Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

# *Supplementary Information*

## Photochemical HER activity of layered metal phospho-sulfides and -selenides

Manaswee Barua, Mohd Monis Ayyub, Pratap Vishnoi, K. Pramoda and C.N.R. Rao *

New Chemistry Unit, Sheikh Saqr Laboratory, School of Advanced Materials, Jawaharlal
Nehru Centre for Advanced Scientific Research, Jakkur P.O., Bangalore -560064, India

Corresponding author email: cnrrao@jncasr.ac.in

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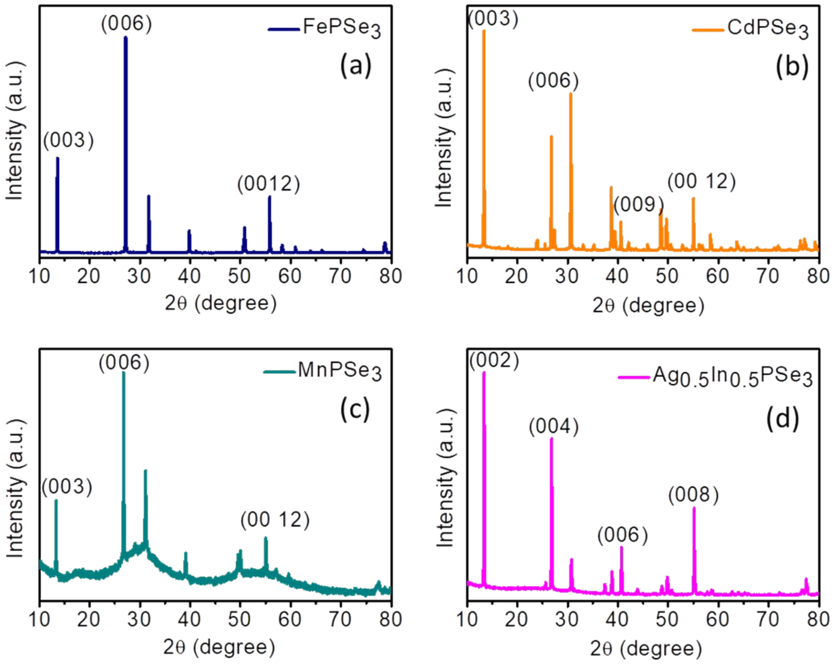

Figure S1: PXRD patterns of $MnPSe_3$, $FePSe_3$, $CdPSe_3$ and $Ag_{0.5}In_{0.5}PSe_3$

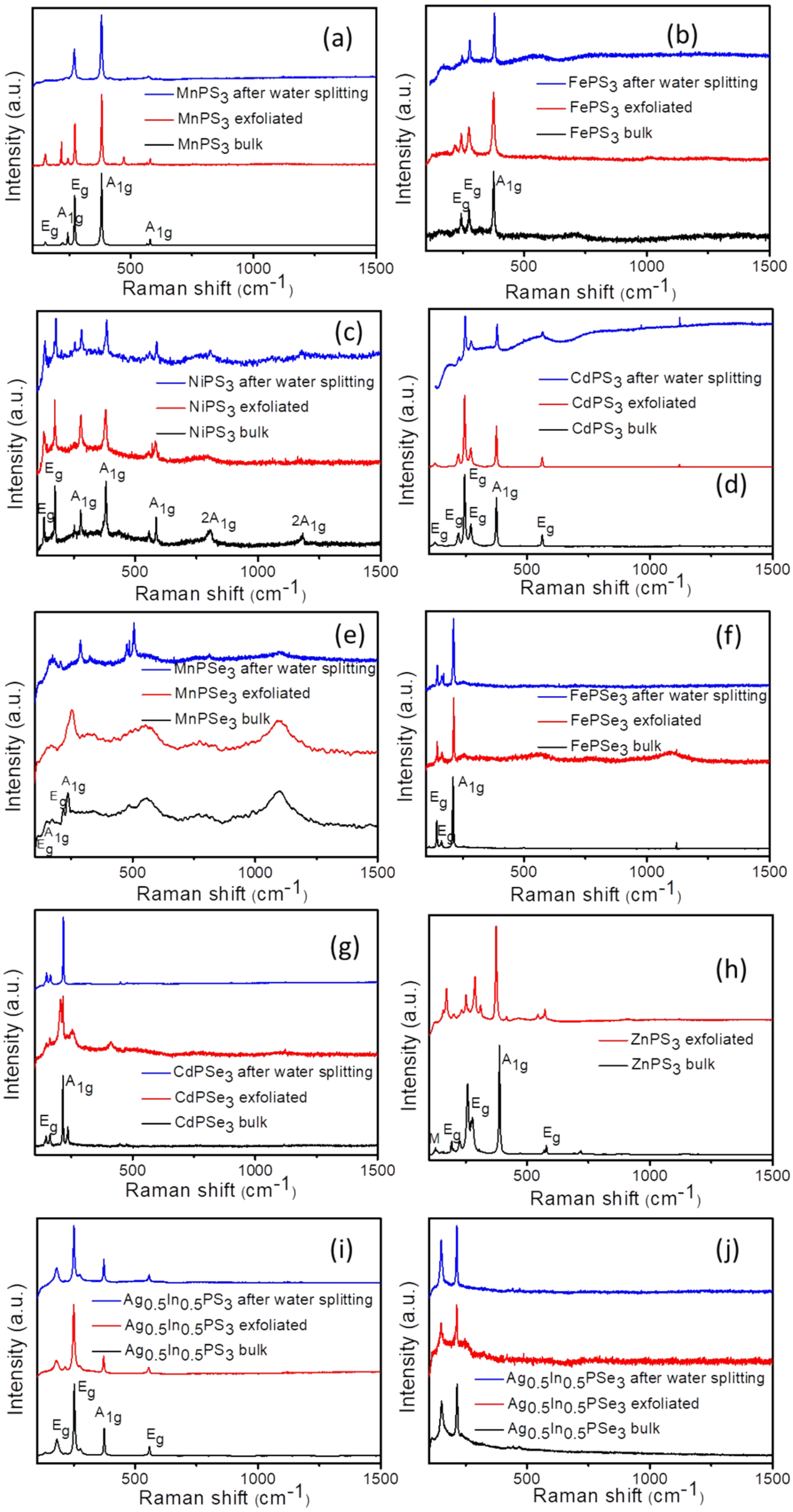

Figure S2: Raman spectra of all synthesized metal phosphosulfides and selenide compounds in bulk form, exfoliated form and after water splitting

