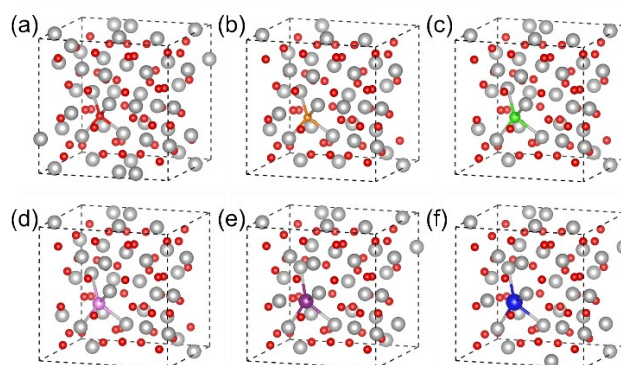


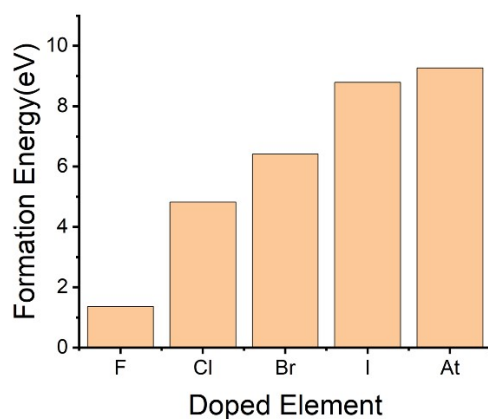
## Supporting information

### 1. Optimized Structures



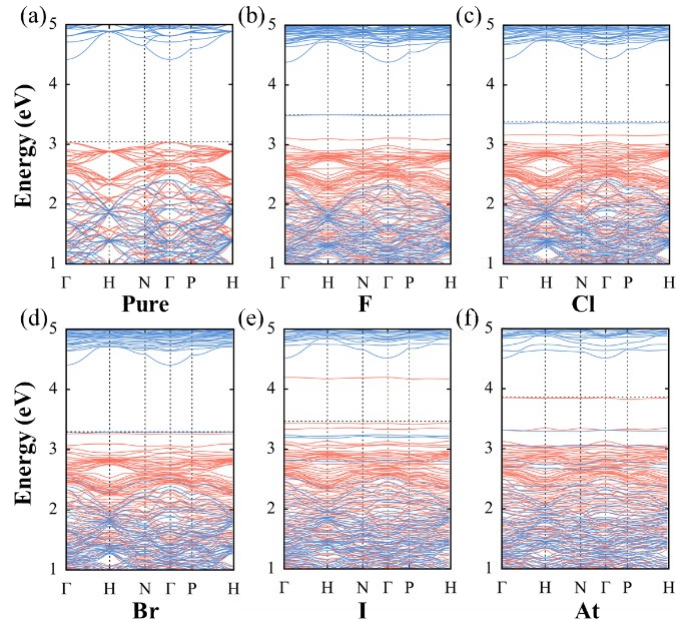
**Figure S1.** The optimized structures of pure  $\beta$ - $\text{Fe}_2\text{O}_3$  (a), and F doped (b), Cl doped (c), Br doped (d), I doped (e), and At doped (f)  $\beta$ - $\text{Fe}_2\text{O}_3$ . Note that all the doped structures are distorted to different degrees.

### 2 Formation energies



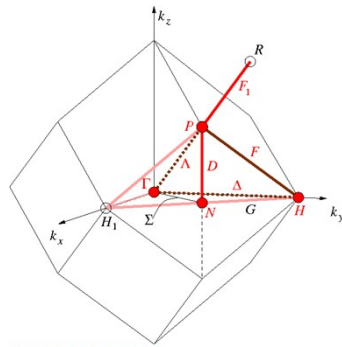
**Figure S2.** The defect formation energies of halogen doped  $\beta$ - $\text{Fe}_2\text{O}_3$ . Note that F and Cl doped structures are more stable than others.

### 3 Band structures



**Figure S3.** (a) Band structure of pure  $\beta\text{-Fe}_2\text{O}_3$ . (b)-(f) Band structures of halogen-doped  $\beta\text{-Fe}_2\text{O}_3$ .

### 4 Reciprocal space



**Figure S4.** The Reciprocal space of  $\beta\text{-Fe}_2\text{O}_3$

### 5 F-doped $\beta\text{-Fe}_2\text{O}_3$

F-doped structure is similar to Cl-doped structure in various aspects such as Density of States (DOS) (Figure S5). The impurity state located at the Fermi level is mainly

composed of Fe3d.

