Hierarchical 3D ZnIn$_2$S$_4$/graphene nano-heterostructures: their in situ fabrication with dual functionality in solar hydrogen production and as anodes for lithium ion batteries†

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Hierarchical 3D ZnIn$_2$S$_4$/graphene (ZnIn$_2$S$_4$/Gr) nano-heterostructures were successfully synthesized using an in-situ hydrothermal method. The dual functionality of these nano-heterostructures i.e. for solar hydrogen production and lithium ion batteries has been demonstrated for the first time. The ZnIn$_2$S$_4$/Gr nano-heterostructures were optimized by varying the concentrations of graphene for utmost hydrogen production. An inspection of the structure shows the existence of layered hexagonal ZnIn$_2$S$_4$ wrapped in graphene. The reduction of graphene oxide (GO) to graphene was confirmed by Raman and XPS analyses. The morphological analysis demonstrated that ultrathin ZnIn$_2$S$_4$ nanopetals are dispersed on graphene sheets. The optical study reveals the extended absorption edge to the visible region due to the presence of graphene and hence is used as a photocatalyst to transform H$_2$S into eco-friendly hydrogen using solar light. The ZnIn$_2$S$_4$/Gr nano-heterostructure that is comprised of graphene and ZnIn$_2$S$_4$ in a weight ratio of 1:99 exhibits enhanced photocatalytically stable hydrogen production i.e. ∼6365 μmol h$^{-1}$ under visible light irradiation using just 0.2 g of nano-heterostructure, which is much higher as compared to bare hierarchical 3D ZnIn$_2$S$_4$. The heightened photocatalytic activity is attributed to the enhanced charge carrier separation due to graphene which acts as an excellent electron collector and transporter. Furthermore, the usage of nano-heterostructures and pristine ZnIn$_2$S$_4$ as anodes in lithium ion batteries confers the charge capacities of 590 and 320 mA h g$^{-1}$ after 220 cycles as compared to their initial reversible capacities of 645 and 523 mA h g$^{-1}$, respectively. These nano-heterostructures show high reversible capacity, excellent cycling stability, and high-rate capability indicating their potential as promising anode materials for LIBs. The excellent performance is due to the nanostructuring of ZnIn$_2$S$_4$ and the presence of a graphene layer, which works as a channel for the supply of electrons during the charge–discharge process. More significantly, their dual functionality in energy generation and storage is quite unique and commendable.

1 Introduction

Graphene, a single layer of carbon arranged in a honeycomb structure has proved to be an exceptionally promising and versatile building block for the design of useful devices and materials because of its fascinating electronic, thermal and mechanical properties, high specific surface area, and easy fabrication from graphite.1 Of the many graphene-based materials that have been reported, those involving inorganic nanocrystals are of particular interest because such a hybrid system has led to many promising applications such as in sensors, photocatalysis, supercapacitors, lithium ion batteries (LIBs), and so on.2

Among all the ternary metal chalcogenides, recently, ZnIn$_2$S$_4$ has been utilized in photocatalysis, charge storage, and thermoelectric energy conversion due to its attractive physical and chemical properties.3–6 The band gap of ZnIn$_2$S$_4$ (2.34–2.48 eV) is well within the visible light region and hence has attracted great interest for visible light-driven photocatalytic degradation
of organic pollutants and water splitting to produce hydrogen.\textsuperscript{3,7,8} The hydrogen is produced from H\textsubscript{2}O or H\textsubscript{2}S splitting using various semiconductor photocatalysts under UV and visible light irradiation. The advantages of producing hydrogen by photocatalysis from highly toxic H\textsubscript{2}S splitting and its necessity are quite known.\textsuperscript{9–12} However, the photocatalytic hydrogen evolution activity over pure ZnIn\textsubscript{2}S\textsubscript{4} is low because of the poor separation efficiency and low migration ability of the photoexcited charge carriers. To enhance the photocatalytic performance of ZnIn\textsubscript{2}S\textsubscript{4}, a variety of efforts have been made, such as doping with metals (Cu, Ag, etc.) and incorporation of multiwalled carbon nanotubes (MWCNTs), GR (reduced graphene oxide) and polymers.\textsuperscript{13–17} Most of the previous studies have found that the hydrogen production performance of ZnIn\textsubscript{2}S\textsubscript{4} photocatalysts can be enhanced by the incorporation of a reasonable amount of graphene.\textsuperscript{15,18–20} Composites with few morphologies have been investigated and enhancement in hydrogen production has been discussed. However, only very limited studies on ZnIn\textsubscript{2}S\textsubscript{4} have been reported so far, hence it is very essential to explore further study for diversified applications. Therefore, graphene is considered to be a high performance support for photocatalysts. Consequently, this encouraged researchers to synthesize the ZnIn\textsubscript{2}S\textsubscript{4}/Gr composites to maximize the photocatalytic activity. Three dimensional hierarchical nanostructures are known for their high surface area, good porosity (due to layered assembly) and high photocatalytic performance. Hence, we synthesized hierarchical ZnIn\textsubscript{2}S\textsubscript{4}/Gr nano-heterostructures for photocatalytic solar hydrogen production. More significantly, considering the hierarchical nanostructure with three dimensional porous assembly of very thin layered nanoscale petals and its intimate contact with graphene, we were very curious to see its electrochemical performance in lithium ion batteries. Hence, the nano-heterostructure is sensibly used as an anode in lithium ion batteries (LIBs).

Currently, lithium-ion batteries (LIBs) are the most efficacious electrochemical energy storage devices due to their salient features such as high energy density, long cycle life and no memory effect.\textsuperscript{21} Nevertheless, the growth of LIBs is still unable to compete with the pace of fast encroachment of portable electronic devices. The further prolific research to improve the LIB technology has navigated to the discovery of a new storage mechanism (conversion reaction) in transition metal oxides and sulphides, which was originated by Poizot et al.\textsuperscript{22} Ensuing this discovery, metal sulfides such as MoS\textsubscript{2},\textsuperscript{23} CoS\textsubscript{2},\textsuperscript{24} CuS,\textsuperscript{25} SnS\textsubscript{2},\textsuperscript{26} etc. have attracted copious attention as the possible alternatives to carbonaceous anode materials due to their higher capacities. However, to the best of our knowledge, the ternary semiconductor chalcogenide, ZnIn\textsubscript{2}S\textsubscript{4} has not been studied as an anode material for LIBs. Being comprised with In\textsubscript{2}S\textsubscript{3}, this layered ternary semiconductor chalcogenide system (ZnIn\textsubscript{2}S\textsubscript{4}) can be a promising alternative. As In\textsubscript{2}S\textsubscript{3} has a defective layered structure with proven high theoretical capacity\textsuperscript{27} and ZnS has reversible lithium insertion/desertion with good stability,\textsuperscript{28} the phase pure ZnIn\textsubscript{2}S\textsubscript{4} has potential as an anode material. We have demonstrated the layered ZnIn\textsubscript{2}S\textsubscript{4} nanostructure with optical properties\textsuperscript{29,30} and were very curious to study transformation in its optical and electrical properties due to formation of nano-heterostructures with graphene. Hence, we have introduced hierarchical 3D ZnIn\textsubscript{2}S\textsubscript{4}/Gr nano-heterostructures with energy generation and storage functionalities i.e. for hydrogen production and as an anode for lithium ion batteries.

