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Introduction

The fabrication of hierarchical nanostructured materials with well-defined structures and morphologies has currently been under growing interest due to the experimental findings that the properties of nanostructured materials are size and morphology dependent.¹ For example, hollow nanostructures have widespread potential applications in drug delivery, catalysis, sensors, lithium ion batteries, ion storage and so on,1-6 because they provide a high specific surface area, favoring a better dispersion. A variety of methods have been developed to synthesize hollow structures; however, it remains a challenge to prepare hollow microspheres, which self-assemble from nanocrystals, with a well-controlled size and morphology for an improved photocatalytic performance. In addition, photocatalysts with a strong absorption in the visible region can show a more efficient utilization of solar energy than UV-light active materials. Also, the development of a visible light active stable photocatalyst (photocorrosion free) has immense significance.7

Architecture of rose and hollow marigold-like ZnIn₂S₄ flowers: structural, optical and photocatalytic study[†]

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In the present investigation, a surfactant-assisted hydrothermal route has been employed to design selfassembled rose and hollow marigold-like Znln₂S₄ flowers. In the absence of the surfactant, uniform (~3–5 µm) marigold-like flowers are observed. The self-alignment of the transparent petals (~3–5 nm thick with a length of ~25–100 nm) leads to the formation of hollow marigold-like flowers, for which a plausible growth mechanism has also been proposed. Moreover, DEA assisted Znln₂S₄ demonstrates a rose flower-like *via* self assembly of hexagonal nanoplates. Structural and optical characterization shows the existence of hexagonal structures with a band gap in the range of ~2.4–2.6 eV. Considering the ideal band gap in the visible region, we have used such unique nanostructured self assemblies of Znln₂S₄ as photocatalysts and demonstrated visible light-driven photocatalytic production of clean hydrogen by toxic hydrogen sulphide, which is abundantly available as a waste gas from oil refineries (15–20%). We believe that continuous efforts in this direction may open up new insights into the design of controllable nanostructures and their potential applications in advanced fields.

> Recently, a new class of multi-component sulphides has also been reported to show a high photocatalytic efficiency.8-11 Among these, $ZnIn_2S_4$ is a n-type semiconductor with a bandgap of 2.4 eV, which possesses photo- and chemical stablility.12 It exhibits a layered structure in the AB_2X_4 (A = Cu, Ag, Zn, Cd, etc.; B = Al, Ga, In; C = S, Se, Te) family, which has attracted considerable attention due to its outstanding electrical and optical properties.¹³ There are several reports of ZnIn₂S₄ in the literature with different morphologies using effective methods/ strategies.13-18 Furthermore, Shen et al. employed nanostructured ZnIn₂S₄ for hydrogen evolution, and the photocatalytic activity of the ZnIn₂S₄ was greatly affected by the crystal plane spacing along the c-axis.17 Considering the importance of the band and crystal structure of ZnIn₂S₄, hierarchically hollow microspheres and faceted growth of nanosheets are usually relevant to the self-assembly process, and are promising in photocatalytic hydrogen evolution. Also, the issue of highly toxic hydrogen sulphide and necessity of producing hydrogen from it by photocatalysis has been described in our previous report.11,19,20 Hence, the fabrication and designing of different morphologies of ZnIn₂S₄ is highly desirable, and their photocatalytic hydrogen generation from hydrogen sulphide will be significant.

> Herein, we have reported nanostructured hollow marigold and rose flower-like ZnIn_2S_4 using polyvinyl pyrrolidone (PVP) and diethyl amine (DEA) as capping agents. The effect of the concentration of PVP and DEA on the morphology has been demonstrated. The possible growth mechanism has also been discussed in detail. Finally, the effect of different morphologies on the photocatalytic hydrogen generation is investigated.

