Crystal Structure and Electron Density of Tantalum Oxynitride, a Visible Light Responsive Photocatalyst

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Tantalum oxynitride (TaON) is investigated by neutron and synchrotron diffraction analysis to clarify the structural and electronic features responsible for the visible-light activity of this material. In combination with density functional theory (DFT) calculations, the present measurements confirm the TaON photocatalyst to be monoclinic with space group $P2_1/c$ (a = 4.94941(4) Å, b = 5.01662(4) Å, c = 5.16430(2) Å, $\alpha = 90°$, $\beta = 99.6107(4)°$, $\gamma = 90°$, V = 126.426(2) Å^3 at 298 K). Complete occupational ordering of the anions occurs in alternate layers normal to the [100] direction. Oxygen and nitrogen atoms in TaON are coordinated with three and four tantalum atoms, respectively. Bond valence sums for the oxygen and nitrogen atomic sites are calculated to be 2.1 and 3.2, respectively. Electron density analyses based on synchrotron data in combination with DFT calculations reveal covalent bonds between Ta and O atoms and between Ta and N atoms. The hybridization of anion 2p and Ta 5d orbitals attributed to the covalent bonds between Ta and O or N atoms results in increased dispersion of the valence band, raising the top of the valence band and leading to a visible-light response. The minimum electron density at the Ta−O bond decreases with increasing bond length, whereas no such trend was observed for the Ta−N bond.

Introduction

Metal oxide photocatalysts have attracted extensive research for the purposes of solar energy conversion and environmental remediation.[1,2] Overall water splitting using a photocatalyst is an attractive solution for the supply of clean and recyclable hydrogen energy, while certain photocatalysts decompose waste materials and hazardous compounds. Although a large number of photocatalysts have been proposed to date, most function only in the ultraviolet (λ < 400 nm) region (e.g., TiO_2[1]) due to the inherently large band gap of metal oxides. Metal oxynitrides are candidates for visible-light responsive photocatalysts, and promising results have been reported for tantalum oxynitride (TaON),[3−6] N-doped TiO_2,[7] and $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$.[8−10] TaON has been demonstrated to be responsive to excitation at wavelengths up to ca. 530 nm, with a suitable band gap (2.3 eV) position for overall water splitting.[3−6]

Armytage and Fender[11] analyzed the crystal structure of TaON by neutron powder diffraction using the Rietveld method at 4 K,[11] through which anion ordering was revealed. Weishaupt et al.[12] subsequently refined the crystal structure using neutron diffraction data collected at room temperature. Fang et al.[13] concluded based on calculations of the band structure of TaON that the anion 2p orbitals are hybridized with Ta 5d states. The band positions of TaON have been more recently investigated by X-ray and ultraviolet photoelectron spectroscopy and electrochemical analyses by Chun et al.[6] These works suggest the importance of covalency in TaON. However, covalent bonding in TaON has yet to be investigated in detail, which can be most effectively conducted by electron-density analysis using X-ray diffraction data.

In the present work, the crystal structure and electron density of an active TaON photocatalyst sample under visible-light excitation are investigated by neutron diffraction for confirmation of anion ordering, and synchrotron powder

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diffraction for high-precision analysis of the crystal structure and electron density. Density functional theory (DFT) is employed for theoretical calculations of the electron density distribution and partial density of states.

Experiments, Data Processing and DFT Calculation. *(1) Sample Preparation.* TaON samples were prepared by heating Ta_2O_5 powder under flowing NH_3 (20 mL min^{-1}) at 1123 K for 15 h. The TaON samples thus obtained were yellow to yellowish-green in color and functioned as a stable and very efficient photocatalyst for oxidation of water into O_2 in the presence of a sacrificial electron acceptor (Ag^+).[3] The chemical composition was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES; Iris Advantage DuO, Thermo Elemental Co.) combined with the use of an oxygen and nitrogen determinator (TC436, LECO). The molar ratio of Ta, O, and N in the prepared samples was determined to be 1.00:1.00(6):1.06(4), indicating the validity of the chemical formula TaON (values in parentheses denote error in the last digit).

