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Theoretical study on cation codoped SrTiO_3 photocatalysts for water splitting

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Abstract

The large band gap of SrTiO_3 is disadvantageous for photocatalytic applications. We therefore study cation codoping to modify the size of the band gap and extend the absorption to visible light. We identify efficient codoping schemes that guarantee charge compensation to avoid creation of localized states. Using the Heyd-Scuseria-Ernzerhof hybrid functional, we analyze the crystal and electronic structures as well as the optical properties. It is found that (Nb/Ta, Ga/In) codoping does not reduce the band gap, in contrast to (Mo/W, Zn/Cd) codoping. The position of the conduction band edge after (Mo, Cd) codoping impedes a high photocatalytic efficiency, whereas (Mo/W, Zn) and (W, Cd) codoping are found to be favorable.

PACS numbers:

Keywords: Density functional theory, oxide, perovskite, doping, photocatalysis

I. INTRODUCTION

Developing approaches that minimize or avoid hazardous substances is key for a sustainable economy. Hydrogen production by solar water splitting as a renewable (green) energy resource and minimization of the environmental pollution by photoreduction of CO_2 are two examples. Although materials for photocatalysis have been studied extensively (both experimentally and theoretically), efficient photocatalysts are still a focus of research. Since most of the metal-oxide photocatalysts, including perovskites, have too large optical band gaps for visible light, many efforts have been directed to a reduction by chemical doping. For example, cation-cation codoping of TiO_2 has been investigated experimentally for (Ni/Zn/Mo, Fe) [1–4], (Co/Nb/Ta, Ni) [5–7], (Y, V) [8], (Sb, Cr) [9], (Rh, Sr) [10] and theoretically for (Ni, Fe) [11], (Rh, Nb) [12], (Mo/W, Mg/Ca) [13], (La, Mn) [14]. Other studies have addressed (La, Ag) codoping of CaTiO_3 [15], (Sn, Ga) codoping of BiFeO_3 [16], and (W, Fe/Mo) codoping of BiVO_4 [17, 18].

SrTiO_3 is a perovskite compound with a band gap of 3.2 eV at room temperature and is able to split water into H_2 and O_2 without the application of an external electric field [19–22]. The large band gap, however, requires ultraviolet radiation, which represents only 3% of the solar spectrum. Strategies for overcoming this problem are anion doping by modifying the O 2p dominated valence band (VB) and cation doping by modifying the Ti 3d dominated conduction band (CB). As both these approaches regrettably suffer from the introduction of localized donor or acceptor states [23–34], codoping strategies are being investigated recently. Cation-anion codoping of (Cr, N) [35] experimentally results in low quantum efficiency. Theoretically, (V/Nb/Ta, N) [36], (Sb, N) [37], (Mo/W, 2N) [38], (La/Ce/Pr/Nd, N) [39], and (Rh, 2F) [40] codoping has been studied, the latter turning out to be appropriate for water splitting. Cation-cation codoping has been addressed experimentally for (Ag, Nb) [41] and (La, Cr) [42], showing that visible light absorption is not possible, and theoretically for (Na/K/V/Nb/Ta, Rh) [36] and (La, Rh) [43], finding that (Rh, V) codoping is advantageous for water splitting. Since the electronegativities of the involved elements determine the band edge energies, we search in this contribution for an efficient visible light active photocatalyst by studying a total of eight codoping schemes: ($\text{Mo}^{6+}/\text{W}^{6+}$, $\text{Zn}^{2+}/\text{Cd}^{2+}$) and ($\text{Nb}^{5+}/\text{Ta}^{5+}$, $\text{Ga}^{3+}/\text{In}^{3+}$). All these schemes guarantee charge compensation to avoid creation of localized states.

In section II the methodology is introduced, in section IIIA pristine and monodoped SrTiO_3 are discussed as reference, and in section IIIB the cation codoping is addressed, with an emphasis on the band structure, optical properties, and photocatalytic efficiency. Finally, section IV gives our conclusions.

