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Nature of β-TaON surfaces at ambient conditions

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ABSTRACT

TaON has been recently identified as a promising water-splitting photocatalyst. Here we present the results of our detailed computational study to understand the exposed surfaces of β-TaON at ambient conditions. By employing periodic density functional theory, structures and electronic properties of all the low index native surfaces of β-TaON were studied. Nature of the β-TaON surfaces at ambient moist conditions was investigated using the ab initio thermodynamics approach. Based on the surface energies computed as a function of temperature (T) and pressure, we obtain the equilibrium shape of the β-TaON single crystal by the Wulff construction and study the exposure of these surfaces as a function of T at moist conditions. The effects of surface hydration and T on the exposure of the low-index surfaces are discussed. This study presents surface models relevant for studying catalytic reactions using β-TaON. Surface reactivity of the most stable surface of TaON is then analyzed.

1. Introduction

Photocatalytic water splitting is a promising route for storing solar energy as chemical energy in H_2 [1–7]. The process of water splitting is endothermic in nature and thus requires a photocatalyst to drive the reaction by coupling this to photo excitation of electrons.

In the rigorous search for a suitable catalyst for water splitting using solar energy, oxynitride materials have drawn considerable attention owing to their appropriate band gap and suitable band positions [5,8–11]. The conduction band (CB) of a metal oxynitride is mainly formed by the empty *d* orbitals of metal atoms.

On the other hand, the valence band (VB) edges of oxynitrides are shifted to more negative potential (with respect to the standard hydrogen electrode, SHE) compared to the metal oxides by the same metal atoms by the presence of N 2*p* mixed states. Thus the band gap of oxynitrides is smaller than that of the corresponding metal oxides. Experimentally reported band gaps of oxynitrides are in the range of 2.0–2.5 eV [5,8,9,12].

As an example, the band gap of TaON measured by ultraviolet photoelectron spectroscopy (UPS) is 2.4 eV, and the CB and the VB edges are situated at -0.2 V and $+2.2$ V (with respect to SHE), respectively, whereas the band gap of Ta_2O_5 is 3.9 eV [9].

Among the oxynitrides, TaON shows high quantum efficiency (34%) when it was used with silver nitride [8]. High H_2 and O_2 evolution activities were also reported when TaON was used with sacrificial reagents [13–15] and a good quantum yield was achieved for overall water splitting using TaON in the presence of metal co-catalysts [16–18]. The effect of crystal defects and the particle size of TaON on the mineralization of chlorophenols was reported experimentally [19]. The authors showed that low defect density of TaON and small particle size promote separation of electron-hole pair and accelerate charge transfer at the interface, thus enhancing the photocatalytic activity. TaON was also shown to do photochemical oxidation of hydrocarbons [19,20].

Photocatalytic reactions on TaON are believed to proceed through migration of photo generated h^+ and e^- produced in the bulk to the active sites on the surfaces where the reactants are adsorbed [3, 21]. Understanding the structure of exposed facets and the morphology of the material at the experimental conditions is crucial for a proper understanding of the photochemical reactions, and for further improvements.

TaON exists mainly as β- and γ-TaON. The monoclinic $\beta-$TaON is the most stable phase and is largely used for catalysis [8,10,22]. The metastable γ-TaON exists in C-centered monoclinic form and is 20 kJ/mol higher in energy than the β-phase [22]. Results of a recent DFT calculation by Harb et al. [23] indicate that TaON is appropriate for water oxidation, and the non-stoichiometric TaON has positive influence on the hydrogen evolution reaction due to the modified band edge positions [23]. Although several experiments and theoretical calculations were devoted to characterize the bulk properties of β-TaON [10,24,25], only a recent article by Bredow and co-workers [26], published during the last stages of preparation of this manuscript, has investigated the β-TaON surfaces. Their hybrid DFT and MSINDO semi-empirical calculations showed that (100) and (111) surfaces are the most exposed surfaces under UHV conditions.

