Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Effect of Mn^{2+} Substitution on the Structure, Properties and HER activity of Cadmium Phosphochlorides

Anand Roy[a], Anjali Singh[a], S. Assa Aravindh[a], Swaraj Servottam[a], Umesh V. Waghmare[a],

and C. N. R. Rao[a]*

[a]New Chemistry Unit, Sheikh Saqr Laboratory, School of Advance materials and Theoretical Science Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, P.O., 560064, Bangalore, India.

Materials

All the materials used in the synthesis were bought from Sigma-Aldrich and used as it is without further purification.

Supporting Figures and Discussion

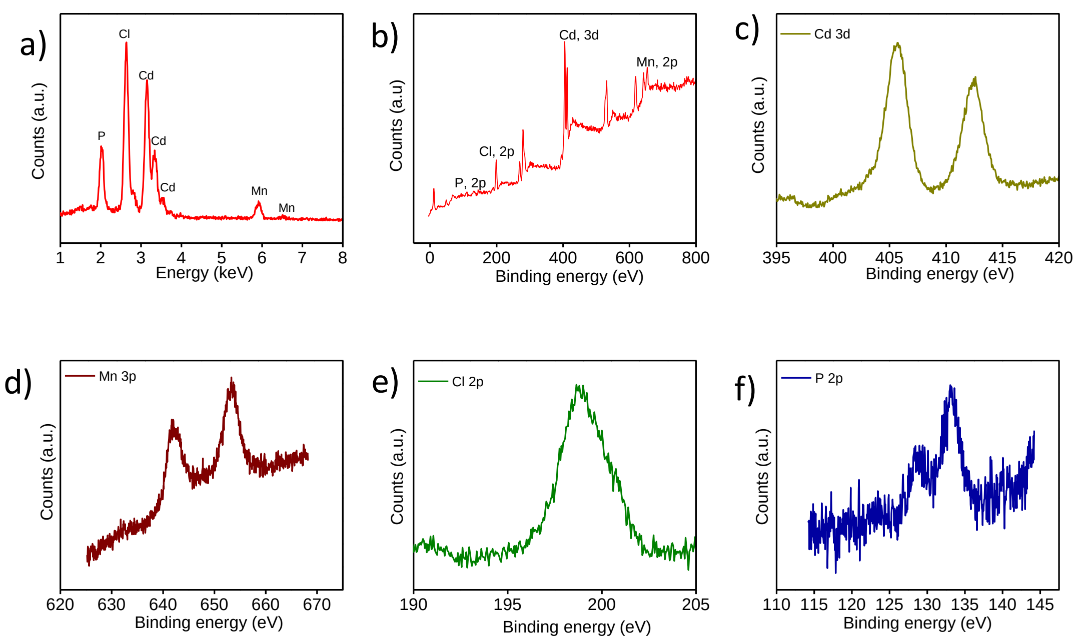

Figure S1. a) EDAX and b) XPS-survey scan spectrum of $Cd_{5.8}Mn_{1.2}P_4Cl_6$, c) to f) core-level spectra of Cd, Mn, Cl, and P.

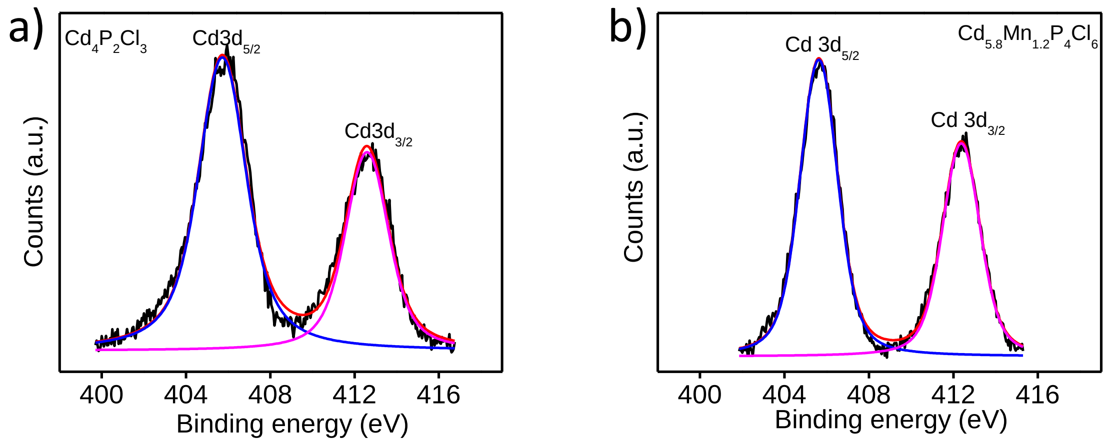

Figure S2. High resolution core-level spectra of Cd-atoms in a) $Cd_4P_2Cl_3$ and b) $Cd_{5.8}Mn_{1.2}P_4Cl_6$ compounds.

