Photocatalytic H_2 evolution from water-methanol system by anisotropic $InFeO_3(ZnO)_m$ oxides without cocatalyst in visible light

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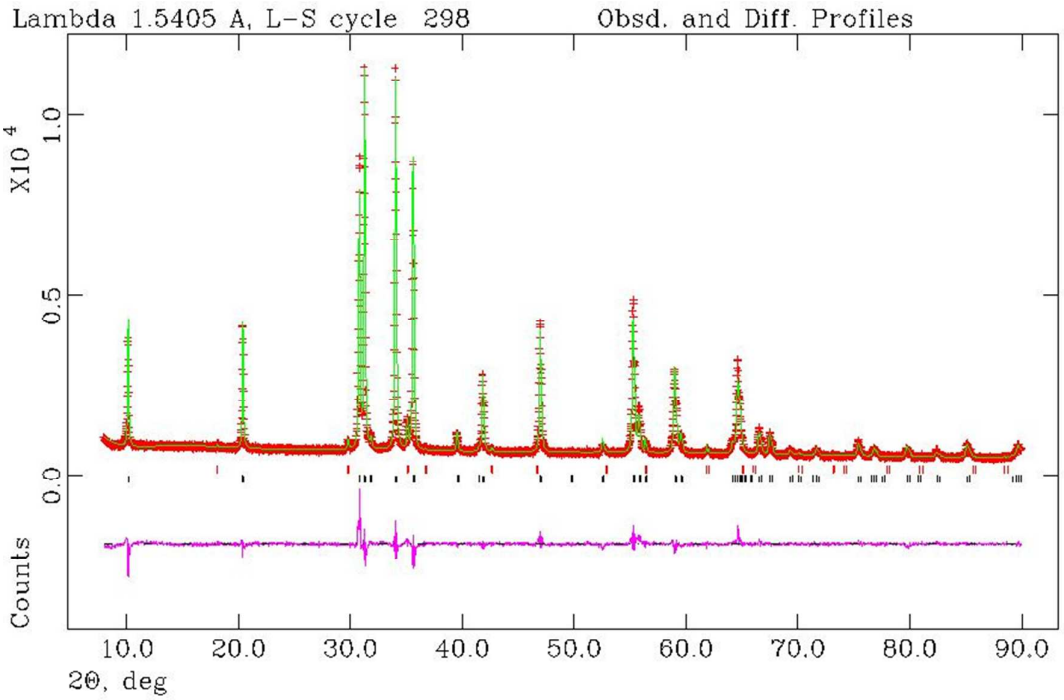
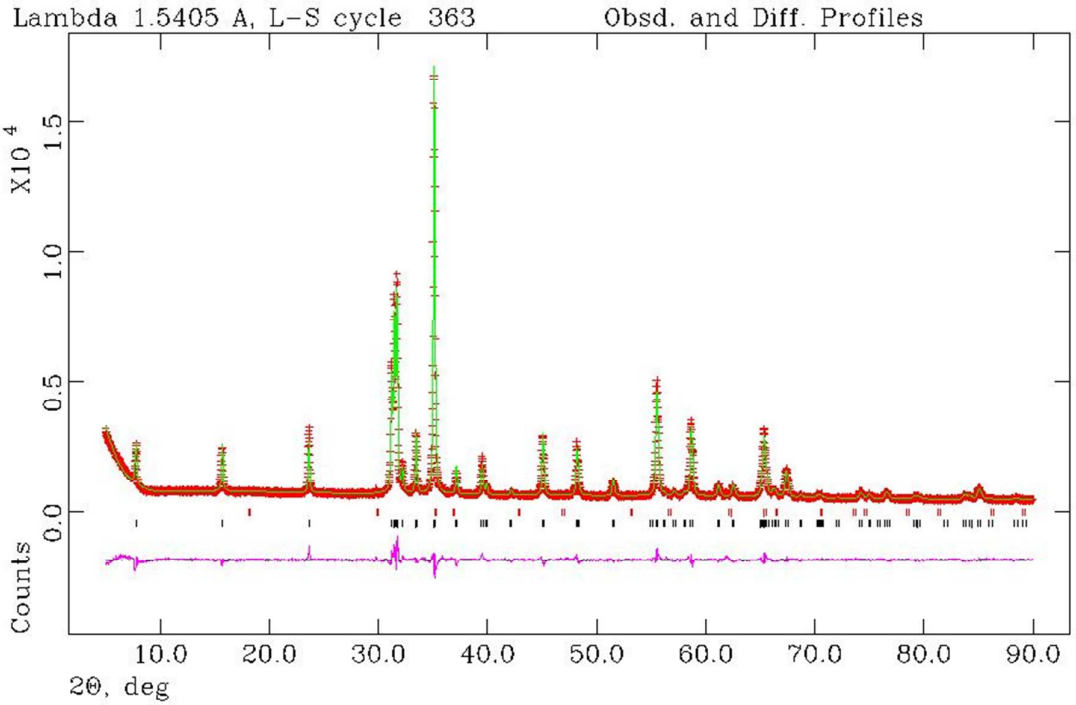
Refinement data





