Protruding Pt single-sites on hexagonal ZnIn$_2$S$_4$ to accelerate photocatalytic hydrogen evolution

Xiaowei Shi$^1$, Chao Dai$^1$, Xin Wang$^1$, Jiayue Hu$^2$, Junying Zhang$^3$, Lingxia Zheng$^1$, Liang Mao$^4$, Huajun Zheng$^1$ & Mingshan Zhu$^2$

Single-site cocatalysts engineered on supports offer a cost-efficient pathway to utilize precious metals, yet improving the performance further with minimal catalyst loading is still highly desirable. Here we have conducted a photochemical reaction to stabilize ultralow Pt co-catalysts (0.26 wt%) onto the basal plane of hexagonal ZnIn$_2$S$_4$ nanosheets (Pt$_{SS}$-ZIS) to form a Pt-S$_3$ protrusion tetrahedron coordination structure. Compared with the traditional defect-trapped Pt single-site counterparts, the protruding Pt single-sites on h-ZIS photocatalyst enhance the H$_2$ evolution yield rate by a factor of 2.2, which could reach 17.5 mmol g$^{-1}$ h$^{-1}$ under visible light irradiation. Importantly, through simple drop-casting, a thin Pt$_{SS}$-ZIS film is prepared, and large amount of observable H$_2$ bubbles are generated, providing great potential for practical solar-light-driven H$_2$ production. The protruding single Pt atoms in Pt$_{SS}$-ZIS could inhibit the recombination of electron-hole pairs and cause a tip effect to optimize the adsorption/desorption behavior of H through effective proton mass transfer, which synergistically promote reaction thermodynamics and kinetics.
W
ter splitting for hydrogen (H₂) generation through solar light has attracted increasing attention since it supplies a significant carbon-neutral technology for zero-emission renewable energy evolution. The design of a photocatalyst with high efficiency and long durability is a focused task for researchers to scale up H₂ evolution reaction (HER) in the past decades. Two-dimensional (2D) hexagonal ZnIn₂S₄ (h-ZIS), a typical ternary chalcogenide with favorable H adsorption features at edge S atoms in (110) facet (ΔG_{T1} = −0.16 eV) and robust resistance to photocorrosion, has been regarded as a promising candidate for photocatalytic water splitting. The current guiding principles for advancing the catalytic performance of h-ZIS are as follows. First, increase the active site density in h-ZIS through preferentially exposing the edge sites. Unfortunately, unleashing the intrinsically high activity of h-ZIS is still retarded by the severe recombination of electron-hole pairs, where only a small quantity of electrons could survive at the active sites. Second, create in-plane sulfur vacancies or dope metallic heteroatoms to substitute Zn atoms. The lifetime of photogenerated electrons is prolonged, and the basal-plane S atoms in those h-ZIS are also stimulated as centers for HER; however, these S sites suffer from less favorable hydrogen adsorption features (ΔG_{T1} = −0.25 eV) despite the increased site density. Apparently, h-ZIS only becomes applicable toward photocatalytic HER when the rapid carrier recombination and limited active site obstacles are simultaneously overcome.

As a lamellar material, the basal plane of h-ZIS provides plenty of platforms for noble-metal nanoparticles loading, especially platinum (Pt), while the scarcity and high cost of the noble-metal co-catalysts tremendously inhibit their large-scale implementation. Alternatively, single-site co-catalysts (SSCs) emerge as a frontier for catalysis science due to their high atom efficiency and outstanding activity. The strong metal-support interaction caused by metal atoms and coordinated atoms would affect the charge distributions and introduce the electronic structure modifications, which influence the electron-hole pairs recombination and the adsorption behavior during the catalytic process, and eventually change their catalytic activity and selectivity. One of the effective strategies for advanced SSCs is to produce more active sites through increasing metal loading with no aggregation, and accordingly, several Pt single-site (PtSS)-based photocatalysts (Pt loading with 8.7 wt% or 12.0 wt%) have exhibited exciting H₂ evolution rate and observable bubbles under visible light irradiation. For practical applications, achieving maximum catalytic performance with minimal noble-metal atoms is essentially required. Recently, Pt SSCs supported on highly curved substrates were successfully prepared as electrocatalyst to mimic the metal sites at the edges and corners of particles. Owing to the accumulation of electrons around Pt regions triggered by the tip effect, an accelerated HER kinetics was achieved. Principally, the generation of tip enhancement is biased onto curvature-rich configurations (typically corner, vertex, or protrusion). Direct anchoring Pt SSCs onto h-ZIS nanosheets, aberration-corrected high angle annular dark field STEM (HAADF-STEM) measurements were carried out on h-ZIS and Pt₀.₃-ZIS nanosheets, forming Pt–S₄ tetrahedron coordination structure with surrounding S atoms. Since the contrast in HAADF-STEM image is proportional to the square of atomic number, Pt is much brighter than Zn, In, and S atoms, and the atomically dispersed bright spots (circled) were observed in h-ZIS and Pt₀.₃-ZIS nanosheets. By alerting the volume of added H₂PtCl₆, Pt loading content could be tuned, as quantified by the inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis (Supplementary Table 1). Additionally, the molar ratio of Zn and In in Pt₀.₃-ZIS was calculated to be 0.225±0.451, which is consistent with the theoretical molar ratio of 1:2.

