

Internal quantum efficiency higher than 100% achieved by combining doping and quantum effects for photocatalytic overall water splitting

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Abstract

Multiple exciton generation (MEG), where two or more electron-hole pairs are produced from the absorption of one high-energy photon, could increase the efficiency of light-absorbing devices. However, demonstrations of the effect are still scarce in photocatalytic hydrogen production. Moreover, many photocatalytic systems for overall water splitting suffer from poor charge carrier separation. Here we show that a CdTe quantum dot/vanadium-doped indium sulfide (CdTe/V-In₂S₃) photocatalyst has a built-in electric field and cascade energy band structure sufficient to effectively extract excitons and separate carriers, allowing MEG to be exploited for hydrogen production. We achieve a tunable energy band structure through quantum effects in CdTe and doping engineering of V-In₂S₃, which induces a 14-fold enhancement in CdTe/V-In₂S₃ interfacial built-in electric field intensity relative to pristine CdTe/V-In₂S₃. We report an internal quantum efficiency of 114% at 350 nm for photocatalytic hydrogen production, demonstrating the utilization of MEG effects. The solar-to-hydrogen efficiency is 1.31%.

Keywords: Photocatalytic overall water splitting; Separation efficiency; Quantum effect; Doping engineering; Multiple exciton effect

30 Introduction

31 Photocatalytic overall water splitting into hydrogen and oxygen is a promising approach for production
32 of hydrogen¹⁻³. Various strategies, such as heterojunction construction⁴⁻⁸, atom doping⁹⁻¹², crystal facet
33 engineering^{13,14} and defect engineering¹⁵⁻¹⁷, have been adopted to enhance the photocatalyst
34 performance. Specially, Z-scheme photocatalyst construction has been demonstrated to be a promising
35 method for facilitating charge separation and improving photocatalyst performance¹⁸⁻²⁰. A Zn–Pt
36 porphyrin conjugated polymer/BiVO₄ Z-scheme photocatalytic system was constructed via *in situ*
37 Sonogashira coupling reaction and exhibited an apparent quantum yield (AQY, i.e. the yield of incident
38 photon to converted electron for photocatalytic H₂ evolution) of 9.85% at 400 nm²¹. A g-C₃N₄/g-C₃N₄
39 Z-scheme heterojunction with tunable boron doping content and nitrogen deficient concentration was
40 designed, achieving an AQY of 23.52% at 420 nm and solar to hydrogen (STH) efficiency of 1.16%³.
41 The charge separation efficiency of these Z-scheme artificial photocatalytic systems is related to the
42 driving force by interfacial internal electric field^{22,23}. However, the low charge carrier separation
43 efficiency and sluggish kinetics of the carrier transport still restrict the photocatalyst performance, and
44 further enhancing the internal electric field intensity is a key issue²⁴⁻²⁷.

45 The multiple exciton generation (MEG) effect, i.e., a nanocrystal quantum dot absorbs a single
46 photon to generate multiple excitons, is another promising strategy to improve the quantum efficiency.
47 Theoretically, an ideal material would produce additional carriers per photon with energies equal to
48 multiples of E_g (e.g., for $E_{hv}=2E_g$, two carriers are generated per photon)²⁸⁻³⁰. However, the quantum
49 efficiency is still inefficient in photovoltage device because it usually requires E_{hv} to be much greater
50 than $2E_g$ to generate an additional carrier per incident photon. Recently, enhancing internal electric
51 field intensity has been proved as a promising strategy to extract excitons generated by MEG effect

52 and improve the photoelectric conversion efficiency²⁸⁻³¹. For example, a photovoltaic system with an
53 internal quantum efficiency (IQE, i.e., the ratio of absorbed incident photons to converted electrons)
54 close to 200% has been developed via chemically attaching a single layer PbS quantum dots on an
55 energy band matched single-crystal-anatase TiO₂ surface²⁹. Depositing the PbS quantum dots on the
56 top of FTO/TiO₂ via a layer-by-layer approach can achieve an IQE that exceeded 100% in
57 photoelectrochemical cells for hydrogen generation³². Nevertheless, limited by the insufficient
58 interfacial charge extraction force, achieving an IQE that exceeded 100% in photocatalytic overall
59 water splitting were rarely reported.