The Raman spectra of these compounds are well known in the literature. The corresponding Raman modes were assigned according to the literature[1-5]. Raman spectra of exfoliated samples and of the samples after water splitting experiment match with that of the corresponding bulk samples. We did not observe any oxide peaks in these samples either after exfoliation or after water splitting suggesting that structural integrity of the compounds is maintained. For the $ZnPS_3$ sample, solid product could not be centrifuged out after water splitting.

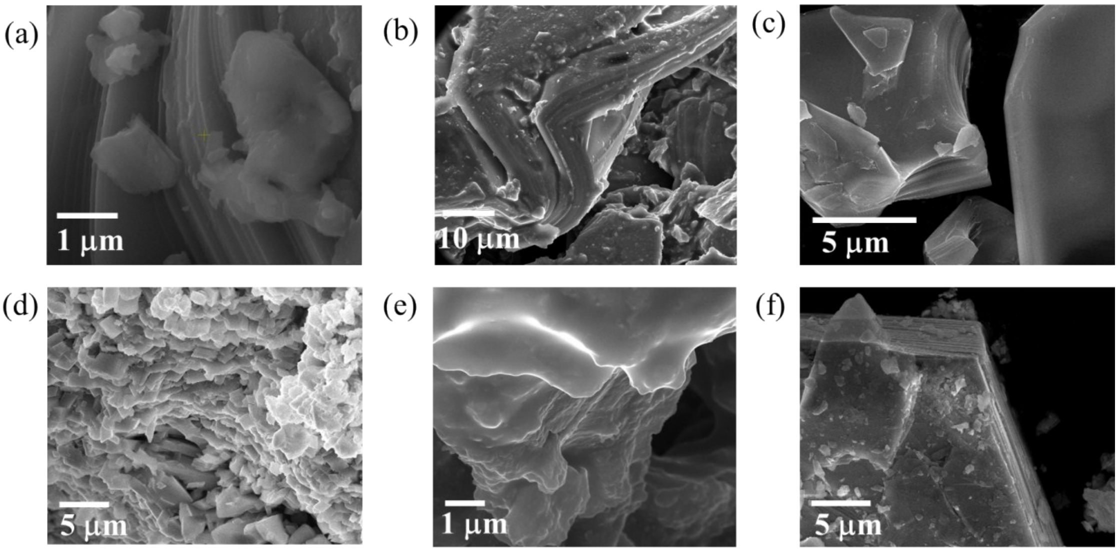

Figure S3: FESEM images of (a) $FePS_3$, (b) $ZnPS_3$, (c) $CdPS_3$, (d) $MnPS_3$, (e) $MnPSe_3$ and (f) $CdPSe_3$

