

Supporting information (SI†)

Effects of Transition Metal Doping on Electronic Structure of Metastable β -Fe₂O₃ photocatalyst for solar-to-hydrogen conversion

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1 Defect formation energies.

The original intention of doping is not to change the structure of the doped matrix, and not to form new substances at the same time. Two problems should be paid attention to in real experiments: the first is that the doping concentration of dopant atom M should not be too large. If the doping concentration is too large, it will no longer be a simple phase but will form other phases; the second is to control the preparation conditions of materials, such as temperature, time, etc. Due to the different formation conditions of different substances, sometimes other substances may be formed even if the concentration of doping is low. These problems that should be paid attention to in the experiment should also be paid attention to in the simulation calculation.

Generally, the defect formation energy of doped M (M=Zr, Sn, Ti) in β -Fe₂O₃ can be

expressed as:

$$E_{M_{Fe}}^f = E_{M_{Fe}}^t - E_{\beta-Fe_2O_3}^t - E_M + E_{Fe} \quad (S1)$$

where $E_{M_{Fe}}^t$ is the total energy of β - Fe_2O_3 doped with M (M=Zr, Sn, Ti), $E_{\beta-Fe_2O_3}^t$ is the total energy of pure bulk β - Fe_2O_3 , E_M and E_{Fe} are the energy of a single atom of doped atoms M (M=Zr, Sn, Ti) and Fe atoms in their elementary substance, respectively.

In principle, formula (S1) is correct, but it does not take into account the fact that new substances may be formed in the experiment. So it needs to be improved, and the improved defect energy formula can be expressed as:

$$E_{M_{Fe}}^f = E_{M_{Fe}}^t - E_{\beta-Fe_2O_3}^t - \mu_M + \mu_{Fe} \quad (S2)$$

where μ_M and μ_{Fe} are the chemical potential of doped atoms M (M=Zr, Sn, Ti) and Fe atoms. How to use μ_M and μ_{Fe} to ensure that M only replaces the position of Fe without forming new substances? The following is an explanation.

First of all, under the condition of thermodynamic equilibrium, pure bulk β - Fe_2O_3 crystal should meet the following condition:

$$2\mu_{Fe} + 3\mu_O = \mu_{\beta-Fe_2O_3} \quad (S3)$$

where μ_{Fe} and μ_O are the chemical potential of Fe atoms and O atoms, $\mu_{\beta-Fe_2O_3}$ is the chemical potential of a single β - Fe_2O_3 unit cell. Under equilibrium conditions, $\mu_{\beta-Fe_2O_3}$ is equal to the total free energy $E_{\beta-Fe_2O_3}^f$ of a single β - Fe_2O_3 unit cell. $E_{\beta-Fe_2O_3}^f$ can be expressed as:

$$E_{\beta-Fe_2O_3}^f = 2E_{Fe} + 3E_O + E_{\beta-Fe_2O_3}^f \quad (S4)$$

where $E_{\beta\text{-Fe}_2\text{O}_3}^f$ is the formation energy of pure bulk $\beta\text{-Fe}_2\text{O}_3$ crystal. So, when $\mu_{\beta\text{-Fe}_2\text{O}_3}$ is equal to $E_{\beta\text{-Fe}_2\text{O}_3}^f$, the relationship is as follows:

$$2\mu_{\text{Fe}} + 3\mu_{\text{O}} = 2E_{\text{Fe}} + 3E_{\text{O}} + E_{\beta\text{-Fe}_2\text{O}_3}^f \quad (\text{S5})$$

When $\Delta\mu_{\text{O}} = \mu_{\text{O}} - E_{\text{O}}$, $\Delta\mu_{\text{Fe}} = \mu_{\text{Fe}} - E_{\text{Fe}}$, the above formula (S5) can be transferred to :

$$2\Delta\mu_{\text{Fe}} + 3\Delta\mu_{\text{O}} = E_{\beta\text{-Fe}_2\text{O}_3}^f \quad (\text{S6})$$

