Suitable Fundamental Properties of $Ta_{0.75}V_{0.25}ON$ Material for Visible-Light-Driven Photocatalysis: A DFT Study

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ABSTRACT: By applying calculations based on density functional theory, and on density functional perturbation theory, together with generalized gradient approximation-Perdew−Burke−Emzerho and screened Coulomb hybrid HSE06 functionals, we predict novel and suitable fundamental parameters of the stable monoclinic $Ta_{0.75}V_{0.25}ON$ semiconductor for solar water splitting. In addition to its predicted bandgap of 2.0 eV in the required zone for solar-driven water splitting, this material reveals a high visible-light absorption coefficient, high static dielectric constant, high hole and electron mobilities along the [001] and [010] crystallographic directions, relatively low exciton binding energy, and suitable band edge energy levels for oxidizing water and reducing protons. The optical, charge-carrier transport, and redox features predicted for this material are found to be considerably better than those obtained for $Ta_3N_5$, which is the most common semiconductor photocatalyst used in visible-light-driven water splitting.

1. INTRODUCTION

Producing hydrogen from water splitting using powder photocatalysts under sunlight is a low-cost, attractive, and scalable technology.1,2 Besides the good crystallinity required for the prepared material, finding a new good candidate photocatalyst for solar water splitting requests at least the following challenging fundamental parameters to be present in the semiconductor as a photon absorber: (1) adequate bandgap energy (greater than 1.23 eV and near 2.0 eV) to absorb a large amount of photons in the visible region, which corresponds to 43% of the direct sunlight at Earth’s surface; (2) static dielectric constant greater than 10 accompanied by a binding energy of the exciton smaller than 25 meV to achieve a good ability for the exciton to be dissociated into free carriers;3−8 (3) smaller hole and electron effective masses than 0.5$m_0$ ($m_0$ denotes the mass of free electron) to obtain good transport properties;9,10 (4) relative band edge energy levels suitable for splitting water, to provide enough driving forces to the created holes and photoexcited electrons for water oxidation and proton reduction.11

It has been clearly demonstrated in previous computational studies12−29 that the calculated fundamental parameters mentioned above of widely used semiconductors in photocatalysis and photovoltaics can accurately predict the experimental data by means of density functional theory (DFT) using the screened Coulomb and hybrid exchange-correlation functional HSE06.30,31 By applying this computational scheme, we have recently shown interesting dielectric, charge-carrier transport, and redox features of ($Ta_{1-y}Nb_y$)ON solid solution materials (0.25 ≤ x ≤ 0.5) for water splitting, whereas they revealed almost UV light absorption features due to their large predicted direct bandgaps in the 2.8−3.0 eV range.23 In addition, we have recently predicted suitable optoelectronic features of VON polymorphs for photovoltaic applications with computed bandgaps of 1.3 and 1.4 eV,26 located in the suitable range for good efficiency.

Getting inspired from the two previous studies, we present here a detailed theoretical investigation on the required physicochemical parameters of ($Ta_{1-x}V_x$)ON ($x$ = 0.125, 0.25, and 0.5) semiconductor compounds that could be used for solar water splitting, following the above invoked accurate first-principles quantum computations. Besides the structure and stability of the studied systems, we studied their optoelectronic and redox properties with various V contents. We also compared the computed data to those acquired for $Ta_3N_5$, which is the most common semiconductor used in visible-light-driven photocatalytic water splitting. The adequate bandgap energy (2.0 eV) predicted for the $Ta_{0.75}V_{0.25}ON$ material as well as the high static dielectric constant, the small hole and electron effective masses, the low exciton binding energy, and the appropriate locations of the conduction and valence bands with respect to the oxidation and reduction potentials of water indicate the potential for this material to be effective in water splitting for hydrogen production under solar energy.

2. COMPUTATIONAL DETAILS

Simulation of $Ta_{(1−x)}V_xON$ structures was performed by considering the monoclinic crystalline structure of $TaON$ (space group $P2_1/c$; Ta is in Wyckoff position 4e) as experimentally identified using the neutron and synchrotron diffraction analysis.21,24,33,34 Several structural configurations...

