrate to the surface and then initiate redox reactions of adsorbents with various reactive species, such as the photogenerated e[−] and h⁺, superoxide (•O₂[−]), singlet oxygen (¹O₂), and hydroxyl radical (•OH).¹⁰ The oxidation of NO can be attributed to the direct reaction with the photogenerated holes and the reaction with •OH radicals.^{11,12} The photocatalytic oxidation of NO to NO₃[−] was reported to be the major process, with NO₂ as an intermediate.^{2,13} However, Sano et al.¹⁴ found that about 61% of NO reacted in 5 h during visible light illumination was oxidized to NO₂ over N-doped TiO₂. Lin et al.¹⁵ also found the formation of NO₂ on platinum ion-doped TiO₂ and that the NO₂ concentration gradually increased with the increase of the wavelength of the irradiation. Because NO₂ is 4–5 times more harmful than NO,¹⁶ it is crucial to suppress the production of gaseous NO₂ during the visible light photocatalytic removal of NO. Because the adsorption significantly affects the photooxidation efficiency of low concentration gas pollutants,¹⁷ the photocatalysts with larger surface area will show higher catalytic activity.

TiO₂ has long been a promising candidate for photocatalysis applications because of its strong photocatalytic oxidation

performance, photostability, natural abundance, and non-toxicity.¹⁸ However, the relatively large band gap of TiO₂ (3.0–3.2 eV) limits its application in the visible light region (400 nm < λ < 750 nm), which accounts for 43% of the incoming solar energy.^{1,13} Therefore, developing visible light-responsive photocatalysts with high efficiency and stability is desirable and has become one of the most important topics in environmental photocatalysis.¹⁹ Metal/nonmetal doping, coupling with other lower band gap semiconductors, hydrogen treatment, and photosensitization with dyes have been applied to enhance the visible light activity of TiO₂.^{20–22} Recent studies have revealed that defect can modulate the light absorption and photocatalytic reactivity of TiO₂.²³

Oxygen vacancy is one of the most important defects in TiO₂.²⁴ It has been shown that the photocatalytic properties including the electronic structure, charge transport, and surface properties of TiO₂ are closely related to oxygen vacancies.^{25–29} The conventional route for the synthesis of TiO₂ with oxygen vacancies is hydrogen thermal treatment or thermal treatment under oxygen-depleted conditions.^{21,30} The specific surface areas of catalysts prepared by this method are relatively small because of the high-temperature calcining. In this study, oxygen-deficient TiO₂ was prepared with a facile and low-temperature method. The catalysts were utilized to remove gaseous NO at the 400 ppbv level in air under visible light (420 nm < λ < 700 nm) irradiation. The relationship between the physicochemical properties and the photocatalytic performance of the as-prepared catalyst is discussed based on the experimental and calculation results.

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2. EXPERIMENTAL SECTION

2.1. Catalyst Synthesis. The oxygen-deficient TiO_2 was synthesized using a sol–gel method.³¹ A measured quantity of tetrabutyl orthotitanate (17.5 mL) was dropped slowly into 90 mL of anhydrous ethanol and 20 mL of deionized (DI) water with vigorous stirring. After complete dissolution, 4 mL of nitric acid was added to catalyze the hydrolysis and condensation reactions. The mixed solution was uniformly agitated for 3 h, and then the precipitate of titanium hydroxide was produced. After drying at 110 °C, the powder was calcined in air at controlled temperatures for 5 h. The as-prepared catalysts calcined at 150, 200, 300, 400, and 500 °C were labeled as TiO_2 -150, TiO_2 -200, TiO_2 -300, TiO_2 -400, and TiO_2 -500, respectively. N- TiO_2 was synthesized according to ref 32. Commercial anatase TiO_2 (purchased from Beijing JAH TECH Co., Ltd., China) was milled with urea at a molar ratio of 1:2 and then calcined at 450 °C for 3 h.

