Supporting Information for

Zn_2NF and Related Analogues of ZnO

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Methods

Synthesis

Synthesis of zinc nitride

In a typical synthesis of Zn_3N_2, Zinc powder (~4 g) was taken in an alumina boat and spread uniformly. The boat was placed in a quartz tube, at the centre of the heating zone in a horizontal tube furnace. The sample was purged with NH_3 (>40 mL/min) for 5h in a quartz tube in order to remove the oxygen and other gases. Then the sample was heated under a continuous flow of NH_3 at 500 °C for 10 h with a temperature ramp rate of 5 °C/min. After the reaction, the sample was naturally cooled down to room temperature. Top layer of the product appears yellow to orange colour and is because of the formation of nitrogen doped ZnO. Layer of by-product of N doped ZnO sample was carefully removed from the partially converted Zn and Zn_3N_2 mixture (black colour) and this process was repeated 3-4 times in the same experimental conditions to achieve complete conversion of Zn to Zn_3N_2. The product was collected and confirmed by PXRD (Figure S11).

Synthesis of Zn_2NF

In a typical synthesis of orthorhombic Zn_2NF, 1:1 mole ratio of Zn_3N_2 (synthesized) and ZnF_2 (commercial) were ground uniformly and pressed as a pellet and the pellet was placed inside a alumina tube. Alumina tube was closed the alumina cap with a tiny opening for the removal of gases. Alumina protects the sample from being exposed to quartz which leads to the formation of zinc silicates. The sample was placed in a quartz ampoule and the sample was kept in a vacuum $3x10^{-5}$ mbar for 20 minutes and sealed. The sample in the sealed ampoule was heated at 350 °C for 1 h and 500 °C for 2 h in a tube furnace. After the reaction, the sample was allowed to cool down to room temperature naturally. The sample was carefully collected from the quartz tube and subjected for characterization. Orthorhombic Zn_2NF structure transforms to tetragonal Zn_2NF structure at temperature above 500 °C.

Synthesis of $ZnO_{0.2}N_{0.5}F_{0.3}$

1:1 mole ratio of Zn_3N_2 (synthesized) and ZnF_2 (commercial) were ground uniformly. The reactant mixture was sealed in a quartz ampoule under $3x10^{-5}$ mbar pressure. The sample was heated at 500 °C for 5 h in a muffle furnace. After the reaction, sample was collected and characterized. (Note: Zn_2SiO_4 impurity should be carefully removed).

Synthesis of N and F doped ZnO

The N and F doped ZnO samples were prepared by two different methods. In the first method, ZnO was treated with NH_4F in NH_3 atmosphere [1] while in the second method ZnF_2 was heated in NH_3 atmosphere at 600 °C. $ZnO_{0.8}N_{0.1}F_{0.1}$ was prepared by heating a reaction mixture of ZnO (160 mg) and NH_4F (~1.5 g) at 600 °C for 2 h in NH_3 flow. $ZnO_{0.4}N_{0.3}F_{0.3}$ was prepared by heating a reaction mixture of ZnO (160 mg) and NH_4F (~1.5 g) at 600 °C for 2h in NH_3 flow (Prior to heating the reaction mixture was kept at room temperature for a day). $ZnO_{0.7}N_{0.07}F_{0.21}$ and $ZnO_{0.6}N_{0.2}F_{0.2}$ were prepared by heating ZnF_2 at 600 °C at flow rate of NH_3, 20 and 40 mL/min respectively. This process was repeated 2-3 times to completely convert ZnF_2 to N and F doped ZnO. In all the reactions the samples were purged with NH_3 for 1h prior to the reaction. These products were characterized by XRD. X-ray diffraction patterns of these materials clearly showed that the N and F doped ZnO samples possess the wurtzite structure similar to ZnO (Figure S12). Unit cell parameters of these N and F doped ZnO samples are lower than that of pristine ZnO. Chemical compositions as well as the environment of the dopants of these samples were studied by X-ray photoelectron spectroscopy (XPS).

Characterization

The X-ray diffraction patterns (XRD) of the samples were recorded with Bruker D8 Diffraction System using a Cu Kα source (λ= 0.154178 nm) and PANalytical monochromatic laboratory x-ray diffractometer (λ = 1.5406 A°). UV-Vis absorption spectra were taken with Perkin Elmer Model Lambda 900 spectrometer. Study state photoluminescence and life time measurements were carried out on the FLSP920 spectrometer, Edinburgh Instruments. XPS studies were carried out with a Mg Ka (1253.6 eV) X-ray source and was used to estimate the composition of the N and F doped ZnO samples.

XPS

The N 1*s* and F 1*s* signals typically appeared at 395.8 and 685.0 eV respectively (Figure S13).

Table S1. Properties of N and F doped ZnO samples.