We have synthesized hierarchical 3D ZnIn\textsubscript{2}S\textsubscript{4}/Gr nano-heterostructures by an in-situ one pot hydrothermal method. Surprisingly, the nanopetals deposited onto the surface of graphene sheets with good intimacy. The enhanced solar hydrogen production from copious H\textsubscript{2}S with higher efficiency has been demonstrated for the first time. Sensibly, the nano-heterostructure has been demonstrated as an anode for Li-ion batteries (LIBs) which is hitherto unattempted. The prima facie observation shows a wider response in the visible region, higher photocatalytic activity and significantly improved Li-storage capacity and cycling stability than bare ZnIn\textsubscript{2}S\textsubscript{4}. The formation mechanism as well as electrochemistry of the nano-heterostructure has also been discussed.

### 2 Experimental methods

#### 2.1 Preparation of graphene oxide (GO)

Graphene oxide was prepared from graphite powder (99.99% S d fine) using the Hummers and Offeman method.\textsuperscript{31}

#### 2.2 Preparation of ZnIn\textsubscript{2}S\textsubscript{4}/Gr nano-heterostructures

ZnIn\textsubscript{2}S\textsubscript{4}/graphene nano-heterostructures were prepared by using a hydrothermal method. Analytical grade zinc nitrate (Zn(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O), indium nitrate (In(NO\textsubscript{3})\textsubscript{3}·3H\textsubscript{2}O) and thiourea were purchased from the local chemical manufacturer (Qualigene Chemicals) and used as received. In a typical synthesis, the as-prepared GO (1%) was dispersed in distilled water and ultrasonicated for half an hour [solution A]. The solutions of precursors Zn(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O (0.1 M), In(NO\textsubscript{3})\textsubscript{3}·3H\textsubscript{2}O (0.2 M) and thiourea (0.4 M) were prepared in distilled water and mixed together [solution B]. Then, solution B is slowly added into solution A followed by stirring for 30 min using a magnetic stirrer. The reaction mixture was then transferred into a Teflon-lined stainless-steel autoclave of 200 ml capacity. The autoclave was filled to 80% of its volume with distilled water and then tightened properly. The autoclave was then kept in an electric oven and maintained at a temperature of 150 °C for 30 h. After the stipulated time, the autoclave was allowed to cool in air before opening. A yellowish precipitate (GZIS2) thus obtained was washed with distilled water and ethanol several times and dried at 70 °C. The procedure is repeated with various amounts of GO (0.5 wt%, 1 wt%, 3 wt% and 5 wt%) to obtain ZnIn\textsubscript{2}S\textsubscript{4}/graphene nano-heterostructures in various proportions. The as-synthesised samples are named as per the graphene to ZnIn\textsubscript{2}S\textsubscript{4} wt% ratio (GZIS0 [0.5:99.5], GZIS2 [1:99], GZIS3 [3:97] and GZIS4 [5:95]). Bare ZnIn\textsubscript{2}S\textsubscript{4} (GZIS0) was synthesized without addition of GO. The other parameters for synthesis of GZIS0, GZIS1, GZIS3, and GZIS4 such as temperature, time and concentration were kept constant. These products were then subjected to XRD, UV-DRS, Raman, XPS, FTIR, FESEM, TEM and PL analyses for their characterization before using it for hydrogen generation.
2.3 Material characterization

The crystalline phases and the crystallite size of the photocatalyst were identified using the X-ray powder diffraction (XRD) technique (XRD-D8, Advance, Bruker-AXS) with Cu Kα radiation. The optical properties of the powder samples were studied using an UV-visible-near infrared spectrophotometer (UV-Vis-NIR, Perkin Elmer Lambda-950). Room temperature microRaman scattering (RS) was performed using a HR 800-Raman spectroscopy, Horiba Jobin Yvon, France, with excitation at 632.81 nm by a coherent He–Ne ion laser and a liquid nitrogen cooled CCD camera to collect and process the scattered data. The nature of chemical bonds formed in ZnIn2S4 and reduction of GO to GR were examined using a X-ray photoelectron spectroscopy (XPS, ESCA-3000, VG Scientific Ltd, England) with the base pressure greater than 1.0 × 10−9 Pa, and Mg Kα radiation (1253.6 eV) was used as an X-ray source operated at 150 W. FTIR spectra were recorded using a Nicolet Magna 550 spectrometer. The morphology of the GR/ZnIn2S4 nanostructures was characterized by field emission scanning electron microscopy (FE-SEM, Hitachi, S-4800) and high resolution transmission electron microscopy (HRTEM, JEOL, 2010F). For HRTEM studies, samples were prepared by dispersing the powder in acetone, followed by sonication in an ultrasonic bath for 2 min and then drop-casting the dispersion on a carbon coated copper grid and by subsequent drying in a vacuum. Photoluminescence (PL) emission spectra were recorded using a HORIBA-JY, F-3 fluorescence spectrophotometer, excited at 400 nm.

2.4 Photodecomposition of H2S

The cylindrical quartz photochemical reactor was filled with 200 ml of 0.25 M aqueous KOH and purged with argon for 1 h. Hydrogen sulphide (H2S) was bubbled through the solution for about 1 h at the rate of 2.5 ml min−1 at 299 K. 0.2 g of each photocatalyst, namely bare ZnIn2S4 (GZIS0) and ZnIn2S4/Gr (GZIS1–GZIS4) nanocomposites were, respectively, introduced one at a time into the reactor and irradiated with a visible light source Xe-lamp (300 W, LOT ORIEL GRUPPE, EUROPA, LSH302) using a cut-off filter λ ≥ 420 nm. The escaped hydrogen sulfide was trapped in a NaOH solution. The amount of hydrogen gas evolved was collected in a graduated cylinder and measured. The evolved hydrogen was then analyzed for its purity using a gas chromatograph (Model Shimadzu GC-14B, MS-5 Å column, TCD, Ar carrier). All the samples (GZIS0–GZIS4) were tested for their photocatalytic activity under identical conditions.