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[†] Electronic supplementary information (ESI) available: Fig. SI-1 and SI-2: XRD study of different concentrations of PVP and DEA capping agents, Fig. SI-3: FESEM images of the samples synthesized using (a and b) 100 and (c and d) 200 ppm PVP as a capping agent. Fig. SI-4: BET surface area and pore width distribution, and Fig. SI-5: error bars of the hydrogen evolution. See DOI: 10.1039/c3ra45767b

Experimental

Synthesis

All the chemicals were analytical grade and used as received without purification. In a typical synthesis of pristine ZnIn₂S₄ (S1), $Zn(NO_3)_2 \cdot 6H_2O$ (5 mmol), $In(NO_3)_3 \cdot 5H_2O$ (10 mmol) and double excess of thiourea (40 mmol) were dissolved in 100 ml distilled water. This solution was then transferred into a 200 ml Teflon lined autoclave. Distilled water was added to maintain an 80% volume of the reactor. The reactor was sealed and kept at 150 °C for 30 h. The autoclave was cooled naturally to room temperature. The product was washed with distilled water and ethanol and finally dried at 70 °C. In addition to this, PVP assisted ZnIn₂S₄ samples were also synthesized in the presence of different amounts of PVP as a capping agent. In this case, 100 ppm, 200 ppm and 300 ppm (S2) PVP was added in the same reaction as described above. Diethyl amine (DEA) assisted ZnIn₂S₄ was synthesized using 0.01 and 0.015 mol (S3) DEA as a capping agent instead of PVP.

Characterization

The as-synthesized products were characterized by an X-ray diffractometer (XRD) (D8, Advance, Bruker AXS model) using Cu K α (λ : 1.5406 Å). The surface morphological studies of the assynthesized samples were carried out using a field emission scanning electron microscope (FESEM, Hitachi S-4800). The single crystalline nature was confirmed using a high resolution transmission electron microscope (HRTEM, Technai G² 20 Twin, FEI). The surface characterization of the ZnIn₂S₄ was carried out using X-ray Photoelectron Spectroscopy (XPS, ESCA-3000, VG Scientific Ltd, England). The UV-Visible Diffuse Reflectance Spectra (UV-DRS) were recorded on a Lambda 950 Perkin Elmer spectrophotometer in the wavelength range from 200-800 nm. The Brunauer-Emmett-Teller (BET) equation was used to calculate the surface area from the adsorption branch. The pore size distribution was calculated by analyzing the adsorption branch of the nitrogen sorption isotherm, using the Barrett-Joyner-Halenda (BJH) method.

Photocatalysis measurements

A cylindrical quartz photochemical thermostatic reactor was filled with 250 ml 0.25 M aqueous KOH and purged with argon for 1 h. Hydrogen sulphide (H₂S) was bubbled through the solution for about 1 h with a rate of 2.5 ml min⁻¹ at 298 K. ZnIn₂S₄ (0.25 g) was introduced into the reactor and irradiated with a visible light source (Xe-lamp (Oriel, 300 W)) with constant stirring. The excess hydrogen sulphide was trapped in the NaOH solution. The amount of hydrogen evolved was measured using a graduated gas burette and analyzed using a gas chromatograph (Model Shimadzu GC-14B, MS-5A column, TCD, Ar carrier).

Results and discussion

Fig. 1 depicts the XRD patterns of the $ZnIn_2S_4$ samples synthesized in the absence of surfactant (S1) and in the

presence of 300 ppm PVP (S2) as well as 0.015 mmol DEA (S3) as a capping agent. The XRD pattern confirms the hexagonal crystal structure with cell parameters a = b = 3.85 Å and c =24.68 Å. This is in agreement with JCPDS data (ICDD-JCPDS card no. 72-0773). The crystallite sizes have been calculated using the Scherrer formula and are found to be ~65, 70 and 32 nm for sample S1, S2 and S3, respectively. The absence of peaks due to impurities such as binary sulphides and oxides indicates the high phase purity of the product. In addition, the XRD patterns of the samples synthesized with different concentrations of PVP and DEA are given in the ESI (SI-1).†