II. METHODS

$2 \times 2 \times 2$ supercells of SrTiO_3 , containing 40 atoms, are employed in all simulations, as illustrated in Figure 1 for pristine, monodoped, and codoped SrTiO_3 . Spin polarized density functional theory is used with projector augmented wave pseudopotentials [44, 45], which take into account the valence states Sr $4s^2 4p^6 5s^2$, Ti $4s^1 3d^3$, O $2s^2 2p^4$, Mo $4p^6 5s^2 4d^4$, W $6s^2 5d^4$, Nb $4p^6 5s^1 4d^4$, Ta $6s^2 5d^3$, Zn $4s^2 3d^{10}$, Cd $5s^2 4d^{10}$, Ga $4s^2 4p^1$, and In $5s^2 5p^1$. For the exchange-correlation functional the generalized gradient approximation in the scheme of Perdew-Burke-Ernzerhof [46] is utilized together with a Monkhorst-Pack $8 \times 8 \times 8$ k -mesh [47] for the structure optimization. The plane wave cutoff energy is set to 600 eV and forces are converged to 0.01 eV/Å with a 10^{-6} eV tolerance of the total energy. Binding energies, electronic structures, and optical properties are studied using the Heyd-Scuseria-Ernzerhof hybrid functional [48] (with mixing coefficient 0.28 and screening coefficient 0.2 Å^{-1}) in order to achieve the best possible agreement with the experimental value of the band gap [49, 50]. A $3 \times 3 \times 3$ k -mesh is utilized in these calculations. The dielectric function $\varepsilon_1(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$, which depends solely on the electronic structure, is employed to investigate the optical properties, with ω being the angular frequency. The imaginary part is calculated from the momentum matrix elements between the occupied and unoccupied states, considering local field effects, and the real part subsequently from the Kramers-Kronig relation. The absorption coefficient then is given by [51]

$$\alpha(\omega) = \sqrt{2}\omega \sqrt{\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega)}. \quad (1)$$

FIG. 1: (Color online) $2 \times 2 \times 2$ supercells of pristine, monodoped, and codoped SrTiO_3 (from left to right). Blue, red, green, and pink/yellow spheres represent Sr, Ti, O, and dopant atoms, respectively.

III. RESULTS AND DISCUSSION

A. Pristine and Monodoped SrTiO_3

The relaxed Sr-O and Ti-O bond lengths of pristine SrTiO_3 are 2.75 Å and 1.95 Å, respectively, which agrees well with previous experimental and theoretical results [29, 38]. The projected density of states (PDOS) is depicted in Figure 2a, showing that the top of the VB is dominated by O states (Ti contributions at lower energy reflect covalent Ti-O bonding) and that the Ti states give rise to the CB with substantial contributions of O states. The Sr DOS is very small in the whole energy range, due to the ionic character of Sr, and the obtained band gap of 3.2 eV is well in line with the experimental value [20].

In order to study later the effect of codoping, it is mandatory to revisit monodoping in SrTiO_3 . We start the discussion with the d^0 dopants. When we replace a Ti atom by Mo/W we obtain a Mo/W-O bond length of 1.94/1.93 Å, which is close to the Ti-O bond length due to the comparable ionic sizes of $\text{Mo}^{6+}/\text{W}^{6+}$ (0.60/0.59 Å) and Ti^{4+} (0.61 Å) [52]. Figure 2b/2c shows for Mo/W-doped SrTiO_3 strongly hybridized n-type defect states at and below the Fermi level, similar to the findings in Ref. [37], which may trap excited electrons and thus enhance the electron-hole recombination [53, 54]. The visible spin polarization is due to two unpaired electrons, as the total magnetic moment is found to be $2 \mu_B$, which are introduced by the Mo/W doping and shift the Fermi level into the CB. The energy difference between the top of the VB and the occupied impurity states amounts to 1.9/2.4 eV.

FIG. 2: (Color online) PDOS for pristine SrTiO_3 (a), and Mo (b), W (c), Nb (d), and Ta (e) monodoped SrTiO_3 .

For Nb/Ta doping the Nb/Ta-O bond length (1.95 Å) again deviates hardly from the Ti-O bond length due to the similar ionic sizes of $\text{Nb}^{5+}/\text{Ta}^{5+}$ (0.64 Å). According to Figure 2d/2e, the extra electron results in an n-type conducting state, in agreement with Ref. [41]. Since the energy difference between the top of the VB and the occupied impurity states is 3.2 eV, doping with Nb/Ta cannot improve the photocatalytic efficiency.

Turning to the d^{10} dopants, the larger ionic sizes of $\text{Zn}^{2+}/\text{Cd}^{2+}$ (0.73/0.95 Å) result in local distortions of the crystal structure with a Zn/Cd-O bond length of 1.98/2.03 Å. The total magnetic moment of $2 \mu_B$ is due to the two introduced holes, which occupy the VB and induce a p-type conducting state. The band gap is narrowed by about 0.8/1.4 eV with respect to pristine SrTiO_3 , see Figure 3a/3b, which extends the absorption to visible light.

