Electronic Supplementary Information

[A] XRD studies of different concentration of PVP and DEA assisted $ZnIn_2S_4$ samples.

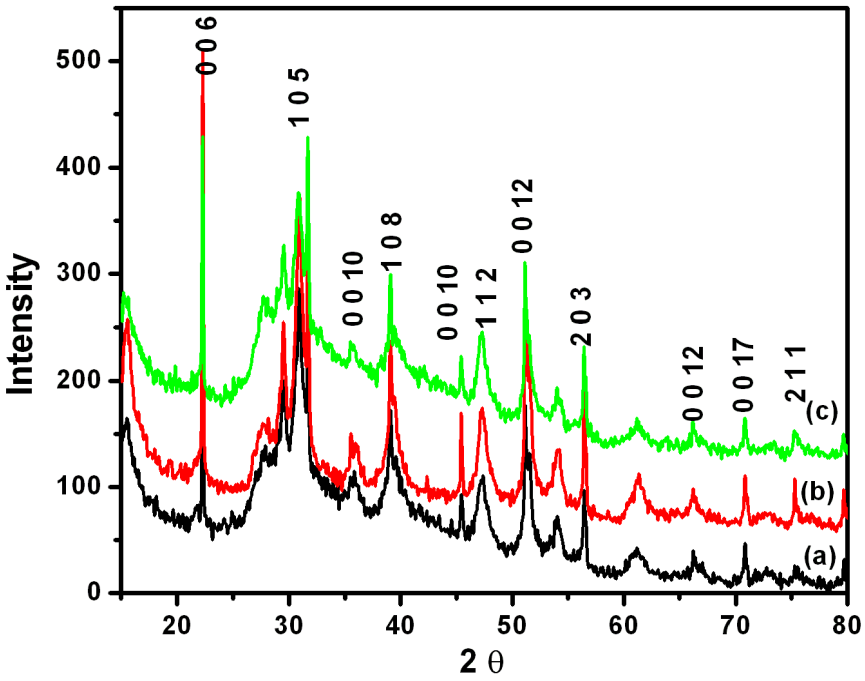

Fig. SI-1 XRD of the samples synthesized for 30h using (a) 100(b) 200 & (c) 300 ppm PVP.

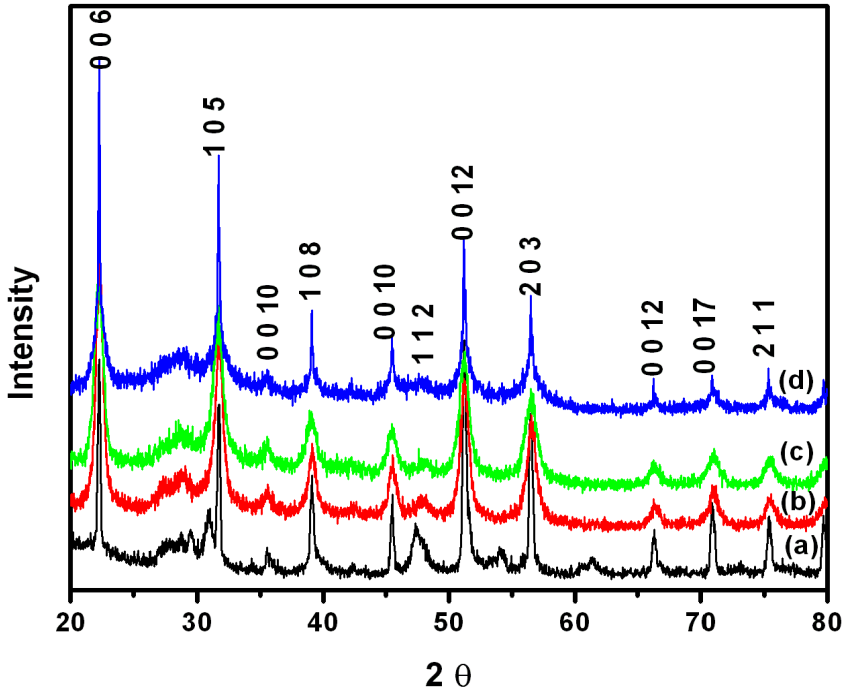

Fig. SI-2 XRD of the samples synthesized for 30 h using (a) 0.005 (b) 0.01, (c) 0.015 and (d) 0.02 mol DEA.