In order to investigate the influence of the size and shape on the optical properties, UV-visible diffuse reflectance spectra (DRS) were recorded. Fig. 2 depicts diffuse reflectance spectra of all samples (S1–S3), which show steep absorption edges in the visible region, indicating the formation of a single phase compound. The steep shape of the visible edge, and the strong absorption in the visible region, also reveal that the absorption band of $ZnIn_2S_4$ is because of the transition from the valence band to the conduction band. The samples without a capping agent (S1) and with PVP (S2) show an absorption edge at ~515 nm with a corresponding band gap of 2.4 eV. Meanwhile, the DEA assisted $ZnIn_2S_4$ sample (S3) shows an absorption edge at ~475 nm (2.6 eV) which is due to the reduced nanoparticle size.

Fig. 3a shows the FESEM image of pristine ZnIn_2S_4 (S1), indicating the formation of uniform marigold flowers originating from well organized petals. The size of the flower is observed to be in the range of 3–5 µm with the thickness of the petal being ~3–5 nm. The observed size of the ZnIn_2S_4 flower clearly indicates a high aspect ratio. A more detailed structural analysis of the present marigold-like ZnIn_2S_4 flower was carried out using a TEM. Fig. 3b shows the TEM micrograph of the petals of the marigold flower. The size of the ZnIn_2S_4 petal is found to be ~50–200 nm, which is observed to be thin and transparent. The selected area electron diffraction (SAED)



Fig. 1 X-ray diffraction patterns of the $ZnIn_2S_4$ synthesized without using surfactant (S1) and with 300 ppm PVP (S2) and 0.015 mol DEA (S3).



Fig. 2 UV-visible diffuse reflectance spectra of the $ZnIn_2S_4$ samples S1, S2 and S3.



Fig. 3 (a) FESEM images of the samples synthesized without using a capping agent (S1) and (b and e) TEM images of the petal of the flower with selective area electron diffraction in (c), (d) HRTEM image with an FFT pattern in (e).

pattern taken from the surface of the $ZnIn_2S_4$ petal (Fig. 3e), demonstrates the single crystalline nature of the $ZnIn_2S_4$ (Fig. 3c). The lattice fringes in the HRTEM image confirm the high crystallinity of the petal, as shown in Fig. 3d. The HRTEM image is taken on the edge of the same petal, and the interplanar spacing (*d*) is observed to be ~3.35 Å which is consistent with the (101) plane of the hexagonal $ZnIn_2S_4$. A fast Fourier transform (FFT) pattern taken from the same area is shown in Fig. 3f. The FFT result indicates a single crystalline nature with a well defined hexagonal pattern. This is agreement with the result shown by the XRD pattern.

FESEM studies of the PVP assisted $ZnIn_2S_4$ samples with different PVP concentrations were also carried out to see the morphological effect. Surprisingly, the variation in

concentration plays an important role in the formation of the hollow marigold flower structures. In the systematic study, at lower PVP concentration (100 ppm), premature distorted flowers are observed (Fig. SI-3a and b⁺). As the concentration of PVP is increased up to 200 ppm, hollow spheres of size \sim 4–6 μ m with a \sim 2.5 µm cavity are obtained (Fig. SI-3c and d†). However, the puffiness of the flower is observed to be much less, due to the compactness of the petal. When the concentration of PVP is further increased up to 300 ppm (S2), interestingly, puffy flowers with hollow cavities are obtained (Fig. 4). The petals of the flower are fully grown and well separated from each other. These highly porous flowers with a cavity represent the hollow nature of the nanoparticles. Fig. 4b-d reveal that the hierarchical nanostructured hollow marigold flowers are assembled by numerous orderly packed nanosheets (petals). Furthermore, a nitrogen adsorption isotherm was carried out for surface area analysis study (Table SI-1 and Fig. SI-4†). BET surface areas of \sim 40 and 55 m² g⁻¹ are found for samples S1 and S2, respectively. The hollow marigold flowers (S2) show a higher surface area due to their cavity, in comparison to the marigold flowers only (S1).