2.2. Characterization. The surface morphology of the catalysts was observed using scanning electron microscopy (SEM, Hitachi, S-3000N) with an acceleration voltage of 10 kV. The samples for SEM imaging were mounted on metal stubs with a piece of conducting tape and then coated with a thin layer of gold film to avoid charging.

The crystalline structure of the catalysts was determined by a powder X-ray diffractometer (XRD; X'Pert PRO, PANalytical, Netherlands) using $\text{Cu K}\alpha$ ($\lambda = 0.154\,06\text{ nm}$) radiation at 40 kV and 40 mA. The data of 2θ from 20° to 80° were collected at 8°/min with the step size of 0.07°.

Raman spectra of the catalysts were recorded at room temperature on a UV resonance Raman spectrometer (UVR DLPC-DL-03), which consisted of three optional exciting lasers (244, 325, and 532 nm), a three-stage grating spectrograph, and a CCD detector cooled by liquid nitrogen. The instrument was calibrated against the Stokes Raman signal of Teflon at 1378 cm^{-1} . A continuous diode pumped solid state (DPSS) laser beam (532 nm) was used as the exciting radiation, and the power output was about 48 mW. The diameter of the laser spot on the sample surface was focused at 25 μm . A 325 nm He–Cd laser was also used as an exciting source for the measurement of UV-Raman. The spectra resolution was 2.0 cm^{-1} . All Raman spectra used in the paper were original and unsmoothed.

X-ray photoemission (XPS) measurements were recorded on a scanning X-ray microprobe (AXIS Ultra, Kratos Analytical, Inc.) using $\text{Al K}\alpha$ radiation.

The X-band electron paramagnetic resonance (EPR) spectra were recorded at room temperature using a Bruker A300-10/12 EPR spectrometer.

The surface area and pore structure (volume and size) of the catalysts were determined with a physisorption analyzer (Autosorb-1C-TCD, Quantachrome) by N_2 adsorption–desorption at 77 K. The surface area (S_{BET}) was determined by applying the Brunauer–Emmett–Teller (BET) method to the adsorption isotherm in the partial pressure range of 0.05–0.35. The pore volume (V_{BJH}) and the pore diameter (D_{BJH}) were determined by the Barrett–Joyner–Halenda (BJH) equation from the desorption isotherm.

The UV–vis diffuse reflection spectra of the catalysts over the range of 200–800 nm were recorded at room temperature with a diffuse reflectance UV–vis spectrophotometer (U-3310, Hitachi), using BaSO_4 as reflectance standard.

The photoluminescence (PL) emission spectra of the samples were measured with a fluorescence spectrophotometer

(Hitachi F-4500) using the 300 nm line of a Xe lamp as the excitation source at room temperature. The scanning speed was 240 nm/min, and the PMT voltage was 400 V. The widths of the excitation slit and emission slit were both 5.0 nm.

2.3. Photocatalytic NO Removal. The photocatalytic experiments for the removal of NO with the resulting samples were performed at ambient temperature in a continuous flow reactor. The volume of the round-shaped reactor which was made of Pyrex glass and covered with a quartz plate was 114 cm^3 ($R = 4.5\text{ cm}$, $h = 1.8\text{ cm}$). A sample dish containing the photocatalyst powders was placed in the center of the reactor. A 500 W commercial xenon arc lamp (Beijing TrusTech Science and Technology Co., China) was used as the simulated solar light source. For the visible light photocatalytic activity test, two optical filters were used to obtain light in the 420–700 nm range, and the integrated light intensity was 35.8 mW/cm^2 (FZ-A, radiometer, Photoelectric Instrument Factor of Beijing Normal University). The lamp was vertically placed outside the reactor above the sample dishes. Furthermore, the temperature of the sample was kept at 25 °C by water circulation. For activity testing, each sample was prepared by coating an aqueous suspension of the photocatalyst onto the dish with a diameter of 5.5 cm. The weight of the photocatalyst used for each experiment was kept at 0.05 g. The dish containing the photocatalyst was pretreated at 60 °C for several hours until complete removal of water in the suspension was achieved and then cooled to room temperature before use. The initial concentration of NO was diluted to about 400 ppb by the air stream. The desired humidity level of the NO flow was controlled at 55% by passing the nitrogen streams through a humidification chamber. The total flow rate was controlled at 1.2 L min^{-1} by mass flow controller. After adsorption–desorption equilibrium among water vapor, gases, and photocatalysts was achieved, and the lamp was turned on. The concentration of NO, NO_2 , and NO_x was continuously measured by a chemiluminescence NO_x analyzer (Thermo Environmental Instruments Inc. Model 42i), which monitors NO, NO_2 , and NO_x (NO_x represents $\text{NO} + \text{NO}_2$) with a sampling rate of 0.7 L min^{-1} .