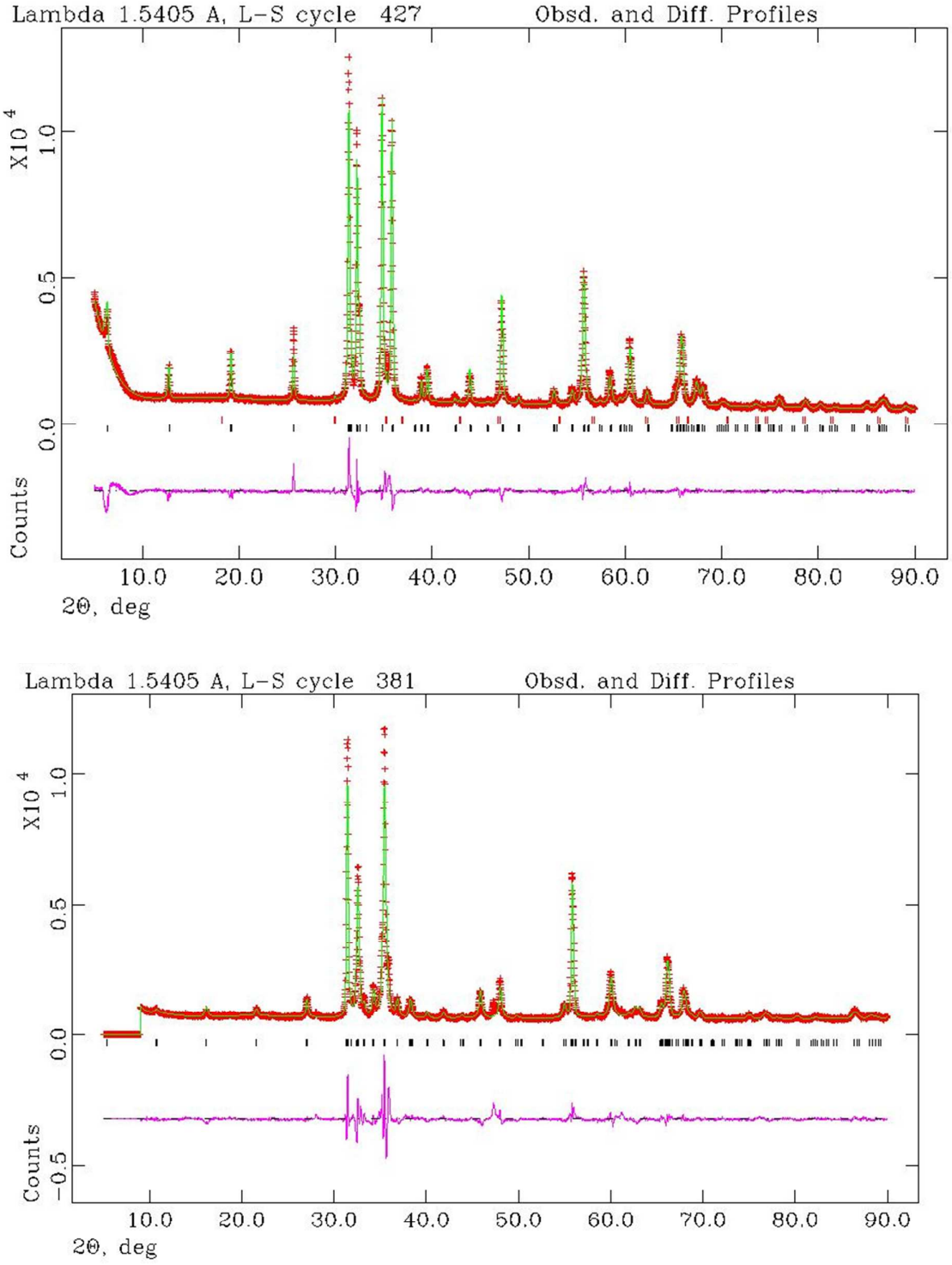


Figure S1. Refinement of the powder XRD patterns of $InFeO_3(ZnO)_m$ (m=1,2,3 and 4)

Table S1: Bond lengths of cation polyhedra in $InFeO_3(ZnO)_m$ as obtained from PXRD refinement

IFZ1		IFZ2		IFZ3		IFZ4	
In-O2(X6)	2.179	In-O1(X6)	2.219	In-O1(X6)	2.203	In-O1(X6)	2.331
Fe-O1(X3)	1.930	Fe-O2(X2)	2.147	Fe-O2(X1)	2.057	Fe-O3(X2)	2.387
Fe1-O1 (X1)	2.320	Fe-O3(X3)	1.911	Fe-O3(X3)	1.917	Fe-O4(X3)	1.901
Fe-O2 (X1)	1.976	Zn1-O1(X1)	1.917	Fe-O3(X1)	2.478	Zn1-O1(X1)	1.664
Zn1-O1 (X3)	1.930	Zn1-O2(X3)	1.965	Zn1-O1(X1)	1.954	Zn1-O2(X3)	2.016
Zn1-O1 (X1)	2.320			Zn1-O2(X3)	1.976	Zn2-O2(X1)	1.926
Zn1-O2 (X1)	1.976			Zn2-O2(X1)	2.057	Zn2-O3(X1)	1.916
				Zn2-O3(X3)	1.971	Zn2-O3(X2)	1.917
				Zn2-O3(X1)	2.478		

