Hierarchical Sheet-on-Sheet ZnIn$_2$S$_4$/g-C$_3$N$_4$ Heterostructure with Highly Efficient Photocatalytic H$_2$ production Based on Photoinduced Interfacial Charge Transfer

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We have realized in-situ growth of ultrathin ZnIn$_2$S$_4$ nanosheets on the sheet-like g-C$_3$N$_4$ surfaces to construct a “sheet-on-sheet” hierarchical heterostructure. The as-synthesized ZnIn$_2$S$_4$/g-C$_3$N$_4$ heterojunction nanosheets exhibit remarkably enhancement on the photocatalytic activity for H$_2$ production. This enhanced photoactivity is mainly attributed to the efficient interfacial transfer of photoinduced electrons and holes from g-C$_3$N$_4$ to ZnIn$_2$S$_4$ nanosheets, resulting in the decreased charge recombination on g-C$_3$N$_4$ nanosheets and the increased amount of photoinduced charge carriers in ZnIn$_2$S$_4$ nanosheets. Meanwhile, the increased surface-active-sites and extended light absorption of g-C$_3$N$_4$ nanosheets after the decoration of ZnIn$_2$S$_4$ nanosheets may also play a certain role for the enhancement of photocatalytic activity. Further investigations by the surface photovoltage spectroscopy and transient photoluminescence spectroscopy demonstrate that ZnIn$_2$S$_4$/g-C$_3$N$_4$ heterojunction nanosheets considerable boost the charge transfer efficiency, therefore improve the probability of photoinduced charge carriers to reach the photocatalysts surfaces for highly efficient H$_2$ production.

Photocatalytic H$_2$ production through water splitting or reduction has received great attention in recent years, since it offers an economical and environmentally friendly strategy to convert solar energy into preservable chemical fuels for mitigating the excessive consumption of non-sustainable fossil fuels such as coal, petroleum and natural gas. To date, various kinds of UV- or visible-response semiconductors, such as TiO$_2$, ZnO, Cu$_2$O, CdS, and so forth, have been developed as photocatalysts for H$_2$ production due to their suitable band potential and catalytic functions. Besides these traditional semiconductor photocatalysts, a large number of semiconducting materials, including metal-organic frameworks (MOFs), polyoxometalate (POM), and metal free compounds, are also being introduced as potential candidates for the new generation of photocatalysts to fulfill the photocatalytic water reduction and oxidation. Among them, the two-dimensional (2D) layered polymer, graphitic carbon nitride (g-C$_3$N$_4$), is considered as the most promising visible-light-active photocatalyst because of its unique electronic structure, high stability, nontoxic nature, and low cost. However, the photocatalytic activity on H$_2$ production over single-component g-C$_3$N$_4$ so far is unsatisfactory due to its limited surface areas, poor light-harvesting efficiency and fast recombination of photoinduced charge carriers. To overcome the above drawbacks, much effort has been devoted to the construction of multi-component heterostructural photocatalysts through coupling other visible-active semiconductor with g-C$_3$N$_4$ nanosheets, in which the heterogeneous interfaces can effectively assist the photoinduced charge-carriers migration and hinder these charge-carriers recombination to enhance the photocatalytic efficiency. Moreover, the surface structures and light-harvesting...
behavior can be also promoted through tailoring the secondary nanostructures of heterostructural photocatalysts. Therefore, design and architecture of g-C3N4-based heterostructural photocatalysts with the matchable bandgap, desired component, and hierarchical nanostructures is still the hot topics in the field of solar-to-fuels conversion.

As an important ternary chalcogenide semiconductor, hexagonal phase ZnIn2S4 with 2D layered structure and narrow bandgap has been extensively investigated in photocatalysis, especially serving as the photosynergistic components in heterojunction photocatalysts. The viewpoint of band structure, the bandgap of ZnIn2S4 (Eg = ~2.6 eV) is smaller than that of g-C3N4 (Eg = ~2.8 eV) while the conduction band (CB) of ZnIn2S4 (ECB = −1.0 V) is higher than that of g-C3N4 (ECB = −1.1 V). Accordingly, when integrating of ZnIn2S4 nanostructure with g-C3N4 nanosheets, a “type I” heterojunction would be formed in their interface, meaning that the CB and valence band (VB) positions of g-C3N4 straddle those of ZnIn2S4. As such, the ZnIn2S4 can be seemed as a “charge sink” to accept the photoinduced charge carriers from adjacent g-C3N4, leading to the improvement of charge separation on g-C3N4 and thereby enhancing its photocatalytic activity. On the other hand, the 2D sheet-like ZnIn2S4 nanostructures could be easily anchored onto the active or flexible 2D substrates, such as F-doped SnO2 (FTO) thin film and reduced graphene oxide (RGO) nanosheets, to form the “sheet-on-sheet” type heterostructure. This kind of hierarchical nanostructure usually exhibits a high surface area, strong light harvesting, and efficient charge mobility due to its unique structure advantages.