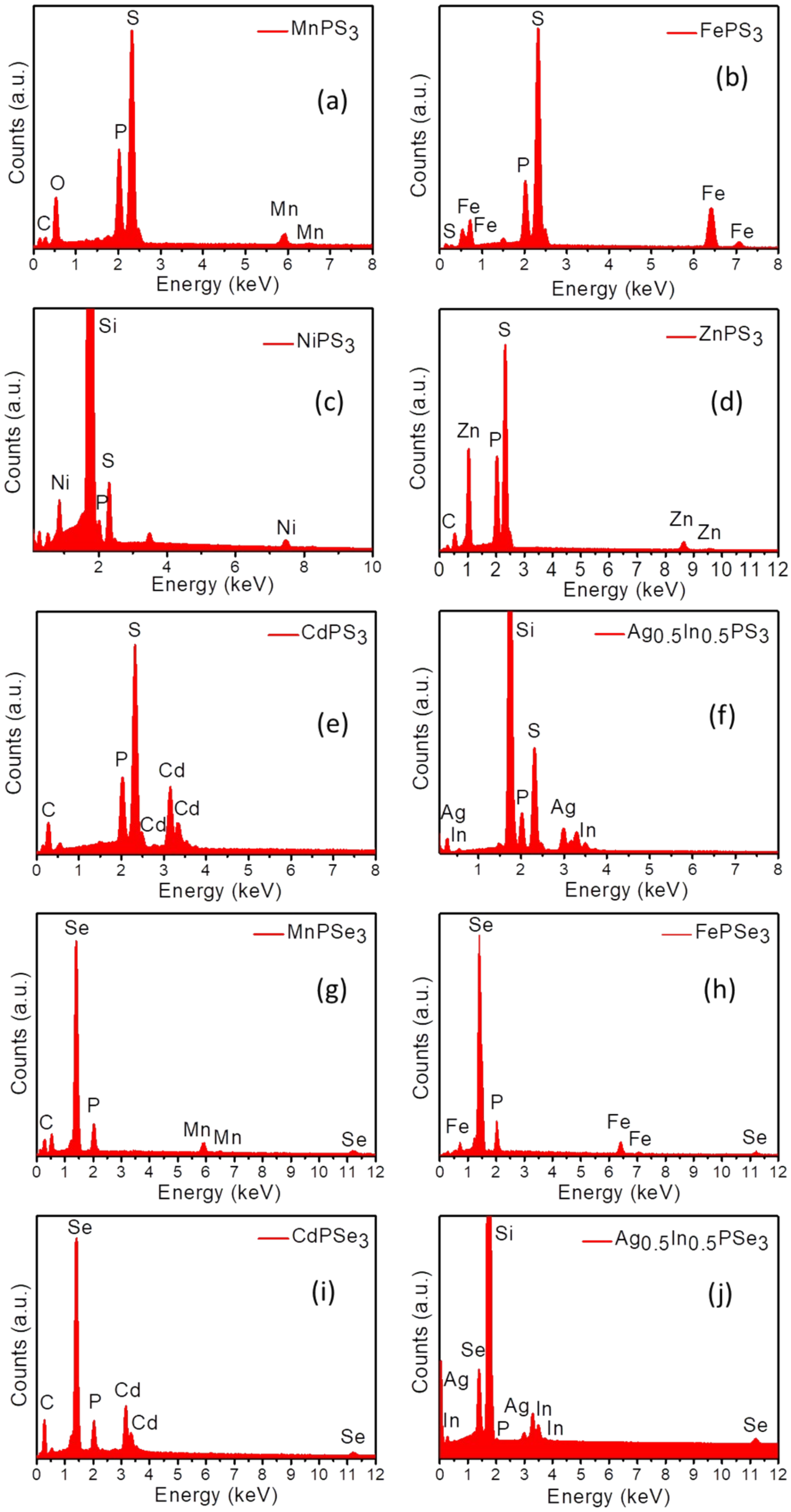

Figure S4: EDAX showing elemental composition of (a) $MnPS_3$, (b) $FePS_3$, (c) $NiPS_3$, (d) $ZnPS_3$, (e) $CdPS_3$, (f) $Ag_{0.5}In_{0.5}PS_3$, (g) $MnPSe_3$, (h) $FePSe_3$, (i) $CdPSe_3$ and (j) $Ag_{0.5}In_{0.5}PSe_3$.(EDAX of the samples were done by either putting sample on carbon tape or silicon substrate.)

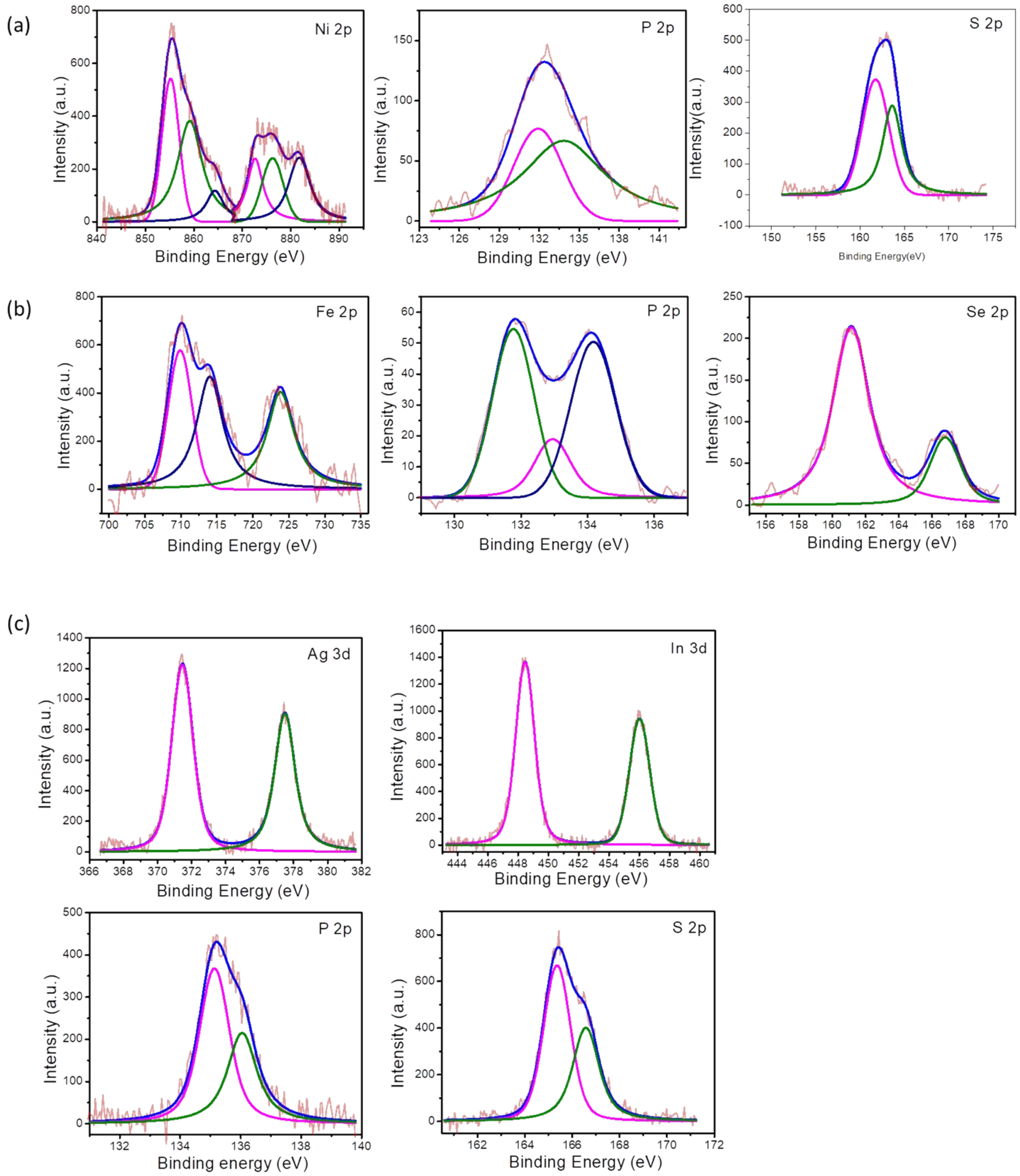

Figure S5: XPS spectra of (a) $NiPS_3$, (b) $FePSe_3$ and (c) $Ag_{0.5}In_{0.5}PS_3$

X-ray photoelectron spectroscopy was done for $NiPS_3$, $FePSe_3$ and $Ag_{0.5}In_{0.5}PS_3$ to study the bonding characteristics.

