Chapter 3

Hierarchical nanostructured ZnIn$_2$S$_4$ for an efficient hydrogen production

3.1 Introduction:

The ternary chalcogenides $AB_mC_n$ (A) Cu, Ag, Zn, Cd, etc.; B) Al, Ga, In; C) S, Se, Te; $m$, $n$: Arabic numerals) have been extensively studied because of their unique optoelectronic and catalytic properties [1-6]. Recently, multi-component metal sulfides have been reported to be more stable and show enhanced photocatalytic activity under visible light irradiation. Very recently, our group reported nanostructured CdIn$_2$S$_4$ and CdLa$_2$S$_4$ for hydrogen generation and/or organic dyes degradation [1, 7-9]. However, these materials comprise cadmium, which is one of the most toxic elements and directly affects human neuron system. In view of this the development of an ecofriendly ternary system has immense importance.

As ZnS is a wide band gap semiconductor and it is well-known for good photocatalytic activity under UV light. In this context, ZnIn$_2$S$_4$ has immense importance as a stable visible light photocatalyst. ZnIn$_2$S$_4$ is the only semiconducting material with a layered structure in the $AB_2X_4$ family which has attracted considerable attention because of its outstanding electrical and optical properties [10]. Its band gap is well within the visible region with substantial chemical stability [11]. Recently, various morphologies of ZnIn$_2$S$_4$ have been obtained by different methods and using surfactants, and have been used as a photocatalysts [10-14]. Despite its good utility, very limited literature has been reported. The fabrication of hierarchical nanostructures using different precursors and surfactants has a significant role in the field of catalysis. Hence, it is very essential to investigate new photocatalysts with the architecture of their hierarchical nanostructures.

The present chapter elucidates architecture of ZnIn$_2$S$_4$ hierarchical nanostructures using different capping agents such as polyvinylpyrrolidone (PVP), Triethylamine (TEA), Diethylamine (DEA) and Cetyltrimethylammoniumbromide (CTAB) by a simple hydrothermal method. Furthermore, the influence of capping agents on the morphologies and optical properties has been discussed. The photocatalytic hydrogen...
productions from ZnIn$_2$S$_4$ are discussed in detail. The hierarchical nanostructures have been used as a photocatalysts for hydrogen production under visible light irradiation. The morphological effect on hydrogen production has been discussed in detail.

3.2 Experimental:

3.2.1 Optimization of controlled synthesis of ZnIn$_2$S$_4$ nanostructures:

In the present studies, various set of experiments have been performed for controlled synthesis of ZnIn$_2$S$_4$ phase via hydrothermal method. Initially, the precursor’s concentration and the reaction duration are varied to optimize the appropriate crystalline phase of ZnIn$_2$S$_4$. All the chemicals are of analytical grade and used without further purification. The zinc nitrate hexahydrate [Zn(NO$_3$)$_2$.6H$_2$O], indium nitrate [In(NO$_3$)$_3$.5H$_2$O] (prepared using indium metal dissolved in nitric acid), and thiourea ((NH$_2$)$_2$CS) are used as a Zn, In and S precursor’s, respectively.

In the typical synthesis of samples S1-S5, 5 mmol Zn(NO$_3$)$_2$.6H$_2$O, 10 mmol In(NO$_3$)$_3$.5H$_2$O and a double excess of (NH$_2$)$_2$CS i.e. 40 mmol were dissolved in 150 mL distilled water. The clear solution was then transferred into 200 mL Teflon-lined autoclave. The autoclave was sealed and kept at 150°C for different reaction period such as 4, 8, 16, 24 and 30 h. Then the reactor is allowed to cool at room temperature naturally. The precipitate was filtered, washed with distilled water several times and finally by absolute ethanol. The prepared sample was dried at 60°C. Detailed experimental parameters for the synthesis of ZnIn$_2$S$_4$ nanostructures are depicted in Table 3.1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Zn:In:S ratio in mmol</th>
<th>Reaction time (hrs)</th>
<th>Phase formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>5:10:40</td>
<td>4</td>
<td>No</td>
</tr>
<tr>
<td>S2</td>
<td>5:10:40</td>
<td>8</td>
<td>No</td>
</tr>
<tr>
<td>S3</td>
<td>5:10:40</td>
<td>16</td>
<td>Partial</td>
</tr>
<tr>
<td>S4</td>
<td>5:10:40</td>
<td>24</td>
<td>Yes</td>
</tr>
<tr>
<td>S5</td>
<td>5:10:40</td>
<td>30</td>
<td>Yes</td>
</tr>
<tr>
<td>S6</td>
<td>1:2:8</td>
<td>30</td>
<td>Yes</td>
</tr>
<tr>
<td>S7</td>
<td>10:20:80</td>
<td>30</td>
<td>Yes</td>
</tr>
</tbody>
</table>
In order to reveal the influence of reaction time on phase formation and resultant morphology, the identical sets of experiments were performed at different time i.e. 4, 8, 16, 24 and 30 h.

XRD patterns of ZnIn$_2$S$_4$ synthesized for different time intervals at 150$^\circ$C were recorded. It was observed that, the complete phase formation was observed beyond 16h. Typically, 8h reaction (S2) shows the formation of only In$_2$S$_3$ which was confirmed from XRD and EDAX (Fig. 3.1A-B).