Received: September 16, 2016
Accepted: November 17, 2016
Published: November 29, 2016
with different V models of TaON, which contains 32 functional units, by substituting various Ta atoms with V. Particular attention was paid to key structures showing well-dispersed or agglomerated V to identify the lowest energy configurations. The generic Ta_{32-3p}V_{3p}O_{32}N_{32} supercell model adopted in the calculations leads to the corresponding stoichiometry Ta_{(1-x)}V_xON (x = p/32). Ta_{(1-x)}V_xON structures with x = 0.125, 0.25, and 0.5 were modeled by giving p values of 4, 8, and 16, respectively. The explored structural configurations were fully relaxed by DFT using the VASP program along with the Perdew–Burke–Emzerhof (PBE) functional and the projector-augmented plane wave approach. The considered valence electrons were 5d^36s^2 for Ta, 3p^63d^44s^1 for V, 2s^22p^4 for O, and 2s^22p^3 for N. A 3 × 3 × 3 Monkhorst–Pack-type k-point grid was considered to sample the Brillouin zone. 

Thermodynamic stability of the explored Ta_{(1-x)}V_xON materials relative to the pure TaON and VON phases was investigated using the reaction indicated in eq 1, respectively.

\[ (1 - x)\text{TaON} + x\text{VON} \rightarrow \text{Ta}_{(1-x)}\text{V}_x\text{ON} \]  

(1)

The reaction energy was computed using eq 2

\[ E_{\text{reaction}} = E_{\text{form}}(\text{Ta}_{(1-x)}\text{V}_x\text{ON}) - (1 - x)E_{\text{form}}(\text{TaON}) - xE_{\text{form}}(\text{VON}) \]  

(2)

where \( E_{\text{form}}(\text{Ta}_{(1-x)}\text{V}_x\text{ON}) \) is the formation energy of Ta_{(1-x)}V_xON, which was computed using eq 3

\[ E_{\text{form}}(\text{Ta}_{(1-x)}\text{V}_x\text{ON}) = E_x(\text{Ta}_{(1-x)}\text{V}_x\text{ON}) - (1 - x)E_x(\text{Ta}) - xE_x(\text{V}) \]  

(3)

As can be seen, eq 3 takes into account the 0 K electronic energy of Ta_{(1-x)}V_xON, Ta, and V solids in the most stable configurations and of N and O molecules in the gas phase and the thermal component of the chemical potentials of nitrogen (\( \Delta \mu_N \)) and oxygen (\( \Delta \mu_O \)), which depend on the temperature and pressure through the entropy and enthalpy terms of each molecule in the gas phase, as indicated in eq 4

\[ \Delta \mu_{ON} = h_{O_2}N_2(T) - T\Sigma_{O_2,N_2}(T) + RT \ln \left( \frac{p(O_2)N_2}{P_0} \right) \]  

(4)

Note that the thermal contributions of each gas phase molecule were calculated with the DMol program by applying the PBE functional in connection with the DNP basis set by systematically including the zero point vibrational energy, whereas those for solids were not considered. The electronic energies of the solid-state molecules were calculated with VASP. Here, \( \Delta \mu_O \) and \( \Delta \mu_N \) were set to −0.22 and −0.18 eV, respectively, to be under standard conditions (\( T = 298 \) K and \( p(O_2) = p(N_2) = 1 \) atm). Positive or negative reaction energy leads to a less or more stable system than TaON or VON. Note that the formation energies of TaON and VON solids in eq 2 were calculated using eq 3 for \( x = 0 \) and 1, respectively.

Investigating the electronic structures of Ta_{(1-x)}V_xON semiconductor compounds was done by DFT with the HSE06 exchange-correlation functional using the VASP software. The optical spectra were simulated using the sum over empty states approach as described in VASP together with HSE06. The absorption coefficient of solids was calculated as in eq 5

\[ \alpha(\omega) = (4\pi/\lambda)k(\omega) \]  

(5)

where \( \lambda \) and \( \omega \) correspond to the frequency and wavelength of the upcoming photon. \( k(\omega) \) represents the imaginary part of the refractive index, which is defined by eq 6

\[ k(\omega) = \left\{ \left[ (\epsilon_i^2 + \epsilon_r^2)^{1/2} - \epsilon_i \right]/2 \right\}^{1/2} \]  

(6)

