

Titanium oxide (TiO_2) is now drawing much attention from engineering and scientific viewpoint. This semiconductor material can be used for photocatalysis, photoelectrolysis, and solar cell devices. However, the pure bulk compound has large band gap 3.2eV(rutile) and is transparent to visible light. Therefore only the small UV fraction of sunlight can be utilized. To overcome this shortcoming, a lot of experimental studies have been carried out. Recently, several experimental results revealed that carbon-doped (C-doped) TiO_2 is photocatalytic under visible light. The mechanism of these doped TiO_2 are discussed and interpreted in several ways, but the detailed microscopic mechanism is still unclear.

To clarify this mechanism, we theoretically investigated the C-doped rutile TiO_2 , as assessed by the band structure (periodic doping assumed), the density of state, and the electronic density of each band. We also carried out these analyses with oxygen-vacancy (O-vacancy) structure. The O-vacancy is the origin of the N-carrier in TiO_2 and widely exists in the ordinary TiO_2 . Since the Ti-N bonding is confirmed by XRD experiment in the case of N-doping, we first examined anion-doping case (substituting oxygen atom by carbon atom).

As a result, we confirmed that the carbon doping results in visible light response. We also clarified that the microscopic mechanism of such response is due to the electron transition from valence band of TiO_2 to impurity state caused by the doped carbon. Since the main reason of photocatalytic reaction is considered to be the strong reduction power of electron hole at valence band, this electron transition is reasonable.

It is also confirmed that the O-vacancy results in carrier electrons in conduction band. Because the energy level of these states is higher than the impurity state, electron from O-vacancy is considered to transfer to the above mentioned impurity state, if possible. As a result, O-vacancy is suspected to prevent the photocatalysis.

Furthermore, we found that neighboring of C-doping and O-vacancy at certain orientation strongly stabilizes the internal energy in comparison with the isolated two. A simple thermodynamic analysis is also carried out and the formation of such C-doping and O-vacancy pair is confirmed to be satisfactory stable under experimental doping rate, defects rate and temperature. Although similar visible light response was seen in C-doping and O-vacancy pair, the electronic transition was found to be quite different from the simple C-doped case. Consequently, C-doping and O-vacancy pair is also suspected to prevent photocatalysis.

In the presentation, we will discuss the structure of C-doping, O-vacancy, and the pair of C-doping and O-vacancy in rutile TiO_2 . Similar analyses for cation-doped case, and anion/cation-doped anatase structure will be also addressed if we have a time.

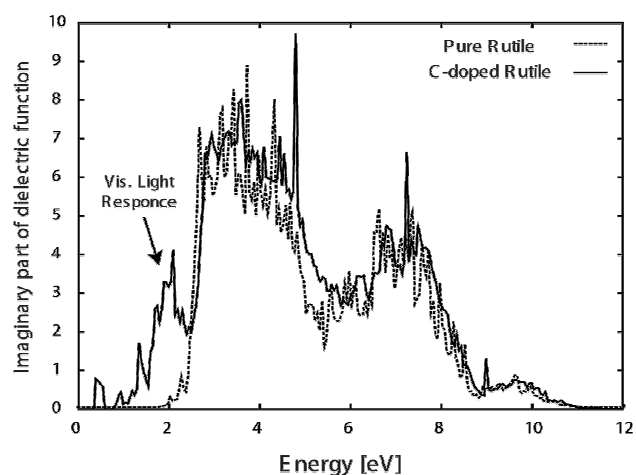


Fig.1: Optical response of pure rutile TiO_2 and C-doped rutile TiO_2 . Unit cell with 8 times larger volume than the primitive cell was employed. The C-doped cell was prepared by substituting one oxygen atom with carbon atom, and by optimizing the structure afterward. It is clearly seen that visible light response was introduced.

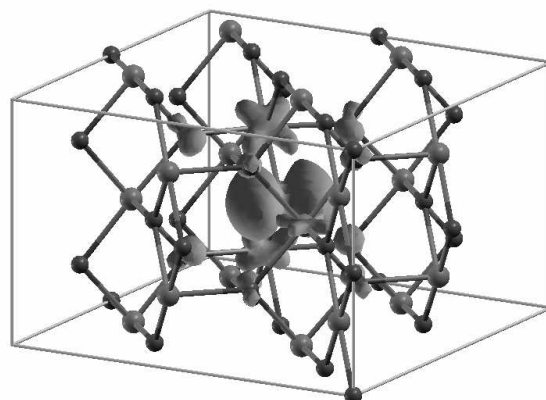


Fig.2: Isosurface plot of the electron density at impurity state. Larger ball and smaller ball show Ti and O atom respectively. At the center of unit cell, doped carbon atom is located (hidden by the isosurface). Around the doped carbon, an impurity state is formed that acts as a trapping state from valence band by optical transition. It is shown that the trapping state has p orbital shape.