**$NiPS_3$**: The XPS spectra show the presence of peaks at binding energies of 855.1 and 872.7 eV corresponding to the 2p3/2 and 2p1/2 levels of $Ni^{2+}$in $NiPS_3$[9,10]. Whereas position of 2p3/2 peak for Ni (852)[6], $Ni_2P$ (853.1)[6], NiS (852.8)[7]and $NiS_2$ (853.6)[8] are absent which rules out the possibility of formation of other compounds. The peaks at binding energies of 859.3, 864.6, 876.2, and 881.7 eV are assigned as satellite 2p peaks of Ni. The region corresponding to the sulphur 2p3/2 and 2p1/2 levels (Figure S5a) shows peaks at binding energies of 161.8 and 163.6 eV, respectively, and the phosphorus 2p3/2 and 2p1/2 levels (Figure S5c) show peaks at binding energies of 132 and133.9, respectively[9, 10].

**$FePSe_3$:** The XPS spectra for Fe 2p region shows peaks at around 709.9 and 723.9 eV due to 2p3/2 and 2p1/2 levels of $Fe^{2+}$ accompanied by the satellite peak at 714.1 eV. Fe peaks in iron phosphides are at ~707[6] which riles out the possibility of the formation of iron phosphides. The peaks at 131.8 and 132.9 eV correspond to the 2p3/2 and 2p1/2 peaks for P respectively while there a peak at 134.2 suggests the presence of $P_4O_{10}$ states due to surface oxidation. Phosphorus peaks in iron phosphides should be at a lower binding energy of 129.5 eV ($Fe_2P$)[6], 129.4 eV ($Fe_3P$)[6],129.8eV ($FeP_2$)[6] which further confirms the absence of any phosphides in the system. The peaks for Se 3p3/2 and Se 3p1/2 levels are observed at ~161.2 and ~166.7 eV respectively[11,12].

**$Ag_{0.5}In_{0.5}PS_3$**: XPS spectra show peaks at binding energies 371.5 and 377.7 corresponding to the 3d5/2 and 3d3/2 levels of Ag. Peaks at binding energy 448.5 and 456 eV correspond to the 3d5/2 and 3d/3/2 levels of In. 3d5/2 level for Ag and In in their sulfides and phosphides are at lower binding energies for Ag (368.1 eV)[13], $Ag_2S$ (368.2 eV)[14], In (443.15 eV)[15] and InP (443.9eV)[16]. The region corresponding to the sulfur 2p3/2 and 2p1/2 levels shows peaks at binding energies of 166.6 and 167.8 eV, respectively, and the phosphorus 2p3/2 and 2p1/2 levels (Figure S5c) show peaks at binding energies of 136.3 and137.2, respectively.

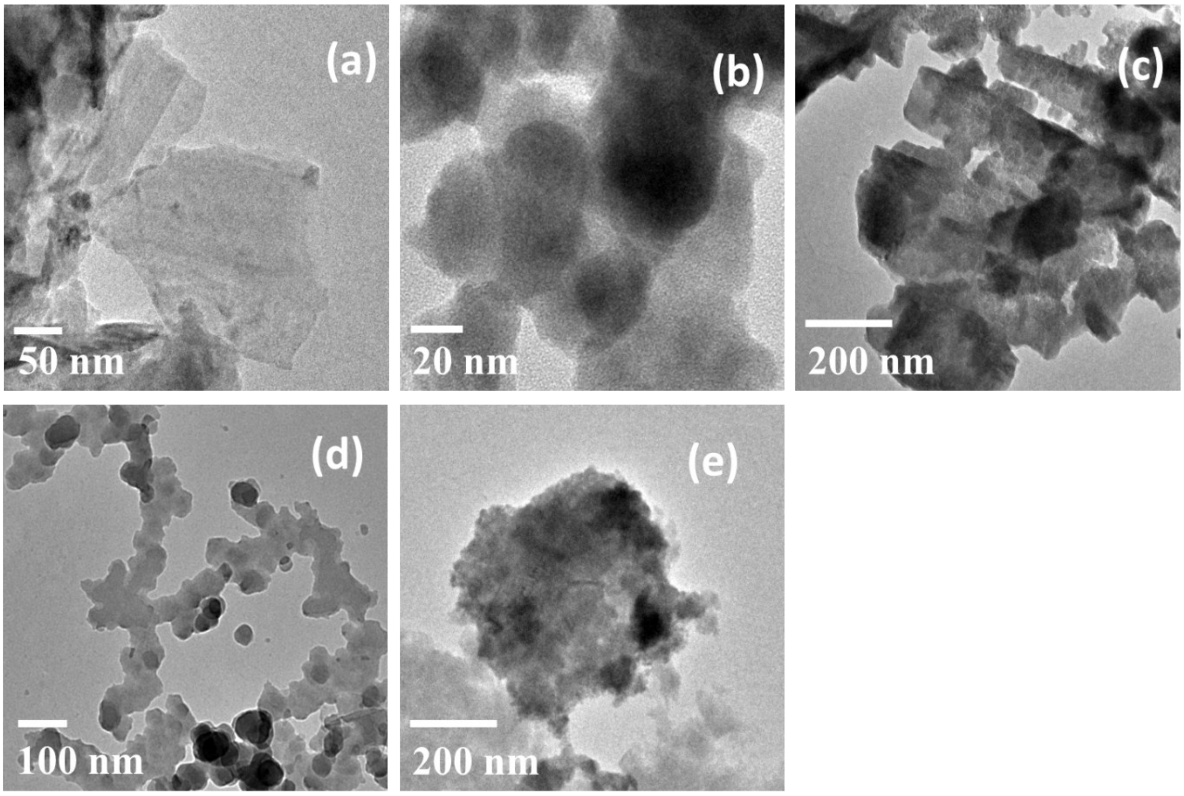

Figure S6: TEM images of (a) $MnPS_3$, (b) $FePS_3$, (c) $CdPS_3$, (d) $MnPSe_3$ and (e) $CdPSe_3$

