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Towards high visible light photocatalytic activity in rare earth and N co-doped SrTiO₃: a first principles evaluation and prediction

Chao Zhang,^{*a} Nan Jiang,^a Shiai Xu,^{ab} Zheng Li,^a Xingliang Liu,^a Tianle Cheng,^a Aixia Han,^a Haitang Lv,^a Wenliang Sun^a and Yunlei Hou^a

The band structure and photocatalytic activity of RE (La, Ce, Pr or Nd) mono-doped and RE–N co-doped SrTiO₃ for band gap reduction are studied systematically using first principles calculations. Based on the evaluation methods proposed by us previously, various RE–N co-doped cases with La–N, Ce–N, Pr–N and Nd–N co-doped in SrTiO₃ are studied. By comprehensive comparison, the favourable co-doping dopants are obtained and the predicted Pr–N co-doped SrTiO₃ shows that it may serve as an effective potential candidate photocatalyst for water splitting under visible light among the four types of RE–N co-doped cases. In addition, the f state electrons from the RE atom may have a greater contribution to the band structure narrowing of the RE–N co-doped SrTiO₃.

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1. Introduction

Currently, there are numerous studies on exploiting the potential of semiconductor-based photocatalysts for water splitting and hydrogen production.^{1,2} As one of the typical perovskites, SrTiO₃ has been extensively studied for its potential application in this area.^{3–5} However, due to the wide band gap (about 3.2 eV) of SrTiO₃, it shows a poor response on its exposure to visible light.⁶ Currently, several researchers are trying to obtain substantially more sunlight by narrowing the band gap of SrTiO₃. A common strategy for band gap reduction is to dope SrTiO₃ structures with various cations or anions.^{7–11} Since mono-doping may cause compensating defects, co-doping has been proposed to overcome these limitations in SrTiO₃.^{12–17}

There have been numerous reports on transition metal ion or noble metal dopants with non-metal co-doping on SrTiO₃ previously. However, the rare-earth with non-metal co-doped SrTiO₃ and their photocatalytic properties have seldom been reported thus far. Only a few research studies mention this topic. Wei *et al.*¹⁸ reported that the donor–acceptor pair recombination by co-doping could maintain the charge balance and promote the photogenerated carriers efficiency for N–La co-doped SrTiO₃ under visible light. Wang *et al.*¹⁹ reported co-doping (N–La, C–Ce, and N–Ce–N) on the electronic structure of SrTiO₃ and found that (N–Ce–N) co-doping can significantly

narrow the band gap of SrTiO₃. Dawson *et al.*²⁰ reported the defect chemistry of RE mono-doped SrTiO₃/CaTiO₃/BaTiO₃ and found that RE doping is energetically preferred in BaTiO₃ and least favourable in SrTiO₃.

Recently, the rare earths have attracted great attention with TiO₂ and have shown their importance in the TiO₂ matrix due to their incompletely occupied 4f and empty 5d states.²¹ The photocatalytic activity of TiO₂ is improved by rare earth (RE) doping and the high oxidation states of RE ions may serve as efficient electron traps.^{22–25} Inspired by this, we think that it is necessary to systematically study the electronic structure and band edge of SrTiO₃ doped with RE elements or co-doped with RE and non-metals. In addition, since the RE elements have similar ionic radii and complex 4f or 5d electrons, it is a great challenge to accurately calculate their electronic structure and predict the best co-doping properties.

Herein, we present a comparative study on the electronic structure and photocatalytic activity of RE and N co-doped SrTiO₃ with RE (La, Ce, Pr or Nd) as a donor and N as an acceptor for band gap reduction. By combining the evaluation methods proposed by us previously,²⁶ we pick the best co-doping dopant among the listed four co-doped cases *via* systematic evaluation and prediction. Moreover, the band structure of the chosen Pr–N co-doped SrTiO₃ shows that it may be a good candidate photocatalyst for water splitting under visible light.

2. Computational methods

Herein, all the calculations carried out were performed *via* density functional theory (DFT) using the CASTEP code.²⁷ The PBE function within GGA was used. The valence electrons and

^aChemical Engineering College, Qinghai University, Xining 810016, China. E-mail: zhangchaoqhu@126.com; Fax: +86-971-5310427; Tel: +86-971-5310427