![XRD pattern of S2 (8 h) and corresponding EDAX pattern (B).](image)

Fig. 3.1(A) XRD pattern of S2 (8 h) and corresponding EDAX pattern (B).

During optimization, it was observed that, there is a partial formation of ZnIn$_2$S$_4$ at 16 h and complete formation at 24 h with low crystallinity (Fig. 3.2a). However, highly crystalline phase of hexagonal ZnIn$_2$S$_4$ (ICSD-JCPDS card No.01-072-0773) was observed at 30 h (Fig. 3.2c).

Although, the XRD pattern of the S3 (at 150$^\circ$C for 16 h) shows few characteristic peaks with low intensity which are attributed to the hexagonal phase of ZnIn$_2$S$_4$ (ICSD-JCPDS card No.01-072-0773), but the complete phase formation is yet to occur (Fig. 3.2a). Furthermore, with increasing reaction duration up to 24 h (S4) pure hexagonal ZnIn$_2$S$_4$ phase has been observed (Fig. 3.2b). But, the crystallinity for this sample is still less and hence, again the reaction is carried out for 30 h (S5) and a pure hexagonal ZnIn$_2$S$_4$ with better crystallinity is obtained (Fig. 3.2c).
Fig. 3.2 XRD of the samples synthesized for (a) 16 h, (b) 24 h and (c) 30 h reaction time using 5:10:40 mmol ratio of Zn:In:S.

The identical procedure has been followed for the synthesis of sample S6 and S7. XRD pattern of S6 synthesized using 1:2:8 mmol precursor ratios (Fig. 3.3A) depict the highly crystalline ZnIn$_2$S$_4$ phase. Although, the precursor concentration was increased by 10 times, no structural change was observed for S7 (Fig. 3.3B).

Fig. 3.3 XRD of the sample synthesized for 30 h using (A) 1:2:8 mmol ratio and (B) 10:20:80 mmol of Zn:In:S.
3.2.1 Phase formation mechanism:

ZnIn$_2$S$_4$ can be grown into a two distinct polymorphs, either hexagonal or cubic lattices; depending on the synthetic method used [15]. The hexagonal polymorph of ZnIn$_2$S$_4$ also exhibits different polytypes due to the different stacking fashions of sulfur atoms [16]. In all polytypes of the hexagonal phase, Zn and half of the In atoms are tetrahedrally coordinated by sulfur atoms, whereas the other half are octahedrally coordinated. However, in the case of the cubic phase of ZnIn$_2$S$_4$, Zn atoms are tetrahedral co-ordinated by sulfur atoms, while In atoms are only octahedral coordinated (Scheme 3.1). A solution coordination model (SCM) was previously proposed to explain the formation of cubic ZnIn$_2$S$_4$ [17]. According to this model, the coordination of the ions formed in solution serves as a template to retain the same coordination as in the solid. Thus, the phase of the solid product is determined by the coordination environment in the solution. The tetrahedral co-ordinations between the S and the two metal ions (Zn$^{2+}$ and In$^{3+}$) results in the formation of a cubic phase. On the basis of the above-mentioned SCM model, we propose a formation mechanism of the as-synthesized hexagonal ZnIn$_2$S$_4$, as illustrated in Scheme-3.2. In solution, In$^{3+}$ and Zn$^{2+}$ can form three different complexes with thiourea (TU) as the tetrahedral [In(TU)$_4$]$^{3+}$ and [Zn-(TU)$_4$]$^{2+}$ and the octahedral [In(TU)$_6$]$^{3+}$. As a result, In$^{−}$S$_6$, In$^{−}$S$_4$, and Zn$^{−}$S$_4$ species are formed under solvothermal/hydrothermal conditions. According to the previous report [18], In$^{−}$S$_6$ and In$^{−}$S$_4$ species were formed and deposited first under thermal conditions, but Zn$^{−}$S$_4$ species were not formed because the solubility product constant (Ksp) of In$_2$S$_3$ and ZnS were 5.7 $×$ $10^{-74}$ and 1.51 $×$ $10^{-21}$ [19,20], respectively. These results were confirmed by XRD pattern (Fig. 3.1A) and EDAX (Fig. 3.1B) of the as-synthesized materials obtained after 8h. Meanwhile, these fresh generated In$^{−}$S$_6$ and In$^{−}$S$_4$ species underwent the process of Oswald ripening, and further combined with the [Zn(TAA)$_4$]$^{2+}$ in situ, resulting in a thermodynamically stable hexagonal ZnIn$_2$S$_4$ rudiment in which the coordination of In$^{3+}$ ions were present in both the octahedral and the tetrahedral forms.
Scheme 3.1 Chemical reaction for ZnIn$_2$S$_4$ formation. Note: For clarity, the charges for the complexes (In, Zn, S) were omitted in the figure.

Furthermore, in order to reveal the effect of capping agents on morphology, shape and size of ZnIn$_2$S$_4$ (optimized phase condition at 5:10:40 mmol concentration) were studied in detail. Different capping agents such as triethyl amine (TEA), diethyl amine (DEA), polyvinylpyrrolidone (PVP) and cetyltrimethylammoniumbromide (CTAB) with their different concentrations were used. The detailed experimental parameters are summarized in Table 3.2.

