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Self-surface charge exfoliation and electrostatically coordinated 2D hetero-layered hybrids

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At present, the technological groundwork of atomically thin two-dimensional (2D) hetero-layered structures realized by successive thin film epitaxial growth is in principle constrained by lattice matching prerequisite as well as low yield and expensive production. Here, we artificially coordinate ultrathin 2D hetero-layered metal chalcogenides via a highly scalable self-surface charge exfoliation and electrostatic coupling approach. Specifically, bulk metal chalcogenides are spontaneously exfoliated into ultrathin layers in a surfactant/intercalator-free medium, followed by unconstrained electrostatic coupling with a dissimilar transition metal dichalcogenide, MoSe₂, into scalable hetero-layered hybrids. Accordingly, surface and interfacial-dominated photocatalysis reactivity is used as an ideal testbed to verify the reliability of diverse 2D ultrathin hetero-layered materials that reveal high visible-light photoreactivity, efficient charge transfer and intimate contact interface for stable cycling and storage purposes. Such a synthetic approach renders independent thickness and composition control anticipated to advance the development of 'design-and-build' 2D layered heterojunctions for large-scale exploration and applications.

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Ultimate two-dimensional (2D) anisotropy with atomically thick layered structure is both an ideal low-dimensional system for fundamental study and an elemental building block for designed assembly^{1–10}. Elaborate functionalities can rationally be tailored with precise molecular scale control through artificial assembly based on judicious selection and coordination of heterogeneous counterparts^{11–14}. Intriguing surface effects and physical–chemical properties have gradually been uncovered in 2D hetero-layered materials owing to their large surface-to-volume ratio and confined thickness at an atomic scale^{15–18}. The 2D materials, specifically metal chalcogenides, possess exquisite photo- and electrochemical capabilities that include energy storage batteries/supercapacitors and energy conversion photo/electrocatalysis systems^{10,19,20}. Unlike electronic transistor devices, these applications generally require large quantities of 2D hetero-layered materials. Though a wide variety of 2D layered semiconductor materials have been exfoliated into individual layers, these layered materials typically undergo large extent of swelling phase induced by intercalator or solvation species^{21–23}. Realization of high-volume exfoliation with ultrathin sheet-like crystallite in a facile manner and clean medium still remains scarce. Moreover, the issue of lattice mismatching hinders composition customization of heterostructures owing to the ineffective direct epitaxial growth of some mismatched metal chalcogenide materials. Collectively, all the aforementioned issues limit the scalability of 2D ultrathin hetero-layered metal chalcogenides towards fundamental exploration and advanced functional applications.

Herein, we readily exfoliate the metal chalcogenide semiconductor ZnIn₂S₄ into single-unit-cell layered structure (ca. 2.5 nm) via a self-surface charge exfoliation in pure water medium. Successive electrostatic coupling with another transition metal chalcogenide (for example, MoSe₂) enables construction of arbitrary ultrathin hetero-layered hybrids in a large scale. Such an approach offers salient features, that is, independent thickness and composition control of individual layer assembly, and no constraint by lattice matching prerequisite into functional ultrathin heterostructures. Distinct emission lifetime reduction and photoluminescence quenching of the hetero-layered hybrid ascertain strong interlayer coupling and efficient charge transfer between the components. Surface and interfacial-dominated photocatalysis, a promising strategy for solar energy conversion^{24–32}, is adopted to demonstrate the reliability of the catalytically rich 2D ultrathin ZnIn₂S₄/MoSe₂ hetero-layered material. The as-synthesized ZnIn₂S₄/MoSe₂ concurrently realize efficient separation and transfer of photogenerated charge carriers, acceleration of surface proton reduction with abundant active sites as well as enhanced visible light absorption that circumvent the limitations of conventional photocatalysts³³. Consequently, the ZnIn₂S₄/MoSe₂ displays high-performance visible-light-driven H₂ evolution activity of 6,454 μmol g^{−1} h^{−1}, ~15 and 4 times as high as that of bulk and bare ZnIn₂S₄ nanosheets, respectively. Importantly, the 2D hetero-layered hybrid shows high stability with prolonged 80 h cycling and catalytic reactivity retention after storing over a few months that further attests to the integrity of the constructed 2D materials for prospective advanced applications. Furthermore, we test the applicability of this approach on other 2D metal sulfides, namely CdIn₂S₄ and In₂S₃ that also show scalable self-surface charge exfoliation. Similarly, the constructed hetero-layered hybrids of CdIn₂S₄/MoSe₂ and In₂S₃/MoSe₂ feature enhanced photocatalytic activity and stability.

Results

Self-surface charge exfoliation of ultrathin ZnIn₂S₄ layers. The ultrathin single-unit-cell ZnIn₂S₄ layers were prepared via a facile low-temperature refluxing method, followed by a water-assisted

surfactant/intercalator-free exfoliation process, as schematically illustrated in Fig. 1a (for more details, see Methods). Scanning electron microscopy (SEM) images of bulk ZnIn₂S₄ in Fig. 1b and Supplementary Fig. 1 reveal a uniform morphology of sheet-like structure. The energy-dispersive X-ray spectroscopy (EDX) (Supplementary Fig. 2) and X-ray diffraction (XRD) (Supplementary Fig. 3) analysis confirm the elemental composition and high purity of the as-synthesized ZnIn₂S₄ with hexagonal phase structure (cell parameters of $a = b = 3.85 \text{ \AA}$, $c = 24.68 \text{ \AA}$, JCPDS No. 65–2,023).

Notably, the dispersion of ZnIn₂S₄ in deionized (DI) water reveals a strong negatively charged surface with a zeta potential value of -36.5 mV (Supplementary Fig. 4). This can be ascribed to the presence of excess amount of S^{2−} that has been adsorbed onto the ZnIn₂S₄ surface during the synthesis process^{34–36}. Other supporting evidences are appended in Supplementary Figs 5 and 6. The self-surface charge within the layered nanostructure significantly weakens the interaction between ZnIn₂S₄ interlayers. Owing to Coulombic repulsion, these layers repel each other and are readily exfoliated with the assistance of shear forces triggered by mild sonication in the absence of any intercalator and surfactant species (Supplementary Fig. 7).

Transmission electron microscopy (TEM) images (Fig. 1c and Supplementary Fig. 8) of the as-exfoliated ZnIn₂S₄ layers display 2D sheet structure with a nearly transparent feature, implying the ultrathin nature of the exfoliated product. This self-surface charge promoted exfoliation can be corroborated by the controlled experiment of ultrasonic exfoliation of ZnIn₂S₄ synthesized from the addition of a stoichiometric amount of S^{2−} (denoted as ZnIn₂S₄-S, see Methods for more details), as illustrated in Supplementary Fig. 9. The as-obtained ZnIn₂S₄-S displays a weak zeta potential of -5.2 mV (Supplementary Fig. 10). Accordingly, the dispersion of ZnIn₂S₄-S can be easily centrifuged after ultrasonication. The TEM image in Supplementary Fig. 11 demonstrates that the ZnIn₂S₄-S is composed of aggregated layers. In addition, negatively charged ZnIn₂S₄ surface can also be validated by a layer electrostatic self-assembly demonstration of the ZnIn₂S₄ nanosheets on positively charged 3-aminopropyltriethoxysilane (APTES)-modified glass substrate (Supplementary Figs 12 and 13). Correspondingly, a pale yellow thin film can be observed only for the strong negatively charged ZnIn₂S₄ (-36.5 mV) coating on the glass surface. SEM image reveals uniform coverage/assembly of strong negatively charged ZnIn₂S₄ nanosheets on the positive APTES-glass substrate. Conversely, no obvious adsorption of the weak negatively charged ZnIn₂S₄-S (-5.2 mV) has been observed on the glass substrate. Altogether, these findings confirm the existence of strong negatively self-charged ZnIn₂S₄ surface that facilitates facile interlayer exfoliation of ultrathin ZnIn₂S₄ nanosheets without the assistance of surfactant/intercalator additives.

