Electronic and optical properties of the doped TiO_2 system*

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Abstract: By the total energy pseudo-potential approach of plane wave, we study the electronic and optical properties of the anatase TiO_2 systems with Sc-doped, oxygen vacancies included, and Sc and oxygen vacancies co-existing, respectively. The obtained results show that the contribution by the doped Sc lies mainly in the valence band, and the light absorption in the visible region is obvious. A Mott phase transformation takes place in the presence of oxygen vacancies, and the light absorption in the visible region is also obvious. In particular, the absorption in the visible region of the co-doped system is enhanced coherently due to the influences both from doped Sc and oxygen vacancies.

Key words: anatase TiO_2; doping; electronic structure; optical properties
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1. Introduction

Titanium dioxide TiO_2 has three different crystal phases[1], i.e., rutile, anatase and brookite. Among them anatase TiO_2 is widely used in the photocatalysed field because of its excellent photocatalysis properties[2]. On the other hand, anatase TiO_2 is a wide forbidden band semiconductor with a band gap of 3.23 eV, so only the ultraviolet (UV) light ($\lambda \leqslant 383$ nm) can be used to excite the electrons from the valence band to the conduction band, and the application efficiency of the sunlight is very low. In fact, the absorption edge can be moved to the red light by impurity levels, so much effort has been paid to make anatase TiO_2's band gap smaller by doping methods for the efficient use of sunlight and improving the photocatalysis property of the system.

The anatase TiO_2 has attracted more attention due to its widespread applications in many fields, such as photovoltaic solar cells and photocatalysis. Choi *et al*.[3] studied TiO_2 doped with transition metals systematically by experiments, and found that the separation efficiency of the photoelectron can be enhanced and the photocatalysis of the system can be improved. Qian *et al*.[4] found that the photocatalysis of TiO_2 can be improved by oxygen vacancies. Yang *et al*.[5] studied Sc doped TiO_2 system, and their results show the light absorption in the short wave region increases with the increase in Sc concentration.

In this paper, we study doped anatase TiO_2 in three different cases, i.e. the substitution of Ti by Sc, oxygen vacancies, and both of them co-existing; the electronic and optical properties of the systems are studied. The obtained results show that the contribution by the doped Sc lies mainly in the valence band, and the light absorption in the visible region is obvious. A Mott phase transformation takes place in the presence of oxygen vacancies, the system transforms into metal from semiconductor and the light absorption in the visible region is also obvious. In particular, the visible light absorptions of the two cases enhance coherently, and thus the photocatalysis of the system can be improved greatly.

2. Model and calculation method

The anatase phase TiO_2 is tetragonal of space group 141/AMD. Ti^{4+} cation is at the center of the octahedron formed by six adjacent O^{2-} anions, and an O^{2-} anion is surrounded by three Ti^{4+} cations, which are at the centers of the three different octahedrons. The lattice constants are $a = b =$ 0.3785 nm, $c = 0.9514$ nm; $\alpha = \beta = \gamma = 90°$[6]. The $2 \times 1 \times 1$ supercell is used in this paper.

We use the total energy pseudo-potential approach of plane wave, the ionic potential is substituted by pseudo-potential[7], the electronic wave function is expanded by the plan wave base cluster and the exchange and correlative potential of electronic-electronic interaction is emendated by the generalized gradient approximation (GGA)[8, 9]. In our calculation, the energy cut-off is set to be 340 eV, the total energy is converged to less than 2.0×10^{-6} eV/atom, and a $3 \times 7 \times 3$ k-point mesh in the brillouin zone is used.

Table 1. Comparison of the optimized results of the primitive cell of TiO_2 and experimental data.