Table 3.2 Detail experimental parameters for synthesis of ZnIn$_2$S$_4$ with capping agents.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Zn:In:S ratio in mmol</th>
<th>Reaction time (h)</th>
<th>Capping agents</th>
<th>Amounts of capping agents</th>
</tr>
</thead>
<tbody>
<tr>
<td>S8</td>
<td>5:10:40</td>
<td>30</td>
<td>PVP</td>
<td>100 ppm</td>
</tr>
<tr>
<td>S9</td>
<td>5:10:40</td>
<td>30</td>
<td>PVP</td>
<td>200 ppm</td>
</tr>
<tr>
<td>S10</td>
<td>5:10:40</td>
<td>30</td>
<td>PVP</td>
<td>300 ppm</td>
</tr>
<tr>
<td>S11</td>
<td>5:10:40</td>
<td>30</td>
<td>DEA</td>
<td>0.01 mol</td>
</tr>
<tr>
<td>S12</td>
<td>5:10:40</td>
<td>30</td>
<td>DEA</td>
<td>0.015 mol</td>
</tr>
<tr>
<td>S13</td>
<td>5:10:40</td>
<td>30</td>
<td>TEA</td>
<td>0.005 mol</td>
</tr>
<tr>
<td>S14</td>
<td>5:10:40</td>
<td>30</td>
<td>TEA</td>
<td>0.01 mol</td>
</tr>
<tr>
<td>S15</td>
<td>5:10:40</td>
<td>30</td>
<td>TEA</td>
<td>0.015 mol</td>
</tr>
<tr>
<td>S16</td>
<td>5:10:40</td>
<td>30</td>
<td>CTAB</td>
<td>100 ppm</td>
</tr>
</tbody>
</table>
In case of the capping agent assisted ZnIn$_2$S$_4$ synthesis (S8-16), all the samples with optimal concentration of capping agent shows hexagonal phase formation take place. PVP and DEA assisted samples (S8-12) also shows a crystalline hexagonal ZnIn$_2$S$_4$ formation (Fig. 3.4 and Fig. 3.5). But, out of the four capping agents, TEA assisted ZnIn$_2$S$_4$ (S13-15) samples exhibits a highly crystalline nature as compared to the others (Fig. 3.6). While XRD pattern of CTAB assisted ZnIn$_2$S$_4$ (S16) shows poor crystallinity (Fig. 3.7).

![Fig. 3.4 XRD of the samples synthesized for 30 h using (a) 100 (b) 200 and (c) 300 ppm PVP.](image)

![Fig. 3.5 XRD of the samples synthesized for 30 h using (a) 0.01, (b) 0.015mol of DEA.](image)
3.3 Result and discussion:

3.3.1 Morphological Study:

The morphology and size of the as-synthesized products was investigated by FESEM technique. As discussed above the phase formation was observed beyond 24 h reaction time and hence, morphological study was performed from sample S4-S16. In case of the sample S4 (24 h), nonuniform solid sphere like morphology was observed (Fig. 3.8a-b). From these images, it is clear that, there is partial growth of ZnIn$_2$S$_4$
spheres. The morphology of ZnIn$_2$S$_4$ obtained for 30 h (Fig. 3.8c-d) shows marigold flowerlike structure. The size of the flower was observed in the range of 3–5 µm with petal thickness ~3–5 nm. Enhancement in observed aspect ratio is due to lower petal thickness and its assembly. Interestingly, some of the flowers have cavity of size ~1.5 µm. We believe that these cavities are formed from the separation of two flowers. Fig. 3b (inset) clearly shows the birth of another small flower from the parent flower. Under certain hydrothermal conditions, the puffiness of the flowers increases due to the further growth of the petals and at a particular time the bigger flower engenders a small flower leaving the cavity behind. This morphological study indicates that the complete growth of flower takes place within 30 h.

![Fig. 3.9 FESEM images of the samples synthesized (a-b) for 24 h, (c-d) for 30 h using 5:10:40 mmol ratio. While, (e) 30 h using 1:2:8 mmol and (f) 30 h using 10:20:80 mmol.](image-url)
FESEM image of the sample synthesized using lower concentration of the precursors (S6) shows decreased in the flower size up to 200 nm (Fig. 3.9e). It is quite well known that, at lower concentration of reactants, the crystal growth slows down due to lower ionic concentration. Hence, less size of flower obtained is justifiable. We also performed the reactions with higher reactant concentration (S7) and its morphological study shows that, there is a formation of bigger size flowers (7-8 µm) with less puffiness as compared to S5(Fig. 3.9f). The formation of bigger flowers clearly indicates fast growth due to higher ionic concentration of precursors. The prima facie observations show that, the morphology and size of ZnIn$_2$S$_4$ is dependent on precursor concentration and reaction duration.

