The electronic and optical properties of Eu/Si-codoped anatase TiO₂ photocatalyst

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The electronic and optical properties of Eu/Si-codoped anatase TiO₂ are investigated using the density functional theory. The calculated results show that the synergistic effects of Eu/Si codoping can effectively extend the optical absorption edge, which can lead to higher visible-light photocatalytic activities than pure anatase TiO₂. To verify the reliability of our calculated results, nanocrystalline Eu/Si-codoped TiO₂ is prepared by a sol-gel-solvothermal method, and the experimental results also indicate that the codoping sample exhibits better absorption performance and higher photocatalytic activities than pure TiO₂. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3692750>]

Titania (TiO₂) has received intense attention as a promising candidate material for photocatalyst applications.^{1,2} However, a large intrinsic band gap of anatase TiO₂ (3.2 eV) allows only a small portion of sunlight in the ultraviolet (UV) light region to be absorbed. Therefore, reducing the band gap of anatase TiO₂ to make it photosensitive to visible-light has become one of the most important goals in photocatalytic applications. It has been suggested that doping with C, N, Si, or Ni would result in a reduced band gap for TiO₂.^{3–6} A few latest researches show that different ions codoping into TiO₂ can further narrow its band gap and enhance its photocatalytic activity.^{7–14} For instance, Jia *et al.* studied the microscopic mechanism for band gap narrowing and the origin of the enhanced visible-light photocatalytic activity in N/S-codoped anatase TiO₂.⁷ Li *et al.* reported the C/H-codoping produces significant band gap narrowing, which leads to higher visible-light photocatalytic efficiency than the C-doped anatase TiO₂.⁹ The research of Su *et al.* suggested that the codoping of TiO₂ with N and Fe leads to the much narrowing of the band gap and greatly improves the photocatalytic activity under visible irradiation.¹⁰ These results indicate that (co)doping is one of the most effective approaches to extend the absorption edge to the visible-light range in anatase TiO₂. However, photocatalytic activity and optical absorption properties of Eu/Si-codoped TiO₂ have no report on the theory and experiment. Thus, the enhanced absorption of the visible-light and photocatalytic activity are expected for Eu/Si-codoped TiO₂.

In this letter, the electronic and optical properties of Eu/Si-codoped TiO₂ were investigated using the density functional theory (DFT) to reveal the synergistic effects of Eu/Si codoping on the mechanism of band gap reducing and the origin of the enhanced visible-light photocatalytic activity. Nanocrystalline Eu/Si-codoped TiO₂ was prepared by sol-gel-solvothermal method, and the higher photocatalytic activity of which was observed in experiments verified the reliability of our calculation.

All the spin-polarized calculations were performed using the projector augmented wave pseudopotentials as implemented in the VASP code.^{15,16} The exchange correlation function was treated by the generalized gradient approximation (GGA) with the Perdew-Wang parameterization (known as GGA-PW91).¹⁷ The Brillouin-zone integrations were approximated by using the special k-point sampling of the Monkhorst-Pack scheme.¹⁸ A cutoff energy of 500 eV and a mesh size of $5 \times 5 \times 5$ were used for geometry optimization and electronic property calculations. Using the block Davidson scheme, both the atomic positions and cell parameters were optimized until the residual forces were below 0.01 eV/Å. It was well-known that the traditional DFT method usually underestimated the band gap for semiconductors. However, the DFT + *U* approach introduced an on-site correction in order to describe systems with localized d and f electrons, which can produce better band gaps in comparison with experimental results. Therefore, our all calculations of the electronic and optical properties were conducted using the GGA + *U* method^{19–22} for both Ti 3d and Eu 4f electrons. It was found that the band gap of pure anatase TiO₂ was 2.9 eV with *U* = 10.0 eV and *J* = 1.0 eV for Ti 3d electrons, and was only weakly dependent on *J* value. This accords well with the experimental value of 3.2 eV.²³

The valence electron configurations considered in this study included Ti (3d²4s²), O (2s²2p⁴), Eu (4f⁷6s²), and Si (3s²3p²). All the doped systems were constructed from a relaxed (2 × 2 × 1) 48-atom anatase TiO₂ supercell, it was shown in Fig. 1(a). As the position of Eu in the TiO₂ lattice was unclear, variety of positions of Eu atoms in the lattice were considered, such as substitutional Eu at the Ti site (Eu@Ti) and O site (Eu@O). In the Si-doped TiO₂, an Ti atom was substituted by an Si atom (Si@Ti).⁵ Similar substitutions were also considered for codoped systems, as Eu locates at either Ti or O site and Si locates at Ti site, namely, Eu@Ti&Si@Ti and Eu@O&Si@Ti. To probe the stabilities of the doped systems, we calculated the defect formation energy (*E_f*) for the doped and codoped systems according to the formulas