The most stable surface is the one which has the lowest surface formation energy. In order to minimize the formation energy of the crystal, surface with lower surface energy predominates in the crystal, which in turn determines the crystal morphology. Exposure of a surface is also influenced by the environmental and thermodynamic parameters. Since β-TaON is synthesized by the reaction of Ta_2O_5 with moist ammonia

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Table 1
Surface energies of the low index surfaces of β-TaON. γ_{hkl} is the surface energy of the (hkl) surface. The band gaps of these surfaces are also presented. See also Tables SI 1 and 9.

Surface	Supercell	γ_{hkl} ($J\ m^{-2}$)	Band gap (eV)
(100)	$Ta_{48}O_{48}N_{48}$ $(3 \times 2 \times 2)$	1.15	1.73
(010)	$Ta_{48}O_{48}N_{48}$ $(2 \times 3 \times 2)$	2.95	0.50
(001)	$Ta_{48}O_{48}N_{48}$ $(2 \times 2 \times 3)$	1.45	1.92
(011)	$Ta_{64}O_{64}N_{64}$ $(2 \times 2 \times 2)$	1.64	1.80
(110)	$Ta_{64}O_{64}N_{64}$ $(2 \times 2 \times 2)$	1.52	1.80
(101)	$Ta_{64}O_{64}N_{64}$ $(2 \times 2 \times 2)$	1.58	1.84
(111)	$Ta_{64}O_{64}N_{64}$ $(2 \times 2 \times 2)$	1.03	2.05

[8], the synthesized β-TaON is exposed to moisture, which could influence the crystal structure.

For modeling and further understanding of the photochemical reactions on β-TaON, it is vital to have the knowledge of the nature of its surfaces and their reactivity. DFT-based quantum chemical calculation is a powerful tool for predicting relative stability of solid surfaces by comparing their surface free energies. By employing periodic DFT calculations we address the structure and electronic properties of β-TaON surfaces and predict the most stable surface of β-TaON among all possible low index surfaces at UHV condition.

We also predict the most stable surface of β-TaON under moist conditions for a range of temperatures and pressures using the ab initio thermodynamics approach [27–30].

2. Methods and models

Bulk β-TaON possesses $P2_1/c$ space group and has a monoclinic unit cell with lattice parameters $a = 4.9581$ Å, $b = 5.0267$ Å, $c = 5.1752$ Å and $\beta = 99.64^\circ$. Bulk structure of β-TaON has sevenfold coordinated Ta atoms, threefold coordinated O atoms and fourfold coordinated N atoms. The bulk structure was generated using the experimental lattice parameters and the fractional coordinates from Ref. [31]. Various surfaces of β-TaON were constructed from the bulk structure by cutting along the planes in different crystallographic directions (*hkl*). Minimum bond breakage of the surface atom and surface compactness criterion were followed [32] during the creation of the surfaces. A periodic slab for a surface calculation was made such that both the surfaces of the slab were equivalent and symmetric with respect to the center of inversion located at the center of the slab. A symmetric slab was chosen in order to avoid any unphysical dipolar interaction between the slabs. Seven low index surfaces were considered here and were modeled using supercells with a vacuum thickness of 10 Å between the two periodically repeated slabs along the normal to the surface. Surface reconstructions of these surfaces were not included in the current study. Bulk TaON was modeled using a $2 \times 2 \times 2$ $Ta_{32}O_{32}N_{32}$ supercell.

All the calculations were performed by employing periodic DFT [33] with its plane-wave formalism as implemented in the CPMD program [34]. We used PBE [35] exchange correlation functional and the core electrons were accounted by the ultra-soft pseudopotentials [36]. The five outer shells of Ta were treated explicitly and the remaining core shells were included in the pseudopotential; see Table SI 5 for more details of the constructed pseudopotential. A plane-wave cutoff of 30 Ry was used in our computations. For structure optimizations, we used simulated annealing of wavefunction and nuclear coordinates using the Car–Parrinello molecular dynamics scheme [37] followed by structural optimization using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm. Five to nine atomic layers of each surfaces of the slab were relaxed depending on the convergence of the surface energy. The band gaps and the projected density of states (PDOS) of β-TaON surfaces were calculated using the Quantum Espresso program [38] with identical pseudopotentials.