Parameter	This work	Ref. [6]	Ref. [10]
a (Å)	3.785	3.785	3.692
c (Å)	9.800	9.514	9.471
d_{eq} (Å)	1.943	1.934	1.893
d_{ap} (Å)	2.009	1.978	1.948
2θ (°)	156.36	156.16	154.4
V (Å^3/ TiO_2)	34.102	34.075	32.27

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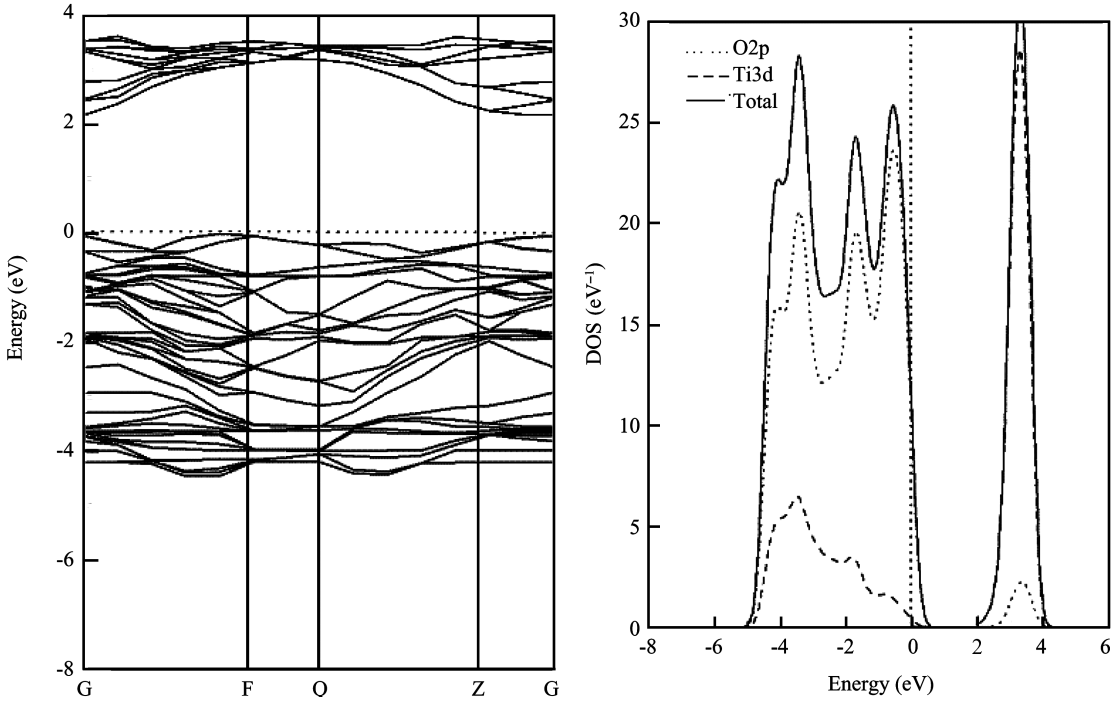

Fig. 1. Band structure and DOS of pure TiO_2.