X-ray diffraction (XRD) patterns and Raman spectra with negligible changes are observed between h-ZIS and Pt-ZIS, suggesting that Pt atoms incorporation does not destroy the crystal structure of h-ZIS (Supplementary Fig. 4). Transmission electronmicroscopy (TEM) and high-resolution TEM (HRTEM) images in Supplementary Fig. 5 depict a sheet-like structure of h-ZIS and the lattice fringe of 0.41 nm corresponds to the (006) facet. After Pt deposition, the obtained Pt-ZIS nanosheets maintain the thickness (3.10–5.11 nm) of pristine h-ZIS recorded by atomic force microscope (AFM) (Supplementary Figs. 6 and 7). As shown in TEM and HRTEM images, no Pt nanoparticles are observed with Pt loading content in the range of 0.1–1.4 wt%, and the energy-dispersive X-ray spectroscopy (EDS) also exhibits homogeneous dispersion of Pt on h-ZIS nanosheets without any aggregation (Fig. 1a–d and Supplementary Figs. 8–10). When further increasing the Pt amount to 3.0 wt%, nanoparticles were formed, which is proved by the green circles and corresponding EDS spectrum (Supplementary Fig. 11). In addition, the lattice fringe of 0.293 and 0.196 nm attribute to the h-ZIS (104) and Pt (200) facet, respectively. To reveal the configuration of Pt co-catalyst on h-ZIS nanosheets, aberration-corrected high angle annular dark field STEM (HAADF-STEM) measurements were carried out on h-ZIS and Pt₀.₃-ZIS. Since the contrast in HAADF-STEM image is proportional to the square of atomic number, Pt is much brighter than Zn, In, and S atoms, and the atomically dispersed bright spots (circled) were observed in h-ZIS and Pt₀.₃-ZIS nanosheets. By alerting the volume of added H₂PtCl₆, Pt loading content could be tuned, as quantified by the inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis (Supplementary Table 1). Additionally, the molar ratio of Zn and In in Pt₀.₃-ZIS was calculated to be 0.225±0.451, which is consistent with the theoretical molar ratio of 1:2.

Results

Structure analysis and characterization. Ultrathin h-ZIS nanosheets with thickness ranging from 2.46 to 4.94 nm were prepared by a hydrothermal method (Supplementary Fig. 1). H₂PtCl₆ aqueous solution was introduced into h-ZIS dispersion with magnetic stirring. The interfacial charges of h-ZIS and Pt species (HPtCl₆⁻ or PtCl₂⁻) were opposite, so they would be spontaneously assembled through electrostatic interaction in the solution, with Pt-ZIS mixture generated (Supplementary Fig. 2). After irradiation under visible light for 60 min, Pt sites were immobilized on h-ZIS, and the mixture was centrifuged and collected (see the Experimental Section and Supplementary Fig. 3). By alerting the volume of added H₂PtCl₆, Pt loading content could be tuned, as quantified by the inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis (Supplementary Table 1). Additionally, the molar ratio of Zn and In in Pt₀.₃-ZIS was calculated to be 0.225±0.451, which is consistent with the theoretical molar ratio of 1:2.

Photon-corrosion resistance to photocorrosion, has been regarded as a promising candidate for photocatalytic water splitting. The current guiding principles for advancing the catalytic performance of h-ZIS are as follows. First, increase the active site density in h-ZIS through preferentially exposing the edge sites. Unfortunately, unleashing the intrinsically high activity of h-ZIS is still retarded by the severe recombination of electron-hole pairs, where only a small quantity of electrons could survive at the active sites. Second, create in-plane sulfur vacancies or dope metallic heteroatoms to substitute Zn atoms. The lifetime of photogenerated electrons is prolonged, and the basal-plane S atoms in those h-ZIS are also stimulated as centers for HER; however, these S sites suffer from less favorable hydrogen adsorption features (ΔG_{T1} = −0.25 eV) despite the increased site density. Apparently, h-ZIS only becomes applicable toward photocatalytic HER when the rapid carrier recombination and limited active site obstacles are simultaneously overcome.

