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All-Electron *GW* Approach for Light-Element-Doped Anatase TiO_2

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All-electron *GW* approach based on the many-body perturbation theory was adopted to determine the electronic structures and understand the mechanism of band gap narrowing for anatase TiO_2 doped with light elements (such as C and N) and its various defect states. It is clearly shown that the band gap could be controlled by the oxygen pressure and doping states, and C, N codoping narrowed the band gap more than monodoping.

TiO_2 is known as a photocatalytic material, and its band gap corresponds to the UV region. Adding visible-light responsive photocatalytic functionality to TiO_2 by doping of impurity elements such as C and N could promote its technological applicability. An example is the TiO_2 coating on Ti dental implants to achieve antibacterial properties, which are induced by its photocatalytic reactions.

In this study, we determine the electronic structures of C- and N-doped anatase TiO_2. To do this, we first construct various models of C and N monodoped and codoped TiO_2 considering the oxygen vacancy(ies) and estimate the stable models through formation energy analysis as a function of the oxygen (O_2) pressure or oxygen chemical potential. Then, for the stable models, *GW* calculations using the all-electron mixed basis approach are performed to analyze the electronic structures and clarify the mechanism of band gap narrowing that originates because of impurity doping. Finally, we discuss a possible way to realize an oxygen pressure condition under which visible-light response TiO_2 can be synthesized.

The *GW* method has been implemented in the TOhoku Mixed Basis Orbitals ab initio program (TOMBO) [1]. TOMBO uses the all-electron mixed basis approach, in which the electronic wave function is expressed by a linear combination of plane waves and atomic orbitals.

The stability of the C- and N-doped models varies depending on the oxygen pressure conditions. Furthermore, the all-electron *GW* calculations indicate that the band gaps of the C- and N-doped models are found to be narrowed primarily owing to impurity levels introduced in the gap. Figure 1 (a) summarizes the stable models and their band gaps as functions of the oxygen pressure at 700K or oxygen chemical potential. It is shown that the band gaps vary by up to 1 eV and that codoping with C and N is more effective for narrowing the band gap when compared with monodoping.

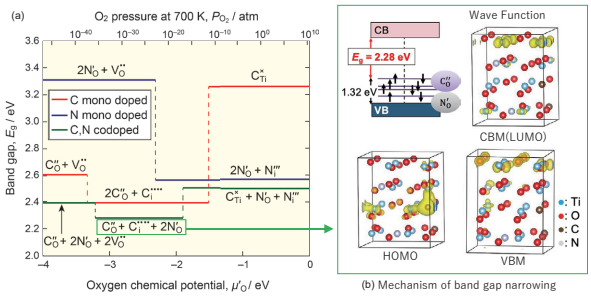

Fig. 1 (a) Relationship between the band gap and oxygen pressure (or oxygen chemical potential) for C- and N-doped anatase TiO_2, and (b) Mechanism of band gap narrowing for the $C_O^{''} + C_i^{\bullet\bullet\bullet\bullet} + 2N_O^{'}$ model.

Among the stably doped models identified in this study, the $C_O^{''} + C_i^{\bullet\bullet\bullet\bullet} + 2N_O^{'}$ model under the medium oxygen pressure condition exhibited the smallest band gap (2.28 eV).

Figure 1(b) shows the mechanism of band gap narrowing for the $C_O^{''} + C_i^{\bullet\bullet\bullet\bullet} + 2N_O^{'}$ model. The band structure shows that the occupied impurity levels derived from $C_O^{''}$ and $N_O^{'}$ in the gap led to a narrowing of the band gap. Selected wave functions of CBM (conduction band minimum), HOMO (highest occupied molecular orbital), and VBM (valence band maximum) are also shown.

A possible means to synthesize TiO_2 could be the thermal oxidation of Ti in the gas mixture of CO-CO_2-N_2 under intermediate oxygen pressure conditions, which suggests that visible light photocatalytic materials based on anatase TiO_2, could be manufactured through C and N codoping [2].

References

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