LaTiO₂N as a Visible-Light (≤ 600 nm)-Driven Photocatalyst (2)

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LaTiO₂N, a Ti-based oxynitride, was studied as a visible-light (420-600 nm)-driven photocatalyst. DFT calculation for LaTiO₂N indicated that the top of the valence band consists predominantly of N 2p orbitals with a small contribution by O 2p orbitals, while the bottom of the conduction band is made up entirely of empty Ti 3d orbitals. LaTiO₂N was synthesized from a La₂Ti₂O₇ precursor at 1123 K under NH₃ flow. The relationship between the preparation condition and the photocatalytic activities of H⁺ reduction to H₂ and H₂O oxidation to O₂ was examined. It was found that the photocatalytic activity for O₂ evolution increased with nitridation time, reaching a maximum at 72 h. Further treatment beyond 72 h lowered the rate of O₂ evolution. The rate of H₂ evolution was almost independent of nitridation time. The relationship between nitridation time and the rate of O₂ evolution is discussed on the basis of X-ray photoelectron spectroscopy (XPS) analyses.

1. Introduction

Photocatalytic reactions are currently applied in various fields to solve energy problems and to meet the increasingly stringent standards set by environmental regulations. Heterogeneous photocatalysts offer great potential for converting photon energy into chemical energy and for decomposing pollutants in air or in solution. In particular, photocatalysts that catalyze overall water splitting under visible light irradiation would have great potential in solar energy applications. However, to date, no effective visible-light-driven photocatalyst for the reaction has been devised. Although some Ti⁴⁺, Nb⁵⁺, and Ta⁵⁺-based oxides such as SrTiO₃, K₂La₂Ti₃O₁₀, K₄Nb₆O₁₇, and NaTaO₃ function as stable and efficient photocatalysts for overall water splitting to form stoichiometric H_2 and O_2 ,¹⁻⁴ these materials are not activated by visible light because the tops of the valence bands are composed of O 2p orbitals with low potential energies, resulting in large band gap energies of over 3 eV.⁵

Recently, (oxy)nitrides containing Ti^{4+} or Ta^{5+} , such as LaTiO₂N,⁶ TaON,⁷ and Ta₃N₅,⁸ have been reported as potential visible-light-driven photocatalysts. These stable inorganic materials are synthesized by nitriding the corresponding metal oxides under NH₃^{9,10} and absorb visible light up to wavelengths of 500–600 nm. Density functional theory (DFT) calculations for TaON and Ta₃N₅ have revealed these materials to have the following common features. The formal electronic configurations of transition metal cations are d⁰, the bottoms of the conduction bands consist of empty d orbitals, and the tops of the valence bands consist mainly of N 2p orbitals.

The present authors have already reported briefly on LaTiO₂N as a photocatalyst.⁶ LaTiO₂N, when irradiated with visible light



Figure 1. Schematic structures of (a) La₂Ti₂O₇ and (b) LaTiO₂N.

 $(\lambda \leq 600 \text{ nm})$ functions as a photocatalyst for the reduction of H⁺ to H₂ and oxidation of H₂O to O₂ in the presence of a sacrificial electron donor (methanol) and acceptor (Ag⁺). These photoreactions were confirmed to proceed via a band gap transition of 2.1 eV on the basis of the wavelength dependence of the activity. In this paper, more detailed results of the preparation conditions and the photocatalytic activity of LaTiO₂N are presented.

The schematic structures of La₂Ti₂O₇, a precursor, and LaTiO₂N are shown in Figure 1. La₂Ti₂O₇ is a monoclinic compound with space group $P2_1$ formed of alternating perovskite-like blocks of *n*TiO₆ octahedron slabs.¹¹ On the other hand, the oxynitride is a triclinic compound with space group P(-1), the same structure as a perovskite oxide represented by ABO₃ (A, B = metal cations), and is composed of a TiO_xN_y octahedral structure (x + y = 6).^{9,12}

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2. Experimental Section

2.1. Synthesis of LaTiO₂N. LaTiO₂N was prepared by nitriding La₂Ti₂O₇ under NH₃ flow.^{6,9,12} La₂Ti₂O₇ was obtained from a corresponding oxide precursor containing stoichiometric amounts of La³⁺ and Ti⁴⁺ cations (1:1) by oxidation at 1423 K for 10 h in air.^{13,14} The resulting La₂Ti₂O₇ powder was nitrided at 1123 K under a flow of NH₃ at 20 cm³ min⁻¹ in a quartz tube reactor. Effluent gas with entrained water produced during nitridation was passed into a silicon oil bubbler at 420 K. The bubbler was directly connected to the nitridation reactor to prevent contamination of water and O₂ in air. The powder obtained after nitridation time.