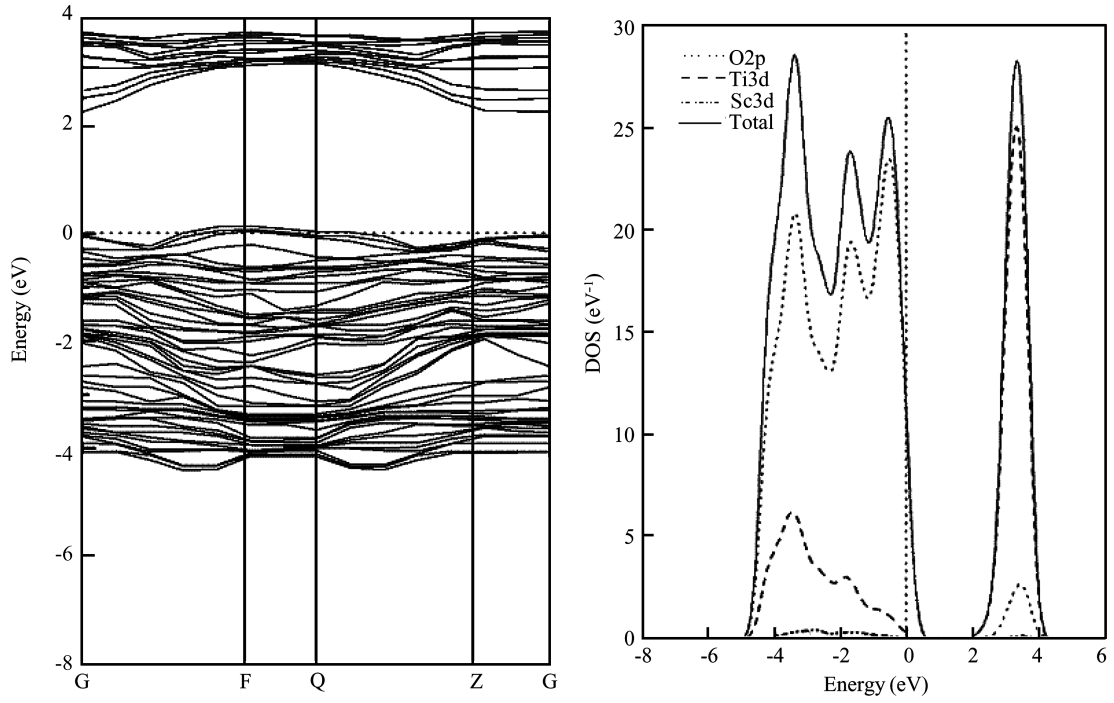

Fig. 2. Band structure and DOS of Sc-doped TiO_2.

3. Results and discussion

The supercell is optimized first in the calculation. The optimized results of the primitive cell of pure TiO_2 are shown in Table 1. Here, d_{eq} and d_{ap} are the lengths of the two different Ti–O bonds, and 2θ is the angle between the two bonds. As can be seen, the optimized geometry parameters are in good agreement with experiments[6], so we can say that our calculation is reasonable.

3.1. Band structure and DOS

For comparison, we first calculate the electronic structure of the pure TiO_2 system. The calculation results are shown in Fig. 1, and Figures 2–4 are the corresponding results for the different doped systems.

It is obvious that pure TiO_2 is an indirect band gap semiconductor with a band gap of 2.17 eV, which is in agreement with the theoretical results by others[11], but is much smaller