^bShanghai Key Laboratory of Advanced Polymeric Materials, Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China



ionic core interaction were calculated by the Perdew–Wang 91 gradient-corrected functional²⁸ and ultra-soft pseudo-potentials.²⁹ The cut-off energy (E_{cut}) was set at 390 eV and a $2 \times 2 \times 2$ Monkhorst–Pack³⁰ k -mesh was adopted. The energy convergence was set to 5×10^{-5} eV per atom. The largest force on atoms was set at $0.1 \text{ eV } \text{\AA}^{-1}$ for convergence and criterion optimization. The stress was less than 0.2 GPa, and the maximum displacement was 5×10^{-4} nm. For the doping cases, a $2 \times 2 \times 2$ SrTiO₃ supercell with 40 atoms was used. N atom for O atom and RE (La, Ce, Pr or Nd) atom for Sr atom substitution was used in the SrTiO₃ structure to model the N or RE mono-doping case. In the case of co-doping, we introduced both N and RE atoms in the SrTiO₃ crystal structure with an N atom for O and RE atom for Sr in the same super structure to model the La–N, Ce–N, Pr–N and Nd–N co-doping. The chosen valence electronic configurations were 4s, 4p and 5s for Sr, 4s and 3d for Ti, 2s and 2p for O, 2s and 2p for N, 5s, 5p, 5d and 6s for La, 4f1, 5s2, 5p6, 5d1 and 6s2 for Ce, 4f3, 5s2, 5p6 and 6s2 for Pr, and 4f4, 5s2, 5p6 and 6s2 for Nd. The DFT + U formalism^{31,32} was employed for the accurate treatment of the correlated f or d electron phenomena with $U = 6.0 \text{ eV}$.²⁸

3. Results and discussion

3.1. RE mono-doping in SrTiO₃

3.1.1. RE mono-doping effects on formation energy and lattice parameters of SrTiO₃. The calculated structure of the un-doped SrTiO₃ crystal was determined first. The optimized structural parameters of the pure SrTiO₃ ($a = b = c = 3.935 \text{ \AA}$) are in good agreement with the experimental data³³ ($a = b = c = 3.905 \text{ \AA}$). For RE mono-doping on SrTiO₃, La prefers to substitute for the Sr site and because the ionic radii of Ce³⁺ (0.103 nm), Pr³⁺ (0.101 nm) and Nd³⁺ (0.100 nm) are similar to La³⁺ (0.115 nm), herein, we mainly consider the RE (La, Ce, Pr or Nd) atom substitute for the Sr site, which is described as La@Sr, Ce@Sr, Pr@Sr and Nd@Sr mono-doped SrTiO₃, respectively. All of the RE atom mono-doped models are labelled in Fig. 1(b).

In order to obtain the formation energy needed for the different mono doped cases, the doping formation energy (E_f) of the different mono-doped cases was calculated according to the listed formulas and the results are shown in Table 1.

Table 1 The calculated formation energies (E_f), and band gaps (E_g) of the different RE dopant mono-doped SrTiO₃

Dopant	E_f (eV)	E_g (eV)	E_g with scissor operator (1.0 eV)
Pure	—	2.20	3.20
La@Sr	−0.25	1.45	2.45
Ce@Sr	−1.17	2.36	3.36
Pr@Sr	−1.16	1.94	2.94
Nd@Sr	−1.04	1.11	2.11

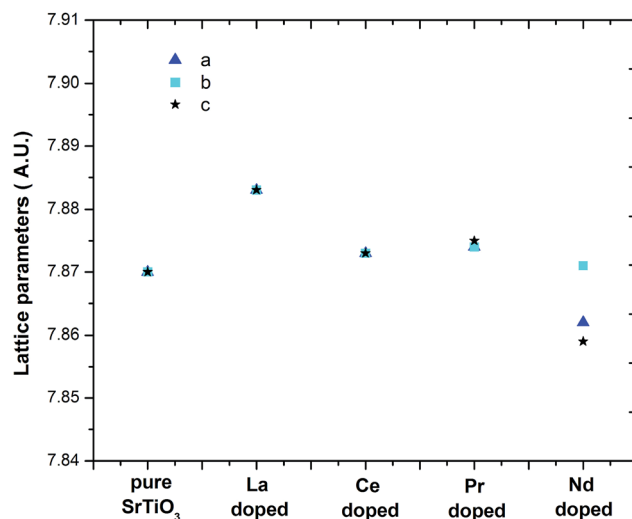


Fig. 2 Lattice parameters (supercell) change with the different types of RE mono-doped SrTiO₃.

$$E_f = E_{\text{N-doped}} - (E_{\text{un-doped}} - \mu_{\text{O}} + \mu_{\text{N}}) \quad (1)$$

$$E_f = E_{\text{La(Ce/Pr/Nd)-doped}} - [E_{\text{un-doped}} - \mu_{\text{Sr}} + \mu_{\text{La}} \text{ (or } \mu_{\text{Ce}}/\mu_{\text{Pr}}/\mu_{\text{Nd}})] \quad (2)$$

The E_f defines the energy of the mono or co-doped dopants in SrTiO₃, and $E_{\text{un-doped}}$, $E_{\text{N-doped}}$, $E_{\text{La-doped}}$, $E_{\text{Ce-doped}}$, $E_{\text{Pr-doped}}$, $E_{\text{Nd-doped}}$, are the total energies of the SrTiO₃ without doping and with N doping, La doping, Ce doping, Pr doping, and Nd