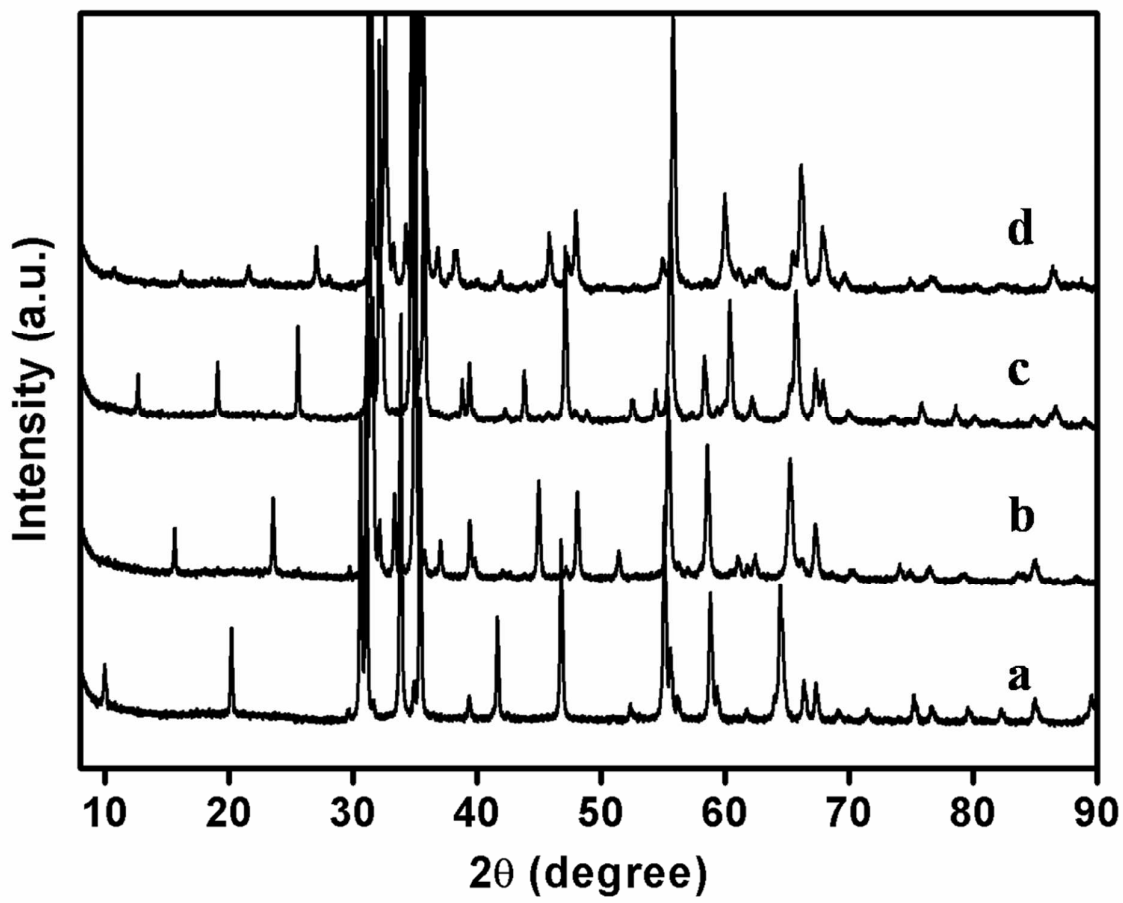


Figure S2. PXRD patterns of of $InFeO_3(ZnO)_m$ (a) m=1, (b) m=2, (c) m=3, and (d) m=4. after 2 hours of Hydrogen evolution reaction

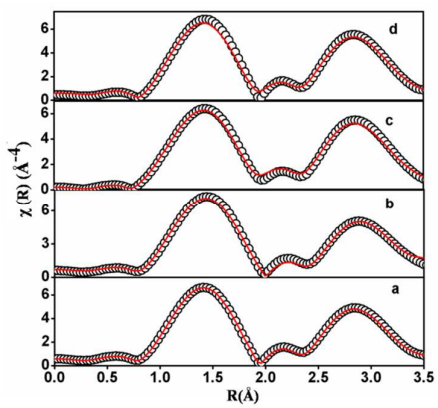


Figure S3. Fourier transformed EXAFS spectra of $InFeO_3(ZnO)_m$ at Zn K-edge (Scatter points) and theoretical fit (Solid line): (a) m=1, (b) m=2, (c) m=3, and (d) m=4. a and b are fitted for pentacoordination whereas c and b are fitted for tetracoordination.

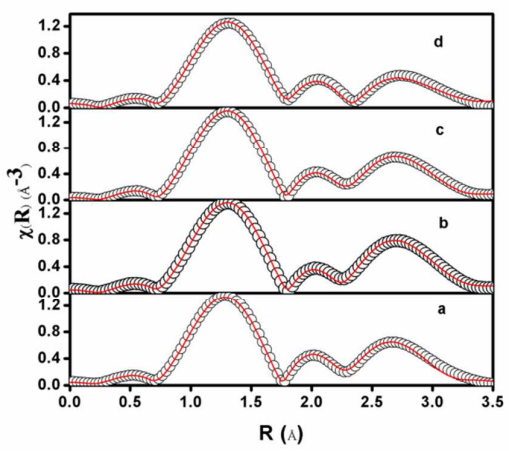


Figure S4. Fourier transformed EXAFS spectra of $InFeO_3(ZnO)_m$ at Fe K-edge (Scatter points) and theoretical fit (Solid line): (a) m=1, (b) m=2, (c) m=3, and (d) m=4.