Sample	Composition	Crystal structure	a (Å)	c (Å)	Band gap (eV)	Color
1	ZnO	Wurtzite	3.252	5.210	3.2	White
2	$ZnO_{0.7}N_{0.07}F_{0.21}$	Wurtzite	3.242	5.195	2.4	Yellow
3	$ZnO_{0.8}N_{0.1}F_{0.1}$	Wurtzite	3.236	5.198	2.2	Orange
4	$ZnO_{0.6}N_{0.2}F_{0.2}$	Wurtzite	3.250	5.207	2.0	Red
5	$ZnO_{0.4}N_{0.3}F_{0.3}$	Wurtzite	3.230	5.191	2.3	Yellow
6	$ZnO_{0.2}N_{0.5}F_{0.3}$	Wurtzite	3.194	5.120	2.8	Pale yellow

Photocatalytic hydrogen evolution

20 mg of the photocatalyst was dispersed in 75 mL of water and transferred to a cylindrical quartz cell with flat-faces. The solution was purged with nitrogen for 30 min to remove the dissolved oxygen. The sample was exposed to visible light (λ>395nm) (Newport Xe Lamp, 400 Watt) and the gas sample was collected at every 30 minutes with a gas-tight Hamilton syringe through the septum and analysed through gas chromatograph (Perkin Elmer, Clarus 580). Water filter (Newport) was used to eliminate the IR fraction of the radiation.

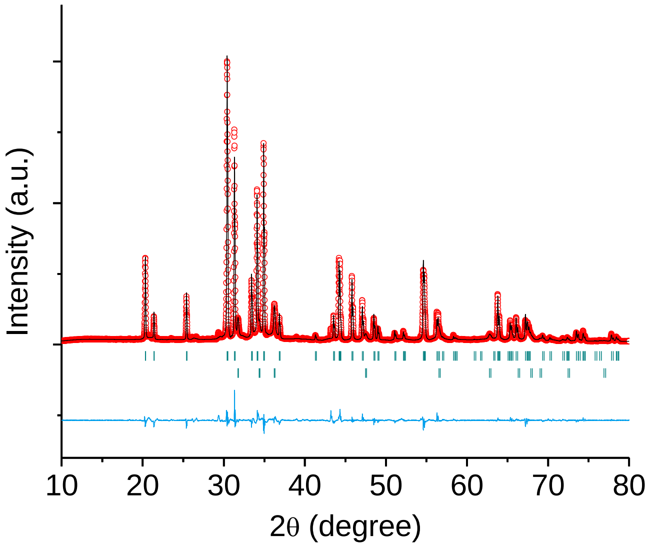

Figure S1. Rietveld refinement of XRD pattern of polycrystalline tetragonal Zn_2NF. Red markers and black solid line indicate the experimental and calculated patterns. Green markers indicate the calculated Bragg peak positions for tetragonal structure (top) and wurtzite structure (bottom).

Table S2. Crystallographic parameters of tetragonal Zn_2NF

		Rietveld refinement parameters				Theory		
Atom	Site.	x/a	y/b	z/c	B_{iso} (Å^2)	x/a	y/b	z/c
Zn1	8b	0.27802	0.35025	0.21904	3.58	0.2837	0.3467	0.2194
F1	4a	0.70923	0.29077	1/4	4.45	0.6937	0.3063	1/4
N1	4a	0.17572	0.17572	0	3.84	0.1660	0.1660	0

Rietveld refinement parameters: Space group $P4_12_12$ (No. 92); a=5.8734 Å, c=6.5324Å; Fitting parameters R_{wp} = 13.5, R_e = 9.26, R_p = 12.5, χ^2 = 2.13

Theory: Space group $P4_12_12$ (No. 92); a=5.74 Å, c=6.40 Å

Table S3. Comparison of selected bond lengths and bond angles obtained by Rietveld refinement and theoretical prediction of tetragonal Zn_2NF

	Experimental	Theory
Bond length (Å)		
Zn-N ring	1.94	1.87
Zn-F ring	2.56	2.37
Zn-N open	1.86	1.87
Zn-F open	2.05	2.06
Zn-O (in ZnO)	1.98	1.97
Bond angle (°)		
N-Zn-F ring	89.3	86.1
Zn-N-Zn ring	106.4	108.3
Zn-F-Zn ring	74.7	79.2

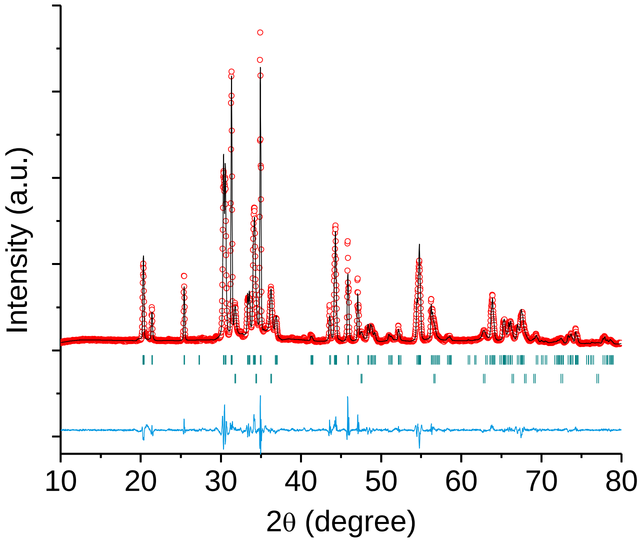

Figure S2. Rietveld refinement of XRD pattern of polycrystalline orthorhombic Zn_2NF. Red markers and black solid line indicate the experimental and calculated patterns. Green markers indicate the calculated Bragg peak positions for orthorhombic structure (top) and wurtzite structure (bottom).