The imaginary part \( \epsilon_i(\omega) \) of the frequency-dependent dielectric function is obtained from the momentum matrix elements of transitions between the various filled to empty states, as in eq 7

\[ \epsilon_i(\omega) = \frac{2e^2}{\Omega} \sum_{i \neq r} \sum_k |\langle \Psi^i_k | \hat{r} | \Psi^r_k \rangle|^2 \delta(E^i_k - E^r_k - \hbar \omega) \]  

(7)

Here, \( k \) is the k-point in the Brillouin zone, \( \Omega \) represents the unit cell volume, \( \omega \) is the incident light frequency, and \( v \) and \( c \) are the respective valence and conduction bands. \( \Psi^i_k \) and \( \Psi^r_k \) represent the eigenstates, \( \hat{r} \) the external field vector with \( r \) the momentum operator. As the dielectric function describes the causal response, the real part \( \epsilon_r(\omega) \) was derived from the imaginary part through the transformation of Kramers–Kronig, see eq 8.

\[ \epsilon_r(\omega) = 1 + \frac{2}{\pi} \int_0^{\infty} \frac{\omega' \epsilon_i(\omega')}{\omega^2 - \omega'^2} d\omega' \]  

(8)

The dielectric constant tensor at high frequency (\( \epsilon_{\infty} \)) of the crystal was obtained by computing the self-consistent response while applying an electric field from the external region, using VASP with HSE06. This method includes local field effects by optimizing the crystal orbitals after applying the electric field. The vibrational dielectric constant (\( \epsilon_v \)) tensor was determined by computing the spectrum of phonons using the density functional perturbation theory (DFPT) approach along with the linear response approach, as ascribed in VASP with the PBE functional. The static dielectric constant tensor (\( \epsilon_0 \)) was then deduced from the addition of both optical and vibrational parts.

The tensors of hole and electron effective masses generated on the energy levels of the band edges of the semiconductor were obtained from the HSE06-computed electronic band structure through eq 9

\[ m^*(i,j) = \pm \hbar^2 \left( \frac{\partial^2 E_n(k)}{\partial k_i \partial k_j} \right)^{-1} (i,j) \]  

(9)

Here, \( i \) and \( j \) represent the reciprocal components and \( E_n(k) \) is the \( k \)-space dispersion relation for the \( n \)-th band level. The second derivatives of the energy with respect to the wave vector in the Brillouin zone were numerically computed by means of the finite difference approach.

The binding energy of the exciton was calculated using the hydrogenic model and eq 10

\[ E_b = \frac{\mu}{m_0^2}R_{11} \]  

(10)

Here, \( R_{11} \) is Rydberg’s constant in the atom of hydrogen (13.6 eV), \( m_0 \) denotes the mass of the free electron, and \( \epsilon_0 \) is the
arithmetic average of the tensor values in the three main crystal orientations, and \( \mu \) is the reduced mass of the exciton given by eq 11

\[
\frac{1}{\mu} = \frac{1}{m_h} + \frac{1}{m_e}
\]

where \( m_h^g \) and \( m_e^g \) denote the geometric averages of the tensor values in the three main crystal orientations.

Figure 1. Depictions of the DFT-optimized lowest energy structures of \((Ta_{1-x}V_x)ON\) materials with various V contents occupying Ta sites (Ta in the Wyckoff position 4e) obtained using PBE: (A) \( x = 0.125 \) or 12.5\% V, (B) \( x = 0.25 \) or 25\% V, and (C) \( x = 0.5 \) or 50\% V. Ta is in light blue, V in green, N in dark blue, and O in red. The substitutional V species at Ta sites are displaced in bigger ball sizes.