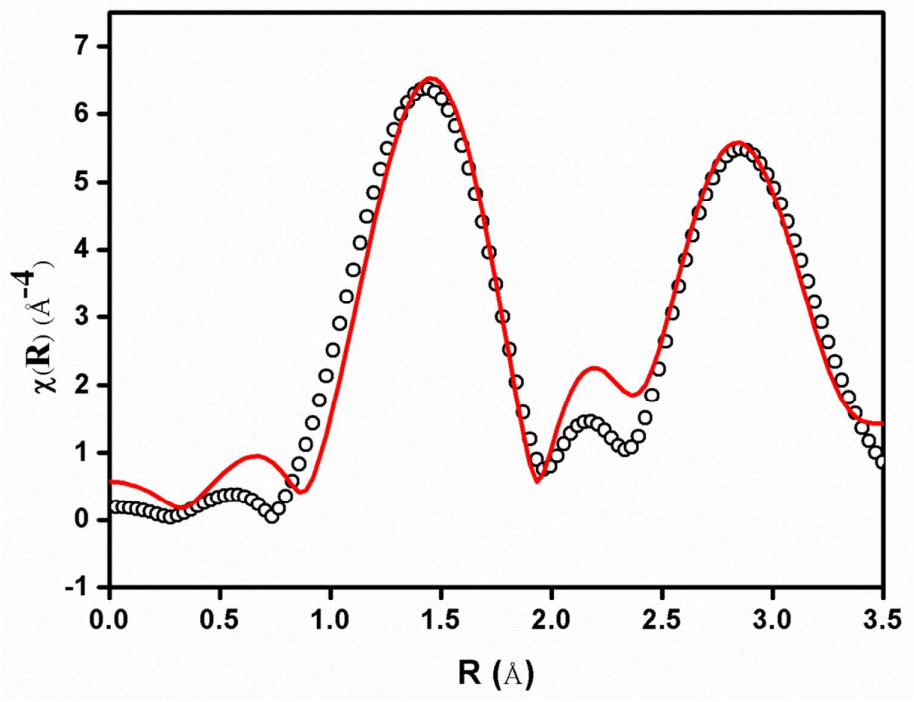


Figure S5. Fourier transformed EXAFS spectra of $InFeO_3(ZnO)_3$ at Zn K-edge (Scatter points) and theoretical fit (Solid line) fitted with TBP structure.

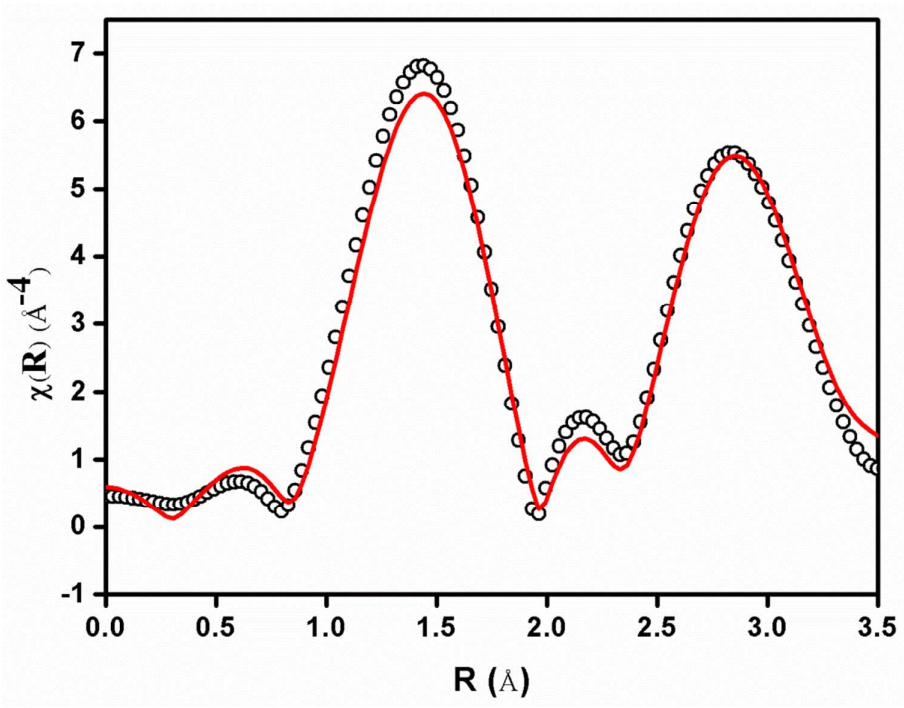


Figure S6. Fourier transformed EXAFS spectra of $InFeO_3(ZnO)_4$ at Zn K-edge (Scatter points) and theoretical fit (Solid line) fitted with TBP structure.