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FIG. 1. (Color online) (a) 48-atom super-cell model for defective anatase TiO_2 shows the location of the dopants. The atom doping sites are marked with Eu and Si. The gray spheres and red spheres represent the Ti and O atoms, respectively. The blue sphere and purple sphere represent Eu and Si atoms, respectively. (b) XRD patterns for the pure and doped TiO_2 .

$$E_f(Y@X) = E_{(Y@X)} - E_{(\text{pure})} - (\mu_Y - \mu_X), \quad (1)$$

$$E_f(Y'@X) = E_{(Y'@X)} - E_{(\text{pure})} - (\mu_{Y'} - \mu_X), \quad (2)$$

$$E_f(Y@X \ Y'@X) = E_{(Y@X \ Y'@X)} - E_{(\text{pure})} - (\mu_Y + \mu_{Y'} - \mu_X - \mu_X), \quad (3)$$

($X = \text{Ti}, \text{O}$; $Y = \text{Eu}, Y' = \text{Si}$),

where E represents the total energy and μ is the chemical potential. The calculated formation energies are listed in Table I. It shows that Eu impurity is preferred to substitute Ti in lattice because of the smallest formation energy in both Eu-doped and Eu/Si-codoped systems.

In order to investigate the electronic properties of Eu and/or Si (co)doping anatase TiO_2 , the total density of states (TDOS) and partial density of states (PDOS) were calculated, and plotted in Fig. 2. For pure TiO_2 , the valence band (VB) is mainly contributed by the O 2p state, while the conduction band (CB) is mainly dominated by the Ti 3d state. For Eu-doped TiO_2 , the overlap of Eu 4f and O 2p states leads to a band gap narrowing. In Si-doped TiO_2 , the VB broadens with the mixing of O 2p and Si 3p states, and the CB bottom has a decline about 0.15 eV. For Eu/Si-codoped TiO_2 , the hybridized states located mainly at the edge of the VB are composed of Eu 4f and Si 3p states while other Eu 4f states are at the edge of the CB. The electron in the VB can be excited to localized impurity states in band gap and subsequently to the CB by visible-light absorption. Consequently, synergistic effect of Eu/Si codoping can lead to a decrease of the photon excitation energy.

It is well-known that optical absorption is a surface property in anatase TiO_2 . However, it is reasonable that the effect of doping on electronic structure and optical absorption properties of anatase TiO_2 are investigated by the bulk anatase TiO_2 ,^{24–26} which partially reflects some experimental results. According to the obtained electronic structures, we calculated the complex dielectric function $\xi = \xi_1 + i\xi_2$. The

TABLE I. Defect formation energies E_f of different doped anatase TiO_2 (in eV).

Doped models	Doped			Codoped	
	Eu@Ti	Eu@O	Si@Ti	Eu@Ti&Si@Ti	Eu@O&Si@Ti
E_f (eV)	1.21	10.55	−8.04	−6.77	1.02

corresponding absorption spectrum was estimated by the following equation:

$$I(\omega) = 2\omega \left(\frac{(\xi_1^2(\omega) + \xi_2^2(\omega))^{1/2} - \xi_1(\omega)}{2} \right)^{1/2}, \quad (4)$$

where I is the optical absorption coefficient, ω is the angular frequency ($E = \hbar\omega$).

The absorption spectrum of the pure and doped systems is calculated, as shown in Fig. 3. It is found that pure anatase TiO_2 can only respond to the UV light and show no absorption activity in the visible-light region. For Eu-doped (Eu@Ti) TiO_2 system, the overlap of impurity states and valence band leads to a good absorption activity in the visible-light region. For Si-doped system, it is clear that the narrowed band gap induces the increasing optical absorption in the UV-light region. For Eu/Si-codoped (Eu@Ti&Si@Ti) system, synergistic effect of Eu/Si codoping can lead to a decrease of the photon excitation energy in the view of electronic structure. Therefore, the absorption of the visible and UV-light is greatly enhanced, which may be responsible for the outstanding photocatalytic activity and the red-shift of optical absorption edge in Eu/Si-codoped anatase TiO_2 .

In order to confirm the better photocatalytic activity of the Eu/Si-codoped anatase TiO_2 compared to that of pure TiO_2 , we further observed the UV-vis absorption spectrum by experiments.

