

1 **Large electronegativity differences between adjacent atomic sites activate and**
2 **stabilize ZnIn₂S₄ for efficient photocatalytic overall water splitting**

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24 **Abstract:** Photocatalytic overall water splitting into hydrogen and oxygen is desirable for long-term
25 renewable, sustainable and clean fuel production on earth. Metal sulfides are considered as ideal
26 hydrogen-evolved photocatalysts, but their component homogeneity and typical sulfur instability cause
27 an inert oxygen production, which remains a huge obstacle to overall water-splitting. Here, a distortion-
28 evoked cation-site oxygen doping of ZnIn_2S_4 (D-O-ZIS) creates significant electronegativity
29 differences between adjacent atomic sites, with S_1 sites being electron-rich and S_2 sites being electron-
30 deficient in the local structure of $\text{S}_1\text{-S}_2\text{-O}$ sites. The strong charge redistribution character activates
31 stable oxygen reactions at S_2 sites and avoids the common issue of sulfur instability in metal sulfide
32 photocatalysis, while S_1 sites favor the adsorption/desorption of hydrogen. Consequently, an overall
33 water-splitting reaction has been realized in D-O-ZIS with a remarkable solar-to-hydrogen conversion
34 efficiency of 0.57%, accompanying a ~91% retention rate after 120 h photocatalytic test. In this work,
35 we inspire an universal design from electronegativity differences perspective to activate and stabilize
36 metal sulfide photocatalysts for efficient overall water-splitting.

37 **Key words:** Overall water splitting; ZnIn_2S_4 ; Electronegativity differences; Active sites;
38 Photocatalytic stability

39

40 **Introduction**

41 The utilization of sunlight and water, two of the most abundant natural resources on earth, for the
42 production of hydrogen (H₂) and oxygen (O₂) at a stoichiometric ratio of 2:1, holds great potential for
43 achieving carbon neutrality ^[1]. Compared with the certain solar hydrogen production techniques, such as
44 photoelectrochemical water splitting, photocatalytic overall water splitting eliminates the need for
45 external bias or circuitry, thereby reducing system costs and mitigating photocatalyst corrosion, stability,
46 and safety concerns ^[2]. Semiconductor-based photocatalytic overall water splitting is an ideal solar-to-
47 chemical energy conversion route ^[3]. Constructing a hybrid photocatalyst can enhance light harvesting
48 and facilitate charge separation ^[4-6]. However, the long reaction paths and random distribution of active
49 sites in hybrid systems limited its photocatalytic activity ^[7-12]. Recently, single photocatalysts, such as
50 SrTiO₃, GaN, Y₂Ti₂O₅S₂, F-C₃N₄, TpBpy covalent organic frameworks, SrTaO₂N, and Ta₃N₅, etc. have
51 been developed to achieve overall water splitting while avoiding the problems of constructing hybrid
52 systems ^[13-20]. However, the development of photocatalysts with high solar to hydrogen (STH)
53 efficiencies in solar hydrogen systems remains a fundamental challenge ^[21-23].

54 Metal sulfides are considered as promising photocatalysts due to their appropriate energy bands,
55 designable structures, and excellent photoelectric properties ^[24-26]. The representative metal sulfides
56 such as ZnIn₂S₄, MoS₂, WS₂, and In₂S₃ have been widely used in the field of photocatalytic water
57 splitting ^[27-29]. Among them, ZnIn₂S₄ (ZIS) is a typical ternary layered metal chalcogenide
58 semiconductor, possessing suitable band gap of about 2.44 eV and conduction band potential of -0.43
59 eV versus Normal Hydrogen Electrode (NHE), which holds the visible-light absorption and strong
60 reduction capacity for H₂ generation from water splitting ^[24]. Many strategies have achieved enhanced
61 H₂ production performance around ZIS photocatalyst, such as constructing a Z-scheme heterostructure

62 of sulfur vacancies ZIS with other semiconductor^[9], fabricating S vacancy induced with atomic Cu
63 doping in ZIS nanosheets ^[23], incorporating anion-site oxygen doping into the sulfur atom sites of ZIS
64 ^[24], and modulating cocatalyst of protruding single Pt atoms ^[7], but they have not been able to attain
65 efficient and stable overall water-splitting reactions. One of the critical challenges faced in enhancing
66 the efficiency for water splitting is the homogeneous composition of active sites and consistent
67 electronic structure in single photocatalyst. Additionally, the sulfur atoms present in a ZIS
68 photocatalyst are highly prone to oxidation by photogenerated holes, leading to its instability. Those
69 bottlenecks result in an inert base that hinders oxygen production and ultimately lead to poor overall
70 water-splitting performance ^[21, 22].

71 Here, a distortion-evoked cation-site O doping of ZIS (D-O-ZIS) was designed to break the
72 homogeneity of its component between adjacent atomic sites and realize high performance overall
73 water splitting. Normally, O atoms tend to occupy the anion site position of ZIS, where no oxygen
74 is produced (Supplementary Fig. 1). O doping in the cation site position is challenging to achieve
75 due to the unfavorable energetics involved. Different from the typical anion-site O doping in ZIS,
76 D-O-ZIS overcomes the high barrier of cation-site O doping by constructing an intermediate,
77 distorted high-energy structure, which facilitates the doping of O atoms into the cation sites (i.e.,
78 distortion-evoked cation-site O doping). The strategy involves thermally inducing atomic
79 migration to generate a distorted edge structure (D-ZIS), which is subsequently treated with O₂
80 plasma to evoke cation-site O doping and create D-O-ZIS (see Fig. 1a and the methods section for
81 a detailed synthesis process). The distortion states and cation-site O doping induced charge
82 redistribution and altered the electronegativity balance of coordinated atomic sites in the O-doped
83 distortion regions. Specifically, the electron-rich S₁ sites and the electron-deficient S₂ sites in the