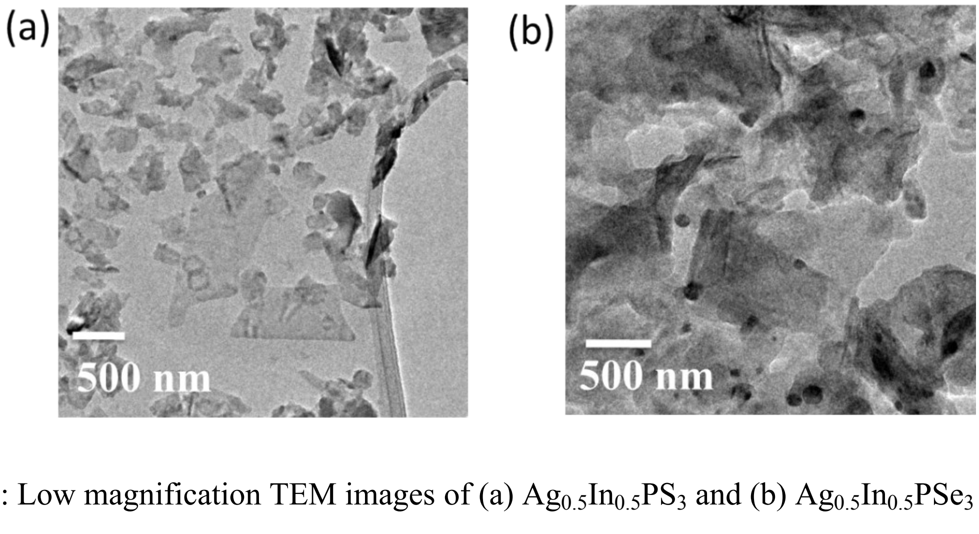

Figure S7: Low magnification TEM images of (a) $Ag_{0.5}In_{0.5}PS_3$ and (b) $Ag_{0.5}In_{0.5}PSe_3$

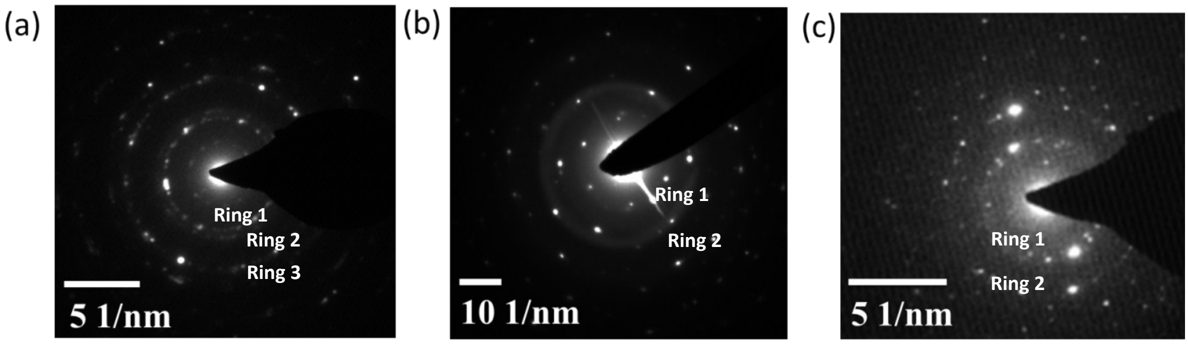

Figure S8: SAED patterns of (a) $NiPS_3$, (b) $FePSe_3$ and (c) $Ag_{0.5}In_{0.5}PS_3$

From the XRD data of a compound, we can find the corresponding d values of the peaks with the help of $2d\sin\theta = \lambda$. d spacing values can also be calculated from the corresponding SAED patterns. Corresponding (hkl) values from d spacing values are assigned using PDF numbers (Table S3).

**$NiPS_3$**

From PXRD

| $2\theta$ | d (Å)= $\lambda/(2\sin\theta)$ | (hkl) |
|---|---|---|
| 14.223 | 6.22 | (001) |
| 28.385 | 3.14 | (002) |
| 31.307 | 2.85 | (130), $(20\bar{1})$ |
| 36.372 | 2.46 | (131), $(20\bar{2})$ |
| 49.705 | 1.83 | $(13\bar{3})$, (202) |
| 54.804 | 1.67 | (060), $(33\bar{1})$ |
| 58.402 | 1.58 | (004) |

The ring with bright spots SAED pattern of any material tells us that the material is polycrystalline in nature. From the radius of these rings we can calculate the d values and hence correlate with the XRD data. The distance between two diagonally placed bright spots is the diameter of the ring (2R 1/nm). Half of this distance is the radius of the ring (R 1/nm). Reciprocal of this radius gives the corresponding d spacing of the ring (d = 1/R nm). We can correlate this d spacing value with the values obtained from the XRD data as shown in the table, and hence assign the (hkl) values.