Moreover, the corresponding selected-area electron diffraction pattern in Fig. 1c inset shows clear bright spots that correspond to the hexagonal structure and single-crystalline characteristic of the ultrathin ZnIn₂S₄ nanosheets. In addition, the high-resolution TEM (HRTEM) image in Fig. 1c inset displays distinct lattice fringes of ca. 0.32 nm, corresponding to the (102) crystallographic plane of ZnIn₂S₄. The typical Tyndall effect observed for the as-exfoliated ZnIn₂S₄ suspension using a red laser (Fig. 1b, inset) indicates the formation of freestanding and highly dispersed ultrathin ZnIn₂S₄ layers. More importantly, the colloid ultrathin ZnIn₂S₄ nanosheets can be easily exfoliated into large scale (Supplementary Fig. 14) that is essential for further utilization.

TEM characterization cannot unambiguously determine the ultimate thickness of the layers. In this context, atomic force microscopy (AFM) is used to provide an estimated quantitative layer thickness. As shown in Fig. 1d, the topography of the

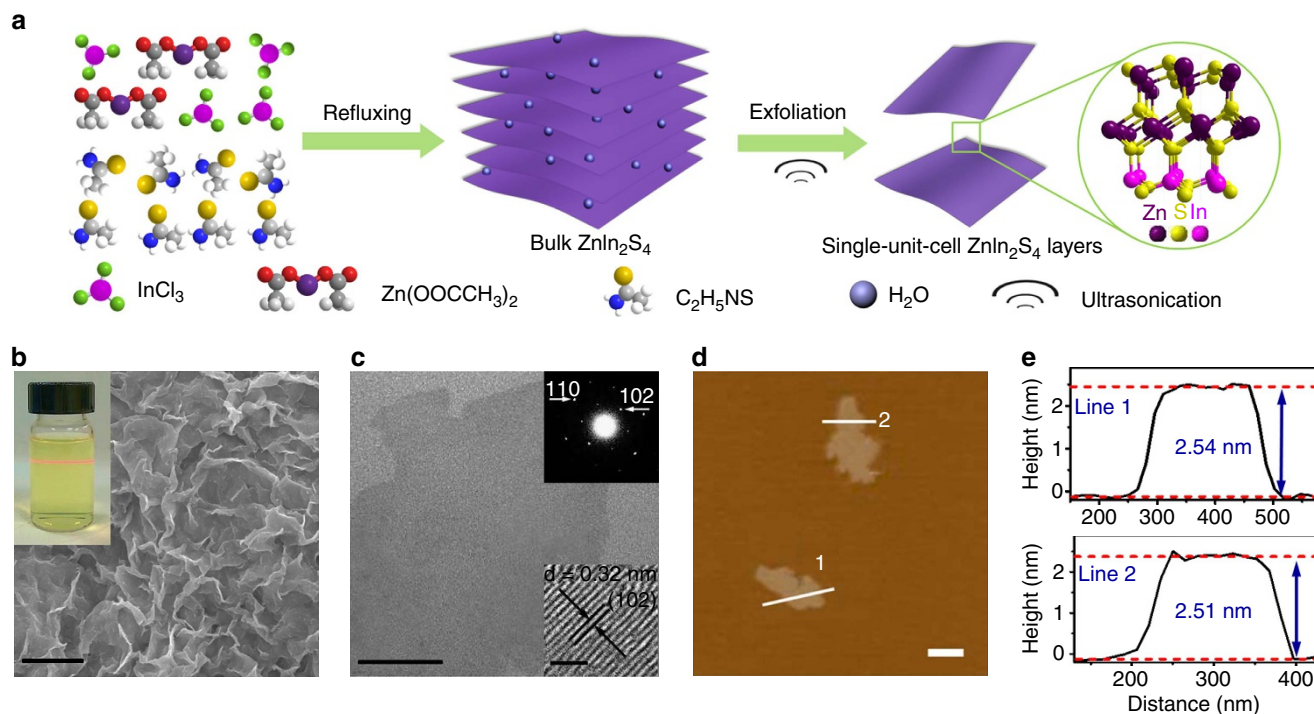


Figure 1 | Schematic illustration of the synthesis of single-unit-cell ZnIn_2S_4 layers and characterization. (a) A self-surface charge promoted exfoliation of clean and freestanding single-unit-cell ZnIn_2S_4 layers in surfactant/intercalator-free medium. (b) Scanning electron microscopy (SEM) image of bulk ZnIn_2S_4 . Scale bar, 2 μm (c) Transmission electron microscopy (TEM) image of single-unit-cell ZnIn_2S_4 layers. Scale bar, 50 nm. (d) Atomic force microscopy (AFM) image and (e) corresponding height images of single-unit-cell ZnIn_2S_4 layers. Scale bar, 200 nm. The inset in b is photograph of Tyndall effect of the ZnIn_2S_4 suspension; insets in c are the corresponding selected-area electron diffraction (SAED) pattern and high-resolution TEM (HRTEM) image of single-unit-cell ZnIn_2S_4 layers.

as-prepared ZnIn_2S_4 presents 2D structure with smooth surface. The corresponding height profiles in Fig. 1e show that the typical thickness of the as-exfoliated layers is ~ 2.5 nm, validating the ultrathin nature of the ZnIn_2S_4 . Considering that the c parameter of ZnIn_2S_4 is 24.68 Å (Supplementary Fig. 15), the thickness of ZnIn_2S_4 is well in agreement with the thickness of a unit cell along the [001] axis³⁷. Thus, it is reasonable to deduce that each ultrathin ZnIn_2S_4 nanosheet with a thickness of ca. 2.5 nm is a single-unit-cell ZnIn_2S_4 atomic layer. According to the diffusion formula of $t = d^2/k^2D$ (d is the particle size, k is a constant, D is the diffusion coefficient of electron-hole pairs)^{5,7}, the ultrathin single-unit-cell ZnIn_2S_4 atomic layer will significantly shorten the diffusion length and time of charge carriers taken to reach the surface, enable the photoexcited electron-hole pairs to transport from the interior to the surface fast, and thus lead to higher charge separation efficiency of the ultrathin ZnIn_2S_4 than its counterpart of bulk ZnIn_2S_4 , as verified by the photocurrent and photoluminescence (PL) analysis in Supplementary Figs 16 and 17.

Generalized synthesis of ultrathin CdIn_2S_4 and In_2S_3 layers.