(2) Neutron Powder Diffraction Experiment and Data Processing. Neutron powder diffraction experiments were performed using the Kinken powder diffractometer in order to ensure high-efficiency and high-resolution measurements. The diffractometer, HERMES,[14] is installed at the JRR-3M Japan Research Reactor of the Japan Atomic Energy Agency (JAEA) in Tokai, Japan, and is operated by the Institute of Materials Research of Tohoku University. Incident neutrons with a fixed wavelength of 1.8150 Å were obtained by a vertically focusing (331) Ge monochromator and a 12′-∞-22′ collimator. Diffraction data were collected at step intervals of 0.1° over a 2θ range of 8−150° using 150 ^{3}He counters set at 1° intervals. Structural refinement was performed using the Rietveld analysis program RIETAN-2000.[15] The peak shape was assumed to be a modified pseudo-Voigt function with asymmetry. The cutoff value was 7.00 × fwhm (full-width at half-maximum). The background of each profile was approximated by a 12-variable polynomial in $2\theta^n$ ($n = 0...11$). The n parameters were refined simultaneously with the unit cell, structural, and profile parameters. The nuclear density of TaON was investigated by the maximum-entropy method (MEM).[16] The MEM calculations were performed using the computer program PRIMA[16] with a 64 × 64 × 64 pixel unit cell.

(3) Synchrotron Powder Diffraction Experiment and Data Processing. Synchrotron X-ray powder diffraction experiments were performed using the multiple-detector system[17] installed at the BL-4B$_2$ beam line of the Photon Factory, High Energy Accelerator Research Organization (KEK), Japan. The experimental set up consisted of a bending-magnet light source, a double-crystal Si(111) monochromator, a focusing cylindrical mirror, and a multiple-detector system with Ge(111) analyzer crystals, Soller slits, and scintillation counters.[17] A monochromatized 1.20200 Å X-ray beam was utilized. Powder diffraction data from the sample at 298 K in air were collected in asymmetric flat-specimen reflection geometry with a fixed incident angle of 7.0°. Scanning parameters were set as follows: step interval, 0.004°; counting time, 3.0 s step^{-1}; diffraction angle 2θ, 8−140°. The crystal structure of the TaON sample was refined by the Rietveld method using RIETAN-2000.[15] As enhancement in asymmetric scan mode is not implemented in RIETAN-2000, the observed intensity data were modified by multiplying by the term $[1 + \{\sin \alpha/\sin(2\theta - \alpha)\}]/2$, where α is the fixed incident angle, in order to obtain data equivalent with those measured in symmetric scan mode.[18] The peak shape was assumed to be a split Pearson VII-type function.[19] The cutoff value was set at 30.00 × fwhm. The background was approximated by a 12-variable polynomial in $2\theta^n$ ($n = 0...11$). The n parameters were refined simultaneously with the unit cell, zero point, scale, profile shape, and crystal structural parameters. The electron density distribution of TaON was investigated by MEM using the 237 structure factors obtained by the Rietveld analysis. MEM calculations were carried out using PRIMA with a 64 × 64 × 64 pixel unit cell. To confirm the validity of the MEM analysis, MPF[16] was also conducted using the structure factors obtained by Fourier transform of the MEM electron density distribution. It is well-known that the MEM can produce a precise electron density distribution that visualizes covalent bonding.[20]

(4) DFT Calculation. The *ab initio* total energy program VASP (Vienna *Ab initio* Simulation Package)[21,22] was employed for calculation of the valence electron-density distribution and partial density of states in TaON. Projector augmented-wave (PAW) potentials were used for Ta, O, and N atoms.[23,24] A plane-wave basis set with a cutoff of 500 eV was used. The calculations were performed using the Perdew−Burke−Ernzerhof (PBE) generalized gradient approximation (GGA) for the exchange and correlation functional.[25] Sums over occupied electronic states were performed using the Monkhorst−Pack scheme[26] on a 5 × 5 × 5 set of the k-point mesh. The crystallographic parameters refined using synchrotron data were used for comparison with the experimental results, without structural optimization in VASP calculations.