FESEM study of PVP assisted ZnIn$_2$S$_4$ samples with different PVP concentrations (S8-S10) are also carried out to examine the effect of PVP on the morphology. Surprisingly, the variation in concentration plays an important role in the formation of hollow marigold flower structures. In the systematic study, at lower PVP concentration i.e 100 ppm (S8), there is a irregular distribution in size and shape of particles (Fig. 3.10a-b). As the concentration of PVP is increased up to 200 ppm, hollow spheres of size ~4-6 µm with ~2.5 µm cavity are obtained (Fig. 3.10 c-d). But, herein puffiness of the flower is still less and petals are more compact in nature. Hence, the concentration of PVP was further increased up to 300 ppm and interestingly puffy flowers with hollow cavity are obtained (Fig. 3.10e-f). The petals of the flower are fully grown and well separated from each other. These flowers are seen to be highly porous (Fig. 3.10e inset) and cavity present in each flower represents the hollow nature of the flower. Figure 3.10f reveals that hierarchical hollow marigold flowers are assembled by numerous orderly packed nanosheets. The corresponding TEM image of the 300 ppm PVP assisted ZnIn$_2$S$_4$ sample shown in Fig. 3.15a-b confirms that the product exhibit hollow structure. Importantly, uniform marigold flowers with size ~ 4.5 µm are observed. TEM image with higher magnification (Fig. 3.15b) reveals that there is an empty space (cavity) present at the center of the flower. It also shows the hollow structure consists of numerous interconnected thin petals. It is also clear form Fig. 3.15c that the petals are of hexagonal shape with size ~200 nm. Continuous sharp hexagons in the selected-area electron diffraction (SAED) pattern illustrated the highly crystalline nature of the ZnIn$_2$S$_4$ hollow marigold flowers (Fig. 3.15d).
Fig. 3.10 FESEM images of the samples synthesized using (a-b) 100 (c-d) 200 and (d-f) 300 ppm PVP as a capping agent and 5:10:40 mmol precursors of Zn:In:S for 30 h.

FESEM images of the DEA assisted ZnIn$_2$S$_4$ samples are shown in Fig. 3.11. There is premature nanoplate like morphology (Fig. 3.11a) is observed for lower DEA concentration i.e. 0.01 mol (S12). Figure 3.11(b) depicts the FESEM images of the sample synthesized using 0.015 mol diethyl amine (DEA). It clearly shows rose flowerlike morphology of the ZnIn$_2$S$_4$ with size of ~ 0.5-1µm. The individual flowerlike structure consists of aggregated hexagonal nanosheets (petals) of thickness ~100 nm. These petals, with a random array, are connected to each other to build a rose flower-like architecture.
Fig. 3.11 FESEM images of the samples synthesized using (a) 0.01 and (b) 0.015 mol DEA as a capping agent and 5:10:40 mmol precursors of Zn:In:S for 30 h.

FESEM images of TEA assisted samples (S13-S15) are shown in Fig. 3.12. With lowest TEA concentration (0.005 mol) shows the distorted flowers with nanoplates having sizes in the range of ~ 0.5–1 mm (Fig. 3.13a-b). Presence of TEA causes the distortion in flowers and it further goes on increasing with higher TEA concentration. The magnified image (Fig. 3.12b) of the same shows petals of a distorted flower are more opened compared to that of S5. The separation between the two petals was observed to be ~ 100–250 nm. Nanoplates with a size ~ 200–300 nm are grown on the surface of the flower. It seems that after complete growth of the flower, the extended unidirectional growth of the nanoplates originates from the petals due to the existence of surfactant traces on the surface.

Figure 3.12(c–d) depicts the FESEM images with different magnifications of S14 which is synthesized using 0.01 mol TEA. It clearly shows nanoplates and nanostrips are stacked into bundles with size ~ 100–500 nm. The observed nanoplate thickness is in the range ~ 50–70 nm. The nanostrips formation can be attributed to splitting of nanoplates at certain reaction temperature and time. The curving nature of the petals disappeared due to increasing the concentration of surfactant and engendered the nanoplates. This indicates that TEA plays a significant role in the formation of different morphologies.

Figure 3.12(e-f) shows FESEM images of sample S15 synthesized using 0.015 mol TEA. These images shows highly distorted flower-like structures. However, the thickness of the petals is observed to be ~30–40 nm. Occasional nanostrip like morphology was also noticed on the surface of the flower. The nanostrip originates from the self-aligned nanoparticle cluster (an inset Fig. 3.12e). A careful examination of
the flowers and plates reveals that the nanopetals thickness is much lower than the nanoplate. This indicates that due to presence of TEA, the growth of the petals slows down and creates distorted flower like morphology as explained in the case of sample S13. As the petal thickness increases, this sustains a surface tension created by the vapour pressure during hydrothermal reaction, ultimately restricting the curving nature of the petal. Hence, when the petal grows beyond ~70 nm and transforms into a plate-like morphology and the petal with thickness below ~50 nm are transformed into flower-like morphology. Formations of such typical 3D structures are dependent on the experimental reaction conditions.

**Fig. 3.12** FESEM images of the samples synthesized using (a-b) 0.005 mol, (c-d) 0.01 mol and (e-f) 0.015mol TEA as a capping agent and 5:10:40 mmol precursors of Zn:In:S for 30h.
Figure 3.13(a-b) depicts FESEM image of 100 ppm CTAB assisted ZnIn$_2$S$_4$ sample (S16), which shows distorted spheres of ZnIn$_2$S$_4$ of size 4-5µm. (Fig. 3.12b). The clusters of aggregated spherical nanoparticles are self assembled and form a sphere like morphology. In comparison with other capping agents, CTAB does not show desirable effect on morphology. However, further study like optimization with respect to reaction time and concentration of CTAB is in progress.