The suitability of self-surface charge exfoliation as a general approach for large-scale preparation of other 2D metal sulfides, that is, CdIn_2S_4 and In_2S_3 , has also been demonstrated. As shown in Supplementary Fig. 18, the CdIn_2S_4 dispersion in DI water shows a strong negative charge with a zeta potential value of -39.7 mV. TEM images in Supplementary Fig. 19 demonstrate the 2D sheet structure of the exfoliated CdIn_2S_4 nanosheets without using any surfactant or intercalator under moderate ultrasonication. The inset in Supplementary Fig. 19 shows HRTEM image where the distinct lattice fringes of 0.33 nm correspond to the (311) crystallographic plane of CdIn_2S_4 . AFM

topography reveals the ultrathin structure of the exfoliated CdIn_2S_4 with the thickness of ~ 2.3 nm (Supplementary Fig. 20). Typical Tyndall effect is observed for the as-exfoliated CdIn_2S_4 suspension (Supplementary Fig. 21), indicating the formation of large-scale freestanding and highly dispersed CdIn_2S_4 layers. Moreover, the respective EDX and XRD analyses in Supplementary Figs 22 and 23 confirm the as-synthesized CdIn_2S_4 nanosheets with cubic phase structure (JCPDS No. 27-0060).

Likewise, this self-surface charge strategy is also exploited to exfoliate In_2S_3 into a large-scale colloidal dispersion of ultrathin nanosheets (Supplementary Fig. 24). Zeta potential measurement displays a strong negatively charged surface (zeta potential of -41.9 mV) of In_2S_3 (Supplementary Fig. 25). TEM images in Supplementary Fig. 26 show 2D sheet structure with distinct lattice fringes (ca. 0.32 nm) of In_2S_3 (311) crystallographic plane. The thickness of the obtained In_2S_3 is ~ 4.5 nm (Supplementary Fig. 27). Moreover, EDX result confirms the elemental composition of In_2S_3 and XRD pattern reveals the pure cubic phase of the synthesized In_2S_3 (JCPDS No. 65-0459) (Supplementary Figs 28 and 29).

Construction of hetero-layered hybrids. Recent advances in creating heterostructures based on 2D atomic crystals by artificial combination of various 2D materials have shown to strongly modulate electronic and optical properties¹⁷. By virtue of the 2D configuration with large surface area, along with its complementary high interfacial contact with other components, the single-unit-cell ZnIn_2S_4 layers provide a favourable platform for the fabrication of hybrid composite^{17,38}. In this context, MoSe_2 nanosheets are integrated with the ultrathin ZnIn_2S_4 via a surface charge promoted self-assembly method that is driven by

strong electrostatic attraction between the negatively charged ZnIn_2S_4 layers and positively charged MoSe_2 (see Methods for more details). The electrostatic self-assembly method efficiently circumvents the requirement of lattice matching of two individual layers for assembling hetero-layer structure^{39,40}. Consequently, a large quantity of hetero-layered $\text{ZnIn}_2\text{S}_4/\text{MoSe}_2$ can be readily obtained (Supplementary Fig. 30). Moreover, this method also imparts strong hetero-interlayer coupling that effectively promotes interfacial charge carriers transfer^{41–43} that will be discussed later.

Figure 2a,b shows the TEM images of MoSe_2 , indicating that the sheets are typically composed of 2–4 layers with an interlayer spacing of 0.65 nm that corresponds to the (002) plane of hexagonal MoSe_2 (refs 44,45). The HRTEM image in Fig. 2c shows a d spacing of 0.28 nm that matches with the interspacing of (100) MoSe_2 (refs 46,47). After the integration of MoSe_2 with the single-unit-cell ZnIn_2S_4 layers, the as-prepared $\text{ZnIn}_2\text{S}_4/\text{MoSe}_2$ yields a hetero-layered structure (Fig. 2d,e). Figure 2f and Supplementary Fig. 31 show HRTEM images of $\text{ZnIn}_2\text{S}_4/\text{MoSe}_2$ that display interlayer spacing of MoSe_2 (0.65 nm) and distinct lattice fringes of ZnIn_2S_4 (0.32 nm), confirming the co-existence and interfacial contact of the two components. In addition, Supplementary Fig. 32 shows overlapping TEM mapping of various elements, also indicating the lamellar structure formation of vertically coordinated ZnIn_2S_4 and MoSe_2 heterostructure. The corresponding EDX spectrum (Fig. 3a) shows the coexistence of Zn, In, S, Mo and Se elements, whereas the EDX mapping (Fig. 3b) demonstrates the homogeneous distribution of these elements throughout the $\text{ZnIn}_2\text{S}_4/\text{MoSe}_2$ composite. Therefore, based on the above analyses, it is reasonable to infer that the ultrathin single-unit-cell ZnIn_2S_4 layers are intimately coupled with the layered MoSe_2 featuring a sheet-on-sheet hetero-layer structure, as schematically reflected in Fig. 3c.

Moreover, the XRD patterns of ZnIn_2S_4 and $\text{ZnIn}_2\text{S}_4/\text{MoSe}_2$ composite (Supplementary Fig. 33) present analogous diffraction peaks of hexagonal phase ZnIn_2S_4 . The absence of typical MoSe_2

peaks (Supplementary Fig. 34) could be ascribed to the relatively low diffraction intensity of MoSe_2 peaks shielded by the strong and broad peaks of ZnIn_2S_4 . Notably, Fig. 3d shows the Raman spectra of ZnIn_2S_4 and $\text{ZnIn}_2\text{S}_4/\text{MoSe}_2$ where a characteristic peak at 240 cm^{-1} corresponding to the 'A_{1g}' band of MoSe_2 (refs 44,48,49) (Supplementary Fig. 35) is observed for $\text{ZnIn}_2\text{S}_4/\text{MoSe}_2$ sample, confirming the formation of a composite with MoSe_2 in the matrix of ZnIn_2S_4 . In addition, the shift of the 'A_{1g}' band of $\text{ZnIn}_2\text{S}_4/\text{MoSe}_2$ as compared with that of bare MoSe_2 (241.1 cm^{-1}) also implies the reduced layer aggregation of MoSe_2 nanosheets in the hybrid composite^{48,49}. The ultraviolet–visible (UV–vis) absorption spectra in Supplementary Fig. 36 show that the $\text{ZnIn}_2\text{S}_4/\text{MoSe}_2$ displays enhancement in visible-light absorption as compared with ZnIn_2S_4 . This can be attributed to the intrinsic background absorption of black-coloured MoSe_2 (Supplementary Fig. 37). To further determine the composition and chemical states of the composite, the $\text{ZnIn}_2\text{S}_4/\text{MoSe}_2$ has been characterized by X-ray photoelectron spectroscopy (XPS). The doublet peaks for Mo 3d at 228.7 and 231.9 eV (top panel of Fig. 3e) can be assigned to the Mo⁺⁴ valence state, whereas the peak at 226.4 eV should be assigned to S 2s (ref. 15). In the Se 3d XPS spectrum (bottom panel of Fig. 3e), the peaks at 54.4 and 55.3 eV are ascribed to Se²⁻ (ref. 47). Meanwhile, the high-resolution XPS spectra of Zn 2p peaks at 1021.8 and 1044.8 eV, In 3d peaks at 445.0 and 452.6 eV and S 2p at 161.9 and 163.0 eV (Supplementary Fig. 38) can be assigned to Zn²⁺, In³⁺ and S²⁻ of ZnIn_2S_4 , respectively^{50–52}. The XPS analysis corroborates the presence of MoSe_2 in the $\text{ZnIn}_2\text{S}_4/\text{MoSe}_2$ composite.

