Computational Condensed Matter 6 (2016) 5–17

Contents lists available at ScienceDirect

Computational Condensed Matter

journal homepage: http://ees.elsevier.com/cocom/default.asp

# Understanding electronic and optical properties of La and Mn co-doped anatase $TiO_2$

Renhui Zhang [a, *], Juan Zhao [b], Yingchang Yang [a], Zhibin Lu [c], Wei Shi [a, **]

[a] Research Center of Material and Chemical Engineering, School of Material and Chemical Engineering, Tongren University, Tongren, 554300, PR China
[b] School of Mathematics and Information Science, Tongren University, Tongren, 554300, PR China
[c] State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Science, Lanzhou 730000, PR China

ARTICLE INFO

*Article history:*
Received 28 February 2016
Received in revised form
12 March 2016
Accepted 12 March 2016
Available online 15 March 2016

*Keywords:*
Electron
$TiO_2$
First-principles
Dipole moment

ABSTRACT

The electronic structures, dipole moment, and optical properties of La-doped, Mn-doped, and La-Mn-doped anatase $TiO_2$ have been investigated by means of GGA + U first-principles method, showing that the absorption coefficients of the La-Mn-doped $TiO_2$ under visible light to be sensitive to the doping positions of La and Mn atoms. La-Mn-$TiO_2$(1) exhibits the largest absorption coefficient in visible light because of the smallest band gap. Additionally, for the La and Mn co-doped $TiO_2$, the large dipole moment of $TiO_6$ octahedron is in prejudice of enhancing the optical responses under the visible light. We successfully probe the interesting optical response mechanism in this work.



## 1. Introduction

Due to the interesting demand for the environmental accountability and energy conversion [1], titanium dioxide ($TiO_2$) was continuously attracting substantial research in solar cells, lithium-ion batteries, purifying water, photolysis of water and optical degradation of organic compound [2–6] because of its strong oxidizing power, cost effectiveness, long term stability, and high catalytic activity [7,8]. However, it had large electronic band gaps of 3.0–3.2 eV [9], which limited its optical absorption in the ultraviolet (UV) region of the solar spectrum. However, the UV light only accounted for less than 5% of the entire solar energy [10]. Although $TiO_2$ was even efficient in utilizing the UV light, its overall solar activity was very limited. Furthermore, the photocatalytic activity depended on the amount of photo-exciting electrons and holes on the surface of the $TiO_2$ for the reaction. However, its photo quantum yield value was very low due to easily recombination of photo-exciting electron-hole pairs. Hence, it was highly desirable to develop $TiO_2$ with high catalytic activity under the visible light.

During the past few decades, tremendous effort has been devoted to the rational design of the better optical absorption of $TiO_2$ under visible-light region through the dopant of metal or non-metal. For instance, V doped $TiO_2$ photocatalyst prepared by the Klodek et al. exhibited excellent photocatalytic activity for photo-oxidation of ethanol [11]. Di Paola et al. reported that the transition metal doped $TiO_2$ samples have an effect on the photocatalytic degradation of organic compounds [12]. Meng et al. declared that N and transition metal co-doped $TiO_2$ exhibited superior photocatalytic activity under visible light. And they also pointed out the relationship between electronic structure and optical properties [13]. Ohno and Umebayashi et al. reported that S doped $TiO_2$ could improve the photocatalytic activity under visible-light irradiation [14–16]. Asahi and Maeda et al. prepared N doped $TiO_2$ films and found that they exhibit excellent photocatalytic activity under visible-light irradiation [17,18]. Indeed, the light absorption edge of the doped $TiO_2$ could be extended to the long wavelength range (mostly visible light range) with the help of these strategies. Unfortunately, the variable experimental conditions and sample preparation methods led to difficultly understanding their intrinsic activation mechanism. Luckily, the simulation method could well overcome the complexity of the experimental conditions and help us to analyze the microscopic information of electronic structure of the doped $TiO_2$, and understand the detailed effect of different doped elements and doped positions on the photocatalytic activity of $TiO_2$.

First-principles method provided a powerful tool to capture

* Corresponding author.
** Corresponding author.
*E-mail addresses:* zrh_111@126.com (R. Zhang), wlxsw@sina.cn (W. Shi).

