THE ELECTRONIC STRUCTURE OF InVO$_4$ PHOTO-CATALYSTS WITH WATER MOLECULE ADSORBED ON THE SURFACE

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Introduction

It is known that an InVO$_4$ photo-catalyst system indicates a visible light response in H$_2$ generation up to the wavelength of approximately 600 nm [1, 2] from water (but no O$_2$) and a BiVO$_4$ system also indicates an visible light response in O$_2$ generation up to the wavelength of approximately 520 nm [3] (but no H$_2$). On the other hand, a YVO$_4$ system shows a good performance in production of both H$_2$ and O$_2$ but only in the ultra-violet region with co-catalyst NiO$_x$ [4]. However, it has not yet been cleared well why they show such contrasting photo-catalytic features. For unraveling this issue, we have stated systematic study on the effect of the water molecule adsorption to the surface of their photo-catalysts on the electronic structure properties of the systems by first principles approach. In this conference, we will report mainly on the locations of the energy levels derived from oxygen atoms located at the slab surface and those belonging to the water molecules adsorbed to InVO$_4$ metal oxide photo-catalyst surfaces.

Crystal structure properties

The InVO$_4$ crystal (an orthorhombic system, the space group Cmcm) [5] includes 4c-V and 6c-In structures (Fig. 1 (a)). The In-O distances of the InO$_6$ octahedron are almost identical at about 2.16 Å. Each VO$_4$ tetrahedron is isolated and not linked to other VO$_4$ tetrahedra. Therefore, the V-V distance is relatively large (4.05 Å). The characteristic V-O distance is 1.66-1.79 Å. The shortest O-O distance is ~ 2.7 Å and the In-In distance is 3.3 Å whereas the In-V distance is ~ 3.5 Å. The InVO$_4$ crystal has a laminated structure in contrast to the YVO$_4$ crystal. The CBM of bulk InVO$_4$ is spanned by mainly V_3d atomic orbitals (~59 %) and In_5s atomic orbitals (~19 %), and the VBM is composed of O_2p (~81 %).

Simulation model

We prepared a slab model exposing the (001) surface of InVO$_4$. The concerned top surface includes four 3c-V structures. Indium sites closest to the top surface are surrounded by six oxygen atoms (6c-In) The super cell includes two conventional unit cells of InVO$_4$ corresponding to a size of 2a × b × c as a slab part.
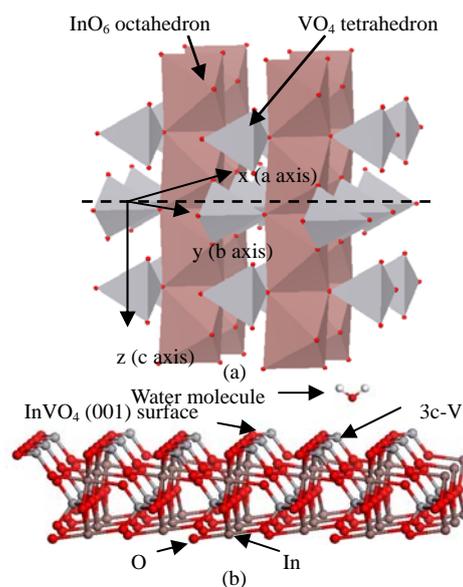

Fig. 1 (a): Crystal structure of InVO$_4$; (b): sketch of the slab surface with a water molecule.

The super cell size is 2a × b × (c + water layers) = 11.53 × 8.542 × 16.5 Å^3 (= 1.62 nm^3). A size of the simulated surface is 2a × b = 98.5 Å^2. It is roughly identical to the size of one mono-molecular H$_2$O layer including ten H$_2$O molecules (10 × 3.1^2 = 96.1 Å^2) in a normal room condition. We have investigated the electronic structures of bulk system, slab system without water molecule and the system with a single water molecule adsorbed on the surface (Fig. 1 (b)). The slab is composed of 8 In, 8 V, and 32 O atoms. The electronic structure properties were checked by using the relaxed systems after they had reached thermal equilibrium stage at 300K.