Photoelectrochemical properties. It has been well accepted that layered transition metal chalcogenides with exposed edge sites can effectively decrease activation energy/overpotential of redox reaction¹⁷ that are desirable for photo-/electrocatalytic processes. According to the energy band structures of ZnIn_2S_4 and MoSe_2 , the photogenerated electrons from the excitation of ZnIn_2S_4 are thermodynamically available for transferring to MoSe_2 . Therefore, it is anticipated that the $\text{ZnIn}_2\text{S}_4/\text{MoSe}_2$ hetero-

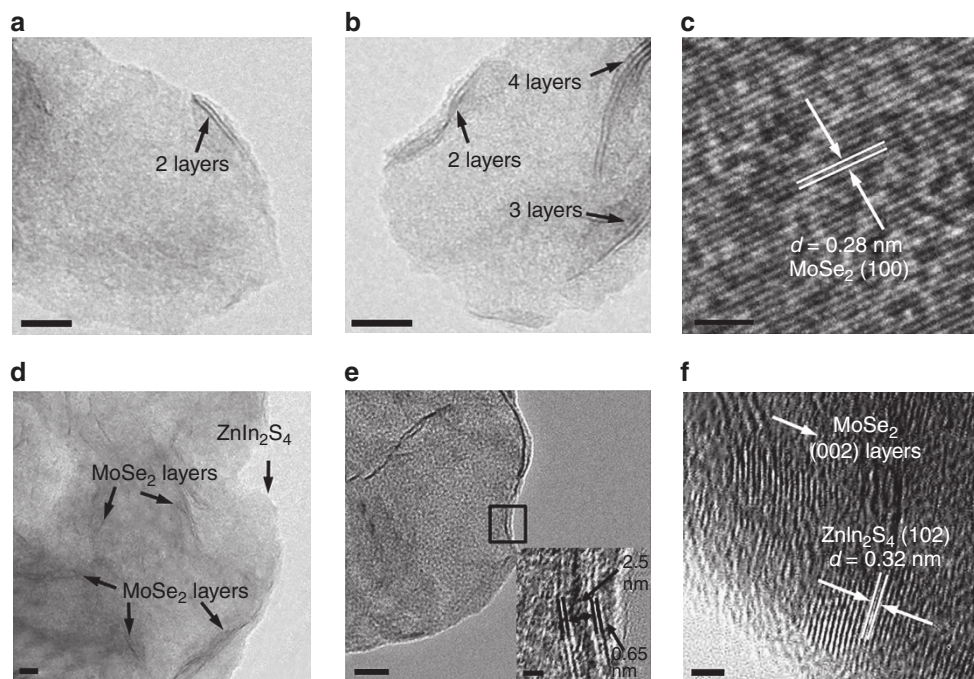


Figure 2 | Morphology and structure of few-layered MoSe_2 and hetero-layered $\text{ZnIn}_2\text{S}_4/\text{MoSe}_2$. (a,b,d,e) Transmission electron microscopy (TEM) images of few-layered MoSe_2 (a,b) and hetero-layered $\text{ZnIn}_2\text{S}_4/\text{MoSe}_2$ (d,e). Scale bar, 10 nm. (c,f) High-resolution TEM (HRTEM) images of MoSe_2 (c) and $\text{ZnIn}_2\text{S}_4/\text{MoSe}_2$ (f). Scale bar, 2 nm. The inset in e is the magnification of the image shown in the black box of Fig. 2e. Scale bar, 2 nm.