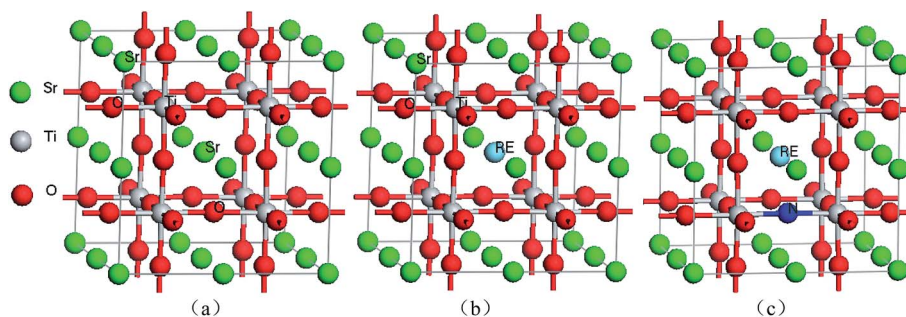


Fig. 1 SrTiO₃ supercell models (a) un-doped $2 \times 2 \times 2$ SrTiO₃ supercell, (b) one RE atom mono-doped $2 \times 2 \times 2$ SrTiO₃ supercell, and (c) RE–N co-doped $2 \times 2 \times 2$ SrTiO₃ supercell (RE = La, Ce, Pr or Nd atom); green, light gray, and red balls represent Sr, Ti, and O atoms, respectively.



doping, respectively. μ_{O} and μ_{N} are the energies of the O and N atom gained from the energies of the O_2 and N_2 molecular orbitals, respectively. μ_{Sr} , μ_{Ti} , μ_{La} , μ_{Ce} , μ_{Pr} and μ_{Nd} are calculated from the bulk Sr (gamma-strontium),³⁴ Ti (alpha-titanium),³⁵ La (hcp, structure),³⁶ Ce (hcp, structure),³⁶ Pr (hcp, structure),³⁶ and Nd (hcp, structure) crystals, respectively.

The smaller the defect formation energy needed, the more favourable the substitution for the dopant. From Table 1, the result shows that the formation energy of La@Sr is -0.25 eV, which is much larger than that of Ce@Sr, Pr@Sr or Nd@Sr. This is reasonable since the ionic radius of La^{3+} (0.115 nm) is larger than that of Ce^{3+} (0.103 nm), Pr^{3+} (0.101 nm) or Nd^{3+} (0.100 nm),