The above analysis implies that once the ZnIn2S4 nanosheets combine with g-C3N4 nanosheets, a significant enhancement on photocatalytic H2 production may be realized through synergistic promotion on the inner charge carriers and outer hierarchical structures. However, little effort has been donated to the synthesis of ZnIn2S4/g-C3N4 heterostructure toward the highly efficient photocatalytic H2 production. Herein, we report a novel kind of “sheet-on-sheet” heterostructure synthesized through in-situ growth of ultrathin ZnIn2S4 nanosheets onto g-C3N4 nanosheets surfaces. After introducing the ZnIn2S4 nanosheets, the specific surface area of g-C3N4 nanosheets is obviously promoted, resulting in providing the more active sites for the photoreaction. Furthermore, the intimate contacted interface between the ZnIn2S4 and g-C3N4 nanosheets facilitates the photoinduced charge-carriers transfer from g-C3N4 to ZnIn2S4 based on the heterojunction effect. By taking of the above features, the as-synthesized ZnIn2S4/g-C3N4 heterojunction nanosheets exhibit a significantly enhanced visible-light photocatalytic H2 production performance as compared to the single component of ZnIn2S4 or g-C3N4 nanosheets.

Results
X-ray diffraction (XRD) patterns of the as-synthesized samples are shown in Fig. 1. Two pronounced diffraction peaks appear at 13.1° and 27.4° for g-C3N4 nanosheets, reflecting to the periodic structure of intra-planar tri-s-triazine packing as the (100) peak, and the interlayer stacking of conjugated aromatic structures as the (002) peak for graphitic materials, respectively. The diffraction peaks of ZnIn2S4 nanosheets can be perfectly indexed as a pure hexagonal phase of ZnIn2S4 (JCPDS No. 65–2023). In the case of ZnIn2S4/g-C3N4 heterojunction nanosheets, the XRD pattern shows diffraction peaks of both ZnIn2S4 and g-C3N4 nanosheets, while the feature peaks of ZnIn2S4 (27.7°) and g-C3N4 (27.4°) are very close and overlap with each other. Note that the diffraction peaks of ZnIn2S4 nanosheets are very weak. This phenomenon may be ascribed to two reasons: (1) the ultrathin 2D nanostructure of ZnIn2S4, leading to the ultra-small size in its c-axis orientation; (2) the low content of ZnIn2S4 component in the heterostructure. Besides, after introducing the ZnIn2S4 by hydrothermal method, the (100) diffraction peak of g-C3N4 becomes more intense, and its position shifts toward the lower diffraction angle (10.8°) (Figure S1). This reveals that some metal ions from ZnIn2S4 surfaces may be connected with the g-C3N4 through the lone-pair electrons of nitrogen in the “nitrogen pots”, thus leading to enlarging the intra-planar separation of ordered tri-s-triazine packing. Moreover, some weak peaks corresponded to the
intermediates of thermal polymerized g-C3N4 are also detected on the XRD pattern of ZnIn2S4/g-C3N4 heterojunction nanosheets, implying that a small part of g-C3N4 nanosheets might be further exfoliated (or reduced) into the structural units of g-C3N4, such as melamine, ammeline, or tri-s-triazine units, due to the longer reaction time for hydrothermal growth of ZnIn2S4 onto g-C3N4 nanosheets16,36.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were performed to directly observe the morphologies and structures of the ZnIn2S4/g-C3N4 heterojunction nanosheets in comparison with the single component of ZnIn2S4 and g-C3N4 nanosheets, as displayed in Fig. 2. The thermal polymerized g-C3N4 shows a bulk structure with smooth surfaces (Fig. 2A), which can be easily exfoliated into the wrinkled sheet-like nanostructures by the ultrasonic treatment in methanol solution (Fig. 2D). Figure 2B reveals significant aggregation of the nanosheets into microspheres with the average diameter of ~1.5 μm for the hydrothermally synthesized ZnIn2S4 sample. Interestingly, when introducing the as-fabricated g-C3N4 nanosheets as the substrates during the hydrothermal process, the ZnIn2S4/g-C3N4 heterojunction nanosheets could be achieved in the form of “sheet-on-sheet” structure (Figure S2 and Figure S3). As observed in Fig. 2C, the layered surfaces of g-C3N4 nanosheet are covered with the high density of secondary ZnIn2S4 nanosheets. These nanosheets with uniformly ultrathin 2D-structure are connected and even across to each other, finally forming the sheet-like networks vertically aligned on the g-C3N4 nanosheet surface. This kind of unique hierarchical heterostructure (65.9 m2 g−1) shows much higher specific-surface-area than the general sheet-like structure for pure g-C3N4 (12.8 m2 g−1), thereby providing more active sites for the photocatalytic reaction.(Figure S4) Moreover, the interspaces among interweaved ZnIn2S4 nanosheets on the g-C3N4 nanosheets may also boost the light-harvesting behavior of this hierarchical heterostructure though the multi-reflection processes on the incident electromagnetic waves25,26,29.