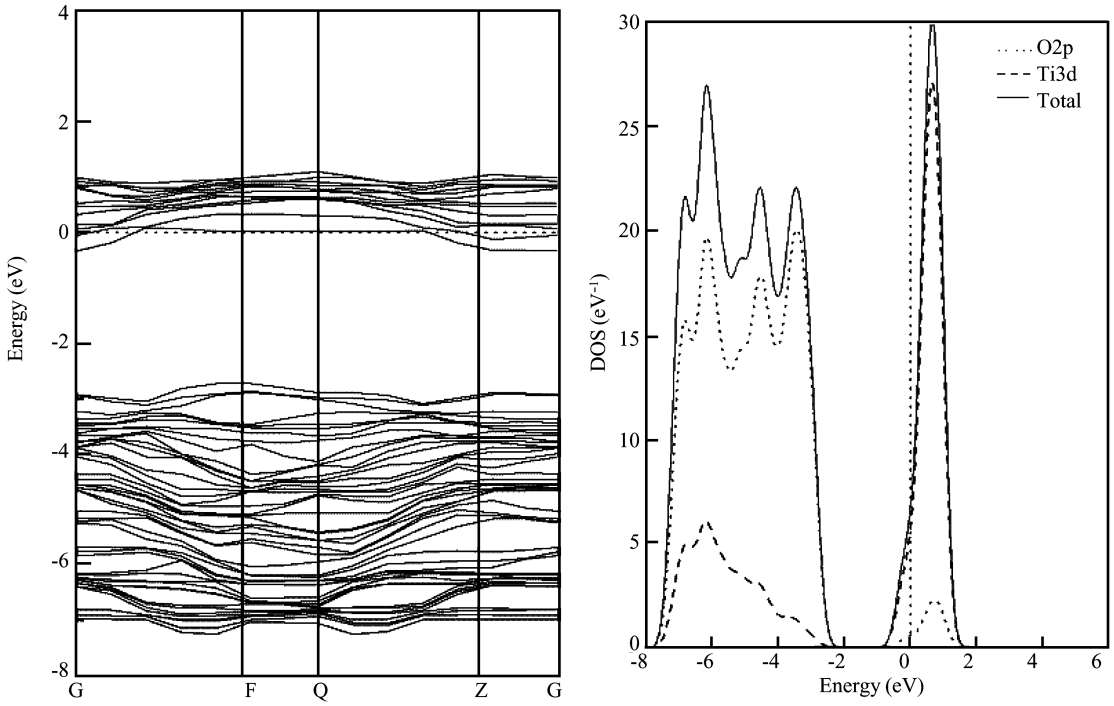

Fig. 3. Band structure and DOS of TiO_2 with oxygen vacancies.

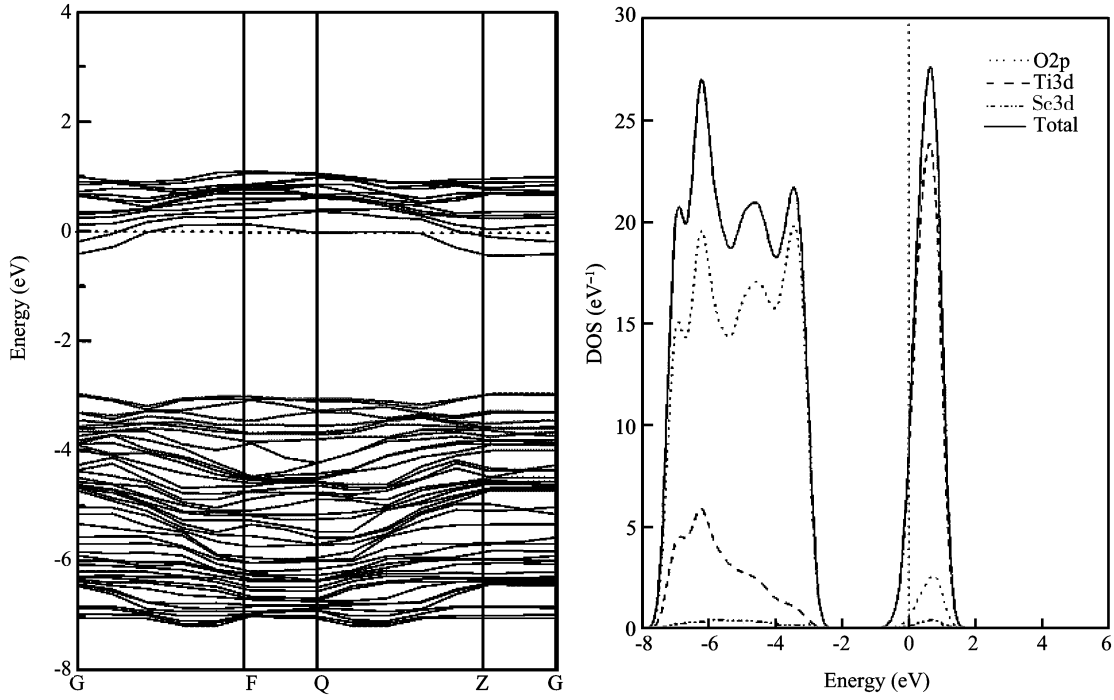

Fig. 4. Band structure and DOS of the doped TiO_2 with both Sc and oxygen vacancies.

than experimental results (3.23 eV). This problem is originated from GGA approximation adopted in the calculation process, and can be corrected by the scissors approximation.