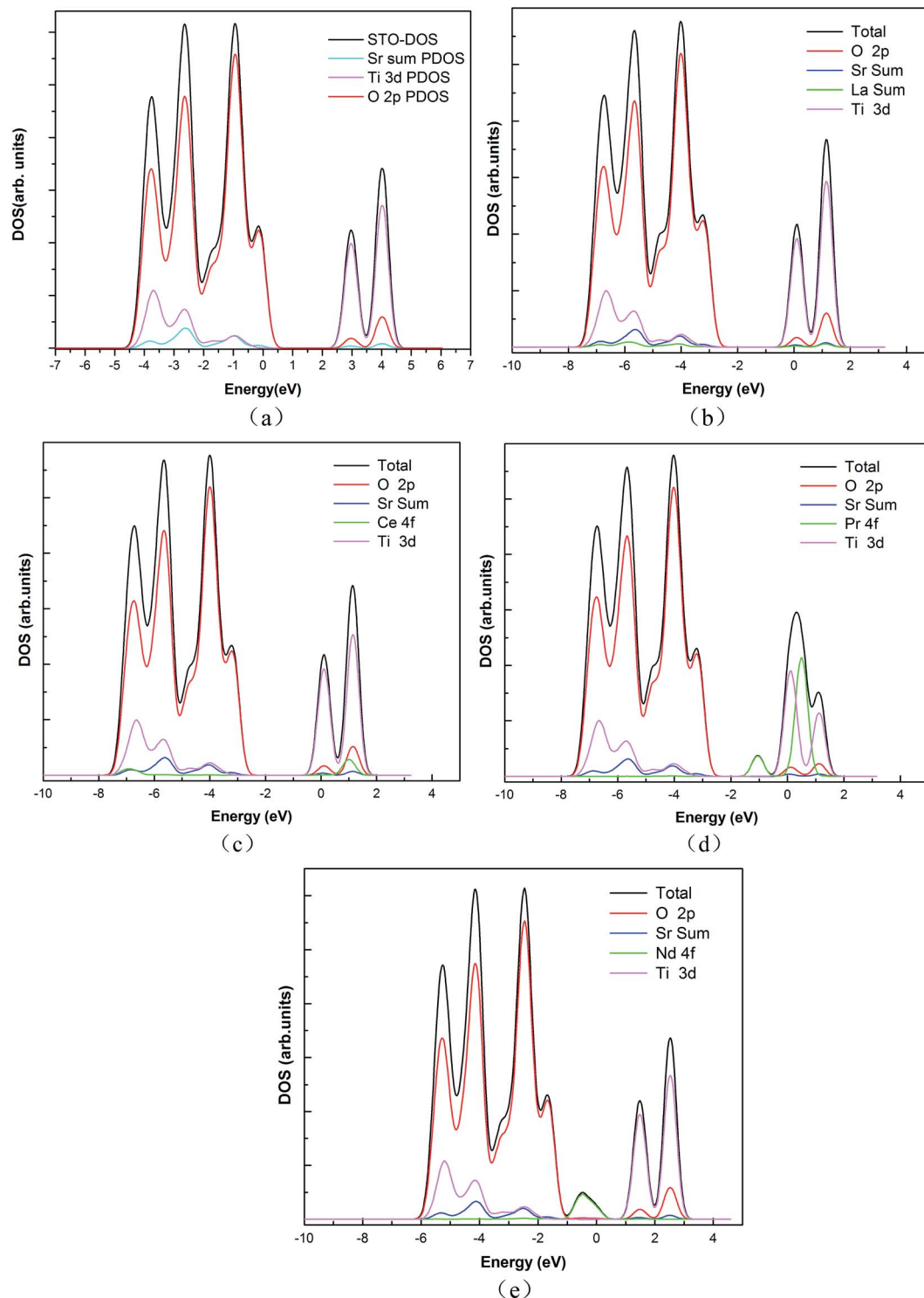


Fig. 3 Calculated DOS for (a) pure SrTiO_3 , (b) substitutional La for Sr doped SrTiO_3 , (c) substitutional Ce for Sr doped SrTiO_3 , (d) substitutional Pr for Sr doped SrTiO_3 , and (e) substitutional Nd for Sr doped SrTiO_3 . The VBM of pure SrTiO_3 is chosen as the energy zero.



which leads to the relative larger formation energy of Sr substituted by La.

The calculated lattice parameters (supercell) of the different RE mono-doped SrTiO₃ are shown in Fig. 2. From the lattice parameters trend we may conclude that La is energetically unfavourable compared with the Ce, Pr or Nd mono-doped cases, which is consistent with the changing trend of the defect formation energy or ionic radius of the four different RE mono-doped SrTiO₃.

3.1.2. RE mono-doping on band structure and band gap of SrTiO₃. The DOS and PDOS for pure and RE mono-doped SrTiO₃ calculated are shown in Fig. 3. It is clear that the VBM is mainly determined by the O 2p and Sr related states and the Ti 3d states mainly contribute to the CBM for undoped SrTiO₃. For the substituted La@Sr, Ce@Sr, Pr@Sr and Nd@Sr mono-doped SrTiO₃, the La@Sr mono-doped case has a relatively small effect on the band structure of SrTiO₃ (Fig. 3(b)), whereas the other three cases have a relatively big effect on the band structure of SrTiO₃. The 4f orbit electrons have a bigger contribution on the band structure narrowing of Pr or Nd mono-doped SrTiO₃. In addition, the f electron of Ce and Pr mainly located in the CB and the f electron of Nd tend to fall between the VB and CB of SrTiO₃, which may be due to the different f electron energies of the Ce, Pr and Nd atoms (Fig. 3(c and e)).

The band gap of the Pr@Sr or Nd@Sr mono-doped SrTiO₃ case shows some degree of narrowing, and in the Ce@Sr mono-doped case, it shows some degree of increase compared with the pure case (Table 1). From Table 1 we can clearly see that the band gap of La (Pr or Nd) mono-doped SrTiO₃ case shows some kind of narrowing, whereas in the Ce mono-doped SrTiO₃ case, it tends to slightly increase.

In order to describe the oxidation and reduction power of the RE mono-doped SrTiO₃, the valence band (VB) bottoms (E_{VB}) and conduction band (CB) bottoms (E_{CB}) were calculated empirically according to formula (3).³⁷ Moreover, the suitable band edge of the catalyst should lie between the water reduction and oxidation potential, which means that the conduction band edge should lie at a potential more negative than the water reduction potential (<0 V vs. NHE at pH 0).

$$E_{\text{CB}} = x_{\text{A}_a\text{B}_b\text{C}_c} - \frac{1}{2}E_{\text{g}} + E_0 \quad (3)$$

where E_{g} is the band gap, E_0 is the scale factor relating the reference electrode redox level to the absolute vacuum scale ($E_0 = -4.5$ eV for a normal hydrogen electrode), and $x_{\text{A}_a\text{B}_b\text{C}_c}$ is the absolute electronegativity of compound $\text{A}_a\text{B}_b\text{C}_c$, where the absolute electronegativity of La (Ce, Pr and Nd) atom was obtained from that reported by Bartolotti.³⁸

The calculated E_{CB} of pure, La mono-doped, Ce mono-doped, Pr mono-doped and Nd mono-doped SrTiO₃ are -1.16, -0.73, -1.19, -0.95, and -0.52 eV, respectively. Thus, the VB tops are 2.04, 1.72, 2.17, 1.99 and 1.59 eV, respectively. From the calculated E_{CB} and E_{VB} in Fig. 4, we conclude that the four types of RE mono-doped SrTiO₃ meet the requirements for water reduction without considering their efficiency, where the La (Pr or Nd) mono-doped case may be the best choice.