TEM image of the ZnIn2S4/g-C3N4 heterojunction nanosheets further confirms that the ultrathin ZnIn2S4 nanosheets with thickness of 4~9 nm are vertically grown onto the g-C3N4 nanosheets surface (Fig. 2E and Figure S3). Figure 2F presents the high-resolution (HR) TEM of an individual ZnIn2S4 nanosheet on g-C3N4 surface, in which the lattice-fringe spacing of 0.41 nm appeared on the side view (perpendicular sheet) can be assigned to the (006) crystal plane of hexagonal ZnIn2S4, while the top view (planar sheet) image shows the interplanar distances of 0.32 nm, belonging to the d-spacing of (102) planes of hexagonal ZnIn2S4. In short, intimate contacted heterojunctions between ZnIn2S4 and g-C3N4 nanosheets are indeed constructed by the in-situ growth process, which may be beneficial for the photoinduced interfacial charge-transfer from g-C3N4 to ZnIn2S4.

Figure 3A presents the Fourier transform infrared (FT-IR) spectra of the as-synthesized ZnIn2S4/g-C3N4 heterojunction nanosheets along with the single ZnIn2S4 and g-C3N4 nanosheets for the purpose of structure comparison. The stretching vibration bands on the spectra of g-C3N4 nanosheets show characteristics similar to those of the reported results13,16,21,23. Accordingly, the peaks appeared between 1200 cm−1 and 1650 cm−1 are attributed to the stretching vibration modes of CN heterocycles. The peak located at 3200 cm−1 is originated to the NH stretching vibration mode, while the 811 cm−1 to the feature vibration mode of s-triazine ring unit. For the ZnIn2S4 sample, only two peaks at 1396 cm−1 and 1610 cm−1, belonging to the surface hydroxyl groups
and absorbed water molecules, can be observed on the FT-IR spectrum. After the growth of ZnIn$_2$S$_4$ nanosheets onto g-C$_3$N$_4$ surfaces, the heterojunction nanosheets show the typical stretching vibration modes of both ZnIn$_2$S$_4$ and g-C$_3$N$_4$ nanosheets. Besides, a series of new vibration bands can be detected simultaneously on the spectrum of ZnIn$_2$S$_4$/g-C$_3$N$_4$ nanosheets, which are in agreement with the vibration bands of melamine and/or ammeline. This further suggests that during the long-time hydrothermal process, a few number of g-C$_3$N$_4$ nanosheets were exfoliated (or reduced) into the sub-structures of g-C$_3$N$_4$. To study in-depth the chemical configurations of the as-synthesized samples, the X-ray photoelectron spectroscopy (XPS) analyses were performed. As observed in Fig. 3B, three main peaks with the binding energies at 284.6 eV, 285.7 eV, and 287.9 eV can be found on the C 1s core-level spectrum of g-C$_3$N$_4$ nanosheets, which are assigned to sp$^2$ C-C bonds of graphitic carbon, sp$^3$-coordinated carbon bonds, and sp$^2$-bonded carbon (N-C = N) of the s-triazine rings, respectively. The binding energy for the C 1s peak at 284.6 eV can be attributed to the adventitious carbon species on the samples and the carbon-containing contaminants, which was used as the reference for calibration. The N 1s signal of g-C$_3$N$_4$ nanosheets also shows three feature peaks, corresponding to the sp$^2$-bonded N (C-N = C) (398.1 eV), tertiary nitrogen N-(C$_3$) groups (399.2 eV), and amino groups (C-N-H) (400.7 eV). Investigations found that the relative intensity of the peaks relating to the N-C = N and C-N = C groups of g-C$_3$N$_4$ nanosheets are decreased after hydrothermal treatment for a long time, indicating that some of the tri-s-triazine units of g-C$_3$N$_4$ were distorted during this process. Meanwhile, when introducing the ZnIn$_2$S$_4$ nanosheets onto g-C$_3$N$_4$ nanosheets to form the heterojunction, both the C 1s and N 1s characteristic signals of g-C$_3$N$_4$ nanosheets shift slightly toward the higher binding energy side. On the contrary, the binding energies of Zn 2p (1022.0 eV for 2p$_{3/2}$ and 1045.5 eV for 2p$_{1/2}$), In 3d (444.9 eV for 3d$_{5/2}$ and 452.5 eV for 3d$_{3/2}$), and S 2p (161.5 eV for 2p$_{3/2}$ and 162.6 eV for 2p$_{1/2}$) for the ZnIn$_2$S$_4$/g-C$_3$N$_4$ heterojunction nanosheets are a little lower than the corresponding values for the pure ZnIn$_2$S$_4$ nanosheets, as shown in Fig. 3D–F. The binding energy shifts for the heterojunction components could be explained by a strong interaction between ZnIn$_2$S$_4$ and g-C$_3$N$_4$ nanosheets. Theoretically, the enhancement