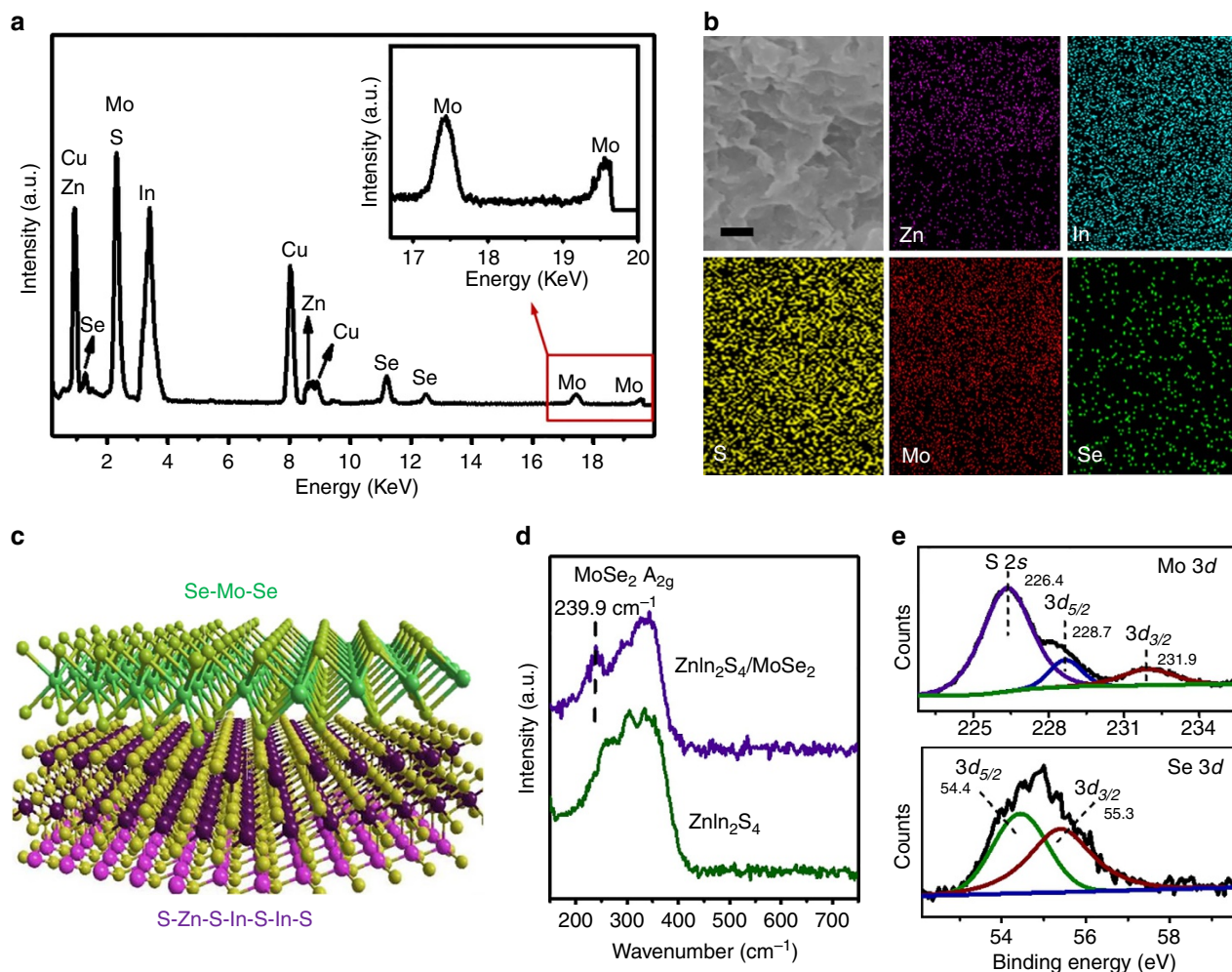


Figure 3 | Characterization of hetero-layered $\text{ZnIn}_2\text{S}_4/\text{MoSe}_2$. (a) Energy-dispersive X-ray (EDX) spectrum and (b) mapping images of the as-prepared $\text{ZnIn}_2\text{S}_4/\text{MoSe}_2$. Scale bar, 200 nm. (c) Schematic illustration of the sheet-on-sheet $\text{ZnIn}_2\text{S}_4/\text{MoSe}_2$ hetero-layer structure. (d) Raman spectra of ZnIn_2S_4 and $\text{ZnIn}_2\text{S}_4/\text{MoSe}_2$. (e) High-resolution X-ray photoelectron spectroscopy (XPS) spectra of Mo 3d and Se 3d.

layered structure not only promotes charge separation and transport driven by junction/interface between the MoSe_2 and the light harvester ZnIn_2S_4 , but also facilitates the proton reduction on the surface of MoSe_2 . To gain more insight into its optoelectronic properties, a series of complementary photo- and electrochemical characterizations were carried out. Figure 4a displays the linear sweep voltammetry curves of $\text{ZnIn}_2\text{S}_4/\text{MoSe}_2$ composite and bulk ZnIn_2S_4 , revealing a higher cathodic current density that is attributed to the reduction of water to H_2 (ref. 53) over hetero-layered $\text{ZnIn}_2\text{S}_4/\text{MoSe}_2$ than bulk ZnIn_2S_4 . Simultaneously, the controlled experiment over bare fluoride tin oxide (FTO) shows no obvious cathodic current under the same potential range (Supplementary Fig. 39). The result indicates that the integration of MoSe_2 with ZnIn_2S_4 accelerates the protonation and subsequent H_2 formation rate of $\text{ZnIn}_2\text{S}_4/\text{MoSe}_2$ as compared with that of bulk ZnIn_2S_4 .

In addition, Fig. 4b displays the time-resolved photoluminescence spectra of bulk ZnIn_2S_4 and hetero-layer structured $\text{ZnIn}_2\text{S}_4/\text{MoSe}_2$, which probe the specific charge carrier dynamics of nanosystems^{54,55}. The emission decay curves of the samples are fitted by biexponential kinetics function (Supplementary Note 1, Supplementary Equation 1) in which two decay components are derived (insets in Fig. 4b) (τ_1 is originated from the nonradiative recombination of charge carriers in the defect states of ZnIn_2S_4 , whereas the longer lifetime component of

τ_2 is caused by the recombination of free excitons in the ZnIn_2S_4). For $\text{ZnIn}_2\text{S}_4/\text{MoSe}_2$, the emission lifetimes of both components ($\tau_1 = 0.31$ ns, $\tau_2 = 0.38$ ns) are shorter than that of the corresponding bulk ZnIn_2S_4 counterpart ($\tau_1 = 0.73$ ns, $\tau_2 = 3.77$ ns). The average emission lifetime (calculated from Supplementary Note 1, Supplementary Equation 2), which reflects the overall emission decay behaviour of sample, has also displayed an obvious decrease for $\text{ZnIn}_2\text{S}_4/\text{MoSe}_2$ (2.43 ns) as compared with that of bulk ZnIn_2S_4 (3.78 ns). Meanwhile, the steady-state PL spectra in Fig. 4d show obvious PL quenching of hetero-layered $\text{ZnIn}_2\text{S}_4/\text{MoSe}_2$ hybrid. The corresponding observations of PL quenching and lifetime reduction suggest the establishment of an electron transfer channel from ZnIn_2S_4 to MoSe_2 in a nonradiative quenching pathway (Fig. 4c)^{54,55}. Accordingly, this leads to efficient interfacial charge transfer and suppression of photoexcited charge recombination in the hetero-layered $\text{ZnIn}_2\text{S}_4/\text{MoSe}_2$ structure.

Furthermore, the electrochemical impedance spectrum of $\text{ZnIn}_2\text{S}_4/\text{MoSe}_2$ (Fig. 4e) shows a smaller semicircular in the Nyquist plot than that of bare ZnIn_2S_4 nanosheets, indicating a lower charge-transfer resistance in the hybrid composite that warrants efficient transportation and separation of charge carriers^{56–59}. As shown in Fig. 4f, the $\text{ZnIn}_2\text{S}_4/\text{MoSe}_2$ displays obvious transient photocurrent response under visible light irradiation. The current density is comparable to recently

