Supporting Information

Cationically Substituted $Bi_{0.7}Fe_{0.3}OCl$ Nanosheets as Li-Ion Battery Anodes

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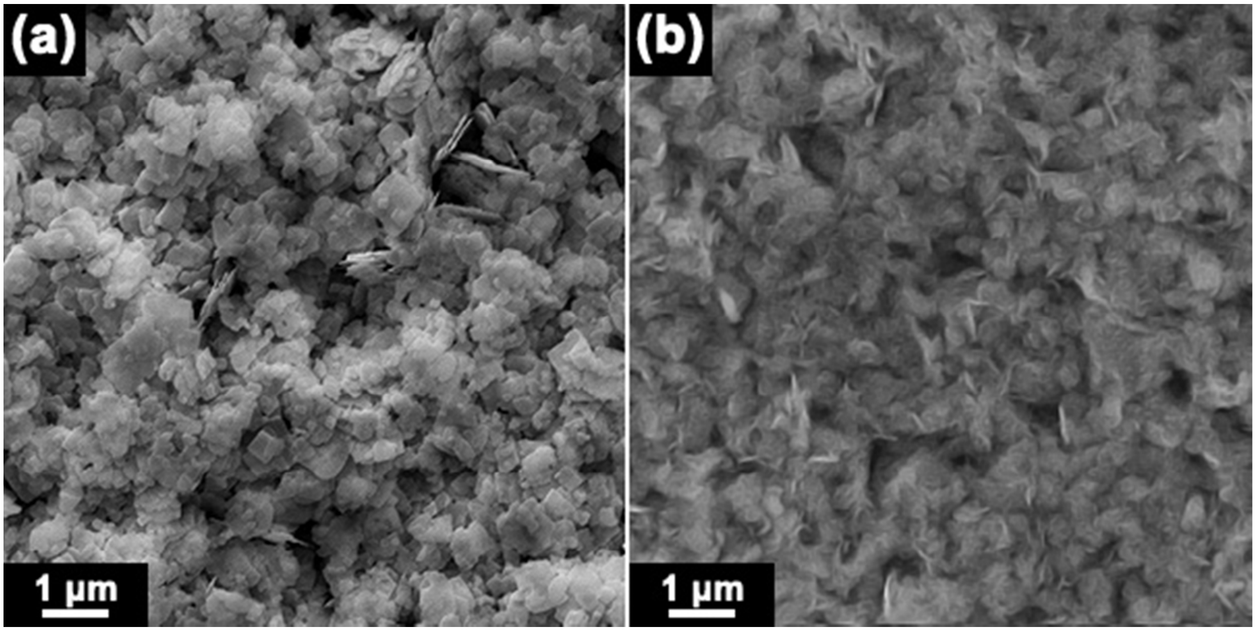

Figure S1. The SEM images shows general morphology of (a) as synthesized $Bi_{0.7}Fe_{0.3}OCl$ and (b) 500 ^{o}C annealed $Bi_{0.7}Fe_{0.3}OCl$ nanosheets.