Table S4. Refined crystallographic parameters of orthorhombic Zn_2NF (PXRD)

Atom	Site.	x/a	y/b	z/c	B_{iso} (Å^2)
Zn1	4a	0.0349	0.3499	0.6559	4.34
Zn2	4a	0.6007	0.2265	0.9074	4.28
F1	4a	0.0526	0.7255	0.1260	4.47
N1	4a	0.9240	0.1798	0.8801	7.58

Space group $P2_12_12_1$ (No. 19); a=5.8501 Å, b=5.8926 Å, c=6.5363 Å; Fitting parameters R_{wp} = 14.9, R_e = 5.42, R_p = 14.2, χ^2 = 7.54

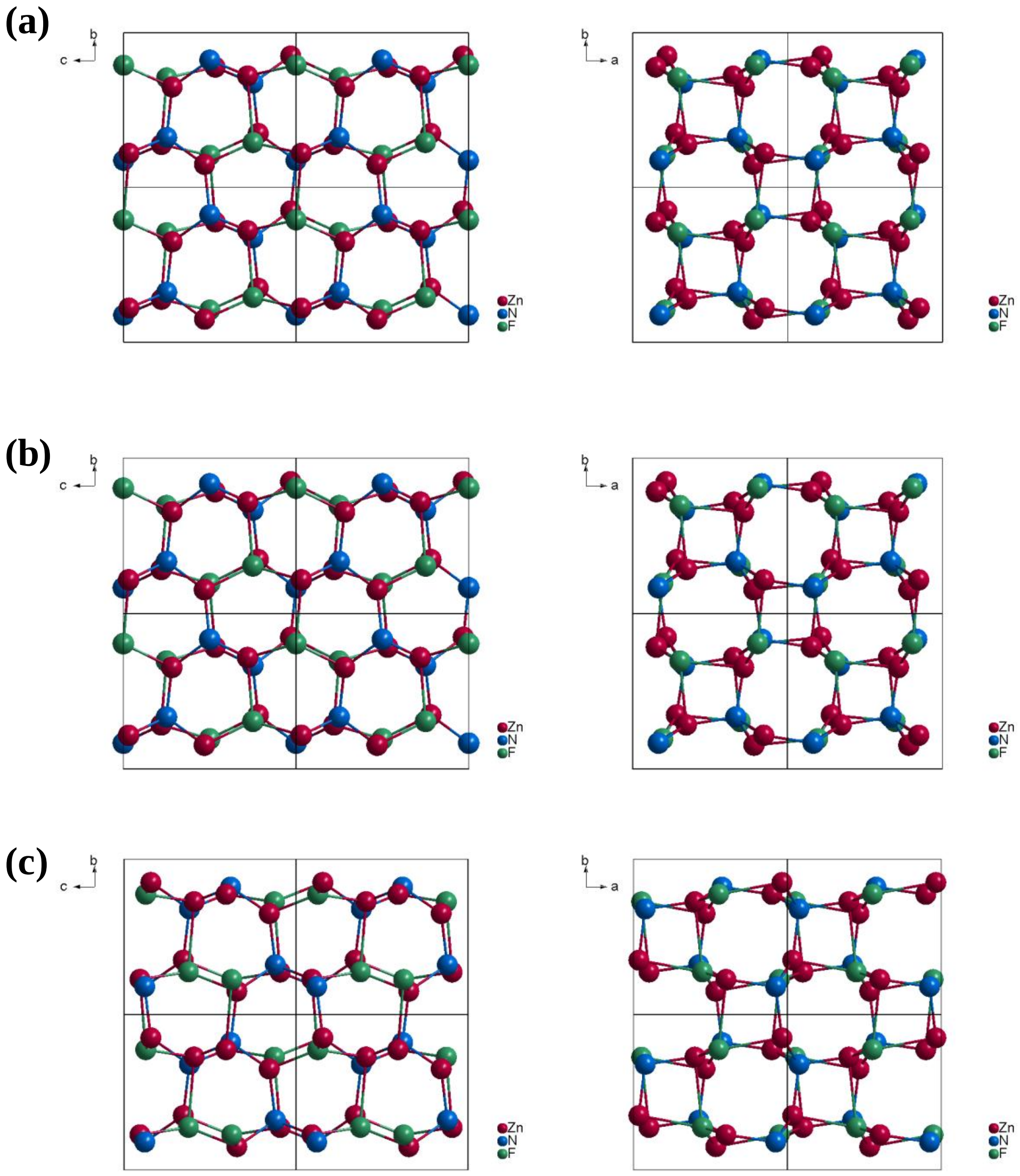

Figure S3. 2 X 2 X 2 supercells of (a) tetragonal Zn_2NF (Experimental) (b) tetragonal Zn_2NF (Theory) and (c) orthorhombic Zn_2NF.