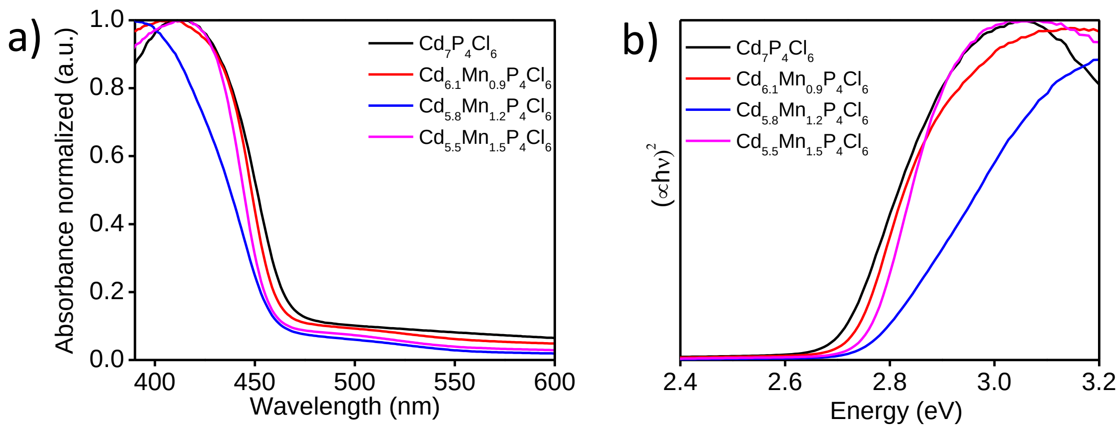

Figure S3. a) Diffuse UV/Vis absorption spectra and b) Tauc plot of pristine and $Cd_{7-y}Mn_yP_4Cl_6$ compounds.

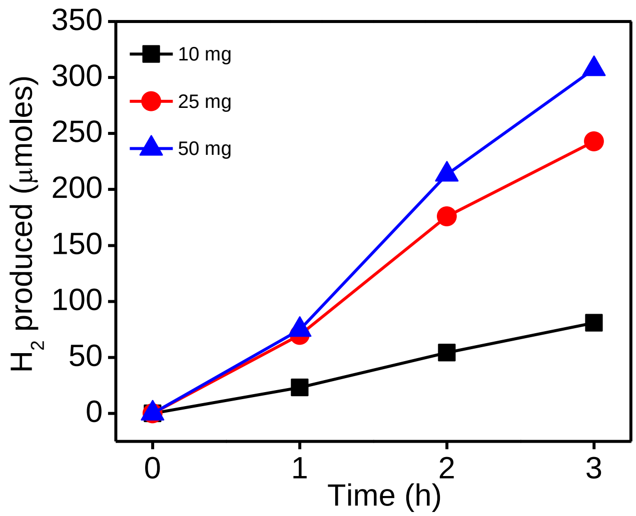

Figure S4. Optimization of the weight of photocatalyst for H_2 generation reaction.

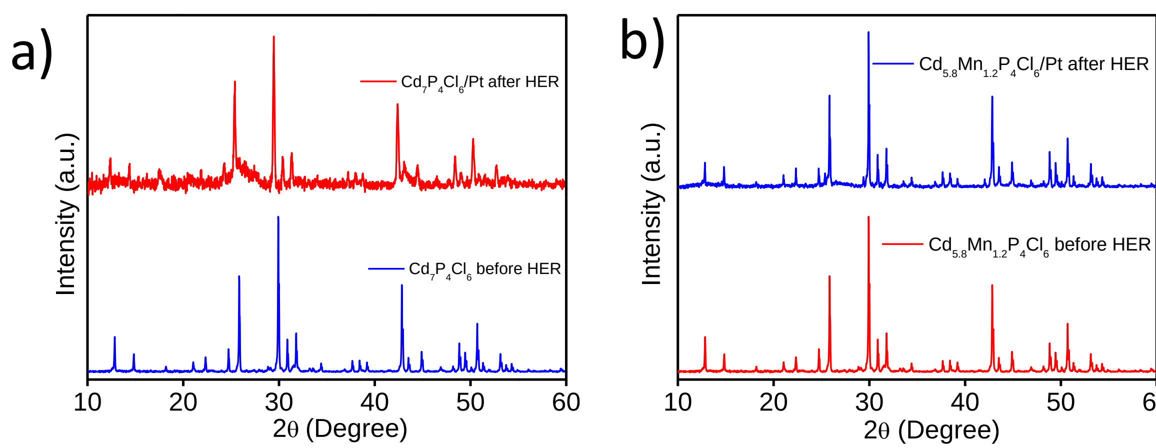

Figure S5. PXRD patterns of a) Pristine $Cd_7P_4Cl_6$ and b) $Cd_{5.8}Mn_{1.2}P_4Cl_6$, after their use in multiple cycles hydrogen evolution reaction.

