## SUPPORTING INFORMATION

# (Ti/Zr, N) codoped hematite towards the enhanced photoelectrochemical activity of water splitting

Haijun Pan,<sup>a,b</sup> Xiangying Meng,<sup>\*a,b</sup> Dongyan Liu,<sup>a,b</sup> Song Li,<sup>a</sup> and Gaowu Qin<sup>\*a</sup>

<sup>a</sup> Key Laboratory for Anisotropy and Texture of Materials (Ministry of Education), Northeastern University, Shenyang 110819, People's Republic of China

<sup>b</sup> College of Sciences, Northeastern University, Shenyang 110819, People's Republic of China

\**Corresponding authors. E-mail:* x\_y\_meng@mail.neu.edu.cn (XYM), qingw@smm.neu.edu.cn (GWQ)

### Concrete procedures on how to choose the optimal structure



Fig. S1 Hexagonal close-packed crystal structure of pure hematite. The gold yellow spheres represent Fe atoms, and red spheres indicate positions of O atoms. The octahedral holes are also drawn, which are represented by white spheres.

As shown in Fig.S1, hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) has a corundum structure with a space group of R-32/C (NO.167), and one unit cell contains 12 Fe and 18 O atoms. Its crystal structure is based on the oxygen hexagonal-close-packed lattice. The Fe atoms with coordinates of (0, 0, z), etc., occupy two-thirds of the octahedral holes in successive oxygen layers, and one-third of the octahedral holes with coordinates of (0, 0, 0), etc., are empty.

To find out the optimal co-doping model, we first investigate the reasonable mono-doped hematite by Ti, Zr, and



**Fig. S2** (a) Interstitial doping. The doped atom (represented by blue) is placed at one of equivalent octahedral holes. (b) Substitutional doping. The first metal atom (noted as M1) is incorporated into the position of a spin-down Fe atom, or the second metal atom (M2) substitutes a spin-up Fe atom, respectively, which is represented with blue spheres. (c) N mono–doped hematite. The O atom is replaced by N atom, which is labeled by green.

N, respectively. When the foreign atom appears in hematite, it may occupy the octahedral hole or substitute the original atom. As for the first case, a foreign atom is placed in one of octahedral holes, which is indicated by blue in Fig. S2a. In the case of substitutional doping, the metal atom (noted as M) is incorporated into the position of a spin-down Fe atom (noted as M1), or substitutes a spin-up Fe atom (noted as M2), respectively. The calculated results indicate that when M1 and M2 are represented by Ti (Zr) atom, the energy of M1 doped model is lower than that of M2 doped model by 0.33eV (0.03eV). As for N dopant, one of equivalent O atoms is substituted, which is displayed in Fig. S2c. After simulations, the following formula is used to calculate the formation energy.<sup>S1</sup>

 $E(M \ doped)_f = E(M \ doped) - E(pure) - \mu_M + \mu_{Fe}$  $E(N \ doped)_f = E(N \ doped) - E(pure) - \mu_N + \mu_0$ 

Table 1 shows the formation energies of substitutional and interstitial doped hematite. Because there are no exchanges of atoms, the formation energy of interstitial doping does not change under O- or Fe- rich environment. All metal doped models show negative formation energies, indicating the intense interaction between dopant and

the host lattice. Among them, interstitial doping is thermodynamically less favorable than interstitial doping, and may eventually evolve into substitutional doping. For N doped hematite, these two different doping models are not energetically stable. However, the formation energy of substitutional doping is still smaller by at least 0.93eV. In conclusion, when the foreign atoms are incorporated into hematite, they are easier to substitute atoms in the crystal lattice.

	dopant	Fe-rich	O-rich
substitutional doping	Ti	-2.44 eV	-3.86 eV
	Zr	-3.63 eV	-5.05 eV
	Ν	4.56 eV	5.51 eV
interstitial doping	Ti	-2.24 eV	-2.24 eV
	Zr	-2.29 eV	-2.29 eV
	Ν	6.46 eV	6.46 eV

Table I The formation energies of substitutional and interstitial doped hematite.



Fig. S3 The (M1, N) codoped model. The dopant M1 is fixed, while the subsequently introduced N is placed at different

positions in each model.

In the next step, we are going to pick out the most stable configuration of codoped hematite. As shown in Fig. S3,

a spin-down Fe atom is firstly replaced by M1. Then, different configurations of co-doped hematite will be obtained by change the position of N atom. There are six layers of oxygen atom in the M1 doped hematite, and each of O atoms in the same layer substituted by N atom will lead to the same configuration of co-doped hematite. Thus, there are six co-doping methods. Finally, co-doped hematite is selected as the most stable structure by comparing energies of these systems in table II.

	(Ti, N)	(Zr, N)
(M1,N1)	-207.15 eV	-208.97 eV
(M1,N2)	-207.33 eV	-209.08 eV
(M1,N3)	-207.43 eV	-208.96 eV
(M1,N4)	-207.46 eV	-209.18 eV
(M1,N5)	-207.29 eV	-209.11 eV
(M1,N6)	-207.13 eV	-209.95 eV

Table II Energies of different co-doped systems.

#### Calculations with $2 \times 2 \times 1$ supercell



Fig. S4 (a)  $2 \times 2 \times 1$  hematite supercell (b)  $2 \times 2 \times 1$  hematite supercell codoped with (Ti/Zr, N)

Fig. S4a shows the 120-atom  $2 \times 2 \times 1$  hematite supercell, which is constructed by doubling the lattice vectors of the primitive cell along *a* and *b*. As shown in Fig. S4b, the  $2 \times 2 \times 1$  hematite supercell codoped with (Ti/Zr, N) is result from expanding the codoped primitive cell of hematite. Different from previous calculations, the Brillouin–zone integration was performed with k meshes of  $3 \times 3 \times 2$ . Except for this, other computational parameters remain unchanged.



Fig. S5 (a) The band structure and (b) density of electronic states (DOS) calculated by  $2 \times 2 \times 1$  hematite supercell. The Fermi level is set to energy zero.



Fig. S6 Band structure and DOS calculated by  $2 \times 2 \times 1$  hematite supercell codoped with (Ti, N) (a and b) and with (Zr, N) (c and d). The Fermi level is set to energy zero.

Fig. S5 shows that the valence band mostly comprises the O 2p states while the conduction band is mostly composed of Fe 3d states. The calculated band gap of undoped hematite is 2.25 eV. The electronic properties obtained by hematite supercell are exactly consistent with that calculated from primitive cell.

The band structures of (Ti/Zr, N) codoped hematite (in Fig. S6a and c) clearly demonstrate that the newly formed energy bands above the top of the host Fe<sub>2</sub>O<sub>3</sub> valence band is the main reason leading to band gap narrowing.

Through the DOS as shown in Fig. S6b and d, it is visible that the newly emerged energy bands is mainly attributed to the *d* electrons of doped metal atom and N 2*p* orbital, which is higher in energy than Fe 3*d* and O 2*p* orbital, respectively. Besides, there are small amounts of O 2p and Fe 3d within it. As for the conduction band, there exists slight difference between these two codoped hematite. The conduction band minimum is composed of the Ti 3d and Fe 3d hybridized state in the case of (Ti, N) codoped hematite, with the majority contribution from the Fe 3d state, while the conduction band minimum is only dominated by the Fe 3d state in the case of (Zr, N) codoped hematite.

#### Reference

S1. J. Wang, H. Sun, J. Huang, Q. Li, J. Yang, J. Phys. Chem. C, 2014, 118, 7451-7457.