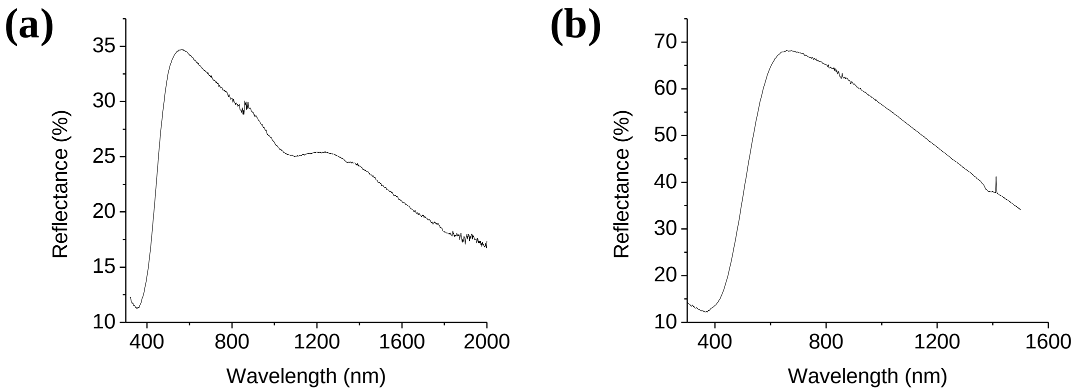

Figure S4. Diffuse reflectance spectra of (a) $ZnO_{0.2}N_{0.5}F_{0.3}$ and (b) $ZnO_{0.7}N_{0.07}F_{0.21}$.

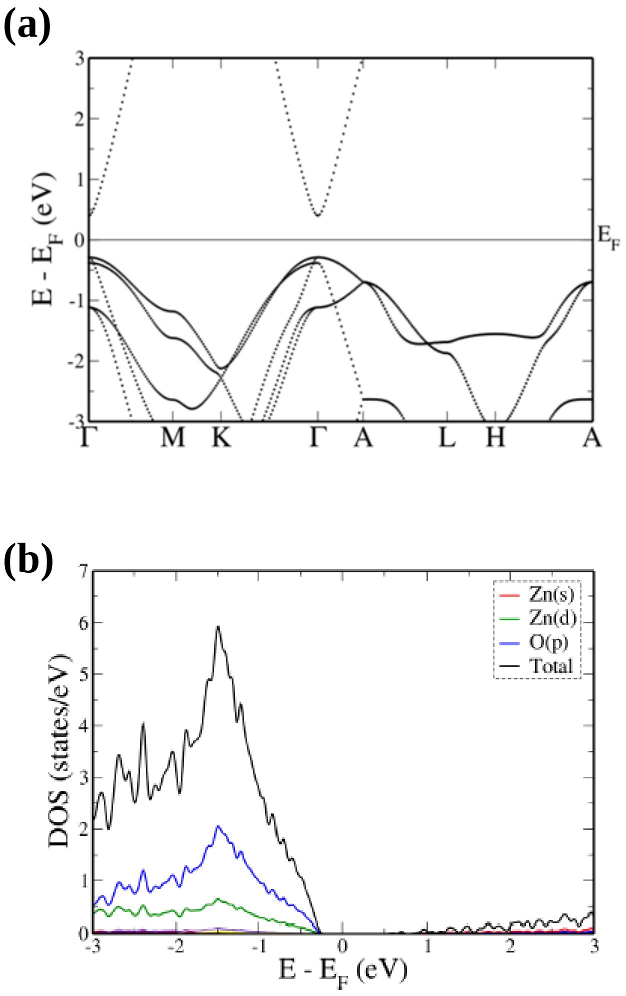

Figure S5. a) Electronic structure and b) density of electronic states of ZnO obtained with LDA calculations [Fermi energy is set at 0 eV].