84 local S₁-S₂-O configuration of D-O-ZIS have manifested optimal adsorption/desorption behavior
85 of H₂ or O₂ during the reaction. The S-O bond of D-O-ZIS, being a hybridized electronic state of
86 S 3*p*-O 2*p*, promotes stable oxygen evolution for overall water-splitting reactions and avoids the
87 common issue of sulfur instability in metal sulfide photocatalysis. Consequently, D-O-ZIS as a
88 single photocatalyst exhibited outstanding photocatalytic overall water-splitting performance with
89 a 0.57% STH, accompanied by an enhanced water-splitting stability of ~91% retention rate after
90 120 h. In this work, this strategy could also effectively activate the oxygen inert of other metal
91 sulfide photocatalysts, such as MoS₂ and In₂S₃, demonstrating the design universality of the metal
92 sulfides from electronegativity differences perspective for overall water splitting.

93 **Results**

94 **Photocatalyst characterization**

95 The photocatalysts were analyzed using scanning electron microscopy (SEM) and transmission
96 electron microscopy (TEM), which revealed nanoflower-like structures consisting of nanosheets (Fig.
97 1b, 1c, Supplementary Fig. 2). High-resolution TEM (HRTEM) images confirmed that the lattice
98 fringes of the sample had an interplanar distance of 0.32 nm, corresponding to the (102) lattice plane
99 of hexagonal phase ZIS (Fig. 1d-f) [8]. D-ZIS and D-O-ZIS exhibited distorted edge shells (Fig. 1d, e,
100 yellow squares) compared to ZIS (Fig. 1f). Line profiles indicated that the thicknesses of D-ZIS and
101 D-O-ZIS distorted edge shells were 1.3±0.3 and 2.2±0.2 nm, respectively (Fig. 1g). Energy-dispersive
102 X-ray spectroscopy (EDX) revealed that Zn, In, S, and O were uniformly dispersed spatially in D-O-
103 ZIS (Fig. 1h), while O atom was hardly detected in ZIS and D-ZIS (Supplementary Fig. 2e, g).
104 Selected area electron diffraction (SAED) patterns further indicated that the structures of D-O-ZIS and
105 D-ZIS were distorted at the edges compared to the ZIS crystal structure (Fig. 1i, Supplementary Fig.

106 2f, h). High-angle annular dark field scanning TEM (HAADF-STEM) line scans for the Zn element
107 showed that Zn vacancies were confined to the edges of D-ZIS and D-O-ZIS, whereas the line scan
108 for O showed that the O atoms doped in D-O-ZIS were primarily localized at the outer edge (Fig. 1j,
109 Supplementary Fig. 2i), and the crystal structure of the D-O-ZIS is consistent with that of ZIS
110 (Supplementary Fig. 2j).

111 We conducted a more detailed analysis of the edge shell structure and O doping characteristics of
112 the photocatalysts. The distorted edge shell structure of D-ZIS, which differed from the ZIS without
113 distortion, was primarily caused by S-S bonds and the introduction of Zn vacancies. S 2*p* X-ray
114 photoelectron spectroscopy (XPS) exhibited higher energy shifts in D-ZIS, with additional peaks
115 assigned to the S-S bond (S_2^{2-}) at 164.4 and 165.3 eV (Fig. 2a) [26]. Electron spin resonance (ESR)
116 spectroscopy of D-ZIS displayed a peak intensity at $g = 2.004$ attributed to the unpaired free electrons
117 trapped in Zn vacancy, confirming the existence of Zn vacancy (Fig. 2b), with a concentration of $\sim 2.3\%$
118 determined by Zn XPS spectra (Supplementary Fig. 3, Supplementary Table 1) [26], which is consistent
119 with the inductively coupled plasma (ICP) emission spectrometer results (Supplementary Table 2). The
120 Fourier-transform of $k^3\chi(k)$ curves for Zn *K*-edge extended X-ray absorption fine structure (FT-EXAFS)
121 spectra showed a Zn-S peak at $R = 1.90 \text{ \AA}$ in D-ZIS, but with reduced intensity compared to ZIS (Fig.
122 2c), indicating the presence of Zn vacancy induced distortion states [23]. This finding was further
123 confirmed by the Zn *K*-edge EXAFS spectra in *k* space, which exhibited a damped oscillation for D-ZIS
124 compared to ZIS (Fig. 2d), and the strong wavelet contour plots (Supplementary Fig. 4) [23, 30-33]. The
125 distorted lattice parameters of the Zn *K*-edge EXAFS fitted results (Supplementary Fig. 5,
126 Supplementary Table 3) confirmed the presence of distortion states induced by the S-S bonds and the
127 altered bond lengths [34-36].