In the data analysis, the NO conversion, NO_2 selectivity, and NO_x conversion were defined as follows:

$$\text{NO conversion} = \frac{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}}{[\text{NO}]_{\text{in}}}$$

$$\text{NO}_2 \text{ selectivity} = \frac{[\text{NO}_2]_{\text{out}}}{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}}$$

$$\text{NO}_x \text{ conversion} = \frac{[\text{NO}]_{\text{in}} - [\text{NO}_x]_{\text{out}}}{[\text{NO}]_{\text{in}}}$$

Since NO_2 is more toxic than NO ,³³ the photocatalyst performance should be evaluated by the NO_x conversion or the NO conversion in conjunction with the NO_2 selectivity.

2.4. Computational Details. DFT calculations were performed using the CASTEP package on the basis of the plane-wave-pseudopotential approach. The Perdew–Burke–Ernzerhof (PBE) of the generalized gradient approximation (GGA) was used as the exchange–correlation function. The interaction between valence electrons and the ionic core was described by the ultrasoft pseudopotential. Calculations were carried out with a Monkhorst–Pack k -point mesh of $(2 \times 2 \times 2)$ and a plane-wave cutoff of 380 eV.

A 108-atom supercell made up by $3 \times 3 \times 1$ unit cell has been used to simulate an anatase bulk crystal. The oxygen vacancy in anatase TiO_2 was modeled by removing one oxygen atom in anatase TiO_2 cells, thus forming the TiO_{2-x} compounds with $x = 0.028$.

The initial geometry configurations were optimized by the Broyden, Fletcher, Goldfarb, and Shanno minimizer for spin-polarized systems with different initial numbers of spin-up and spin-down electrons. The spin occupation numbers were then optimized during the electronic iterations. The energetic convergence threshold for the self-consistent field (SCF) is 5.0×10^{-7} eV/atom. The convergence tolerance parameters of optimized calculations were a maximum energy of 5.0×10^{-6} eV/atom, a maximum force of 0.01 eV/Å, a maximum stress of 0.02 GPa, and a maximum displacement of 0.0005 Å.

The DFT+U method can describe the electronic structure, band gaps, and defect states of TiO_2 more correctly compared with the DFT method.^{34,35} Therefore, after finishing the geometry optimizations, the DFT+U method was used to calculate the band structures and the projected density of states (PDOS) of TiO_2 and TiO_{2-x} . A self-consistent Hubbard U correction of 3.3 eV for the d electrons of Ti atoms has been calculated.³⁶

The oxygen vacancy formation energy is computed from

$$E_{\text{vac}} = E(\text{TiO}_{2-x}) - E(\text{TiO}_2) + \frac{1}{2}E(\text{O}_2)$$

where $E(\text{TiO}_{2-x})$ is the total energy of TiO_2 with an oxygen vacancy and $E(\text{TiO}_2)$ is the total energy of TiO_2 . The formation energy is referenced to half the total energy of molecular O_2 .