And under Fe-rich conditions:

$$\mu_{\text{Fe}} = \mu_{\text{Fe}(\text{bulk})} \quad (\text{S7})$$

$$\mu_{\text{O}} = \mu_{\beta\text{-Fe}_2\text{O}_3} - \mu_{\text{Fe}(\text{bulk})} \quad (\text{S8})$$

Under O-rich conditions:

$$\mu_{\text{O}} = \mu_{\text{O}(\text{O}_2)} \quad (\text{S9})$$

$$\mu_{\text{Fe}} = \mu_{\beta\text{-Fe}_2\text{O}_3} - \mu_{\text{O}(\text{O}_2)} \quad (\text{S10})$$

The result of defect formation energies is shown in Figure S1. It shows that it is favorable to dope Zr, Sn, Ti into substitutional site under O-rich conditions. In the case of Ti-doped, the defect formation energy is the minimum, while that of Sn-doped is the maximum. Based on the results of defect formation energies, the equilibrium impurity concentrations (or the solubility in host) of Ti will be relatively higher than that of other impurities.

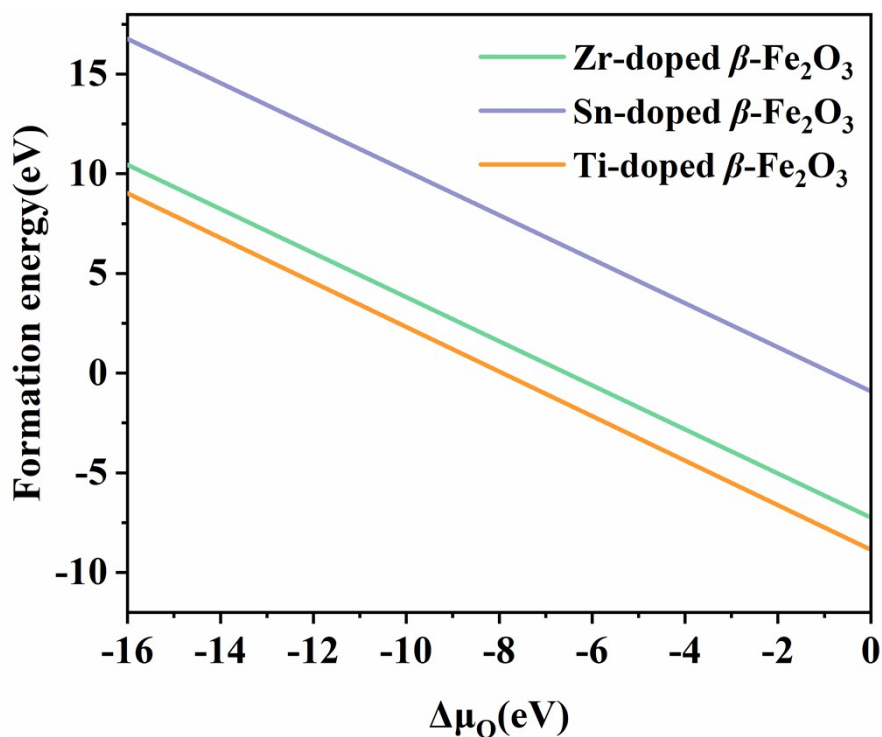


Figure S1. Defect formation energies of Zr, Sn, Ti doping into $\beta\text{-Fe}_2\text{O}_3$.

2 The bond length of FeO_6 distorted octahedron structure.

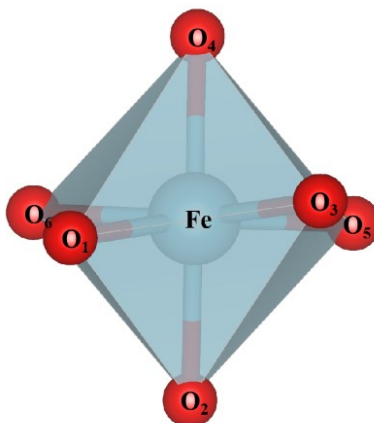


Figure S2. The model of FeO_6 distorted octahedron structure.