2.5 Electrochemical measurements

For electrochemical measurements, electrodes of ZnIn2S4 (GZIS0) and its nano-heterostructure with graphene (GZIS2) were fabricated using a slurry casting process. The slurry was prepared by mixing the active material (ZnIn2S4 or ZnIn2S4/graphene), Super P, and the binder at a weight ratio of 7.5 : 1.5 : 1. The resulting slurry was coated onto a copper foil (current collector) and dried overnight under vacuum at 70 °C. Furthermore, 2032 coin type cells were assembled in an argon filled glove-box. The Li metal was used as counter and pseudo-reference electrodes while the prepared electrode was a working electrode. A solution of 1 M LiPF6 dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1 : 1, v/v) was used as the electrolyte. The electrochemical properties of the obtained electrodes were investigated using cyclic voltammetry (CV) in the potential range of 0.0 to 3.0 V vs. Li/Li+ at a scan rate of 0.1 mV s−1 using a potentiostat (Gamry – PC-750). In addition, the cells were galvanostatically charged and discharged from 0.01 to 3 V vs. Li/Li+ using an automatic battery cycler (Won-A-Tech-WBCS 3000). The impedance analysis of the cells was conducted before and after charge–discharge cycling using an impedance analyzer (ZIVE SP2 instrument; Won-A-Tech) in the frequency range of 1 Hz–1 MHz with an amplitude of 10 mV. All experiments and tests were conducted at 25 °C.

3 Results and discussion

The structural study of nano-heterostructures was performed by XRD and the corresponding patterns are shown in Fig. 1. The diffraction peaks of bare hierarchical ZnIn2S4 (GZIS0) and ZnIn2S4/Gr (GZIS1–GZIS4) nano-heterostructures could be well indexed as a hexagonal ZnIn2S4 (JCPDS 72-0773) pertaining to the typical diffraction peaks of (006), (102), (108), (0012), (110) and (203) crystal planes at 2θ = 21.6°, 27.7°, 38.2°, 44.2°, 47.4° and 56.0°, respectively. The absence of impurity peaks corresponding to binary sulphides and oxides indicates the phase purity of the product. The XRD results revealed that graphene did not affect the crystal phase of ZnIn2S4. However, no diffraction peaks corresponding to either GO or graphene are observed in the XRD patterns of ZnIn2S4/Gr nanocomposites, which may be due to their low content.

The optical properties of bare ZnIn2S4 (GZIS0) and ZnIn2S4/Gr (GZIS1–GZIS4) nano-heterostructure samples have been determined from the UV-vis diffuse reflectance spectra (UV-DRS), shown in Fig. 2. The sample of bare hierarchical ZnIn2S4 shows as absorption edge at about 525 nm and its energy gap is estimated to be 2.4 eV.
Although the introduction of graphene into ZnIn$_2$S$_4$ does not obviously change the band gap of ZnIn$_2$S$_4$, absorbance in the visible-light region increases with increasing graphene content. This is quite well known\textsuperscript{32} and in agreement with the color change of the ZnIn$_2$S$_4$/Gr nanocomposites from yellow to dirty yellow with increasing graphene amount. Because of the increased absorbance, more efficient utilization of the solar energy can be realized. Therefore, we can infer that the introduction of graphene into ZnIn$_2$S$_4$ is effective for the visible-light response of the ZnIn$_2$S$_4$/Gr nano-heterostructures.

Raman spectroscopy is a powerful nondestructive tool to characterize carbonaceous materials, particularly for distinguishing the ordered and disordered states of carbon structures. The significant structural changes occurring during chemical processing from GO to graphene are also reflected in their Raman spectra. Thus, we characterized the GO, bare ZnIn$_2$S$_4$ (GZIS0), and ZnIn$_2$S$_4$/Gr (GZIS1–GZIS4) nano-heterostructures by Raman analysis and the results are shown in Fig. 3. The Raman spectrum displays two prominent peaks at around 1325 cm\textsuperscript{-1} and 1595 cm\textsuperscript{-1} which correspond to the disordered sp\textsuperscript{2} carbon (D-band) and the well-ordered graphite (G-band), respectively, suggesting that the structure of graphene is maintained in the heterostructure. The ratio of $I_D/I_G$ for the nano-heterostructures (GZIS1–GZIS4) is determined to be 1.18, 1.36, 1.17 and 1.14, much higher than that observed for the original GO (0.91). Since, the ratio of $I_D/I_G$ is an indicator of the degree of graphitization of carbonaceous materials, the higher $I_D/I_G$ observed for the as-prepared nano-heterostructures as compared to that of GO suggests a successful reduction of GO to graphene in the nano-heterostructures.\textsuperscript{33}

The reduction of GO to graphene and the electronic state of the ZnIn$_2$S$_4$/Gr (GZIS2) nano-heterostructure are shown in Fig. 4. Fig. 4a shows the high resolution C 1s spectrum of GO, where three peaks of C 1s can be de-convoluted. The peak at 284.6 eV is attributed to the sp\textsuperscript{2} carbon atom (C–C, C–C and C–H groups), while the peak at 286.7 eV is assigned to the C from the C–O and C=O groups.\textsuperscript{34} The peak located at 288.5 eV is closely associated with the O=C–OH species.\textsuperscript{35} Compared with the C 1s spectrum of GO, the peaks of C=O–H, C=O and O=C–OH for the GZIS2 sample still exist with decreased peak intensity, implying the substantial reduction of GO after the hydrothermal reaction (Fig. 4b). Meanwhile, a new peak at 287.6 eV can be observed, which is attributed to the Zn–O–C bond.\textsuperscript{36} As shown in Fig. 4c–e, the characteristic binding energy of 1045.5 eV for Zn\textsuperscript{2+} 2p\textsubscript{3/2}, 445.0 eV for In\textsuperscript{3+} 3d\textsubscript{5/2}, 452.6 eV for S\textsuperscript{2–} 3p\textsubscript{2} are observed in the XPS spectra of the GZIS2 nano-heterostructure. Additionally, the average O/C atomic ratio of the Gr/ZnIn$_2$S$_4$ (GZIS2) sample is 0.21 which is much smaller than 0.37 for pure GO. The decrease of the O/C atomic ratio further confirms the partial reduction of GO. The presence of a small amount of hydrophilic groups on the surface of graphene, such as hydroxyl and carboxyl, can be helpful to enhance the photocatalytic activity.\textsuperscript{37} Furthermore, evidence for the degree of reduction of oxygen functional groups is confirmed from the FT-IR spectra of GO and ZnIn$_2$S$_4$/Gr (GZIS1–GZIS4) nano-heterostructures.