Figure 3. (A) FT-IR spectra of the as-synthesized samples: (a) g-C$_3$N$_4$ nanosheets, (b) 15 wt% ZnIn$_2$S$_4$/g-C$_3$N$_4$ heterojunction nanosheets, and (c) ZnIn$_2$S$_4$ nanosheets; XPS spectra of the as-synthesized samples: (B) C 1s core-level spectra; (C) N 1s core-level spectra: (a) g-C$_3$N$_4$ nanosheets, (b) 15 wt% ZnIn$_2$S$_4$/g-C$_3$N$_4$ heterojunction nanosheets; (D) Zn 2p core-level spectra; (E) In 3d core-level spectra; (F) S 2p core-level spectra: (b) 15 wt% ZnIn$_2$S$_4$/g-C$_3$N$_4$ heterojunction nanosheets, and (c) ZnIn$_2$S$_4$ nanosheets.
of binding energy means the weakened electron screening effect caused by the decreased electron concentration, while the increase in electron concentration leads to the decrease of binding energy due to the promoted electron screening effect. Thus, in this case, it is reasonable to conclude that the higher and lower binding energy shifts are ascribed to the decreased electron concentration of g-C3N4 nanosheets and increased electron concentration of ZnIn2S4 nanosheets due to the strong interaction between the g-C3N4 to ZnIn2S4 nanosheets based on the interfacial charge transfer.

The optical properties of the as-synthesized samples were investigated through UV-vis absorption spectra which converted from the corresponding diffuse reflectance (DR) spectra by means of the Kubelka-Munk function. As shown in Fig. 4, the absorption edges of g-C3N4 and ZnIn2S4 nanosheets appears at ~443 and ~476 nm, corresponding to the band energies of ~2.8 and ~2.6 eV, respectively. These values are consistent with the reported values of g-C3N4 and ZnIn2S4 nanosheets15,17–19,28,33,34. In the case of ZnIn2S4/g-C3N4 heterojunction nanosheets, two obvious absorption bands ascribed to the characteristic absorption of g-C3N4 and ZnIn2S4 nanosheets can be found on the absorption curve of Fig. 4b. Moreover, the absorption peaks of ZnIn2S4 nanosheets become more intense with increase of ZnIn2S4 content in the heterojunction nanosheets (Figure S5), further confirming that the ZnIn2S4/g-C3N4 heterojunction nanosheets with controllable component contents were obtained.