The valence band and the conduction band are primarily contributed to by the 3d states of Ti (Ti3d) and the 2p states of O (O2p). The valence band is mostly contributed to by O2p states, and the conduction band is mostly contributed to by Ti3d states. The substitution of Ti by Sc is the p-type doping and the contribution by the doped Sc mainly lies in the valence band (Fig. 2).

The presence of oxygen vacancies (Fig. 3) plays the role of n-type doping, which lifts the Fermi level of the system. The Fermi level lies within the conduction band. The system undergoes the Mott phase transformation[12].

In the Sc and oxygen vacancies co-existing case (Fig. 4), the results are similar to that in the sole oxygen vacancies case,

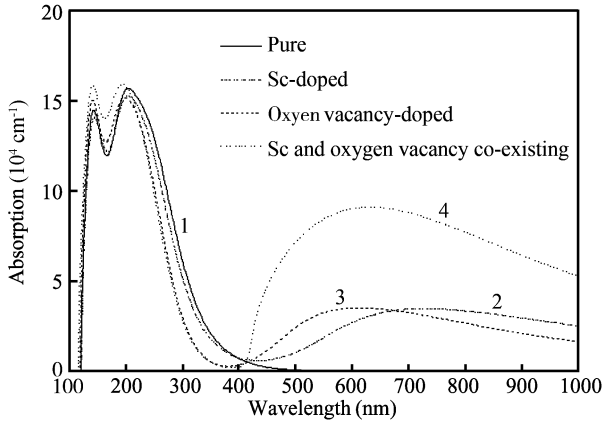

Fig. 5. Absorption spectra of pure TiO_2 and different doped systems.

the contribution by doped Sc is mainly in the valence band. Compared with the sole Sc doped case, the contribution to the valence band by the Sc in the co-existing case is enhanced.

3.2. Optical properties

For comparison with experiment, the scissor approximation must be taken into account during the calculation of optical properties. The corrected band gap of TiO_2 is set to be the experiment result 3.23 eV, i.e. correction value is 1.06 eV (the value is also used for the doped systems).

Absorption spectra of pure TiO_2 and different doped systems are shown in Fig. 5. The calculated absorption edge of pure TiO_2 is at about 380 nm, which is in good agreement with available experimental data. For all the systems, the absorptions in the ultraviolet light (UV) region are similar. For the doped systems, new absorption peaks in the visible region appear. In the Sc doping case, the absorption edge moves to the red light direction. As a matter of fact, the radius of Sc is bigger than that of Ti, the relaxation takes place after Sc doping, and the distance between Ti^{4+} and O^{2-} becomes smaller, so the spectral response of the system is extended to the visible region. Another point, it can be seen from Fig. 2 that the contribution by the doped Sc mainly lies in the top valence band, more electrons can be supplied to jump to the conduction band, thus the absorption in the visible region is enhanced. In the presence of oxygen vacancies, the density of states near the Fermi level is heightened, and more electrons from the valence band can be accepted, so the absorption in the visible region is enhanced. In the visible region, absorption in the Sc doping case and that in the oxygen vacancies case enhance coherently, the absorption in the co-existing case is boosted greatly, absorption coefficient reaches 9.1×10^4 cm^{-1}. Thus, photocatalysis of the co-doped system is improved obviously.

4. Conclusion

We have studied the anatase TiO_2 systems with Sc-doped, oxygen vacancies included, and Sc and oxygen vacancies co-existing, respectively. The obtained results show that the contribution by the doped Sc lies mainly in the valence band, and the light absorption in the visible region is obvious. A Mott phase transformation takes place in the presence of oxygen vacancies, the system transforms into metal from semiconductor, and the light absorption in the visible region is also obvious. Especially, the absorption in the visible region of the co-doped system is enhanced coherently due to the influences both from doped Sc and oxygen vacancies.

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