http://dx.doi.org/10.1016/j.cocom.2016.03.001

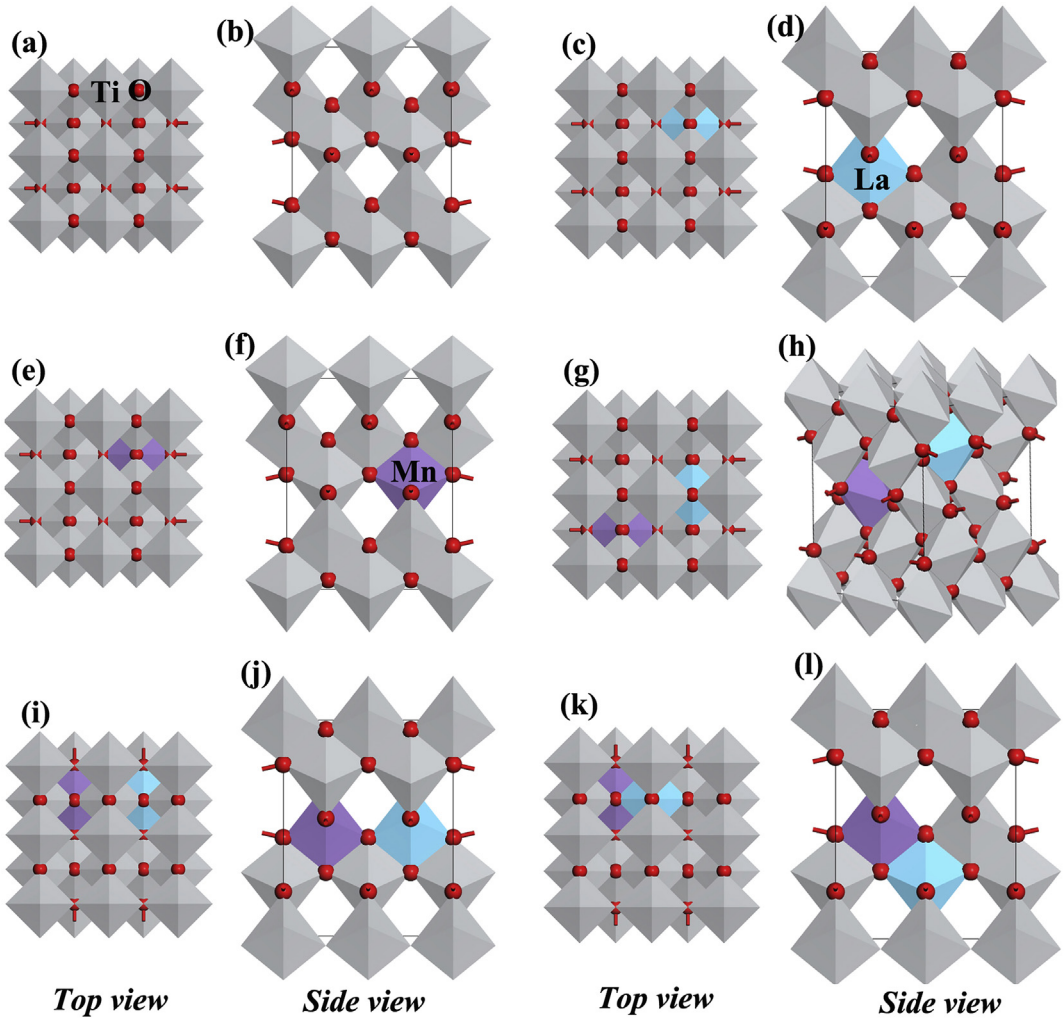


**Fig. 1.** Models of $TiO_2$ (a) top view, (b) side view, La-$TiO_2$ (c) top view, (d) side view, Mn-$TiO_2$ (e) top view, (f) side view, La + Mn-$TiO_2$(1) (g) top view, (h) side view, La + Mn-$TiO_2$(2) (i) top view, (j) side view, La + Mn-$TiO_2$(3) (k) top view, (l) side view.

atomic details and gained a deeper insight into the intrinsic activation mechanism of $TiO_2$ under visible light region. Yang et al. reported that the effect of N concentration on the formation energies and electronic band structure of N-doped $TiO_2$ has been investigated on the basis of first-principles calculations [19]. And Yang et al. also studied the photocatalytic activity of S and P doped $TiO_2$ under visible light from first-principles [20]. Weng et al. investigated the electronic structure and optical properties of the Co doped anatase $TiO_2$ based on the first-principles method [21]. Moreover, we have successfully probed the activation mechanism of C-N, N-La, and N-transition metal co-doped $TiO_2$ based on the first-principles method in our previous investigations [22–24]. Additionally, Li et al. [25–27]systematically investigated the band gap engineering of early transition-metal-doped anatase $TiO_2$, electronic, optical and photocatalytic behavior of Mn, N doped and co-doped $TiO_2$, and effects of oxygen vacancy on 3d transition-metal doped anatase $TiO_2$. Nowadays, more and more researchers payed attention to photo-activation mechanism of the anion or cation or anion and cation doped $TiO_2$ [28–30]. Lin et al. studied the photocatalytic performance of Mn and Fe codoped $TiO_2$ film [31], they found that two transition metals codoped $TiO_2$ improved synergistically the photocatalytic efficiency of $TiO_2$. A very limited number of investigations have considered the combined effect of using Mn and La as codopants. Also, we found that N-La, N-Mn co-doped $TiO_2$ exhibited excellent optical absorption under visible light, and La and Mn co-doped $TiO_2$ could improve its optical absorption under visible light.

Herein, we systematically investigate the electronic structure, dipole moment, electron localization function (ELF) and optical properties of La and Mn co-doped $TiO_2$ using GGA + U first-principles method, and try to probe the photo-activation mechanism of La and Mn co-doped $TiO_2$.

## 2. Computational method and details

Fig. 1a and b shows the top and side views of $TiO_2$ respectively. Fig. 1c–f shows the top and side views of La or Mn mono-doped $TiO_2$. Ti atom is replaced by La or Mn atom, the atom fraction is 6.67%. The top and side views of La and Mn co-doped $TiO_2$ is plotted in Fig. 1g–l, Ti atoms are replaced by La and Mn atoms, the atom fraction is 13.3%. La and Mn co-doped $TiO_2$ are marked as La + Mn-$TiO_2$(1), La + Mn-$TiO_2$(2), La + Mn-$TiO_2$(3) in the work. The pseudo atomic calculations perform for La $5s^25p^65d^16s^24f^0$, Mn $3d^54s^2$, O $2s^22p^4$, Ti $3s^23p^63d^24s^2$.

The first-principles calculations are performed using the CASTEP module in Materials Studio 6.0. The energy plane-wave pseudopotential total calculation method is carried out for all the calculations based on the density functional theory. The generalized-