Figure 3.13 FESEM images of the ZnIn$_2$S$_4$ sample synthesized for 30h using 100ppm CTAB.

3.3.2 TEM Study:

Figure 3.14(a-b) depicts the TEM images of the petal of the marigold flower which observed in a FESEM image of sample S5. It shows that the ZnIn$_2$S$_4$ petals are very thin and transparent. The length of petal measured from TEM images was observed to be in the range of ~50–200 nm. The bright spots in the SAED pattern (an inset Fig. 3.14a) indicate highly crystalline nature of the petals. These spots represent the corresponding planes which are present in the XRD pattern of ZnIn$_2$S$_4$. HR-TEM image taken along the petal edge (Fig. 3.14b) and observed interplanar distance ~2.5 Å corresponding to (105) plane of hexagonal ZnIn$_2$S$_4$ phase and growth direction take place along the [001] direction.

Figure 3.14c depicts the TEM image of the nanoplates (S5). It clearly shows the small hexagonal plates of ~50–100 nm in size. Corresponding SAED pattern consists of six bright spots which represents the hexagonal alignment (Fig. 3.14d). The d values calculated from SAED pattern are in good agreement with the XRD result.
Fig. 3.14 (a) TEM image of Petal of the flower with an inset is diffraction pattern, (b) is synthesized without using capping agent, while (c) is TEM image of plate & (d) is diffraction pattern of plate like ZnIn$_2$S$_4$ sample synthesized using TEA as a capping agent.

Fig. 3.15 (a-c) TEM images of the samples synthesized with using 300 ppm PVP as a capping agent and (d) is electron diffraction pattern.
3.3.3 Growth Mechanism:

Flowers and Nanosheets:

The formation of hierarchical nanostructures with marigold flower-like morphology is quite possible in a aqueous media as investigated by Kale et al [1]. Regarding the formation of the spherical (marigold flower) structure, the geometric building blocks may play a key role, because no surfactants were used during the synthesis. A simple array of such crystals (petals) will easily generate a curvature and develop into a marigold flower-like structure (Scheme 3.3a). Further, the formation of ZnIn$_2$S$_4$ using TEA as a surfactant gave a slightly different morphology. It is quite well known that triethylamine (TEA) as a surfactant affects on the shape and size of the material [21]. Due to low TEA concentration, no significant variation was observed in the flower size; however puffiness has been increased considerably (Scheme 3.3b). The intermediate reaction (2) is basically accelerated in the presence of TEA, which ultimately results in growth rate of ZnIn$_2$S$_4$ nanoparticle. Hence, the overgrowth and puffiness observed is quite understandable. After increasing the concentration of TEA, we found a drastic change in the particle morphology and size. The bonding strength of the co-ordination between TEA and surface atoms of ZnIn$_2$S$_4$ nanoparticles (NP) increases with decreasing particle size. Hence, the overall growth of petals has been suppressed drastically which is attributed to the formation of smaller plates instead of flowers (Scheme 3.3c). Additionally, Van der Waals forces of attraction are also greater among larger size particles which can easily overcome the reduced energy barrier once a few surfactants are removed leading to their faster aggregation. Therefore, a stronger NP-TEA bond at the surface will act against the weaker Van der Waals forces of attraction between petals which could account for the formation of smaller nanoplates instead of micron-sized flowers [21]. Further, at higher TEA concentrations, the reaction slows down due to the strong steric hindrance created by the excess TEA (0.015 mol). Hence, a distorted flower-like structure was obtained. FESEM image (Fig. 3.12(e-f)) shows flowers with dispersed small curving petals and partially grown plates on the top surface of the petal (Scheme 3.3d). The FESEM image (Fig. 3.12a inset) also depicts premature growth of plates of the petal of the flowers in the form of self-aligned nanoparticles. This indicates that excess TEA accelerates the unidimensional growth, i.e. formation of plates and nanostrips.
In the extension of this work we replaced TEA by Diethyl amine (DEA) as a capping agent. At lower concentration of DEA (0.01 mol), the three dimensional growth is observed and hence, aggregated spherical nanoparticles align and shows premature nanoplates (Fig. 3.11a). As concentration of DEA increases (0.015 mol), two dimensional (2D) growth of the nanoparticles is accelerated. Hence at prolong reaction time, due to Ostwalled ripening phenomenon hexagonal plate like structure is found. At equilibrium condition these hexagonal plates are self organized and assembly of rose flowerlike structure is formed (Fig. 3.11b). Interestingly, at higher concentration of DEA due to the lower vapor pressure, there is no strain created on the plate and hence the curving ability is suppressed. Hence, instead of marigold structure, the rose like structure is obtained.

![Scheme 3.3 Schematic illustration of the possible growth mechanism of ZnIn₂S₄ Flowers and Nanoplates.](image)

**Hollow flowers:**

According to the earlier reports [22-24], it is observed that PVP is a well known surfactant to obtain the hollow nanostructured materials. On the basis of the above results, we proposed that synergistic effect of PVP is the prime factor for the formation
of hollow marigold ZnIn$_2$S$_4$ flowers. In the absence of PVP instead of hollow, compact marigold flowers are obtained which indicates PVP is playing key role for the formation of hollow structure. A possible growth mechanism is proposed in Scheme 3.4.