FIG. 3: (Color online) PDOS for Zn (a), Cd (b), Ga (c), and In (d) doped SrTiO₃.

Indeed, it has been found experimentally that Zn doping can improve the photocatalytic properties [55, 56]. The Ga³⁺/In³⁺ ionic sizes of 0.62/0.82 Å result in Ga/In-O bond lengths of 1.97/2.06 Å and a total magnetic moment of 1 μ_B is created by the loss of one electron as compared to Ti⁴⁺. The PDOS in Figure 3c/3d shows spin polarized O states at the top of the VB. Since the band gap has not changed significantly, the photocatalytic efficiency is not improved.

B. Codoped SrTiO₃

Additional n-type doping of p-type monodoped SrTiO₃ can increase the photocatalytic activity [57] by avoiding recombination centres (Mo/W monodoping), CB shifts (Zn/Cd monodoping), and partially occupied valence states (Ga/In monodoping), due to charge compensation in n-p pairs. In order to evaluate this idea, we first study the structure and stability of the codoped materials. In the case of (Mo/W, Zn) codoping the Mo/W-O bond is shortened to 1.90 Å and the Zn-O bond elongated to 2.01/2.02 Å, as compared to monodoping. The defect pair binding energy is used to determine the relative stability with

FIG. 4: (Color online) PDOS for (Mo, Zn) (a), (Mo, Cd) (b), (W, Zn) (c), (W, Cd) (d), (Nb, Ga) (e), (Nb, In) (f), (Ta, Ga) (g), and (Ta, In) (h) codoped SrTiO_3 .

respect to the monodoped structures [58],

$$E_b^{M1,M2} = E_{M1} + E_{M2} - (E_{M1,M2} + E_{\text{SrTiO}_3}), \quad (2)$$

where $E_{M1,M2}$, E_{M1} , E_{M2} , and E_{SrTiO_3} are the total energies of the codoped, first and second monodoped, and pristine systems, respectively. We obtain $E_b^{\text{Mo/W,Zn}} = 4.45/5.80$ eV, the

positive value indicating that codoping is favorable over monodoping due to charge compensation. Cation-cation codoping also turns out to be favorable over catio-anion codoping (for example, $E_b^{Mo/W,2N} = 4.04/4.03$ eV [29]), because the ionic sizes of the cations fit better to that of Ti. For (Mo/W, Cd) codoping the Mo/W-O bond length again is shorter (1.92/1.91 Å) and the Cd-O bond length longer (2.13 Å) than found for monodoping, but $E_b^{Mo/W,Cd} = 4.18/5.57$ eV is less than $E_b^{Mo/W,Zn}$. For (Mo/W, Zn/Cd) codoping the previously discussed defect states are depopulated so that the PDOS in Figure 4a-d resembles that of pristine SrTiO₃ except for the fact that the states forming the VB edge tend to separate from the rest of the VB. The top of the VB consists still predominantly of O states. Since the band gap is reduced, 1.8/1.6 eV for (Mo, Zn/Cd) codoping and 2.3/2.1 eV for (W, Zn/Cd) codoping, the absorption of visible light is enhanced. We obtain charge compensated non-magnetic materials, because all electrons are paired. Table I summarizes the effective masses of the light and heavy charge carriers at the band edges.

For (Nb/Ta, Ga/In) codoping we find Nb/Ta-O and Ga/In-O bond lengths of 1.97 Å and 1.97/2.09 Å, respectively, i.e., slightly longer than in the corresponding monodoped compounds. The defect pair binding energies turn out to be $E_b^{Nb/Ta,Ga} = 3.47/3.82$ eV and $E_b^{Nb/Ta,In} = 3.78/3.84$ eV, i.e., less than for (Mo/W, Zn/Cd) codoping. At the top of the VB again the O states dominate and the bottom of the CB consists mainly of Ti and O

TABLE I: Effective mass (in units of the free electron mass) at the band edges of pristine and codoped SrTiO₃.

	hole, light	hole, heavy	electron, light	electron, heavy
pristine	0.71	5.2	0.46	5.8
(Mo, Zn)	0.38	42.6	0.16	1.9
(Mo, Cd)	0.12	38.2	0.25	2.4
(W, Zn)	0.12	50.6	0.08	0.5
(W, Cd)	0.22	46.7	0.09	0.4
(Nb, Ga)	0.09	6.7	0.05	13.3
(Nb, In)	0.45	7.4	0.38	38.6
(Ta, Ga)	0.08	6.1	0.02	9.4
(Ta, In)	0.06	7.0	0.04	17.5

states, see Figure 4e-h. Similar to (Mo/W, Zn/Cd) codoping, we find no magnetic moment due to charge compensation. Since there are no defect states, the band gap is too large (3.5 eV) for absorbing visible light. Therefore and since the ionic sizes of $\text{Mo}^{6+}/\text{W}^{6+}$ and Zn^{2+} are comparable to that of Ti^{4+} (important from the experimental point of view), (Mo/W, Zn/Cd) codoping is the best candidate to enhance the photocatalytic properties.