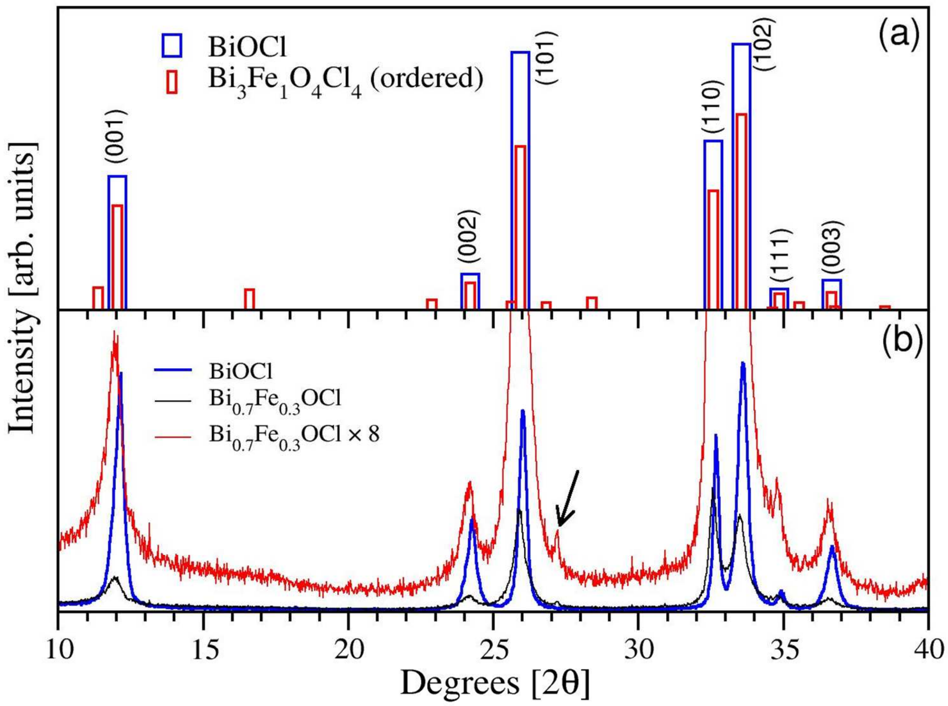

Figure S2. Simulated XRD for a 1x2x1 supercell of BiOCl with an ordered substitution of Fe on one of the four equivalent Bi sites (top panel). Experimental XRD of pure and Fe 30% substituted BiOCl (bottom panel).