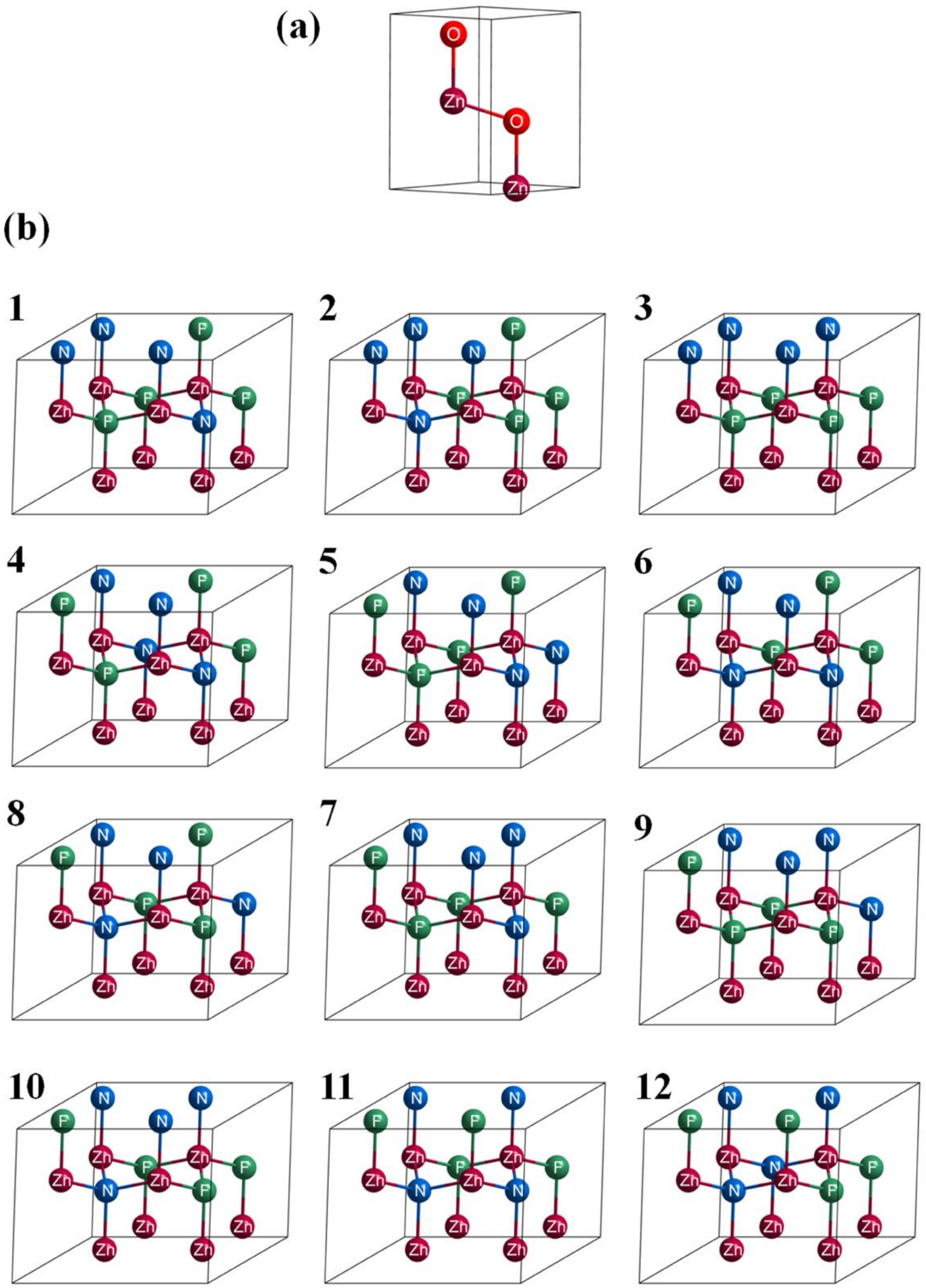

Figure S6. a) Conventional unit cell of wurtzite ZnO, and b) 12 symmetry inequivalent configurations of Zn_2NF (hexagonal) with a 2x2x1 supercell [Color code: Maroon - Zn, red - O, blue - N and green - F].

