Electronic Supplementary Information (ESI)

First-principles calculation method

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First-principles calculations were performed using Vienna ab initio simulation package (VASP) based on density functional theory (DFT).[1] Electron-ion interaction was modelled by projector augmented wave (PAW) potentials.[2] Exchange and correlation effects for structural relaxation were approximated by generalized gradient approximation (GGA)[3] with Perdew-Burke-Ernzerhof (PBE)[4]. The cutoff energy was set to be 400 eV in all calculations for plane-wave basis restriction. K-points were sampled under Monkhorst-Pack for Brillouin-zone integration.[5] For (001) surface model, $(\sqrt{2}\times\sqrt{2})R45^{o}$ surface unit cell and 11 atomic layers with the same top and bottom terminations were used. Similarly, for (111) surface model, 2×2 surface unit cell and 11 atomic layers with the same top and bottom terminations were used. For both models, three topmost surface layers on both top and bottom terminations are relaxed with all other atoms being fixed to simulate bulk. The forces acting on all relaxed atoms <0.05 eV/Å are reached for ionic relaxation and self-consistency accuracy of 10^{-4} eV for electronic loops. Surface magnetic anisotropy was calculated by non-collinear calculations via considering spin-orbital coupling using the algorithm implanted in VASP by Hobbs *et al*.[6] For all non-collinear calculations, self-consistency accuracy of 10^{-6} eV is reached for electronic convergence.

The most stable surface termination of Fe_3O_4 (001) and (111) were selected for study on surface magnetic anisotropy. Extensive work has been done to evaluate stability of different Fe_3O_4 surface terminations in literature. Pentcheva *et al.* concluded (001)-Fe_{oct}-termination is the most stable for (001) surface according to DFT calculation and thermodynamic analysis.[7] By using spin-density functional theory, Grillo *et al.* reported (111)-Fe_{tet1}-O_1-termination is the most energetically favored for (111) surface.[8] As a result, (001)-Fe_{oct}- and (111)-Fe_{tet1}-O_1-surface model (see Fig. S1 below) were built for further study on magnetic anisotropy. Energy $E_{\perp}$ when applying magnetic field perpendicular to surface was calculated by aligning magnetic dipole out of surface as seen in Fig. S1(a) and (c). Similarly, energy $E_{\parallel}$ when applying magnetic field parallel to surface was obtained by aligning magnetic dipole in surface. Several in-surface directions of magnetic dipole were investigated. The direction of magnetic dipole with the lowest $E_{\parallel}$ was finally determined as seen in Figure S1(b) and (d) for (001) and (111) surface model respectively. Surface magnetic anisotropy K_S is further obtained using the equation $K_S=\frac{E_{\perp}-E_{\parallel}}{2A}$ for each model, where A is surface area of model on each side.

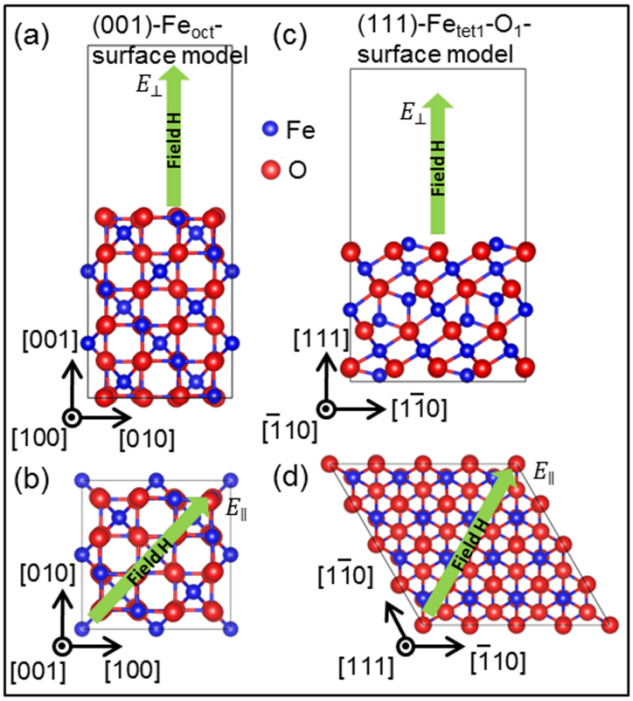

Fig. S1 (a) and (c): cross-sectional view of atomic structures of (001)-Fe_{oct}- and (111)-Fe_{tet1}-O_1-surface model respectively. The green arrows indicate the directions of magnetic dipole when applying magnetic field out of surface. (b) and (d): top view of atomic structures of (001)-Fe_{oct}- and (111)-Fe_{tet1}-O_1-surface model respectively. The green arrows indicate the directions of magnetic dipole when applying magnetic field in surface.

References

1 G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169-11186.
2 P. E. Blöchl, *Phys. Rev. B*, 1994, **50**, 17953-17979.
3 J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh and C. Fiolhais, *Phys. Rev. B*, 1992, **46**, 6671-6687.
4 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.
5 H. J. Monkhorst and J. D. Pack, *Phys. Rev. B.*, 1976, **13**, 5188-5192.
6 D. Hobbs, G. Kresse and J. Hafner, *Phys. Rev. B*, 2000, **62**, 11556-11570.
7 R. Pentcheva, F. Wendler, H. L. Meyerheim, W. Moritz, N. Jedrecy and M. Scheffler, *Phys. Rev. Lett.*, 2005, **94**, 126101.
8 M. E. Grillo, M. W. Finnis and W. Ranke, *Phys. Rev. B*, 2008, **77**, 075407.