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calculations were carried out to determine the energies of Pt atoms on various sites. Six different locations were established, including Zn-S hollow site, Zn atop, S atop on Zn-S plane, In-S hollow site, In atop, and S atop on In-S plane, respectively, and Zn-S hollow site with the largest adsorption energy is confirmed to be the most stable location for Pt atom occupation (Supplementary Figs. 15–17). The distribution of Pt atoms on h-ZIS and their propensity to agglomerate was also examined by calculating the energy difference between an isolated Pt atom and a Pt dimer (ΔEₐ), in which the total energy of the isolated configuration was used as reference energy. As shown in Supplementary Fig. 18, it is more favorable for the Pt atoms to be isolated at Zn-S hollow site due to the positive ΔEₐ of 2.03 eV, which fully supports the experimental observations of the Pt single atom in Pt₀.₃-ZIS. Based on the DFT-optimized structure, a STEM simulation on Pt SSCs dispersed h-ZIS was performed. The simulated result is in good agreement with the experimental HAADF-STEM image, demonstrating that Pt single sites prefer to chemisorb above the Zn-S hollow site in h-ZIS basal plane (Fig. 1h and 1i).

Electronic states of atoms in Pt-ZIS. Elemental composition and chemical states of Pt-ZIS were characterized by X-ray photoelectron spectroscopy (XPS). The high-resolution Zn 2p and In 3d XPS peaks corresponding to h-ZIS, Pt₀.₃-ZIS, and Pt₃.₅-ZIS exhibit little shift (Supplementary Fig. 19). The S 2p spectrum for h-ZIS shows two peaks at 161.8 and 163.0 eV, respectively. After loading Pt single sites, a blue-shift of ~0.4 eV in Pt₀.₃-ZIS is observed, indicating that the electrons are transferred from Pt to h-ZIS and enriched around S atom. This also proves that the decoration of Pt single atoms would modulate the electronic structures of h-ZIS (Fig. 2a)²⁰,²⁷. With the increasing amount of Pt to 3.0 wt%, a smaller blue-shift of about 0.3 eV is detected. For the Pt 4f spectra, Pt/C exhibits three peaks at 71.90, 71.77, and 73.19 eV, which correspond to the Pt⁰, Pt²⁺, and Pt⁴⁺ state, respectively (Fig. 2b)¹⁶. In contrast, the Pt₀.₃-ZIS mainly contains Pt⁴⁺ species (72.10 eV), revealing the formation of a higher coordination number with the Pt-S bonds than the Pt-Pt bonds²⁸–³⁰. Interestingly, both Pt⁰ and Pt⁴⁺ peaks appear in the spectrum of Pt₃.₅-ZIS (70.90 and 72.09 eV), which is probably owing to the well-constructed both Pt single atoms and nanoparticles²⁹. The detailed information for XPS fits is listed in Supplementary Tables 2–5.

Furthermore, X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure spectroscopy (EXAFS) were conducted to investigate the local atomic structure and electronic environment of Pt species in Pt-ZIS. EXAFS results in Fig. 2c show k²-weighted Fourier transforms from the Pt L₃-edge EXAFS oscillations of Pt₁.₄-ZIS and Pt₃.₅-ZIS in comparison to that of Pt foil and PtO₂ (k²-weighted χ(k) signals in Supplementary Fig. 20). The only prominent shell in Pt₁.₄-ZIS locating at near 2.0 Å without any Pt–Pt contribution in the range of 2–3 Å testifies the atomically dispersed Pt on h-ZIS¹⁷,³⁰, whereas an additional peak at about 2.6 Å arises in Pt₃.₅-ZIS, closing to that of Pt–Pt contribution. To gain visual illustrations of Pt coordination conditions, wavelet transform (WT) of the k²-weighted EXAFS spectra, a reflection of structure information in the resolution of k space and R space, are shown in Fig. 2d. Pt₁.₄-ZIS exhibits the maximum WT intensity at 1.8–2.1 Å in R space and 3–6 Å in k space, ascribing to Pt–S bond in the first coordination shell³¹,³². While a new WT intensity maximum near 2.5–2.8 Å and 9–11 Å suggests the coexistence of Pt–S and Pt–Pt bonds in Pt₃.₅-ZIS. The Fourier-transform EXAFS curves and the corresponding fitting results in Supplementary Fig. 21 and Supplementary Table 6 give the Pt–S coordination number of 2.6 for Pt₁.₄-ZIS, implying a similar coordination condition of
Pt–S₃ in PtSS-ZIS as depicted by HAADF-STEM image and DFT simulations. The XANES spectra of Pt L₃-edge show that the white-line intensity of Pt₁.₄-ZIS is lower than that of PtO₂, but higher than that of Pt₃.₀-ZIS and Pt foil, demonstrating the Pt atoms are in an oxidation state originating from covalent Pt–S bonds, which is consistent with XPS results (Supplementary Fig. 22). Moreover, we investigated the CO adsorption behavior on different photocatalysts using Fourier-transform infrared (FTIR) spectroscopy to provide additional information about the dispersion and chemical state of Pt (Fig. 2e–g). For Pt₀.₃-ZIS, only a weak vibration band appears at 2093 cm⁻¹ corresponding to CO adsorption on Ptδ+33,34. While the adsorption of CO also produces a strong vibration band at 2033 cm⁻¹ and another weak band at 1961 cm⁻¹ for Pt₁.₄-ZIS. The main band at 2033 cm⁻¹ can be ascribed to linearly bonded CO on Pt₀ sites, and the band at 1961 cm⁻¹ is caused by CO adsorbed on the interface between Pt clusters and the support33. All these characterizations provide compelling evidence that our protocol affords Pt₀.₃-ZIS with only positively charged Pt single atoms, while Pt₃.₀-ZIS with both single atoms and Pt nanoparticles.

