Supporting Information: Photo-Oxidation of Water on Defective Hematite(0001)

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We have carried out density of states (DOS) calculations for the defect-free, O vacancy and N-doped systems using fully relaxed symmetric 2×2 slabs (e.g., Figure S2).

In agreement with a previous density-functional (PBE+U) work,[1] our calculations show that there are gap states appearing in the case of the defect-free surface, typically, states are located around the Fermi level.

O vacancies or N dopants make the surface states close to the Fermi level less pronounced, however, the gap states become slightly more dispersed. To estimate the number of gap states we determine $n = \int_{E_1}^{E_2} DOS(\epsilon) d\epsilon$, where the same energy window $[E_1, E_2]$ is indicated by arrows in Figure S1. We found that the ideal and O vacancy surfaces have

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similar gap states, about 34 states (per unit cell), while the N doped surface has about 31. These data suggest that O vacancies or N dopants do not produce more gap states, but modify the distribution of gap states of the ideal surface.

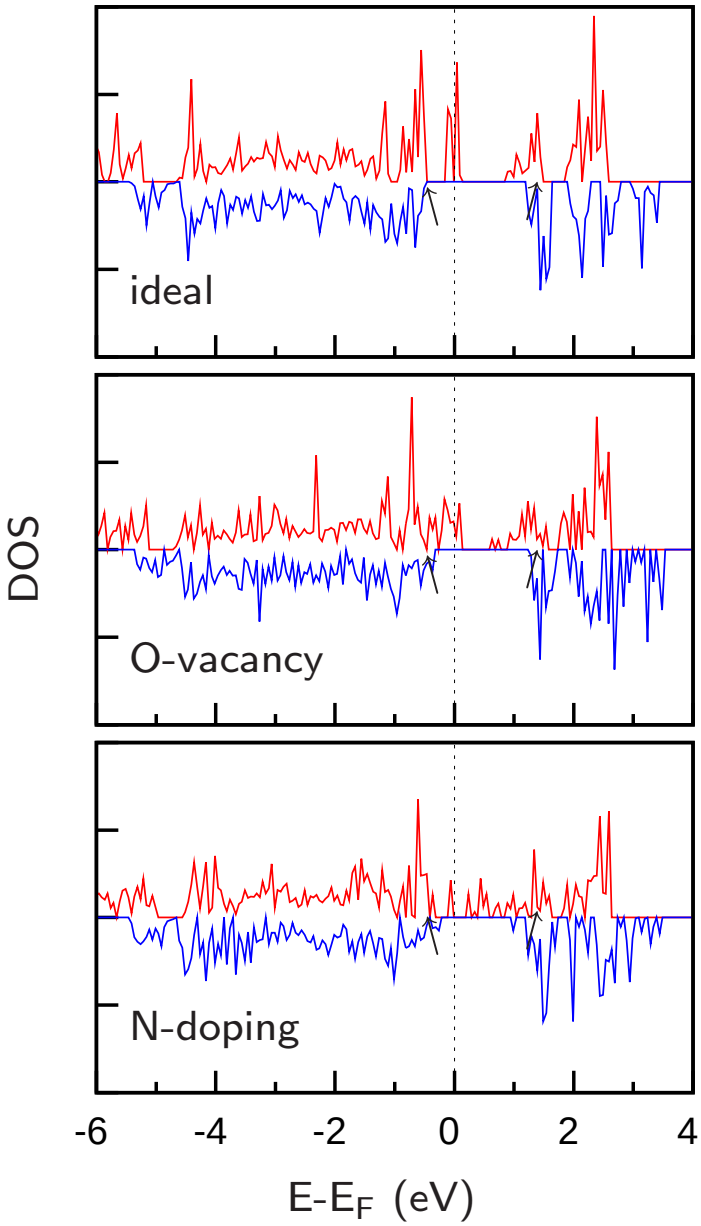

Figure S1: DOS of the ideal, O vacancy and N-doped systems, the Fermi level is set at zero. The arrows indicate the energy gap.