The FT-IR spectrum of GO shows C–O (1739 cm\textsuperscript{-1}), C–C (1623 cm\textsuperscript{-1}), O–H (1417 cm\textsuperscript{-1}) and C–O (1049 cm\textsuperscript{-1}) (Fig. S1a, ESI†).\textsuperscript{18,38} Furthermore, in Fig. S1b–e (ESI†), the peak at 1739 cm\textsuperscript{-1} which is assigned to the C–O vibration observed in GO totally disappeared in GZIS1–GZIS4 nano-heterostructures, while that at 1052 cm\textsuperscript{-1} significantly decreases, indicating that GO has been successfully reduced to graphene during the synthesis process.\textsuperscript{20,39} The above XPS, Raman and IR studies as well as our recent report\textsuperscript{12} firmly show the presence of graphene.

Field emission scanning electron microscopy (FE-SEM) and high resolution transmission electron microscopy (HR-TEM) have been used to analyze the ZnIn$_2$S$_4$/Gr nano-heterostructure (GZIS2)
as shown in Fig. 5. Fig. 5a shows the FESEM images of bare hierarchical ZnIn$_2$S$_4$ (GZIS0), in which most of the nanosheets are curled and stacked with each other. Bare ZnIn$_2$S$_4$ (Fig. 5a) shows the hierarchical 3D nanostructured marigold flowers of 4–8 μm in diameter, which is an assembly composed of numerous thin nanopetals with the thickness of few nanometers (1–2 nm). It is very difficult to mount petals vertically so that we could not measure the thickness of petals. Fig. 5b shows the typical wavy GO sheets. When GO is added during the synthesis of the ZnIn$_2$S$_4$/Gr (GZIS2) nano-heterostructure, the morphology of the as-synthesized ZnIn$_2$S$_4$/Gr nano-heterostructures is little different from that of bare ZnIn$_2$S$_4$ (Fig. 5c). Surprisingly, the hierarchical porous layered nanostructure with graphene has been observed. From Fig. 5a and c, we can clearly see the ultrathin curled ZnIn$_2$S$_4$ nanopetals grown on the graphene sheet (looks like a honeycomb porous structure) and the average length of ZnIn$_2$S$_4$ nanopetals is about 50 nm and above. This implies that graphene can act as a structure directing agent transforming ZnIn$_2$S$_4$ micro-flowers into a micro-porous assembly via the growth of very ultrathin nanopetals. A more enlightening feature of the ZnIn$_2$S$_4$/Gr nanopetal structure can be seen from HRTEM images (Fig. 5d–g). The ultrathin ZnIn$_2$S$_4$ nanopetals are interconnected with each other on the graphene sheet to form a ZnIn$_2$S$_4$/Gr nano-heterostructure (Fig. 5d and e).

The clear lattice-fringe spacing of 0.321 nm can be assigned to the (102) plane of hexagonal ZnIn$_2$S$_4$ (Fig. 5f). The selected area electron diffraction (SAED) pattern shown in Fig. 5g indicates that the ZnIn$_2$S$_4$/Gr nano-heterostructures possess a polycrystalline structure. The electron diffraction dots can be indexed as the (110), (102) and (006) planes of the hexagonal phase of ZnIn$_2$S$_4$. These observations are consistent with the XRD results (Fig. 1). The formation mechanism of ZnIn$_2$S$_4$/Gr nano-heterostructures is illustrated in Scheme 1.

GO is prepared by Hummer’s method via pristine graphite (Scheme 1b), and Zn(NO$_3$)$_2$, In(NO$_3$)$_3$ and thiourea were mixed in distilled water for the synthesis of the ZnIn$_2$S$_4$/Gr nanocomposite (GZIS2). During ultrasonic pretreatment, (Scheme 1c) van der Waals interactions between the GO layers are overpowered leading to the separation of GO sheets. It is well known that GO has lots of hydrophilic functional groups (e.g. –OH, –COOH) on its surface, which can act as the adsorption sites for Zn$^{2+}$ and In$^{3+}$ cations$^{20,40}$ (Scheme 1d). These surface adsorbed cations can further react with S$_2$–/C$_0$ anions to form ZnIn$_2$S$_4$ nuclei on the surface of graphene which is shown in Scheme 1e. Due to the intrinsic lamellar structure of the hexagonal ZnIn$_2$S$_4$ phase$^{41}$, the as-formed ZnIn$_2$S$_4$ nuclei exhibit one dimensional growth and led to the formation of nanopetals on the surface of GR as the reaction continued to 30 h (Scheme 1f and g).

![Fig. 4](image_url) High resolution XPS patterns of (a) C 1s of GO (b) C 1s, (c) Zn 2p, (d) In 3d, and (e) S 2p for GZIS2.

![Fig. 5](image_url) FESEM images of (a) bare ZnIn$_2$S$_4$ (GZIS0), (b) GO, and (c) GZIS2; TEM images (d–f) and (g) SAED pattern of (GZIS2).

![Scheme 1](image_url) Schematic representation of the formation mechanism of the ZnIn$_2$S$_4$/Gr nano-heterostructure.
The overall formation reaction of hexagonal layered ZnIn$_2$S$_4$ using zinc and indium precursors and thiourea under hydrothermal conditions is explained as follows.

\[
\text{Zn(NO}_3\text{)}_2 + 2\text{In(NO}_3\text{)}_3 + 8(\text{NH}_2\text{)CS} + 16\text{H}_2\text{O} \\
\rightarrow \text{ZnIn}_2\text{S}_4 + 8\text{HNO}_3 + 8\text{CO}_2 + 16\text{NH}_3 + 4\text{H}_2\text{S} \quad (1)
\]

The degree of ionization of zinc and indium nitrates is relatively higher in polar solvents like water and hence petite nuclei are formed in the supersaturated solution and further growth of nanoparticles occurs with time (Scheme 1e). These new nanoparticles impulsively agglomerated to minimize their surface energy which further grow anisotropically along the 2D directions and confer thin nanopetals.