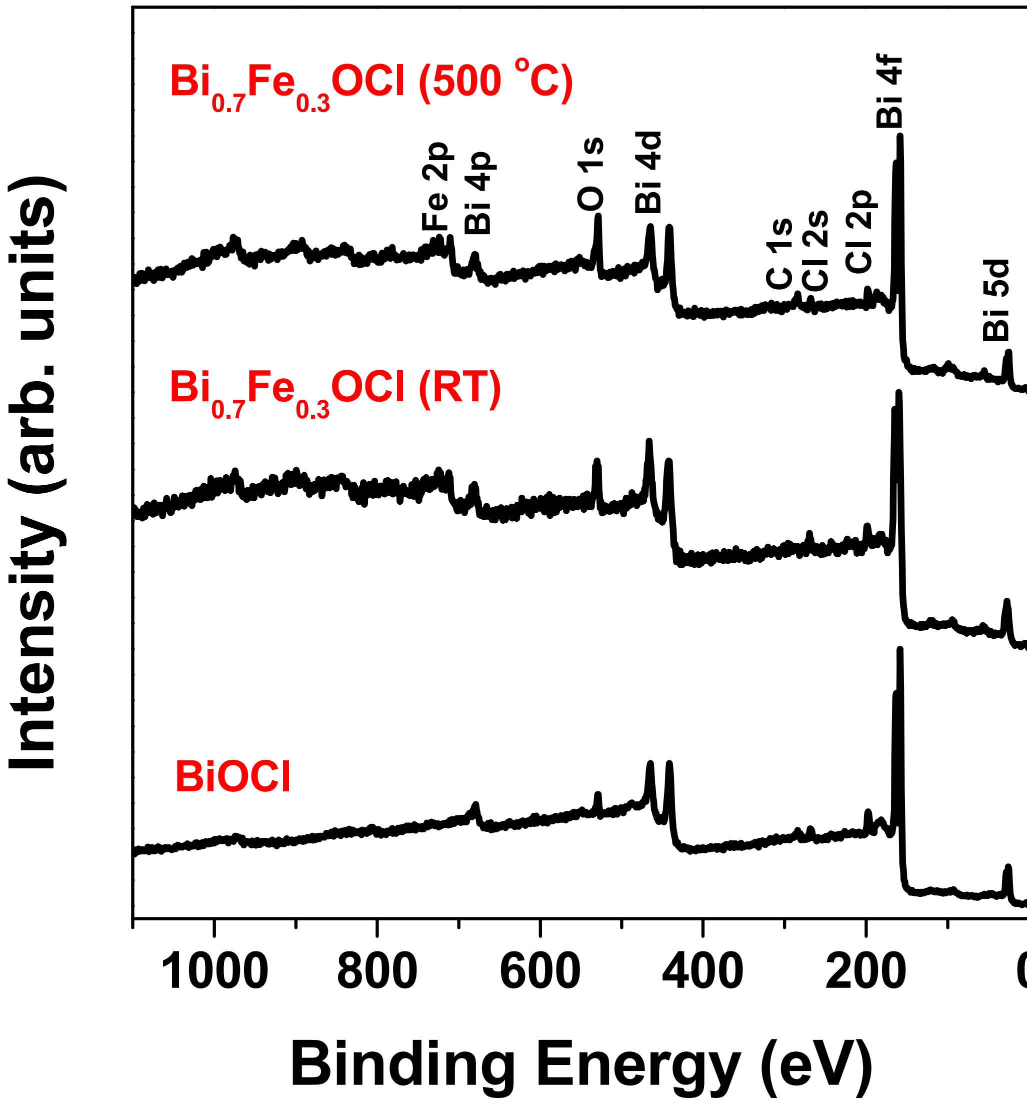

Figure S3. XPS survey spectra of BiOCl, as synthesized Fe doped BiOCl and 500 ^{o}C annealed samples.

S4: Chemistry of $Bi_{0.7}Fe_{0.3}OCl$ formation

$Bi_{0.7}Fe_{0.3}OCl$ nanosheets can be successfully formed by room temperature hydrolysis of $Bi(NO_3)_3$ and $FeCl_3$ under acidic conditions (pH 3). Generally, $Bi(NO_3)_3$ in D.I. water, dissociates to give Bi^{3+} ion and this Bi^{3+} readily hydrolyzes to form BiO^+, which is unstable in the presence of Cl^- anions, and precipitates as crystalline BiOCl.[1] On the other hand, the interaction of $FeCl_3$ in aqueous environment is highly pH dependent. At low pH conditions, $[Fe(OH)]^{2+}$, $[Fe(OH)_2]^+$, $[Fe_2(OH)_2]^{4+}$ ions are formed leading to formation of FeOOH.[2-5] The FeOOH can react with Cl^- to form FeOCl in the same medium. This possible reaction sequence has been reported wherein, FeOOH is successfully converted to FeOCl and $Fe_2(OH)_3Cl$ in low pH conditions.[6-8]

Based on our XPS spectra, there is no detectable Fe^{2+} ionic state. Therefore, we suggest FeOCl is formed in $Bi_{0.7}Fe_{0.3}OCl$ medium. In addition, the post thermal annealing step provides enough free energy for efficiently incorporating Fe^{3+} into BiOCl lattice. The entire reaction mechanism is suggested as follows:

$$FeCl_3 + 2H_2O \rightarrow FeOOH + 3HCl \qquad (1)$$

$$FeOOH + HCl \rightarrow FeOCl + H_2O \qquad (2)$$

$$2Bi(NO_3)_3 + 2HCl + 2H_2O \rightarrow 2BiOCl + 6HNO_3 \qquad (3)$$

Overall adding (1) + (2) + (3), we obtain,

$$FeCl_3 + 2Bi(NO_3)_3 + 3H_2O \rightarrow 3Bi_{0.66}Fe_{0.33}OCl + 6HNO_3 \qquad (4)$$

The experimentally obtained composition of $Bi_{0.7}Fe_{0.3}Cl$ is close to the ideal $Bi_{0.66}Fe_{0.33}OCl$ derived from the chemical reaction sequence given above.