In order to examine the hollow cavity and crystalline nature of the 300 ppm PVP assisted ZnIn_2S_4 sample, TEM analysis was carried out. The TEM images in Fig. 5a and b confirm the hollow structure, which is in good agreement with the SEM results. A magnified TEM image (Fig. 5b) reveals that hollow microspheres, with hierarchical nanostructures assembled with nanosheets, were obtained. Significantly, very thin hexagonal petals of ZnIn_2S_4 with length $\sim 1 \ \mu\text{m}$ are found around the cavity. Fig. 5c shows a high resolution image taken from the edge part, and the magnified HRTEM image (inset Fig. 5c) depicts the lattice fringes of $\sim 3.29 \ \text{Å}$ associated with the (101) plane of the hexagonal ZnIn_2S_4 . The corresponding electron diffraction pattern (Fig. 5d) depicts not only the formation of a single crystalline ZnIn_2S_4 nanostructure but also gives some indication that the blur diffraction ring pattern may be due to a



Fig. 4 FESEM images of the sample synthesized using PVP as a capping agent (S2).



Fig. 5 (a–c) TEM images of the samples synthesized with 300 ppm PVP (S2) as a capping agent and (d) the electron diffraction pattern.



Fig. 7 (a and b) TEM images of the $ZnIn_2S_4$ sample synthesized using diethyl amine as a capping agent (S3), (c) HR-TEM image of nanosheets and (d) an electron diffraction pattern.

slightly low crystallinity. Furthermore, detailed observations reveal that these electron diffraction spots form a hexagonal geometry in the SAED pattern, which is due to the hexagonal $ZnIn_2S_4$.

Fig. 6a and b depict the FESEM images of the sample synthesized using diethyl amine (DEA) as a capping agent (S3). This clearly shows the rose flower-like morphology of the $ZnIn_2S_4$ with a size of 0.5–1 µm. The individual flower-like structures consist of aggregated hexagonal nanosheets (petals) of thickness ~50 nm. These petals, with a random array, are connected to each other to build a rose flower-like architecture.

Fig. 7a and b depict the TEM images of the same sample (S3). The presence of a hexagonal sheet with sharp edges is clearly observed. The HR-TEM image shows visible lattice fringes with an inter-planar distance of ~4.11 Å (Fig. 7c), which represents the (006) plane, indicating the [001] direction, *i.e. c*-axis oriented growth of the $ZnIn_2S_4$. The electron diffraction (ED) pattern (Fig. 7d) indicates that the nanosheet had a low crystallinity, which may be due to smaller crystallites.



Fig. 6 FESEM images of the sample synthesized in the presence of (a) 0.01 and (b) 0.015 mol DEA as a capping agent.

The size, shape and growth kinetics of $ZnIn_2S_4$ can be explained on the basis of the capping agents and their concentration under hydrothermal conditions, which are given in the following section.

Reaction mechanism

The current hydrothermal synthesis of $ZnIn_2S_4$ is carried out using $Zn(NO_3)_2 \cdot 6H_2O$, $In(NO_3)_3$ and thiourea as precursors, while PVP and DEA act as the capping agents in water. The Zn^{2+} and In^{3+} cations (R1) combine with the capping agents (CA) to form $[Zn (CA)]^{2+}$ and $[In (CA)]^{3+}$ complexes (R2). The formation and dissociation reactions of complexes are reversible (R2). Meanwhile, the thiourea (NH_2CSNH_2) hydrolyzes in the aqueous solution to yield H_2S (R3), which further dissociates to generate S^{2-} anions ((R4) and (R5)). The dissociation/hydrolysis reactions of complexes and NH_2CSNH_2 accelerate at higher temperatures.