2.2. Characterization of Catalysts. The prepared samples were studied by X-ray powder diffraction (XRD, Rigaku Geigerflex RAD-B, Cu K α), scanning electron microscopy (SEM, S-4700, Hitachi), energy-dispersive X-ray spectroscopy (EDX, EMAX 7000, Horiba), and UV-visible diffuse reflectance spectroscopy (UV-vis DR, V-560, Jasco). The surface of the prepared sample was examined by X-ray photoelectron spectroscopy (XPS, ESCA 3200, Shimadzu). The binding energy was corrected against Au 4f_{3/2} (83.8 eV). The amount of N in a sample was measured by elemental analysis (CHNS-932, LECO).

2.3. Photocatalytic Reactions. The reactions were carried out in a Pyrex reaction vessel connected to a closed gas circulation and evacuation system. Photoreduction of H⁺ to H₂ and photooxidation of H₂O to O₂ in the presence of a sacrificial electron donor (methanol) and acceptor (Ag⁺) were examined as test photoreactions. H₂ evolution was examined in an aqueous solution (200 mL) containing 0.20 g of the sample loaded with 3 wt % of Pt and 20 mL of methanol. The sample was reduced in H₂ at 573 K after loading with Pt from [Pt(NH₃)₄]Cl₂ by impregnation. For a typical photooxidation of water into O₂, the reaction was performed in an aqueous AgNO₃ solution (0.01 mol dm⁻³, 200 mL) containing 0.20 g of the catalyst and 0.20 g of La₂O₃ powder, a basic oxide added to maintain the solution at a pH of approximately 8 during the reaction (see section 3.3). The reaction solution was evacuated several times to remove air and then irradiated with a 300-W Xe lamp equipped with a cutoff filter. The evolved gas was analyzed by gas chromatography. Quantum efficiencies (Φ) were calculated using the following equation:

$$\Phi$$
 (%) = (AR/I) × 100

where A is a coefficient for a particular photoreaction (for H₂ evolution, A = 1;¹⁵ for O₂ evolution, A = 4), R is the H₂ and O₂ evolution rate (molecules h⁻¹), and I is the rate of introduction of incident photons into a reaction vessel. The absorption rate of incident photons was measured using a Si photodiode, typically 9.6 × 10²¹ photons h⁻¹ at 420 < λ < 600 nm. It was assumed that the quantum efficiencies were constant in the wavelength range of 420–600 nm for both reactions. Therefore, the quantum efficiencies obtained in this work are regarded as averaged apparent quantum efficiencies.

3. Results and Discussion

3.1. DFT Electronic Structure Calculations. The electronic structure of LaTiO₂N was calculated using a planewave-based DFT program, CASTEP.¹⁶ The core orbitals were replaced by ultrasoft core potentials,¹⁷ and La 5s²5p⁶5d¹6s², Ti 3s²3p⁶4s²-3d², N 2s²2p³, and O 2s²2p⁴ electrons were treated explicitly. The kinetic energy cutoff was set at 260 eV. The atomic



Figure 2. Four models of atomic arrangement for $(\text{LaTiO}_2\text{N})_4$. In model A, Ti atom has "axial" Ti–N bonds. In models B and C, Ti atom has "equatorial" Ti–N bonds with trans and cis configurations, respectively. In model D, Ti atom has "axial" and "equatorial" mixed Ti–N bonds. Models A–D preserve P(-1) symmetry.

coordinates were referenced from Clarke et al.12 The unit cell consisted of (LaTiO₂N)₄ with three distinct sites for N atoms. Four N atoms were placed in a unit cell. The P(-1) crystal symmetry was preserved to give models A-D in Figure 2. Each unit cell contained 160 electrons. Model C gave the lowest total energy of -14519.98 eV, and relative energies measured from that of model C were 1.21, 0.22, and 0.44 eV for models A, B, and D. The calculated band gap energies for models A-D were 0.63, 0.66, 0.67, and 0.66 eV, respectively. Although current DFT methods predict smaller band gaps than are seen experimentally, this discrepancy is very large when applied to oxynitrides. Major reason is ascribed to the fact that the N atoms are placed randomly to the O atom sites and only the averaged atomic coordinates are available from the literature.¹² The unit cell structure for model C was optimized with a constraint of lattice parameters. The total energy only decreased by 0.82 eV, but the band gap greatly increased to 1.57 eV, which is 75% of the experimental value (2.1 eV).