Results and Discussion

All reflections in the neutron and synchrotron powder diffraction profiles (Figures 1 and 2) were indexed as belonging to a monoclinic cell, indicating a single phase of baddeleyite-type TaON. Rietveld analyses of the neutron and synchrotron diffraction data were thus performed assuming a baddeleyite-type structure.[11,12] In a preliminary analysis of

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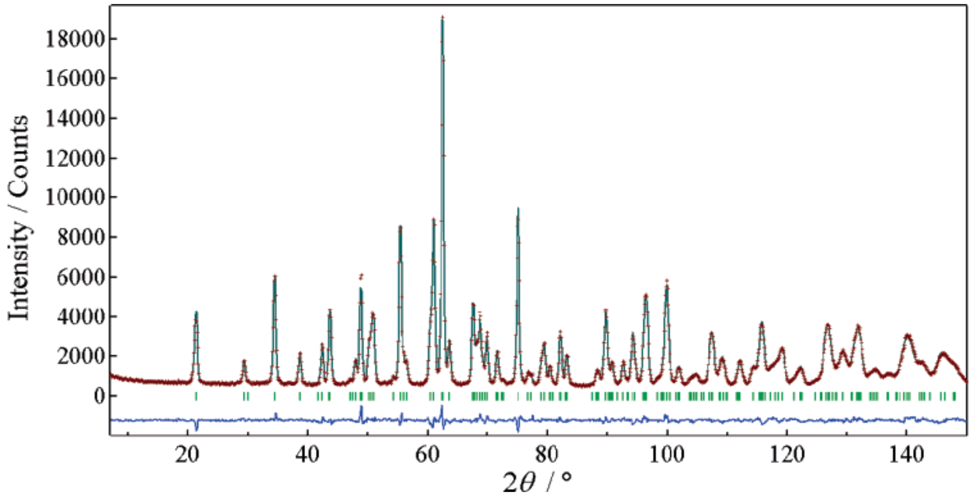

Figure 1. Rietveld pattern determined from neutron powder diffraction data for TaON at 299 K. Plots denote observed data, the green line denotes calculated profiles, and the blue line denotes the difference. Vertical lines indicate possible Bragg peaks of the monoclinic TaON phase.

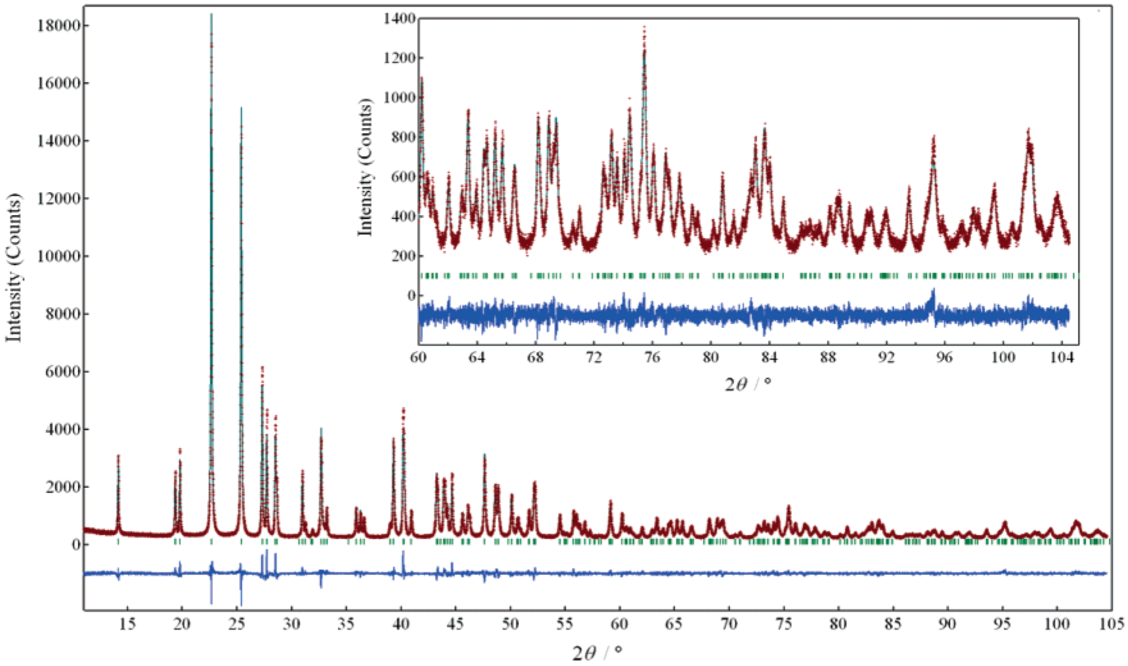

Figure 2. Whole powder pattern for the first MPF analysis of synchrotron powder diffraction data for TaON at 298 K. Plots denote observed data, the green line denotes calculated profiles, and the blue line denotes the difference. Vertical lines indicate possible Bragg peaks of the monoclinic TaON phase.