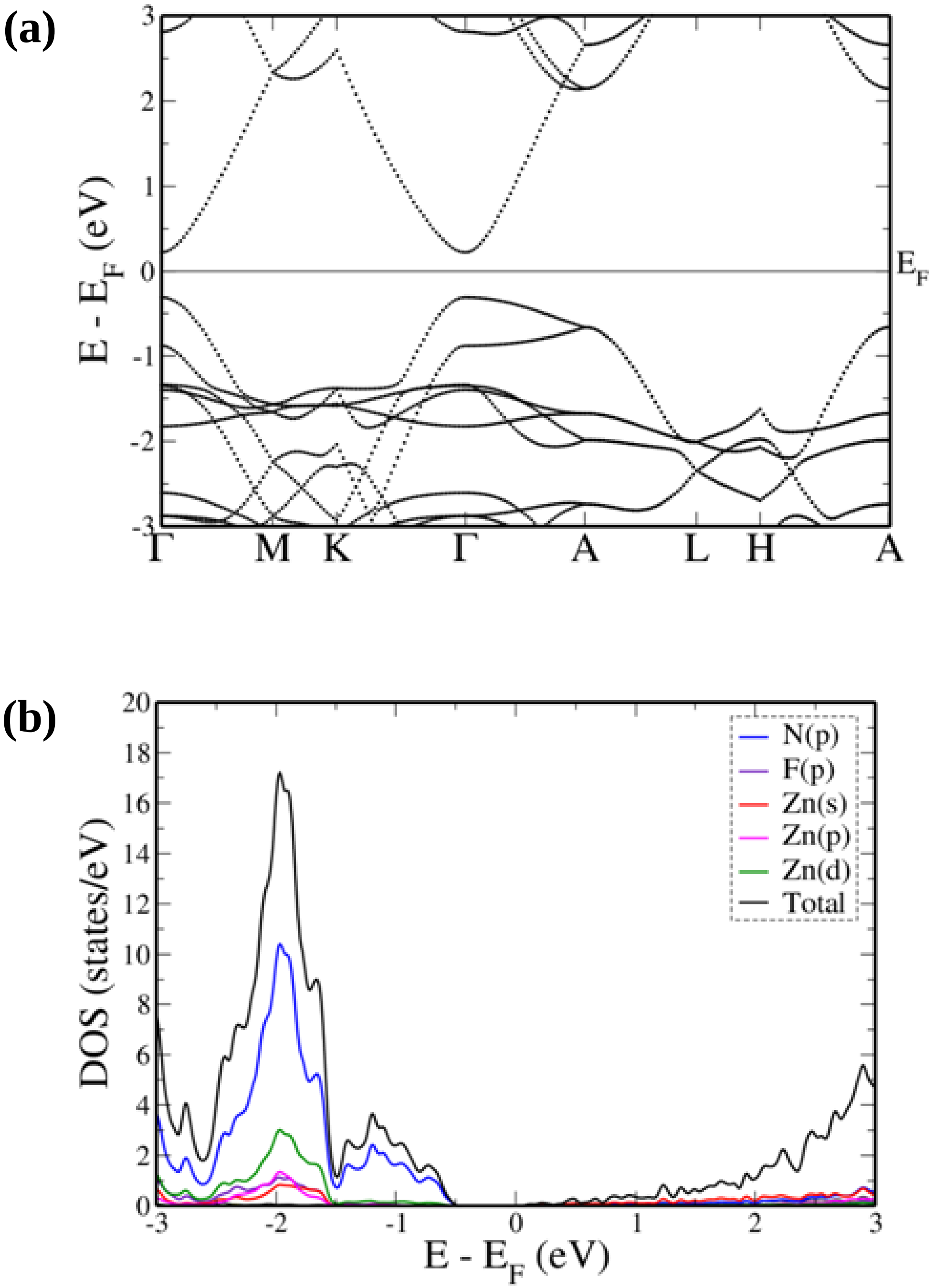

Figure S7. a) Electronic structure and b) density of electronic states of Zn_2NF (lowest energy configuration of hexagonal structure, i.e. 4) [Fermi energy is set at 0 eV].