Table 1. Reaction Energies at Room Temperature (in eV) and Lattice Constants Obtained with PBE of the Lowest Energy \((Ta_{1-x}V_x)ON\) Structures Reported in Figure 1

| stoichiometry       | structure | reaction energy (eV) | cell lengths (Å) and angles (deg) |
|---------------------|-----------|----------------------|-----------------------------------|
|                     |           |                      | \( a \)   | \( b \)   | \( c \) | \( \alpha \) | \( \beta \) | \( \gamma \) |
| TaON                | Expt\(^{1,14}\) |                      | 4.96      | 5.02      | 5.17  | 90       | 99.8      | 90       |
| TaON                | Expt\(^{16}\) |                      | 4.95      | 5.01      | 5.16  | 90       | 99.6      | 90       |
| TaON                | (DFT)     |                      | 4.97      | 5.03      | 5.18  | 90       | 99.7      | 90       |
| \( Ta_{0.75}V_{0.25}ON \) | (1A)     | 0.23                 | 4.94      | 5.01      | 5.15  | 90       | 99.7      | 90       |
| \( Ta_{0.75}V_{0.25}ON \) | (1B)     | -0.23                | 4.92      | 4.97      | 5.13  | 90       | 99.6      | 90       |
| \( Ta_{0.75}V_{0.25}ON \) | (1C)     | -0.57                | 4.85      | 4.88      | 5.07  | 90       | 99.3      | 90       |

Figure 2. Electronic density of states of \((Ta_{1-x}V_x)ON\) materials with different V concentrations obtained with HSE06: (a) \( x = 0 \), (b) \( x = 0.125 \), (c) \( x = 0.25 \), and (d) \( x = 0.5 \).

\( Ta_{0.75}V_{0.25}ON \)—vacuum interface was simulated by building a \((2a \times 1b)\) slab containing eight atomic layers with a vacuum along the \( c \) direction to select the (001) surface. The slab was fully optimized by maintaining the cell parameters constant at the bulk relaxed values. The thickness of vacuum was carefully refined to neglect any possible electron interaction of the two opposite slab borders. Moreover, the slab thickness required to reproduce the bulk bandgap was also carefully checked.
thickness of 20 Å for the slab (eight atomic layers) and a thickness of 20 Å for the vacuum well reproduced the bulk signature of this semiconductor compound. The absolute energy of vacuum was deduced from the calculation of the averaged local potential along planes that are parallel to the (001) surface of Ta$_{0.75}$V$_{0.25}$ON using the HSE06 functional, as described in VASP. The correction of possible errors generated by the periodic conditions was done by adding dipole corrections to the total local potential calculation.  

3. RESULTS AND DISCUSSION

3.1. Characterization of Crystal Structure and Thermodynamics. The stability of the explored (Ta$_{1-x}$V$_x$)$_3$ON structures was examined to check whether it was thermodynamically possible to incorporate V at Ta sites into the monoclinic lattice of Ta$_3$ON. Figure 1 presents the DFT-optimized lowest energy (Ta$_{1-x}$V$_x$)$_3$ON structures for $x = 0.125, 0.25$, and 0.5, whereas Table 1 summarizes their computed reaction energy and cell parameters.

The optimized cell constants of Ta$_3$ON reproduce very well the experimental data. Its structural configuration consists of sharing irregular TaO$_5$N$_4$ polyhedra by edges. Each Ta is linked to three O and four N with bond lengths of Ta−O located in the 2.03−2.15 Å range and bond lengths of Ta−N in the 2.06−2.13 Å range. With respect to the (Ta$_{1-x}$V$_x$)$_3$ON materials for $x = 0.125, 0.25$, and 0.5, the most stable configurations show dispersed V species with V−V distances varying from 5.0 to 7.23 Å. Upon geometry relaxation, the new V locations were very slightly displaced as compared with the initial locations of Ta inside the lattice of Ta$_3$ON. This gives very similar lattice constants as found in the monoclinic phase of Ta$_3$ON (Table 1). Discussing now the energetics of the lowest energy structures with $x = 0.125, 0.25$, and 0.5, we can clearly see that their calculated reaction energies are negative with values of −0.08, −0.23, and −0.57 eV, respectively (see Table 1). This result indicates that these materials seem to be thermodynamically more stable than Ta$_3$ON or VON. Other geometrical configurations for $x = 0.125, 0.25$, and 0.5, with more separated V by shorter V−V distances going from 3.22 to 3.95 Å, showed slightly less stability by 0.06, 0.07, and 0.09 eV than the previous cases, respectively.

