

Structure Related Photocatalytic Properties of TiO₂

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The band structures and the densities of states at the Fermi energy for rutile, anatase and brookite phases are investigated along with the structure-photocatalytic relationship by using DFT method. Bands are less dispersive in anatase phase than in rutile phase, and they are almost flat in brookite phase. As a result, the DOS value near the Fermi energy for brookite is highest among three types of TiO₂, which means that the numbers of electrons near the Fermi energy are largest in brookite. The calculation shows that brookite phase may exhibit highest photocatalytic efficiency among three types of TiO₂.

Key Words: TiO₂, Brookite, DOS, Photocatalyst

Introduction

Titanium dioxide has three different structure types ; rutile, anatase, and brookite. All of these crystalline forms of TiO₂ occur in nature as mineral, but only rutile and anatase have been able to be synthesized in pure form at low temperature until recent days.¹ Therefore, anatase and rutile phases which belong to the tetragonal crystal system are widely studied on their syntheses, characterizations and photocatalytic properties.²⁻⁴ So far anatase phase is known to exhibit higher photocatalytic efficiency compared with rutile phase. Only little efforts have been made on the synthesis, characterization and properties of brookite phase which is belonging to the orthorhombic crystal system.⁵⁻⁷ The poor result on brookite phase is due to the difficulty in preparing the pure brookite-type TiO₂ without mixture of rutile or anatase phase. Recently, the method to synthesize pure brookite phase TiO₂ was reported,⁸ which means that versatile studies on the brookite phase can be ignited. In this paper, the band structures and densities of states (DOS) near the Fermi energy for rutile, anatase and brookite phase are calculated and investigated along with the structure-photocatlaytic relationship.

Calculation

The first principle calculations were performed for the three types of TiO₂ crystals within the density functional theory⁹ (DFT) formalism, using the Cambridge Serial Total Energy Package (CASTEP) software.¹⁰ The CASTEP software solves the Kohn-Sham equations with periodic boundary conditions and the pseudopotential method as an approximation of the atomic core-valence electron interaction, while the electronic wavefunctions are expanded in a plane wave basis. The Kohn-Sham band structure underestimates systematically the band gap often by more than 50%. However, the result shows a good representation, especially in band dispersion. We adopted the normalized conserving pseudopotentials provided within the package and the generalized gradient density approximation of Perdew, Burke and Ernzerhof (GGA-PBE)¹¹

for the exchange-correlation functional. The Brillouin zone was sampled with the Monkhorst-Pack scheme¹² using a k point separation of 0.04 Å⁻¹ in a 6 × 6 × 6 grid in reciprocal space. A plane wave energy cutoff of 500 eV and an energy convergence limit of 1×10⁻⁷ eV/atom were used in total energy calculations, guaranteeing a high level of convergence. The adopted structure of rutile, anatase and brookite was tetragonal, tetragonal and orthorhombic, respectively.

Results and Discussion

The bond distances of Ti-O and O-O in rutile, anatase and brookite are shown in Table 1. Generally, the degree of orbital interactions within a bond decreases with increasing the bond distance. Ti-O and O-O bond distances are longest in brookite, while those are shortest in rutile phase. It is expected, therefore, the orbital interaction is expected to be strong in rutile, but weak in brookite, which in turn results in the increase of the band width as rutile < anatase < brookite. Figures 1a and 1b show the band dispersion curve and density of states (DOS) of rutile structure, respectively. Bands around the Fermi energy are strongly dispersive and the DOS value within the window of ±1.0 eV of the Fermi energy is less than 5 e⁻/eV, as expected with the bond distances.