128 The incorporation of O atoms induced the formation of more Zn vacancies, resulting in
129 increased distortion states in D-O-ZIS. XPS and Raman spectroscopy confirmed O doping in D-O-
130 ZIS, with an O atom concentration of 5.8% as confirmed by O 1s spectra (Fig. 2a, Supplementary
131 Fig. 3). ESR and Zn *K*-edge FT-EXAFS data suggested an increase in Zn vacancies in D-O-ZIS (Fig.
132 2b, 2c), with a concentration of ~3.7% (Supplementary Fig. 3c). A weak peak at about 1.39 Å
133 assigned to the Zn-O coordination in D-O-ZIS [24]. The Zn *K*-edge EXAFS of D-O-ZIS in *k* space
134 showed minimal oscillation, indicating an increase in distortion states in the structure (Fig. 2d) [34,
135 37]. This is consistent with the formation of Zn vacancies induced by O doping in theoretical
136 calculations (Supplementary Fig. 6). We further verified cation-site O atom doping in Zn atom sites
137 of D-O-ZIS using S *K*-edge X-ray absorption near-edge structure (XANES) spectra, which revealed
138 an S-O coordinated bond at 2481.8 eV (Fig. 2e) [34, 36]. The rising S pre-edge showed a higher energy
139 shift from 2467.5 for pristine ZIS to 2468.9 eV for D-ZIS due to S-S anti-bond formation. Doping
140 with O, which possesses stronger electronegativity, led to a further shift of the S pre-edge to 2470.5
141 eV for D-O-ZIS, generating a higher valence state of coordinated S atom [34], and hence, the
142 electronegativity difference within the S-O bond. The O *K*-edge XANES spectra verified the
143 existence of the S-O bond as an S 1s–O 2p δ^* anti-bond (Fig. 2f) [34, 37]. Density Functional Theory
144 (DFT) calculation simulations of distortion states and O doping structures (Fig. 2g) revealed that the
145 lattice parameters matched the XANES fitted results (Supplementary Fig. 5, Supplementary Table
146 3). Distortion-evoked cation-site O doping in ZIS has a formation energy (E_f) of 5.99 eV for distorted
147 configurations with high energy structures containing S-S bonds and Zn vacancies. Cation-site O
148 doping has a negative energy of -3.45 eV. This suggests that distortion structures lower the energy
149 required for cation-site O doping in Zn atom sites, making it energetically favorable.

Photocatalytic overall water splitting performance

The photocatalytic performance of samples was evaluated for an overall water-splitting reaction from pure water with Pt and CoO_x used as co-catalysts. Loading of co-catalysts can greatly enhance the photocatalytic activity of D-O-ZIS for water splitting by constructing matched energy band between D-O-ZIS and cocatalysts and reducing the free energy of hydrogen and oxygen adsorption (Supplementary Fig. 7-9). When exposed to light irradiation at AM 1.5G (100 mW cm⁻²) with optimized Pt and CoO_x loading, H₂ and O₂ were steadily produced over D-O-ZIS, achieving evolution amounts up to 373.2 and 177.6 μmol within 12 h reaction, respectively (Supplementary Fig. 9, 10, Fig. 3a). Meanwhile, during the photocatalytic process, H₂ and O₂ are less prone to adsorb onto D-O-ZIS/Pt/CoO_x, accompanied by a 14% reduction observed after a 12-hour dark reaction (Supplementary Fig. 11-13) [1, 38, 39]. ZIS and D-ZIS cannot split water into H₂ and O₂ with co-catalyst loading and activity attenuation occurs in each cycle (Supplementary Fig. 14). The apparent quantum yield (AQY) of D-O-ZIS for overall water splitting was investigated (Supplementary Fig. 15, Supplementary Table 4), and calculated to be 14.90% at 400 nm (Fig. 3b, Supplementary Table 5), higher than that of ZIS (1.40%) or D-ZIS (3.11%) (Supplementary Fig. 16, Supplementary Tables 6, 7). The solar to hydrogen (STH) efficiency was measured at AM1.5G (100 mW cm⁻²) simulated sunlight irradiation with a mean value of 0.57% (Fig. 3c, Supplementary Table 8), which outperforms most of the recently reported single photocatalysts (Supplementary Fig. 17, Supplementary Table 9) and ZIS based composite photocatalysts (Supplementary Fig. 18, Supplementary Table 10).

We further investigated the photocatalytic performance of single D-O-ZIS without adding Pt and CoO_x cocatalysts (Supplementary Fig. 19, Supplementary Table 11). The system still produced H₂ and O₂ evolution, with values of 76.8 and 36.0 μmol, respectively. The STH efficiency yielded value

172 of 0.12% (Supplementary Table 12) and is the highest of the investigated photocatalysts without
173 loading any cocatalysts (Supplementary Fig. 17). In contrast, ZIS and D-ZIS only produced H₂ and
174 showed a decrease in catalytic activity in each cycle (Supplementary Fig. 20). The overall water-
175 splitting activity of D-O-ZIS was further confirmed by performing H₂ or O₂ evolution half-reactions.
176 D-O-ZIS exhibited H₂ or O₂ evolution during the half-reactions, while no O₂ was detected on ZIS and
177 D-ZIS (Supplementary Fig. 21). The ¹⁸O isotopic measurement for D-O-ZIS confirmed that the
178 generated O₂ was due to water splitting (Supplementary Fig. 22) [4].