The band dispersion relation and density of states are shown in Figure 3 for the optimized structure of model C. The orbitals are numbered and the 80 occupied orbitals are classified into eight bands. The lowest band consists of the Ti 3s orbitals. The Ti 3p and La 5s bands appear in almost the same energy range. The O 2s band then appears, followed by the La 5p band. The N 2s band lies in an energy region 5-6 eV higher than the O 2s band. The valence bands are comprised of O 2p orbitals for the lower-energy side and N 2p orbitals for the higher-energy side. The splitting of these orbitals is less remarkable compared to that between the O 2s and N 2s orbitals. Figure 4 shows the



Figure 3. Band dispersion and density of states for optimized structure of model C of LaTiO₂N. A total of 80 occupied orbitals are classified into eight bands.

four density contour maps from the lower to the upper parts of the valence band.

The bottom of the conduction band is made up of Ti 3d orbitals. Then the La 4f and also 5d orbitals appear in a little higher energy range. Figure 5 shows the four density contour maps for orbitals 81, 90, 91, and 100. The Ti 3d orbitals are dominant for the former two, and the La 4f, 5d orbitals are major contribution for the latter two.

With the optimized structure of model C, the bandgap energy of 1.57 eV was estimated. The effect of optimization is not a simple decrease in Ti–N bond lengths. The sum of four Ti–O bond lengths and two Ti–N bond lengths increased by ca. 0.1 Å. By the optimization, Ti atoms move asymmetrically, that is, one Ti–N(O) bond length reduces and the other one is stretched.

3.2. XRD, SEM, TEM, and UV-vis Spectra. Figure 6 shows the XRD patterns for samples obtained by nitriding La2-Ti₂O₇ at 1123 K for several time periods. After 48 h of nitridation, the structure of La2Ti2O7 disappeared and the XRD pattern became characteristic of a perovskite-type LaTiO₂N.9 Nitridation for more than 48 h increased the diffraction peak intensities yet did not promote impurity phases. The bulk atomic ratios of Ti/La, O/La, and N/La for each sample are shown in Figure 7. The Ti/La ratios were measured by EDX, while the O/La and N/La ratios were estimated on the basis of the quantity of N in the samples by elemental analysis and the charge balance among La3+, Ti4+, O2-, and N3-: assuming that the charge valance is set up among La³⁺, Ti⁴⁺, O²⁻, and N³⁻ in a sample without defects, the O/La ratio was estimated. The O/La ratio values could contain some error. The N/La ratio increased with nitridation time to a constant (N/La = 0.96) after 94 h. This result indicates that nitridation for more than 94 h yields nearstoichiometric LaTiO₂N.

SEM and TEM images of the samples before and after nitridation for 72 h are shown in Figures 8 and 9. The introduction of N^{3-} into $La_2Ti_2O_7$ from NH₃ results in a rough LaTiO₂N morphology. There is no noticeable difference in

morphology among the samples prepared by nitridation for more than 48 h. The TEM image and electron diffraction pattern of LaTiO₂N reveal that well-crystallized LaTiO₂N was formed by nitridation for 72 h.

Figure 10 shows the UV-vis spectra for the samples. The absorption edge of $L_{22}Ti_2O_7$ is found to be ca. 320 nm, and the band gap energy is estimated to be 3.9 eV. The UV-vis spectra of the sample after nitridation consists of two broad bands located above and below 600 nm, and both bands increase with nitridation time. There is no significant difference in the UV-vis spectra among the samples obtained by nitridation for more than 72 h. Heating a sample, prepared by nitridation for 72 h, at 573 K for 24 h in air produced no change in the XRD pattern but reduced the band intensity above 600 nm, as shown in spectrum e in Figure 10. Absorption in the near-infrared region above 600 nm is attributable to a small amount of Ti³⁺ species. Therefore, the band gap transition is estimated to extend to as long as ca. 600 nm, indicating that the band gap energy is 2.1 eV.