Nanocrystalline pure, Si-, Eu-, and Eu/Si-codoped TiO_2 were prepared by a sol-gel-solvothermal method. First, a desired amount (0.2973 g) of europium nitrate hexahydrate was dissolved in 31.73 ml of glacial acetic acid solution under stirring. Then, 5.96 ml of tetraethyl orthosilicate was dropwise added into the solution with stirring for 1 h. Second, 22.69 ml of tetrabutyl titanate was also dropwise added into the solution with continuous stirring for 2 h, and the solution was heated in an oven and kept at 140 °C for 14 h. Finally, the precipitate obtained was dried in a vacuum oven at 70 °C for 48 h. To evaluate the photocatalytic activity of samples, photocatalytic experiments were carried out in an inner-irradiation-type reactor. A 500 W long-arc xenon lamp surrounded with a water cooling system was fixed in the center of the reaction cell. 0.2 g of photocatalyst was suspended in 200 ml of a methylene blue (MB) solution (20 mg/l) under stirring magnetically. The mixture was kept in the dark for

FIG. 2. (Color online) Calculated TDOS and PDOS of different doped TiO_2 . The top of the valence band of pure anatase TiO_2 is taken as the reference level. Curves above and below the horizontal axis refer to the up-spin and down-spin DOS, respectively.

30 min to establish an adsorption-desorption equilibrium before the light radiation. The amount of MB in the solution was determined on the basis of its characteristic optical absorption at 665 nm using an UV-vis spectrophotometer based on Lambert-Beer's law.

The crystalline phase was identified by x-ray diffraction (XRD) (Rigaku D/MAX-2400). The Brunauer-Emmett-Teller (BET) surface area of the samples was measured through nitrogen adsorption at 77 K (Nova 2000e). The UV-vis absorption spectra were obtained on an UV-vis spectro-

photometer (UV-3600), using BaSO_4 as the reference sample.

Fig. 1(b) shows the XRD patterns of the samples of pure, Si-, Eu-, and Eu/Si-codoped TiO_2 . It is found that all of the diffraction peaks are contributed by the anatase TiO_2 phase and no other visible impurity peak can be distinguished in the pattern of pure or doped sample. The BET surface areas for pure, Si-, Eu-, and Eu/Si-codoped TiO_2 are 84.33, 252.31, 221.48, and 320.58 m^2/g , respectively. Obviously, with the coexistence of Eu and Si in TiO_2 , the surface

FIG. 3. (Color online) The optical absorption curves of (a, a') pure, (b, b') Si-doped, (c, c') Eu-doped, (d, d') Eu/Si-codoped TiO_2 . The left and right figures represent the absorption spectra obtained by calculations and experiments, respectively.

FIG. 4. (Color online) Photocatalytic degradation ratio of MB in the presence of the pure and doped nanocrystalline TiO_2 .

area is increased to $320.58 \text{ m}^2/\text{g}$, about four times of that of pure TiO_2 powders.

The optical absorption spectra of the pure and doped systems are obtained by experiments, and shown in Fig. 3. Compared with the pure TiO_2 , it is clear that the incorporation of Si into TiO_2 lattice induces the enhanced optical absorption in the UV-light region. For Eu-doped system, it shows good absorption activity in the visible-light region. For Eu/Si-codoped TiO_2 , the optical absorption curve shows that codoped TiO_2 with Eu and Si can greatly enhance the absorption of UV and visible-light, which indicates synergistic effect of Eu/Si codoping. However, there are small misalignments between the experimental and theoretical results, which may be due to neglect of the anisotropy of the absorption coefficient and the well-known limitation of DFT. But, from the perspective of qualitative analysis, the experimental results are consistent with the calculations.

The photocatalytic activity of the pure and doped samples was evaluated by monitoring the degradation of MB, as shown in Fig. 4. The “Blank” shows that MB almost cannot be degraded under the visible-light irradiation without catalysts, indicating that the photolysis can be ignored. The Si-doped sample presents the best photocatalytic activity while the degradation rate of TiO_2 is apparently reduced after doping with Eu. This is because the impurity states of Eu 4f are also easy to become the recombination center of electron-hole pairs. For Eu/Si-codoped TiO_2 sample (see Fig. 4), the improvement of photocatalytic activity in the codoping sample can be attributed to the enhanced absorption of visible and UV-light. Therefore, the Eu/Si-codoped sample exhibits the better photocatalytic activity than the pure and Eu-doped sample, lower than the Si-doped sample.

In summary, we have studied the electronic and optical properties of Eu/Si-codoped TiO_2 based on DFT calculations. The synergistic effects of Eu/Si codoping may further

reduce the electrons excited energy from VB to CB under the visible-light irradiation, which enhances the photocatalytic activity and the red-shift of absorption edge. The photocatalytic and optical absorption properties obtained by experiments reveal that Eu/Si-codoped TiO_2 has a much stronger absorption and photocatalytic activity than the pure TiO_2 , which verifies the reliability of the calculation results.

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