the neutron diffraction data, refinement gave an occupancy factor at the N site g(N) of 0.966(3). However, the fit in the Rietveld analysis of the synchrotron data was not good using this occupancy for g(N), and chemical analysis did not reveal such a deficiency in N. All the occupancy factors were therefore fixed at unity in the final refinement. Isotropic harmonic atomic displacement parameters were used for all atoms. In a preliminary analysis, the atomic displacement parameters U for the three atoms were refined independently. However, as the refined atomic displacement parameter was negative, final refinement was conducted assuming $U(\mathrm{Ta}) = U(\mathrm{N}) = U(\mathrm{O})$, where $U(\cdot)$ denotes the atomic displacement parameter. The calculated intensity obtained after final refinement was in good agreement with the observed data (Figures 1 and 2). The refined crystallographic parameters and reliability factors obtained using neutron and synchrotron powder diffraction data are shown in Tables 1 and 2. The refined crystallographic parameters obtained using neutron data are closely consistent with the values obtained using synchrotron data.

Table 1. Refined Crystallographic Parameters and Reliability Factors for Neutron Powder Diffraction Data of TaON Measured at 299 K[a]

			atomic coordinates		
atom	site	occupancy: g	x	y	z
Ta	4*e*	1.0	0.2926(3)	0.0449(3)	0.2146(3)
O	4*e*	1.0	0.0617(4)	0.3271(3)	0.3461(3)
N	4*e*	1.0	0.4438(2)	0.7565(3)	0.4800(2)

[a] Unit cell: monoclinic $P2_1/c$, $a = 4.9498(2)$ Å, $b = 5.0179(2)$ Å, $c = 5.1652(2)$ Å, $\alpha = 90°$, $\beta = 99.610(2)°$, $\gamma = 90°$, $V = 126.489(7)$ Å^3. Atomic displacement parameters: $U(\mathrm{Ta}) = U(\mathrm{N}) = U(\mathrm{O}) = 0.0027(4)$ Å^2. $R_{\mathrm{wp}} = 4.41\%$, GOF = 1.65, $R_{\mathrm{I}} = 1.13\%$, $R_F = 0.44\%$. Wavelength = 1.8150 Å.

Figure 3 shows the crystal structure drawn with refined crystallographic parameters using NTa_4 tetrahedra and OTa_3 triangles. The neutron and synchrotron data sets both indicate that the TaON material has a baddeleyite-type structure

Table 2. Refined Crystallographic Parameters and Reliability Factors for Synchrotron Powder Diffraction Data of TaON Measured at 298 K[a]

			atomic coordinates		
atom	site	occupancy: *g*	*x*	*y*	*z*
Ta	4*e*	1.0	0.29197(5)	0.04477(5)	0.21486(6)
O	4*e*	1.0	0.0662(7)	0.3273(5)	0.3443(6)
N	4*e*	1.0	0.4447(8)	0.7557(7)	0.4808(9)

[a] Unit cell: monoclinic $P2_1/c$, $a = 4.94941(4)$ Å, $b = 5.01662(4)$ Å, $c = 5.16430(2)$ Å, $\alpha = 90°$, $\beta = 99.6107(4)°$, $\gamma = 90°$, $V = 126.426(2)$ Å^3. Atomic displacement parameters: $U(\mathrm{Ta}) = U(\mathrm{N}) = U(\mathrm{O}) = 0.0031(4)$ Å^2. Reliability factors in the Rietveld analysis: $R_{wp} = 6.04\%$, GOF = 1.40, $R_I = 1.14\%$, $R_F = 0.48\%$. Reliability factors in the first MEM analysis: $R_F = 0.33\%$, $wR_F = 0.30\%$. Reliability factors in the first MPF analysis: $R_{wp} = 6.06\%$, GOF = 1.41, $R_I = 0.81\%$, $R_F = 0.33\%$. Wavelength = 1.20200 Å.