[B] FESEM images of different concentration of PVP assisted $ZnIn_2S_4$ sample.

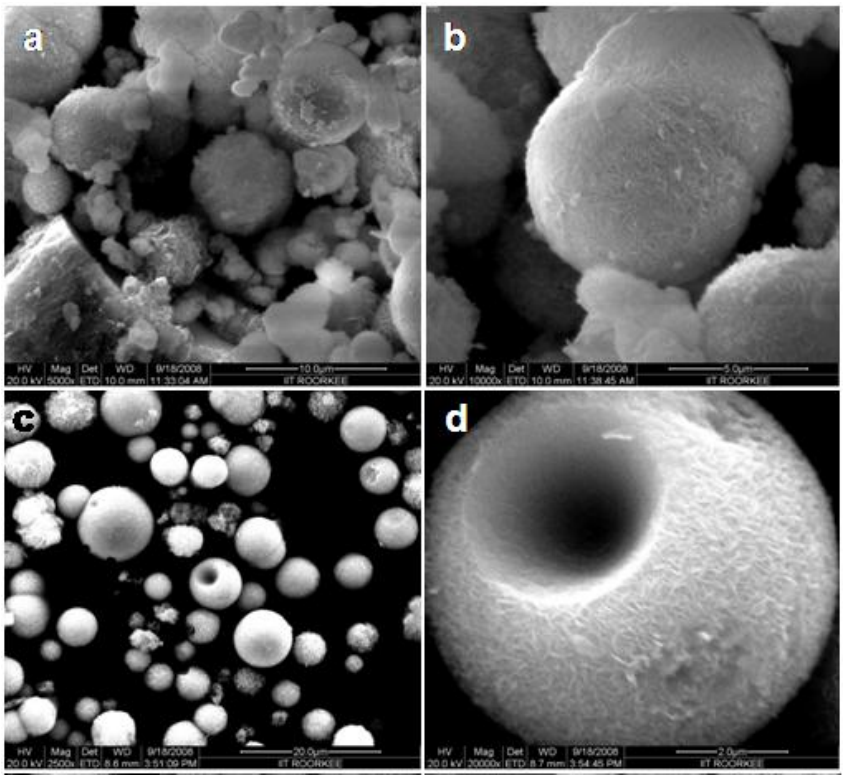

Fig. SI-3: FESEM images of the samples synthesized using (a-b) 100 and (c-d) 200 ppm PVP as a capping agent.

Table SI-1 Surface area study of the samples S1, S2 and S3.

Sample Name	Surface Area $m^2 g^{-1}$
S1	40
S2	55
S3	21

[C] BET surface area and pore width size distribution.