Discussion
Photocatalytic H2 production activities of the as-synthesized samples were evaluated under visible light (λ > 400 nm) irradiation by using triethanolamine (TEOA) as the sacrificial reagent to quench the photoinduced holes. The H2 production rates of pure g-C3N4 nanosheets, pure ZnIn2S4 nanosheets, and ZnIn2S4/g-C3N4 heterojunction nanosheets with various ZnIn2S4 ratios are summarized in Fig. 5A, in which the heterojunction nanosheets show the enhanced H2 production rates as compared to the single heterojunction components. It implies that in situ growth of ZnIn2S4 nanosheets onto g-C3N4 nanosheets could noticeably improve the photocatalytic activities on H2 production. Even with only 2.5 wt% ZnIn2S4 nanosheets, the heterojunction nanosheet displays a H2 production rate of 5.2 μmol h−1, which is more than 6 times higher than that of pure g-C3N4 nanosheets (0.8 μmol h−1). The poor photoactivity of g-C3N4 nanosheets for the H2 production is mainly ascribed to its limited light-harvesting efficiency and fast recombination of photoinduced charge carriers18,19. The optimal photocatalytic activity was achieved on 15 wt% ZnIn2S4 with a H2 production rate of 14.1 μmol h−1. This value is ~17.6 times higher than that of pure ZnIn2S4 nanosheets. Accordingly, the apparent quantum efficiency of this optimal sample is estimated as 0.28% under irradiation at 420 nm. Note that only 5 mg of 15 wt% ZnIn2S4/g-C3N4 heterojunction nanosheets was used for H2 production in our work. However, when the ZnIn2S4 content is higher than 15 wt%, a further increase in ZnIn2S4 content (20 wt%) leads to a rapid decrease in the photocatalytic activity for H2 production. This photoactivity reduction can be attributed to the increased opacity (so-called shield effect), resulting in a decrease of irradiation passing through the suspension photoreaction solution12,25,29,31,40,41. As observed in Fig. 5B, the significant enhancement of photocatalytic activity for the heterojunction sample can be further confirmed by the time-dependent H2 production behaviors. It could be found that the H2 production amounts linearly increases with the irradiation time. After visible light irradiation for 2h, the H2 production yield of 15 wt% ZnIn2S4-decorated g-C3N4 nanosheet could reach 28.2 μmol, which is greatly superior to the pure g-C3N4 and ZnIn2S4 nanosheets. The enhanced photocatalytic performance on H2 production could be explained by two main reasons: (1) the reduced recombination process of photoinduced charge carriers on g-C3N4 and increased amount of charge carriers on ZnIn2S4 based on the interfacial charge transfer; (2) the higher specific-surface-area and enhanced light absorption for
the unique “sheet-on-sheet” heterostructure as aforementioned. However, it should be pointed out that in comparison with the pure ZnIn$_2$S$_4$ nanosheets (132.0 m$^2$ g$^{-1}$), the heterojunction nanosheets (65.9 m$^2$ g$^{-1}$) show the lower specific-surface-area, but the higher photoactivity. Meanwhile, the g-C$_3$N$_4$ nanosheets treated by the hydrothermal process in the absence of ZnIn$_2$S$_4$ precursor show a lower photocatalytic H$_2$ production rate (0.41 μmol/h) as compared to the pure (untreated) g-C$_3$N$_4$ nanosheets (Figure S6), because of the poor photoactivities of the exfoliation or reduction of g-C$_3$N$_4$ with the ultra-small structures, such as melamine, ammeline, or tri-s-triazine units$^{16,36}$. These observations also the indirect evidence that the dynamics process of photoinduced charge transfer occurring on the interface between the ZnIn$_2$S$_4$ and g-C$_3$N$_4$ nanosheets may be crucial to the photocatalytic H$_2$ production activities of heterojunction nanosheets. At low ZnIn$_2$S$_4$ content, a well dispersion of ZnIn$_2$S$_4$ nanosheets on the g-C$_3$N$_4$ nanosheets could be formed. In this way, the increase of ZnIn$_2$S$_4$ content would induce more ZnIn$_2$S$_4$ nanosheets assembled onto the g-C$_3$N$_4$ surface, which generates larger contact area between the ZnIn$_2$S$_4$ and g-C$_3$N$_4$ nanosheets, thereby allowing more efficient interfacial charge transfer. However, excess ZnIn$_2$S$_4$ loading causes considerable reduction of light absorption for the covered g-C$_3$N$_4$, and decreases its excitation process for interfacial charge transfer. Therefore, a balance would be built between ZnIn$_2$S$_4$ loading amount and ZnIn$_2$S$_4$/g-C$_3$N$_4$ contact area, which can maximize the photocatalytic H$_2$ production for the heterojunction nanosheets. Through the sequential remediation of heterojunction components, we concluded an optimal loading of 15 wt% ZnIn$_2$S$_4$ onto g-C$_3$N$_4$, which exhibited the highest photocatalytic activity in our work.