The calculated band gap of 2.1 eV is somewhat smaller than the experimental band gap of 3.2 eV, which is due to the origin of the Kohn-Sham method, as mentioned in introduction. Figures 2a and 2b demonstrate the band dispersion curve and density of states (DOS) of anatase structure, respectively. The band gap of 2.1 eV is almost similar to that of rutile, but bands are definitely less dispersive for the anatase phase compared

Table 1. The bond distances of Ti-O and O-O in Rutile, Anatase, and Brookite

	Ti-O (Å)	O-O (Å)
Rutile	1.91-1.94	2.43
Anatase	1.92-1.95	2.43
Brookite	1.87-2.04	2.49

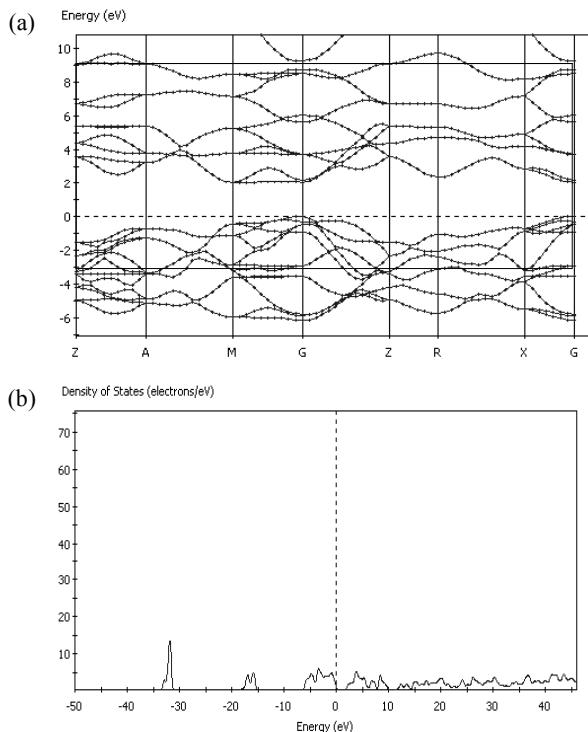


Figure 1. Calculated (a) band dispersion curve and (b) Density of States of rutile TiO_2 . G, X, M, Z, R, A represent (0, 0, 0, 0), (0, 0, 0, 0.5), (0.5, 0.5, 0.5), (0, 0, 0.5, 0.5), (0.5, 0.5, 0.5), (0.5, 0.5, 0.5) position, respectively, in the reciprocal lattice. The horizontal dashed line in dispersion curve and the vertical dashed line in DOS represent the Fermi energy.

with rutile phase, thereby exhibiting higher DOS value of about 15 e⁻/eV within the window of ± 1.0 eV of the Fermi energy. This means that anatase phase possesses larger number of electrons around the Fermi energy. The photocatalytic activity arises from the hydroxyl radicals and peroxide ions prepared through the following reactions:

1. $TiO_2 + h \rightarrow TiO_2 (e^-CB + h^+VB)$
 2. $TiO_2 (h^+VB + e^-CB) \rightarrow TiO_2$ (recombination)
 3. $TiO_2 (h^+VB) + OH^- \rightarrow TiO_2 + OH^-$
 4. $TiO_2 (e^-CB) + O_2 \rightarrow TiO_2 + O_2^-$
- CB : conduction band of TiO_2
VB : valence band of TiO_2

The degree of photocatalytic activity of TiO_2 is proportional to the number of electrons emitted by ultraviolet energy. The probability of electron emission is strongly related to the electron density near the Fermi energy. Therefore the higher photocatalytic efficiency of anatase phase compared with rutile phase is understood.

Figures 3a and 3b exhibit the band dispersion curve and density of states (DOS) of brookite structure, respectively. The band gap of 1.7 eV is somewhat less than those of anatase and rutile. Surprisingly, bands are almost flat and the DOS value within the window of ± 1.0 eV of the Fermi energy in brookite-type TiO_2 is bigger than that in rutile or even in anatase phase. The photocatalytic efficiency of the material depends on the crystallinity of the material, surface area, shape of the particle, band gap, and the amount of electrons around

