$La_2Ti_2O_7$ 광촉매의 전자구조와 물분해 활성

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Electronic Structure of La2Ti2O7 and Its Photocatalytic Activity in Water Splitting

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Introduction

Despite a number of studies about photocatalytic materials for water splitting, satisfactory explanation for their high activity have not been obtained. Recently, among lanthanide titanites, La2Ti2O7 have been reported to have good photocatalytic activity in water splitting reaction under UV irradiation when combined with nickel oxide. In our previous paper, we concluded that its high photocatalytic activity resulted from both layered structure and its peculiar electronic structure that the slab constructing the layered structure has hyper-valency different from conventional perovskite oxide such as SrTiO3. La2Ti2O7 with monoclinic structure with a space group of P21 is classified into layered perovskite oxide. It has been accepted generally that the peculiar structure of photocatalyst materials plays a crucial role in photocatalytic water splitting reaction, as shown in many other photocatalysts such as K4Nb6O17, BaTi4O9, La2Ti2O7 etc. However, we have to consider another factor, electronic structure of photocatalyst, since its optical property is determined by its electronic structure. Here we report the electronic structure of La2Ti2O7 with very high photocatalytic activity under UV irradiation and the relationship between its electronic structure and photocatalytic activity.

Experiment

Sample Preparation and Photocatalytic Reaction

For the preparation of the La2Ti2O7 photocatalysts, stoichiometric mixture of La2O3 (Aldrich 99.999%) and anatase-TiO_2 (Aldrich 99.99%) was mixed and ground in mortor in the presence of ethanol and dried in an oven. The dried powders were pressed in the form of a pellet. Pellets were calcined at 1323 K for 10 h in static air. Calcined samples were converted to the active photocatalysts (NiO/Ni/Perovskite) by loading 1.0 wt % of Ni metal from nickel nitrate solution by incipient-wetness impregnation method. The photocatalytic decomposition of water was carried out at room temperature and atmospheric pressure in a closed gas circulation system using a high pressure Hg lamp (450 W) placed in an inner irradiation-type quartz reaction cell. The catalyst (0.2g) was suspended in distilled water (500 mL) containing 500 ml by magnetic stirring. The amount of H_2 and O_2 were determined by a gas chromatograph equipped with TCD (molecular sieve 5A column).

Characterization of Photocatalyst

The crystal structure of the sintered powder was determined by X-ray diffraction (XRD, Mac Science Co., M18XHF) and the band gap energy was measured by UV-Vis diffuse reflectance spectroscopy (Shimadzu, UV 525).

Electronic Structure Calculation

The electronic structure calculation is based on the FLAPW method which uses the genaralized gradient approximation (GGA), an improvement of the local spin density approximation (LSDA) within density functional theory, known to be an efficient and accurate scheme for solving many-electron problem of a crystal. Wien97 package was used in this study.

Result and Discussion

La2Ti2O7 is a member of an homologous series of layered structures built from (110) perovskite slabs differing in thickness and bounded by crystallograpic shears in the perovskite [100] direction. Adjacent slabs are offset from one another by half of one TiO6 octahedron height and the octahedron connectivity is broken at the shear interface. At room temperature, the space group of this material is P21 and the unit cell has one axis double that observed in the alkali-metal niobates (Ca2Nb2O7) and tantalates (Sr2Ta2O7), i.e. b= 2 * a_o (cubic perovskite) = 7.8 A; the shortest axis is apparently common to all members to this structural family, $a=2^{1/2}a_o$ (cubic perovskite) = 5.6A. The schematic diagram of monoclinic La2Ti2O7 with space group of P21 is shown in Fig. 1. The atomic coordinates for calculation of electronic structure were adopted from the literature.

The muffin tin radius for La, Ti and O was chosen 2.3, 1.7, 1.6, respectively in this calculation. The conversionce parameter RKmax was set to 6.0, which gave the 19999 plane waves in the monoclinic phase. The calculation was iterated to self-consistency using interacive diagnolization with the charge convergence criterion of 0.001. The length of reciprocal lattice vectors are 4.926, 6.862, 2.958. The numbers of mesh points in the Brillouin zone is 48 and the division of the reciprocal lattice vectors (intervals) is 4×6×2 meshes, generating 12 inequivalent k-points.