Besides, this optimal ZnIn$_2$S$_4$/g-C$_3$N$_4$ heterojunction nanosheets also shows fairly stable photoactivity for H$_2$ production. In Fig. 5C, the H$_2$ production rate remains consistent even at the prolonged time period for 12 h. Meanwhile, the recycling ability for the 15 wt% ZnIn$_2$S$_4$/g-C$_3$N$_4$ heterojunction nanosheets was further studied by performing a three-run test of photocatalytic H$_2$ production. Figure 5D shows that no notable decreases

Figure 5. (A) Photocatalytic H$_2$ production under visible light irradiation over (a) g-C$_3$N$_4$ nanosheets; (e) 15 wt% ZnIn$_2$S$_4$/g-C$_3$N$_4$ heterojunction nanosheets, and (g) ZnIn$_2$S$_4$ nanosheets; (B) comparison of visible-light-driven H$_2$ production rate over different samples: (a) g-C$_3$N$_4$ nanosheets, (b) 2.5 wt%, (c) 5 wt%, (d) 10 wt%, (e) 15 wt%, (f) 20 wt% ZnIn$_2$S$_4$/g-C$_3$N$_4$ heterojunction nanosheets, and (g) ZnIn$_2$S$_4$ nanosheets; (C) photocatalytic H$_2$ production curve with prolonged irradiation time over 15 wt% ZnIn$_2$S$_4$/g-C$_3$N$_4$ heterojunction nanosheets; (D) cycling test of photocatalytic H$_2$ production over 15 wt% ZnIn$_2$S$_4$/g-C$_3$N$_4$ heterojunction nanosheets.
of H₂ evolution were detected during the three-run test, powerfully verifying the good stability of 15 wt% ZnIn₂S₄/g-C₃N₄ heterojunction nanosheets for using as the photocatalysts.

To provide more evidence on the photoinduced charge transfer occurring in the heterojunction interface, the surface photovoltage spectroscopy (SPS) and photoluminescence (PL) spectroscopy of ZnIn₂S₄/g-C₃N₄ heterojunction nanosheets were investigated in comparison with those of pure g-C₃N₄ nanosheets. As shown in the inset of Fig. 6A, a poor response appears on the SPS curve of pure g-C₃N₄ nanosheets, indicating very low efficiency on the photovoltaic conversion. However, the photon absorption and conversion processes have been proven by the photoelectrochemistry in our previous work. Thus, the low photovoltage of g-C₃N₄ nanosheets can be attributed to the Schottky interface contact between the g-C₃N₄ and ITO glass in the absence of electrolyte, which leads to the limited electron transfer process from the g-C₃N₄ to ITO glass electrode. After decoration of ZnIn₂S₄ onto g-C₃N₄ nanosheets, the SPS signal in the region from 300 to 450 nm is remarkably enlarged, suggesting the promoted charge generation and separation based on the semiconductor heterojunction effect. This phenomenon can be further understood through the steady-state and transient PL spectroscopy. In Fig 6B, the pure g-C₃N₄ nanosheet shows a strong emission peak with the center at ~450 nm. However, as compared to the g-C₃N₄ nanosheets, the emission process of ZnIn₂S₄/g-C₃N₄ heterojunction nanosheets suppresses significantly, revealing either the faster migration process with the shorter lifetime or the slower recombination process with the longer lifetime for the photoinduced charge carriers. To shed more light on this issue, we tried to fit the time-resolved transient PL spectroscopy based on the multi-exponential kinetics function expressed as follow:

\[
I(t) = A_1 \cdot \exp(-t/\tau_1) + A_2 \cdot \exp(-t/\tau_2)
\]

