Supplementary Information

Bulk-terminated or reconstructed Fe_3O_4(001) surface: water makes a difference

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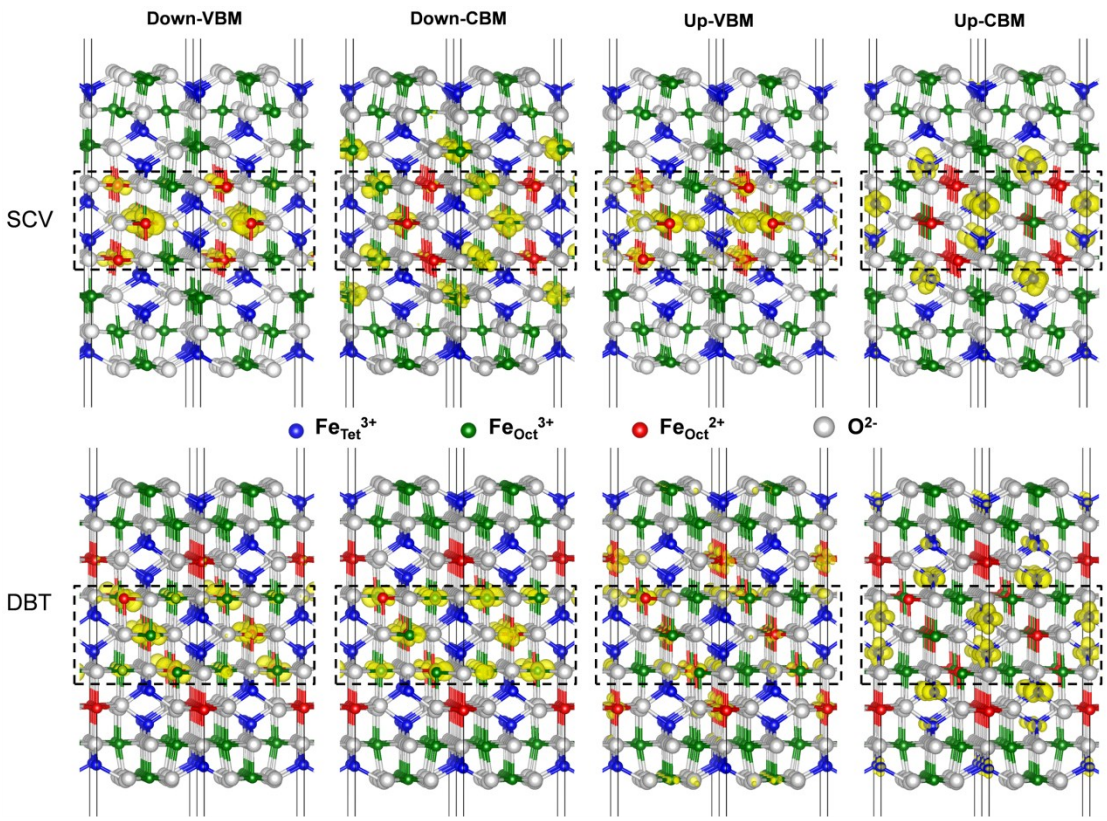

Figure S1. The charge density plot for the valence band maximum (VBM) and conduction band minimum (CBM) of spin-up and spin-down electrons of different $Fe_3O_4(001)$ surfaces, i.e. surface with subsurface cation vacancy (SCV) (shown in the upper part) and surface with a bulk truncation (DBT) (shown in the lower part).