179 We also evaluated the photocatalytic stability test for the ZIS, D-ZIS, and D-O-ZIS after a 120 h
180 reaction. The results showed that D-O-ZIS retained ~91% of its original photocatalytic gas evolution
181 rate, demonstrating stability of overall water splitting performance (Fig. 3d), while ZIS and D-ZIS
182 decay almost to zero. The photo-corrosion degree of photocatalysts induced by S leaching after the
183 photocatalytic reaction was evaluated by S 2*p* XPS (Fig. 3e). The S 2*p* spectra of D-O-ZIS showed the
184 smallest binding energy shift of 0.02 eV while preserving the pretest intensity compared to ZIS (0.62
185 eV shift) and D-ZIS (0.59 eV shift) with reduced intensities and oxidation product of SO₄²⁻, indicating
186 that S leaching in D-O-ZIS was significantly suppressed [26, 29]. The HRTEM image and structural
187 analysis of D-O-ZIS after testing revealed stable distortion features (Fig. 3f, Supplementary Fig. 23),
188 maintaining the shell thickness of about 2±0.2 nm, while ZIS and D-ZIS exhibited S leaching
189 characteristics (Supplementary Fig. 24). Additionally, we found that S *K*-edge and O *K*-edge XANES
190 for D-O-ZIS showed negligible changes in characteristic peaks after testing (Supplementary Fig. 25),
191 further indicating its structural stability for photocatalytic reactions (further discussion of stability
192 mechanism in photocatalytic working principle of activation and stability section). This design strategy
193 can activate the oxygen-inert properties of other metal sulfide photocatalysts, including MoS₂ and In₂S₃.

194 This demonstrates the universal applicability of metal sulfides in overall water splitting from an
195 electronegativity difference perspective (Supplementary Fig. 26).

196 **Kinetics of charge transport and separation**

197 The optical and electrical characteristics of the samples were investigated to determine the mechanism
198 of the improved photocatalytic activity. The UV–vis absorption spectrum of D-O-ZIS showed intense
199 optical absorption of the visible region and a redshift compared to ZIS (Supplementary Fig. 27). By
200 introducing distortion and O doping into ZIS, D-O-ZIS exhibited the smallest carrier transport
201 activation energy of 0.13 eV (Fig. 4a), which is favorable for charge transport and was calculated using
202 the Arrhenius equation (Supplementary Fig. 28) ^[40, 41]. To evaluate the carrier separation dynamics,
203 the internal electric field intensity of photocatalysts was analyzed via the potential shift from 0 V to
204 the bias intersection voltage (V_i) based on the conductivity test ^[42-45]. D-O-ZIS showed the strongest
205 internal electric field with the largest potential shift at -0.20 V (Fig. 4b, Supplementary Fig. 29). The
206 internal electric field intensity was further estimated using transient photoelectric measurements and
207 the intensity of D-O-ZIS was 5.1 and 2.0 times stronger than that of ZIS and D-ZIS, respectively (Fig.
208 4c, Supplementary Fig. 30) ^[42]. Additionally, D-O-ZIS exhibited the greatest charge separation ability
209 with a prolonged average carrier lifetime of 42.71 ns and charge separation efficiency of 39.6%,
210 influenced by the internal electric field (Supplementary Fig. 31) ^[42].

211 We calculated the energy band during the photocatalytic process to elucidate the enhanced internal
212 electric field intensity and kinetics of charge transport and separation. The energy band structures were
213 determined through UV–vis diffuse reflectance spectra and ultraviolet photoelectron spectroscopy (UPS)
214 (Fig. 4d) ^[43]. The Fermi level (E_F) of the photocatalyst was found to upshift with increasing distortion
215 states and O doping. During the photocatalytic process, the photocatalyst and solution with different

216 electric potentials are in contact (E_F : photocatalyst; E_s : 0.34 eV for water solution), which creates a space-
217 charge region at the interfaces ^[46, 47]. We estimated the space charge region width (W) using a Mott-
218 Schottky plot ^[46] from Supplementary Fig. 7b and found that D-ZIS and D-O-ZIS showed wider widths
219 of 1.53 and 2.33 W when the depletion region width of ZIS was set as W . The enhanced space charge
220 region width is ascribed to the increased E_F difference ($\Delta\phi$), which is consistent with the trends of the
221 internal electric field. The wider space-charge regions between the photocatalyst and solution interfaces
222 reduced hole drift distance on D-O-ZIS, which provided a strong driving force for charge separation ^{[40,}
223 ^{42]}.

224 The changes in average potentials and internal electric field intensity were further verified by
225 DFT. The E_F raised in D-O-ZIS due to the increased distortion states and O doping (Supplementary
226 Fig. 32), which is consistent with experimental findings. The electrostatic potential difference reflected
227 the internal electric field intensity, which increased proportionally to the E_F difference between the
228 photocatalyst and solution interfaces (Supplementary Fig. 33). Further analysis of the dipole moment
229 revealed that the dipole moment changed significantly along the x, y, and z directions in D-O-ZIS,
230 inducing a dipole of structure and adding asymmetry to the local structure, thus increasing the internal
231 electric field (Fig. 4e) ^[40]. These findings confirmed that the increasing distortion states and O doping
232 in D-O-ZIS enhanced the internal electric field, providing a strong driving force for charge separation.

233 **Photocatalytic working principle of activation and stability**

234 *In situ* Raman spectroscopy was used to monitor the changes occurring on the surface of D-O-ZIS.
235 The Raman signal for S-H adsorption at 2519 cm^{-1} was observed over the potential range from 0.02
236 to -0.12 V versus Reversible Hydrogen Electrode (RHE) to track hydrogen evolution process (Fig. 5a)
237 ^[48-50]. The S-H peak appeared at 0.02 V and became stronger as the potential increased. The peak at