3.3. Photocatalytic Reactions. Figure 11 shows the time courses of O2 evolution on LaTiO2N under visible light irradiation ($\lambda > 420$ nm) in an aqueous AgNO₃ solution under several pH conditions. LaTiO₂N prepared by nitridation for 72 h was used in the reaction because this LaTiO₂N sample exhibited the highest activity for O_2 evolution (see section 3.4). O₂ evolution did not take place in the dark. When the pH was maintained at about 8 by the addition of La₂O₃ (Figure 11a), O₂ evolved efficiently with a small amount of N₂ formation, as demonstrated in our previous paper.⁶ In the presence of a basic oxide, La₂O₃, the pH of the solution during the photoreaction is buffered at pH = 8-9 by the dissolution (La₂O₃ is a basic oxide), and the efficient oxidation of water by (oxy)nitrides including LaTiO2N proceed under such relatively high concentration of OH^{-.6-8} The initial quantum efficiency (QE) was estimated to be 1.5%. Although the N₂ evolution may suggest some degradation of the catalyst, it is attributed to surface



Figure 4. Density contour maps of the valence band: (A) density for the lowest orbital in the valence band 45 and dominant contribution from O 2p orbitals; (B) density for orbital 55 and mutual contribution from O 2p and N 2p orbitals; (C) density for orbital 75 and mutual contribution from O 2p and N 2p orbitals; (D) density for the highest occupied orbital 80 and larger contribution from N 2p orbitals.

nitrogen species because the evolution rate became almost negligible after 2 h. The estimated amount of surface nitrogen is about 11 μ mol, which is very similar to the amount of N₂ that evolves during photocatalytic reactions.¹⁸ Ca²⁺-doped LaTiO₂N modified by an IrO₂ colloid exhibited much higher activity (QE = 5%)⁶ with excellent stability, demonstrating the functionality of this material.⁶ A similar effect was also observed for LaTiO₂N loaded with the IrO₂ colloid.

The strong pH dependence of O₂ evolution from LaTiO₂N is noteworthy. Figure 11b,c shows gas evolution on the same LaTiO₂N (72 h of nitridation) sample in an aqueous AgNO₃ solution without La₂O₃. The pH of the solutions was adjusted before the reactions to 6.0 and 9.0 with 0.01 M HNO₃ and NaOH aqueous solutions. The pH of the solutions after the reaction is indicated in the figure. In the case of pH 6.0, the rate of O₂ evolution was suppressed remarkably and O₂ evolution was accompanied by the evolution of about 50 μ mol of N₂. In fact, only 2.1 μ mol of O₂ evolved over 5 h, and the pH of the solution indicates that about 10.0 μ mol of H⁺ was produced for the evolution of about 2.5 μ mol of O₂, as given by the reaction

$$4\mathrm{Ag}^{+} + 2\mathrm{H}_{2}\mathrm{O} \rightarrow 4\mathrm{H}^{+} + \mathrm{O}_{2} + 4\mathrm{Ag}^{0}$$

This is in good agreement with the amount of evolved O₂ (2.1



Figure 5. Density contour maps of the conduction band: (A) density for the lowest unoccupied orbital 81 and exclusive contribution from Ti 3d orbitals; (B) density for orbital 90 and almost all density on Ti 3d orbitals; (C) density for orbital 91 and primary contribution from La 4f and 5d orbitals; (D) density for orbital 100 and primary contribution from La 4f and 5d orbitals.



Figure 6. XRD patterns for (a) $La_2Ti_2O_7$ and samples obtained by nitriding $La_2Ti_2O_7$ at 1123 K after nitridation for (b) 22, (c) 48, (d) 72, (e) 94, and (f) 120 h.

 μ mol). The decrease in pH is therefore attributed to the production of H⁺ through the oxidation of water. However, it is noted that degradation of LaTiO₂N proceeds to some extent in an acidic solution to form N₂, following the reaction

$$2N^{3-} + 6h^+ \rightarrow N_2$$

In an alkaline solution (Figure 11c, initial pH = 9.0) without



Figure 7. Variation in Ti/La, O/La, and N/La atomic ratios of samples with nitridation time.



