Supplementary Information

Synergistic Effects of dopant (Ti or Sn) and Oxygen Vacancy on the Electronic Properties of Hematite: a DFT Investigation †

Haijun Pan,*[ab] Dongbiao Ao ,[a] and Gaowu Qin[c]

a. School of Resources and Materials, Northeastern University at Qinhuangdao, Qinhuangdao 066004, People's Republic of China E-mail:panhaijun@neuq.edu.cn

b. Hebei Provincial Laboratory for Dielectric and Electrolyte Functional Materials, Qinhuangdao 066004, People's Republic of China

c. Key Laboratory for Anisotropy and Texture of Materials, Northeastern University, Shenyang 110819, People's Republic of China

Hematite has been widely studied as one of the most promising photoanodes in photoelectrochemical decomposition of water. At present, a prevailing strategy of coupling dopant (Ti or Sn) and oxygen vacancy has been proposed by experiments, which effectively improves its photocatalytic activity. In order to clarify the intrinsic reasons for the improvement of photochemistry activity, the density functional theory is adopted to calculate the formation mechanism and electronic properties of hematite with doping ion and oxygen vacancy. The result shows that the doped atom is beneficial to the formation of oxygen vacancy in hematite, thus forming a stable structure containing doping ion and oxygen vacancy. Due to the synergistic effects of dopant and oxygen vacancy, the bandgap of hematite decreases, and donor levels are introduced into the bandgap, which lead to the increase of carrier concentration. In the system with doped Ti and oxygen vacancy, donor levels are introduced at 1.47 eV and 1.73 eV under the bottom of the conduction band, respectively. For the case containing Sn and oxygen vacancy, the donor level is introduced at 1.75 eV from the conduction band minimum. Our results elaborate the reasons for the enhancement of carrier densities in terms of electronic structure, and provide some guidance for the future modification of photocatalyst.

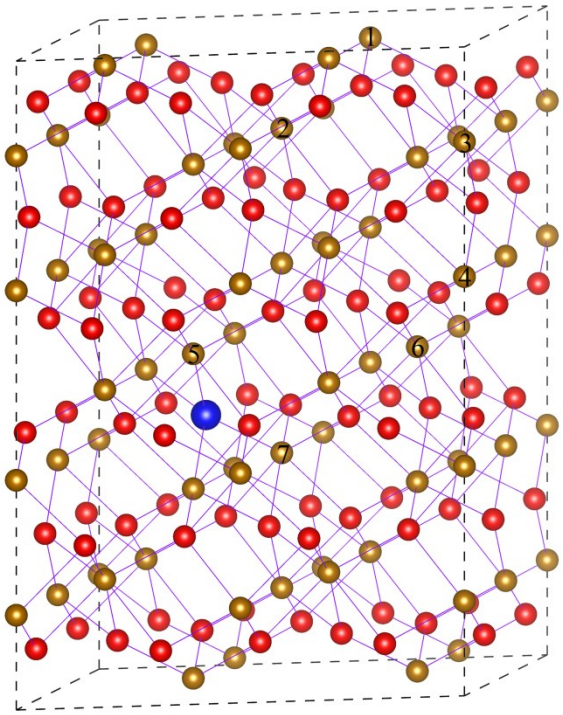

Fig. S1 Possible combination of V_O and dopant atom (Ti or Sn) in 2×2×1 supercell of Fe_2O_3. The Fe atom and O atom are represented by golden yellow and red spheres, respectively. V_O is represented by blue sphere. In each model, the V_O is fixed, while the introduced dopant is placed at different positions marked by numbers.

Table S1 The total energy of the 2×2×1 supercell of Fe_2O_3 with V_O and Ti at different position.

Models	Position of Ti atom	Totoal energy (eV)
Model 1	1	-819.7313
Model 2	2	-819.8584
Model 3	3	-819.7257
Model 4	4	-819.7950
Model 5	5	-818.0045
Model 6	6	-820.0070
Model 7	7	-819.5649

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Table S2 The total energy of the 2×2×1 supercell of Fe_2O_3 with V_O and Sn at different position.