Fig. 2 shows the total DOS and partial DOS of monoclinic La2Ti2O7. The core band exists from -18 to 12eV, which consists of mainly O2s and La5p. The valence band exists from -4 to 0eV, while main portion of conduction band exists from 3.2 to 10eV, although the continuous band exists even at energy higher than 10eV due to O2p. The band gap energy (the forbidden band gap between VB and CB) was about 3.2eV, which is a little underestimated value and comes from the some flaws of GGA. The valence band consists of mainly O2p, which is a little hybridized with Ti3d, which reflects that only small portion of Ti3d takes part in the interaction with O2p to construct the valence band. However, the conduction band consists of mainly Ti3d covering from 3.2 to 10eV, which split into two band of e_g and t_{2g}. La4f covers the conduction band from 5 to 6eV, which is completely localized from the Ti3d orbital. La 5d hybridized a little with Ti3d covers the latter part of conduction band from 8 to 10eV. O2p orbital also contributes to the conduction band and splits into two energy like Ti3d, which reflects that there is some electronic interaction between O2p and Ti3d. The electronic structure of 4 inequivalent La is similar for La, Ti and O atoms, which means that the bond distances between the environment atoms are not so different, as shown in Fig. 1. Fig. 3 shows the electronic band structure of monoclinic La2Ti2O7. The valence band from -4 to 0eV and conduction band from 0 to 10eV is shown in this figure. It is clear from this band structure that the band gap appears between the the highest value of VB and tthe lowest point of CB at the same Γ point.

As reported by our previous paper, photocatalytic activity of monoclinic La2Ti2O7 is much higher than TiO2, although the surface area of La2Ti2O7 (less than $2m^2/g$) is much lower that that of TiO2 P25 (more than $50m^2/g$). We also calculated the electronic structure of TiO2 with rutile structure. The band gap energy from this calculation was about 1.9eV, which is also underestimated value like monoclinic La2Ti2O7. The experimental band gap energy from UV-DRS was 3.2eV. The main difference in electronic structure between monoclinic La2Ti2O7 and TiO2 is the shape of conduction band and the valence band is not affected by La addition to TiO2, since La atom does not contribute to the valence band. The width of conduction band of La2Ti2O7 is 6.8eV, which is a little longer than that of TiO2 (6eV), because of the La 5d. In addition, the La5f orbital is located on the middle zone (5 to 6eV) of conduction band, which can connect smoothly the completely split-conduction band of TiO2. Photocatalytic activity of monoclinic La2Ti2O7 might be enhanced due to the wider conduction band than that of TiO2. As the conduction band is wider, the chance of electron-hole could be kept from being recombinated.

Conclusion

The electronic structure of La2Ti2O7 was calculated using GGA to DFT for the first time and the wider conduction band by La addition to TiO2 could play an important role in retardation of electron-hole recombination, and further the enhanced photocatalytic activity in water splitting.

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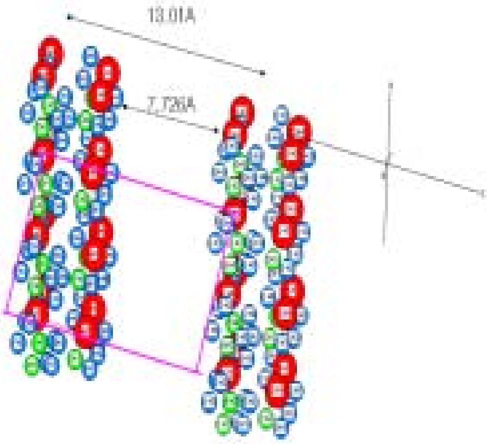

Fig. 1 Schematic Diagram of Monoclinic $La_2Ti_2O_7$

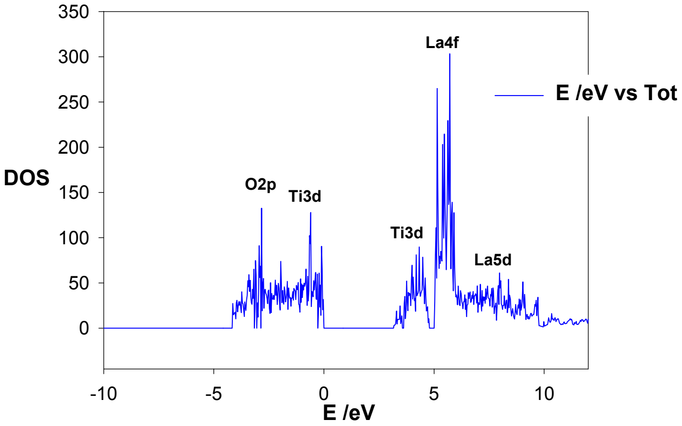

Fig. 2 Total Density of States of Monoclinic $La_2Ti_2O_7$

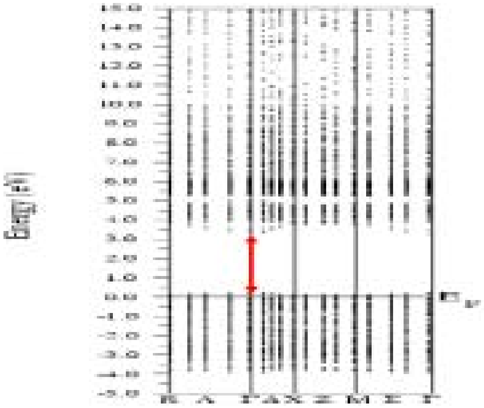

Fig. 3 The electronic band structure of monoclinic La2Ti2O7