Figure 8. SEM images of (a) $La_2Ti_2O_7$ and (b) $LaTiO_2N$ (72 h nitridation).



Figure 9. TEM images and electron diffraction patterns of $La_2Ti_2O_7$ and $LaTiO_2N$ (72 h nitridation).



Figure 10. UV-vis DR spectra of (a) $La_2Ti_2O_7$, samples obtained by nitriding $La_2Ti_2O_7$ at 1123 K after nitridation for (b) 22, (c) 48, and (d) 72 h, and sample obtained (e) by heating $LaTiO_2N$ (72 h of nitridation) in air at 573 K for 24 h.

 La_2O_3 , the initial rate of O_2 evolution was higher than that in the acidic solution but O_2 evolution ceased after 2 h. The pH was reduced to 3.8 by the end of reaction. These results are interpreted as follows. Under basic conditions, oxidation of water on LaTiO₂N produces O_2 and H⁺, thereby lowering the pH of the solution. When the solution becomes acidic, O_2 evolution



Figure 11. O₂ evolution from LaTiO₂N under visible light irradiation (>420 nm) for LaTiO₂N (72 h of nitridation) = 0.2 g, AgNO₃ solution = 0.01 mol dm⁻³, 200 mL: (a) La₂O₃ = 0.2 g, initial pH = 8.4; (b) without La₂O₃, initial pH = 6.0; (c) without La₂O₃, initial pH = 9.0.

slows and finally stops. The amount of evolved N₂ was almost the same (ca. 50 μ mol) in both experiments (Figure 11b,c), suggesting similar degradation of the catalyst.

Figure 12 shows the time courses of H₂ evolution on LaTiO₂N (72 h) under visible light irradiation ($\lambda > 420$ nm) in aqueous



Figure 12. H₂ evolution from LaTiO₂N under visible light irradiation (>420 nm) for Pt-coated LaTiO₂N (72 h of nitridation) = 0.2 g, methanol solution = 200 mL (distilled water 180 mL, methanol 20 mL): (a) without La₂O₃; (b) La₂O₃ = 0.2 g.



Figure 13. Evolution rates of H_2 and O_2 from LaTiO₂N prepared with various nitridation times (>420 nm): (H₂) Pt-coated LaTiO₂N (0.2 g), methanol solution (200 mL; distilled water 180 mL, methanol 20 mL); (O₂) LaTiO₂N (0.2 g), La₂O₃ (0.2 g), AgNO₃ solution (200 mL, 0.01 mol dm⁻³).

methanol solutions with and without La₂O₃ (initial pH = 6.5 and 7.6). In both cases H₂ evolution was observed, but N₂ was not detected by gas chromatography, indicating that LaTiO₂N reduces H⁺ to H₂ without appreciable degradation.

3.4. Variation in Photocatalytic Activity with Nitridation Time. Figure 13 shows the dependence of the rates of H_2 and O_2 evolution under visible light irradiation on nitridation time. The rates plotted in this figure were obtained during the initial stages of the reactions (1-2 h). The rate of O_2 evolution increases with nitridation time up to a maximum rate at 72 h. Further nitridation results in a decrease in activity for water oxidation. In contrast, after 48 h, the rate of H_2 evolution becomes independent of nitridation time. H_2 and O_2 evolution occurs and a LaTiO₂N phase emerges at 22 h (according to XRD), as shown in Figure 6. The evolution rates increase with



Figure 14. Dependence of surface Ti/La, O/La, and N/La atomic ratios on nitridation time for LaTiO₂N.



Figure 15. AES spectra of Ta foil behind $La_2Ti_2O_7$ powder in the quartz reactor (a) before nitridation and (b) after nitridation under NH₃ flow (20 cm³ min⁻¹) at 1123 K for 120 h.

the growth of LaTiO₂N crystal. However, the formation of stoichiometric LaTiO₂N reduces the rate of O_2 evolution.