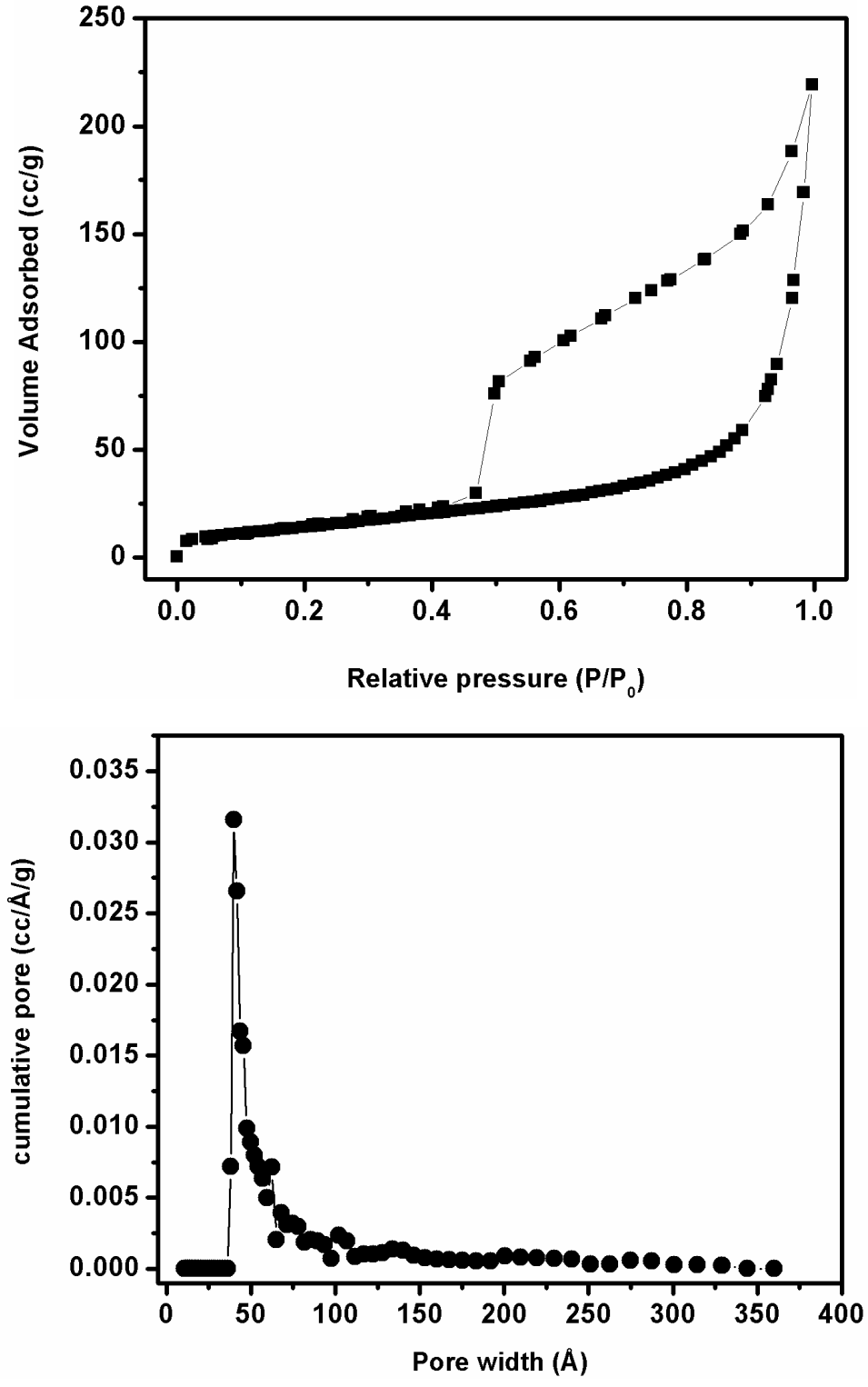

Fig. SI-4 BET surface area (A) and pore width size distribution (B) of sample S2 (hollow marigold).