238 1194 cm^{-1} corresponding to $^*\text{OOH}$ adsorption on D-O-ZIS during oxygen evolution was observed in
239 Fig. 5b [48], which intensified gradually over the anodic potential range from 0.06 to 0.25 V versus
240 RHE. The redshifts of S-H (from 2519–2535 cm^{-1}) and $^*\text{OOH}$ (from 1194–1210 cm^{-1}) were attributed
241 to the significant Stark tuning phenomenon and adsorption of interfacial species, including H_2O , OH^- ,
242 and H^+ species [50]. Two-dimensional contour plots also showed that the S-H and $^*\text{OOH}$ vibrations on
243 D-O-ZIS intensified with time (Fig. 5c, d). The determined shift rates for the S-H and $^*\text{OOH}$ vibrations
244 in D-O-ZIS are 114 $\text{cm}^{-1} \text{V}^{-1}$ and 84 $\text{cm}^{-1} \text{V}^{-1}$, respectively (Fig. 5e). Raman signals (S-H and $^*\text{OOH}$)
245 were detected at -0.12 V and 0.25 V potentials, respectively, for ZIS, D-ZIS and D-O-ZIS (Fig. 5f).
246 The S-H signal was stronger for D-O-ZIS than that of ZIS or D-ZIS, and the $^*\text{OOH}$ signal was only
247 detected for D-O-ZIS. Meanwhile, the O 1s XPS spectrum after photocatalytic tests showed a signal
248 of $^*\text{OOH}$ in D-O-ZIS (Supplementary Fig. 34), further confirming the activity of overall water-
249 splitting reactions in D-O-ZIS.

250 DFT calculations were performed to gain insight into the effects of distortion states and cation-
251 site O doping. The calculated Bader charge over the structures revealed a strong charge redistribution
252 in the regions of distortion states and O doping. In the ZIS structure, a charge transfer occurred from
253 the Zn atom (0.861|e|) to the S atom ($-0.805|e|$) (Fig. 5g). In the D-ZIS structure, the charges on the S_1
254 and S_2 atoms were significantly redistributed ($-0.194|e|$ for S_1 and $-0.332|e|$ for S_2) in the dipolar bond
255 of the S_1 – S_2 center. Electrons were transferred from nearby Zn atoms (0.853|e|, 0.847|e|) to the S_1 and
256 S_2 sites in D-ZIS, and the Zn vacancy acted as an electron trap (Fig. 5h) [51]. Cation-site O doping in
257 D-O-ZIS resulted in a large electronegativity, causing the charge on the coordinated S_2 site to become
258 more positive (1.024|e|), even higher than the charge on the Zn atom (0.865|e|). The charge on the S_1
259 site was $-0.410|e|$, indicating a significant difference in electronegativity between the adjacent sites

260 (Fig. 5i). These findings are consistent with the XANES results of the O atom coordinated as S-O
261 configuration (Fig. 2e). The additional charge transfer (from S₂ atoms to O atoms and electrons
262 extracted at the Zn vacancy) improved charge mobility and generated a more positive charge center of
263 the S₂ site, which may switch the active sites in the local structure.

264 To understand the role of active centers in catalytic processes, we investigated the distribution of
265 charge density in the valence band maximum (VBM) and conduction band minimum (CBM) [23, 28].
266 ZIS exhibited uniformly distributed charge densities in both the VBM and CBM (Fig. 6a). However,
267 the VBM and CBM charge densities of D-ZIS were localized at the S₁–S₂ sites, Zn vacancy, and
268 unsaturated S atoms (Fig. 6b). Meanwhile, the CBM charge density of D-O-ZIS was localized at the S₁–
269 S₂–O sites and Zn vacancy, while the VBM charge density was significantly decreased at the S₂ sites.
270 This indicates that electrons could be easily photoexcited to the conduction band, resulting in electron
271 depletion at the S₂ site (Fig. 6c) [22]. Therefore, the photogenerated holes accumulation at the S₂ sites and
272 electrons trap at the S₁ sites and Zn vacancy induced charges that were spatially separated within atomic
273 sites, providing a strong driving force for efficient electron–hole separation on D-O-ZIS.

274 The partial density of states (PDOS) calculation was conducted to investigate the structure of
275 distortion states and O doping in D-O-ZIS. The PDOS of D-O-ZIS showed S 3*p*–O 2*p* bonding
276 resonances near the Fermi level (E_F), with hybridized electronic states dominating the feature
277 (Supplementary Fig. 35) [23]. The electronic states of the S 3*p* and O 2*p* increased at E_F, and the
278 surrounding S atom was also activated compared to D-ZIS and ZIS in the S₁–S₂–O configuration of
279 D-O-ZIS (Fig. 6d). D-O-ZIS showed a high degree of overlap for the intermediates (OH*, O*, and
280 *OOH) adsorbed on the S₂ p-band, indicating strong interactions during the oxygen production process
281 (Supplementary Fig. 36) [18]. The optimum hydrogen adsorption-free energy (ΔG_{H*}) was –0.07 eV at

282 the S₁ site and -0.13 eV at the Zn vacancy, indicating that the S₁ site is more conducive to hydrogen
283 adsorption/desorption than the Zn vacancy in D-O-ZIS, while D-ZIS showed an optimum ΔG_{H^*} of
284 -0.63 eV at the S₁ site and ZIS of -1.10 eV at S site (Fig. 6e), and their adsorption models are depicted
285 in Supplementary Fig. 37-39. The free energy barrier of O* adsorption at the S₂ site in D-O-ZIS was
286 low (0.31 eV) compared to the energy barriers in ZIS (1.27 eV) and D-ZIS (0.97 eV), which enhances
287 the oxygen evolution reaction (Supplementary Fig. 40). Furthermore, the O₂ evolution activity on
288 metal atoms (i.e., Zn sites) was investigated in D-O-ZIS, excluding the role of metal sites as oxygen
289 production sites (energy barrier 0.85 eV) in this photocatalyst design (Supplementary Fig. 41). By
290 investigating structures with varying Zn vacancy levels and O doping (Supplementary Fig. 42), the
291 D-O-ZIS significantly optimized the adsorption of key intermediates for H₂ and O₂ evolution
292 (Supplementary Fig. 43). Consequently, D-O-ZIS exhibited hydrogen and oxygen species adsorbed at
293 the S₁ and S₂ site, respectively, which would promote an overall water-splitting reaction.

