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Citation: Applied Physics Letters 101, 062106 (2012); doi: 10.1063/1.4745193
View online: http://dx.doi.org/10.1063/1.4745193
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/101/6?ver=pdfcov
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Enhanced optical absorption and photocatalytic activity of anatase TiO₂ through (Si,Ni) codoping

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(Received 2 April 2012; accepted 27 July 2012; published online 9 August 2012)

The electronic and optical properties of (Si,Ni)-codoped anatase TiO₂ are investigated using the density functional theory. The calculated results indicate that the synergistic effects of (Si,Ni) codoping can effectively extend the optical absorption edge, which can lead to higher visible-light photocatalytic activity than pure anatase TiO₂. To verify the reliability of our calculated results, nanocrystalline (Si,Ni)-codoped TiO₂ is synthesized by a sol-gel-solvothermal method, and experimental results also show that the (Si,Ni)-codoped sample exhibits better absorption performance and higher photocatalytic activities than pure TiO₂. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4745193]

Titania (TiO₂) has received intense attention as a promising candidate material for solar energy conversion and photocatalyst applications.3–2 However, the universal applications of TiO₂ are restricted to ultraviolet (UV) light (λ < 385 nm) due to the wide band gap of anatase TiO₂ (∼3.2 eV). 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, S, and Ni would result in a reduced band gap for TiO₂.3–5

A few latest researches show that different ions codoping into TiO₂ can further narrow its band gap and enhance its photocatalytic activity.6–13 For example, Li et al. reported the C/H-codoping produces significant bandgap narrowing, which leads to higher visible-light photocatalytic efficiency than the C-doped anatase TiO₂.8 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-light irradiation.9 These results indicate that codoping 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 (Si,Ni)-codoped TiO₂ have no report on the theory and experiment. Thus, the enhanced optical absorption and photocatalytic activity are expected for (Si,Ni)-codoped TiO₂.

In this letter, the electronic and optical properties of (Si,Ni)-codoped TiO₂ were investigated based on the density functional theory (DFT) to reveal the synergistic effects of (Si,Ni) codoping on the mechanism of band gap reducing and origin of the enhanced visible-light photocatalytic activity. Nanocrystalline (Si,Ni)-codoped TiO₂ was synthesized by sol-gel-solvothermal method. It was found that the (Si,Ni)-codoped TiO₂ showed excellent photocatalytic activity for the degradation of methylene blue (MB), which 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.14,15 The exchange correlation function was treated by the generalized gradient approximation (GGA) with the Perdew-Wang parameterization (known as GGA-PW91).16 A cutoff energy of 500 eV and a Monkhorst-Pack k-point mesh of 9 × 9 × 9 was used for geometry optimization, electronic, and optical properties 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 is well-known that the traditional DFT method usually underestimates the band gap for semiconductors. However, the DFT+U approach introduces an on-site correction in order to describe systems with localized d electron, which can produce better band gaps in comparison with experimental results. Therefore, our all calculations of the electronic and the optical properties were conducted using the GGA+U method18–21 for both Ti 3d and Ni 3d 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.22

The valence electron configurations considered in this study included Ti (3d²4s²), O (2s²2p⁴), Si (3s²3p³), and Ni (3d⁸4s²). All the doped systems were constructed from a relaxed (2 × 2 × 1) 48-atom anatase TiO₂ supercell, shown in Fig. 1(a). As the position of Ni in the TiO₂ lattice was unclear, variety of positions of Ni atoms in the lattice were considered, such as substitutional Ni at the Ti site (Ni@Ti) and O site (Ni@O). Theoretical results confirmed that Si atom was incorporated as cation in the TiO₂ lattice, an Ti atom was substituted by an Si atom (Si@Ti).23 Similar substitutions were also considered for codoped systems, as Si locates at Ti site and Ni locates at either Ti or O site.

