

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

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Introduction

Metal oxynitrides are candidates for visible-light responsive photocatalysts, and promising results have been reported for TaON, N-doped TiO₂, and (Ga_{1-x}Zn_x)(N_{1-x}O_x). 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. In the present work, the crystal structure and electron density of an active TaON photocatalyst sample under visible-light excitation are investigated by synchrotron powder 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 (PDOS). (Yashima *et al.*, *Chem. Mater.*, **19**, 588-593 (2007)).

Experiments

Synchrotron x-ray powder diffraction experiments of TaON were performed at 298 K using the multiple-detector system installed at the BL-4B₂ beam line of the Photon Factory, High Energy Accelerator Research Organization (KEK), Japan. A monochromatized 1.20200 Å x-ray beam was utilized. The crystal structure of the TaON was refined by the Rietveld method with a computer program RIETAN-2000 (Izumi & Ikeda, 2000). Electron-density distribution of TaON was investigated by a maximum-entropy method (MEM, PRIMA (Izumi & Dilanian, 2002)) and DFT calculations.

Results and discussion

The synchrotron data indicate that the TaON material has a baddeleyite-type structure (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, $\alpha = 90^\circ$, $\beta = 99.6107(4)^\circ$, $\gamma = 90^\circ$, and $V = 126.426(2)$ Å³ (298 K). Occupational ordering of the anions occurs in alternate NTa₄ and OTa₃ layers normal to the [100] direction. The coordination numbers of Ta, N and O atoms are 7, 4 and 3, respectively. 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 show covalent bonding between Ta and O atoms (Fig. 1(a) and (b)) and that between Ta and N atoms (Fig. 1(c) and (d)). The electron density distribution obtained using synchrotron data (Figs. 1(a) (c)) is consistent with the valence electron density distribution determined by DFT calculations (Figs. 1(b) (d)). 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 PDOS indicates that 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. 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.

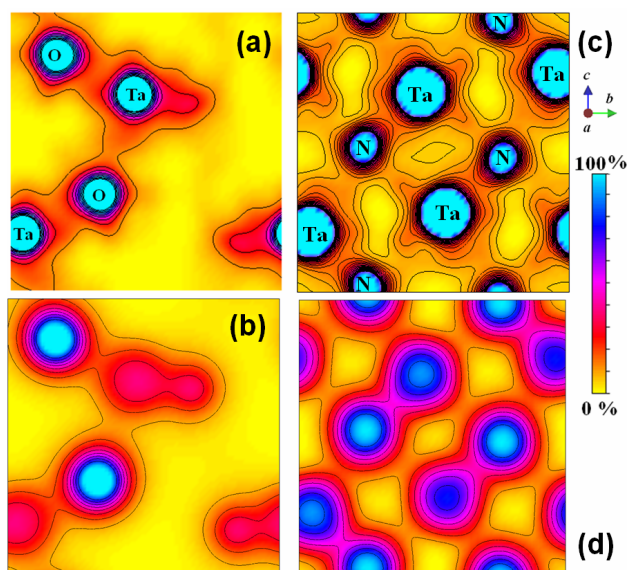


Fig.1. (a) Electron density and (b) valence electron density distributions on the b - c plane of TaON over the range $0 < x < 1/4$. (c) Electron density and (d) valence electron density distributions on the b - c plane of TaON over the range $1/4 < x < 3/4$.

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