294 We further performed the redox potential and free energy of sulfur ions oxidation by the
295 photogenerated holes to elucidate the stability mechanism. The sulfur ions of ZIS or D-ZIS were easily
296 oxidized and devitalized by photoinduced holes due to the redox potential of S²⁻/S⁰ (0.48 eV), while
297 the sulfur ions in S₁-S₂-O had a lower redox potential of S¹⁻/S⁰ (0.42 eV) for D-O-ZIS with weak
298 oxidation driving force (Supplementary Fig. 44). The energy barrier for sulfur ions oxidation in S₁-
299 S₂-O configuration was 0.68 eV for D-O-ZIS, higher than that in D-ZIS (0.42 eV), and ZIS (0.37 eV),
300 indicating that the sulfur ions in S₁-S₂-O configuration were difficult to oxidize by photogenerated
301 holes (Fig. 6f). Additionally, the oxidation energy barrier of sulfur ions for D-O-ZIS (0.68 eV) was
302 higher than the oxygen production free energy of 0.31 eV (Supplementary Fig. 40), which suggests
303 that D-O-ZIS preferred to generate oxygen during water-splitting reactions instead of being oxidized

304 by photogenerated holes.

305 We proposed the work principle of overall water-splitting on D-O-ZIS photocatalyst (Fig. 7), and
306 the catalytic mechanisms of ZIS and D-ZIS were illustrated in Supplementary Fig. 45. Firstly, D-O-
307 ZIS absorbs incident photon to produce photogenerated charge carriers. The photogenerated electron-
308 hole pairs are efficiently separated driven by the internal electric field due to the strong dipole of the
309 distortion-evoked cation-site O doping structure, and then transferred to the active S₁-S₂-O sites to
310 undergo a redox reaction. Due to the optimized energy bands, the CB of D-O-ZIS is negative enough
311 (-0.51 eV) to produce H₂, while the VB is positive enough (1.64 eV) to produce O₂. The strong charge
312 redistribution character and large electronegativity differences between S₁ and S₂ atomic sites activate
313 stable oxygen reactions at S₂ sites and avoids the common issue of sulfur instability in metal sulfide
314 photocatalysis, while S₁ sites favor the adsorption/desorption of hydrogen. The co-catalysts of Pt and
315 CoO_x loading further enhance the photocatalytic activity of D-O-ZIS by promoting charges separation
316 and reducing the free energy of hydrogen and oxygen adsorption. Consequently, D-O-ZIS as a single
317 photocatalyst realizes efficient overall water splitting with high stability.

318 **Discussion**

319 This work proposes an electronegativity difference strategy to activate and stabilize ZIS for
320 photocatalytic overall water-splitting, achieving a remarkable 0.57% solar-to-hydrogen conversion
321 efficiency along with high stability. A distortion-evoked cation-site O doping in Zn atom sites of D-O-
322 ZIS generates significant electronegativity differences between adjacent atomic sites, with S₁ sites
323 being electron-rich and S₂ sites being electron-deficient in the local S₁-S₂-O structure. The strong
324 charge redistribution character activates stable oxygen reactions at S₂ sites and hydrogen
325 adsorption/desorption at S₁ sites. Our study showcases the universal applicability of activating and

326 stabilizing metal sulfides photocatalysts, such as ZIS, MoS₂ and In₂S₃, for efficient photocatalytic
327 overall water-splitting through distortion-evoked cation-site O doping strategy from the perspective of
328 electronegativity differences.

329 **Methods**

330 **Synthesis of photocatalysts**

331 Synthesis of ZnIn₂S₄ (ZIS). The synthesis of ZIS typically involves the following procedure ^[7]: 1 mmol
332 of ZnCl₂, 2 mmol of In(NO₃)₃, and 4 mmol of thioacetamide were dissolved in 35 mL of deionized
333 water and stirred vigorously for 30 minutes. The mixed solution was then transferred to a 50 mL Teflon-
334 lined autoclave and heated at 180 °C for 12 hours. After cooling to room temperature, the resulting
335 yellow suspension was collected and washed with ethanol and deionized water four times, respectively.
336 Finally, the product was dried at 60 °C overnight before further use.

337 Synthesis of distorted ZIS (D-ZIS). The D-ZIS was synthesized starting from ZIS, using a thermal
338 migration strategy. The synthesis process involved heating the precursor material of ZIS at 500 °C for
339 30 minutes under an atmosphere of Ar/H₂ (1 bar). Once the reaction was completed, the resulting
340 powder product was allowed to cool naturally to room temperature, after which it was collected and
341 washed several times using ethanol and deionized water. The product was then dried at 60 °C under
342 vacuum overnight to ensure complete removal of any remaining solvent before further analysis.

343 Synthesis of distortion-evoked cation-site oxygen doping of ZIS (D-O-ZIS). For the synthesis of D-O-
344 ZIS, the resulting D-ZIS was treated with Ar/O₂ (5%) flow at 500 °C for 10 minutes. The resulting
345 powder was then collected and washed three times with ethanol and deionized water, respectively,
346 before being dried under vacuum at 60 °C.

