

Mg-doped TiO₂ for dye-sensitive solar cell: An electronic structure study

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Abstract. Recently, there has been a renewed interest in TiO₂ anatase as charge transfer layer in dye-sensitized solar cells (DSSC). In this work, the electronic structure of Mg-doped TiO₂ anatase was explored in the framework of density functional theory (DFT). The results showed that the substitution of Mg²⁺ ions for Ti⁴⁺ ions was quite easy in comparison with non metallic doping case. It induced small lattice expansions about 0.3% along a and b axis and 0.1% along c axis which can be explained in terms of internal stress around the impurity site and the anisotropic softy of the material. The effects of Mg impurity on the bulk and surface electronic structures were also discussed in details. It caused a negative shift of the conduction band edge -1.16 eV and 1.142 eV for bulk and surface respectively. The Fermi level was also shifted 1 eV to the negative energy. Such effects were suggested to improve short-circuit current J_{SC} of DSSCs but decrease the open-circuit voltage V_{OC}.

I. Introduction

Since the last decade, Dye-sensitized solar cells (DSSCs) has emerged as a brilliant candidate for high efficiency photoelectric devices which required simple fabrication technology and possibly low cost [1]. The most important component of a DSSC is a film of TiO₂ nanocrystals mixed with dye-sensitized molecules. It plays the crucial role in harvesting solar energy and generating photoelectric current. Therefore, TiO₂ has been intensively studied on purpose of increasing energy conversion efficiency.

Doping TiO₂ is a promising way to improve DSSC efficiency because it can easily shift the band edge and Fermi level of the material and thus change the electron transfer properties [2]. For example, the band gap of TiO₂ was 0.89 eV narrowed by S doping because of impurity states at the top of valence band [3]. Iodine doping moved the mixed states of Ti 3d and O 2p 0.16 eV to higher energy and thus reduced the band gap of the material [4]. Al, W-codoping [5] was reported to improve both open-circuit voltage V_{OC} and short-circuit current J_{SC} of DSSCs by suppressing dark current and

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improving electron trap-detrap mechanism, respectively. More recently, Liu et al. [6] and Feng et al. [7] proposed Nb- and Ta-doped TiO₂ nanomaterials for fabricating DSSCs. The Nb-doped TiO₂ photoanode [8] exhibited a negative shift of the flat band potential of TiO₂ and improved short-circuit current. Meanwhile, Ta-doped TiO₂ nanowire based DSSCs [9] have an open-circuit voltage improved owing to the positive shift of the TiO₂ Fermi level.

Information on electronic structure provides a good guideline to optimize efficiency of DSSCs via doping way. Our work was aimed at getting a deep insight into the electronic structure of a Mg doped TiO₂ anatase material in the framework of density functional theory (DFT). Mg is of the alkaline earth metallic series which were used to dope into TiO₂ anatase in order to improved photoactivities of the material [10]. The results in the literature showed that Mg is the best one of the series which can substitute for Ti in bulk. In this paper, effects of Mg doping on electronic structure as well as electron photo-injection and transportation will be discussed on the base of our *ab initio* calculation results.

2. Calculation details

This research was in the framework of density functional theory (DFT). In DFT method, the electron energy is separated into several components: the kinetic energy E^T , the electron-nuclear interaction E^V , the Coulomb repulsion E^J , and an exchange-correlation term E^{XC} which accounts for the remainder of electron-electron interaction (which is itself divided into separate exchange and correlation components).

$$E = E^T + E^V + E^J + E^{XC} \quad (1)$$

Then the variable principle requires that the distribution of electron density in the system should minimize the energy of the system. Kohn-Sham equation [11], Schrodinger equation of DFT method, was deduced in such way:

$$\left\{ \frac{-\Delta^2}{2} - V_n + V_e + \mu_{xc} \right\} \phi_i = \varepsilon_i \phi_i \quad (2)$$

Because of the mutation dependence between electron density and electron-electron interaction, this equation can be solved by self-consistent field (SCF) scheme. In DFT method, all of the energy components correspond to the classical energies of charge distribution except the last E^{XC} . This component arises from the anti-symmetry of the quantum mechanical wave function of electron (exchange functional EX), and the dynamic correlation in the motions of the individual electrons (correlation functional EC). With this inclusion, the DFT method achieves a significantly greater accuracy than the Hartree-Fock (HF) method at only modest increase in computation time.