3.2. Bandgap Narrowing and Visible-Light Optical Absorption Enhancement with Increasing V Concentration. Figure 2a displays the calculated electronic structure using HSE06 for Ta$_3$ON and 3.0 eV as a bandgap value was predicted, and this was reasonably close to the measured one of 2.8 eV. The valence band edge energy levels mainly consist of N 2p states with little implications of Ta 5d and O 2p states. The conduction band edge energy levels consist of unoccupied Ta 5d orbitals. For this semiconductor, the energy of the bandgap involves direct optical transitions from N 2p$^6$ to Ta 5d$^6$ orbitals.

For (Ta$_{1-x}$V$_x$)$_3$ON, the HSE06-computed bandgaps are much narrower than that obtained for Ta$_3$ON (see Figure 2b−d). Bandgaps of 2.3 and 2.0 eV are obtained when V concentration is increased to 12.5 and 25%, respectively (see Figure 2b,c). An additional increase in the V concentration to 50% again reduces the bandgap energy up to 1.6 eV, as displayed in Figure 2d. The electronic analyses show lower density of Ta 5d orbitals accompanied by higher V 3d density orbitals in the conduction band while increasing the V concentration (Figure 2b−d). As a consequence, the conduction band states located within a wide energy range of these compounds are predominant by unoccupied V 3d orbitals (Figure 2b−d). As expected, in all cases, the upper part of the valence band states is principally made by N 2p orbitals similarly as obtained in Ta$_3$ON. Therefore, the lowest energy bandgap energy of these materials originates from direct N 2p$^6$−V 3d$^0$ orbital excitations. The impact of the spin−orbit interaction on the electronic structures of these materials was also checked and very small bandgap energy reductions, 0.01 eV only, were found.

We have also investigated the light absorption properties of the considered (Ta$_{1-x}$V$_x$)$_3$ON materials by calculating their UV−visible optical absorption coefficient in terms of incident photon wavelength. For Ta$_3$ON, an absorption onset at around 400 nm was revealed from the computed spectrum (Figure 3a).

Abs. \( (x \times 10^{19} \text{cm}^{-2} \text{eV}^{-1}) \)

Wavelength (nm)

Figure 3. Absorption edges of (Ta$_{1-x}$V$_x$)$_3$ON compounds simulated with HSE06 for (a) 0% V, (b) 12.5% V, (c) 25% V, and (d) 50% V. The calculated spectrum shown in pink (curve (e)) corresponds to Ta$_3$N$_5$.
holes and photoexcited electrons. On the basis of these conditions, we mainly focused, in what follows, on the Ta0.75V0.25ON material with this optimal composition to investigate the dielectric constant, charge-carrier transport, and band edge energy positions with respect to water-splitting limits. We systematically compared the computed results with those obtained for Ta3N5.

3.3. Optical/Static Dielectric Constant and Hole/Electron Effective Mass Tensors of Ta0.75V0.25ON: Comparison with Ta3N5. The calculated nonzero values of the high-frequency and static dielectric constant tensors of the Ta0.75V0.25ON crystal in the three principal directions together with those obtained for Ta3N5 are reported in Table 2. For Ta0.75V0.25ON, we found $\varepsilon_0$ values of 28.1, 41.7, and 28.0 in the three respective [100], [010], and [001] principal directions with an averaged value of 32.6. As the obtained value is quite higher than 10, this indicates that the Ta0.75V0.25ON crystal has excellent dielectric properties. Interestingly, the static dielectric constant is dominated by the vibrational component (see Table 2 for more details), which may come from the high electronegativity of nitrogen and oxygen leading to important Born charges generated in this system. Our computed static electronegativity of nitrogen and oxygen leading to important Born charges generated in this system. Our computed static electronegativity of nitrogen and oxygen leading to important Born charges generated in this system. Our computed static electronegativity of nitrogen and oxygen leading to important Born charges generated in this system. Our computed static electronegativity of nitrogen and oxygen leading to important Born charges generated in this system. Our computed static electronegativity of nitrogen and oxygen leading to important Born charges generated in this system.