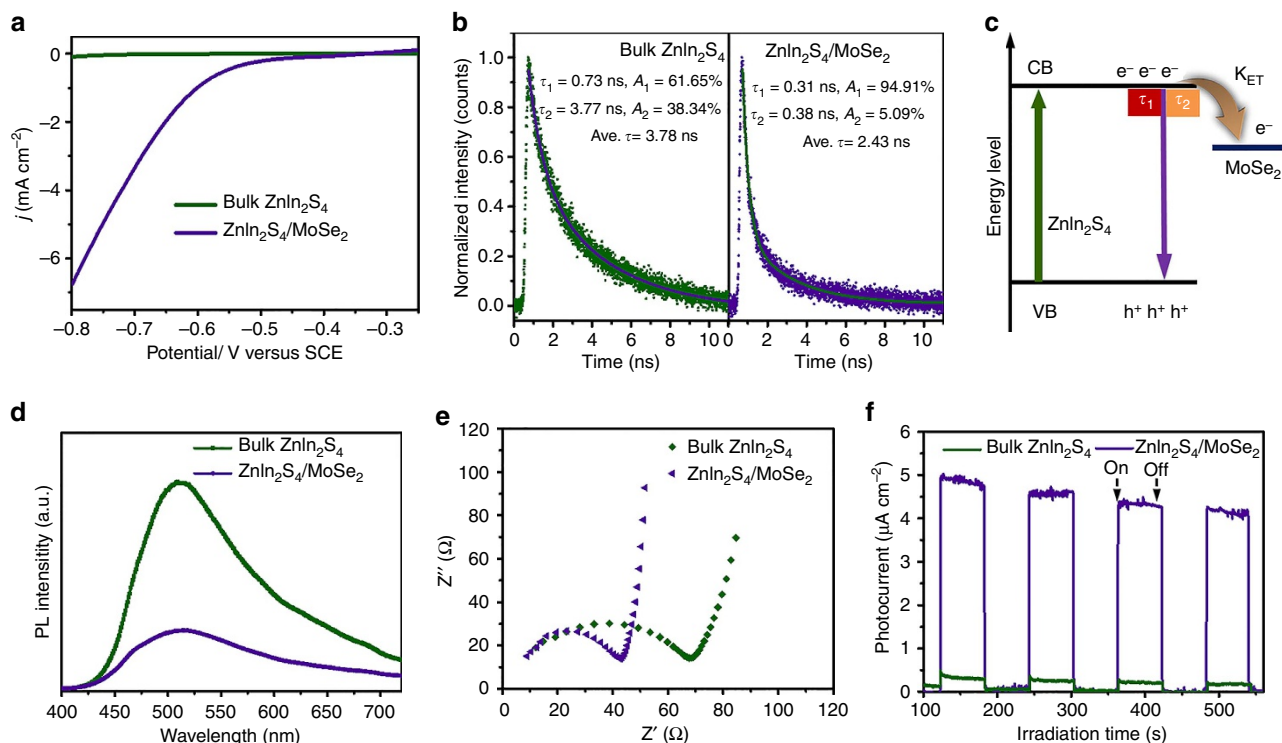


Figure 4 | Photoelectrochemical properties. (a) Linear sweep voltammetry (LSV) curves, (b) time-resolved transient photoluminescence (PL) decay (excitation at 400 nm and emission at 495 nm), (c) schematic illustration of the interfacial charge carrier transfer, (d) steady-state PL spectra, (e) electrochemical impedance spectroscopy Nyquist plots and (f) transient photocurrent responses of bulk ZnIn₂S₄ and hetero-layered ZnIn₂S₄/MoSe₂ composite. CB, conduction band; VB, valence band.

reported 2D-based photocatalyst systems (Supplementary Table 1). In addition, it is notable that the ZnIn₂S₄/MoSe₂ displays ca. 22-fold photocurrent enhancement as compared with bulk ZnIn₂S₄ under the same experimental condition, and this is a marked improvement that suggests the structure and composition advantage of the hetero-layered ZnIn₂S₄/MoSe₂ composite in promoting the separation and transportation of photogenerated charge carriers. Collectively, these commendable photo- and electrochemical properties support efficient electron-hole pair separation and high surface reaction rate of the ZnIn₂S₄/MoSe₂ hetero-layered structure.

Photocatalytic H₂ production performance. Recent experimental results and theoretical predictions suggest that metal chalcogenides are a class of promising inexpensive, earth-abundant and visible responsive catalyst alternatives. However, nonoptimal interfacial contact and bulk metal chalcogenides structure limit catalytic activity owing to poor electronic coupling effect and low active sites exposure. Correspondingly, the constructed metal chalcogenide heterostructure that is thinned down to a few layers with incorporated electrostatic coupling is evaluated by photocatalytic H₂ production. The photocatalytic performance provides a useful and explicit evaluation to assert the structural integrity and stability of the 2D hetero-layered structure.

The photocatalytic activity, H₂ generation of the ultrathin ZnIn₂S₄ layers and ZnIn₂S₄/MoSe₂ hetero-layered nano hybrids was performed under visible light irradiation ($\lambda > 400$ nm) using lactic acid as the hole scavenger. As shown in Fig. 5a, the single-unit-cell ZnIn₂S₄ layers show a H₂ evolution rate of $\sim 1,748 \mu\text{mol g}^{-1} \text{h}^{-1}$ that is fourfold of the pristine bulk ZnIn₂S₄ ($446 \mu\text{mol g}^{-1} \text{h}^{-1}$), indicating enhanced activity of the ultrathin layers. In addition, the photoactivity of the ultrathin

ZnIn₂S₄ is also demonstrated to be much higher than the H₂ generation rate of the hydrothermal synthesized ZnIn₂S₄ nanoflowers (Supplementary Fig. 40) of ca. $260 \mu\text{mol g}^{-1} \text{h}^{-1}$. The augmented photoactivity of ZnIn₂S₄ nanosheets can be attributed to its unique 2D ultrathin structure that lowers charge-transfer resistance and shortens the diffusion pathway of charge carriers, thus favouring the fast and efficient separation of photogenerated charge carriers (Supplementary Figs 16 and 17).

Furthermore, significant improvement in H₂ generation was established after coupling of MoSe₂ layers to the ultrathin ZnIn₂S₄ nanosheets forming hetero-layered composites. The amount of H₂ evolved increases with MoSe₂ content up to 1% (Fig. 5b). The as-obtained ZnIn₂S₄/1%MoSe₂ displays the highest H₂ evolution rate of $6,454 \mu\text{mol g}^{-1} \text{h}^{-1}$, that is ~ 15 and 4 times as high as that of bulk ZnIn₂S₄ and ZnIn₂S₄ nanosheets, respectively. Notably, the photoactivity is considerably higher than that of the reference photocatalysts, that is, ZnIn₂S₄/1%Pt ($4,353 \mu\text{mol g}^{-1} \text{h}^{-1}$) and ZnIn₂S₄/1%MoS₂ ($3,860 \mu\text{mol g}^{-1} \text{h}^{-1}$), as shown in Fig. 5c,d. Pt and MoS₂ are two exemplary co-catalysts that have been used in reported literature for photocatalytic H₂ evolution. The result highlights the effectiveness of MoSe₂ that surpasses the classic Pt and MoS₂, as a co-catalyst in promoting photocatalytic H₂ evolution^{44,60}. Importantly, the hetero-layered ZnIn₂S₄/MoSe₂ displays good stability. The cycling test over the optimal ZnIn₂S₄/1%MoSe₂ (Fig. 5e) shows negligible photoactivity loss after 20 consecutive cycles with accumulatively 80 h under visible light irradiation. Moreover, after storing in ambient conditions for 3 months, the ZnIn₂S₄/1%MoSe₂ retains a high photoactivity as that of the fresh sample (Supplementary Fig. 41). The high photoreactivity and stability of the 2D hetero-layer ZnIn₂S₄/1%MoSe₂ hybrid provide direct evidence of the large exposed active surface and strong electronic coupling between the interlayers.