Initially, Zn-PVP and In-PVP complexes are formed through the coordinative bonding with the carbonyl oxygen of PVP. At elevated temperature, thiourea starts to release H$_2$S as sulphur source. This H$_2$S slowly reacts with Zn$^{2+}$ and In$^{3+}$ ions by replacing PVP ligand and forms ZnIn$_2$S$_4$ nuclei. Here, the ZnIn$_2$S$_4$ nuclei capped with PVP at the surface and hence restricted growth of flowerlike morphology is observed. In this case the precursors are capped with PVP and the nanoparticles then aggregate into bigger particles to decrease the surface energy. At supersaturation condition, the crystallites on/near the outermost surface of aggregates will continue to growth at slow rate [25]. This continuous growth of aggregates confers the spherical self assembly having core with smaller nanoparticles and exterior layer with a bigger nanoparticles (Scheme 3.4a). As the concentration of PVP increased up to 300 ppm, the excess of PVP on ZnIn$_2$S$_4$ nuclei in the core is diffused at 150°C to the exterior layer (Fig3.10e-f). In this stage, Ostwalled ripening takes place in which aggregation of primary nuclei followed by outward mass transfer through the growth of larger crystallites from those of smaller size and migration of crystallites from inner core to outer shell. In this process inner core completely consumed and hollow cavity created due to the diffusion. During this process, the excess PVP present in the core try to evacuate out at 150°C to release the pressure created by PVP. Hence, some of the mass of ZnIn$_2$S$_4$ diffused from the core by leaving the cavity behind. This phenomenon creates hollowness to the flowerlike assembly which is clearly seen in FESEM and TEM images. (Fig. 3.10f and Fig. 3.15b). The flower like assembly shows porous structure due to the steric effect of the PVP molecules, the aggregated nanoparticles are loosely compacted. Hence, we find there are many voids in the interior of the spherical aggregates [24].
Scheme 3.4 Schematic illustration of the possible growth mechanism of ZnIn$_2$S$_4$ hollow flowers

3.3.4 Optical study:

To investigate the possible influence of the size and shape of nano and macro-material on the optical properties, the UV-vis diffuse reflectance spectra (DRS) has been employed. It is commonly observed that all the samples shows a steep absorption edges in the visible region. Absorption edge and corresponding band gap of the samples (S3-S16) are summerized in the adjacent table (Table 3.3-3.6). The optical bandgap of the samples is in the range of ~2.4-2.9 eV, which are close to the bulk bandgap (2.3 eV) [13, 26].

Figure 3.16A depicts UV-Vis DRS spectra of samples S3-S7 respectively. The band gap of sample S3, S4, S5 and S7 was observed to be 2.4 eV (515 nm), however the band gap of S6 is observed to be 2.53 eV (Table 3.3). The blue shift obtained for S6 is due to nanocrystalline nature of the sample, which appear because of the lower precursor concentration. Additionally, sample S3 dose not show single steep absorption due to some immnpurity levels i.e.partial formation of ZnIn$_2$S$_4$ confirmed by XRD (Fig. 3.2a).

Figure 3.16B depicts the UV-Vis DRS spectra of the PVP assisted ZnIn$_2$S$_4$ samples (S8-S10). The absorption edge is observed to be 520 nm for sample S8 and S9 with corresponding band gap of 2.4 eV. The sample S10 shows absorption edge at 502 nm with corresponding band gap 2.47 eV (Table 3.4). The blue shift in the absorption edge...
is due to lower particle size. These results indicate PVP assisted sample does not show considerable shift in the absorption w.r.t the samples synthesized without capping agent.

Figure 3.16C depicts the UV-Vis DRS spectra of DEA assisted ZnIn$_2$S$_4$ samples (S11-S12). Sample S11 and S12 shows absorption edges at 500 and 480 nm, respectively (Table-3.5). The blue shift observed in case of S12 is due to the nanocrystalline nature which is obtained because of higher concentration of capping agent (DEA).

The UV-Vis DRS spectra of TEA assisted ZnIn$_2$S$_4$ samples (S13-S15) are shown in Fig. 3.16D. The absorption edge cut off has been blue shifted with increasing concentration of TEA (see Table 3.6). As we increase the concentration of capping agent, there is a control on crystal growth and hence lower crystallite size is obtained for higher concentration of capping agent. The blue shift observed is due to this lower particle size. In a nutshell overall blue shift is observed in case of TEA assisted ZnIn$_2$S$_4$.

![UV-Visible diffuse reflectance spectra of ZnIn$_2$S$_4$ samples synthesized without using capping agent](image)

**Fig. 3.16A** UV-Visible diffuse reflectance spectra of ZnIn$_2$S$_4$ samples synthesized without using capping agent (a) S3 (b) S4, (c) S5, (d) S7 and (e) S6, **Table 3.3** absorption wavelength and corresponding band gap of respective samples.
Fig. 3.16B UV-Visible diffuse reflectance spectra of PVP assisted ZnIn$_2$S$_4$ samples (a) S8, (b) S9 and (c) S10. Table 3.4 absorption wavelength and corresponding band gap of respective samples.