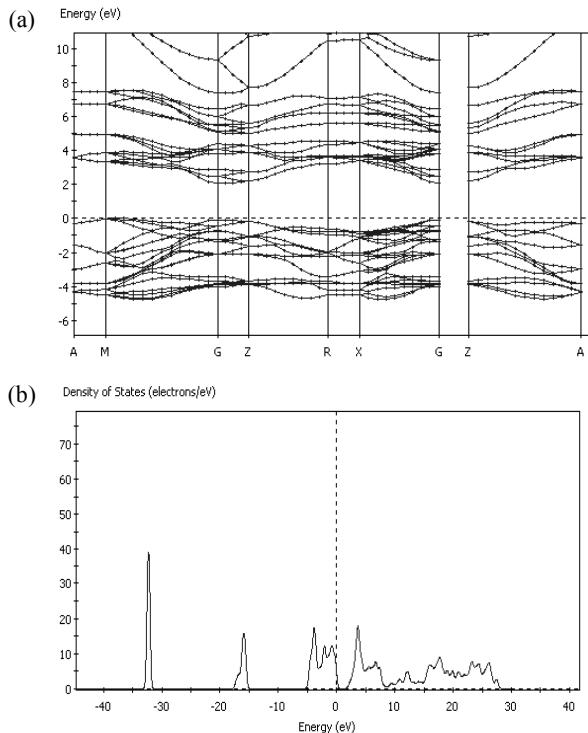


Figure 2. Calculated (a) band dispersion curve and (b) Density of States of anatase TiO_2 . G, X, M, Z, R, A represent (0, 0, 0, 0), (0, 0, 0, 0.5), (0.5, 0.5, 0.5), (0, 0, 0.5, 0.5), (0.5, 0.5, 0.5), (0.5, 0.5, 0.5) position, respectively, in the reciprocal lattice. The horizontal dashed line in dispersion curve and the vertical dashed line in DOS represent the Fermi energy.

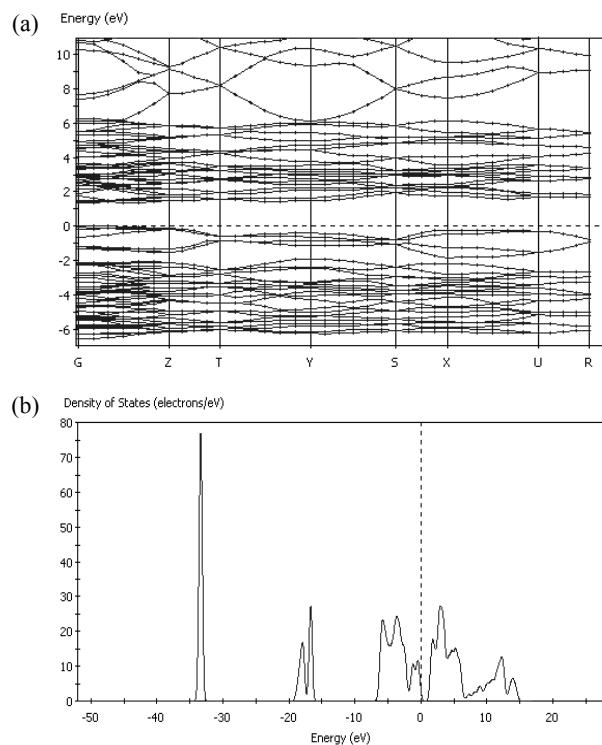


Figure 3. Calculated (a) band dispersion curve and (b) Density of States of brookite TiO_2 . G, X, T, Y, S, U, Z represent (0, 0, 0, 0), (0, 0, 0, 0.5), (-0.5, 0.0, 0.05), (-0.5, 0.0, 0.0), (-0.5, 0.5, 0.0), (0.0, 0.5, 0.5), (0.0, 0.0, 0.5) position, respectively, in the reciprocal lattice. The horizontal dashed line in dispersion curve and the vertical dashed line in DOS represent the Fermi energy.

the Fermi energy. The calculated DOS results suggest that the photocatalytic efficiency of highly crystallized brookite phase TiO_2 might be better than that of anatase when the structural conditions are similar. Not only experiments on the syntheses and characterizations of doped TiO_2 ¹³⁻¹⁴ but also developments of new materials such as brookite phase should be followed.

Conclusion

Band structures and DOS near the Fermi energy for rutile, anatase and brookite phase are calculated and investigated. The band width near the Fermi energy is smallest in the brookite-type TiO_2 , and therefore the DOS value near the Fermi energy is largest in the brookite-type TiO_2 . This means that the electron-hole separation can arise most actively in brookite phase. Consequently, it is expected the brookite-type TiO_2 is expected to exhibit the highest photocatalytic efficiency among three types of TiO_2 when the structural conditions are similar.

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