Finally, these nanopetals grow larger and denser (Scheme 1f) along with the reduction of GO, simultaneously.\(^{18}\)

GO is reduced to graphene by ammonia released from the decomposition of thiourea.\(^{12}\) Finally, these ZnIn$_2$S$_4$ nanopetals grew larger and interconnect with each other possibly via chemisorption to form the ZnIn$_2$S$_4$/Gr nano-heterostructure. The growth of nanopetals and its hierarchical vertical assembly resembles a honeycomb-like structure predominantly positioned on graphene (Fig. 5c). Such a unique nano-heterostructure has porosity as well as layers along the graphene with good intimacy. This nano-heterostructure offers a larger surface area with more number of active sites. Considering the unique properties of the ZnIn$_2$S$_4$/Gr nano-heterostructure, it has been used as a photocatalyst for H$_2$S splitting for hydrogen production under solar light and as an anode in lithium ion batteries for the first time.

3.1 Photocatalytic hydrogen evolution

The photocatalytic activity of the bare hierarchical nanostructured ZnIn$_2$S$_4$ (GZIS0) and ZnIn$_2$S$_4$/Gr (GZIS1–GZIS4) nano-heterostructure samples for hydrogen generation via photodecomposition of H$_2$S was performed. Table 1 shows the hydrogen evolution rate from the photodecomposition of H$_2$S using bare ZnIn$_2$S$_4$ (GZIS0) and ZnIn$_2$S$_4$/Gr (GZIS1–GZIS4) nano-heterostructures. Fig. 6 shows the time dependent hydrogen evolution of all the samples. The linearity of the graph clearly shows the stable hydrogen production. Control experiments indicated that no appreciable hydrogen production was detected in the absence of irradiation of the photocatalyst, suggesting that hydrogen was produced only through photocatalytic reactions on the photocatalyst surface.

The photocatalytic activity of bare ZnIn$_2$S$_4$ (GZIS0) showed a lower hydrogen evolution rate, i.e. \(\sim 4012\ \mu\text{mole h}^{-1}\) while the

\[\text{ZnIn}_2\text{S}_4/\text{Gr (GZIS1–GZIS4) nano-heterostructures showed 6076, 6365, 5844 and 5263 \mu\text{mole h}^{-1}, respectively. The maximum H}_{2}\text{ evolution (i.e. 6365 \mu\text{mole h}^{-1}) was obtained for the GZIS2 sample. When the amount of incorporated graphene exceeds 1.0 wt%, the photocatalytic hydrogen evolution rate over ZnIn}_2\text{S}_4/\text{Gr (GZIS3–GZIS4) decreases. This is mainly due to the fact that the relatively high weight ratio of graphene in ZnIn}_2\text{S}_4/\text{Gr nano-heterostructures (GZIS3–GZIS4) would increase the opacity and shield light, lowering the efficiency of light passing through the depth of the reaction solution, thus leading to decreased photoactivity. This is also called a light ‘shielding effect’ and has been widely observed in Gr–semiconductor composite photocatalysts.}^{12,37,42–44}\]

Therefore, similar to other graphene/semiconductor nanocomposites, an appropriate graphene loading amount is required to achieve the utmost photocatalytic activity. As seen from Fig. 6, graphene has a significant influence on the photocatalytic activity of ZnIn$_2$S$_4$/Gr nano-heterostructures.

However, the overall ZnIn$_2$S$_4$/Gr sample i.e. GZIS2 shows higher activity among the reported metal oxide and sulfide semiconductors studied so far.\(^{12,45,46}\) Based on the above results, it is obvious that a suitable amount of graphene can significantly improve the photocatalytic performance including the activity and the stability of ZnIn$_2$S$_4$/Gr nano-heterostructures as compared with bare ZnIn$_2$S$_4$.

The major reaction steps in this mechanism under visible-light irradiation are described in the following equations:

\[
\text{H}_2\text{S} + \text{OH}^- \rightarrow \text{HS}^- + \text{H}_2\text{O} \quad (2)
\]

\[
\text{Semiconductor ZnIn}_2\text{S}_4/\text{graphene} \\
\rightarrow \text{ZnIn}_2\text{S}_4 (\text{h}^+)_{\text{VB}} + \text{graphene (e}^-)_{\text{CB}} \quad (3)
\]

\[
\text{Oxidation reaction: 2HS}^- + \text{ZnIn}_2\text{S}_4 (2\text{h}^+)_{\text{VB}} \rightarrow 2\text{S} + 2\text{H}^+ \quad (4)
\]

\[
\text{Reduction reaction: 2H}^+ + \text{graphene (2e}^-)_{\text{CB}} \rightarrow \text{H}_2 \quad (5)
\]
The possible photocatalytic mechanism of ZnIn$_2$S$_4$/Gr is systematically described in Scheme 2. Under visible light irradiation; electrons are excited from the valence band (VB) of ZnIn$_2$S$_4$ to the conduction band (CB) which creates holes in the VB. These photo-generated electrons in the CB of ZnIn$_2$S$_4$ tend to transfer to graphene leading to electron–hole separation. These free transferred electrons react with protons and form hydrogen. Because of the excellent conductivity of graphene, the introduction of graphene can benefit the charge transfer in the ZnIn$_2$S$_4$/Gr nano-heterostructure and thus lower the charge recombination.$^{37}$

This can be verified by the photoluminescence (PL) spectra. The PL spectra of the as-prepared bare ZnIn$_2$S$_4$ (GZIS0) and ZnIn$_2$S$_4$/Gr (GZIS1–GZIS-4) nano-heterostructures are shown in Fig. 7. The excited wavelength is determined to be 400 nm and the bare ZnIn$_2$S$_4$ has a strong emission peak at about 550 nm. The PL intensities of ZnIn$_2$S$_4$/Gr (GZIS1–GZIS4) nano-heterostructures decreased with the addition of graphene. Among all the samples, the lowest photoluminescence intensity was observed for the GZIS2 sample, leading to the spatial separation of electrons and holes. We therefore conclude that the enhanced photocatalytic activity of the GZIS2 sample is mainly attributed to more effective charge separation through trap (h$^+$) formation in ZnIn$_2$S$_4$ and transportation (e$^-$) to graphene i.e. lowers the recombination of electrons and holes. The lowering of the recombination effect can also be explained by considering the energy level diagram of the ZnIn$_2$S$_4$/Gr nano-heterostructure, as shown in Scheme 2. The conduction band of ZnIn$_2$S$_4$ can be shown at $-0.84$ V while the valence band would be at 1.56 V (vs. NHE).$^{47}$ The Fermi level of graphene (0.08 V vs. NHE)$^{48}$ is more positive than the conduction bands of ZnIn$_2$S$_4$, which means that the photogenerated electrons can transfer from the CB of ZnIn$_2$S$_4$ to graphene. In the next step, the electrons derived from the CB of ZnIn$_2$S$_4$ to graphene are further transported to substrate H$^+$ ions to form H$_2$. Therefore, the synergetic effect of (1) the extended visible light absorption edge due to incorporation of graphene, (2) the efficient use of high charge carrier transport properties of graphene which is in close contact with ZnIn$_2$S$_4$ and (3) suitable positions of ZnIn$_2$S$_4$ and graphene in the energy band diagram leads to efficient charge separation and subsequent decomposition of H$_2$S to produce H$_2$ under visible light irradiation. More significantly, the hierarchical nanostructure is an assembly of thin nanosheets or petals which are more likely to have layered features with graphene. The hierarchical nanostructures of ZnIn$_2$S$_4$ (thin petals) have more surface in intimate contact with graphene which accelerate the easy and fast electron transport.