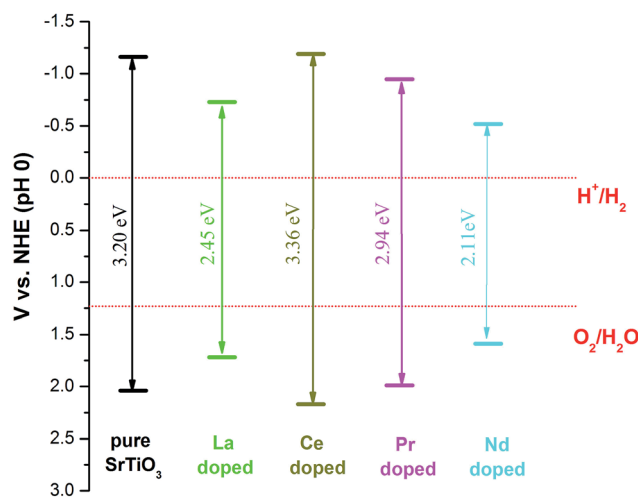


Fig. 4 Calculated E_{CB} and E_{VB} of RE mono-doped SrTiO₃ compared with the water reduction potential (<0 V vs. NHE at pH 0).

3.2. RE co-doping in SrTiO₃

3.2.1. RE co-doping effects on formation energy and lattice parameters of SrTiO₃. The formation energy needed for the different RE-N co-doped cases can be calculated similarly to that of the RE mono-doped cases, as previously described, with some revisions to the formula (formula (4)).

$$E_{\text{f}} = E_{\text{La}(\text{Ce/Pr/Nd})\text{-N-co-doped}} - [E_{\text{un-doped}} - \mu_{\text{O}} - \mu_{\text{Sr}} + \mu_{\text{N}} + \mu_{\text{La}}(\text{or } \mu_{\text{Ce}}/\mu_{\text{Pr}}/\mu_{\text{Nd}})] \quad (4)$$

The calculated atomic structures of the different RE-N co-dopings on SrTiO₃ are shown in Fig. 1(c) and the lattice parameters (supercell) of the different RE-N co-doped SrTiO₃ are listed in Table 2.

From Table 2, it can be seen that the obtained formation energy of the La-N co-doped case is much larger than the other three Ce(Pr/Nd)-N co-doped cases. The change trend is similar to that of the RE mono-doped case.

For the RE-N co-doping cases, the binding energy should also be considered, which can describe the coupling strength of the RE-N co-doping cases. The defect pair binding energies were calculated according to the formula mentioned by Wei *et al.*¹⁸ The obtained binding energies are 1.84 eV, 1.34 eV, 1.91 eV and 1.11 eV for La-N, Ce-N, Pr-N and Nd-N co-doped SrTiO₃. This, La-N and Pr-N may be more stable for SrTiO₃ co-doping just from this point of view.

Table 2 The RE-N co-doping formation energies (E_{f}), binding energies (E_{b}) and band gaps (E_{g}) of SrTiO₃

Dopant	E_{f} (eV)	E_{b} (eV)	E_{g} (eV)	E_{g} with scissor operator (1.0 eV)
Pure	—	—	2.20	3.20
La-N co-doped	8.27	1.84	1.02	2.02
Ce-N co-doped	3.36	1.34	1.01	2.01
Pr-N co-doped	2.49	1.91	0.99	1.99
Nd-N co-doped	3.35	1.11	0.23	1.23



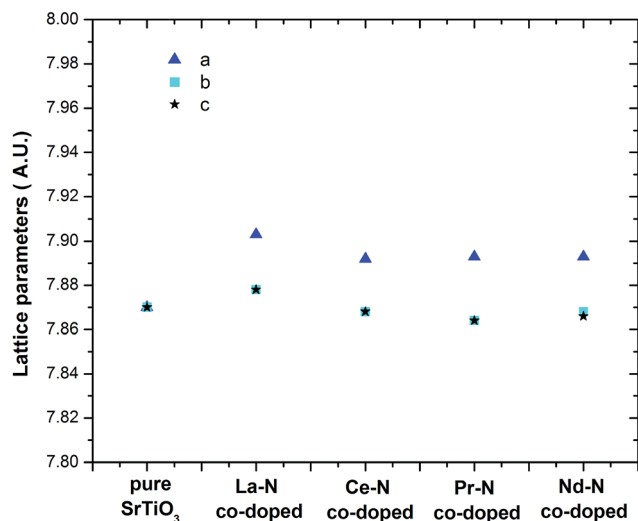


Fig. 5 Lattice parameter (supercell) changes with different types of RE-N co-doped SrTiO₃.