Flat band potential was calculated using the equation, Vfb=EA-Eref+1/2Eg

Where Vfb is the flat band potential, EA is the electron affinity of the individual atom, Eref is the energy of free electrons on the hydrogen scale, Eref= 4.5 eV and Eg is the band gap of the material

For IFZ1 ($InFeO_3(ZnO)_1$), EA=((X_{In}) * (X_{Fe})*(X_{Zn})*$(X_o)^4)^{1/7}$

Where $X_{In,}$ $X_{Fe,}$ $X_{Zn,}$ X_o are the electronegativities in mulliken scale of Indium, Iron, Zinc and Oxygen respectively. The detailed calculation is given below

X_{In} = 3.1 eV

X_{Fe} = 4.06 eV

X_{Zn} = 4.45 eV

X_o = 7.53 eV

Band gap of IFZ1 is 2.85 eV

EA = $(3.1 \times 4.06 \times 4.45 \times (7.53)^4)^{1/7}$

= 5.6364 eV

Vfb = 5.6364 - 4.5 + (½ x 2.85)

= 2.56 eV

For IFZ2 ($InFeO_3(ZnO)_2$)

EA = $(3.1 \times 4.06 \times (4.45)^2 \times (7.53)^5)^{1/9}$

= 5.6676eV

Vfb =5.6676 - 4.5 + (½ x2.96)

= 2.64eV

For IFZ3 ($InFeO_3(ZnO)_3$)

EA = $(3.1 \times 4.06 \times (4.45)^3 \times (7.53)^6)^{1/11}$

= 5.6894eV

Vfb = 5.6894- 4.5 + (½ x2.97)

= 2.67eV

For IFZ4 ($InFeO_3(ZnO)_4$)

EA = $(3.1 \times 4.06 \times (4.45)^4 \times (7.53)^7)^{1/13}$

=5.7045 eV

Vfb = 5.7045- 4.5 + (½ x3.022) = 2.71eV

Chromatograms

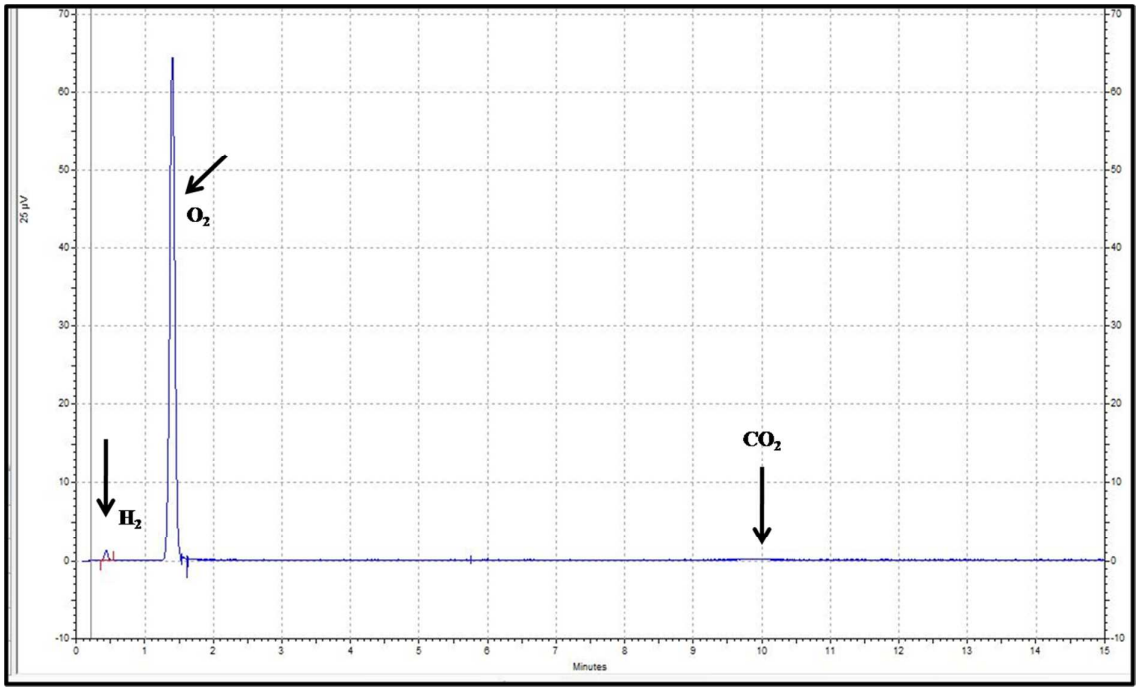


Figure S7. Hydrogen evolution of IFZ1 under dark from 20% methanol 80% water mixture for 2h