These layered features are possible only with a moderate amount of graphene. Further increasing the amount of graphene reduces the layered feature due to stacking of graphene and favors the shielding effect as discussed above. Hence, the hierarchical nanostructure and their heterostructures have significance in enhancing the hydrogen production. The stability of the prepared ZnIn$_2$S$_4$/Gr (GZIS2) photocatalyst was investigated by recycling the GZIS2 sample for the hydrogen generation by H$_2$S splitting (Fig. S2, ESI†). The photodecomposition of H$_2$S was repeated for three successive cycles (each for 7 h). No significant decrease in the photocatalytic activity was observed during the consecutive cycles, which indicates the better stability of the prepared GZIS2 photocatalyst. The XRD, Raman and XPS analyses of the recycled catalyst (GZIS2) did not show any change in the phase purity and the amount of graphene content, which implies good stability of the catalyst (Fig. S3–S5, ESI†). Overall, we observed that the ZnIn$_2$S$_4$/Gr (GZIS2) nano-heterostructure was found to be an efficient photocatalyst for solar hydrogen production from H$_2$S and are hitherto un-demonstrated.

### 3.2 Electrochemical study

After studying the structural, morphological and electronic properties of the hierarchical ZnIn$_2$S$_4$/Gr nano-heterostructure, in addition to hydrogen production, we have also examined the applicability of the bare hierarchical ZnIn$_2$S$_4$ and the
nano-heterostructure showing excellent hydrogen production performance i.e. GZIS2 for Li ion battery application. The electrochemical properties of the hierarchical ZnIn$_2$S$_4$/Gr nano-heterostructure is evaluated by cyclic voltammetry at a scanning rate of 0.1 mV s$^{-1}$ in the potential range from 3.0 to 0.01 V vs. Li$^+$/Li (Fig. 8b), initially. For comparison, we have also presented the results of bare hierarchical ZnIn$_2$S$_4$ (Fig. 8a) prepared by the same procedure under the same electrochemical conditions. For the GZIS0 electrode, in the first cathodic scan, the peaks at 1.6 and 0.95 correspond to the reduction of ZnIn$_2$S$_4$ to metallic In and Zn, and the formation of Li$_2$S (reaction (6)). Another broad cathodic peak between 0.6 and 0.05 V was observed in the first cathodic scan, which is due to subsequent reaction of lithium ions with Zn and In metals (reaction (7)). There may be formation of a solid electrolyte interface (SEI) film on the surface of the electrode during the first cathodic scanning process, which is responsible for the irreversible capacity. On the other hand, in the case of GZIS2 (Fig. 8b), shifting of the peaks at a lower potential but with increased current are observed. In addition the broad peak in the potential range 0.3–0.5 V vs. Li/Li$^+$ is believed to associate with the formation of Li$_x$In alloys such as Li$_x$In$_{1.5}$, Li$_x$In$_{2.5}$, Li$_x$In$_{3}$, and xLi$_x$Zn$_{3-x}$. Furthermore, the peak at 0.0 V can be ascribed to the conversion of Li$_x$Zn to LiZn. The increase in the current for all the reactions is attributed to the increased electron conduction by the usage of graphene as a current collector.

\[
\begin{align}
\text{ZnIn}_2S_4 + 8\text{Li}^+ + 8e^- & \rightarrow \text{Zn} + \text{In} + 4\text{Li}_2S & (6) \\
\text{Zn} + x\text{Li} + xe^- & \rightarrow \text{Li}_x\text{Zn} & (7) \\
\text{In} + x\text{Li} + xe^- & \rightarrow \text{Li}_x\text{In} & (8)
\end{align}
\]

During the anodic scanning process, 4 peaks for each GZIS0 and GZIS2 are observed in the potential range 0.4–1.9 V, which indicates that Li is delithiated in several steps. It is presumed that the peak at 0.5 V is due to delithiation from the Zn alloy, whereas the peak at higher 0.65 V is due to delithiation from Li$_x$In. The additional oxidation peaks in the voltage range 1.05–2.4 V are due to multistep regeneration of zinc sulphide and indium sulphide. The reactions during the anodic scan are expressed in eqn (9)–(12). From the second cycle, there is a decline in some individual peaks of both the samples leading to losses in the reversible capacity. In the subsequent discharge–charge processes, the cathodic and anodic peaks are stable, which indicates that the Li$_x$Zn and Li$_x$In alloying and dealloying are reversible. These results indicate that GZIS0 and GZIS2 show several phases with an increase in the lithium content.

\[
\begin{align}
\text{Li}_x\text{In} & \rightarrow \text{In} + x\text{Li}^+ + xe^- & (9) \\
2\text{In} + 3\text{Li}_2S & \rightarrow \text{In}_2\text{S}_3 + 6\text{Li}^+ + 6e^- & (10) \\
\text{Li}_x\text{Zn} & \rightarrow \text{Zn} + x\text{Li}^+ + xe^- & (11) \\
\text{Zn} + \text{Li}_2S & \rightarrow \text{ZnS} + 2\text{Li}^+ + 2e^- & (12)
\end{align}
\]

Fig. 9 shows the typical galvanostatic cycling profile of the bare nanostructured ZnIn$_2$S$_4$ (GZIS0) and the ZnIn$_2$S$_4$/Gr nano-heterostructure (GZIS2) at a specific current of 100 mA g$^{-1}$. For the GZIS2 electrode, we can see two obvious potential plateaus in the discharge process at about 1.4 V and 0.9 V (vs. Li/Li$^+$), which might be due to the reduction reactions of In$^{3+}$ to In$^{2+}$ and In$^{2+}$ to In$^0$, respectively, whereas the potential plateau in the range of 0.6–0.9 V (vs. Li/Li$^+$) corresponds to the lithiation process of ZnS. A similar potential plateau can also be seen in the charge–discharge profile of the GZIS0 electrode. Considering the plateau potential observed for GZIS0 and GZIS2 electrodes, the contribution of the lithiation reaction for In$_2$S$_3$ and ZnS to the total discharge capacity can be realized. The first discharge and charge capacities are 1134 and 523 mA h g$^{-1}$ for the GZIS0 electrode and 1106 and 645 mA h g$^{-1}$ for the GZIS2 nano-heterostructure. The initial loss observed in the capacity of both the electrodes is due to the incomplete conversion reaction and irreversible loss of lithium ions due to the formation of the SEI film. For appraisal, the charge–discharge curve for baseline graphene is given in Fig. S6 (ESI†). The reversible capacity for baseline graphene is observed to be 300 mA h g$^{-1}$. Considering the amount of graphene (1%) in the ZnIn$_2$S$_4$/graphene composite, its contribution in the reversible capacity of the nano-heterostructure is quite small and can be neglected.