Figure 5 (left) shows that pristine SrTiO_3 can absorb ultraviolet light but not visible light (450-800 nm). This problem is overcome by (Mo/W, Zn/Cd) codoping, in agreement with the earlier discussion, with absorption coefficients of $9.6 \times 10^4 \text{ cm}^{-1}$, $12.3 \times 10^4 \text{ cm}^{-1}$, $12.4 \times 10^4 \text{ cm}^{-1}$, and $13.5 \times 10^4 \text{ cm}^{-1}$, respectively, at a wavelength of 450 nm. The most important criterion for water splitting by photocatalysis is the relative position of the band edges, i.e., the VB edge must lie below the $\text{O}_2/\text{H}_2\text{O}$ oxidation level and the CB edge above the H^+/H_2 reduction level. For fixed VB edge, the photocatalytic efficiency is enhanced when the CB edge approaches the H^+/H_2 reduction level. Figure 5 (right) gives the calculated band edge energies with respect to the normal hydrogen electrode (NHE) [20] and shows that pristine SrTiO_3 can be used for photocatalytic water splitting. However, the large band gap excludes absorption of visible light. For (Mo/W, Cd/Zn) codoped SrTiO_3 the VB edge is located below the $\text{O}_2/\text{H}_2\text{O}$ oxidation level, indicating the ability to release O_2 in the water splitting process. The CB edge of (Mo, Cd) codoped SrTiO_3 lies below the H^+/H_2

FIG. 5: (Color online) Absorption coefficients (left) and band edge energies (right) of pristine and codoped SrTiO_3 .

FIG. 6: (Color online) Absorption coefficients (left) and band edge energies (right) of pristine and codoped SrTiO_3 .

reduction level so that the material is not capable of releasing H_2 . On the other hand, in the case of (Mo/W, Zn) and (W, Cd) codoping the CB edge comes close to the H^+/H_2 reduction level, giving rise to good photocatalytic properties. Considering the size of the band gap and band edge energies together, we predict that (W, Cd) codoping will lead to the best performance. We show in Fig. 6 absorption coefficients ($7.8 \times 10^4 \text{ cm}^{-1}$, $8.4 \times 10^4 \text{ cm}^{-1}$, $11.1 \times 10^4 \text{ cm}^{-1}$, and $13.2 \times 10^4 \text{ cm}^{-1}$, respectively, at a wavelength of 450 nm) and band energies of state-of-the-art materials in the literature [36, 59–62]. (W, Cd) codoping turns out to be clearly superior to (Rh, Nb/Sb/Ta) codoping. While it performs similar to (Rh, V) codoping, Rh is scarce and therefore much too expensive for most purposes, in contrast to both W and Cd.

IV. CONCLUSIONS

Density functional theory has been used to examine the structure, electronic states, and optical properties of cation mono and codoped SrTiO_3 . For the Heyd-Scuseria-Ernzerhof hybrid exchange correlation functional the band gap of pristine SrTiO_3 turns out to be in good agreement with the experimental value. (Nb/Ta, Ga/In) codoping does not improve the photocatalytic properties due to an enlarged band gap, whereas (Mo/W, Zn/Cd) codoping

reduces the band gap as compared to pristine SrTiO_3 . Due to charge compensation, (Mo/W, Zn/Cd) codoping avoids in-gap defect states. (Mo, Cd) codoping leads to the smallest band gap but the energetical position of the CB edge prevents photocatalytic water splitting (the bottom of the CB is shifted to lower energy, while the VB edge remains unaffected). The calculated absorption coefficient verifies improved photocatalytic properties of (Mo/W, Zn) and (W, Cd) codoped SrTiO_3 . Our results indicate that (W, Cd) codoping provides the best combination of band gap size and band edge energies for water splitting. The computational approach followed in the present work turns out to be powerful in guiding development of efficient photocatalysts by cation codoping strategies.

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