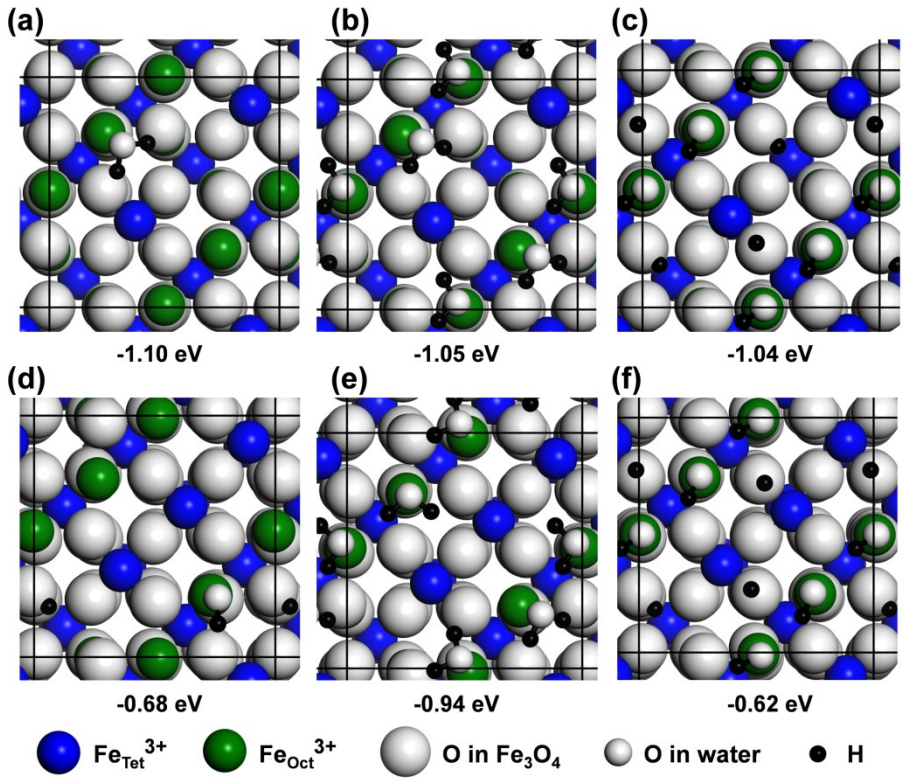

Figure S2. Top views of selective configurations of water adsorption on DBT and SCV surfaces with different coverage. (a) Single undissociated water molecule on DBT surface. (b) Four undissociated water molecules on DBT surface. (c) Four dissociated water on DBT surface. (d) Single partially dissociated water molecule on SCV surface. (e) Four undissociated water molecules on SCV surface. (f) Four dissociated water on SCV surface. Big blue, green and white balls represent Fe_{Tet}^{3+}, Fe_{Oct}^{3+} and O in Fe_3O_4, respectively. Small white and black balls represent O and H from water. The black squares represent the $(\sqrt{2} \times \sqrt{2})R45°$ unit cell used in the calculations. The adsorption energies per water molecule are listed under the corresponding structures.

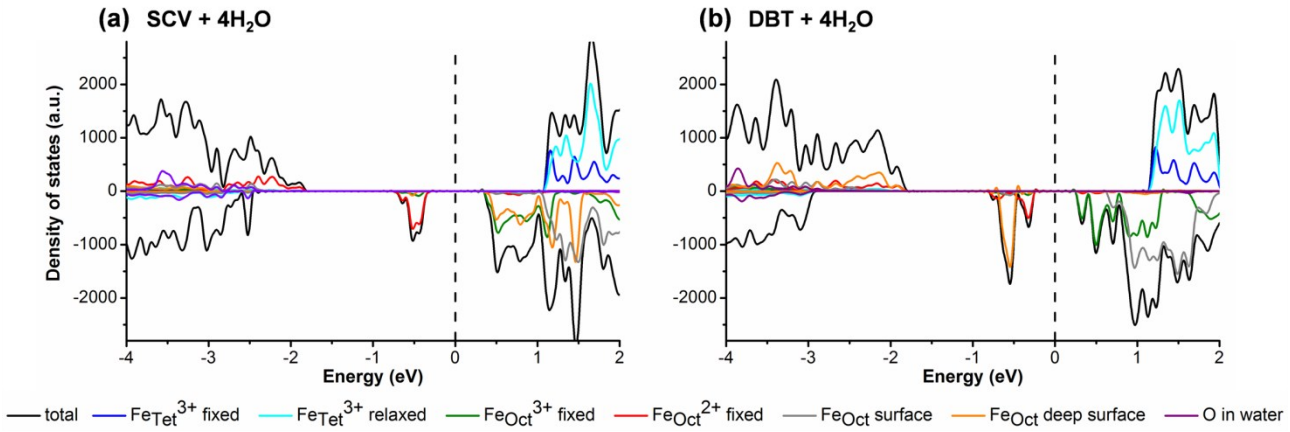

Figure S3. Projected density of states (PDOS) on different kinds of Fe ions and O ions in the SCV and DBT slab models with full coverage of water adsorption in the mixed mode. Legend of colors is on the bottom of the panels. The black lines represent the total DOS. The blue and cyan lines represent PDOS on the d states of Fe_{Tet}^{3+} in the fixed layers and relaxed layers, respectively. The green and red lines represent PDOS on the d states of Fe_{Oct}^{3+} and Fe_{Oct}^{2+} in the fixed layers. The gray lines represent PDOS on the d states of Fe_{Oct} in the surface layers (layer1 + layer3 + layer15 + layer17). The orange lines represent PDOS on the d states of Fe_{Oct} in the deep surface layers (layer5 + layer13). The purple lines represent PDOS on the oxygen atoms in water. The Fermi level is scaled to zero as indicated by the dashed black lines.

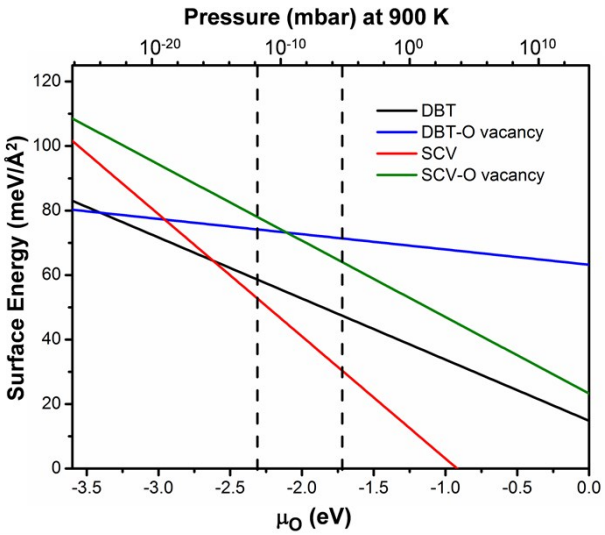

Figure S3. Surface energy of different surface models as a function of oxygen chemical potential. μ_O has been converted into pressures at 900 K. The energy reference for μ_O is set to be half the total energy of an isolated O_2 molecule. The black and blue lines represent the DBT surfaces with and without oxygen vacancy. The red and green lines represent the SCV surfaces with and without oxygen vacancy. Vertical dashed lines indicate a reasonable range of oxygen chemical potential or O_2 partial pressure in experiments[1]. The DBT surface with oxygen vacancy can be stable only in an extremely poor oxygen condition (chemical potential smaller than -3.5 eV) and the SCV surface with oxygen vacancy is less stable than DBT surface with oxygen vacancy.

References

1. R. Bliem, E. McDermott, P. Ferstl, M. Setvin, O. Gamba, J. Pavelec, M. A. Schneider, M. Schmid, U. Diebold, P. Blaha, et al. *Science*, 2014, **346**, 1215-1218.