$$Zn(NO_3)_2 + In(NO_3)_3 + H_2O \rightarrow Zn^{2+} + In^{3+}$$
 (R1)

$$Zn^{2+} + In^{3+} + CA \rightarrow [Zn(CA)]^{2+} + [In(CA)]^{3+}$$
 (R2)

$$NH_2CSNH_2 \rightarrow NH_2CN + H_2S$$
 (R3)

$$H_2S + H_2O \leftrightarrow H_3O^+ + HS^-$$
(R4)

$$HS^{-} + H_2O \leftrightarrow H_3O^{+} + S^{2-}$$
(R5)

The released Zn^{2+} , In^{3+} and S^{2-} ions combine to form $ZnIn_2S_4$ nuclei, as expressed by (R6):

$$Zn^{2+} + In^{3+} + S^{2-} \rightarrow ZnIn_2S_4 \tag{R6}$$

 Zn^{2+} , In^{3+} and S^{2-} ions are released gradually (R2–R5), which controls the nucleation rate of $ZnIn_2S_4$ and hence the numbers of $ZnIn_2S_4$ nuclei formed in the initial stage are limited. Accordingly, there are still large amounts of unreacted Zn^{2+} , In^{3+} and S^{2-} ions in the reaction solution, in the form of $[Zn(CA)]^{2+}$, $[In(CA)]^{3+}$ and NH_2CSNH_2 , respectively. Depending on the concentration of the capping agent and the reaction time, these unreacted forms release ions to develop a particular morphology, which is explained in the "growth mechanism" section.

Growth mechanism

In our previous report,¹⁹ we discussed a detailed mechanism for the formation of marigold flowers and nanosheets of $ZnIn_2S_4$. Here in this report, we obtained hollow marigold flowers of $ZnIn_2S_4$, which has hitherto not been attempted, and hence our focus is more on this unique morphology. It is reported^{21–23} that PVP is a well known surfactant for obtaining hollow nanostructured materials. On the basis of the above results, we propose that the synergistic effect of PVP is the prime factor for the formation of the hollow marigold $ZnIn_2S_4$ flowers. In the absence of PVP compact marigold flowers are obtained, which indicates that PVP plays a key role in the formation of the hollow structure. A possible growth mechanism is proposed in Scheme 1.

Initially, Zn–PVP and In–PVP complexes are formed through coordinative bonding with the carbonyl oxygen of the PVP. At elevated temperatures, thiourea starts to release H_2S as a sulphur source. This H_2S slowly reacts with Zn^{2+} and In^{3+} ions by replacing the PVP ligand, and forms $ZnIn_2S_4$ nuclei. Here, the $ZnIn_2S_4$ nuclei are capped with PVP at the surface, and hence restricted growth of the flower-like morphology is observed. In this case, the precursors are capped with PVP and the nanoparticles then aggregate into bigger particles to decrease their surface energy. At supersaturation conditions, the crystallites on/near the outermost surface of the aggregates will continue to grow at a slow rate.²⁴ This continuous growth of aggregates confers a spherical self assembly, having



a core with smaller nanoparticles and an exterior layer with bigger nanoparticles (Scheme 1a). As the concentration of PVP increases up to 300 ppm, the excess of PVP on the ZnIn₂S₄ nuclei in the core is diffused at 150 °C to the exterior layer (Fig. 4). At this stage, as per the Ostwald ripening phenomenon, there is an aggregation of the primary nuclei, followed by an outward mass transfer through the growth of larger crystallites from those of smaller size, and the migration of crystallites from the inner core to the outer shell. In this process the inner core is completely consumed and a hollow cavity is created due to diffusion. During this process, the excess PVP present in the core is relinquished at 150 °C, to release the pressure created by the PVP. Hence, some of the mass of the ZnIn₂S₄ diffuses from the core. Due to this reason, a hole or cavity is created on the flower. This phenomenon creates the hollowness in the flower-like assembly which is clearly seen in the FESEM and TEM images (Fig. 4 and 5a and b). The flower-like assembly shows a porous structure due to the steric effect of the PVP molecules. Hence, we find there are many voids in the interior of the spherical aggregates.23