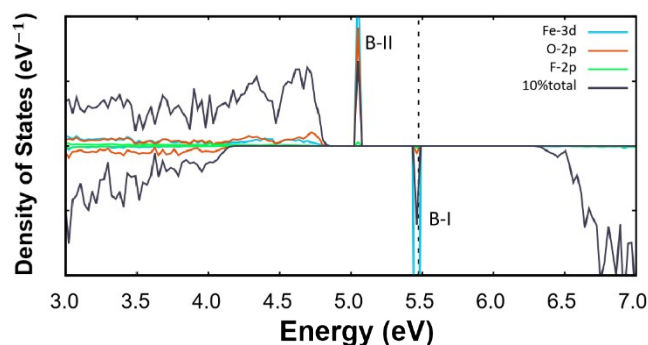


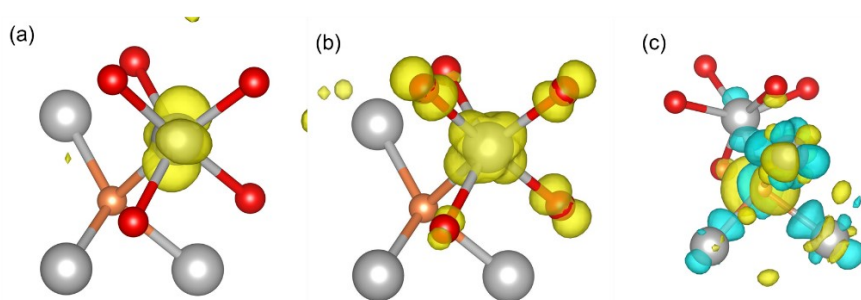
Figure S5. Density of states (DOS) of F doped  $\beta$ -Fe<sub>2</sub>O<sub>3</sub>

The band which located around fermi level is named B-I, and the band which located between VBM and fermi level named B-II, and

The charge density contour plot of B-I is displayed in Figure S6 (a). Electrons are located at Fe atom, the impurity state is located between VBM and Fermi level and is composed of Fe3d and Fe3d and O2p.

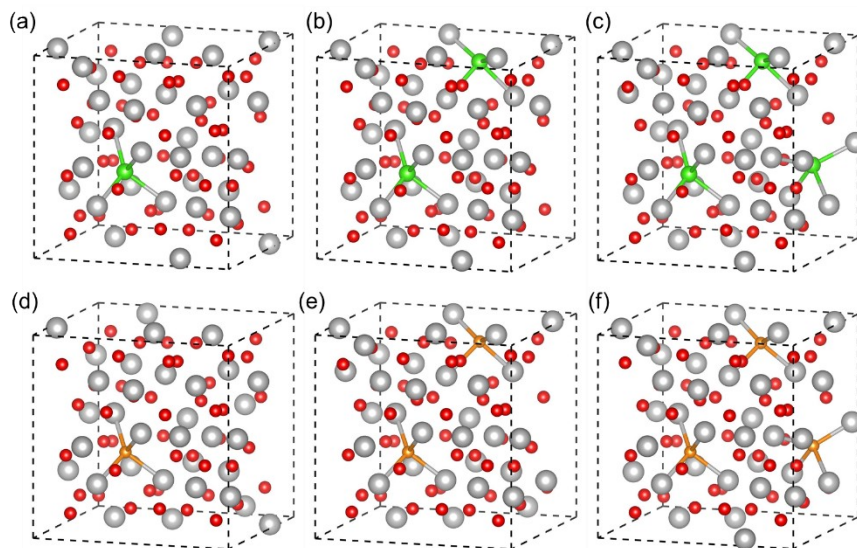
The charge density contour plot of B-II is displayed in Figure S6 (b). These electrons are located Fe and O atom. The differential charge diagram is plotted in Figure S5 (c) with isosurface 0.005 e bohr<sup>-3</sup>.

This result because the F atom have the same valence electron structure with Cl atom. The valence electron will bond with Fe atoms firstly, thus the B-II was formed. But the valence electron of F atom is more a redundant electron than the O atom. The redundant electron will transform to Fe atom, and formed the B-I.