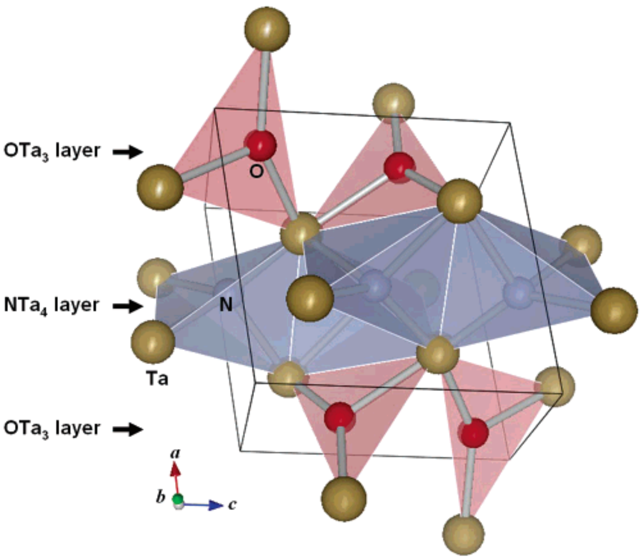

Figure 3. Refined crystal structure of the TaON photocatalyst. Brown, red, and gray spheres denote Ta, O, and N atoms, respectively. OTa_3 triangles and NTa_4 tetrahedra are shown. Complete occupational ordering of O and N atoms occurs in alternate layers normal to [100].

(space group, $P2_1/c$), with estimated unit cell parameters of $a = 4.94941(4)$ Å, $b = 5.01662(4)$ Å, $c = 5.16430(2)$ Å, $\alpha = 90°$, $\beta = 99.6107(4)°$, $\gamma = 90°$, and $V = 126.426(2)$ Å^3 (298 K). Occupational ordering of the anions occurs in alternate NTa_4 and OTa_3 layers normal to the [100] direction. The coordination numbers of Ta, N, and O atoms are 7, 4, and 3, respectively. The NTa_4 tetrahedron is linked with four corner-shared NTa_4, four edge-shared NTa_4, two corner-shared OTa_3, and one edge-shared OTa_3. The OTa_3 triangle is linked with twelve corner-shared NTa_4, one edge-shared NTa_4, three corner-shared OTa_3, and one edge-shared OTa_3. These results indicate that the nitrogen atoms prefer to be four-coordinated in TaON, while oxygen atoms prefer to have three neighbors, which is consistent with previous neutron diffraction[11,12] and electronic structure studies.[13] The bond valence sums of NTa_4 and OTa_3 are estimated to be 3.2 and 2.1, which are consistent with the valences of N and O ions, respectively. Bond valence parameters of 2.01 and 1.92 are assumed here for NTa_4 and OTa_3, respectively.[27] Occupational ordering is therefore apparent in TaON, with N and O atoms present at different positions. In contrast, $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ photocatalysts exhibit occupational disorder with both N and O atoms located at the same site.[9,10] The occupational ordering in TaON is due to the existence of three- and four-coordinated crystallographic sites.

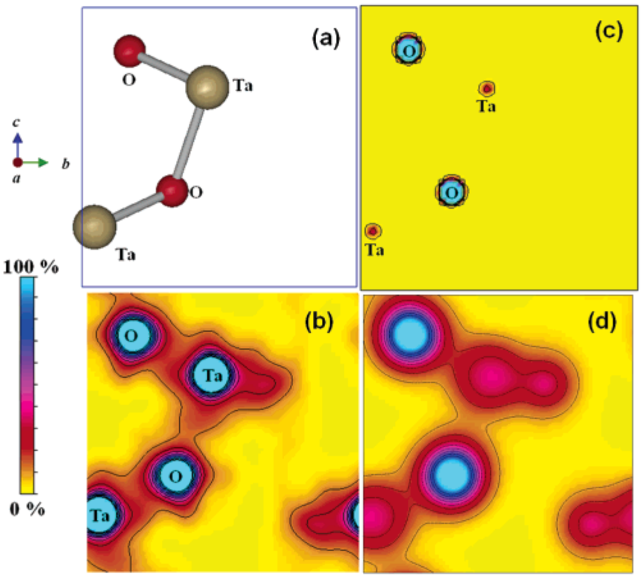

Figure 4. (a) Refined crystal structure, (b) electron density, (c) nuclear density, and (d) valence electron density distributions on the *b*−*c* plane of TaON over the range $0 < x < 1/4$. Full scale (by color) corresponds to electron and nuclear densities of 71 Å^{-3} and 28 fm Å^{-3}. Electron (b) and nuclear (c) densities were obtained by MEM analyses of synchrotron and neutron powder diffraction data, respectively. Valence electron density (d) was obtained by DFT calculation.