3. RESULTS AND DISCUSSION

3.1. Photocatalytic NO Removal Activity. The reaction of NO with air was negligible when control experiments were

Figure 1. NO_x , NO, and NO_2 concentration as a function of irradiation time in the presence of TiO_2 -200.

performed with or without light in the absence of photocatalyst (residence time 5.7 s). Figure 1 shows the NO_x , NO, and NO_2 concentration against irradiation time in the presence of TiO_2 -200 under visible light irradiation. When the concentration of NO was steady, the NO gas was introduced into the reactor under dark conditions. The adsorption of NO on the photocatalyst was completed in 5 min, and then the concentration of NO recovered to 400 ppb. The concentration

Figure 2. NO conversion, NO_x conversion, and NO_2 selectivity at 0.5 h for various catalysts.

Figure 3. XRD patterns of (a) uncalcined sample, (b) TiO_2 -150, (c) TiO_2 -200, (d) TiO_2 -300, (e) TiO_2 -400, (f) TiO_2 -500, and (g) P25.

Table 1. Summary of Physicochemical Properties of the Catalysts

catalysts	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	pore vol ($\text{cm}^3 \text{g}^{-1}$)	av pore size (nm)	XRD particle size ^a (nm)
P25	57.3	0.1628	11.36	21.2 (31.6)
uncalcined	236.8	0.2060	3.480	7.9
TiO_2 -150	245.3	0.2181	3.556	8.4
TiO_2 -200	282.7	0.2549	3.607	8.1
TiO_2 -300	243.5	0.2439	4.000	8.4
TiO_2 -400	145.2	0.1958	5.393	9.2
TiO_2 -500	58.6	0.0998	6.807	16.9 (35.7)

^aDetermined using Scherrer's equation (applicable from 3 to 200 nm). The value in parentheses is the particle size of rutile.

of NO decreased from 400 to 120 ppb in 2 min when the photocatalyst was irradiated under visible light. As can be seen in Figure 1, the concentration of NO was constant during the irradiation time; however, the concentration of NO_2 increased to 50 ppb after 30 min.

The NO conversion, NO_x conversion, and NO_2 selectivity at 0.5 h for various samples are displayed in Figure 2. It can be seen that NO could be photocatalytically oxidized even on pure P25 under visible light irradiation. This is because P25 is a mixture consisting of anatase and rutile phases, and oxygen vacancies could thus be created at the boundaries of anatase and rutile grains, resulting in "oxygen deficiency doping".³⁷ As shown in Figure 2, the conversion of NO was in the range of 55–65% over different photocatalysts; however, the selectivity of NO_2 (14.92%) was the lowest over TiO_2 -200, and therefore

Figure 4. Visible Raman spectroscopy of samples prepared at various temperatures with the excitation line at 532 nm.

Figure 5. Peak position and fwhm of the anatase E_g mode as a function of sample preparation temperatures and for commercial anatase.

Figure 6. EPR spectra of TiO₂-200 and TiO₂-500.

the conversion of NO_x (53.96%) was the highest over TiO₂-200. The activity of TiO₂-200 was 2 times higher than that of P25. The activity of TiO₂-200 was also better than that of N-TiO₂ (the conversion of NO_x is 28.7%). Table S1 shows the conversion of NO_x for various catalysts irradiated for different times. It can be seen that the conversion of NO_x for various catalysts gradually decreased with time in all cases due to the

surface of the photocatalysts being covered by nitric acid and nitrates, which was confirmed by FTIR spectra of catalysts after 6 h photoreaction (Figure S1). However, the activity of TiO₂-200 was even 4 times higher than that of P25. This was mainly caused by the low selectivity of NO₂ on TiO₂-200 (Table S2), i.e., the high oxidation rate of NO₂ to HNO₃. From the following characteristic of the catalysts, the reasons for the NO₂ formation suppression of TiO₂-200 should be the largest surface area for the adsorption of NO₃⁻ and the effective charge separations for the oxidation of NO₂. To investigate the stability of photocatalytic activity of TiO₂-200, catalysts after photocatalytic reactions were collected by water scrubbing, centrifugation, and dried for the subsequent photoreaction cycle. It was confirmed that no severe degradation of the photocatalytic performance was observed after two cycles (see Figure S2).