Photocatalytic H₂ evolution performances. With protrusion-shaped SSCs in hand, we next explored their photocatalytic HER activities in an aqueous solution with 10 vol% triethanolamine (TEOA) as the sacrificial agent under visible light (λ > 420 nm) irradiation. According to Fig. 3a, all Pt-loaded h-ZIS photocatalysts exhibit higher H₂ evolution performance than the counterpart (h-ZIS: 19.67 μmol h⁻¹ with 20 mg photocatalyst). The optimized rate (350.1 μmol h⁻¹) is acquired at Pt₀.₃-ZIS, which is about 17.8 times enhanced than that of pristine h-ZIS. When Pt loading content exceeds 0.₃ wt%, the activity experiences a decrease, and the catalytic efficiency of each Pt site is reduced (Supplementary Fig. 23). In addition, h-ZIS with sulfur vacancies (h-ZIS-V₅) was synthesized through the treatment of NaBH₄ in a water bath. Benefiting from the existence of localized states caused by sulfur vacancies, h-ZIS-V₅ performs a narrower bandgap (2.66 eV) and a longer average fluorescence lifetime (5.86 ns) than h-ZIS (2.79 eV and 3.02 ns) (Supplementary Figs. 24 and 25). As a result, the photocatalytic activity of h-ZIS is enhanced after creating sulfur vacancies. Then Pt₀.₃-ZIS-V₅ (0.₂₈ wt% Pt) was also prepared by the same photochemical procedure (Supplementary Fig. 26). The obviously decreased ESR signal of Pt₀.₃-ZIS-V₅ and the calculated adsorption energy reveal that Pt single atoms incline to be trapped at defect sites rather than protrude out of h-ZIS-V₅ surface (Supplementary Figs. 26, 27). The recorded H₂ generation rate for Pt₀.₃-ZIS-V₅ is only about half of that for Pt₀.₃-ZIS (Fig. 3b). These results imply that the excellent catalytic activity of Pt₀.₃-ZIS could be mainly...
attributed to the protrusion-like Pt species on 2D h-ZIS. Similar to the trend of visible light, Pt0.3-ZIS also displays a boosted activity under simulated solar light with a total H2 generation of 3504 μmol within 6 h, whereas only 245.7 μmol H2 is formed by h-ZIS (Supplementary Fig. 28). Additionally, Pt0.3-ZIS could introduce acceptable HER performance even in pure water and the H2 evolution rate is ~24.04 μmol h−1 (1202 μmol h−1 g−1) under visible light irradiation (Supplementary Fig. 29). Dependence of apparent quantum efficiency (AQE) at each wavelength for Pt0.3-ZIS derived from the amount of generated H2 was estimated by various band-pass filters (Fig. 3c and Supplementary Table 7). The AQE matches well with the absorption spectrum of Pt0.3-ZIS, and reaches up to 50.4% at 420 nm. Experiments in dark or without photocatalysts show no H2 evolution, demonstrating that H2 is generated by the photocatalysis processes. Such high AQE and catalytic HER activity of Pt0.3-ZIS is far beyond the majority of representative photocatalysts (details see the comparisons in Fig. 3d and Supplementary Table 8). Furthermore, Pt0.3-ZIS almost maintains its photocatalytic H2 evolution rate at the initial level after continuous irradiation for 50 h (Fig. 3e). The characterizations including XRD, XPS, TEM, and HAADF-STEM, demonstrate that the structures undergo negligible changes, manifesting high stability of Pt0.3-ZIS (Supplementary Figs. 30–33).