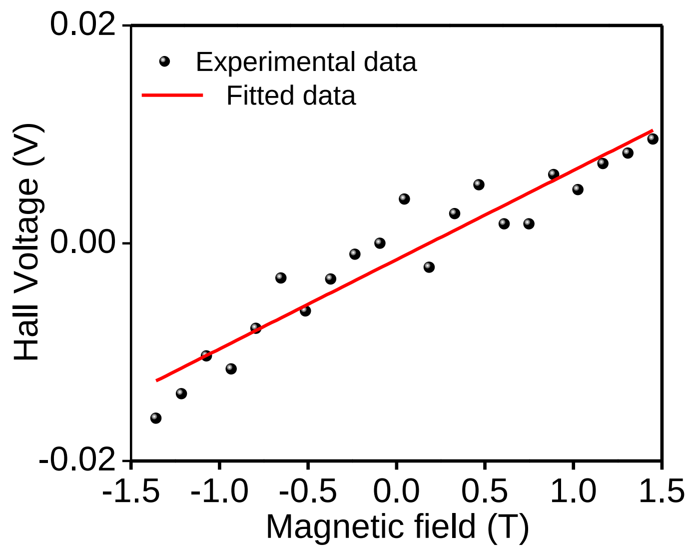

Figure S6. Variation of Hall voltage with applied magnetic field in $Cd_{5.8}Mn_{1.2}P_4Cl_6$. Positive slope confirms p-type conductivity of sample.

Apparent quantum yield calculation

The apparent quantum yield has been calculated considering the entire number of incident photons used in the photochemical reaction (entire spectrum in which photocatalyst is active). Photon flux (number of photons entering the reaction cell) was calculated using the irradiance meter (New Port) please see **Figure S6.**

For $Cd_{5.8}Mn_{1.2}P_4Cl_6$; Band gap ~2.62 eV, corresponding to the absorption edge wavelength of 472 nm. The number of incident photons were calculated integrating photons available from 395 nm (λ >395 nm, UV cut-off filter used to allow only visible-light photons) to 472 nm (absorption edge or cut-off wavelength of $Cd_{5.8}Mn_{1.2}P_4Cl_6$ beyond which there will not be any absorption). From the lamp spectra number of photons

Number of photons entering cylindrical sample cell (diameter = 4.5 cm) = $\int_{395}^{472} F d\lambda$= 1.7359×10^{17} photons/second

HER activity of $Cd_{5.8}Mn_{1.2}P_4Cl_6$ = 247.8 μmol/h = $0.413X10^{17}$ H_2/second

$$AQY\ (\%) = 2 \times \frac{Number\ of\ evolved\ hydrogen}{Number\ of\ incident\ photons} \times 100 = 2 \times \frac{0.413\times10^{\wedge}17}{1.735\times10^{\wedge}17} \times 100 = 47.60\ \%$$

Similarly, the quantum yield for pristine $Cd_7P_4Cl_6$ and $Cd_4P_2Cl_3$ compounds were calculated.

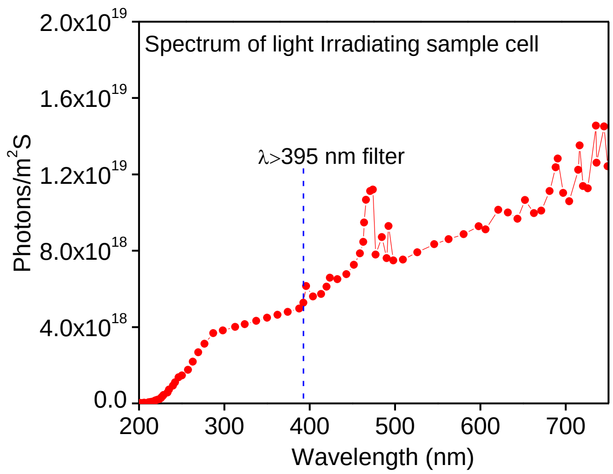

Figure S7. The spectrum of light-source used for the hydrogen evolution reaction.

Table S1: Comparative rate of photocatalytic hydrogen evolution reaction (HER) of photocatalysts.

Photocatalyst	Reaction condition	HER activity (μmol/h)	Reference
CdS-commercial	Na_2S-Na_2SO_3; Visible light	1.04	1[1]
CdS-nanoparticles	Na_2S-Na_2SO_3; Visible light	4.69	1
TiO_2	Na_2S-Na_2SO_3; Visible light	0.59	1
$Cd_{6.1}Mn_{0.9}P_4Cl_6$	Na_2S-Na_2SO_3; Visible light	42.5	Present work
$Cd_{5.8}Mn_{1.2}P_4Cl_6$	Na_2S-Na_2SO_3; Visible light	52.1	Present work
$Cd_{5.5}Mn_{1.5}P_4Cl_6$	Na_2S-Na_2SO_3; Visible light	58.8	Present work
$Cd_{5.8}Mn_{1.2}P_4Cl_6$/Pt	Na_2S-Na_2SO_3; Visible light	247.8	Present work

References

1.A. Roy, A. Singh, S. A. Aravindh, S. Servottam, U. V. Waghmare and C. N. R. Rao, *Angew. Chem. Int. Ed.*, 2019, **58**, 6926-6931.