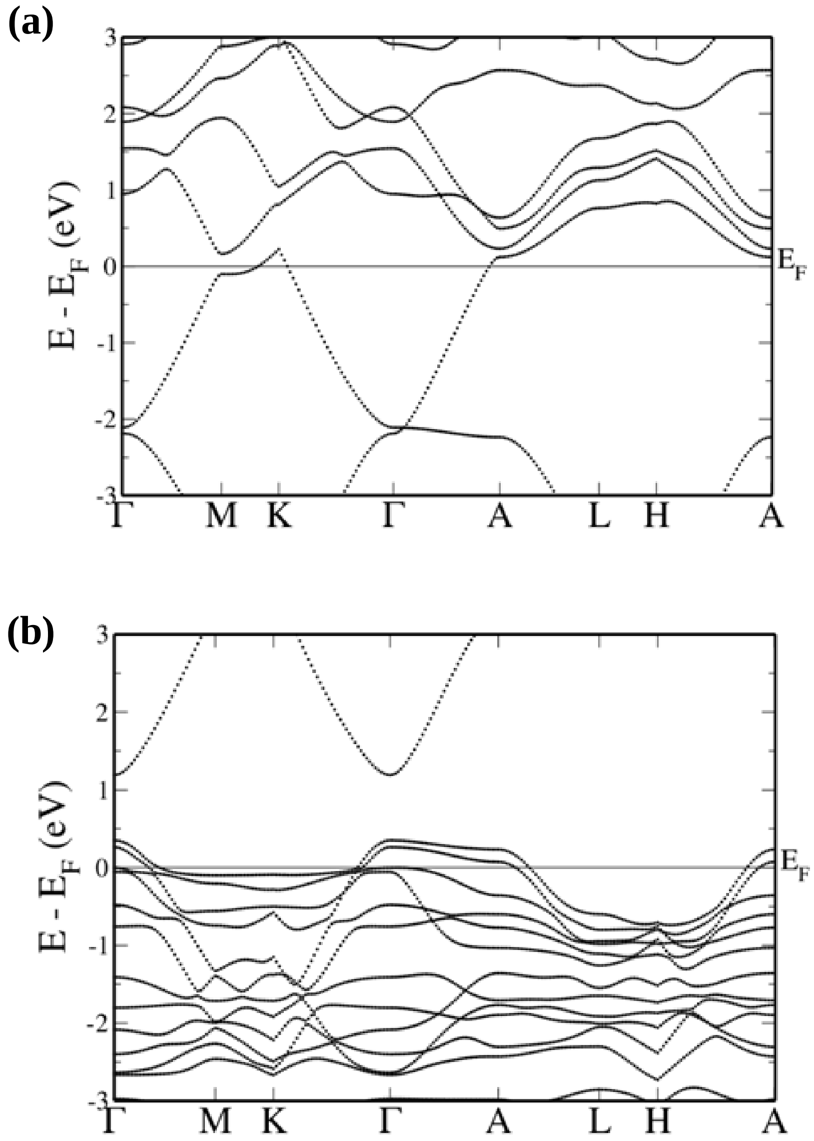

Figure S8. Electronic structure of a) $Zn_8ON_4F_3$ (hexagonal) and b) $Zn_8ON_3F_4$ (hexagonal), showing their p and n-type character [Fermi energy is set at 0 eV].

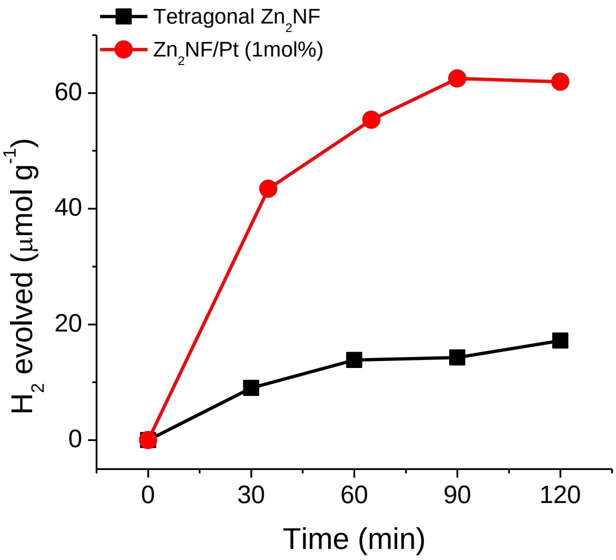

Figure S9. Photocatalytic hydrogen evolution of tetragonal Zn_2NF/Pt and tetragonal Zn_2NF.

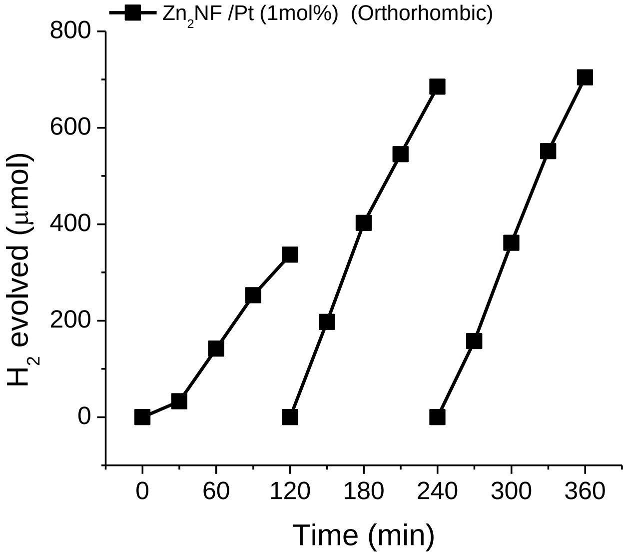

Figure S10. Stability test of photocatalytic hydrogen evolution on orthorhombic Zn_2NF/Pt in the presence of Na_2S-Na_2SO_3 under visible-light irradiation.

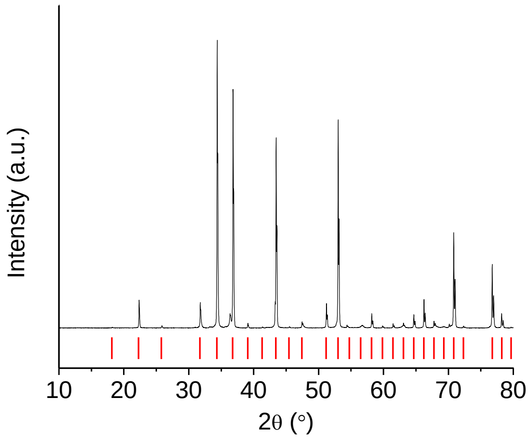

Figure S11. X-ray diffraction pattern of the Zn_3N_2. Vertical red markers indicate the calculated peak positions.

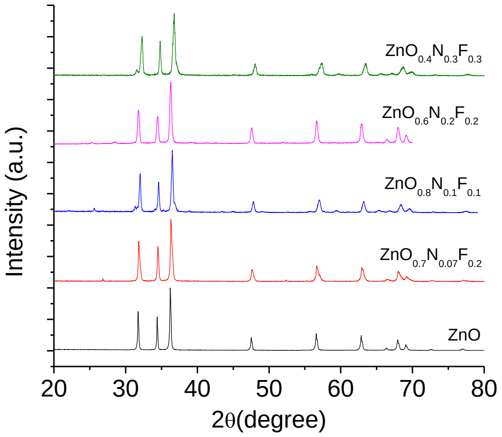

Figure S12. Comparison of X-ray diffraction patterns of $ZnO_{1-x}(N,F)_x$ samples with various amounts of N and F.