3.2. Catalyst Characterization. Figure 3 illustrates the XRD patterns of the catalysts with different calcination temperatures and commercial P25. The crystal structures of catalysts calcined at various temperatures were mainly anatase (JCPDS no. 21-1272), and small peaks of brookite (2θ = 30.8°, [121], JCPDS no. 29-1360) were also found (Figure 3B). However, the most intense peak from brookite TiO₂ (2θ = 25.3° [120], 2θ = 25.7° [111]) overlapped with that of anatase [101]. The rutile phase began to appear at 500 °C. The crystalline defects of the mixed structure (coexistence of anatase and brookite phases) should be more pronounced than for the pure anatase structure. Furthermore, the crystallite size of the catalysts was determined from the half-width of peaks by using Scherrer's formula ($d = 0.9\lambda/\beta \cos \theta$) on the basis of the anatase [101] peak, as shown in Table 1. The crystallite sizes of anatase phases were increased with the increasing of calcination temperature. SEM results also confirm the increase of particle size with calcination temperature (Figure S3). The formation of anatase at low temperature was due to the effect of HNO₃ added during the catalyst synthesis, which would rearrange the amorphous aggregates to form the crystalline phases even at room temperature.^{38,39}

Visible Raman spectra of catalysts prepared at various calcining temperatures are displayed in Figure 4. It should be pointed out that the residual of a carbonaceous species on the TiO₂ surface results in a strong fluorescence on TiO₂ calcined below 400 °C (Figure S4). The content of carbonaceous species should decrease as the temperature increases owing to the oxidation of the carbon content, which is evidenced in TGA-DSC-MS results (see Figure S5 and Table S3). Therefore, the Raman spectra of catalysts calcined below 400 °C were collected after in-situ photo treatment of the samples in air, which can remove the carbonaceous species. Raman shifts at 146, 399, 515, and 639 cm⁻¹ attributed to the Raman-active modes of anatase with the symmetries of E_g, B_{1g}, A_{1g}, and E_g, respectively, were observed for all TiO₂ samples. These results indicate that the surface of catalysts calcined at various temperatures were in an anatase state.

The E_g feature of anatase (symmetric stretching vibration of O–Ti–O) at 146 cm⁻¹ was studied in detail (Figure 4 inset). The peak position and full width at half-maximum (fwhm) showed a strong dependence on the calcining temperatures (Figure 5). The blue-shift of the peak position and broadening of fwhm for catalysts prepared at low temperatures compared with commercial anatase may be due to the formation of oxygen vacancies in the nonstoichiometric TiO₂.^{40,41} UV Raman spectroscopy was found to be more sensitive to the

Figure 7. (A) UV-vis diffuse reflectance spectra and (B) plots of transformed Kubelka–Munk function versus the energy of absorbed light for catalysts calcined at different temperature.

Figure 8. Photoluminescence (PL) emission spectra of the catalysts.

Figure 9. Optimized geometries of bulk anatase and of an oxygen vacancy in a (100) plane are given in (A) and (B), respectively. The red and blue spheres represent O and Ti atoms, respectively. Atomic distances are given in angstroms.

surface region of TiO₂ than visible Raman spectroscopy and XRD because TiO₂ strongly absorbs UV light.⁴² The UV Raman spectra also indicate that the surface of catalysts

calcined at various temperatures was in an anatase state and that oxygen vacancies were formed for catalysts prepared at low temperatures (Figures S6 and S7). In order to further confirm the existence of oxygen vacancy, EPR spectra of TiO₂-200 and TiO₂-500 are shown in Figure 6. The symmetric signal at $g = 2.004$ for TiO₂-200 is assigned to oxygen vacancy.²⁴ These oxygen vacancies may be formed as a result of the presence of carbonaceous species.^{42,43} In order to differentiate the role of carbon doping, the C 1s XPS spectra were recorded. No C 1s peak at ~ 281 eV (Ti–C bond⁴⁴) was observed (Figure S8), strongly suggesting that carbon does not enter the TiO₂-phase.