To see if the O vacancy or N dopant directly contributes to the gap states we calculate the integrated local density of states (ILDOS) in the energy window $[E_1, E_2]$ marked by arrows in Figure S1:

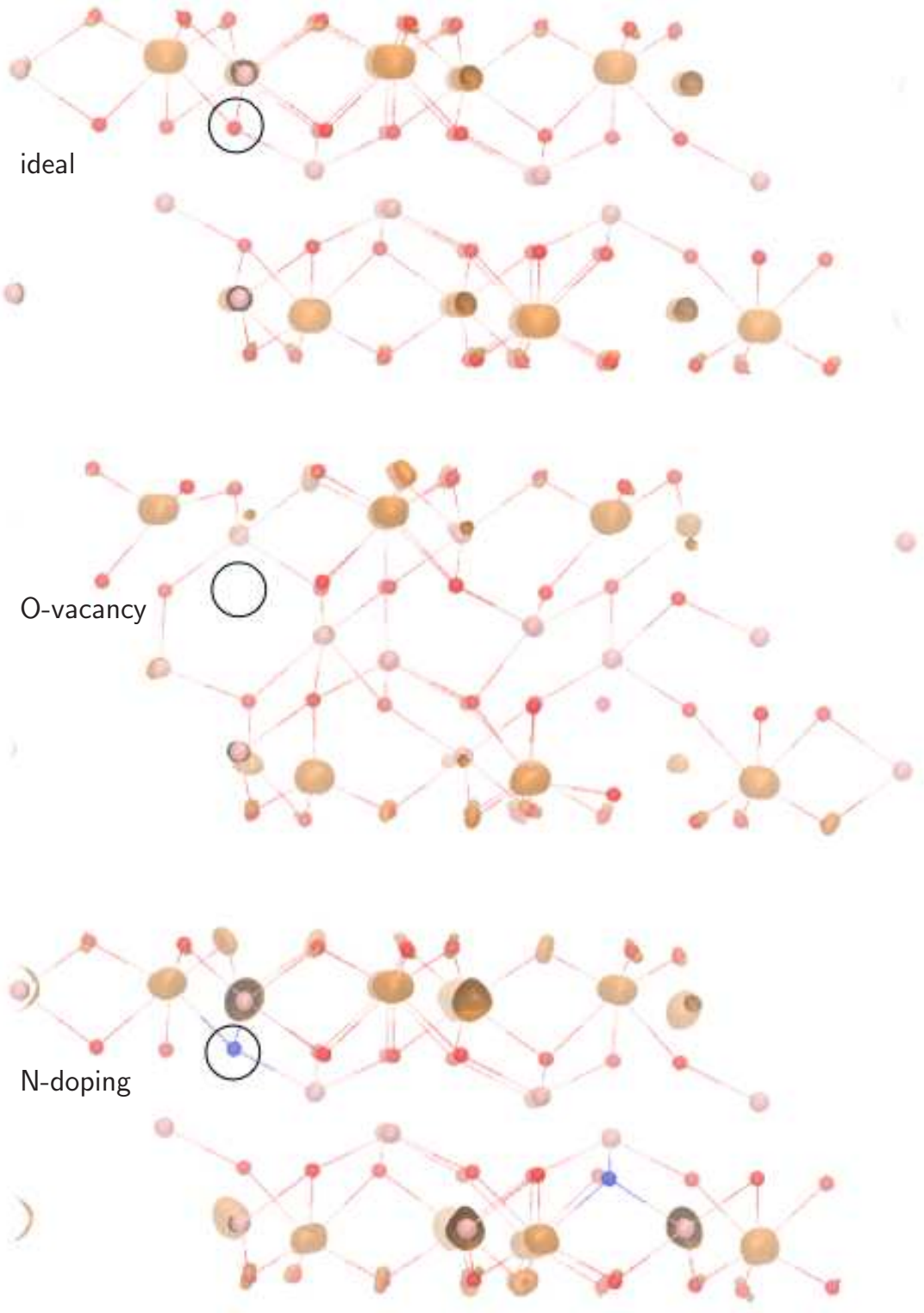

Figure S2: ILDOS (orange, isosurface value at 0.2 au) of the defect-free, O vacancy, and N doped surfaces. The black circles indicate the native O atom, the O vacancy and the N dopant.

$$ILDOS(\mathbf{r}) = \int_{E_1}^{E_2} LDOS(\mathbf{r},\epsilon)d\epsilon, \quad (1)$$

where the local density of states LDOS is given by

$$LDOS(\mathbf{r},\epsilon) = |\psi(\mathbf{r},\epsilon)|^2 \quad (2)$$

In Figure S2 we show the ILDOS of the three cases. In the defect-free case, the gap states mainly contributed by the outermost O and Fe atoms. In the case of O vacancy or N dopant, gap states are also mainly from the outermost O and Fe atoms, and clearly, the no gap state is contributed by the O vacancy or N dopant.

References

(1) Kiejna. A.; Pabisiak, T. Surface properties of clean and Au or Pd covered hematite (α-Fe_2O_3) (0001). *J. Phys.: Condens. Matter* **2012**, 24, 095003