Due to its outstanding performance, we dispersed Pt0.3-ZIS into ethanol solution and then drop-casted onto FTO substrate (1.5 × 2 cm2) to form a thin film (~3 μm thick) with excellent transmittance (Supplementary Figs. 34 and 35). As a proof-of-concept, the resultant Pt0.3-ZIS film was employed as a photocatalyst for H2 production. No H2 is generated before irradiation, while small H2 bubbles start to appear continuously when turning on the light (Fig. 3f, g and Supplementary Movies 1, 2). The H2 generation rate over the film achieves as high as 0.967 L h−1 m−2 (43.17 mmol h−1 m−2) under visible light irradiation, outperforming numerous recent reported photocatalysis films, such as C3N4 film (0.19 L h−1 m−2) and PtSS-MOF (0.398 L h−1 m−2), which dictates an enormous potential for real applications21,35.

Insight of the increased photocatalytic activity. To shed light on the origin of enhanced activity, three elementary processes in photocatalysis HER, namely light absorption, charge separation, and interfacial H2 catalysis, are taken into consideration. The optical absorption properties were examined by ultraviolet-visible
(UV-vis) diffuse reflectance spectra. An absorption edge at around 440 nm corresponding to the bandgap of about 2.85 eV, is observed for Pt0.3-ZIS. It is slightly larger than that of pristine h-ZIS (2.79 eV), revealing a blue-shift absorption edge of h-ZIS upon Pt stabilizing (Fig. 4a and b). These results are similar to those achieved from the photocurrent action spectra of different photocatalysts film electrodes (Supplementary Fig. 36). Even though the light absorption is enhanced in the visible range with further increasing the amount of Pt (Pt3.0-ZIS), the measured photocurrent action spectrum of Pt3.0-ZIS is quite different from its UV-vis absorbance, in which there is almost no photocurrent at 500 nm. Additionally, the AQE of Pt3.0-ZIS was also recorded (Supplementary Fig. 37 and Table S7). Consistent with the photocurrent action, the AQE of Pt3.0-ZIS does not follow well with the UV-vis spectrum and only a little amount of H2 is generated at 500 nm. Considering that the Pt colloids exhibit broadband optical absorption from ultraviolet to the visible light region, we can conclude that Pt nanoparticles formed in Pt3.0-ZIS could extend the light absorption, but have limited contributions to the photocatalytic performances of h-ZIS. The digital images demonstrate an obvious color change from ivory to pale yellow for h-ZIS and Pt0.3-ZIS, and finally to dark brown for Pt3.0-ZIS. The relationship between VBM, Ef, and E_vac, and the UPS spectra of different photocatalysts are shown in Fig. 4c. The vacuum level (E_vac) should be located 21.2 eV above the cutoff energy (E_cutoff) of the spectrum. The relative locations of valence band maximum (VBM) are calculated to be −6.14 eV (h-ZIS) and −6.12 eV (Pt0.3-ZIS) compared with E_vac according to UPS spectra (Fig. 4d). As a result, h-ZIS and Pt0.3-ZIS display the conduction band minimum (CBM) potential of −3.35 and −3.27 eV, respectively (Fig. 4e). The detailed band positions are illustrated in Supplementary Table 9. The elevation of CBM endows the photoexcited electrons in Pt0.3-ZIS with a higher reduction ability to react with hydrogen ions and form molecular hydrogen in HER compared with h-ZIS. This favorable feature of the band structure is advantageous to prohibit the recombination of...
electron-hole pairs, and is responsible for the enhanced photocatalytic performance of Pt0.3-ZIS.

The electron dynamics involved in photocatalysis were revealed by time-resolved diffuse reflectance (TDR) spectroscopy, a robust technique to provide direct evidence for the effect of Pt loading on charge separation in semiconductors37,38. The pump light with a central wavelength of 420 nm was used, which is effective for photoinduced an interband transition in h-ZIS. It turns out that probing in the wavelength range of 900–1200 nm yielded similar TDR spectra, featuring free or trapped photoexcited electrons (Supplementary Fig. 38)39,40. And a set of representative data obtained at 1150 nm combined with the biexponential fitting results are illustrated. In Fig. 4f, the two-time constants for h-ZIS are $\tau_1 = 12.5$ ps (52.7%) and $\tau_2 = 567$ ps (47.3%), respectively, and the weighted average lifetime is 554 ps. In comparison, the characterized two-time constants for Pt0.3-ZIS (Figure 1k) are $\tau_1 = 0.259$ ps (97.0%) and $\tau_2 = 16.6$ ps (3.0%) and Pt3.0-ZIS (Figure 1k) is $\tau_1 = 0.782$ ps (89.2%) and $\tau_2 = 31.6$ ps (10.8%). This lead to much shorter average lifetime of 11.1 and 26.4 ps, respectively. In general, the average recovery lifetime is considered as a crucial indicator for evaluating the separation efficiency of photoexcited electron-hole pairs, and such a shortened lifetime indicates the opening of an additional pathway for electron transfer after Pt deposition31,42. Based on the mean transient decay times of h-ZIS (τTDR), Pt0.3-ZIS (τh), and Pt3.0-ZIS (τh), we can determine the injection rate through the equation as $k_{et} = (1/\tau_1) - (1/\tau_{TDR})$, where $x$ represents the weight ratio of Pt (33,34). It is highlighted that the $k_{et}$ of Pt0.3-ZIS is 8.8 × 10$^{-6}$ s$^{-1}$, to be almost 2.4 times faster than that of Pt3.0-ZIS (3.6 × 10$^{-6}$ s$^{-1}$). In addition, as a more significant parameter for photocatalytic activity, the efficiency of electron injection ($\eta_{inj}$) from h-ZIS to Pt is calculated as $\eta_{inj} = 1 - \tau_x/\tau_{TDR}$, and Pt0.3-ZIS affords a higher $\eta_{inj}$ ($\eta_{inj} = 98.0\%$) than that of Pt3.0-ZIS ($\eta_{inj} = 95.2\%$).