For benchmarking, the lattice parameters of β-TaON were optimized and the surface energies were recomputed using the optimized lattice parameters, but the changes are only marginal (see Table SI 6 and 7). The convergence of the surface energy with respect to the *k*-points was also performed and the results are presented in Table SI 8: Γ-point computations of surface energies with the supercells chosen for all the surfaces (see Table 1 and Table SI 1)were adequate for identifying the most exposed surface and to compute their relative stabilities.

The surface energies of the slabs are also converged with respect to the number of layers parallel to the surface (Table SI 9).

The surface energy (γ) was calculated by

$$\gamma = \frac{E_{slab} - E_{bulk}}{2A} \tag{1}$$

where E_{slab} and E_{bulk} are the energies of the supercell and the bulk, respectively, and A is the surface area.

We used the ab initio thermodynamic approach [27–30] to compute γ in the presence of water at a given temperature T and partial pressure of water p_{H_2O}. To employ this approach the following equilibrium was considered:

$$\text{Surface}_{hkl} + nH_2O \rightleftharpoons [nH_2O.\text{Surface}_{hkl}] \tag{2}$$

Surface free energy change is defined by free energy change per unit area for the above process.

$$\Delta\gamma_{hkl} = \frac{\Delta G}{2\,A_{hkl}} \tag{3}$$

where ΔG and $\Delta\gamma_{hkl}$ are the free energy change and surface free energy change on adsorption. A_{hkl} is the area of the surface in the crystallographic hkl direction. From Eq. (3), the surface energy of the composite surface can be obtained as

$$\gamma_{hkl} = \gamma^0_{hkl} + \frac{1}{2\,A_{hkl}}\left(G_{H_2O/TaON} - G_{TaON} - N_{H_2O}\mu_{H_2O}\right) \tag{4}$$

where

$$\Delta\gamma_{hkl} = \gamma_{hkl} - \gamma^0_{hkl} \tag{5}$$

and

$$\begin{aligned}\Delta G &= G_{H_2O/TaON} - G_{TaON} - G_{H_2O} \\ &= G_{H_2O/TaON} - G_{TaON} - N_{H_2O}\mu_{H_2O}.\end{aligned} \tag{6}$$

Here G_i is the Gibbs free energy for the component i and γ^0_{hkl} denotes surface energy of the neat surface (in the absence of water). μ_{H_2O} is the chemical potential of water and N_{H_2O} is the number of water molecule adsorbed on the chosen slab. This equation can be rewritten in terms of the binding energy of water, $E^b_{H_2O}$, and relative chemical potential of water, $\Delta\mu_{H_2O}$, under the assumption that entropy changes and volume changes are negligible, which is a reasonably good approximation for solid surfaces [27].

$$\gamma_{hkl} \approx \gamma^0_{hkl} + \frac{\theta_{hkl}}{2}\left(-E^b_{H_2O} - \Delta\mu_{H_2O}\right) \tag{7}$$

θ_{hkl} denotes the surface water coverage per nm^2 and is calculated as N_{H_2O}/A_{hkl}. The binding energy of water is defined as the adsorption energy per water as expressed in Eq. (8).

$$E^b_{H_2O} = -\frac{1}{N_{H_2O}}\left(E_{H_2O/TaON} - E_{TaON} - N_{H_2O}E_{H_2O}\right) \tag{8}$$

Eq. (7) defines a relationship between the surface energy and the water chemical potential. Knowing the total energies, E_is from DFT, one can predict the stability of the surface using Eq. (7) with respect