Table S1. The bond length $\Delta d(\text{Fe-O})/\text{\AA}$ of FeO_6 distorted octahedron structure.

	$\Delta d(\text{Fe-O}_1)$	$\Delta d(\text{Fe-O}_2)$	$\Delta d(\text{Fe-O}_3)$	$\Delta d(\text{Fe-O}_4)$	$\Delta d(\text{Fe-O}_5)$	$\Delta d(\text{Fe-O}_6)$
pure	2.00311	2.07985	2.00311	2.07985	2.06725	2.06725
Zr-doped	1.98469	2.08807	1.99574	2.06697	2.12918	2.06832
Sn-doped	1.97713	2.13821	2.00051	2.05615	2.10616	2.06425
Ti-doped	1.99446	2.08361	1.99098	2.06346	2.11208	2.06234

3 The k-point path.

Details for the k-point path of $\beta\text{-Fe}_2\text{O}_3$ are shown below.

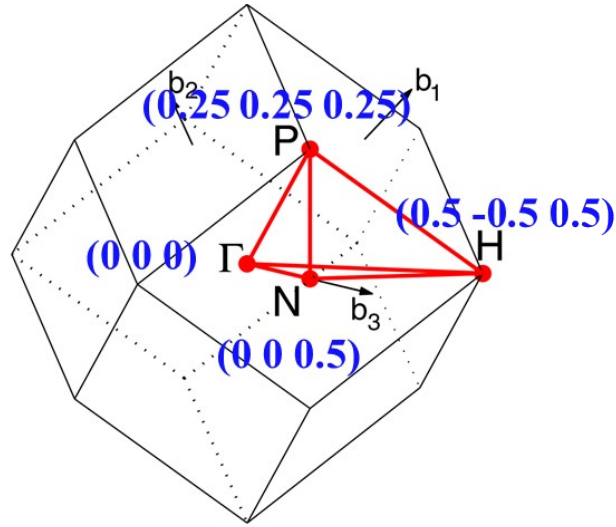


Figure S3. The k-point path of $\beta\text{-Fe}_2\text{O}_3$.

Table S2. Symmetry k-points of $\beta\text{-Fe}_2\text{O}_3$.

	$\times b_1$	$\times b_2$	$\times b_3$
Γ	0	0	0
H	0.5	-0.5	0.5
N	0	0	0.5
P	0.25	0.25	0.25

4 Effective mass.

By fitting the top of the valence band and the bottom of the conduction band, the degree of curvature of the bands edge can be obtained. The degree of curvature characterizes the dynamic response characteristics of the carriers in $\beta\text{-Fe}_2\text{O}_3$ to the external field, and is usually expressed by effective mass. The effective mass obtained by fitting the top of the valence band characterizes the dynamic response characteristics of material holes, and the bottom of the conduction band characterizes the dynamic response characteristics of electrons. Considering that effective mass

varies in different directions of the Brillouin zone, effective masses of electron and hole of β -Fe₂O₃ are calculated along some possible directions. As shown in Figure 2, β -Fe₂O₃ is a direct band gap semiconductor. The valence band maximum (VBM) and the conduction band minimum (CBM) for β -Fe₂O₃ crystal are located at the center of the reduced Brillouin zone Γ point. Due to the symmetry of the Brillouin zone of β -Fe₂O₃, it is only necessary to consider directions connecting with some high-symmetry points. Effective masses of the electron and hole along three directions, $\Gamma(0\ 0\ 0) \rightarrow H(0.5\ -0.5\ 0.5)$, $\Gamma(0\ 0\ 0) \rightarrow N(0\ 0\ 0.5)$, and $\Gamma(0\ 0\ 0) \rightarrow P(0.25\ 0.25\ 0.25)$ are calculated. The effective mass of carrier (referenced to the electron rest mass m_0) can be calculated from the relation:

$$m = \frac{\hbar^2}{2|a|} \quad (S11)$$

where \hbar is the reduced Planck's constant, a is the second derivative of the curve in valence band (for holes) and conduction band (for electrons).