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101, 062106-1 © 2012 American Institute of Physics
(Si@Ti&Ni@Ti and Si@Ti&Ni@O). To determine the relative stabilities of the doped systems, we calculated the defect formation energies ($E_f$) for the monodoped and codoped systems according to the formulas

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

(1)

$$E_f(Si@Ti&Ni@O) = E_{(Si@Ti&Ni@O)} - E_{(pure)} - (\mu_{Si} + \mu_{Ni} - \mu_Y - \mu_Y),$$

(2)

where $X$ = Si, Ni, $Y$ = Ti, O, $E$ represents the total energy, and $\mu$ is the chemical potential. The chemical potential of O atom ($\mu_O$) is determined by the energy of an O$_2$ molecule. The calculated formation energies are listed in Table I. It shows that Ni impurity is preferred to substitute O in lattice because of the smallest formation energy in both Ni-doped and (Si,Ni)-codoped systems. Moreover, the charge analyses indicate that the impurities atoms of Si and Ni present a positive valance state, which is consistent with the experimental results.

To investigate the electronic properties of Si and/or Ni (co)doping anatase TiO$_2$, the total density of states (TDOS) and partial density of states (PDOS) were plotted in Fig. 2. It shows that the valence band (VB) is dominated by O 2p states while the conduction band (CB) consists mainly of Ti 3d states for pure anatase TiO$_2$. In Si-doped (Si@Ti) TiO$_2$, the CB broadens with the mixing of Ti 3d and Si 3s states, and the CB bottom has a decline about 0.5 eV, which can lead to a band gap narrowing. For Ni-doped (Ni@O) TiO$_2$, it can be observed that the band gap decreases by about 0.2 eV and most Ni 3d states are located in the band gap compared with the pure anatase TiO$_2$, which may be due to stronger interactions between the Ni 3d and O 2p orbitals. For (Si,Ni)-codoped (Si@Ti&Ni@O) TiO$_2$, a series of impurity states (Ni 3d) appear in the band gap, and all of impurity energy levels are located above the valence band maximum and below the conduction band minimum. Moreover, the band gap narrowed by 0.5 eV compared with the pure anatase TiO$_2$. Therefore, synergistic effect of (Si,Ni) doping can lead to a decrease of the photon excitation energy and shift the optical absorption edge to the visible-light region.

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$_2$, which partially reflects some experimental results. According to the obtained electronic structures, we calculated the complex dielectric function $\varepsilon = \varepsilon_1 + i\varepsilon_2$. The corresponding absorption spectrum was estimated by the following equation:

$$I(\omega) = 2\omega \left( \frac{(\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega))^{1/2} - \varepsilon_1(\omega)}{2} \right)^{1/2},$$

(3)

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

The optical 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 ultraviolet (UV) light and shows no absorption activity in the visible-light region. For Si-doped (Si@Ti) TiO$_2$, it is clear that the narrow band gap induces the increasing optical absorption in the UV-light region. For Ni-doped (Ni@O) TiO$_2$, there are a series of impurity states (Ni 3d orbital) appearing in the forbidden gap, which leads to a more significant the absorption of visible-light. For (Si,Ni)-codoped (Si@Ti&Ni@O) TiO$_2$ system, synergistic effect of (Si,Ni) doping induces a band gap narrowing and a series of impurity states appearing in the band gap, which can lead to a decrease of the photon excitation energy in the view of electronic structure. Therefore, the absorption of UV- and visible-light are greatly enhanced, and there is a large visible-light absorption wave packet at 600±50 nm, which may be responsible for the outstanding photocatalytic activity and the red-shift of optical absorption edge in (Si,Ni)-codoped anatase TiO$_2$.

In order to confirm the better photocatalytic activity of the (Si,Ni)-codoped TiO$_2$ compared to that of pure TiO$_2$, we further observed the UV-vis absorption spectrum by experiments.

**TABLE I.** Defect formation energies $E_f$ for different doped anatase TiO$_2$ systems.

<table>
<thead>
<tr>
<th>Doped models</th>
<th>Si@Ti</th>
<th>Ni@Ti</th>
<th>Ni@O</th>
<th>Si@Ti&amp;Ni@Ti</th>
<th>Si@Ti&amp;Ni@O</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_f$ (eV)</td>
<td>1.6452</td>
<td>8.0914</td>
<td>2.6591</td>
<td>9.6748</td>
<td>2.8120</td>
</tr>
</tbody>
</table>

FIG. 1. (a) 48-atom supercell model for defective anatase TiO$_2$ shows the location of the dopants. The atom doping sites are marked with Si and Ni. The blue spheres and red spheres represent the Ti and O atoms, respectively. The blue sphere and purple sphere represent Si and Ni atom, respectively. (b) XRD patterns for the pure and doped TiO$_2$.  