347 Photocatalytic overall water-splitting reaction test

348 To perform photocatalytic reactions, we used a reaction vessel with a gas-closed circulation and
349 evacuation system. Before each reaction, we dispersed 35 mg of photocatalysts in 50 mL of pure water
350 and evacuated the air from the vessel, replacing it with Ar gas. We then conducted photocatalytic H₂
351 and O₂ evolution in a quartz reactor using a 300 W Xe lamp for irradiation. The evolved gases were
352 pumped and detected by a Shimadzu GC-2014c gas chromatography with a thermal conductivity
353 detector. We measured the STH efficiency under simulated sunlight at AM1.5G illumination (100 mW
354 cm⁻²). The STH efficiency was determined according to the following Equation (1):

$$355 \text{ STH (\%)} = (R(\text{H}_2) \times \Delta G_r) / (P \times S) \times 100\% \quad (1)$$

356 Here, $R(\text{H}_2)$, ΔG_r , P , and S denote the H₂ evolution rate, the reaction Gibbs energy during the water
357 splitting reaction, the light energy flux under the AM1.5G irradiation, and the irradiated sample area,
358 respectively. The value ΔG_r used for the calculations is 237 kJ mol⁻¹ for the liquid water in the
359 reaction system. The value of P is 100 mW cm⁻². The value S is 3.6 cm².

360 Data Availability

361 All data generated in this study are provided in the article and Supplementary Information, and the raw
362 data generated in this study are provided in the Source Data file. Source data are provided with this
363 paper.

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512 **Author contributions**

513 These authors contributed equally: X. X., Y. L., X. X. and X. L. conceived the idea. X. L. supervised
514 the project. X. X. performed the synthesis, characterization, and photocatalysis. Y. L., Y. Z. and Y.
515 Wang performed the photo-electrochemical experiments. X. C., Y. Wei, C. D., J. S., R. W., P. G., J. Y.,
516 J. Z., A.J. S., and M.-M. T. analyzed the data and commented on the manuscript.

517

518 **Competing Interests**

519 The authors declare no competing interests.

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532 **Figures**

533 Fig. 1. **Photocatalyst synthesis and morphology characterization.** **a** Schematic of the synthetic process for ZIS,
534 D-ZIS, and D-O-ZIS. The yellow, blue, orange, and green spheres represent the S, Zn, In, and O atoms, respectively.
535 The enlarged image shows the edge structure of samples; **b** SEM image of D-O-ZIS; **c** TEM image of D-O-ZIS; **d**
536 HRTEM image of D-O-ZIS (The lattice fringe enlargement of Fig. 1c). The arrow denotes the distortion in edge. The
537 yellow dashed square denotes shell thickness of ~ 2.2 nm for D-O-ZIS; **e** HRTEM image of D-ZIS. The arrow denotes
538 the distortion in edge. The yellow dashed square denotes shell thickness of ~ 1.3 nm for D-ZIS; **f** HRTEM image of
539 ZIS. The yellow dashed square denotes shell thickness of ~ 0 nm for ZIS; **g** The respective line profiles on the edge
540 of ZIS, D-ZIS, and D-O-ZIS from the outer edge to the core in Fig. 1d-f; **h** The corresponding EDX mapping images
541 of D-O-ZIS. The scale bar is 500 nm; **i** SAED pattern of D-O-ZIS edge. The scale bar is 5 nm^{-1} ; **j** The element
542 distribution and HAADF-STEM line scans of Zn, In, S, and O elements from the outer edge to the core for D-ZIS
543 and D-O-ZIS. Source data are provided as a Source Data file.

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545 Fig. 2. **Geometric and local electronic structures of photocatalysts.** **a** XPS spectra of S 2*p* in ZIS, D-ZIS, and D-
546 O-ZIS; **b** ESR spectra of ZIS, D-ZIS, and D-O-ZIS; **c** The Fourier transform curves of k^3 -weighted Zn *K*-edge EXAFS
547 spectra of ZIS, D-ZIS, and D-O-ZIS; **d** Zn *K*-edge EXAFS spectra of ZIS, D-ZIS, and D-O-ZIS in *k* space; **e**
548 Normalized S *K*-edge XANES spectra of ZIS, D-ZIS, and D-O-ZIS. Embedded is an enlargement of S *K*-edge pre-
549 edge; **f** Normalized O *K*-edge XANES spectra of D-O-ZIS; **g** The schematic process of the local structure
550 transformation of D-O-ZIS to form distortion and cation-site O doping; Meanwhile, the corresponding bond lengths
551 were depicted on the structures. The structures are shown in top view. Source data are provided as a Source Data file.