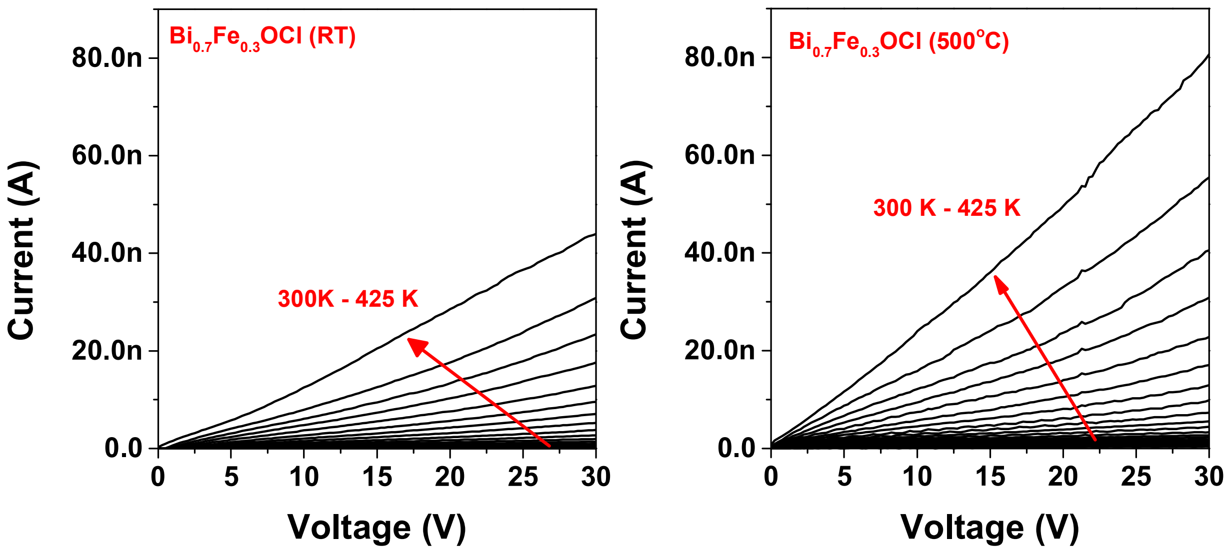

Figure S4. Temperature dependent I-V characteristics of as synthesized (left) and 500 ^{o}C annealed $Bi_{0.7}Fe_{0.3}OCl$ (right) samples. The I-V characteristics of pure BiOCl have been reported in our previous publication.[9]