The cycling properties of the ZnIn$_2$S$_4$/Gr nano-heterostructure (GZIS2) and the bare ZnIn$_2$S$_4$ (GZIS0), at current densities of 75 mA g$^{-1}$ and 150 mA g$^{-1}$ are shown in Fig. 10a. For some
materials activation is needed to achieve a stable cycle life at higher current density. Hence in the present work, first 25 cycles at a lower current density in the cycling data are obtained for the activation of the materials and then the material is cycled at a higher current density to determine the cyclability of the material. A much better cycling stability of the composites\textsuperscript{53} and significantly improved capacity can be observed for the ZnIn\textsubscript{2}S\textsubscript{4}/graphene nano-heterostructure electrode.

In Fig. 10a, the capacities of GZIS2 are higher than those of GZIS0, which might be attributed to (1) the presence of ZnIn\textsubscript{2}S\textsubscript{4} nanopetals between graphene sheets effectively preventing the agglomeration of graphene sheets and consequently retaining their high active surface area which is favorable for increasing the Li\textsuperscript{+} storage capacity of the composites\textsuperscript{53} and (2) the flexible graphene provides a large contact surface area and acts as a scaffold for the growth of a ZnIn\textsubscript{2}S\textsubscript{4} nanopetal porous structure, which further not only alleviates the volume change during the charge–discharge reaction but also efficiently prevents the pulverization of electrode materials upon continuous cycling.\textsuperscript{2,54}

After 25 cycles at an applied current of 75 mA g\textsuperscript{-1}, the reversible charge capacities are 603 and 465 mA h g\textsuperscript{-1} for GZIS2 and GZIS0 electrodes, respectively. Interestingly, it is noted that both the electrodes, when cycled at a higher current of 150 mA g\textsuperscript{-1}, attain the maximum and minimum of 424 and 454 mA h g\textsuperscript{-1} for GZIS0 and GZIS2, respectively, at the 100\textsuperscript{th} cycle. The charge capacities recorded for GZIS2 and GZIS0 after 220 cycles are 590 mA h g\textsuperscript{-1} and 320 mA h g\textsuperscript{-1}, compared to their initial reversible capacities of 645 and 523 mA h g\textsuperscript{-1}, respectively. The decline in capacity during the first few cycles might be due to an activation of porous materials, which is caused by the trapping of lithium ions in the ZnIn\textsubscript{2}S\textsubscript{4} frameworks in the initial cycles and then released gradually upon cycling.\textsuperscript{55,56}

Furthermore, the increase in the charge storage capacity after 130 cycles is observed for GZIS2. The process may be assigned to the gradual access of more electrolyte molecules into the meso-and micro-pores of the active material. The porous structure formed by the growth of curled nanopetals on the graphene surface provides the extra space, allowing storage of more lithium ions, which further buffers the large volume change to some extent and decrease the lithium ions’ diffusion distance simultaneously, leading to an improvement in the cycling capacity retention upon extended cycling.\textsuperscript{57,58} Moreover the electrochemical grinding can reduce the particle size of ZnIn\textsubscript{2}S\textsubscript{4} with the number of cycles, increasing the resultant surface area available for the Li-storage reaction, and hence an increment in the capacity even after 130 cycles.

It is also seen that the capacity retained by the ZnIn\textsubscript{2}S\textsubscript{4}/graphene nano-heterostructure (92\%) is higher than the bare nanostructured ZnIn\textsubscript{2}S\textsubscript{4} (61\%) after 220 cycles, corroborating the stability of the composite at higher applied current. Furthermore, to investigate the reversibility of the material, the coulombic efficiency was calculated as shown in Fig. 10b. The coulombic efficiency of bare ZnIn\textsubscript{2}S\textsubscript{4} and the ZnIn\textsubscript{2}S\textsubscript{4}/Gr nano-heterostructure in the first cycle was observed to be 46 and 59\%, respectively. The coulombic efficiency of GZIS2 in the first cycle was higher than that of GZIS0. The synergetic effect of graphene sheets and ZnIn\textsubscript{2}S\textsubscript{4} petals is responsible for the excellent electrochemical properties of the overall electrode via the maximum utilization of electrochemically active graphene and ZnIn\textsubscript{2}S\textsubscript{4} petals. After few cycles, the coulombic efficiency of GZIS2 reaches 99\%, indicating good reversibility of the ZnIn\textsubscript{2}S\textsubscript{4}/Gr nano-heterostructure.

Fig. 9 First discharge–charge profile of a Li-ion battery half-cell containing bare ZnIn\textsubscript{2}S\textsubscript{4} (GZIS0) and the ZnIn\textsubscript{2}S\textsubscript{4}/graphene nano-heterostructure (GZIS2).