The calculated formation energies are listed in Table I. Therefore, synergistic effect of (Si,Ni) codoping can lead to a decrease of the photon excitation energy and shift the optical absorption edge to the visible-light region.
Firstly, a desired amount (0.1938 g) of nickel nitrate hexahydrate was dissolved in 31.70 mL of glacial acetic acid solution under stirring. Then, 7.44 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, and a 500 W long-arc xenon lamp was used as the simulated solar light source.

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 2000 e). The UV-vis absorption spectra were obtained using an UV-vis spectrophotometer (UV-3600) and using BaSO$_4$ as the reference sample.
Fig. 1(b) shows the XRD patterns of the samples of pure, Si-, Ni-, and (Si,Ni)-codoped TiO\textsubscript{2}. It is found that all of the diffraction peaks are contributed by the anatase TiO\textsubscript{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-, Ni-, and (Si,Ni)-codoped TiO\textsubscript{2} are 84.33, 252.31, 224.52, and 321.20 m\textsuperscript{2}/g, respectively. Obviously, with the coexistence of Si and Ni in TiO\textsubscript{2}, the surface area of TiO\textsubscript{2} powders is increased to 321.20 m\textsuperscript{2}/g, about four times of that of pure TiO\textsubscript{2} powders.

The optical absorption spectra of the pure and doped systems are obtained by experiments, shown in Fig. 3. Compared with the pure TiO\textsubscript{2}, it is clear that the incorporation of Si into TiO\textsubscript{2} lattice induces the enhanced optical absorption in the UV-light region. For Ni-doped system, it shows good absorption activity in the visible-light region. For (Si,Ni)-codoped TiO\textsubscript{2} system, the optical absorption curve shows that codoped TiO\textsubscript{2} with Si and Ni can greatly enhance the absorption of UV- and visible-light, which indicates synergetic effect of (Si,Ni) codoping. However, there are some misalignments between the experimental and theoretical results. In particular, there is a disparity between the DFT codoped results at 600 nm with experiment, which may be due to the shortcomings of the DFT leading to an unfaithful prediction for the impurity state. But, from the perspective of qualitative analysis, the experimental results are consistent with the calculations.

The photocatalytic activity of the pure and doped samples were evaluated by monitoring the degradation of MB, as shown in Fig. 4. The “Dark environment” shows that MB almost cannot be degraded using catalysts without the visible-light irradiation. 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\textsubscript{2} is reduced after doping with Ni. This is because the impurity states of Ni 3d is also easy to become the recombination center of electron-hole pairs. For (Si,Ni)-codoped TiO\textsubscript{2} sample (see Fig. 4), the improvement of photocatalytic activity in the coding sample can be attributed to the enhanced absorption of UV- and visible-light. Therefore, the (Si,Ni)-codoped sample exhibits better photocatalytic activity than the pure and Ni-doped sample, lower than the Si-doped sample.

In summary, we have studied the electronic and optical properties of (Si,Ni)-codoped TiO\textsubscript{2} based on DFT calculations. The synergistic effects of (Si,Ni) 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 (Si,Ni)-codoped TiO\textsubscript{2} has a much stronger absorption and photocatalytic activity than the pure TiO\textsubscript{2}, which verifies the reliability of the calculation results.

This work was supported by the National Science Foundation of China under Grants (Nos. 10647008, 50971099, 20876125, and 21176199), the Research Fund for the Doctoral Program of Higher Education (Nos. 20096101110017 and 20096101110013), Key Project of Natural Science Foundation of Shaanxi Province of China (Nos. 2010JZ002 and 2011JM1001). Yanming Lin would like to thank Dr. Kesong Yang and Dr. Run Long for helpful discussions on the topic.