Computational frame work

First-principles thermal relaxation simulations were performed within the Car-Parrinello scheme (CPMD) [6] using a Becke-Lee-Yang-Parr gradient corrected approach. The valence-core interaction was taken into account via norm-conserving Troullier-Martins pseudopotentials for V, In, and O atoms. For H, a Car-von Barth pseudopotential was used. In the case of V, the use of semi-core states was needed in order to obtain a good description of both the geometry and

the energetics. For In, non-linear core correction was included. The electrons of V 3s, 3p, 3d, 4s; In 5s, 5p; O 2s, 2p; H 1s were included in the valence electrons. Valence wavefunctions were expanded in plane waves with an energy cut-off of 80 Ry. A fictitious electronic mass of 1200 a.u. and an integration step of 5.0 a.u. ensured a good control of the conserved quantities. After the thermal relaxations, we compute the electronic structures by diagonalizing the Kohn-Sham matrix.

Results

In the thermal relaxation process in the system with a single water molecule, we observed water molecule dissociation at the 3c-V site. Whenever a water molecule approaches the exposed V atoms of 3c-V structures, a strong interaction occurs between V and the lone pair of electrons of the O atom of the H_2O molecule. Soon later, not only is the O_{water} atom attracted by the $V_{surface}$ but the H_{water} atoms are also drawn to the $O_{surface}$ atoms to form hydrogen bonds. Then the water molecule was firmly captured by the $V_{surface}$ and $O_{surface}$ and the water molecule was adsorbed dissociatively. At the moment the water molecule dissociated, the distance between the O_{water} and the $V_{surface}$ was about 1.9 Å. After the dynamics for about 1 psec, the geometry of the system was optimized. The separated hydroxyl -O-H from the water molecule was bound to 3c-V forming VO_4 tetrahedral structure and the other hydrogen atom was bound to $O_{surface}$. The V-O equilibrium distances of the VO_4 are ~ 1.8 Å (Fig. 2).

Fig. 3 indicates the electronic structures of (a) the $InVO_4$ bulk crystal, (b) slab system without water molecule and (c) that with the dissociated water molecule on the surface, respectively. In (b) and (c), the energy levels including large weight of the wavefunctions of O_2p located at the slab surface
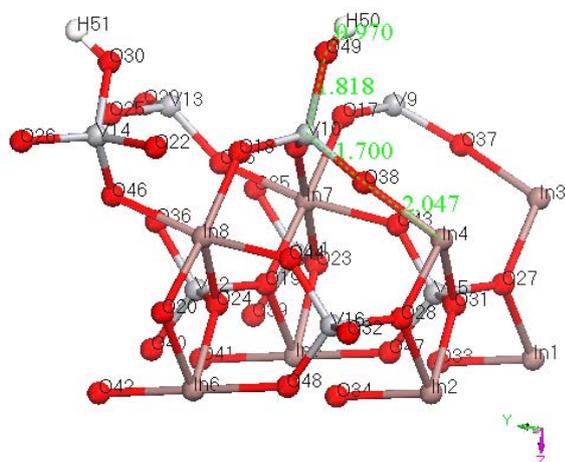

Fig. 2 Diagram of water molecule adsorption on the top surface formed by 3c-V structures. Atomic distance is Å unit.
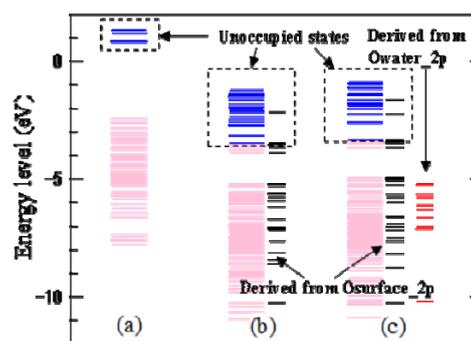

Fig. 3 The electronic structures of (a) the $InVO_4$ bulk crystal, (b) slab system without water molecule and (c) that with the dissociated water molecule on the surface, respectively.

are indicated just in the right side of the whole energy levels. In addition to those levels, the energy levels including large weight of the orbitals of O_2p of the adsorbed water molecule is shown in (c). The (c) indicates that the occupied energy levels derived from an adsorbed water molecule are located in relatively lower positions than those from the oxygen atoms which are located at the slab surface.

Conclusions

Throughout our studies, it has been found that the O_2p orbitals located at the slab surface span the surface level in the $InVO_4$ photo-catalyst system and the level is located at higher position than the energy levels derived from the adsorbed water molecules. This fact should lead to suppressing the direct oxidization of the O^{2-} belonging to the adsorbed water molecule. It may lead to understanding the reason why $InVO_4$ photo-catalyst system can not produce O_2 and provide us some clues to improve the system so as to generate O_2 in visible light wavelength region.

References

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