Models	Position of Ti atom	Totoal energy (eV)
Model 1	1	-811.5719
Model 2	2	-811.6007
Model 3	3	-811.5736
Model 4	4	-811.6730
Model 5	5	-810.0023
Model 6	6	-811.8476
Model 7	7	-810.1797

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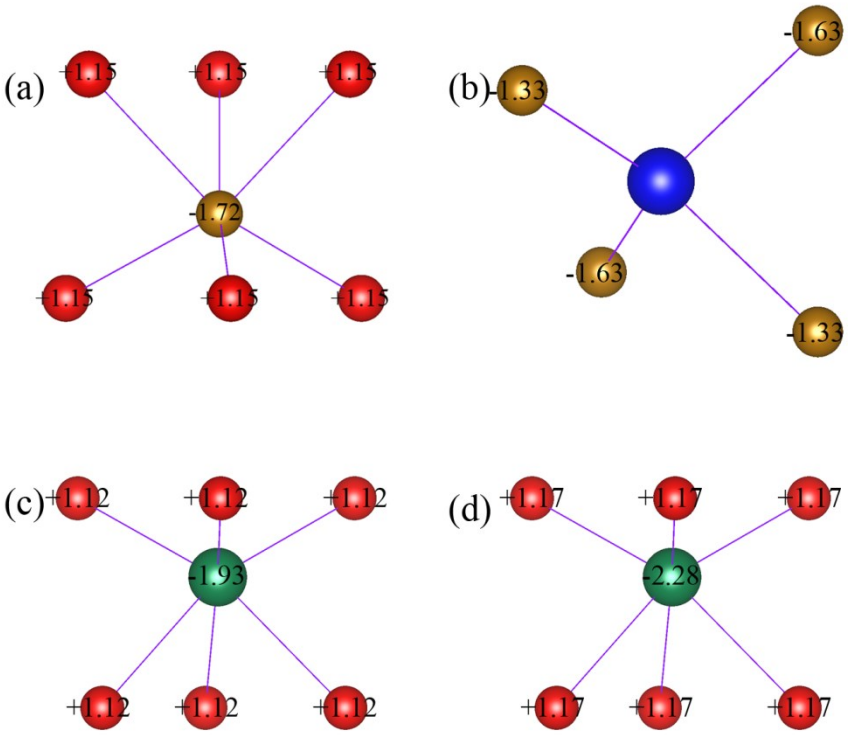

Fig. S2 The charge transfer between atoms in Fe_2O_3: (a) perfect crystal, (b) containing V_O, (c) containing Ti and (d) containing Sn. The positive sign represents the charge obtained by an atom relative to a neutral atom, while a negative sign represents the loss of charge.

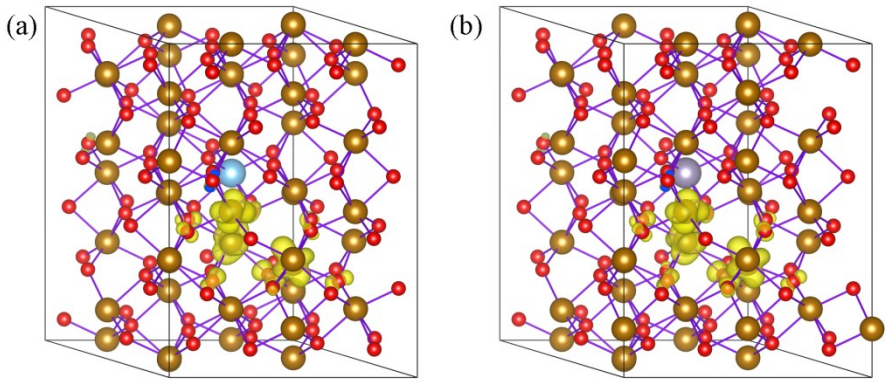

Fig. S3 The partial charge density of donor state of (a) (Ti_{Fe}+V_O)-Fe_2O_3 (b) (Sn_{Fe}+V_O)-Fe_2O_3.