Additionally, steady-state photoluminescence (PL) spectra were recorded (Supplementary Fig. 39). Loading Pt onto h-ZIS results in significant PL quenching for Pt-ZIS, and Pt0.3-ZIS exhibits the lowest PL intensity among the photocatalysts, which presently, the photocurrent intensity of Pt0.3-ZIS is around 6.5 and Pt3.0-ZIS shows the smallest semicircle diameter and separation in Pt 0.3-ZIS was also concluded (47,48). The efficiency of charge separation in Pt0.3-ZIS was also confirmed by photocatalytic activation of peroxymonosulfate (PMS) to degrade antibiotic ornaments (ONZ) pollutants (Supplementary Fig. 41). For Pt0.3-ZIS, the degradation efficiency of ONZ is 1.8 and 1.7 times and the utilization efficiency of PMS is 2.4 and 1.8 times than h-ZIS and Pt3.0-ZIS, respectively. The effective electrons injection from Pt0.3-ZIS to PMS molecules generate more reactive species, contributing to the higher photocatalytic performance than h-ZIS and Pt3.0-ZIS. These results disclose that more rapid and efficient directional migration of photogenerated electrons is realized by isolated Pt atoms decoration, partly accounting for Pt0.3-ZIS with the greatly enhanced photocatalytic performance38,48.

DFT calculations were further carried out to dive fundamental insight into the effect of atomic Pt decoration. The charge density difference isosurface images reveal a strong charge redistribution at Pt-bonding region after the presence of protrusion-like single Pt atom on the basal plane of h-ZIS, and the calculated Bader charge shows that 0.06 e is transferred from Pt to S atoms in the h-ZIS substrate, confirming the strong interaction between Pt and h-ZIS (Fig. 5a and b)30. It is also observed that the Pt–S coordination has obvious charge transfer along the z direction. When the Pt adsorbate hybridizes with the p band of S, the adsorbate state split into localized bonding and antibonding states. In the projected density of states (PDOS) profile for PtSS-ZIS, the dominant feature is Pt 5d-S 3p bonding resonances below the Fermi level and forming hybridized electronic states (Fig. 5c). Such states are considered as the electron acceptor states that could endow PtSS-ZIS with metallic conductive character to inhibit the recombination of electron-hole pairs49. Moreover, the antibonding states of PtSS-ZIS with the position all above the Fermi level involve in constructing conduction band, which probably leads to the upshift of CBM19. This enlarged bandgap for PtSS-ZIS is consistent with the UV-vis absorption spectra and UPS spectra. Hence, theoretical calculations suggest that the covalent Pt–S coordination bond within PtSS-ZIS forms additional charge-transfer channels to improve the charge mobility, causing an enhanced photocatalytic activity.