Table 2. High-Frequency ($\varepsilon_{\infty}$) and Static ($\varepsilon_0$) Dielectric Constant Components in the Three Principal Directions of Ta0.75V0.25ON and Ta3N5 Crystals Obtained with PBE and HSE06

|          | Ta0.75V0.25ON | Ta3N5 | Ta0.75V0.25ON | Ta3N5 |
|----------|---------------|-------|---------------|-------|
| [100]    | 10.3          | 9.0   | 28.1          | 33.2  |
| [010]    | 12.8          | 8.7   | 41.7          | 37.6  |
| [001]    | 11.3          | 8.0   | 28.0          | 51.5  |

To evaluate the possibility of the exciton to be dissociated to free holes and electrons by considering the material Ta0.75V0.25ON, we have calculated the exciton binding energy using the hydrogenic model. A low value of 4.7 meV was obtained for Ta0.75V0.25ON, which is lower than the thermal energy at 298 K, and hence, a facile separation of exciton to free holes and electrons could be achieved using Ta0.75V0.25ON. Because our computed value of this material is very close to 4.4 meV, as was obtained for Ta3N5, the ability of the exciton to be dissociated to free charge carriers using the Ta0.75V0.25ON material is expected to be good and similar to that of Ta3N5.

With respect to the calculated hole and electron effective mass tensors of Ta0.75V0.25ON and Ta3N5, crystals, high anisotropies are found in the obtained values along the three crystallographic directions as shown in Table 3. The smallest hole effective mass of Ta0.75V0.25ON is found to be in the [001] direction with a value of 0.20$m_0$. The lowest effective mass of electron of 0.38$m_0$ was obtained in the [010] direction. As a result, the highest mobility of holes could be in the [001] orientation, whereas the highest electron mobility could be in the direction as shown. Both effective masses are smaller than $0.5m_0$, good transport properties of charge carriers are expected in these two particular crystal orientations. We stress here that the migration of electrons and holes seems to be easy along these two particular orientations; therefore, the separation of electrons and holes could be achieved at this compound surface. In contrast, the effective masses of holes in the [100] and [010] orientations and those of the electrons in the [100] and [001] directions are quite large; therefore, the transport properties of holes and electrons are expected to be poor in these two directions. Interestingly, our lowest effective masses computed for Ta0.75V0.25ON ($m^h_0 = 0.12m_0$, $m^e_0 = 0.18m_0$) are found to be much lower than those obtained for Ta3N5 ($m^h_0 = 0.84m_0$, $m^e_0 = 0.62m_0$), yielding much better transport properties than Ta3N5.

Table 3. Electron ($m^e_0$) and Hole ($m^h_0$) Effective Masses along the Three Principal Directions of Ta0.75V0.25ON and Ta3N5 Crystals Obtained with HSE06

|          | Ta0.75V0.25ON | Ta3N5 | Ta0.75V0.25ON | Ta3N5 |
|----------|---------------|-------|---------------|-------|
| [100]    | 1.93          | 3.38  | 1.43          | 1.94  |
| [010]    | 1.17          | 0.84  | 0.38          | 0.62  |
| [001]    | 0.20          | 0.84  | 0.73          | 0.62  |

$m_0$ is the mass of the free electron.

4. CONCLUSIONS

In the context of screening possible materials for photocatalytic water splitting, we have investigated the thermodynamic stability as well as the redox and optoelectronic properties of (Ta$_{1-x}$V$_x$)$_{2-x}$ON solid solution semiconducting compounds (with $x = 0.12S$, 0.2S, and 0.5S) by means of calculations based on DFT (together with the perturbation approach DFPT) using both GGA-PBE and screened Coulomb hybrid HSE06 functionals.

Our study predicted Ta0.75V0.25ON as a promising photocatalyst for splitting of water driven by solar light, with an adequate bandgap of 2.0 eV, high absorption efficiency, a static
dielectric constant greater than 10, smaller hole and electron effective masses than \(0.5m_0\) along the [001] and [010] crystallographic directions respectively, binding energy of the exciton lower than 25 meV, and suitable energy levels of band edges for water-splitting limits. The obtained solar energy absorption and redox features of \(\text{Ta}_{0.75}\text{V}_{0.25}\text{ON}\) were clearly better than those acquired for \(\text{Ta}_3\text{N}_5\), which is the most common semiconductor photocatalyst used in visible-light-driven water splitting.

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**ACKNOWLEDGMENTS**

The research for this paper was conducted in the King Abdullah University of Science and Technology (KAUST). The authors warmly acknowledge the High Performance Computing department (HPC) at KAUST for the CPU time attributed to this research work.

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