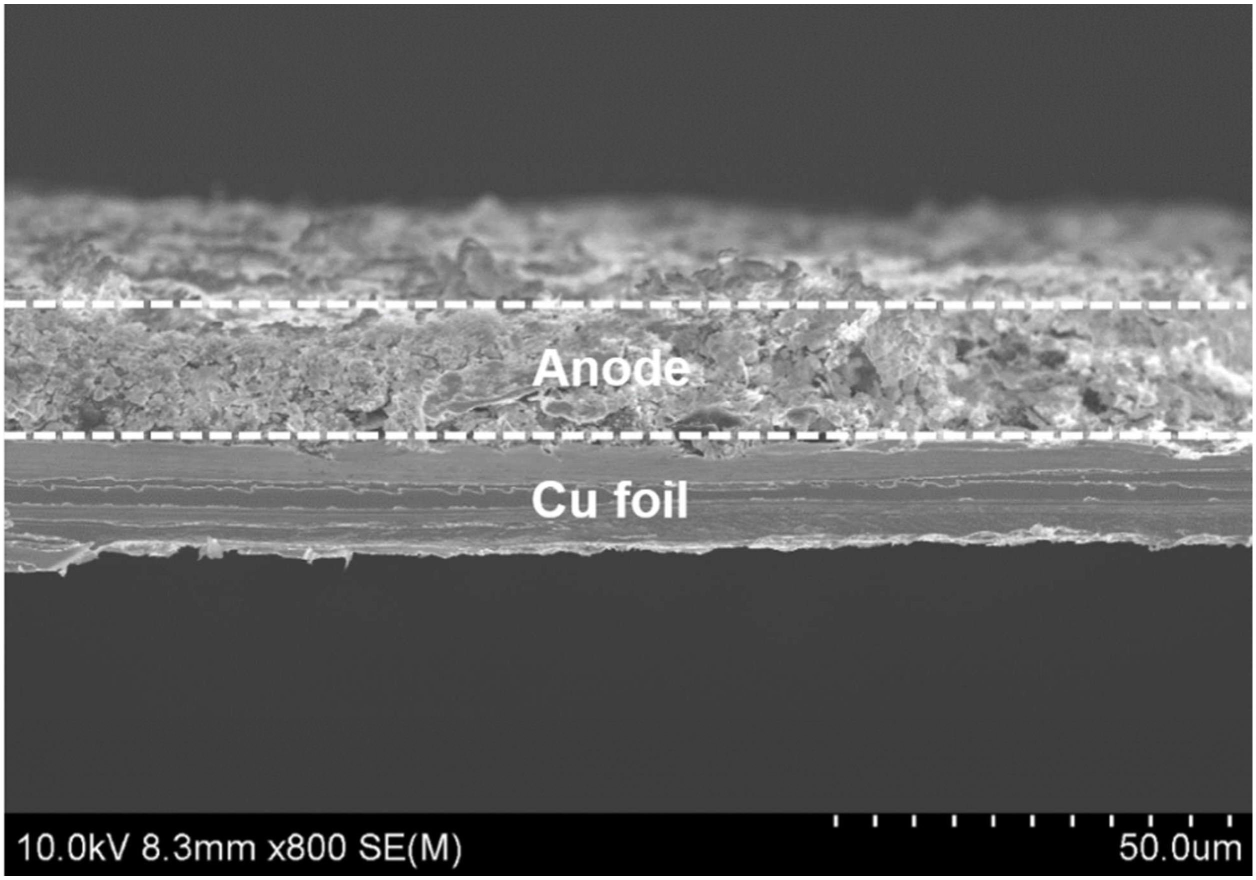

Figure S5. Cross-section SEM image of Li ion battery anode (average thickness ~20 µm) on Cu foil.

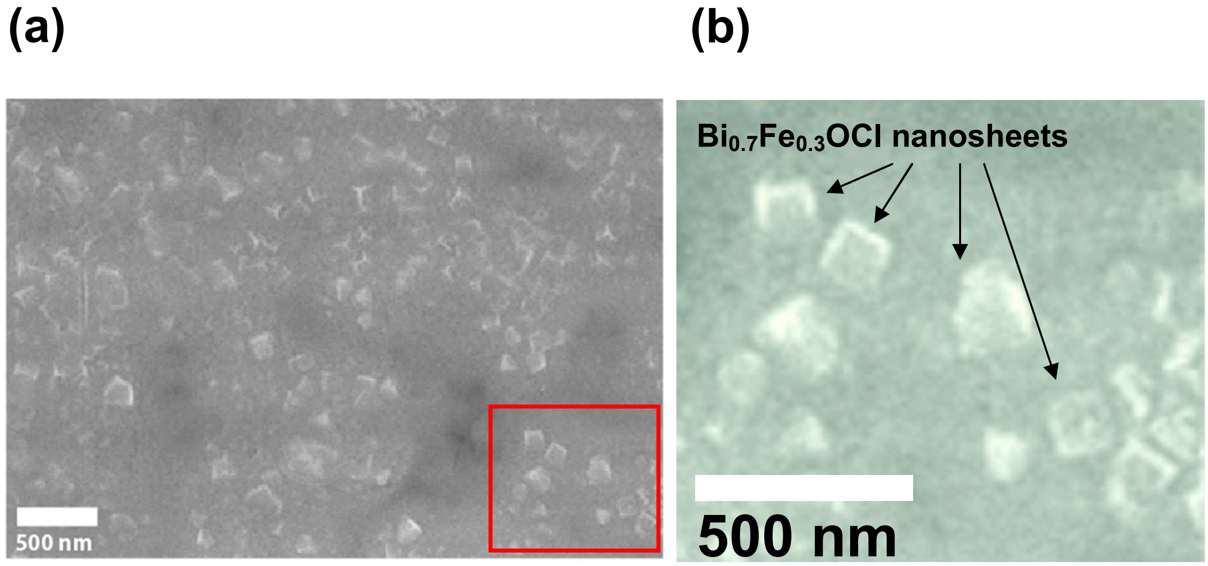

Figure S6. SEM image of post-test, $Bi_{0.7}Fe_{0.3}OCl$ nanosheets mixed in the PVDF + carbon black binder. (b) A zoomed image of the red box from image in (a) showing the intact square-like shapes of the $Bi_{0.7}Fe_{0.3}OCl$ nanosheets.