[D] Error bar of the hydrogen evolution rate for all samples

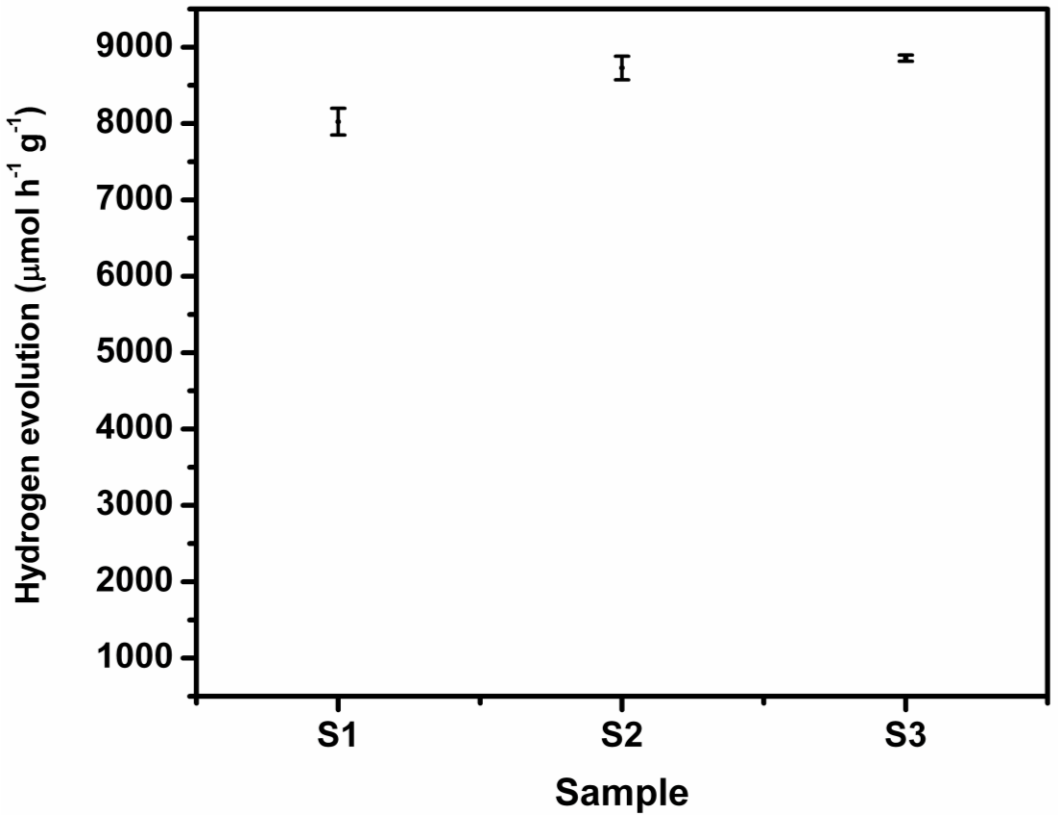

Fig. SI-5 Error bar of the hydrogen evolution of samples S1, S2 and S3.

[E] Photocatalytic mechanism:

The sample S1 showed less photocatalytic activity in comparison to sample S2 and S3, this may due to the compactness of flowers with absence of hollow cavity. Such dense petals are arranged in a compact flower structures which affects on charge separation and migration of photogenerated carriers, which is generally depend on crystallinity rather than the surface area.[11, 25] Additionally, the size of the solid (S1) and hollow (S2) flowers are much higher than the rosy flowers (S3). So, the larger size also play role to getting slightly lower activity in case of hollow marigold flowers. Thus, overall $ZnIn_2S_4$ nanostructures with optimize size, shape and crystalline nature gives a significant photocatalytic efficiency.

Table SI-2 Photocatalytic activity of $ZnIn_2S_4$ for H_2 evolution.

Sample	S1	S2	S3
H_2 ($\mu mol\ h^{-1}g^{-1}$)	8022	8682	8818

The H_2S splitting under the visible light is takes place as follows.

In 0.25 M KOH solution with a pH of 12.5, the weak diprotic acid H_2S (two pKa values are 7.0 and 11.96) dissociates and maintains equilibrium with hydrosulfide HS^- ions (R7). The $ZnIn_2S_4$ absorbs light and generates electron-hole pairs (R8). The photogenerated valence band hole (h^+_{VB}) upon band gap excitation of powder $ZnIn_2S_4$ oxidizes the HS^- ion to disulfide ion (S_2^{2-}), liberating a proton from the HS^- ion (R9). The conduction band electron (e^-_{CB}) from $ZnIn_2S_4$ photocatalyst reduces protons to produce molecular hydrogen (R10).

$H_2S + OH^- \leftrightarrow HS^- + H_2O$ (R7)

Semiconductor $ZnIn_2S_4 \leftrightarrow h^+_{VB} + e^-_{CB}$ (R8)

Oxidation reaction: $2HS^- + 2h^+_{VB} \leftrightarrow S_2^{2-} + 2H^+$ (R9)

Reduction reaction: $2H^+ + 2e^-_{CB} \leftrightarrow H_2$ (R10)

The efficiency of our photocatalyst was confirmed by the experiment which showed that in absence of photocatalyst as well as in dark condition, no evolution of hydrogen gas was observed from 0.25 M KOH solution flushed with H_2S gas under the visible light irradiation. Overall the photocatalytic activity has been enhanced due to the unique rose and hollow marigold flower like morphology.