From SAED

| Ring no. | 2R (1/nm) | R (1/nm) | d (Å) | Possible (hkl) values |
|---|---|---|---|---|
| 1 | 7 | 3.5 | 2.85 | (130), $(20\bar{1})$ |
| 2 | 8 | 4.1 | 2.4 | (131), $(20\bar{2})$ |

| | | | | |
|---|---|---|---|---|
| 3 | 12 | 6 | 1.66 | $(13\bar{3})$, (202) |

**$FePSe_3$**

From PXRD

| 2θ | d (Å) = λ/2sinθ | (hkl) |
|---|---|---|
| 13.6 | 6.5 | (003) |
| 27.16 | 3.28 | (006) |
| 31.78 | 2.8 | (113) |
| 39.82 | 2.26 | (116) |
| 50.82 | 1.8 | (119) |
| 55.78 | 1.65 | (00 12) |
| 58.26 | 1.58 | (036) |
| 60.92 | 1.52 | (223) |
| 63.88 | 1.46 | (11 12) |
| 74.42 | 1.27 | (229) |
| 78.7 | 1.21 | (11 15) |

From SAED

| Ring no. | 2R (1/nm) | R (1/nm) | d (Å) | Possible (hkl) values |
|---|---|---|---|---|
| 1 | 7.2 | 3.6 | 2.8 | (113) |
| 2 | 12 | 6 | 1.66 | (00 12) |

**$Ag_{0.5}In_{0.5}PS_3$**

From PXRD

| 2θ | d (Å) = λ/2sinθ | (hkl) |
|---|---|---|
| 13.84 | 6.4 | (002) |
| 26.68 | 3.34 | (103) |
| 32.46 | 2.75 | (112) |
| 38.76 | 2.32 | (105) |
| 40.46 | 2.22 | (114) |
| 41.94 | 2.15 | (006) |
| 45.42 | 1.99 | (210) |
| 51.76 | 1.76 | (116) |
| 56.96 | 1.61 | (008) |
| 59.78 | 1.545 | (220) |
| 60.76 | 1.52 | (222) |

From SAED

| Ring no. | 2R (1/nm) | R (1/nm) | d (Å) | Possible (hkl) values |
|---|---|---|---|---|
| 1 | 6 | 3 | 3.33 | (103) |
| 2 | 9.797 | 4.89 | 2.03 | (210) |

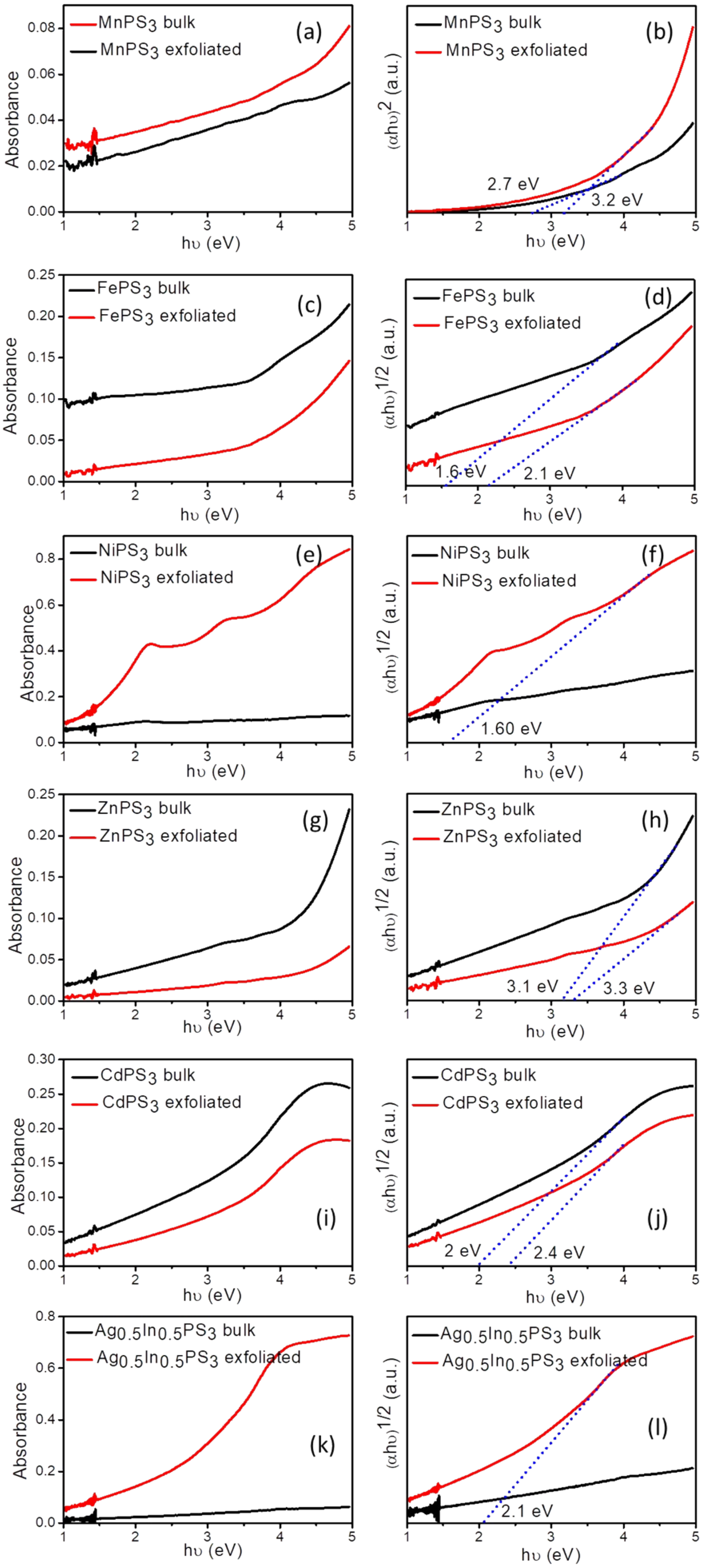
(a)
MnPS3 bulk
MnPS3 exfoliated
Absorbance
0.00
0.02
0.04
0.06
0.08
hυ (eV)
1
2
3
4
5
(b)
MnPS3 bulk
MnPS3 exfoliated
(αhυ)2 (a.u.)
2.7 eV
3.2 eV
hυ (eV)
(c)
FePS3 bulk
FePS3 exfoliated
Absorbance
0.00
0.05
0.10
0.15
0.20
0.25
hυ (eV)
(d)
FePS3 bulk
FePS3 exfoliated
(αhυ)1/2 (a.u.)
1.6 eV
2.1 eV
hυ (eV)
(e)
NiPS3 bulk
NiPS3 exfoliated
Absorbance
0.0
0.2
0.4
0.6
0.8
hυ (eV)
(f)
NiPS3 bulk
NiPS3 exfoliated
(αhυ)1/2 (a.u.)
1.60 eV
hυ (eV)
(g)
ZnPS3 bulk
ZnPS3 exfoliated
Absorbance
0.00
0.05
0.10
0.15
0.20
0.25
hυ (eV)
(h)
ZnPS3 bulk
ZnPS3 exfoliated
(αhυ)1/2 (a.u.)
3.1 eV
3.3 eV
hυ (eV)
(i)
CdPS3 bulk
CdPS3 exfoliated
Absorbance
0.00
0.05
0.10
0.15
0.20
0.25
0.30
hυ (eV)
(j)
CdPS3 bulk
CdPS3 exfoliated
(αhυ)1/2 (a.u.)
2 eV
2.4 eV
hυ (eV)
(k)
Ag0.5In0.5PS3 bulk
Ag0.5In0.5PS3 exfoliated
Absorbance
0.0
0.2
0.4
0.6
0.8
hυ (eV)
(l)
Ag0.5In0.5PS3 bulk
Ag0.5In0.5PS3 exfoliated
(αhυ)1/2 (a.u.)
2.1 eV
hυ (eV)