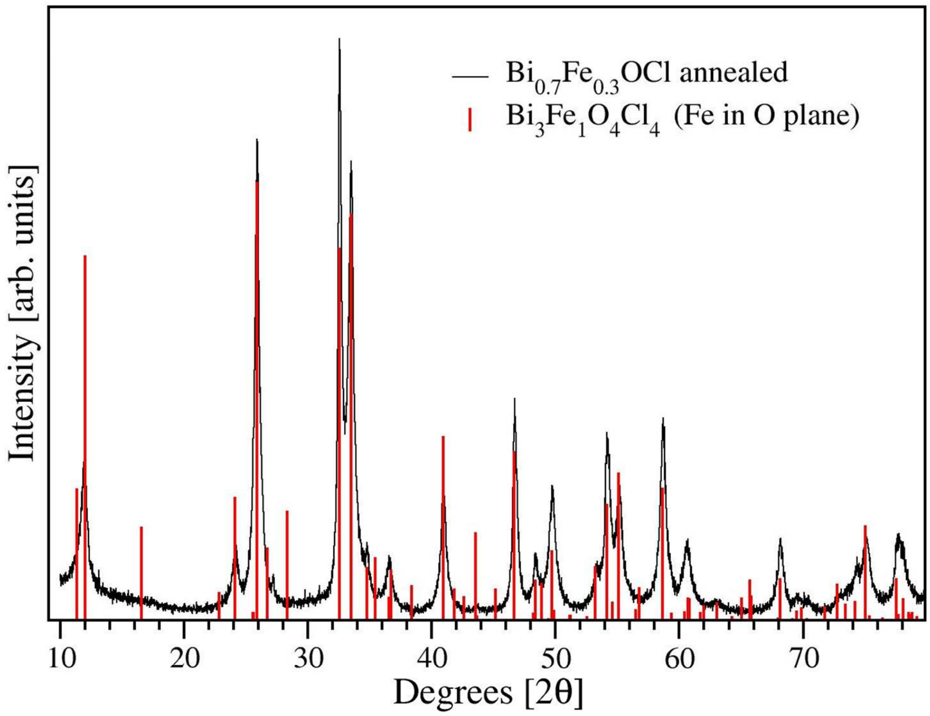

Figure S7. Simulated XRD for a 1x2x1 supercell of BiOCl with composition $Bi_3Fe_1O_4Cl_4$ from the DFT-relaxed structure where Fe moves from the Bi plane to the O plane.