To disclose the underlying interfacial catalytic contribution of PtSS-ZIS, the dominant feature is Pt 5d-S 3p bonding resonances below the Fermi level and forming hybridized electronic states (Fig. 5c). Such states are considered as the electron acceptor states that could endow PtSS-ZIS with metallic conductive character to inhibit the recombination of electron-hole pairs49. Moreover, the antibonding states of PtSS-ZIS with the position all above the Fermi level involve in constructing conduction band, which probably leads to the upshift of CBM19. This enlarged bandgap for PtSS-ZIS is consistent with the UV-vis absorption spectra and UPS spectra. Hence, theoretical calculations suggest that the covalent Pt–S coordination bond within PtSS-ZIS forms additional charge-transfer channels to improve the charge mobility, causing an enhanced photocatalytic activity. To disclose the underlying interfacial catalytic contribution of PtSS-ZIS, the dominant feature is Pt 5d-S 3p bonding resonances below the Fermi level and forming hybridized electronic states (Fig. 5c). Such states are considered as the electron acceptor states that could endow PtSS-ZIS with metallic conductive character to inhibit the recombination of electron-hole pairs49. Moreover, the antibonding states of PtSS-ZIS with the position all above the Fermi level involve in constructing conduction band, which probably leads to the upshift of CBM19. This enlarged bandgap for PtSS-ZIS is consistent with the UV-vis absorption spectra and UPS spectra. Hence, theoretical calculations suggest that the covalent Pt–S coordination bond within PtSS-ZIS forms additional charge-transfer channels to improve the charge mobility, causing an enhanced photocatalytic activity. To disclose the underlying interfacial catalytic contribution of PtSS-ZIS, the dominant feature is Pt 5d-S 3p bonding resonances below the Fermi level and forming hybridized electronic states (Fig. 5c). Such states are considered as the electron acceptor states that could endow PtSS-ZIS with metallic conductive character to inhibit the recombination of electron-hole pairs49. Moreover, the antibonding states of PtSS-ZIS with the position all above the Fermi level involve in constructing conduction band, which probably leads to the upshift of CBM19. This enlarged bandgap for PtSS-ZIS is consistent with the UV-vis absorption spectra and UPS spectra. Hence, theoretical calculations suggest that the covalent Pt–S coordination bond within PtSS-ZIS forms additional charge-transfer channels to improve the charge mobility, causing an enhanced photocatalytic activity.
protrusion-like single atoms could continuously enrich protons, which issues an improvement in proton mass transfer, thus boosting the kinetics of H₂ production on the Pt single atom²²,²⁶,⁵⁰,⁵². Active blocking experiment by introducing thiocyanate ion (SCN⁻) into the catalyst system dictates a drastically decreased H₂ generation rate from 350.1 to 27.44 μmol h⁻¹ with the increase of KSCN concentration, confirming that Pt single atoms indeed serve as the centers for HER (Supplementary Fig. 46). Based on calculations, the adsorbed Pt single sites onto the surface of h-ZIS manifests a fast formation and release of molecular hydrogen, leading to an outstanding catalytic activity.

**Discussion**

By combining experimental results with theoretical calculations, the high catalytic performance of Pt₀.₃-ZIS accompanied with long durability is confirmed. The enhanced H₂ generation rate is due to the atomic protrusion-like Pt atoms with triple roles in the photocatalytic HER. First, single Pt atoms immobilized onto h-ZIS could tune the band structure of h-ZIS on upshifting the CBM, providing a larger reduction driving force. Second, the atomically dispersed Pt are acted as electron wells to accelerate charge separation and transportation. Third, the tridimensional protrusions induce effective proton mass transfer to the active Pt site and an almost thermoneutral ΔG° for HER, which is also supported by the smallest overpotential of Pt₀.₃-ZIS among J–V curves (Supplementary Fig. 47). A reasonable photocatalytic mechanism for HER from water is proposed (Supplementary Fig. 48). Upon light irradiation, the electron and hole pairs are generated and then migrate from the interior to the surface of h-ZIS. Due to the covalent Pt–S coordination bond, electrons are injected from the neighboring S atoms into Pt single atoms efficiently, followed by the reaction with...
adsorbed protons to generate H₂. Simultaneously, the holes in h-ZIS are consumed by TEOA.

In summary, compared to the conventional defect-trapped-SSCs, atomically dispersed Pt sites are immobilized onto the basal plane of h-ZIS nanosheets to generate catalysts by a facile photochemical strategy. The efficient water reduction activity over Pt₀.₃-ZIS proceeds via regulated band structure, improved charge separation, reduced H₂ evolution overpotential, and advanced protons mass transfer. The demonstration herein of constructing tridimensional protrusions through immobilizing ultralow content Pt SSCs onto 2D h-ZIS nanosheets presents a promising, cost- and energy-efficient avenue for boosting photocatalysis H₂ evolution, and this prototype potentially would stimulate innovative ideas of enabling future ambient HER catalysts of industrial interest. The phenomenon of triggering tip enhancement by high-curvature nano-textures could function as a general prescription to enhance the performances of catalysts achieved in other reactions, such as organic pollutants degradation, O₂ reduction, CO₂ reduction, and N₂ fixation.

Methods

Synthesis of hexagonal ZnIn₉S₄ (h-ZIS) nanosheets. In a typical synthesis, 68 mg ZnCl₂ (Aladdin, 99.95%), 293 mg InCl₃·4H₂O (Aladdin, 99.9%), and 300 mg trisodium citrate (Aladdin, 99.0%) are dissolved into 25 mL of deionized water and 5 mL of glycol (Shanghai LingFeng Chemical Reagent Co. LTD, AR). After being drastically stirred for 30 min at room temperature, 150 mg triothiocadmate (TAA, SCR, AR) is then added into the solution. After another 30 min stirring, the heterogeneous solution was transferred into a 50 mL Teflon-lined stainless steel autoclave and maintained at 120 °C for 12 h in an oven. After natural cooling, the products were collected by centrifugation, rinsed twice with ethanol and distilled water, and then freeze-dried.