where \(\tau_1\) and \(\tau_2\) are the fluorescent lifetime, and \(A_1\) and \(A_2\) are the corresponding amplitudes. As listed in the insets of Fig. 6C,D, the short lifetime component for \(\tau_1\) is originated from the nonradiative recombinatin of charge-carriers in the defect states of g-C₃N₄, while the longer lifetime component for \(\tau_2\) is caused by the free excitons recombinatin in the g-C₃N₄ body. In the case of ZnIn₂S₄/g-C₃N₄ heterojunction nanosheets, the emission lifetime for the component \(\tau_1\) (3.3 ns) is longer than the corresponding lifetime of g-C₃N₄ nanosheets (3.1 ns), while its component \(\tau_2\) (12.3 ns) is shorter than the component for g-C₃N₄ nanosheets (14.7 ns). To gain further understanding on this phenomenon, the average emission lifetimes, relating to the overall emission decay behaviors of the samples, were also evaluated through the following equation:

\[
\frac{1}{\tau} = \frac{A_1}{\tau_1} + \frac{A_2}{\tau_2}
\]
\[ \tau_A = \frac{A_1 \cdot \tau_1^2 + A_2 \cdot \tau_2^2}{A_1 \cdot \tau_1 + A_2 \cdot \tau_2} \]

It is clearly that after loading the ZnInS₂ nanosheets, the average lifetime of g-C₃N₄ nanosheets is shortened from 10.45 ns to 8.97 ns. The combination of decreased emission lifetime and quenched PL indicates the emergence of a nonradiative pathway from the electron transfer between ZnInS₂ and g-C₃N₄ nanosheets. According to the energy band structures of these semiconductors (Fig. 6E), it could be deduced that the photoinduced electrons transfer from the conduction band (CB) of g-C₃N₄ to the CB of ZnInS₂ nanosheets. This assumption is in agreement with the emission quenching phenomenon of g-C₃N₄ nanosheets after decorating the ZnInS₂ nanosheets. The rate constant for the interfacial electron-transfer (kₑ) can be estimated by the expression:

\[ k_e(g-C_3N_4 \rightarrow ZnInS_2) = \frac{1}{\{\tau_A\}_{ZnInS_2(g-C_3N_4)}} - \frac{1}{\{\tau_A\}_{g-C_3N_4}} \]

Obviously, the \( k_e \) value is approximately \( 1.6 \times 10^7 \) S⁻¹. As illustrated in Fig. 6E, the CB and valence band (VB) positions of g-C₃N₄ straddle those of ZnInS₂, forming the “type I” heterojunction interface. When this heterojunction is excited by visible light with the photon energy higher or equal to the band gaps of both ZnInS₂ and g-C₃N₄ nanosheets, the photoinduced electrons and holes of g-C₃N₄ nanosheets would move to the CB and VB of ZnInS₂ nanosheets, respectively. As such, the recombination process on the photoinduced charge carriers of g-C₃N₄ could be suppressed effectively by the photosynergistic effect of ZnIn₂S₄/g-C₃N₄ heterojunction. Accordingly, the amount of photoinduced charge carriers on ZnInS₂ is remarkably increased based on the photoinduced interfacial charge transfer. During the photocatalytic H₂ production process, the photoinduced electrons accumulated on the CB of ZnInS₂ could initiate the catalytic proton reduction to H₂. Accordingly, the photoinduced holes transfer from the VB of g-C₃N₄ to the VB of ZnInS₂ were quenched by the sacrificial reagent of TEOA (or directly quenched by the sacrificial reagent on the VB of g-C₃N₄). In this way, the effective charge transfer at the interface between the ZnInS₂ and g-C₃N₄ nanosheets results in the enhanced photocatalytic activity on H₂ production.

In summary, a series of ZnIn₂S₄/g-C₃N₄ heterojunction nanosheets with various contents of ZnInS₂ have been successfully synthesized through in-situ growth of ultrathin ZnInS₂ nanosheets onto g-C₃N₄ nanosheets fabricated by a traditional thermal polymerization and followed ultrasonic dispersion method. The unique “sheet-on-sheet” heterostructure obtained by vertically loading ZnInS₂ nanosheets onto the g-C₃N₄ fabricated by a traditional thermal polymerization and followed ultrasonic dispersion method. The unique “sheet-on-sheet” heterostructure obtained by vertically loading ZnInS₂ nanosheets onto the g-C₃N₄ nanosheets surfaces leads to the enlarged reactive sites and enhanced light absorption ability. More importantly, the formation of “type I” heterojunction can effectively suppress the photoinduced charge recombination of g-C₃N₄ through the interfacial charge transfer, as evidenced by the electron microscopic analyses, steady-state and time-resolved transient photoluminescence decay investigations. As a result, the ZnInS₂/g-C₃N₄ heterojunction nanosheets exhibited considerable enhancement on the photocatalytic activity for H₂ production as compared the single component nanosheets. It is believed that our study provides a promising strategy to develop the new generation of hierarchical heterostructure photocatalysts for highly efficient solar-to-fuels conversion and environmental remediation.