Figure S9: Absorption spectra and the corresponding Tauc plots of (a-b) $MnPS_3$, (c-d) $FePS_3$, (e-f) $NiPS_3$, (g-h) $ZnPS_3$, (i-j) $CdPS_3$, (k-l) $Ag_{0.5}In_{0.5}PS_3$

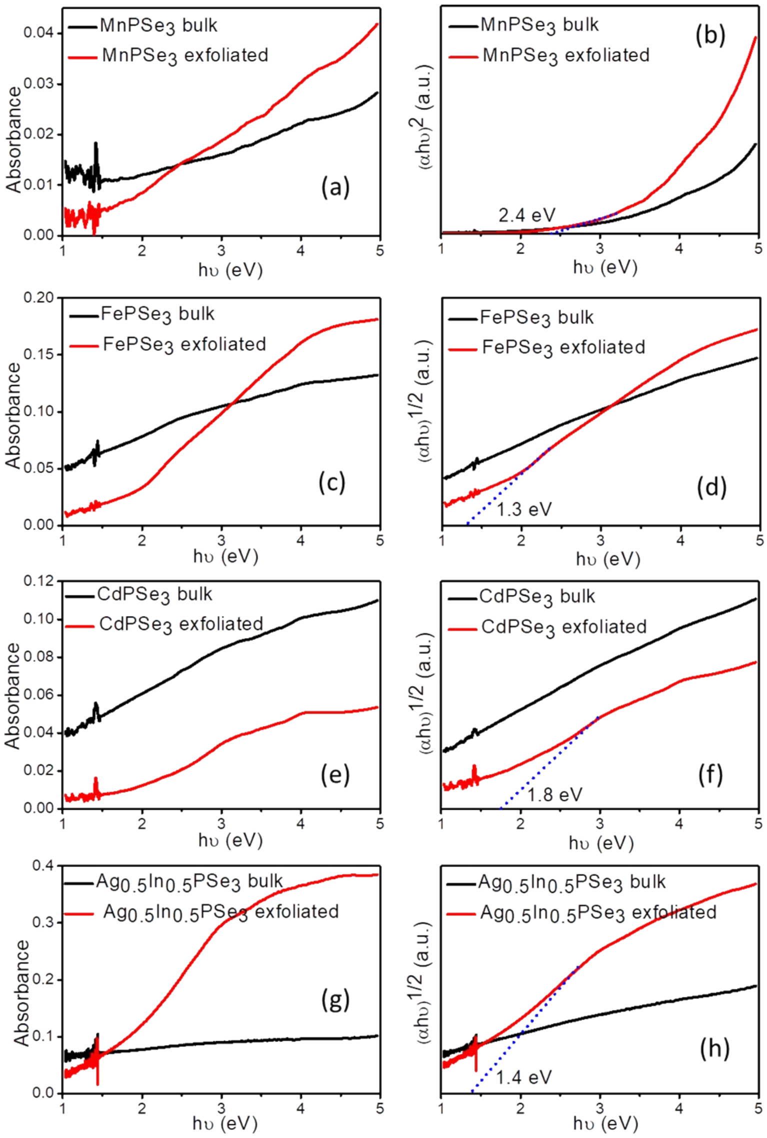

Figure S10: Absorption spectra and the corresponding Tauc plots of (a-b) $MnPSe_3$, (c-d) $FePSe_3$, (e-f) $CdPS_3$, (g-h) $Ag_{0.5}In_{0.5}PSe_3$

Absorption spectra of the bulk and exfoliated samples were calculated using very dilute solutions. The mathematical relation between absorbance (A) and absorption coefficient (α) is given by Lambert-Beer law, according to which

$$A = \alpha c l \quad (1)$$

where c = concentration of solution , l= path length

From the absorption spectra, we calculated the $\alpha$ values using equation (1)

The band gap energy between valence band and conduction band for an allowed transition is given by Tauc equation as:

$$(\alpha h\nu)^{1/n} = B\,(h\nu - E_g) \qquad (2)$$

where $h\nu$ = incident photon energy, $E_g$ = band gap, n, B = constants

For direct transitions, n= ½ for indirect transitions n=2

On plotting $(\alpha h\nu)^{1/n}$ vs $h\nu$, $E_g$ is determined by extrapolating a tangent to $\alpha h\nu = 0$ from the point of inflection.