The lattice parameters (supercell) of the different RE-N co-doped SrTiO₃ were also calculated, and the result is shown in Fig. 5. From the calculated result it can be seen that the lattice parameter *a* has a larger change than that of *b* or *c*, which is

different from that of the RE mono-doped cases. This type of difference mainly originates from the N substitution for the O site, which also means that this type of substitution is more difficult than the RE substitution for the Sr site.

3.2.2. RE-N co-doping effects on band structure and band gap of SrTiO₃. To get a better understanding of the electronic structure of the different RE-N co-doped cases of SrTiO₃, we calculated the electronic band structure of the La-N, Ce-N, Pr-N and Nd-N co-doped SrTiO₃. From the obtained band structure, it can be seen that the La-N, Ce-N and Pr-N co-doped SrTiO₃ tend to be a direct band gap semiconductor. In addition, no single donor or acceptor level appears between the VB and CB, which means that the electron of the donor level from the RE element (La/Ce/Pr or Nd) passivates the same amount of holes on the acceptor level from N (Fig. 6(a-c)).

We also calculated the total DOS and PDOS for the RE-N co-doped SrTiO₃, as shown in Fig. 7. From the PDOS of Ce or Pr-N co-doped SrTiO₃, we find that the N 2p states form an effective complementarity with that of the Ce or Pr 4f states, which can effectively reduce the band gap (shown in Fig. 7(c and d)). However, the band structure almost tends to have conductor character for the Nd-N co-doped case, which may be due to the fact that the energy of the complete 4f states just falls between the VB and CB of SrTiO₃ after the co-doping (shown in Fig. 7(d)).

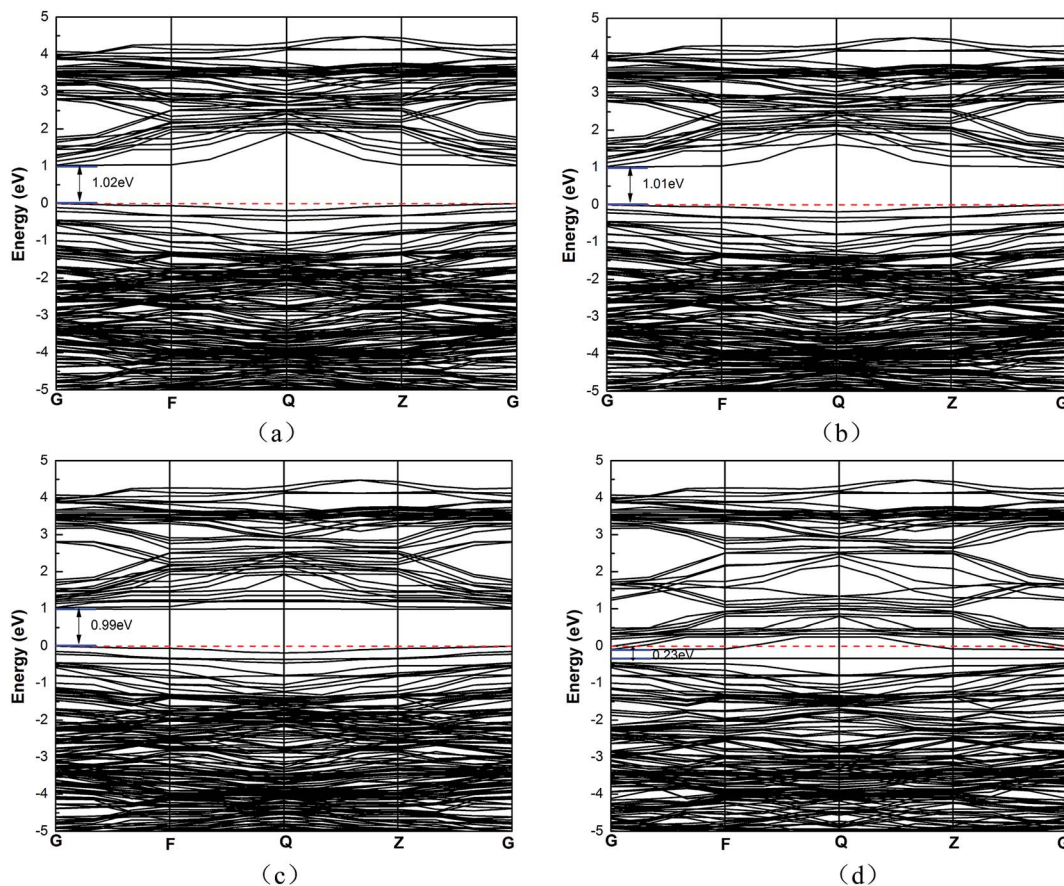


Fig. 6 Band structure plots of (a) La-N co-doped $2 \times 2 \times 2$ SrTiO₃ super-cell, (b) Ce-N co-doped $2 \times 2 \times 2$ SrTiO₃ super-cell, (c) Pr-N co-doped $2 \times 2 \times 2$ SrTiO₃ super-cell and (d) Nd-N co-doped $2 \times 2 \times 2$ SrTiO₃ super-cell.