In an extension of this work, we also used diethyl amine (DEA) as a capping agent. At lower concentrations of DEA (0.01 mol), three dimensional growth is observed and hence, aggregated spherical nanoparticles align and show premature nanoplates. As the boiling point of DEA is higher than water, the overall vapour pressure is less than water alone. Hence, growth is restricted to form a random flower-like structure. As the concentration of DEA increases up to 0.015 mol, two dimensional growth of the nanoparticles is accelerated. Hence, at prolonged reaction time, due to the Ostwald ripening phenomenon a hexagonal plate-like structure is conferred. At equilibrium conditions, these hexagonal plates are self organized and the assembly of rose flower-like structure is conferred. Interestingly, at higher concentrations of DEA due to the lower vapor pressure, there is no strain created on the plate, and hence the curving ability is suppressed.18 Therefore, instead of the marigold structure, the rose flower-like structure is obtained.

XPS study

The surface characterization of the hollow marigold flower-like $ZnIn_2S_4$ was performed using X-ray photoelectron spectroscopy (XPS). The binding energies obtained were corrected for specimen charging by referencing carbon 1s to 284.6 eV. Fig. 8a depicts the survey spectra while Fig. 8b–d show the core lines fixed at 1022 eV (Zn2p 3/2), 445 eV (In3d5/2) and 162 eV (S2p3/2) 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 matched to the theoretical one. No other peaks pertaining to any trace impurities were observed.

Photocatalytic activity

The photocatalytic activity of all the $ZnIn_2S_4$ (S1–S3) samples for hydrogen generation *via* the photodecomposition of H_2S was



Fig. 8 XPS patterns of the as-synthesized $ZnIn_2S_4$ at 150 °C for 30 h using 300 ppm PVP as a capping agent (S2) (a), survey spectra and high-resolution spectra for (b) Zn2p (c) In3d, (d) S2p.

measured in 0.25 M KOH solution. Table SI-2† depicts the comparison of the amount of hydrogen generated by the photocatalysts under identical conditions. As ZnIn₂S₄ is a well known visible light active photocatalyst, it shows activity for hydrogen generation via H2S spitting under solar light. Here, we compared the activity of the ZnIn₂S₄ samples with respect to their morphologies. The sample synthesized in the absence of a capping agent (S1) which has a solid marigold flower-like morphology shows the lowest activity (8022 μ mol h⁻¹ g⁻¹). In the case of the PVP-assisted ZnIn₂S₄ sample (S2), porous marigold flowers with a hollow cavity are obtained. This could increase the overall surface area of the flower, which is responsible for obtaining a higher photocatalytic activity (8682 μ mol h⁻¹ g⁻¹) as compared to the solid flower (without a cavity). Finally, the sample synthesized using DEA assistance (S3) demonstrates the highest photocatalytic activity (8818 μ mol h⁻¹ g^{-1}). The error bar of the hydrogen evolution rate for these samples is mentioned in ESI Fig. SI-5.† A detailed discussion about the mechanism and effect of morphology on the activity is included in the ESI SI-E.†

Conclusions

In a nutshell, the effect of capping agents and their concentration on the morphology of $ZnIn_2S_4$ was observed. A solid marigold flower-like structure is observed without any capping agent, whereas higher concentration of PVP creates a hollow marigold flower-like structure. However, DEA assisted $ZnIn_2S_4$ shows self assembly of hexagonal plates *i.e.* a rose flower-like morphology. Furthermore, the photocatalytic activity for hydrogen generation under visible light irradiation using H_2S splitting has been demonstrated for these $ZnIn_2S_4$ morphologies. The rose-like $ZnIn_2S_4$ nanoflowers showed relatively high photocatalytic activity in comparison with the hollow marigold-like $ZnIn_2S_4$ nanoflowers.

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