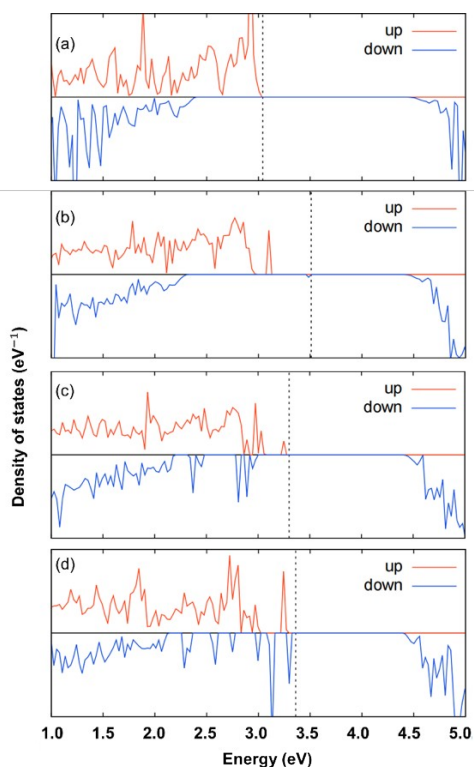
**Figure S6.** The charge density contour plot of the impurity state located at Fermi level with isosurface value of 0.01 e bohr<sup>-3</sup> (a). The charge density contour plot of the impurity state located between VBM and Fermi level with the isosurface value of 0.01 e bohr<sup>-3</sup> (b). The differential charge diagram of F doped  $\beta$ -Fe<sub>2</sub>O<sub>3</sub> with the isosurface value of 0.05 e bohr<sup>-3</sup> (c)

## 6 Doped systems with different doping concentrations



**Fig S7** The optimized geometric structures of Cl doped  $\beta$ - $\text{Fe}_2\text{O}_3$  with concentrations of 1.25% (a), 2.50% (b), and 3.75% (c). The optimized geometric structures of F doped  $\beta$ - $\text{Fe}_2\text{O}_3$  with concentrations of 1.25% (d), 2.50% (e), and 3.75% (f).

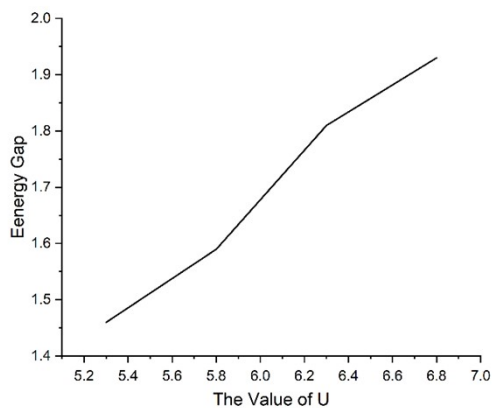
To investigate the effect of doping concentrations on the electronic properties, we calculated the density of states at the F doping concentrations of 1.25%, 2.50%, and 3.75% (Figure S8). Notably, the density of states increase significantly with increasing the F dopant concentrations; at the dopant concentration of 3.75%, the interval between the impurity band and the valence band disappears, which directly causes valence band increase. the increase will improve the electron density at the impurity band and promote the light absorption. Because the density of impurity electron is too low under 1.25%, so I want to improve the density of electron by increase the density of halogen atom. These trends are similar to Cl doped systems,