<table>
<thead>
<tr>
<th>Code</th>
<th>UV cutoff (nm)</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (0.05M 100ppm PVP)</td>
<td>520</td>
<td>2.4</td>
</tr>
<tr>
<td>b (0.05M 200ppm PVP)</td>
<td>520</td>
<td>2.4</td>
</tr>
<tr>
<td>c (0.05 M, 300ppm PVP)</td>
<td>502</td>
<td>2.47</td>
</tr>
</tbody>
</table>

Fig. 3.16C UV-Visible diffuse reflectance spectra of DEA assisted ZnIn$_2$S$_4$ samples (a) S11 and (b) S12. Table 3.5 absorption wavelength and corresponding band gap of respective samples.

<table>
<thead>
<tr>
<th>Code</th>
<th>UV cutoff (nm)</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (0.01 mol, DEA)</td>
<td>500</td>
<td>2.48</td>
</tr>
<tr>
<td>b (0.015mol, DEA)</td>
<td>480</td>
<td>2.58</td>
</tr>
</tbody>
</table>
3.3.5 **X-Ray photoelectron Spectroscopy (XPS) analysis:**

The surface characterization of ZnIn$_2$S$_4$ was performed using X-ray Photoelectron Spectroscopy (XPS). The binding energies obtained were corrected for specimen charging by referencing carbon 1S to 284.5 eV. As shown Fig. 3.17 b-d, the core lines were fixed at 444.9 eV (In3d$^{5/2}$), 161.8 eV (S2p$^{3/2}$) and 1021.5 eV (Zn2p$^{3/2}$) respectively. This implies the existence of chemical states In$^{3+}$, S$^{2-}$ and Zn$^{2+}$. The molar ratio based on the peak surface area was observed to be 1: 2.3: 4 (Zn: In: S) which is very closely matching with the theoretical one. No other peaks pertaining to any trace impurities were observed.

**Table 3.6** absorption wavelength and corresponding band gap of respective samples.

<table>
<thead>
<tr>
<th>Code</th>
<th>UV cutoff (nm)</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (0.005 mol, TEA)</td>
<td>484</td>
<td>2.56</td>
</tr>
<tr>
<td>b (0.01 mol, TEA)</td>
<td>465</td>
<td>2.68</td>
</tr>
<tr>
<td>c (0.015 mol, TEA)</td>
<td>434</td>
<td>2.9</td>
</tr>
</tbody>
</table>

**Fig.3.16D** UV-Visible diffuse reflectance spectra of TEA assisted ZnIn$_2$S$_4$ samples (a) S13, (b) S14 and (c) S15.
3.3.6 Photocatalytic Activity:

Photocatalytic activities for hydrogen generation using H$_2$S splitting were observed for the as-synthesized ZnIn$_2$S$_4$ samples. Table 3.4 reveals the yield of hydrogen for the selected catalysts and the results are compared with the activities obtained for standard visible light active photocatalysts i.e. CdS and CdIn$_2$S$_4$. While, Fig. 3.18 depicts the plots of hydrogen evolution rate (µmolh$^{-1}$) versus irradiation time (min) of the corresponding samples. From these results, ZnIn$_2$S$_4$ samples show superior yield of hydrogen, except CTAB assisted one. It is noteworthy that among all ZnIn$_2$S$_4$ samples, S14 (0.01 mol TEA assisted) shows significant hydrogen evolution rate without any promoters, which is much higher than earlier reported values. [1-18, 26–31]

The TEA-assisted ZnIn$_2$S$_4$ demonstrate a better photocatalytic activity than normal ZnIn$_2$S$_4$ (S5). It is quite well known that morphology of the materials also plays a vital role in photocatalysis [32-34]. Sample S5 has a marigold flowerlike morphology with cavity; these flowers are compact which ultimately suppresses the transport of electrons to the surface which may be the reason for having slightly less activity. For S13, the distorted flowers of ZnIn$_2$S$_4$ are extremely puffy and seem to be crystalline as compared

![Fig.3.17 XPS patterns of as synthesized ZnIn$_2$S$_4$ at 150°C for 30 h using 0.01 mol TEA (S3) (a) survey spectrum and high-resolution spectra for (b) In3d, (c) S2p, (d) Zn2p](image-url)
to S5 and hence, the higher hydrogen evolution rate obtained. The highest hydrogen evolution was obtained for S14 because of the existence of highly crystalline nanoplates and nanostrips. The obtained surface area is definitely higher for the nanoplate and nanostrip morphologies. In the case of S15, mixed morphology is obtained, i.e. flowers with nanostrips. The compact flowers with overgrowth of small spherical particles on the surface of the petals hamper the overall crystallinity which ultimately gives slightly less photocatalytic activity. This is the first time we have achieved extremely high hydrogen production using H$_2$S under solar light especially for ZnIn$_2$S$_4$. The repeatability of the photocatalyst was examined and we obtained the same hydrogen evolution rates. The stability of the photocatalyst has also been examined by reusing the photocatalyst sample (S14). XRD of the reused catalyst (Fig. 3.19) did not show a change in the phase of the ZnIn$_2$S$_4$.