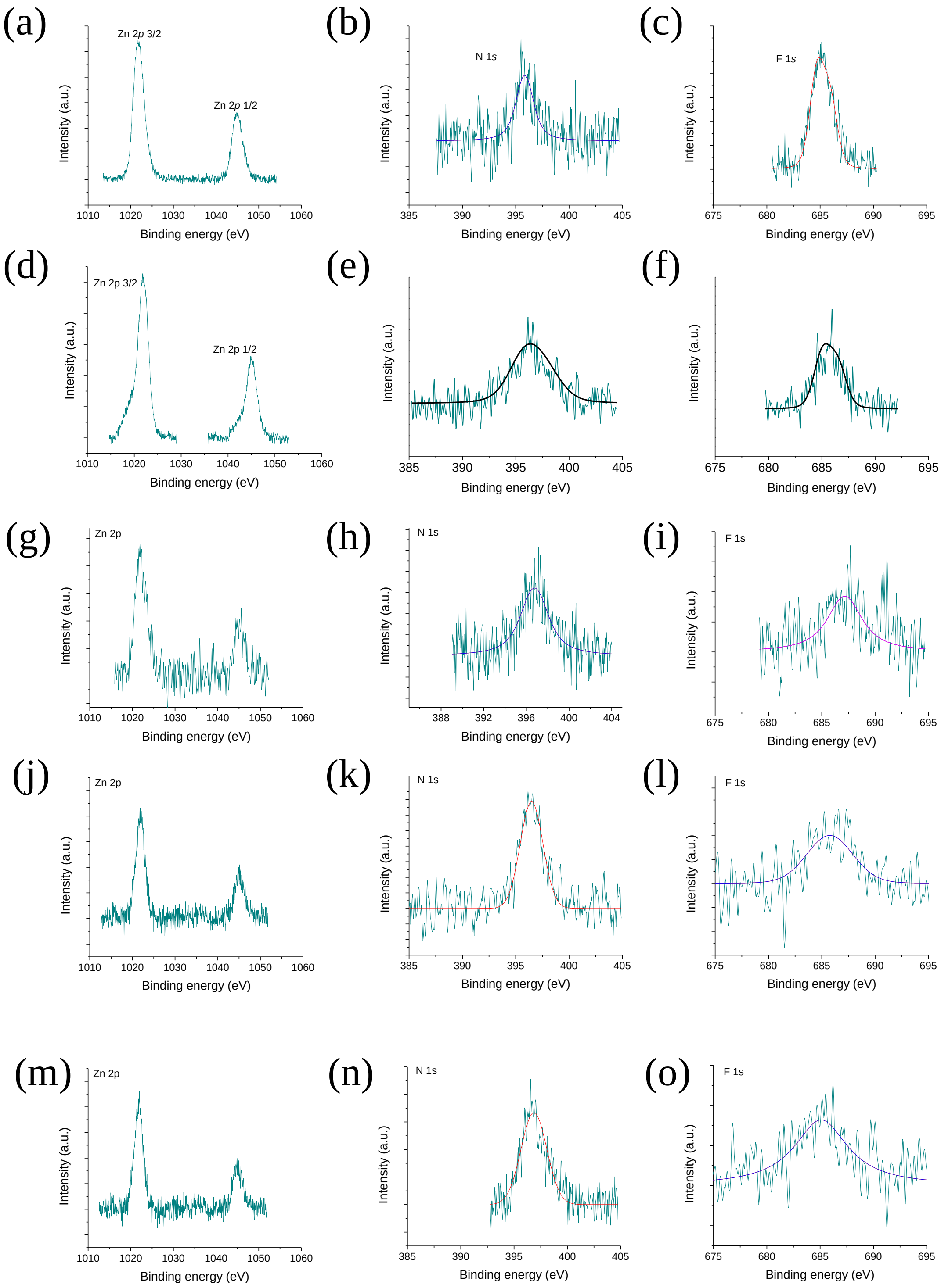

Figure S13. HR-XPS spectra of (a-c) $ZnO_{0.7}N_{0.07}F_{0.21}$ (d-f) $ZnO_{0.8}N_{0.1}F_{0.1}$,(g-i) $ZnO_{0.6}N_{0.2}F_{0.2}$ (j-l) $ZnO_{0.4}N_{0.3}F_{0.3}$ and (m-o) $ZnO_{0.2}N_{0.5}F_{0.3}$.

References

(1) Lingampalli, S. R.; Rao, C. N. R. *J. Mater. Chem. A* **2014**, *2*, 7702-7705.