Fig. 10 (a) Specific capacity and (b) coulombic efficiency of bare ZnIn\textsubscript{2}S\textsubscript{4} (GZIS0) and the ZnIn\textsubscript{2}S\textsubscript{4}/graphene nano-heterostructured (GZIS2) electrode with cycling.
Fig. 11 shows the rate performance of the ZnIn$_2$S$_4$/Gr nano-heterostructure anode at different specific current values of 75, 150, 300, 600, 1200, 2400, and 4800 mA g$^{-1}$. For comparison, the rate performance of the bare nanostructured ZnIn$_2$S$_4$ anode was also tested under the same conditions. Furthermore, to avoid the induced effect due to the activation of the electrode, the cells cycled at 75 mA g$^{-1}$ for 10 cycles were used for the rate capability test. The GZIS2 electrode exhibited good rate capability with the average charge capacities of 625, 550, 495, 435, 368, 324, and 275 mAh g$^{-1}$ at specific current values of 75, 150, 300, 600, 1200, 2400 and 4800 mA g$^{-1}$, respectively. Interestingly, the small decrease in charge capacity was found at high specific current values of 2400 and 4800 mA g$^{-1}$, and the electrode maintained 52% (2400 mA g$^{-1}$) of the initial charge capacity. On the other hand, the average charge capacities obtained for GZIS0 are 509, 410, 326, 300, 264, 235 and 196 at specific current values of 75, 150, 300, 600, 1200, 2400 and 4800 mA g$^{-1}$, respectively. Moreover, the GZIS2 electrode nearly recovered its original charge capacity, when the current returned to the initial value (75 mA g$^{-1}$). The excellent discharge capacity at high specific current is attributed to the porous nature of the ZnIn$_2$S$_4$/Gr nano-heterostructure, which provides the pathway for the diffusion of electrolyte and the high conductivity of graphene allows fast electronic kinetics at high applied current. The specific capacity of the GZIS2 nano-heterostructure is enhanced, and their cycling stability and rate capability are also significantly improved. In order to understand the reason behind the superior electrochemical properties of the ZnIn$_2$S$_4$/Gr nano-heterostructure compared to that of nanostructured ZnIn$_2$S$_4$, ac impedance measurements are performed before and after cycling (Fig. 12).

As shown in Fig. 12, for the electrode after cycle, the high-frequency semicircle corresponds to the internal resistance $R_i$ of the SEI film, and the semicircle in the medium frequency region is assigned to the charge-transfer resistance $R_{ct}$ of the electrode/electrolyte interface. The inclined line corresponds to the lithium-diffusion process within the bulk of the electrode material. It can be seen that the SEI film resistance $R_i$ and the charge-transfer resistance $R_{ct}$ of the GZIS2 electrode are 24 and 17 Ω, which are significantly lower than those of GZIS0 (38 and 30 Ω) after 220 cycles. Moreover, the GZIS2 electrode exhibited a larger initial resistance than the resistance after cycling, suggestive of the activation and enhanced kinetics of the reaction. Those facts confirm that the incorporation of graphene can preserve the high conductivity of the ZnIn$_2$S$_4$/Gr nano-heterostructure electrode and greatly enhance rapid electron transport during the electrochemical lithium insertion/extraction reaction, resulting in significant improvement in the electrochemical properties. This novel kind of ZnIn$_2$S$_4$/Gr nano-heterostructure with high reversible capacity, excellent cyclic stability, and high-rate capability would find wide applications as a promising anode material for LIBs. Surprisingly, the naked hierarchical nanostructured pristine ZnIn$_2$S$_4$ itself showed good performance for the first time and is also better as compared to the reported ZnS and In$_2$S$_3$. The culprit is the hierarchical nanostructured layered structure of ZnIn$_2$S$_4$. The puffy flowers have a very porous structure due to nanopetal 3D assembly. This may accelerate the lithium intercalation which leads to good charged capacity. Curiously, the attempt at nano-heterostructures also leads to an enhanced charge capacity with good cyclability and high reversible capacity. The presence of ZnIn$_2$S$_4$ nanopetals between graphene sheets effectively prevents the agglomeration of graphene sheets and consequently retains their high active surface area, which is favorable for increasing the Li$^+$ storage capacity of the composites. The vertical growth of petals in between graphene (looks like honeycombs) may also serve as channels for lithium intercalation. As discussed above, graphene has provided sites for the growth of ZnIn$_2$S$_4$ nanopetals forming a porous structure, which further acts as a buffer space to accommodate the volume expansion/contraction of active materials during the Li$^+$ insertion/extraction process and also efficiently prevents the pulverization of electrode materials upon continuous cycling.
heterostructure, GZIS2 (1:99), showed a high H₂-production rate. The dispersion of ZnIn₂S₄ over the entire graphene sheet is believed to result from efficient electron transport during the charge–discharge process. In addition, the existence of a graphene layer, which works as a channel for the supply of electrons during the charge–discharge process, has been fabricated by an in situ hydrothermal method. The single step method is quite eco-friendly without any surfactant and toxic reducing agents. The reduction of GO and the growth of ZnIn₂S₄ on graphene sheets was performed simultaneously. This nano-heterostructure is used for efficient visible-light active hydrogen production by H₂S splitting which is hitherto un-attempted. The as-prepared ZnIn₂S₄/Gr nano-heterostructure, with considerable stability. Considering the hierarchical porous nanostructured pristine ZnIn₂S₄ shows good layered 3D nanostructure. The excellent performance of the sample is due to the nanostructure of ZnIn₂S₄ and the presence of a graphene layer, which works as a channel for the supply of electrons during the charge–discharge process. In addition, the dispersion of ZnIn₂S₄ over the entire graphene sheet is believed to improve the performance of the material.

4 Conclusions

In a nutshell, a series of hierarchical 3D ZnIn₂S₄/Gr nano-heterostructures with different percentages of graphene have been fabricated by an in situ hydrothermal method. The single step method is quite eco-friendly without any surfactant and toxic reducing agents. The reduction of GO and the growth of ZnIn₂S₄ on graphene sheets was performed simultaneously. This nano-heterostructure is used for efficient visible-light active hydrogen production by H₂S splitting which is hitherto un-attempted. The as-prepared ZnIn₂S₄/Gr nano-heterostructure, GZIS2 (1:99), showed a high H₂-production rate i.e. ~ 6365 μmole h⁻¹ which is much higher than the pristine ZnIn₂S₄. The enhanced hydrogen evolution is due to efficient charge transfer and charge carrier separation due to graphene. The results demonstrate that the nano-heterostructure is an excellent material for H₂-production activity under solar light with considerable stability. Considering the hierarchical porous and layered structure, it has also been demonstrated as an anode for LIBs for the first time. The ZnIn₂S₄/graphene nano-heterostructure exhibits 645 mA h g⁻¹ for the initial cycle and 590 mA h g⁻¹ after 220 cycles, with high specific capacity, superior cyclability, and excellent rate capability, thereby corroborating its use as an anode material for LIBs. The naked hierarchical nanostructured pristine ZnIn₂S₄ itself shows good performance in lithium ion batteries due to the hierarchical layered 3D nanostructure. The excellent performance of the sample is due to the nanostructure of ZnIn₂S₄ and the presence of a graphene layer, which works as a channel for the supply of electrons during the charge–discharge process. In addition, the dispersion of ZnIn₂S₄ over the entire graphene sheet is believed to improve the performance of the material.

Conflicts of interest

The authors hold no financial conflicts of interest.

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