Our calculation was performed buy DMol³ package which provides a numerical basic set. The Exchange-correlation potential is formulated by Pedrew and Wang (GGA-PWC) [12]. The Kohn-Sham equation is solved with convergence criterion of total energy 10^{-6} (1Ha=27.21138 eV). MonkhorstPack k-point meshes [13] of 3x3x3 and 2x4x1 were used for bulk and surface calculation, respectively. The self-consistent electron potential terms were all electron Coulomb potentials which

included relativistic effects of core electrons. Relaxation processed was done until the residual forces were below $0.002 \text{ Ha}/\text{\AA}$ and maximum energy change below 10^{-5} Ha . Such a Kohn-Sham equation and SCF process were applied to the two following models. A P1 symmetric supercell of $2 \times 2 \times 1$ $I41/amd$ unit cells (Fig. 1a, b) with three dimension periodic boundary condition (PBC) was used for bulk calculations. In order to model doped bulk materials, one site of Ti was substituted by one impurity atom, i.e. one Mg atom. Then the stoichiometric formula of the doped material is $\text{Ti}_{15}\text{MgO}_{32}$ which is corresponding to 6.67% doping case. The second model was for (110) surface. It was composed of a TiO_2 slab which was cut along (110) direction and 8 \AA thick embedded into vacuum which was 28 \AA thick (Fig. 2a, b). Stoichiometric formula of doped surface was $\text{Ti}_{15}\text{MgO}_{30}$ which means two-oxygen-vacancy surface.

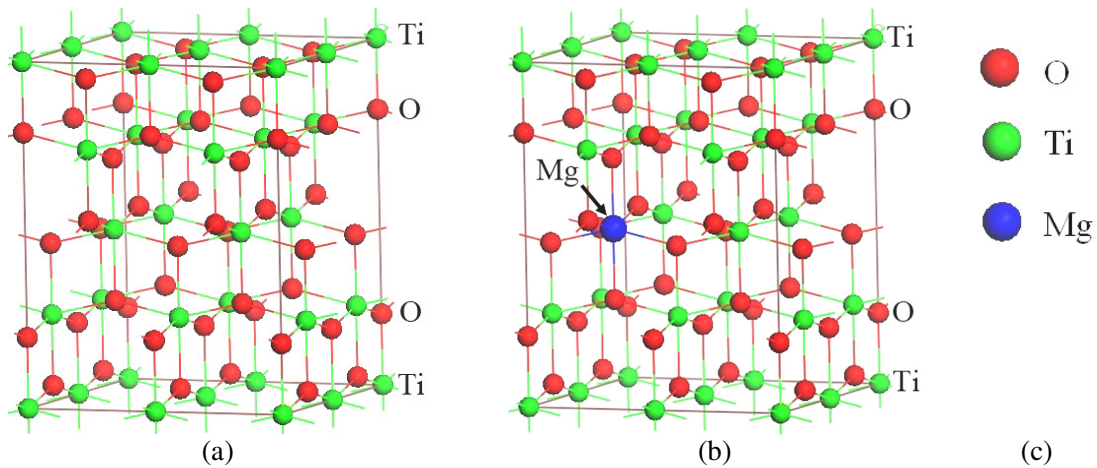


Fig. 1. Supercell structure of pure TiO_2 (a) and doping Mg (b)

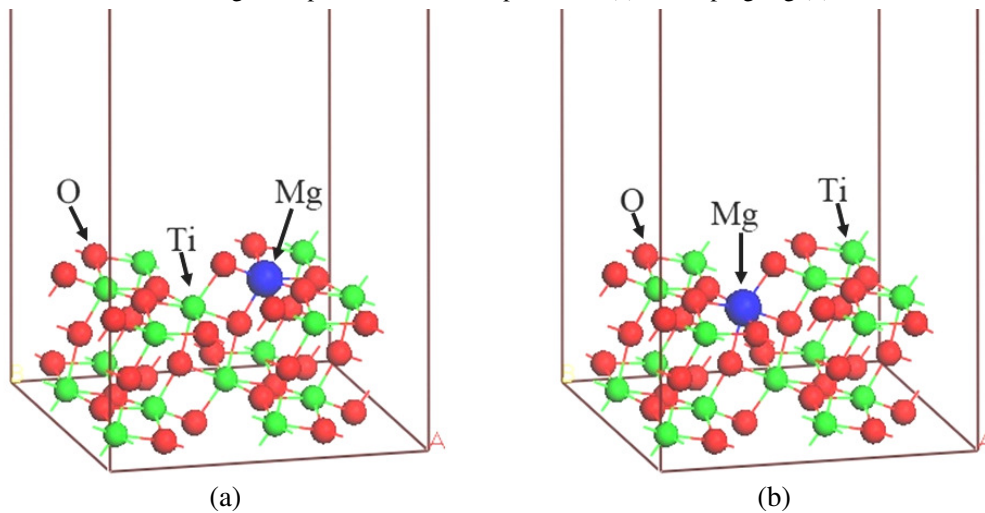


Fig. 2. Supercell for modeling TiO_2 surface anatase (101): substitute Mg for Ti_{5C} (a) and substitute Mg for Ti_{6C} (b).

3. Result and discussion

3.1. Calculations on pure TiO₂ material

Fig. 3a shows the band structure of pure anatase TiO₂. The calculated band gap is $E_g^{undoped} = 2.12$ eV, which is smaller than the experimental one $E_g^{exp} = 3.2$ eV [14]. The optimized cells parameters are $a=b=3.813 \text{ \AA}$ $c=9.78 \text{ \AA}$ which are larger than the experiment ones $a=b=3.78 \text{ \AA}$ $c=9.19 \text{ \AA}$ [15], those are well-known failures of local density approximations in DFT.

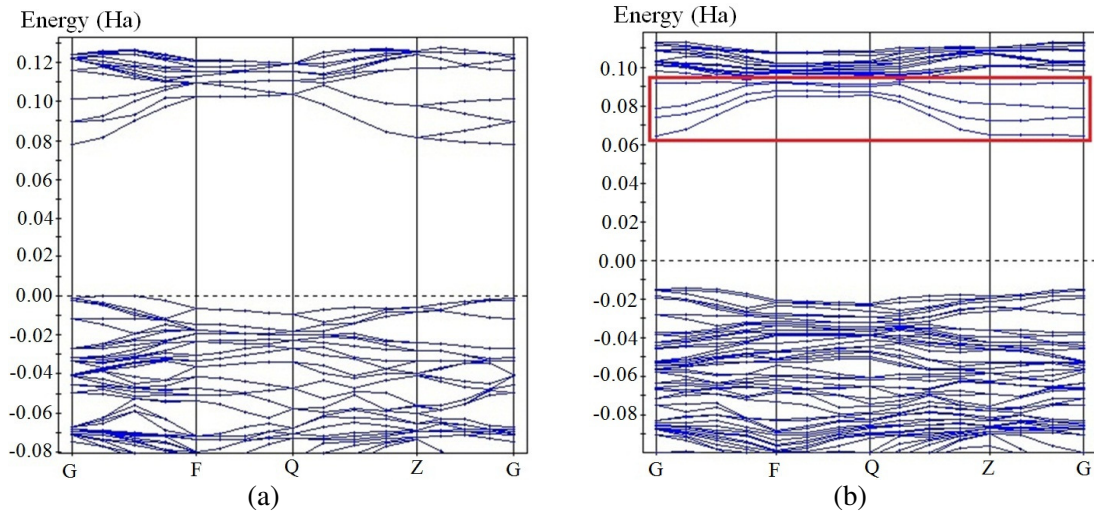


Fig. 3. Band structure of bulk TiO₂: non-doped (a) and doped Mg (b) (1 Ha=27.21138 eV).

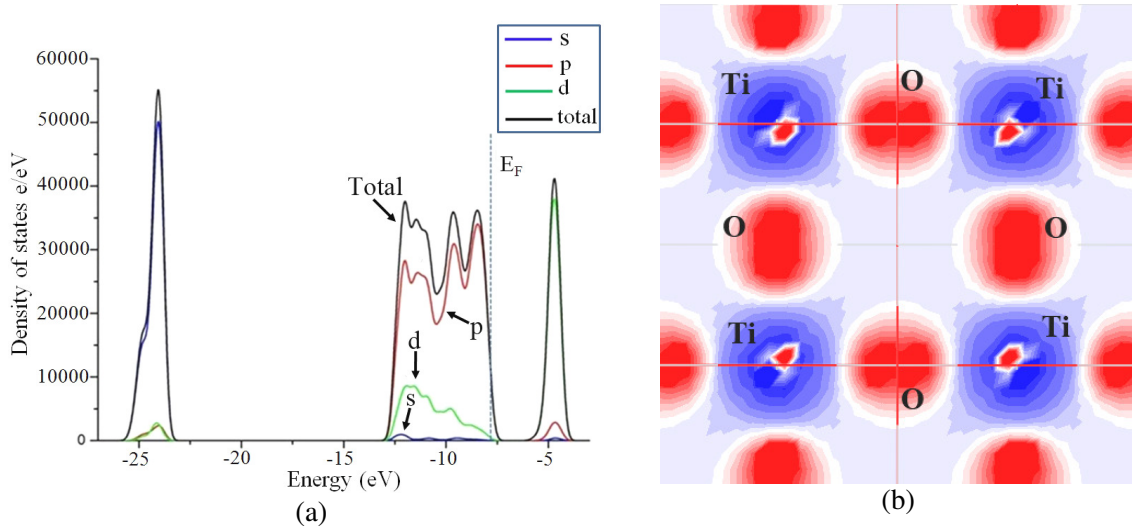


Fig. 4. Density of states of pure TiO₂ anatase (a) and Its electron deformation density (b).

The top of valence band (VB) approximately locates near the G-point and the bottom of the conduction band (CB) locates at the G-point, which means that TiO₂ anatase has an indirect band gap. Our result is in good agreement with those ones of Ju-Young Park et al. Which predicted an indirect band gap of 2.1 eV [16] and of Yin et al which gave rise to an indirect band gap of 1.88 eV [17]. Fig. 4a represents the density of states for pure TiO₂. The core states are highly-dense and locate in a narrow energy band between -26.5 eV and -23 eV. They are primarily oxygen 2p states (91%). There are also 9% of them titanium 2p, 3d states. The VB locates between -13.5 eV and -7 eV. It is composed mainly of the oxygen 2p states (83%) and titanium 3d states (17%). The CB ranging from -5.5 eV to -3 eV originates from titanium 3d states (92%) with the remaining small amount of oxygen 2p. According to this, the overlap between Ti states and O states is so small that the Ti-O bonding should be considered to be strongly polarized or ionic. The electron deformation density $\Delta\rho$ shown in Fig.4b gives a good visualization of the ionic nature of TiO₂ crystal bonding. Here, $\Delta\rho$ is the difference between electron density of TiO₂ crystal $\rho_{crystal}$ and the total of electron density of isolated atoms ρ_i : $\Delta\rho = \rho_{crystal} - \sum_i \rho_i$. The blue region around Ti atom is corresponding to $\Delta\rho < 0$, i. e. electron donating, and the red one around O atom is corresponding to $\Delta\rho > 0$, i. e. electron accepting. There is no shared electron region which is corresponding to covalence bonding between O and Ti.