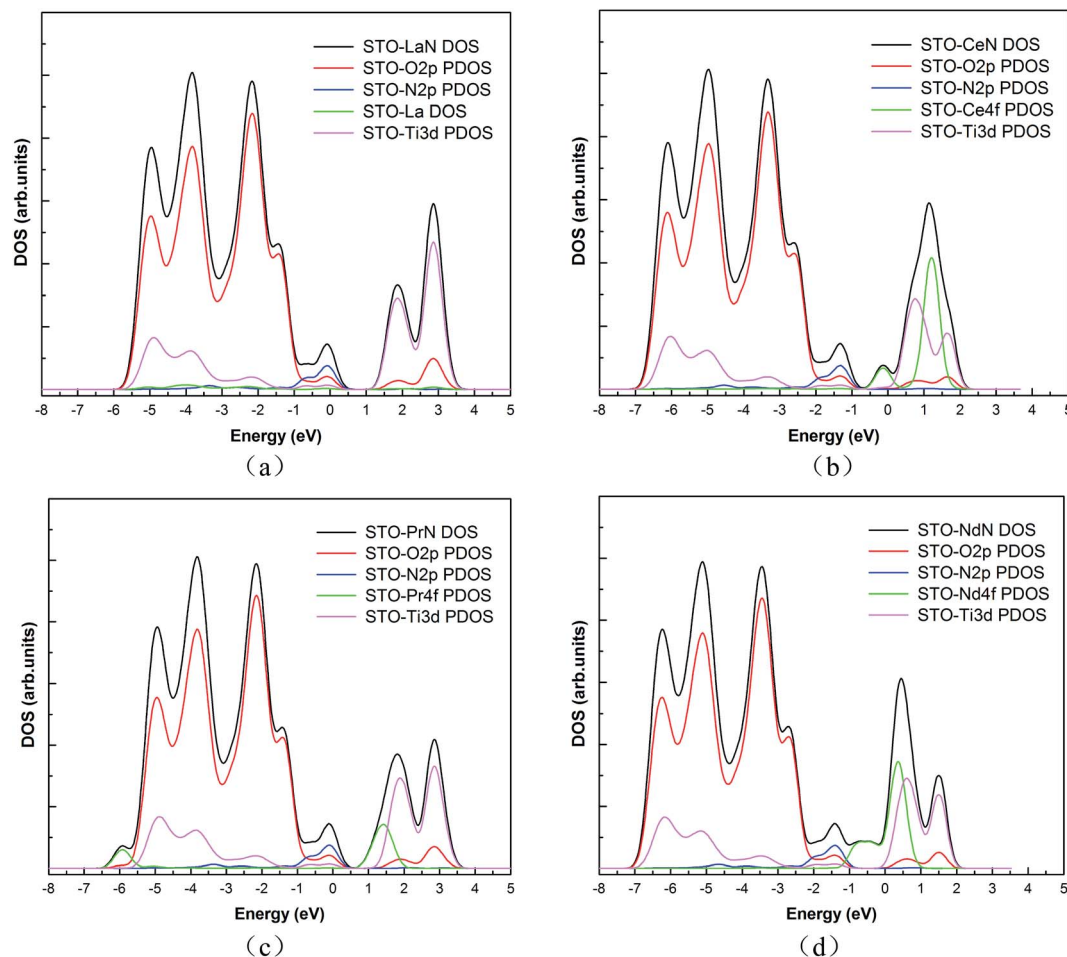


Fig. 7 Calculated DOS and PDOS for (a) La–N co-doped SrTiO_3 , (b) Ce–N co-doped SrTiO_3 , (c) Pr–N co-doped SrTiO_3 , and (d) Nd–N co-doped SrTiO_3 . The VBM of pure SrTiO_3 is chosen as the energy zero.

The band gap of the RE–N co-doped SrTiO_3 can be seen in Table 2. It is clear that the four types of RE–N co-doped SrTiO_3 cases all tend to have a narrowing trend compared with that of pure SrTiO_3 , which is different from that of the RE mono-doped cases. This difference indicates that the RE–N co-doped cases may have a greater impact on the band gap compared with that of the RE mono-doped cases, and thus RE–N co-doping may be a better strategy.

It is difficult to select a suitable RE–N co-doping from the abovementioned four types of co-doping cases just from the value of the band gap; we also have to consider the precise band edge of the valence band (VB) bottoms (E_{VB}) and conduction band (CB) bottoms (E_{CB}) of the co-doped case. Thus, the E_{VB} and E_{CB} of the RE–N co-doped cases were calculated also using formula (3).