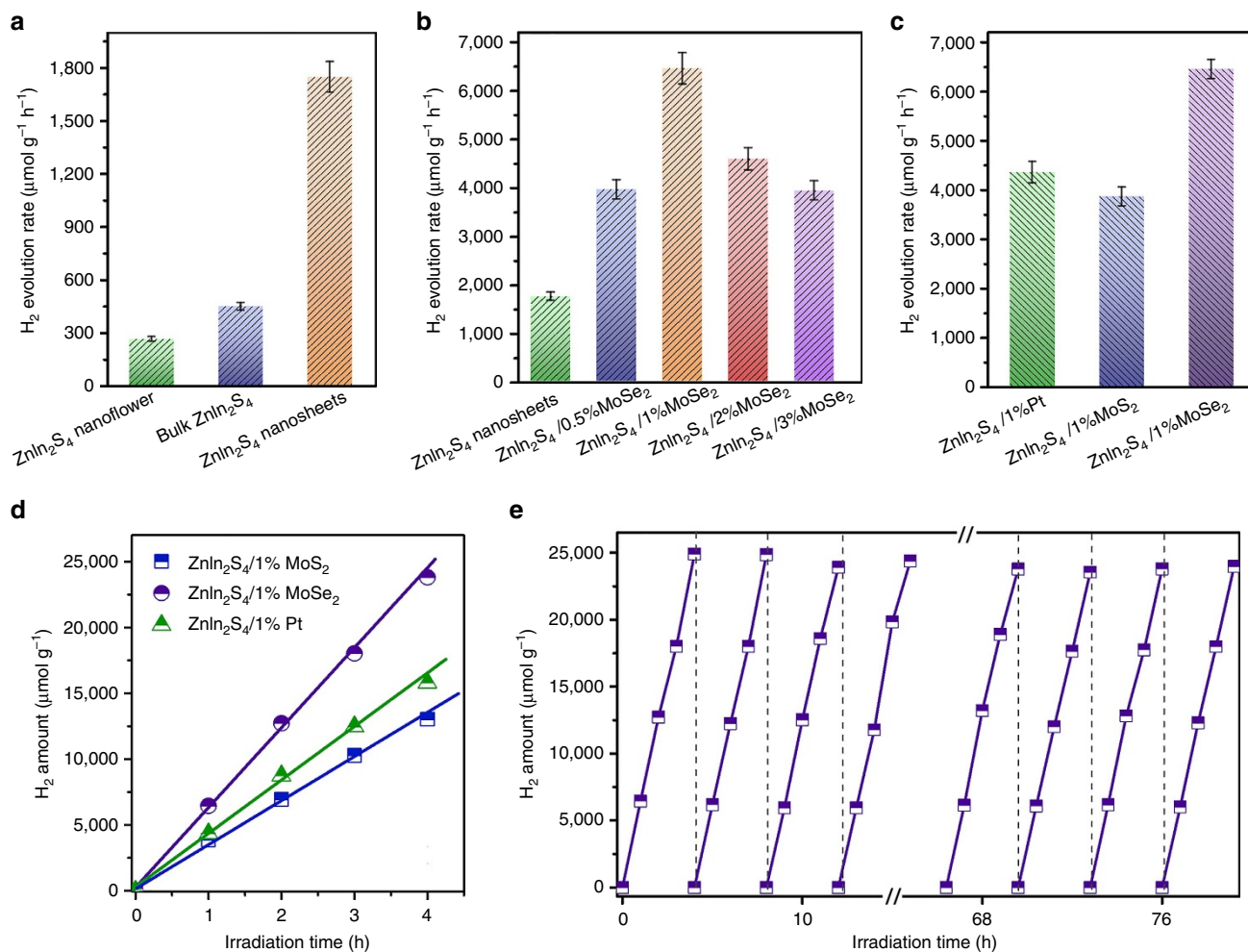


Figure 5 | Photocatalytic H₂ production performance. (a,b) Photocatalytic H₂ evolution over ZnIn₂S₄ nanoflowers, bulk ZnIn₂S₄ and single-unit-cell ZnIn₂S₄ layers (a), and ZnIn₂S₄/MoSe₂ composites with different weight ratios of MoSe₂ (b). (c,d) Comparison of photocatalytic H₂ evolution activities over ZnIn₂S₄/1%Pt, ZnIn₂S₄/1%MoS₂ and ZnIn₂S₄/1%MoSe₂. (e) Recycling photoactivity test of ZnIn₂S₄/1%MoSe₂. Note that the error bars represent the photoactivity s.d. values calculated from triplicate experiments.

Besides, photocatalytic H₂ activities of ultrathin CdIn₂S₄ and In₂S₃ layers also exceed that of their bulk counterparts (Supplementary Fig. 42). Self-assembly construction of 2D hetero-layer hybrids, that is, CdIn₂S₄/MoSe₂ and In₂S₃/MoSe₂, also verifies the enhanced photoactivity and stability. Essentially, the coupling of ultrathin CdIn₂S₄ and In₂S₃ with a few layers of MoSe₂ co-catalyst has enhanced the H₂ evolution activity (Supplementary Fig. 43). The rates of H₂ evolved over the optimal CdIn₂S₄/1%MoSe₂ and In₂S₃/1%MoSe₂ are ~9- and 10-fold of bare CdIn₂S₄ and In₂S₃ nanosheets, respectively. In addition, the photoactivities of the resulted metal sulfide/MoSe₂ (CdIn₂S₄/1%MoSe₂ and In₂S₃/1%MoSe₂) are also much higher than those of the reference photocatalysts, that is, metal sulfide/Pt and metal sulfide/MoSe₂ (Supplementary Fig. 44). Furthermore, the cycling tests of the optimal CdIn₂S₄/1%MoSe₂ and In₂S₃/1%MoSe₂ show negligible photoactivity degradation after 20 consecutive cycles with accumulatively 80 h under visible light irradiation (Supplementary Fig. 45).

Discussion

Although prior literature has already reported exfoliated 2D layered metal chalcogenides commonly induced by intercalator osmotic swelling, self-surface charge exfoliation into single-unit-cell thick layer structure in pure water is unprecedented. Successive artificially coupled hetero-layered structure with

ultrathin and intimate interface characteristics, guided by unconstrained electrostatic coordination of a dissimilar metal chalcogenide, is demonstrated in this work. In contrast, thin-film epitaxial growth is strongly influenced by the surface of the substrate and degree of lattice matching. This limits the production yield and imposes a high cost of 2D hetero-layer metal chalcogenide for practical implementation. To test the hypothesis of the satisfactorily high quality of the as-prepared 2D hetero-layer, surface and interfacial-dominated photocatalysis is used as an ideal testbed for reliability verification. Diverse 2D ultrathin metal sulfide/MoSe₂ hetero-layered materials reveal outstanding visible-light photoreactivity and efficient charge transfer exceeding that of metal sulfide/Pt and metal sulfide/MoSe₂ reference photocatalysts. More remarkably, the ultrathin hetero-layer structures demonstrate highly stable contact interface promising for long-term cycling and storage purposes.

In summary, we have developed a scalable method to artificially coordinate ultrathin metal chalcogenide hetero-layer structure via a combination of pristine self-surface charge exfoliation and electrostatic coupling of dissimilar layers. This generic approach to the preparation of 2D hetero-layered hybrids is attractive as it allows selection of individual constituent materials and thickness control, opening up the possibility of 'design-and-build' 2D layered heterojunction for large-scale theoretical exploration and practical applications.

Methods

Materials. Zinc acetate dehydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, $\geq 98\%$), sodium molybdate dehydrate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, $\geq 99\%$) and hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, 99.99%) solution were obtained from Sigma-Aldrich. Indium chloride (InCl_3 , 99.995%), L(+) lactic acid (90%) and selenium (99.5+%) were obtained from ACROS Organics. Thioacetamide ($\text{C}_2\text{H}_5\text{NS}$, $>98\%$) was obtained from TCI. All of the reagents were used as received without further purification. The DI water used in the catalyst preparation was from local sources.

Synthesis of single-unit-cell ZnIn_2S_4 layers. Single-unit-cell ZnIn_2S_4 layers were fabricated by a facile low-temperature refluxing method followed by a moderate exfoliation. In detail, 1.5 mmol of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and 3 mmol of InCl_3 were added into 250 ml DI water and stirred for 30 min. Subsequently, an excess amount of thioacetamide (TAA, 8 mmol) was added into the above solution and stirred for another 30 min. The solution was then heated to 95°C and maintained at that temperature for 5 h under vigorous stirring. The resulted precipitation was collected by centrifugation, rinsed with water for 2 times and re-dispersed into 200 ml DI water. The dispersion was sonicated continuously for 30 min and then centrifuged at 6,000 r.p.m. for 5 min to remove aggregates. After that, the colloidal single-unit-cell ZnIn_2S_4 layers were obtained. For each set of experimental synthesis, ~ 0.6 g of ZnIn_2S_4 can be obtained. The comparative sample of ZnIn_2S_4 -S was synthesized via the same procedure except that a stoichiometric amount of TAA (6 mmol) was added during the synthesis process.