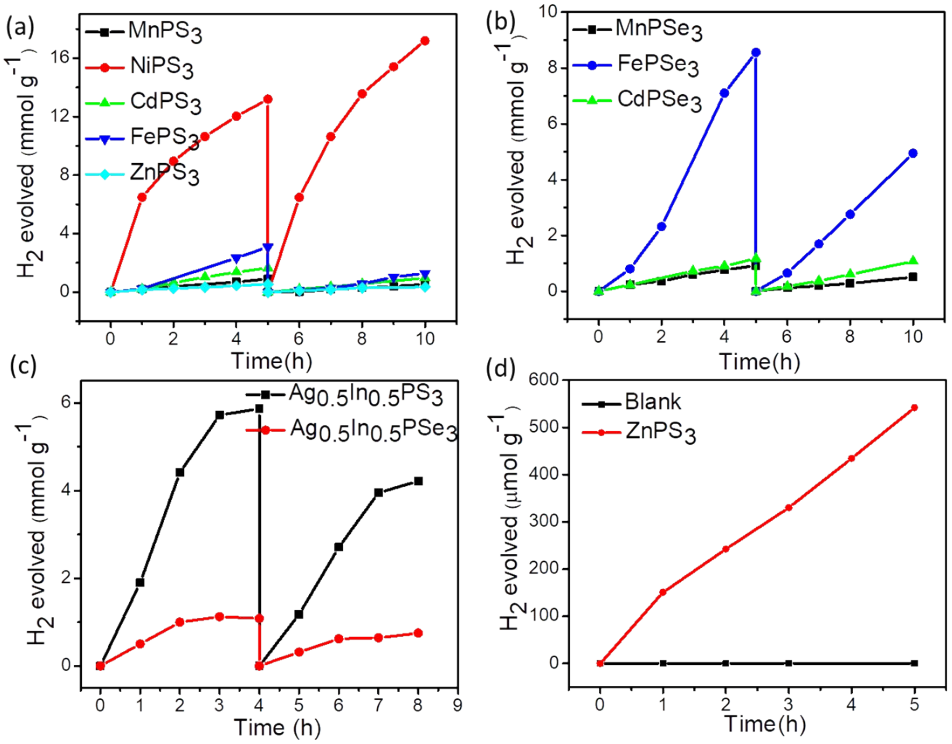

Figure S11: (a-c) HER cycling studies for $MPX_3$ compounds, (d) HER blank reaction

For cycling studies the reaction was stopped at 5 hours. The vessel was then purged with inert gas, photosensitizer was added and irradiation was continued.

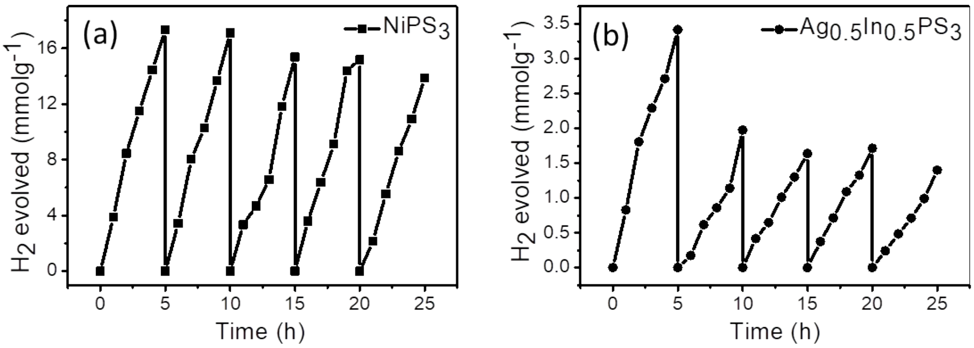

Figure S12: Prolonged HER cycling studies for (a) $NiPS_3$ and (b) $Ag_{0.5}In_{0.5}PS_3$

Table S1: Band gaps of the synthesized $MPX_3$ compounds

| **Compounds** | **Band gap (eV)** |
|---|---|
| $MnPS_3$ | 3.2 |
| $FePS_3$ | 2.1 |
| $NiPS_3$ | 1.6 |
| $ZnPS_3$ | 3.3 |
| $CdPS_3$ | 2.4 |
| $MnPSe_3$ | 2.4 |
| $FePSe_3$ | 1.3 |
| $CdPSe_3$ | 1.8 |
| $Ag_{0.5}In_{0.5}PS_3$ | 2.1 |
| $Ag_{0.5}In_{0.5}PSe_3$ | 1.4 |

Table S2: Photocatalytic HER activities of the synthesized $MPX_3$ compounds

| **Compounds** | **$H_2$ yields (mmol $h^{-1}g^{-1}$)** |
|---|---|
| $MnPS_3$ | 0.2 |
| $FePS_3$ | 0.6 |
| $NiPS_3$ | 2.6 |
| $ZnPS_3$ | 0.1 |
| $CdPS_3$ | 0.3 |
| $MnPSe_3$ | 0.2 |
| $FePSe_3$ | 1.7 |
| $CdPSe_3$ | 0.2 |
| $Ag_{0.5}In_{0.5}PS_3$ | 1.9 |
| $Ag_{0.5}In_{0.5}PSe_3$ | 0.5 |

Table S3: Reference PDF numbers used for matching the PXRD patterns

| **Material** | **PDF number** |
|---|---|
| $MnPS_3$ | 33-903 |
| $FePS_3$ | 33-672 |
| $NiPS_3$ | 33-952 |
| $ZnPS_3$ | 84-996 |
| $CdPS_3$ | 83-466 |
| $Ag_{0.5}In_{0.5}PS_3$ | 39-517 |
| $FePSe_3$ | 33-671 |
| $MnPSe_3$ | 89-264 |
| $CdPSe_3$ | 34-5 |
| $Ag_{0.5}In_{0.5}PSe_3$ | 81-614 |

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