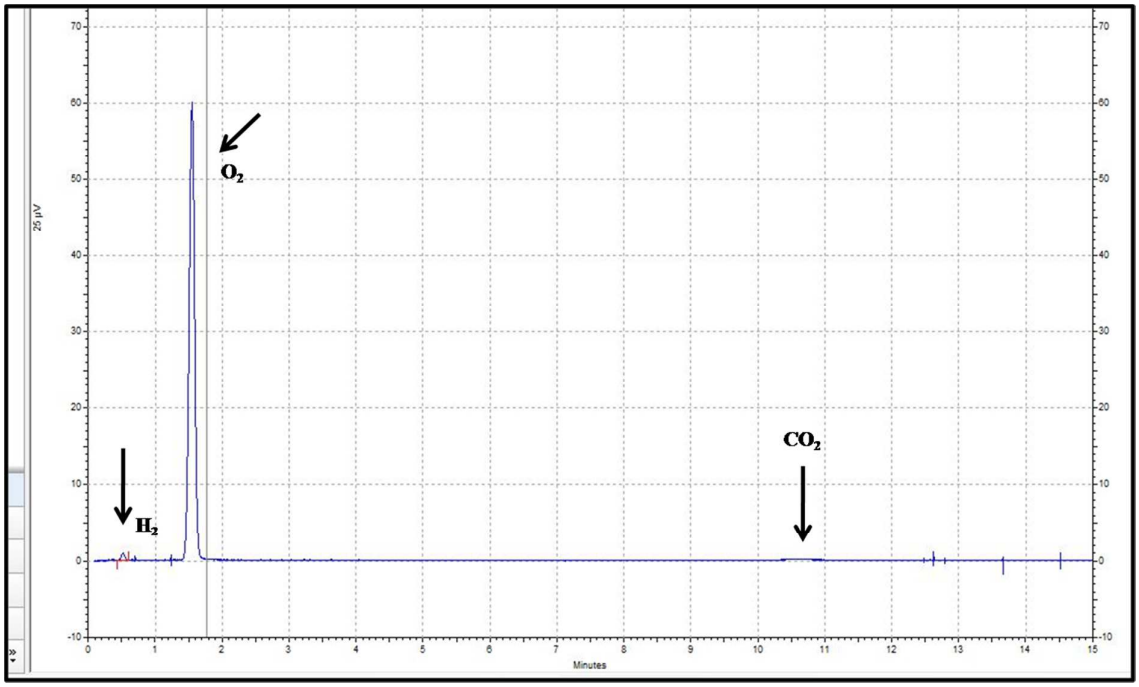


Figure S8. Hydrogen evolution of IFZ1 under visible light irradiation from a 5 ml methanol without water.