In case of PVP assisted (S10) and DEA assisted (S12) ZnIn$_2$S$_4$ samples, both samples are also shows increment in the activity (4340 and 4409 µmolh$^{-1}$, respectively) than normal ZnIn$_2$S$_4$ (S5) (4011 µmolh$^{-1}$). Due to the porous and hollow nature of PVP assisted sample, it shows higher activity than normal ZnIn$_2$S$_4$ though the size of both the samples is nearly same. While in case of DEA-assisted sample, a sheet like morphology helps to enhance the activity. But the enhancement is not to a great extent, because the sheets are very compact and may be affecting on the adsorption of H$_2$S molecules and fewer surfaces are in contact with the light. Lowest activity for H$_2$ generation is observed for CTAB-assisted ZnIn$_2$S$_4$ sample, as this sample shows poor crystalline nature and there are some impurities also present and its morphology very nonuniform to achieve high yield.

The photocatalytic activity of CdS was also studied under the identical conditions. The maximum hydrogen production rate achieved was 847 µmol h$^{-1}$, which is found to be much lower than ZnIn$_2$S$_4$. The photocatalytic activity obtained is also much higher than our previous report on In$_2$S$_3$ [31]. I have also performed photocatalytic experiments using ZnS, but we could not get any hydrogen evolution under solar light. It is noteworthy that I am reporting the hydrogen production using ZnIn$_2$S$_4$ via hydrogen sulphide for the first time. As such naked ZnIn$_2$S$_4$ conferred extremely good photocatalytic activity because of the layered hexagonal structure. In the hexagonal structure of ZnIn$_2$S$_4$, the atoms are arranged in layers at six equally separated levels along the c-axis. Each of the Zn ions are in a tetrahedral environment of four S atoms.
(Zn–S4); In\(^{3+}\) ions are in two environments, an octahedral environment of six S atoms (In–S6) and a tetrahedral environment of four S atoms (In–S4)] [13,18]. This layered structure is also responsible for the good photocatalytic activity over a naked ZnIn\(_2\)S\(_4\).

**Fig. 3.18** Photocatalytic hydrogen generation study for ZnIn\(_2\)S\(_4\) samples.

**Table 3.7** Results of photocatalytic activities of different samples of ZnIn\(_2\)S\(_4\) and comparison with standard catalysts.

<table>
<thead>
<tr>
<th>Code</th>
<th>Sample description</th>
<th>(\text{H}_2) in (\mu\text{mol h}^{-1}) 0.5 g(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Without capping agent</td>
<td>4011</td>
</tr>
<tr>
<td>b</td>
<td>0.005 mol TEA assisted ZIS</td>
<td>4491</td>
</tr>
<tr>
<td>c</td>
<td>0.01 mol TEA assisted ZIS</td>
<td>5429</td>
</tr>
<tr>
<td>d</td>
<td>0.015 mol TEA assisted ZIS</td>
<td>4374</td>
</tr>
<tr>
<td>e</td>
<td>100 ppm CTAB assisted ZIS</td>
<td>1000</td>
</tr>
<tr>
<td>f</td>
<td>0.015 mol DEA assisted ZIS</td>
<td>4409</td>
</tr>
<tr>
<td>g</td>
<td>300 ppm PVP assisted</td>
<td>4340</td>
</tr>
<tr>
<td>h</td>
<td>CdIn(_2)S(_4)</td>
<td>3238</td>
</tr>
<tr>
<td>i</td>
<td>CdS commercial</td>
<td>847</td>
</tr>
</tbody>
</table>
3.4 Conclusions:

The ZnIn$_2$S$_4$ has been synthesized using hydrothermal method. The different capping agents have been used and their effect on morphology, optical properties and photocatalytic activities is investigated. The conclusion of the results and observations are as follow.

1. Structural study showed hexagonal phase of ZnIn$_2$S$_4$ is in all samples.

2. FESEM results depict the formation of uniform marigold flowerlike morphology in absence of capping agent.

3. Effect of the capping agents such as PVP, DEA and TEA was observed for morphological change. Hollow marigold flowerlike morphology is obtained in case of PVP assisted ZnIn$_2$S$_4$. While, rose flowerlike morphology is observed in presence of DEA. Interestingly, uniform and highly crystalline nanoplates have been observed in presence of TEA as a capping agent. These types of hierarchical nanostructures of ZnIn$_2$S$_4$ are obtained for the first time.

4. Optical study clearly indicates all the samples shows strong absorption in the visible region with band gap in the range of ~2.4-2.9 eV. The capping agent assisted sample shows blue shift in the absorption edge due to the reduced particle size. This result indicates that the capping agent strongly affects on the optical properties of ZnIn$_2$S$_4$ due to control over the particle size.
5. The as synthesized ZnIn$_2$S$_4$ samples were used for ecofriendly photocatalytic hydrogen generation via H$_2$S splitting under the solar light irradiation.

6. All the samples show promising hydrogen generation rate as compared to the previous reports. The capping agent assisted samples show higher photocatalytic activity than bare ZnIn$_2$S$_4$. Nanoplate like ZnIn$_2$S$_4$ sample obtained using TEA as a capping agent showed the excellent photocatalytic activity for hydrogen generation (5429 µmol h$^{-1}$).
References: