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Title: Activation of specific sites on cubic nanocrystals: a new pathway for controlled epitaxial growth towards catalytic applications

A method has been developed for controlled epitaxial growth on cubic nanocrystals by selectively activating their surface via etching. This method enables the growth of a noble metal with high catalytic activities on another type of cheaper metal.

As featured in:

Theoretical design of highly active SrTiO$_3$-based photocatalysts by a codoping scheme towards solar energy utilization for hydrogen production†

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SrTiO$_3$ is a promising photocatalyst for the production of hydrogen from water splitting under solar light. Cr doping is an effective treatment for adjusting its absorption edge to the visible-light range, although the performance of Cr-doped SrTiO$_3$ is strongly affected by the oxidation number of the Cr ions. In this study, we theoretically predict that elevating the Fermi level, i.e., n-type carrier doping in SrTiO$_3$, can stabilize the desirable oxidation number of chromium (Cr$^{3+}$), contributing to a higher activity for H$_2$ evolution. Our computational results, based on hybrid density-functional calculations, reveal that such an n-type condition is realized by substituting group-V metals (Ta, Sb, and Nb), group-III metals (La and Y), and fluorine atoms for the Ti, Sr, and O sites in SrTiO$_3$, respectively. From our systematic study of the capability of each dopant, we conclude that La is the most effective donor for stabilizing Cr$^{3+}$. This prediction is successfully evidenced by experiments showing that the La and Cr codoped SrTiO$_3$ dramatically increases the amount of H$_2$ gas evolved from water under visible-light irradiation, which demonstrates that our guiding principle based on Fermi level tuning by the codoping scheme is valid for the design of advanced photocatalysts.

Introduction

There has recently been much interest in the potential use of photocatalytic materials in the production of clean-energy fuels and the reduction of environmental pollutants.¹ Since the discovery of the Honda–Fujishima effect,² TiO$_2$ has been extensively studied and applied to various commercial products, mainly for decomposing harmful chemicals or antifouling coatings. However, its application to fuel production is still limited due to the insufficient efficiency of overall water splitting for H$_2$ evolution.²⁻³ It is therefore a challenge to find a highly active photocatalyst to meet today’s demands for alternative energy resources. The perovskite strontium titanate (SrTiO$_3$ or STO) is a promising photocatalyst because of several advantages, such as high chemical stability and abundance of the constituent elements. The valence-band and conduction-band edges of STO are favorably situated for overall water splitting:¹⁻⁷ the valence-band maximum (VBM) is much lower than the oxidation potential of water, and the conduction band minimum (CBM) is ~0.8 eV (at pH = 0) higher than the standard hydrogen electrode potential (SHE).⁷ The sufficiently large band offset of the CBM with respect to SHE, which is much larger than that of anatase TiO$_2$ (0.1–0.2 eV), is a great benefit for the chemical reactions of photoexcited electrons with protons on the surface: 2H$^+$ + 2e$^-$ → H$_2$. Nevertheless, the photoabsorption range of STO is restricted to ultra-violet light because of its relatively wide band gap (3.25 eV), and the majority of sunlight, i.e. visible light is hardly utilized in photocatalytic reactions on pristine STO. One approach to overcome this problem is to induce a red-shift of the absorption edge while keeping the position of the CBM unchanged, in order to maintain its potential for proton reduction. Chromium (Cr) is of particular interest as an effective dopant for activating visible-light absorption in wide-gap semiconductor oxides.⁸⁻¹⁴ In fact, Cr-doped STO can work continuously and stably under visible light for more than 500 hours, and therefore possesses

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great potential for future solar hydrogen production.\textsuperscript{10-12} Importantly, Cr-doped STO is active only when the Cr ions possess a lower oxidation number (Cr\textsuperscript{3+}), while it is inactive for higher oxidation states of Cr.\textsuperscript{11,12} Thus, the stabilization of Cr\textsuperscript{3+} is a key strategy for enhancing the photocatalytic performance of Cr-doped photocatalysts.

Recently, we have theoretically shown that the desirable oxidation state Cr\textsuperscript{3+} predominates in n-type STO,\textsuperscript{15} namely the condition at which the Fermi level ($\epsilon_F$) is located near the CBM. The negatively charged substitutional Cr at the titanium site (Cr\textsubscript{Ti}), which was identified as the source of Cr\textsuperscript{3+} in Cr-doped STO, gives rise to fully occupied states above the VBM. Fig. 1(a) shows schematically the electronic structures associated with substitutional Cr at a Ti site with two different charge states (Cr\textsubscript{0}T and Cr\textsubscript{3+}T). In a low $\epsilon_F$ condition, the neutral charge state Cr\textsubscript{0}T, which corresponds to a high oxidation state of the Cr ion, is stabilized and photo-exited electrons are likely to be trapped in unoccupied gap states, degrading photocatalytic reactions. By contrast, shifting $\epsilon_F$ towards the conduction band eliminates the trapping centers due to the realization of the desirable charge state Cr\textsubscript{3+}T. Our computational results revealed that the occupied gap states associated with Cr\textsubscript{Ti} play an important role both in the photoresponse under visible light and in the elimination of electron trapping centers.\textsuperscript{19}

Previously, some experimental reports showed that the photocatalytic performance of Cr-doped STO is improved by codoping with antimony (Sb),\textsuperscript{19} tantalum (Ta),\textsuperscript{21} or niobium (Nb),\textsuperscript{11} or by pretreatment in a reducing H\textsubscript{2} atmosphere.\textsuperscript{21} In all of these treatments, the concentration of Cr\textsuperscript{3+} is expected to increase because of the electron carrier doping upon incorporation of these elements into STO. Although the effect of Cr\textsuperscript{3+} has been clearly addressed in our previous work,\textsuperscript{15} knowledge of the role played by codopants is still lacking. Since STO is also a promising semiconductor for oxide electronics,\textsuperscript{26,27} carrier doping of this technologically important material is of great interest to a wide range of researchers. In particular, n-type doping of this wide band-gap semiconductor is a key target in many different fields of research,\textsuperscript{19-21} and the most suitable donor for STO remains to be identified.

Here, we systematically investigate the effects of doping STO with the group-V metals Ta, Sb, Nb, and vanadium (V), the group-III metals lanthanum (La) and yttrium (Y), and the halogen fluorine (F), in order to theoretically identify the most effective donor in STO and the best candidate codopant for stabilizing Cr\textsuperscript{3+} in Cr-doped STO.

The above-mentioned metal dopants can be readily incorporated into the STO lattice thanks to the similarity of their ionic radii to those of the host elements. For instance, the ionic radii of La\textsuperscript{3+} (1.16 Å) and Nb\textsuperscript{5+} (0.64 Å) are very close to those of Sr\textsuperscript{2+} (1.26 Å) and Ti\textsuperscript{4+} (0.61 Å), respectively, that is, the group-V metals preferentially occupy the Ti site rather than the Sr site, while the group-III metals tend to occupy the Sr sites. Our theory, based on hybrid density-functional calculations, predicts that La is the best donor among the candidate elements in terms of electron doping ability and the ability to stabilize Cr\textsuperscript{3+}. The prediction is successfully validated by our experiments, which clearly show that La and Cr codoped STO exhibits the best performance for hydrogen evolution from water splitting under visible-light irradiation among the candidate materials examined in this work.

### Methods of calculation

Our calculations were based on density-functional theory with the hybrid-functional of Heyd, Scuseria, and Ernzerhof (HSE),\textsuperscript{23} which was implemented in the Vienna Ab initio Simulation Package (VASP) code.\textsuperscript{24} In the HSE approach, the Coulomb potential in the exchange energy of the Perdew, Burke, and Ernzerhof (PBE)\textsuperscript{24} functional is divided into short-range and long-range parts with a screening length of 10 Å. The long-range part and correlation potential are represented by the PBE functional, while the short-range part is mixed with the non-local Hartree–Fock (HF) exchange. We reproduced the experimental band gap of STO (3.25 eV) by using the HF mixing parameter of 28%. The HSE functional has been shown to improve the band gap of semiconductors and give a good description of the electronic structure and formation energies of defects and impurities.\textsuperscript{25,26} The cutoff energy of 400 eV was used for the plane-wave basis set. The defect calculations were performed using a (3 $\times$ 3 $\times$ 3) 90-atom supercell and a 2 $\times$ 2 $\times$ 2 grid of Monkhorst-Pack special $k$ points for the Brillouin zone integration. The effects of spin polarization were included in all calculations involving unpaired electrons.

The solubility of a donor-type impurity must be sufficiently high under a given sample growth condition. The formation...
energy is the key quantity that must be calculated to investigate the stability of a dopant, and is given by the following equation:

\[ E_f(X_i) = E_{tot}(X_i^d) - E_{tot}(STO) + \mu_{Ti} - \mu_X + q
\]

Here, \( E_{tot}(X_i^d) \) is the total energy of a STO supercell containing an impurity \( X \) \((X = Ta, Sb, Nb, or V)\) at the Ti site with \( q \) charge state, and was obtained by our density-functional calculations with a 90-atom supercell in the same way as that in case of Cr doping. \( E_{tot}(STO) \) is the total energy of perfect STO, obtained using the same supercell. \( E_{F} \) is the Fermi level referenced to the bulk VBM, which corresponds to the energy of the electron reservoir for charged impurities. A correction was applied to \( E_{F} \) to account for the difference in electrostatic potential between the bulk and the defect-supercell. The impurity \( X \) was taken from a reservoir with energy \( \mu_X \), and the substituted Ti atom was placed in a reservoir with energy \( \mu_{Ti} \). The energies \( \mu_X \) and \( \mu_{Ti} \) thus represent the chemical potentials, and depend on the experimental growth or annealing conditions. The procedure for estimating \( \mu_{X} \) will be addressed at great length later. When STO is grown under equilibrium conditions, the chemical potentials of the constituent atoms, which are referenced to the values of their elemental forms, must satisfy the equilibrium condition \( \mu_{Sr} + \mu_{Ti} + 3\mu_O = \Delta H(STO) = -16.2 \text{ eV} \), where \( \Delta H(STO) \) is the formation enthalpy of STO. The formation of unwanted compounds, such as \( \text{SrO} \), can be avoided by imposing the condition \( \mu_{Sr} + \mu_O < \mu_{SrO} \). Similar bounds were imposed for \( \text{SrTiO}_3 \), \( \text{TiO}_2 \), and \( \text{Ti}_2\text{O}_3 \). Analogous forms of eqn (1) can be written for the substitutional \( \text{La}_{Sr} \), \( \text{Y}_{Sr} \), and \( \text{F}_{O} \). The above-mentioned conditions yield the range of chemical potentials that allow the stable growth of STO, which can be represented by a domain in the two-dimensional space defined by \( \mu_{Sr} \) and \( \mu_{Ti} \) (dark-shaded areas in Fig. 1(b) and 1(c)).

Results and discussion

Here we initially examine the effect of an upward shift of \( E_{F} \) on the stabilization of \( \text{Cr}_{Ti} \). Fig. 1(b) and 1(c) illustrate the Cr impurities that give the lowest formation energy at each chemical potential condition of \( (\mu_{Sr}, \mu_{Ti}); \text{Cr}_{Ti} \), \( \text{Cr} \) substituted for \( \text{Sr} \) \((\text{Cr}_{Sr})\), and \( \text{Cr} \) at an interstitial site \((\text{Cr}_{i})\). These are shown in Fig. 1(b) for \( E_{F} = 0.3 \text{ eV} \) \((p\text{-type STO})\) and in Fig. 1(c) for \( E_{F} = 3.0 \text{ eV} \) \((n\text{-type STO})\). Here, \( \mu_O \) is uniquely determined at each point \((\mu_{Sr}, \mu_{Ti})\) through the above-mentioned equilibrium condition. For \( p\text{-type STO} \), \( \text{Cr}_{Ti}^{3+} \) and \( \text{Cr}_{Ti}^{4+} \) are the dominant species under the stable growth condition, as illustrated by the dark-shaded domain in Fig. 1(b). By contrast, for \( n\text{-type STO} \) where \( E_{F} \) is located near the CBM, the dark-shaded domain is associated only with \( \text{Cr}_{Ti}^{3+} \) (Fig. 1(c)). This suggests that a higher concentration of \( \text{Cr}_{Ti}^{3+} \), which is advantageous for photocatalytic activity, can be obtained under \( n\text{-type conditions}. \) However, such an \( n\text{-type condition is} \) not achieved without external doping, as addressed in the following. In order to determine realistic values of the chemical potentials, \( \mu_O \) was estimated by including contributions from enthalpy and entropy. \( \mu_O \) is expressed as

\[ \mu_O(T, P_0) = \{(H_0 + \Delta H(T)) + T(S_0 + \Delta S(T))/2 \}

where the tabulated values for standard \( \text{O}_2 \) enthalpy at \( T_0 = 298 \text{ K} \) and \( P_0 = 1 \text{ atm} \) \((H_0 = 8.7 \text{ kJ mol}^{-1}) \) and entropy \((S_0 = 205 \text{ J mol}^{-1}) \) are used, \( \Delta H(T) = C_p(T - T_0) \) and \( \Delta S(T) = C_p \ln(T/T_0) \). Using the ideal gas law for \( T\geq 298 \text{ K} \), \( C_p = 3.5k_B \) is used for the heat-capacity per diatomic molecule. The experimental growth conditions of STO described in ref. 12, at a calcination temperature of \( 1100 \text{ °C} \) and a pressure of 1 atm, yields \( \mu_O = -1.57 \text{ eV} \). The equilibrium growth condition is now given as \( \mu_{Sr} + \mu_{Ti} = -16.2 + 3 \times 1.57 = -11.50 \text{ eV} \), which is represented by the dotted lines in Fig. 1(b) and 1(c). The chemical potentials \( \mu_{Ti} = -6.05 \text{ eV} \) and \( \mu_{Sr} = -5.45 \text{ eV} \) (represented by solid circles in Fig. 1(b) and 1(c)) then give the least favorable condition for \( \text{Cr}_{Ti} \) at the boundary of the shaded domain associated with the stable growth condition.

Here, we address how to estimate the chemical potential of the dopants \( \mu_{X} \), which is an important factor in determining the impurity solubility. Fig. 2 illustrates the thermodynamically stable phases for the relevant transition metal (TM) compounds over the range of possible growth conditions between the O-poor limit \((\mu_O = -5.27 \text{ eV})\) and the extreme O-rich limit \((\mu_O = 0)\). \( \mu_{X} \) can be derived from the formation enthalpy of its limiting phase which is subject to an upper bound. For instance, for the realistic growth condition \( \mu_O = -1.57 \text{ eV} \) (dashed-dotted line in Fig. 2), \( \mu_{Cr} \) is determined by the formation enthalpy of \( \text{Cr}_2\text{O}_3 \) that is, \( 2\mu_{Cr} + 3\mu_O \leq \Delta H(\text{Cr}_2\text{O}_3) \), where the upper bound of \( \mu_{Cr} = (\mu_{CrO}_3 - 3\mu_O)/2 \) if \( \mu_{Cr} \) is pushed higher than the upper bound, \( \text{Cr}_2\text{O}_3 \) will form in addition to the \( \text{Cr} \) incorporated in the STO lattice. Using a similar procedure, the upper bound for \( \mu_{X} \) where \( X = Ta, Sb, Nb, V, La, \) and \( Y \) can be determined.

Fig. 3 shows the calculated formation energies of the \( Cr \)-related defects for these realistic chemical potentials, indicating that \( \text{Cr}_{Ti} \) is a more stable form of chromium than the other forms \((\text{Cr}_{Sr} \text{ or } \text{Cr}_{i})\) for a wide Fermi level range, as we discussed in our previous paper. Under a thermodynamic equilibrium condition, the charge neutrality must be satisfied when the concentrations of the positively charged \( \text{Cr}_{Ti}^{3+} \) and the negatively charged \( \text{Cr}_{Ti}^{4+} \) are balanced. This determines the pinning level of
than that of TaTi. We found that SbTi, TaTi, and NbTi do not stabilize Cr introduce in-gap states when positively charged (Sb+ and Nb+, respectively) but are closer to that of Ti than that of Sr, preferential substitution at the Ti site is expected. This is supported, for example, by the fact that the calculated formation energy of TaSr is more positive than that of O2− (1.40 Å), suggesting that O2− is readily substituted by F−. In a similar fashion to the other shallow donors, the extra electron of F0 in Cr-doped STO is found to occupy the extended state located at the bottom of the conduction band, whereas F0 does not form any in-gap states. We note that interstitial F (F+) is energetically unstable, having a much higher formation energy than F0. The density of states (DOS) for TaTi, TaSr, NbTi, NbSr, LaSr, YSr, and F0 in the positive charge state, showing that they do not introduce in-gap states, are shown in the ESL [15].

We now discuss the capability of the codopants to stabilize Cr3+ and enhance the photocatalytic activity of STO. The first factor to consider is that the codopants should not cause trapping centers for photoexcited electrons. This is true for the Ta, Nb, Sb, Y, La, and F impurities that are incorporated into STO (based on the assumption that the dominant forms of the Ta, Nb, Sb, Y, La, and F impurities are Ta0, Nb0, Sb0, Y0, La0, and F0, respectively). By contrast, the incorporated V impurity creates deep states in the gap and should therefore be excluded from the candidate codopants. The second factor to consider when choosing suitable codopants is their solubility. The donor impurities are activated only when their solubility in the host material is sufficiently high. From Fig. 4, it is clear that LaSr has the lowest formation energy (highest solubility) among the examined donors under the realistic growth condition corresponding to μO = −1.57 eV, which determines the upper bound of the chemical potential of each dopant as discussed before; TiO2, NbTi, V0, SbTi, Y0, and La0 Sr are limited by the formation of the binary metal oxides Ta2O5, Nb2O5, V2O5, Sb2O5, Y2O3, and La2O3, respectively (see Fig. 2). The solubility of F0 is limited by the formation of SrF2. In other words, the chemical potential of a dopant must be carefully estimated from the limiting phase, since it significantly affects the solubility of the dopant.

In Cr-doped STO, the pinned Fermi level (εF = 0.92 eV) is relatively low, and the majority of the CrTi3+ is present in the neutral charge state (CrT152) as mentioned above. Under this condition, the photocatalytic activity of Cr-doped STO is depressed. However, the photocatalytic activity is triggered when CrTi3+ is stabilized, an upward shift of the pinned εF should
The concentration of Cr in order to estimate the relative concentrations of Cr\(_0\) the favorable charge state Cr\(_{\text{Ti}}\) can be computed from the binding energy, positive over the entire range of \(E_F\), such that the impurities shown in Fig. 4 were sufficiently added a constant value to the formation energies of the codopant, Cr\(_0\) respectively. The donor impurity with a lower formation energy gives a higher position of the pinning level. The position of the pinning level with respect to VBM significantly affects the relative concentrations of Cr\(_0\) and Cr\(_{\text{Ti}}\), as shown in Fig. 5.

Under thermal equilibrium, the concentration of Cr\(_{\text{Ti}}^0\) can be expressed as \(N_{\text{sites}} \exp(-E_f^{\text{doped}}/k_B T)\), where \(N_{\text{sites}} (\sim 1.67 \times 10^{12} \text{ cm}^{-3})\) is the number of available Ti sites in STO that can be substituted by Cr atoms. The negative formation energy of Cr\(_{\text{Ti}}\), shown in Fig. 3, gives a concentration that is too high for an impurity, indicating that the actual \(\mu_{\text{Cr}}\) is much lower than the upper bound estimated by our calculations; to obtain a positive value of \(E_f^{\text{doped}}\), the actual \(\mu_{\text{Cr}}\) should be at least 0.9 eV lower than the value of \(\mu_{\text{Cr}}\) taken from Cr\(_2\)O\(_3\). Therefore, in order to estimate the relative concentrations of Cr\(_{\text{Ti}}^0\) and Cr\(_{\text{Ti}}\) for different values of the pinned \(E_f\) (Fig. 5), we consistently added a constant value to the formation energies of the impurities shown in Fig. 4 such that \(E_f^{\text{doped}}\) became positive over the entire range of \(E_f\). Without the incorporation of the codopant, Cr\(_{\text{Ti}}^0\) remains the predominant species (solid square in Fig. 5). Codoping successfully shifts the pinning level towards the CBM, and the majority of Cr\(_{\text{Ti}}\) is replaced by the favorable charge state Cr\(_{\text{Ti}}\) at the \(E_f\) for Sb\(_{\text{Ti}}\) substitution. The concentration of Cr\(_{\text{Ti}}\) scales exponentially as a function of the pinned \(E_f\); we found the best and worst dopants for increasing the concentration of Cr\(_{\text{Ti}}\) to be La and Y, respectively.

We also investigated the possibility of the formation of a neutral defect-complex by coupling Cr\(_{\text{Ti}}\) with a codopant, which can be computed from the binding energy,

\[
E_b = E_f^{\text{doped}} - E_f^{\text{neutral}}(\text{LaSr}) - E_f^{\text{neutral}}(\text{LaSr})_0
\]

Here, \(E_f^{\text{neutral}}(\text{LaSr})\) is the formation energy of the donor impurity, such as Sb\(_{\text{Ti}}\), and \(E_f^{\text{neutral}}(\text{LaSr})_0\) is the formation energy of the Cr\(_{\text{Ti}}\)-D complex, in which Cr\(_{\text{Ti}}\) and D\(_+\) occupy adjacent sites. A positive value of \(E_b\) indicates that the Cr\(_{\text{Ti}}\)-D complex is lower in energy than the isolated Cr\(_{\text{Ti}}\) and D\(_+\) constituents. We found that the calculated binding energies for all the neutral complexes were relatively small (the highest value was \(\sim 0.3\) eV). For instance, \(E_b^{\text{neutral}}(\text{LaSr})_0\), \(E_b^{\text{neutral}}(\text{LaSr})\) of Cr\(_{\text{Ti}}\) and \(E_b^{\text{neutral}}(\text{LaSr})_0\), \(E_b^{\text{neutral}}(\text{LaSr})\) of Cr\(_{\text{Ti}}\) experience only a weak driving force to bind to each other. Once Cr and La are incorporated into a sample, under thermal equilibrium (high temperature) they will be confined to their energetically favorable sites (the Ti and Sr sites, respectively); only a small proportion of these dopants will form a complex. This can be clarified as follows. Under equilibrium growth conditions, we can estimate the proportion of the formed Cr\(_{\text{Ti}}\)-La\(_{\text{Sr}}\) complex by the following detailed balance:

\[
\frac{[\text{Cr}_{\text{Ti}}\text{La}_{\text{Sr}}]}{[\text{Cr}_{\text{Ti}}\text{La}_{\text{Sr}}]^0} = 
\exp\left(-\frac{E_b}{k_B T}\right)
\]

**Fig. 5** Calculated relative concentration of Cr\(_{\text{Ti}}\) defects, derived from hypothetical formation energies, as a function of Fermi level \(E_F\). The pinned \(E_F\) results from the charge-neutrality condition for codoped (circles) and non-codoped (square) Cr-doped STO.

**Fig. 6** Photocatalytic H\(_2\) evolution from water splitting of Cr and D codoped SrTiO\(_3\) under visible light irradiation, where D = La, Sb, Y, and Nb. All codoped samples were prepared using 5 mol% of Cr and 5 mol% of D.

**Fig. 7** X-ray photoelectron spectra of Cr 2p of (a) La–Cr, (b) Sb–Cr, (c) Y–Cr, and (d) Nb–Cr doped SrTiO\(_3\). The peaks assigned to Cr\(^{3+}\) and Cr\(^{4+}\) are indicated by dashed and dotted lines, respectively.
\[
\frac{[\text{Cr}_{\text{Ti}}][\text{La}_{\text{Sr}}]}{([\text{Cr}_{\text{Ti}}]-[\text{La}_{\text{Sr}}])} = \frac{N_{\text{sites}}}{N_{\text{config}}} \exp(-E_0/k_BT)
\]

where \([\text{Cr}_{\text{Ti}}],[\text{La}_{\text{Sr}}]\), and \([([\text{Cr}_{\text{Ti}}]-[\text{La}_{\text{Sr}}])\) are the concentrations of \text{Cr}_{\text{Ti}}, \text{La}_{\text{Sr}}, and \([([\text{Cr}_{\text{Ti}}]-[\text{La}_{\text{Sr}}])\), respectively. \(N_{\text{config}}\) is the number of configurations that can be formed, which is 8 for the \text{Cr}_{\text{Ti}}-\text{La}_{\text{Sr}} complex. Using the temperature of 1373 K and \([\text{La}_{\text{Sr}}] \sim 2.9 \times 10^{17} \text{ cm}^{-3}\), determined from the charge-neutrality condition described above, we obtained \([([\text{Cr}_{\text{Ti}}]-[\text{La}_{\text{Sr}}])]/[\text{Cr}_{\text{Ti}}] \sim 5.0 \times 10^{-4}\), which means that only 0.05% of \text{Cr}_{\text{Ti}} participates in the formation of the complex. During the cooling process, \text{Cr}_{\text{Ti}} and \text{La}_{\text{Sr}} remain on their sites if they are assumed to be immobile, and thus the proportion of dopants forming a stable complex remains small. Notably, the calculated binding energies of the complexes between the dopants in STO are much smaller than those in \text{TiO}_2.\(^{29}\) Our results show that the incorporated donor impurities in \text{Cr}-doped STO are unlikely to form complexes with \text{Cr}_{\text{Ti}}, and thus can be considered isolated. The photoabsorption properties of the codoped samples can hence still mainly be attributed to \text{Cr}_{\text{Ti}}.

Previous experimental results have shown that codoping \text{Cr}-doped STO with \text{Ta},\(^{34,35}\) \text{Sb},\(^{34}\) or \text{Nb},\(^{35}\) significantly enhances the photocatalytic activity, whereas codoping with \text{V}\(^{3+}\) decreases the activity, in good agreement with our calculations. It has also been found that \text{Cr}^{3+} is stabilized under \text{O}-deficient conditions,\(^{36}\) which enhances the \(n\)-type condition. Our results are not only applicable to the stabilization of active \text{Cr} ions in the \text{Cr}-doped STO photocatalyst, but can also provide a route towards the fabrication of \(n\)-type STO. Our study clearly shows that \(n\)-type STO can be realized by doping with \text{Nb} or \text{La}, both of which have high solubility under the realistic growth condition discussed above. Indeed, it has long been realized that doping \text{STO} with \text{Nb} or \text{La} induces a transition from an insulator to an \(n\)-type semiconductor.\(^{34,35}\) The dopants \text{Ta}, \text{Sb}, and \text{Y} also act as shallow donors, although their solubility in \text{STO} is limited due to their relatively high formation energies compared to those of \text{Nb} and \text{La} (see Fig. 4). As in other oxides, such as \text{ZnO},\(^{44}\) \text{Fe} is a shallow donor in \text{STO} and is highly soluble under \text{O}-deficient conditions. By contrast, \text{Fe} is a deep acceptor with a high formation energy, and thus cannot contribute to \(p\)-type conductivity in \text{STO}. Theoretical studies of electron-doped \text{STO} have also been carried out and are consistent with our results.\(^{34,35}\)

Now we demonstrate the photocatalytic performance of \text{Cr}-doped \text{STO} codoped with \text{La}, \text{Nb}, \text{Sb}, and \text{Y}, which are theoretically predicted to be the best to the worst codopants for increasing \text{Cr}_{\text{Ti}}, in that order. The detail of experiments can be found in the ESI.\(^{1}\) We found that all codoped samples can absorb light in the visible region, as shown in Fig. S1.\(^{1}\) Fig. 6 shows the photocatalytic activities of \text{Cr}-doped \text{STO} codoped with \text{La}, \text{Nb}, \text{Sb}, and \text{Y} for \text{H}_2 evolution from water splitting under visible light irradiation. \text{Cr}-doped \text{STO} codoped with \text{La} (\text{La-Cr:STO}) showed the highest activity, in excellent agreement with our theoretical prediction. However, the \text{H}_2 evolution activity of \text{Nb-Cr:STO} is the lowest, which is inconsistent with our prediction. This discrepancy might result from the presence of other types of \text{Nb}-related defects, such as \text{Nb} interstitials or its complexes, and the carrier concentration of doped electrons is not sufficiently high to shift the Fermi level up to the expected position under our growth condition. However, the identification of the most stable \text{Nb}-related defect in \text{STO} is beyond the scope of this work.

In contrast, although the \text{H}_2 evolution activity of \text{Sb-Cr:STO} was much lower than that of \text{La-Cr:STO}, it is still higher than that of \text{Nb-Cr:STO}. This could be attributed to the fact that \text{Sb} does not have partially filled \(d\) states, and thus its related defects, if formed, are unlikely to cause carrier recombination. \text{Y-Cr:STO} exhibits \text{H}_2 evolution activity comparable to that of the \text{Sb-Cr:STO} sample at the beginning of the photochemical reaction. However, the activity gradually decreases with longer irradiation time (Fig. 6). This is qualitatively consistent with our prediction that the activity of \text{Y-Cr:STO} is lower than that of \text{Sb-Cr:STO}. As mentioned above, the \text{La-Cr:STO} possesses the highest amount of \text{Cr}_{\text{Ti}} compared to the other codoped samples and thus is a highly active photocatalyst under visible-light irradiation; recently, via a synthesis improvement and a reaction-environment modulation, \text{La-Cr:STO} was found to exhibit a high quantum yield of 25.6% \((\lambda = 425 \pm 12 \text{ nm})\) for \text{H}_2 evolution,\(^{18}\) which lends strong support to the findings of our study herein. Next we discuss the effect of donor impurities on the oxidation state of \text{Cr} in the codoped samples.

X-ray photoelectron spectroscopy (XPS) measurements were performed to investigate the oxidation state of doped \text{Cr}. Fig. 7 shows the XPS spectra of \text{Cr 2p} of the codoped samples. All the codoped samples showed a peak at about 576.4 eV, which is very close to the peak assigned to \text{Cr}^{3+} at 576.7 eV, however, some of our samples showed the peak assigned to \text{Cr}^{6+} at 579.2 eV.\(^{18}\) The relative intensity of XPS allows us to understand the effect of the codopant on the oxidation state of doped \text{Cr} as follows. \text{La-Cr:STO} and \text{Nb-Cr:STO} showed a high peak intensity of \text{Cr}^{3+}, while the peaks assigned to \text{Cr}^{6+} are almost negligible, in agreement with our calculations that codoping with either \text{La} or \text{Nb} should efficiently increase the concentration of \text{Cr}^{3+}. However, based on our experimental result, codoping with \text{Nb} does not enhance the photocatalytic activity even though the concentration of \text{Cr}^{3+} is high, indicating that codoping with \text{Nb} possibly leads to the formation of other types of defects which cause carrier recombination. \text{Sb-Cr:STO} showed a relatively low peak intensity of \text{Cr}^{3+}, while a small shoulder of the peak assigned to \text{Cr}^{6+} was observed. \text{Y-Cr:STO} clearly showed a high peak intensity of \text{Cr}^{6+} compared to that of \text{Cr}^{3+}, in agreement with our theory (Fig. 5) and experiment (Fig. 6).

Conclusions

In summary, we have systematically studied the capability of several dopants (\text{V}, \text{Nb}, \text{Ta}, \text{La}, \text{Y}, and \text{F}) for the enhancement of the photocatalytic performance of \text{Cr}-doped \text{SrTiO}_3. Based on our density-functional calculations for the stability of the donor-type impurities, \text{La} substituted for \text{Sr} (\text{La}_{\text{Sr}}) was predicted to be the best donor for shifting the Fermi level towards the conduction band of \text{SrTiO}_3. The \(n\)-type condition is advantageous for increasing the concentration of negatively charged \text{Cr}_{\text{Ti}} (\text{Cr}^{3+}), which is the key oxidation state for activating
photocatalytic reactions. The prediction from theory has been successfully evidenced by our experiments showing that La and Cr codoped SrTiO$_3$ shows markedly high activity for H$_2$ evolution from water splitting under visible-light irradiation compared to the other candidate dopants (Nb–Cr, Sb–Cr, or Y–Cr). Furthermore, our computational results show that the other substitutional defects, SbTi, TaTi, NbTi, Y$_8$Sr, and FO, are also shallow donors, although they are less soluble in SrTiO$_3$ than La$_{10}$ is, whereas V$_{Ti}$ creates deep states in the band gap and is unable to produce the $n$-type condition. By combining theoretical and experimental investigations, our guiding principle of Fermi level tuning by a doping scheme was found to be reliable for the design of Cr-doped SrTiO$_3$, and represents a significant step forward in the development of advanced photocatalysts.

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Notes and references