Each sample was investigated by XPS to clarify the dependence of the rate of O₂ evolution on nitridation time. The surface atomic ratios of Ti/La, O/La, and N/La of each sample are shown in Figure 14. These atomic ratios were obtained from the peak intensities of La 3d, Ti 2p, O 1s, and N 1s orbitals in the XPS spectrum for each sample. During the initial 22 h of nitridation, the surface N/La ratio increases rapidly to 0.6, and after 22 h, the amount of surface N gradually reaches saturation (N/La = 0.85) at somewhat less than the bulk concentration, as shown in Figure 7 (N/La = 0.96). The bulk Ti/La ratio remains almost unchanged (Ti/La = 1) with nitridation, as shown in Figure 7, whereas the surface Ti/La ratio is reduced to about 0.7 by nitridation for 120 h. After nitridation for 120 h, the quartz tube holding the sample in the nitridation reactor was colored dark blue, suggesting that some material was leached from the sample into the flow of NH₃ during nitridation. To detect the desorbed species, a Ta foil was placed behind the sample powder in the reactor and nitridation was carried out at 1123 K for 120 h under 20 cm³ min⁻¹ flow of NH₃. Figure 15 shows the Auger electron spectroscopy (AES) differential spectra of the Ta foil before and after nitridation. A peak assigned to the Ti LMM Auger electron transition emerges clearly after nitridation, indicating that surface Ti is desorbed during nitridation. Although the desorption mechanism remains

unclear, the deep blue color of the reactor implies that reduced Ti species are liberated from the surface. One possible explanation for the sharp activity drop with nitridation longer than 120 h is the desorption of surface Ti. The rate of O₂ evolution increases with the formation of LaTiO₂N, but a considerable amount of surface Ti desorbs during the long nitridation period, and thereby photocatalytic activity for the oxidation of water decreases. Another possibility is the increase of defects. As shown in Figure 14, the Ti/La ratio decreased from an initial stage of nitridation, and the O₂ evolution rate drop with nitridation longer than 120 h cannot be ascribed to only Ti removal. LaTiO₂N is formed by reduction of La₂Ti₂O₇, followed by nitriding, and at the nitridation temperature (1143 K), a considerable amount of NH₃ is decomposed to N₂ and H₂. Many defects would occur by nitriding for a long period under such a reductive atmosphere, resulting in a decrease in photocatalytic activity. Nitridation in the presence of a small amount of oxidant, such as H₂O or O₂, may prevent surface Ti from desorbing and thereby improve the photocatalytic activity of LaTiO₂N.

No significant difference in the rate of H_2 evolution was observed among the present samples for all nitridation periods, although the observed formation of perovskite LaTiO₂N is known to be essential for H_2 evolution. This difference between O₂ evolution and H_2 evolution is thought to be due to the differing behavior of active sites for water oxidation and reduction.

4. Conclusion

According to DFT calculations, LaTiO₂N is revealed to have a valence band with a top composed mainly of N 2p orbitals with a small contribution by O 2p orbitals, while the bottom of its conduction band consists of Ti 3d orbitals. In an alkaline solution, LaTiO₂N efficiently oxidizes water into O₂ under visible light (≤ 600 nm) irradiation, while in an acid solution, it does not function as a viable photocatalyst. H₂ evolution on LaTiO₂N proceeds without a strong dependence on the pH of the solution. A perovskite phase of LaTiO₂N was observed and is essential for maintaining the photocatalytic activity of this catalyst. Nitridation of La₂Ti₂O₇ at 1123 K for more than 72 h formed near-stoichiometric LaTiO_{2.06}N_{0.96} in the bulk, but the surface concentration of Ti was found to decrease with nitridation time, resulting in lower activity for water oxidation. **Acknowledgment.** This work was supported by the Core Research for Evolutional Science and Technology (CREST) program of the Japan Science and Technology Corporation (JST).

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(18) The amount of surface nitrogen species was estimated as follows: N₂ (mol) = { $s_{(cat)}(2.67/2)(3.13 \times 10^{-19}) \text{ m}^2$ }/A_N, where $s_{(cat)}$ is the surface area of LaTiO₂N used in the photocatalytic reaction (BET surface area 11 m² g⁻¹). The catalyst surface was assumed to consist entirely of (100) oriented crystals and to contain 2.67 N atoms per $3.13 \times 10^{-19} \text{ m}^{2.12} A_N$ is Avogadro's number. The amount of surface nitrogen species was determined by XPS to be 8.0 μ mol. Using the surface atomic ratio (O/N = 2.26:0.71) obtained by the peak intensities of La 3d, Ti 2p, O 1s, and N 1s in the XPS spectrum gives a value of 8.0 μ mol of nitrogen species.