Synthesis of hetero-layered $\text{ZnIn}_2\text{S}_4/\text{MoSe}_2$ structure. MoSe_2 was synthesized via a one-step hydrothermal method⁴⁴. The surface modification of MoSe_2 was carried out as follows: 50 mg MoSe_2 was dispersed in 100 ml ethanol and sonicated continuously for 1 h. Then, 0.25 ml of APTES was added into the above MoSe_2 dispersion. The mixture was heated at 60°C for 4 h under mild stirring. The resulted product was rinsed with ethanol for 3 times and redispersed in 100 ml DI water with the aid of ultrasonication for 1 h. After that, the dispersion was centrifuged at 6,000 r.p.m. for 5 min to remove aggregates. Then, the colloidal APTES-modified MoSe_2 with positive surface charge was obtained. The 2D hetero-layer composite can be built up by dipping of MoSe_2 nanosheet suspension into colloidal ZnIn_2S_4 of constraint supply or controlled amount of dilute solution. In brief, the APTES-modified MoSe_2 was added dropwise into the negatively charged ZnIn_2S_4 colloid slowly. Driven by the strong electrostatic attractive interaction, the ultrathin ZnIn_2S_4 nanosheets can self-assemble with the MoSe_2 layers, forming intimately integrated $\text{ZnIn}_2\text{S}_4/\text{MoSe}_2$ hetero-layer structure.

Synthesis of ultrathin CdIn_2S_4 and In_2S_3 layers. Ultrathin CdIn_2S_4 layers were fabricated via the similar facile low-temperature refluxing method followed by moderate exfoliation. In detail, 1.5 mmol of $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and 3 mmol of InCl_3 were added into 250 ml DI water and stirred for 30 min. Subsequently, an excess amount of thioacetamide (TAA, 8 mmol) was added into the above solution and stirred for another 30 min. The solution was then heated to 100°C and maintained at that temperature for 12 h under vigorous stirring. The resulted precipitation was collected by centrifugation, rinsed with water for 2 times and redispersed into 200 ml DI water. The dispersion was sonicated continuously for 30 min and then centrifuged at 6,000 r.p.m. for 5 min to remove aggregates. After that, the colloidal ultrathin ZnIn_2S_4 layers were obtained. Ultrathin In_2S_3 layers were synthesized via the same method as that of synthesizing ZnIn_2S_4 layers without the addition of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ precursor.

Synthesis of hetero-layered $\text{CdIn}_2\text{S}_4/\text{MoSe}_2$ and $\text{In}_2\text{S}_3/\text{MoSe}_2$. The hetero-layered $\text{CdIn}_2\text{S}_4/\text{MoSe}_2$ and $\text{In}_2\text{S}_3/\text{MoSe}_2$ were synthesized following the same procedure as that of preparing of $\text{ZnIn}_2\text{S}_4/\text{MoSe}_2$.

Characterization. The XRD patterns of the samples were collected on a Philips X-ray diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.541 \text{ \AA}$). UV-vis absorption spectra were recorded on a Shimadzu UV-3600 UV-vis spectrophotometer. XPS measurement was performed on a Thermo Scientific ESCA Lab 250 spectrometer that consists of a monochromatic Al $\text{K}\alpha$ as the X-ray source, a hemispherical analyser and sample stage with multiaxial adjustability to obtain the surface composition of the samples. All of the binding energies were calibrated by the C 1s peak at 284.6 eV. Zeta-potential (ζ) measurements of the samples were determined by dynamic light scattering analysis (Zeta sizer 3000HSA) at a room temperature of 25°C . SEM images were taken on a JEOL JSM-7001F field emission scanning electron microscope. HRTEM images, EDX and elemental mapping images were obtained on a JEOL JEM-2100 electron microscope. The steady-state PL spectra were recorded on a Shimadzu RF-5301PC under the excitation of 400 nm. Tapping-mode AFM measurement was performed on a commercial SPM instrument (MPF-3D, Asylum Research, CA, USA).

Time-resolved photoluminescence measurement was performed under excitation of 400 nm fs pulses. The excitation source is a mode-locked Ti:sapphire laser (Chameleon Ultra II, Coherent) working with repetition rate of 80 MHz and pulse duration of 140 fs. The second harmonic generation of 700 nm output from the laser was employed to excite the samples. The photoluminescence of the

samples was collected and detected by a photon-counting photomultiplier (PMA, Picoquant). The emission centred at 495 nm was selected by a monochromator (SpectroPro 2300i, Princeton Instrument). The PL decay dynamics were achieved by a time-correlated single photon counting module (TCSPC PicoHarp 300, Picoquant).

Photoelectrochemical measurements were performed in a conventional three-electrode quartz cell. A Pt plate was used as counter electrode, and Ag/AgCl electrode/saturated calomel electrode were used as reference electrode, whereas the working electrode was prepared on FTO conductor glass. The sample powder (3 mg) was ultrasonicated in 0.5 ml of *N,N*-dimethylformamide (supplied by Sigma-Aldrich) to disperse it evenly to get a slurry. The slurry was spread onto FTO glass with the area of 1 cm^2 . After air drying, the working electrode was further dried at 90°C for 2 h to improve adhesion. The electrolyte was 0.2 M aqueous Na_2SO_4 solution (pH = 6.8). Linear sweep voltammetry curves were performed in a mixed solution of 10% (v/v) lactic acid and 0.2 M aqueous Na_2SO_4 solution.

Photocatalytic H_2 evolution measurements. With the aid of ultrasonication, 5 mg of photocatalyst, 9 ml DI water and 1 ml lactic acid were mixed in a 25 ml quartz cylindrical reaction cell to form a homogeneous suspension. Then, the reactor was purged with argon gas for 10 min before illumination with a 300 W xenon arc lamp ($\lambda > 400 \text{ nm}$). The evolved H_2 was analysed using an online gas chromatograph (GC-2014AT, Shimadzu Co., Japan) equipped with a thermal conductivity detector.

The recycling test of catalytic H_2 evolution over the as-prepared photocatalyst was performed as follows. After the reaction of the first run under visible light irradiation, the suspension was purged with argon gas for 10 min. The process was carried out for four more cycles. After every five cycles, the photocatalyst was centrifuged and mixed with fresh 9 ml DI water and 1 ml lactic acid for continuous test.

Data availability. The data that support the findings of this study are available from the corresponding author on request.

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Author contributions

G.W.H. proposed the research direction and supervised the project. M.-Q.Y. designed and performed the experiments. Y.-J.X. performed XPS measurement and provided helpful suggestions in conducting the study. W.H.L. and K.Y.Z. carried out AFM characterization and analysis. H.Z. and Q.-H.X. performed the PL lifetime measurement and analysis. G.W.H. and M.-Q.Y. wrote and revised the manuscript. All authors participated in discussion and reviewed the manuscript before submission.

Additional information

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