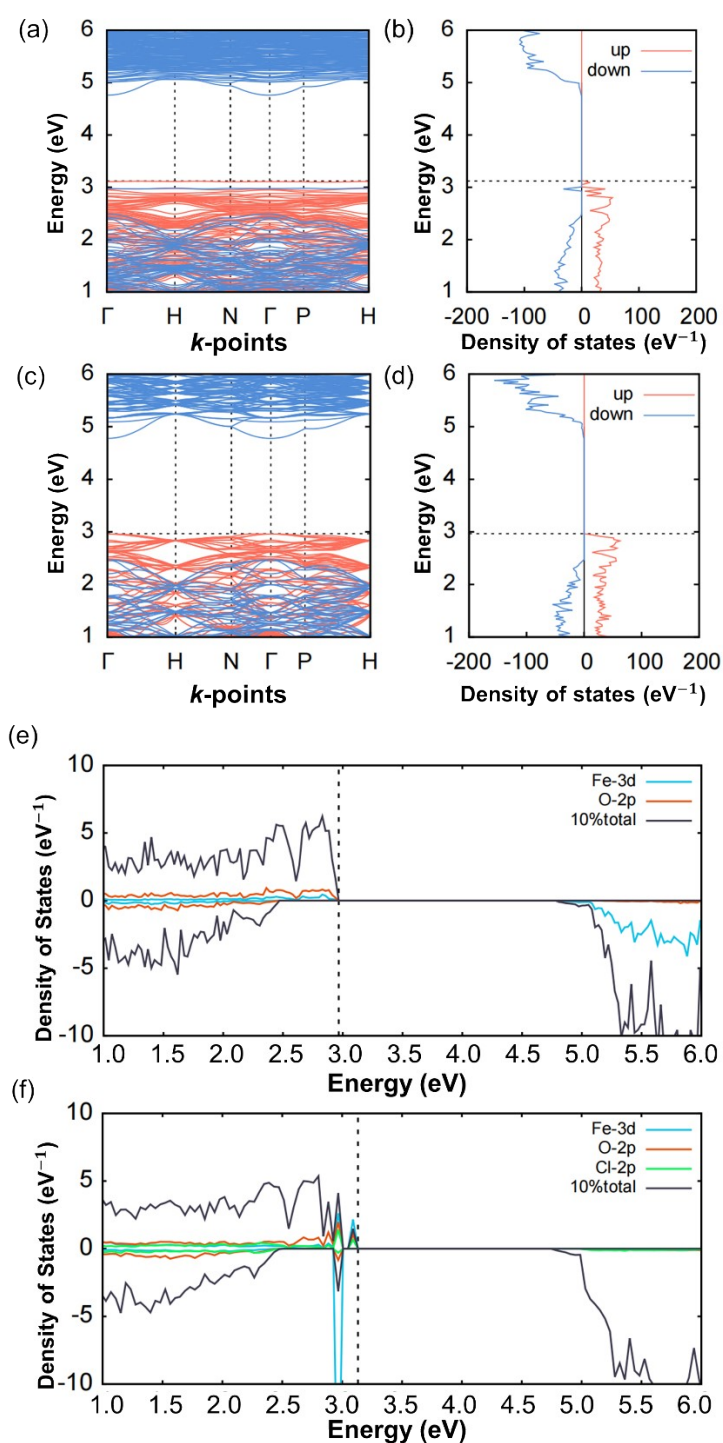
**Figure S8** DOS diagrams of (a) pure, (b) 1.25% F-doped, (c) 2.50% F-doped, and (d) 3.75% F-doped  $\beta$ - $\text{Fe}_2\text{O}_3$ . The density in the purple area increases with increasing F concentrations.

## 7 Testing the value of U

In order to investigate the effect of the U, different values of U from 5.3 to 6.8 are additionally tested. Notably, the band gap monotonic increases with the U value (Figure S10). Especially, when the U is determined to 6.6, the energy gap (1.9 eV) is equal to the experiment value, and the results obtained using U=6.6 (Figure S11) yield essentially the identical tendency with that of U=5.3.



**Figure 10.** The calculated band gap values at different values of U



**Figure S11** (a) Band structure of pure  $\beta\text{-Fe}_2\text{O}_3$ . (b) Electronic density of states of pure  $\beta\text{-Fe}_2\text{O}_3$ . (c) Band structure of Cl-doped  $\beta\text{-Fe}_2\text{O}_3$ . (d) Electronic density of states of Cl-doped  $\beta\text{-Fe}_2\text{O}_3$ . (e) Electronic partial density of states of pure  $\beta\text{-Fe}_2\text{O}_3$ . (f) Electronic density of states of Cl-doped  $\beta\text{-Fe}_2\text{O}_3$ . The  $U$  value is set at 6.6. Note that these results show essentially the identical tendency with those of  $U=5.3$

## 8 Reciprocal space table

**Table S1.** Reciprocal space base vector.

Reciprocal cell vectors (1/Å)			
b	x	y	z
b1	-	0.6584388143	0.6584388143
	0.0000000000		
b2	0.6584388143	0.0000000000	0.6584388143
b3	0.6584388143	0.6584388143	0.0000000000

**Table S2.** The high symmetry points of the path of  $\Gamma$ -H-N- $\Gamma$ -P-H.

Point	x	y	z
$\Gamma$	0.0000000000	0.0000000000	0.0000000000
H	0.5000000000	-0.5000000000	0.5000000000
N	0.0000000000	0.0000000000	0.5000000000
P	0.2500000000	0.2500000000	0.2500000000