Generally, the overall photocatalytic activity of a semiconductor is mainly related to the ability of the photocatalysts to adsorb target pollutants, the photoabsorption ability in the available light energy region, and the separation and transport rate of the photogenerated electrons and holes in the catalysts. To illustrate the reason for the enhanced visible light photocatalytic activity of TiO₂-200, the Brunauer–Emmett–Teller (BET) specific surface areas, pore volumes, and average pore size of various catalysts are summarized in Table 1. TiO₂-200 possessed the largest surface area (283 m²/g) of the catalysts studied. The pore volume of TiO₂-200 was also larger than other catalysts. An initial increase in the surface area up to 200 °C could be due to the formation of small pores due to the expulsion of H₂O and CO₂ (confirmed by the TG-MS data in Figure S5) from the oxidation of the carbonaceous species in the catalysts during the calcination. The decrease of surface areas at higher calcination temperature could be attributed to the sintering of the catalyst. The large surface area can probably facilitate the mass transfer of reactants (NO) or reaction intermediates and can provide more sites for the adsorption of products.

UV-vis diffuse reflectance spectra (DRS) were measured to determine the band gap energy of the synthesized catalysts (Figure 7). The UV-vis spectra of TiO₂-150, TiO₂-200, and TiO₂-300 show a broad absorbance in the visible region. In addition, the absorbance varied in the order TiO₂-200 > TiO₂-150 > TiO₂-300. The absorbance in the visible light region up to 800 nm may be due to the presence of carbonaceous species, which act as a photosensitizer.⁴⁵ Assuming the material to be an indirect semiconductor, plots of $(F(R_{\infty})/h\nu)^{1/2}(F(R_{\infty}) = (1 - R_{\infty})^2/2R_{\infty})$, where R_{∞} is diffuse reflectance and $h\nu$ is the photon energy) versus the energy of absorbed light afford the band gaps of as-prepared catalysts (Figure 7B). The band gap energies of TiO₂-150, TiO₂-200, TiO₂-300, TiO₂-400, and

Figure 10. DFT+U density of states for (A) TiO_2 and (B) TiO_{2-x} . The energy zero is taken as the Fermi level and displayed with a green dashed line.

TiO_2 -500 calculated by the transformed Kubelka–Munk function were 2.97, 2.77, 3.06, 3.14, and 3.06 eV, respectively. The narrowing of the band gap of TiO_2 may be due to the formation of oxygen vacancies,^{19,24} which was confirmed by the following computational results. As can be seen in Figure 2, TiO_2 -200 with its strong absorbance in the visible region and narrow band gap showed the highest photocatalytic activity in NO removal under visible light.

During the photocatalytic process, charge transfer and recombination are two competing reaction pathways, so it is important to suppress the recombination rate and accelerate charge transfer in order to enhance the photocatalytic activity. The photoluminescence (PL) emission spectra can be used to understand the fate of photogenerated electrons and holes in semiconductor particles since PL emission results from the recombination of free carriers.^{46,47}

PL emission spectra of the catalysts are shown in Figure 8 revealing that the peaks are nearly identical in shape and position for all of the catalysts. The PL intensity of TiO_2 -150, TiO_2 -200, and TiO_2 -300 was significantly reduced, indicating that the electron–hole recombination on the surface of these catalysts was largely inhibited to generating more photoelectrons and holes to participate in the photocatalytic reaction. This may be due to the formation of oxygen vacancies (confirmed by the Raman spectrum in Figure 5 and EPR spectra in Figure 6) that trap electrons, resulting in a decreased PL intensity.⁴⁸ The weaker electron–hole recombination on the surface of TiO_2 -200 means more photoelectrons and holes are generated to participate in the photocatalytic reaction.