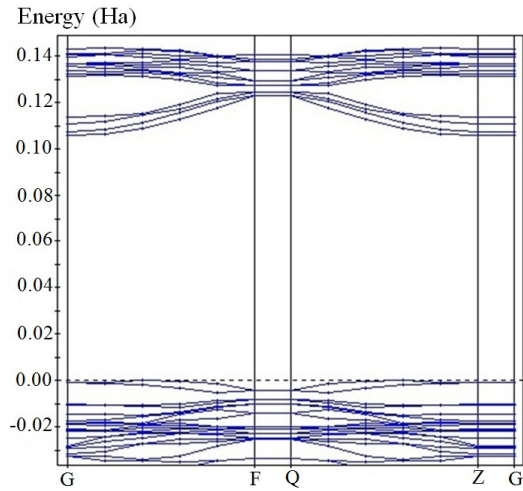
The limitation of crystal by (110) surface gave rise to significant change in band structure as observed from our calculation on vacuum slab supercell (Fig. 5a). It should be noted that there are two oxygen vacancies on the as-built surface which would corresponding to 4-electrons doping if there were no change in oxidization state of Ti. Actually, these electron-impurity states do not appear in the calculated band structure. We suggest that these excess electrons oxidized the surface Ti⁴⁺ ions. Consequently, the proportion of Ti 3d states between VB and CB is two times increased approximately (in case of bulk TiO₂ the contributions of Ti 3d states is 46% in VB and 54% in CB, on the contrary the proportion is 64% and 36% in case of TiO₂ surface) as shown in Ti 3d partial DOS (Fig.5b). According to this, it is believe that Ti⁴⁺ ions were oxidized to Ti³⁺ as observed by previous experiments [5]. There is a nearly separated band at the bottom of the CB which was not observed in bulk TiO₂. It belongs to surface Ti 3d states as deduced from the partial DOS analysis (Fig. 5). We assign the separation of surface Ti 3d band to the transformation of octahedron-like to pyramid-like coordination at surface due to surface oxygen vacancies.

3.3. Calculations on doped material

For the doped material, we calculated the substitution energy $E_{sub} = E_{Mg-doped} + E_{Ti} - E_{Non-dop} - E_{Mg}$. The substitution energy 8.2 eV for bulk material which is smaller than that of P substitution (12.08 eV) implies that Mg substitution reaction is easier than P one [18]. In contrast, the substitution energy is negative and quite large in value in case of surface site substitution, indicating that the substitution reaction can naturally occur. Alkaline earth doped TiO₂ compounds were prepared by Yuexiang Li et al [10]. It was observed that the substitution was the easiest for Mg²⁺ case while Be²⁺ tended to insert into interstitial site, Ca²⁺ was harder to substitute Ti⁴⁺ and able to induce lattice

deformation. The large ions, i. e. Ba^{2+} and Sr^{2+} hardly insert into crystal lattice and prefer to stay on surface.

The calculated average unit cell sizes are 0.3% increased for a and b and 0.1% for c, i.e. $a=b=3.825 \text{ \AA}$ $c= 9.792 \text{ \AA}$ when one Ti in $2 \times 2 \times 1$ supercell is substituted by one Mg (Table. 1). The increase of lattice parameter can be explained in term of local lattice distortion induced by impurity site. The ionic radius of Mg^{2+} $r_{\text{Mg}^{2+}} = 0.86 \text{ \AA}$ [19] is larger than Ti^{4+} $r_{\text{Ti}^{4+}} = 0.745 \text{ \AA}$ [19]. Then the substitution of the larger ion for the smaller ion led to an internal stress around the impurity site.



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