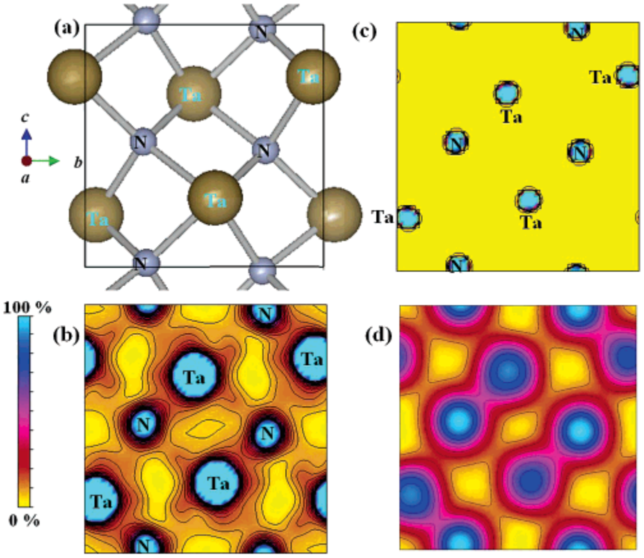

Figure 5. (a) Refined crystal structure, (b) electron density, (c) nuclear density, and (d) valence electron density distributions on the *b*−*c* plane of TaON over the range $1/4 < x < 3/4$. Full scale (by color) corresponds to electron and nuclear densities of 67.1 Å^{-3} and 45.1 fm Å^{-3}. Electron (b) and nuclear (c) densities were obtained by MEM analyses of synchrotron and neutron powder diffraction data, respectively. Valence electron density (d) was obtained by DFT calculation.

Figure 4 shows the refined crystal structure, MEM electron density distribution, MEM nuclear density distribution, and VASP valence electron density distribution on the *b*−*c* plane of the TaON photocatalyst over the range $0 < x < 1/4$. The nuclear density map shows an atom near the stable position, while the MEM and VASP valence electron density maps clearly show covalent bonding between Ta and O atoms. The electron density distribution obtained using synchrotron

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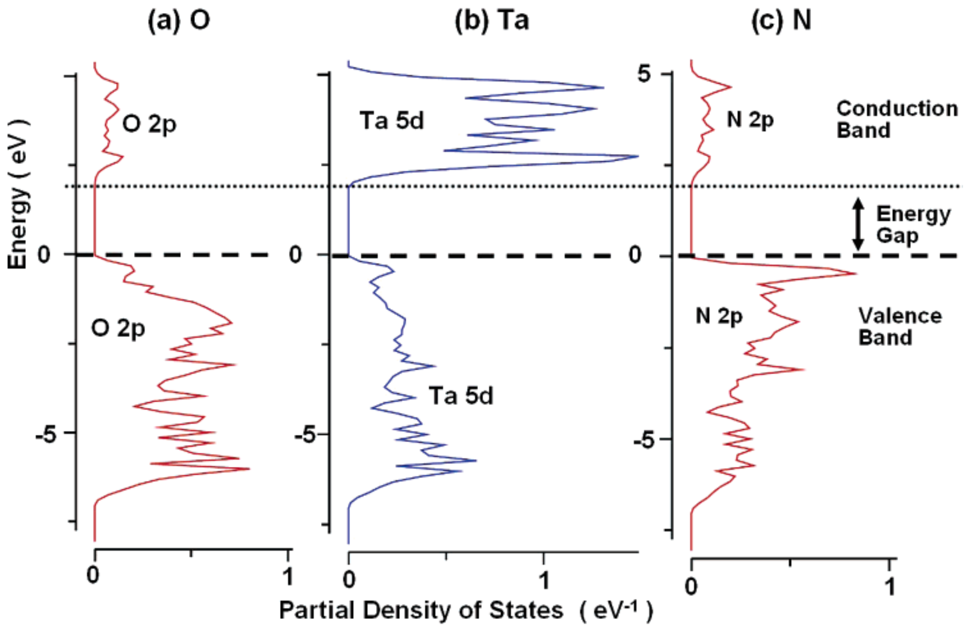

Figure 6. Part of a diagram of partial DOS for (a) O 2p, (b) Ta 5d, and (c) N 2p orbitals in TaON as determined by the VASP program.

data (Figure 4b) is consistent with the valence electron density distribution determined by DFT calculations (Figure 4d).