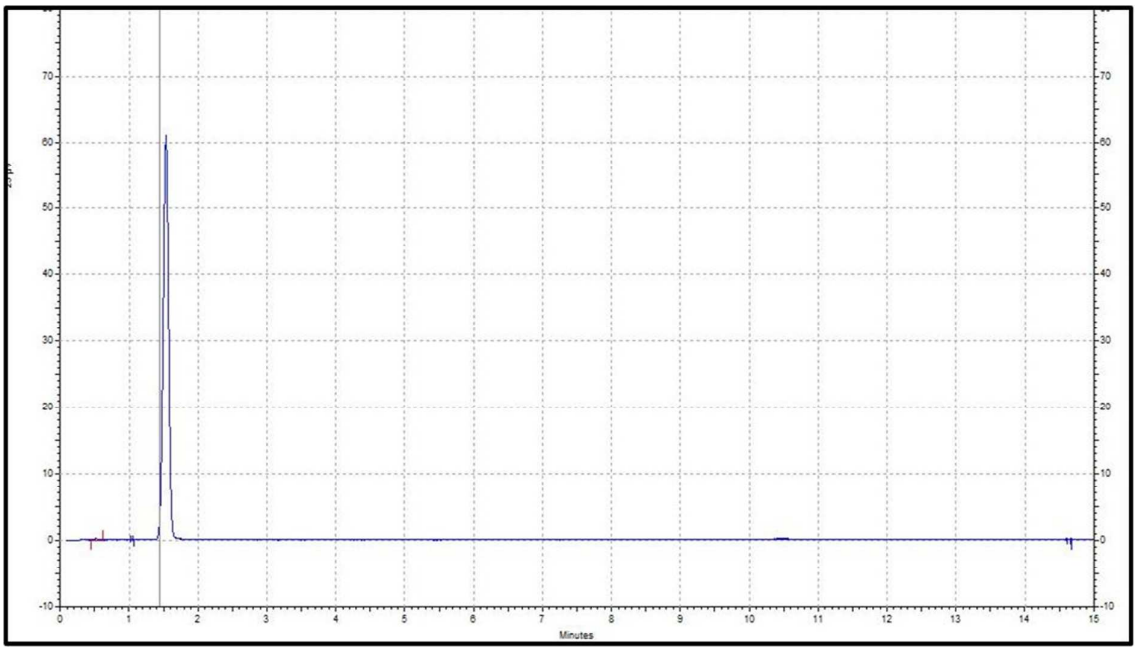


Figure S9. Chromatogram of reaction product of visible light irradiated IFZ1 from water without adding methanol

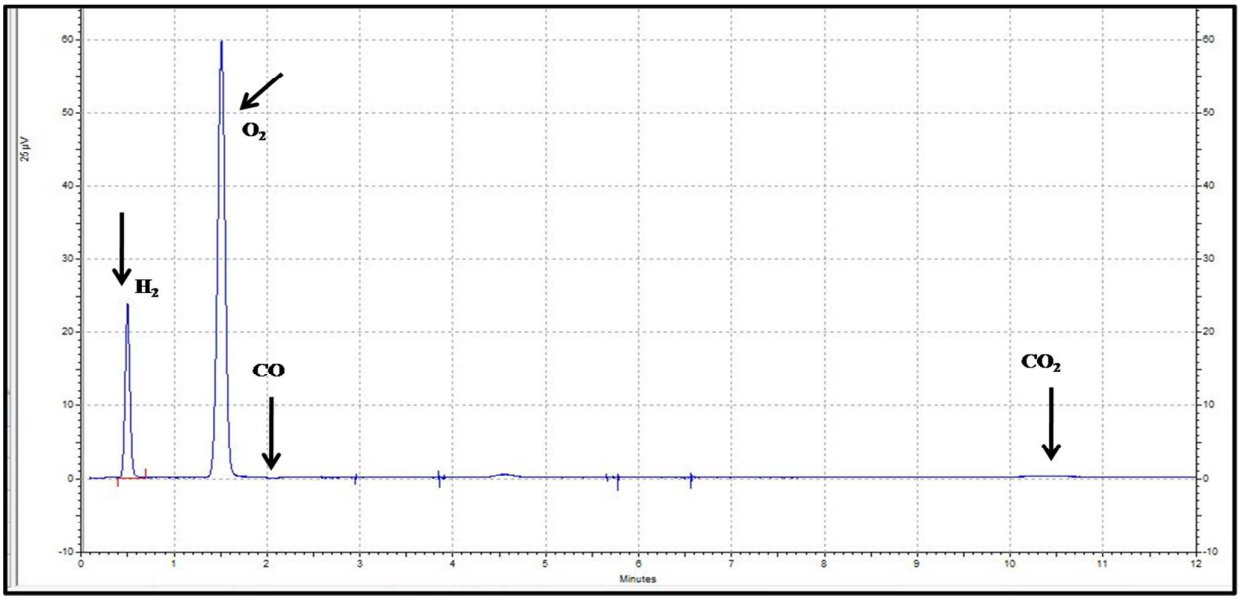


Figure S10. Hydrogen evolution of IFZ1 under visible light irradiation from 12% methanol 88% water mixture for 2h