3.3. Computational Results. Anatase has a tetragonal crystal structure with space group $I4_1/\text{AMD}(141)$. The calculated lattice parameters of pure TiO_2 model are $a = b = 3.812$ Å and $c = 9.653$ Å at ambient conditions, which are in good agreement with experiment values of $a = b = 3.782$ Å and $c = 9.502$ Å.⁴⁹ These results indicate that our calculation methods are reasonable, and the calculated results are authentic.

Figures 9A and 9B show the geometry of Ti and O atoms located on a (100) plane of anatase and their rearrangement after the vacancy formation, respectively. These figures show that the removal of an O atom induces a dramatic change in the local geometry around the vacancy site: one of the nearest-neighbor O atoms breaks indeed its bond with a Ti atom and approaches two nearest-neighbor Ti atoms by strengthening the corresponding Ti–O bonds and becoming 2-fold coordinated (O_{2c}). The significant lattice distortion

changes the dipole moments and internal field is introduced, which can promote the separation of photogenerated electron–hole pairs and improve the photocatalytic activity. This was consistent with the PL results. The formation energy of the V_{Ox} in anatase, 4.27 eV, agrees with previous estimates.⁵⁰

The band structure of the TiO_2 and TiO_{2-x} was obtained by the DFT+U calculations, as shown in Figure S9. The calculated band gap of pure anatase TiO_2 is 2.44 eV, which is still lower than the experimental value of 3.20 eV. Although a value of $U = 8$ on Ti atoms can recover the bulk anatase band gap,⁵¹ it is so large that the impure states cannot be properly described.⁵² The choice of $U = 3.3$ was motivated by the work of Mattioli et al.³⁶ that have applied DFT+U to the study of TiO_2 containing oxygen vacancy, in which this value of U have been found to be suitable for the description of oxygen vacancy. The calculated band gap of TiO_{2-x} is 2.27 eV, which is narrower than that of TiO_2 . This means oxygen vacancy can lead to the narrow of band gap, which was consistent with the experimental results.

To further understand the origin of the band gap variation, the total density of states (DOS) and projected density of states (PDOS) were calculated and plotted in Figure 10 for TiO_2 and TiO_{2-x} with up-spin DOS above zero and down-spin DOS below zero. In the TiO_2 , the valence band is dominated by the O 2p state, while the conduction band by the Ti 3d state. In the TiO_{2-x} the Fermi level locates at the bottom of the conduction band, which is a typical n-type doping. The oxygen vacancy in TiO_{2-x} does not induce impurity level within the band gap but splits the Ti-3d states nearby the Fermi level. This splitting comes from the reduction of Ti^{4+} to Ti^{3+} by the oxygen vacancy. The splitting of Ti-3d states is responsible for the narrowing of the band gap. The calculated results give a good explanation for the experimental observed band gap narrowing and electron–hole recombination slowdown.

4. CONCLUSIONS

Oxygen-deficient TiO_2 was prepared with a facile low-temperature method. XRD results indicated that the structure of oxygen-deficient TiO_2 synthesized below 500 °C is a mixture of anatase and brookite phases. Raman and EPR results showed that oxygen vacancies were formed as a result of the presence of carbonaceous species. TiO_2 -200 showed the highest photocatalytic activity for the removal of NO_x under visible light ($420 \text{ nm} < \lambda < 700 \text{ nm}$) irradiation. The large surface area of TiO_2 -200 can provide more sites for the reaction of NO and the adsorption of oxidation products. The oxygen vacancies of TiO_2 -200 can effectively narrow the band gap and enhance the

separation of photogenerated electrons and holes. The first-principles density functional theory (DFT) calculation confirms that the existence of oxygen vacancies leads to the light absorption in the visible region and effective separating of photogenerated electron–hole pairs

■ ASSOCIATED CONTENT

■ Supporting Information

Tables S1–S3 and Figures S1–S9. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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