Synthesis of hexagonal ZnIn₉S₄ thin layers with S-vacancy (h-ZIS-Vₓ). The as-obtained h-ZIS (100 mg) was dissolved into 50 mL storage bottle containing 0.1 M NaBH₄ (Shinpochemical Pharm Chemical Reagent Co., Ltd, AR). The mixture was heated at 60 °C in a water bath. After 5 min, the resultant dispersion was centrifuged and then freeze-dried.

Synthesis of Pt-loaded h-ZIS and h-ZIS-Vₓ atomic layers (Pt-ZIS and Pt-ZIS-Vₓ). In a typical procedure of photochemical loading Pt on h-ZIS, 20 mg thin layers h-ZIS and different amounts of H₂PtCl₆ (4 mg mL⁻¹) were dispersed in an aqueous solution containing 45 mL H₂O and 5 mL triethanolamine (TEOA, XiLong Scientific, AR). Subsequently, the suspension is bubbled with argon gas through the reactor for 30 min to completely remove the dissolved oxygen and ensure that the reactor is in an anaerobic condition. The dispersion was kept stirring with a magnetic stirrer during visible light irradiation (λ > 420 nm). After the light treatment for 60 min, the sample was centrifuged and washed by deionized water twice and then freeze-dried. By alerting the volume of H₂PtCl₆ solution, the Pt content relative to h-ZIS was adjusted to about 0.1, 0.3, 0.7, 1.4, and 3.0 wt%, which were named as Pt₀.₁-ZIS, Pt₀.₃-ZIS, Pt₀.₇-ZIS, Pt₁.₄-ZIS, and Pt₃.₀-ZIS, respectively. For the synthesis of Pt₀.₃-ZIS-Vₓ, the procedure was similar to that of Pt₀.₃-ZIS except changing h-ZIS to h-ZIS-Vₓ.

Preparation of Pt₀.₃-ZIS thin films. Typically, Pt₀.₃-ZIS (30 mg) powder was dispersed into ethanol (2 mL) and then sonicated for 10 min to obtain a colloidal solution. The film was drop-cast from 400 µL of the colloidal solution onto roughened glass (1.5 × 2 cm²). Then, the film was dried in a vacuum oven at the temperature of 60 °C.

Photocatalytic hydrogen production. Twenty milligrams of photocatalysts was dispersed in 45 mL aqueous solution containing 10 v/v% TEOA using an ultrasonic bath. Subsequently, the suspension was bubbled with argon gas through the reactor for 30 min to completely remove the dissolved oxygen and ensure that the reactor was in an anaerobic condition. The samples were irradiated under visible light using a 300 W Xenon lamp for H₂ generation (PLS-SXE300D, Beijing Perfection Technology Co., Ltd, 300 mw cm⁻²). The reaction temperature is kept at about 8 °C. The visible light is filtered with a nominal 420 nm cutoff filter. The volume of H₂ was measured by Shimadzu GC-8A gas chromatograph equipped with an M5A column and thermal conductivity detector. The apparent quantum efficiency (AQE) was calculated using the following equation,

\[
\text{AQE(%) = } \frac{N_f}{N_p} \times 100\% = \frac{2 \times n_{H_2} \times N_A \times h \times \varepsilon}{S \times \tau \times A} \times 100\% \tag{1}
\]

where \(N_p\) is the total incident photons, \(N_{H_2}\) is the total reactive electrons, \(n_{H_2}\) is the amount of H₂ molecules, \(N_A\) is Avogadro constant, \(h\) is the Planck constant, \(\varepsilon\) is the speed of light, \(S\) is the irradiation area, \(P\) is the intensity of irradiation light, \(\tau\) is the photoconversion time, and \(\lambda\) is the wavelength of the monochromatic light. For the stability test, the photocatalyst was continuously irradiated for 50 h. The turnover frequency (TOF) was calculated according to the following equation:

\[
\text{TOF} = \frac{n_f}{n_{Pt} \times \tau} \tag{2}
\]

Data availability

All data relevant to this study are available from the corresponding author upon reasonable request. The source data are provided as a Source data file. Source data are provided with this paper.

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Author contributions

X.S. and M.Z. constructed and planned the whole project. X.S., C.D., and X.W. performed the synthesis, characterization, and photocatalysis. X.S. and C.D. performed the XAS in terms of XANES and EXAFS tests. X.W. performed the in situ FTIR tests. J.H. performed the photodegradation and photo-electrochemical experiments. L.M. and J.Z. conducted the DFT calculations. X.S. and L.M. writing—original draft, M.Z., L.Z., and H.Z. writing—review and editing. All authors analyzed the data and commented on the manuscript.

Competing interests

The authors declare no competing interests.

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