The calculated E_{CB} of the La–N co-doped, Ce–N co-doped, Pr–N co-doped and Nd–N co-doped SrTiO_3 were -0.52 , -0.52 , -0.48 and -0.08 eV, respectively, and thus the VB tops were 1.50 , 1.49 , 1.51 and 1.15 eV, respectively. The precise band edges of the E_{VB} and E_{CB} of La–N, Ce–N, Pr–N and Nd–N co-doped SrTiO_3 are shown in Fig. 8. From the obtained E_{CB} and E_{VB} , we could deduce that the band edges of La–N, Ce–N and Pr–

N co-doped SrTiO_3 are located just out of the NHE potential and could well meet the requirements for water splitting and hydrogen production.

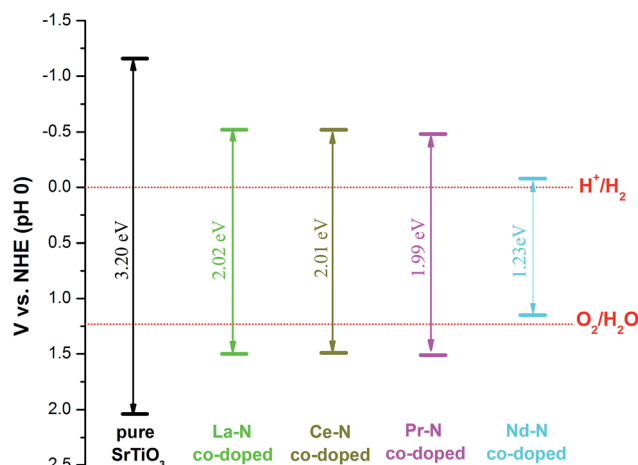


Fig. 8 The calculated E_{CB} and E_{VB} of the RE–N co-doped SrTiO_3 compared with the water reduction potential (<0 V vs. NHE at pH 0).



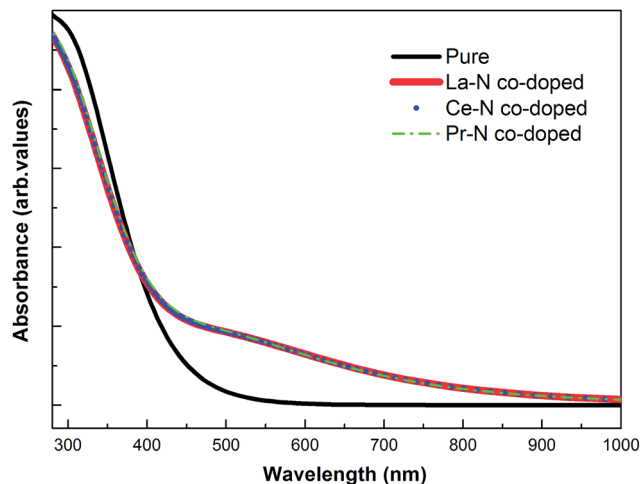


Fig. 9 Calculated optical absorption curves for pure, La-N, Ce-N, and Pr-N co-doped SrTiO₃.

3.2.3. Optical properties. The optical properties can be calculated from the dielectric function $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$, and the imaginary part of the dielectric constant (ϵ_2) can be calculated theoretically based on DFT.³⁹ A rigid scissor operator correction of 1.0 eV was adopted for the absorption spectra calculation. Then, the optical absorption coefficients for La-N, Ce-N, Pr-N and Nd-N co-doped SrTiO₃ and pure SrTiO₃ were calculated, and the obtained results are listed in Fig. 9. From the calculated absorption data, it can be seen that the absorption edge tends to redshift compared with the un-doped case for the co-doping of La-N, Ce-N, and Pr-N.

3.3. Prediction and picking the favorable RE-N co-doping dopants on SrTiO₃

As described before, it is insufficient to predict one RE-N co-doping case from the given La-N, Ce-N, Pr-N or Nd-N co-doping systems as the best candidate. Based on the three basic rules proposed by us previously,²⁶ we choose the best co-doping dopant among the listed four co-doped cases *via* systematic evaluation and prediction. By comprehensively combining the band gap, the precise band edge of E_{VB} and E_{CB} , the formation energy and binding energy of the different RE-N co-doping cases, the Pr-N co-doped dopant may be a good potential candidate for the co-doping of SrTiO₃ among the La-N, Ce-N, Pr-N and Nd-N co-doped cases, which may serve as an effective potential candidate photocatalyst.

4. Conclusion

We present a comparative calculation on the electronic structure and photocatalytic of RE (La, Ce, Pr or Nd)-N co-doped SrTiO₃ for band gap reduction. Based on the evaluation methods proposed by us previously, various types of RE-N co-doping cases with La-N, Ce-N, Pr-N and Nd-N co-doped in SrTiO₃ are studied. The obtained favourable co-doping dopant and the predicted Pr-N co-doped SrTiO₃ shows that it may serve as an effective potential candidate photocatalyst for water

splitting under visible light among the four RE co-doped cases. In addition, the f state electrons from the RE atom may have a greater contribution to the band structure narrowing of the RE-N co-doped SrTiO₃.

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