Figure 5 shows the corresponding results for the range $1/4 < x < 3/4$. The nuclear density map shows an atom near the stable position, and the MEM and valence electron density maps clearly indicate covalent bonding between the Ta and N atoms. Again, the synchrotron-based electron density distribution (Figure 5b) is in agreement with the DFT-based valence electron density distribution (Figure 5d). These results suggest a two-dimensional network consisting of covalent bonds between Ta and N atoms, while the results of Figure 4 indicate a two-dimensional network of covalent bonds between Ta and O atoms. The networks of Ta−N and Ta−O covalent bonds are arranged alternately along the *a*-axis, corresponding to the ordering of NTa_4 tetrahedra and OTa_3 triangles (Figure 3).

Figure 6 shows the results of DFT calculations of the electronic structure of TaON. Shown is part of the partial density of states (DOS) diagram for O, Ta, and N electrons in TaON. These results indicate that the top of the valence band is mainly composed of O 2p and N 2p orbitals hybridized with Ta 5d orbitals, whereas the bottom of the conduction band is composed of Ta 5d orbitals hybridized with N 2p and O 2p orbitals. These features are consistent with previous reports.[13,28] The hybridization of O 2p and N 2p orbitals with Ta 5d orbitals can be attributed to the covalent bonds between O or N and Ta atoms, which have been confirmed by the present synchrotron results. Figure 6 shows a large dispersion of the valence band (ca. 7 eV) by the hybridization of O 2p and N 2p orbitals with Ta 5d orbitals in TaON. The visible-light response of TaON is thus attributable to the larger dispersion of the valence band, which raises the top of the valence band.

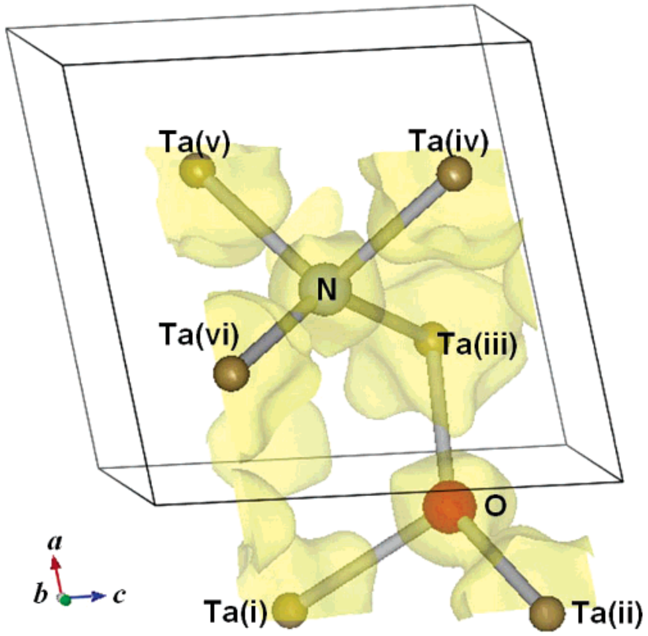

Figure 7. Part of the refined crystal structure and isosurface of electron density at 1.0 Å^{-3} in TaON ($-0.3 < x < 0.75$, $0.35 < y < 1.0$, $0.2 < z < 0.9$). Atomic coordinates of Ta(i), Ta(ii), Ta(iii), Ta(iv), Ta(v), Ta(vi), O and N atoms are listed in Table 3.

Figure 7 shows part of the refined crystal structure and isosurface of electron density at 1.0 Å^{-3}. The bond length and minimum electron density at the bond in TaON were estimated from the refined crystal parameters and electron density distribution as shown in Table 3. For the Ta−O bonds, the minimum electron density at the bond decreased with increasing bond length (closed circles and dashed line in Figure 8). No such trend was apparent for the Ta−N bonds. For the N−Ta(vi) and N−Ta(iii) bonds, the data followed the dashed line in Figure 8. The fractional coordinates and positions of the Ta(vi) and Ta(iii) atoms are shown in Table 3 and Figure 7, respectively. The minimum electron density at the N−Ta(iv) bond (0.91 Å^{-3}) was higher than that on the line (0.7 Å^{-3}), suggesting large covalency.