**Methods**

**Materials synthesis.** The graphitic carbon nitride (g-C₃N₄) was obtained by a traditional thermal polymerization method. 10g of melamine powder was grinded for 60 min in a mortar and then transferred to an alumina crucible with a cover. Afterward, the crucible was heated to 550 °C with a rising rate of 20 °C min⁻¹ and kept for 2 h at the required temperature under semiclosed environment, resulting in the bulk g-C₃N₄ with faint-yellow color. ZnInS₂/g-C₃N₄ heterojunction nanosheets were synthesized by in-situ growth of ultrathin ZnInS₂ nanosheets onto g-C₃N₄ nanosheets through the interfacial charge transfer, as evidenced by the electron microscopic analyses, steady-state and time-resolved transient photoluminescence decay investigations. As a result, the ZnInS₂/g-C₃N₄ heterojunction nanosheets exhibited considerable enhancement on the photocatalytic activity for H₂ production as compared the single component nanosheets. It is believed that our study provides a promising strategy to develop the new generation of hierarchical heterostructure photocatalysts for highly efficient solar-to-fuels conversion and environmental remediation.

**Characterization methods.** X-ray diffraction (XRD) patterns of the as-synthesized samples were measured by a Shimadzu XRD-6000 X-ray diffractometer with a Cu Ka line of 0.1541 nm. Scanning electron microscopy (SEM; XL-30 ESEM FEG, Micro FEI Philips) and transmission electron microscopy (TEM; JEOL JEM-2100) were employed to observe the morphologies and structures of the samples. Energy dispersive X-ray (EDX)
The sandwich structured photovoltage cell.

the process, the sample was put between the indium tin oxide (ITO) glass and stainless steel electrodes to form a

spectroscopy being attached to scanning electron microscopy (SEM) was used to analyze the composition of products. Fourier transform infrared (FT-IR) spectra were recorded on a Magma 560 FT-IR spectrometer with a resolution of 1 cm−1. X-ray photoelectron spectroscopy (XPS) was carried out on a VG-ESCALAB LKII instrument with a Mg Kα ADES (hν = 1253.6 eV) source at a residual gas pressure below 10−9 Pa. UV-vis diffuse reflectance spectra (DRS) were taken with a Lambda 750 UV/Vis/NIR spectrophotometer (Perkin Elmer, USA). The specific surface areas of the products were measured with a Micromeritics ASAP-2020 instrument and analyzed by the Brunauer–Emmett–Teller (BET) method. Decay curves of the as-fabricated products were obtained on a FLS920 fluorescence lifetime spectrophotometer (Edinburgh Instruments, UK) under the excitation of a hydrogen flash lamp with the wavelength at 325 nm (nF900; Edinburgh Instruments). The surface photovoltage spectroscopy (SPS) was performed on PL-SPS1000 instrument (Beijing Perfectlight Technology Co., Ltd). During the process, the sample was put between the indium tin oxide (ITO) glass and stainless steel electrodes to form a sandwich structured photovoltage cell.

Photocatalytic H2 production. The photocatalytic H2 production tests were performed in a 35-mL quartz reactor. Typically, 5 mg of the as-synthesized samples were suspended in 10-mL triethanolamine (TEOA, 15 vol%) aqueous solution. This suspension was sealed in the quartz reactor by a rubber plug, and then purged with argon gas for half an hour to drive away the residual air. Subsequently, the reactor was exposed under a 300-W Xe lamp (PLS-SXE300UV) coupled with a 400 nm cut-off filter. The gas product composition from the upper space above the liquid in the quartz reactor was periodically analyzed by a gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) (Beifen-Ruili Analytical Instrument, SP-3420A). The apparent quantum efficiency (QE) was estimated by using the following equation.

\[ AQE = \frac{2 \times \text{number of evolved hydrogen molecules}}{\text{number of incident photons}} \times 100\% \]

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