552

553 **Fig. 3. Photocatalytic overall water splitting performance.** **a** Time-dependent photocatalytic overall water splitting
554 over D-O-ZIS in pure water under standard AM 1.5 illumination (100 mW cm^{-2}), Pt and CoO_x used as cocatalysts, Pt
555 to CoO_x wt% ratio of 1:4, the photocatalyst mass was 35 mg and the photocatalytic activity was evaluated via the
556 total hydrogen and oxygen yield of a cycle, the time of each cycle is 12 h. Error bars represent the standard deviations
557 from the statistic results of three sets of experiments; **b** Wavelength-dependent of AQY during photocatalytic overall
558 water splitting based on D-O-ZIS. AQY denotes the apparent quantum yield that was calculated using equations (2)
559 and (3) in Supplementary Information and details shown in Supplementary Table 5, Pt and CoO_x used as cocatalysts,
560 Pt to CoO_x wt% ratio of 1:4; **c** The STH efficiency of D-O-ZIS with cocatalysts (Pt, CoO_x) loading for photocatalytic
561 overall water splitting. The STH value was evaluated 12 times with separate samples as shown in Supplementary
562 Table 8 and calculated using Equation (1) in main text. The centre line represents the median, the top and bottom box
563 represent the upper and lower quartile, respectively, the small rectangle represents the mean value and the
564 maximum/minimum values are indicated by the top/bottom bars; **d** Photocatalytic gas yield of ZIS, D-ZIS, and D-O-
565 ZIS before and after photocatalytic overall water splitting test in pure water. Error bars represent the standard
566 deviations from the statistic results of three sets of experiments; **e** The S $2p$ XPS spectra of ZIS, D-ZIS, and D-O-ZIS
567 before and after 120 h photocatalytic test. The vertical bars indicate the difference in intensity before and after test; **f**
568 HRTEM image of D-O-ZIS after 120 h photocatalytic test. Source data are provided as a Source Data file.

569

570 **Fig. 4. Charge transport and separation kinetics.** **a** Carrier transport activation energy of ZIS, D-ZIS, and D-O-
571 ZIS (derived from in-situ Electrochemical impedance spectroscopy plots in Supplementary Fig. 28); **b** Electronic
572 conductivity measured via cyclic voltammetry at scanning rate 50 mV s^{-1} . The black dotted line represents the V_i of
573 ZIS. The blue dotted line represents the V_i of D-ZIS, and the red dotted line represents the V_i of D-O-ZIS. The plots
574 are derived from Supplementary Fig. 29; **c** Internal electric field intensity of ZIS, D-ZIS, and D-O-ZIS (according to
575 the Supplementary Fig. 30, assuming the intensity of ZIS to be “1”); **d** Schematic of the detailed band structures,
576 band bending, and space charge region for ZIS, D-ZIS, and D-O-ZIS. Energy of conduction band: (E_{CB}), valence
577 band (E_{VB}) and Fermi level (E_F) are depicted in diagram, potential versus Normal Hydrogen Electrode (NHE). A
578 minimal degree of band bending and driving force exist on the surface of ZIS due to the dangling bond with
579 unsaturated sulfur atoms on its surface. A mild band bending can be detected in D-ZIS. The D-O-ZIS has significantly
580 strong band bending. E_F difference between the photocatalyst and solution: $\Delta\phi$, Fermi level of water solution (E_S).
581 The detailed energy band calculation of photocatalyst seen in Supplementary Fig. 7. The width of space charge region
582 calculation is obtained from Supplementary Fig. 7b and details seen in Supplementary Information. **e** The calculated
583 dipole moments of ZIS, D-ZIS, and D-O-ZIS along three different structural directions. Source data are provided as
584 a Source Data file.

585

586 Fig. 5. **Photocatalytic hydrogen and oxygen evolution process investigated by *in-situ* Raman spectra.** **a** *In-situ*
587 Raman spectra of photocatalytic hydrogen evolution process on D-O-ZIS. A series of Raman spectra at different
588 potential (0.02– -0.12 V versus RHE) exhibit the dynamic variation of hydrogen evolution process; **b** *In-situ* Raman
589 spectra of photocatalytic oxygen evolution process on D-O-ZIS. A series of Raman spectra at different potentials
590 (0.06–0.25 V versus RHE) exhibit the dynamic variation of oxygen evolution process; **c** 2D contour maps of Raman
591 vibrations of hydrogen evolution process; **d** 2D contour maps of Raman vibrations of oxygen evolution process; **e**
592 Raman shifts and area ratios of the S-H bonds and *OOH vibrations versus potentials at the D-O-ZIS surface; **f**
593 Intensity difference of the Raman signals of S-H vibrations and *OOH vibrations versus identical potentials of -0.12
594 V and 0.25 V, respectively, for the samples during hydrogen evolution and oxygen evolution processes. The charge
595 on atoms from Bader charge calculation for **g** ZIS structure, **h** D-ZIS structure, and **i** D-O-ZIS structure. The negative
596 value is referred to obtain electrons, while the positive value means losing electrons. The structures are shown in top
597 view. The bottom is a partial display of the corresponding structure. Source data are provided as a Source Data file.
598

599 **Fig. 6. Photocatalytic overall water splitting working principle determined by DFT.** Distribution of partial charge
600 density near the edge of conduction band and valence band of **a** ZIS, **b** D-ZIS, and **c** D-O-ZIS. The iso-surface value
601 is $0.015 e \text{ \AA}^{-3}$. The structures are shown in top view. **d** PDOS of different S atoms of S₁, S₂, surrounding normal S,
602 and O atoms in D-O-ZIS, and S₁ and S₂ atoms in D-ZIS, and S atom in ZIS; Fermi level (E_F); **e** The computed values
603 of ΔG_{H^*} at different sites in ZIS, D-ZIS, and D-O-ZIS; **f** The free energy of sulfur ions oxidation in ZIS, D-ZIS, and
604 D-O-ZIS. The included configurations are the S atom leaching by photogenerated holes oxidation from pristine
605 structure. Source data are provided as a Source Data file.
606

607 **Fig. 7. Photocatalytic overall water splitting working principle.** The local structure is shown in top view, and the
608 bottom is a partial display of the corresponding structure. Conduction band (CB), Valence band (VB). Source data
609 are provided as a Source Data file.
610