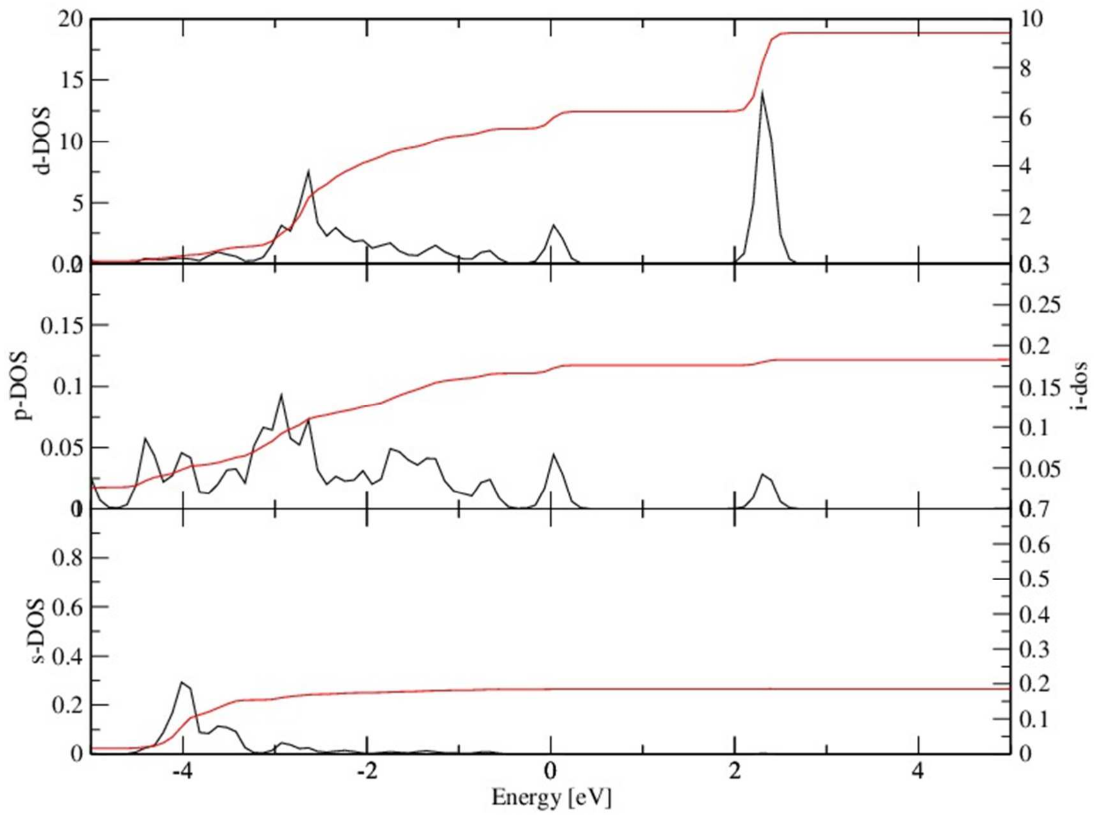

Figure S8. Fe DOS for 1x2x1 supercell with Fe in the Bi plane (unrelaxed structure).

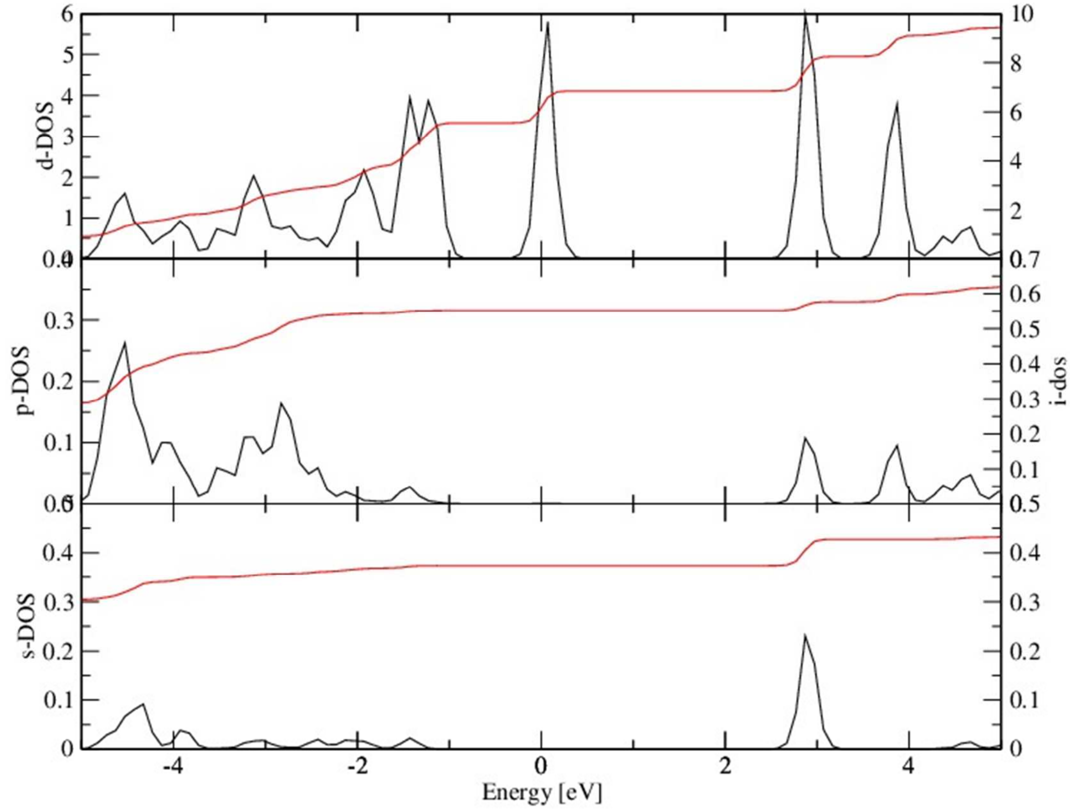

Figure S9. Fe DOS for 1x2x1 supercell with Fe in the O plane (relaxed structure).

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