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Table 3. Bond Length and Minimum Electron Density at the Bond in TaON

bond	bond length (Å)	minimum electron density ($Å^{-3}$)	atomic coordinate of Ta atom		
O−Ta[(i)]	2.147(3)	0.78	$-x$,	$y + 1/2$,	$-z + 1/2$
O−Ta[(ii)]	1.988(3)	1.09	$-x$,	$1 - y$,	$1 - z$
O−Ta[(iii)]	2.060(3)	0.95	x,	$-y + 1/2$,	$z + 1/2$
N−Ta[(iii)]	2.147(4)	0.74	x,	$-y + 1/2$,	$z + 1/2$
N−Ta[(iv)]	2.188(4)	0.91	$1 - x$,	$1 - y$,	$1 - z$
N−Ta[(v)]	2.069(4)	0.81	$1 - x$,	$y + 1/2$,	$-z + 1/2$
N−Ta[(vi)]	2.053(4)	0.98	$-x$,	$1 + y$,	z

Atomic coordinates of O and N are −0.0662, 0.6727, 0.6558 and 0.4447, 0.7557, 0.4808, respectively. The x, y, z is the atomic coordinate of Ta: 0, 0, 0. Atomic configurations are shown in Figure 7.

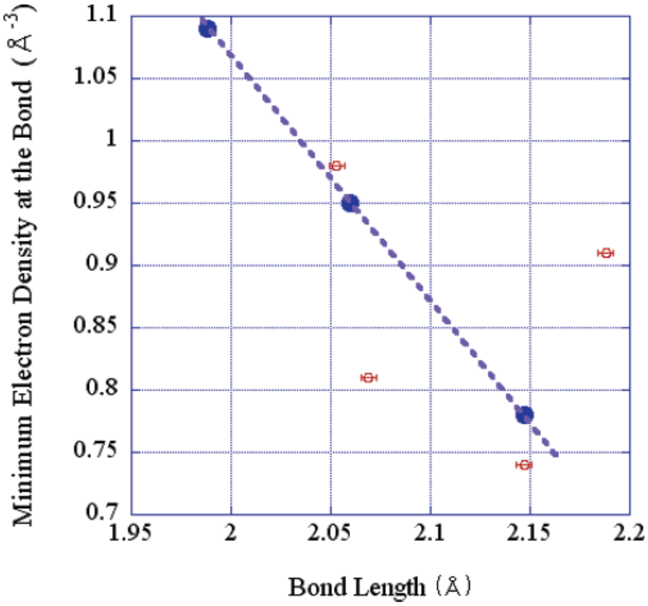

Figure 8. Relationship between bond length and minimum electron density at the bond in TaON. Filled blue and open red circles denote O−Ta and N−Ta bonds, respectively. The dashed line is shown as a guide.

The present work has demonstrated covalent bonding at the Ta−O and Ta−N bonds based on electron density analysis of TaON using synchrotron diffraction data combined with DFT calculations. The DFT calculations also reveal hybridization of the anion 2p and Ta 3d states, resulting in widening of the conduction and valence bands and thus lower band gap energy. The band gap energy determined by the present DFT calculations (2.1 eV) is in good agreement with that indicated by ultraviolet−visible reflectance spectra (2.3 eV).[3−6] The small band gap energy of TaON allows the material as a photocatalyst to be activated by the absorption of visible light down to wavelengths of 530 nm. It is considered that the covalent bonding of the Ta−O and Ta−N bonds is critical to the visible-light photocatalytic activity of TaON.

Concluding Remarks

Tantalum oxynitride (TaON), a promising visible-light responsive photocatalyst, was investigated by neutron and synchrotron powder diffraction and DFT studies. Oxygen and nitrogen atoms in TaON were found to be coordinated with three and four tantalum atoms, and the bond valence sums for the oxygen and nitrogen atomic sites were calculated to be 2.1 and 3.2, respectively. Electron density analysis based on synchrotron diffraction data in combination with DFT calculations clearly showed covalent bonding between Ta and O atoms and between Ta and N atoms. The results demonstrate two-dimensional networks of Ta−O and Ta−N covalent bonds arranged alternately along the [100] direction, corresponding to the occupational ordering of anions. The hybridization of anion 2p and Ta 5d orbitals attributable to the covalent bonds between Ta and O or N atoms results in enhanced dispersion of the valence band, raising the top of the valence band and realizing the visible-light response in TaON. The minimum electron density at the O−Ta bond decreases with increasing bond length, while the N−Ta bond does not exhibit such a systematic change. The high minimum electron density at the N−Ta(iv) bond suggests high covalency. Hybridization of the anion 2p and Ta 5d states around these bonds is expected to be responsible for the small band gap energy, allowing photocatalysis to occur at visible wavelengths of up to 530 nm.

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