60 Here, vanadium-doped indium sulfide (V-In₂S₃) with optimized optoelectronic properties and
61 CdTe quantum dots with tunable bandgaps were studied. The increase in the V-dopant content and
62 quantum dot size causes the Fermi level of V-In₂S₃ to gradually upshift and that of CdTe to gradually
63 downshift, inducing a robust built-in electric field at the interface of CdTe/V-In₂S₃ for carrier/exciton
64 extracting. Meanwhile, a cascade energy band structure is formed by introducing CoO_x as cocatalyst
65 into CdTe/V-In₂S₃ photocatalyst. Under the synergistic effect of robust built-in electric field, cascade
66 energy band structure, and tunable bandgaps of CdTe quantum dot, the CdTe/V-In₂S₃ hybrids provided
67 a sufficient driving force for the extraction of MEG-generated excitons and achieved an effective
68 utilization of MEG effect. As a result, an IQE of 114% and AQY of 73% were achieved at 350 nm,
69 and an excellent photocatalytic overall water splitting activity was obtained (STH efficiency = 1.31%).

70 **Catalyst synthesis and characterization**

71 CdTe/V-In₂S₃ hybrids with tunable V-dopant contents and different CdTe quantum dot sizes were
72 synthesized to elucidate the role of doping and quantum effects in photocatalytic overall water splitting.
73 The V-In₂S₃ samples with different V-dopant contents exhibit a nanoflower-like structure consisting of

74 multiple thin nanosheets (**Supplementary Fig.1**). The X-ray diffraction (XRD) patterns of V-In₂S₃
75 show the characteristic peaks of the In₂S₃ cubic phase (JCPDS no.32-0456) (**Fig. 1a**). The increase in
76 the NH₄VO₃ content in the precursor causes a progressive positive shift in the XRD peak of the (440)
77 plane of V-In₂S₃, suggesting that the V-dopant introduction alters the In₂S₃ crystal structure. X-ray
78 photoelectron spectroscopy (XPS) was used to investigate the V-In₂S₃ structure. Along with the In–S
79 peaks, an additional V–S peak is observed at 517.26 eV in the V 2p XPS curve of V-In₂S₃ (**Fig. 1b and**
80 **Supplementary Fig. 2**), indicating the successful introduction of V atoms into the In₂S₃ nanostructure
81 in the In sites of the In₂S₃ crystal lattice^{33,34}. The peak intensity of the V–S bond gradually increases
82 with the V-dopant content (from 0% to 3.1%) (**Supplementary Table 1**). The V-dopant introduction
83 was also observed by Raman spectroscopy. The V–S Raman peak occurs along with the A_{1g}, E_g, and
84 B_{2g} characteristic peaks of In₂S₃ and gradually intensifies, confirming the presence of the V dopant in
85 V-In₂S₃ (**Fig. 1c and Supplementary Fig. 3**)^{35,36}.

86 Size-tailored CdTe quantum dots were prepared using a laser manufacturing technique in liquid
87 (**Supplementary Fig. 4**). The quantum dot size changed from 2.8 to 5.0 nm by adjusting the irradiation
88 time, which was confirmed using scanning transmission electron microscopy (STEM)
89 (**Supplementary Figs. 5–9**)³⁷. The increase in the quantum dot size causes its fluorescence emission
90 peak to red-shift from 570 to 623 nm (**Fig. 1d**) with a gradual color change from green to red under a
91 365-nm UV lamp irradiation (**Supplementary Fig. 10**), confirming the successful synthesis of the
92 size-tailored CdTe quantum dots³⁸. The absorption edge gradually red shifts with the increase in the
93 quantum dot size, which enhances light harvesting.

94 UV photoelectron spectroscopy (UPS) was used to study the change in the position of the energy
95 band of the developed CdTe quantum dots and V-In₂S₃. The Fermi level of the CdTe quantum dot and

96 V-In₂S₃ were calculated using the plots of the UPS spectra showing the secondary electron cut-off (**Fig.**
97 **1e**)³⁹. The Fermi level of V-In₂S₃ upshifts with the increase of V doping, and that of the CdTe
98 downshifts with increasing the quantum dot size (**Fig. 1f**). By simultaneously increasing the V doping
99 and the quantum dot size, the difference in the Fermi level between V-In₂S₃ and the CdTe quantum dot
100 increases. The energy band matching reveals that the maximum Fermi level difference occurs in V-
101 In₂S₃-3 and CdTe-4.2 (**Supplementary Figs. 11–14 and Supplementary Table 2**). A further increase
102 of V doping or quantum dot size results in the appearance of either a second phase (VS₂)
103 (**Supplementary Fig. 15**) or an energy mismatch in the band structure between V-In₂S₃ and CdTe.

104 CdTe/V-In₂S₃ hybrids were developed using an electrostatic self-assembly method to anchor the
105 CdTe quantum dots onto the surface of V-In₂S₃. For example, in the CdTe-4.2/V-In₂S₃-3 hybrid, the
106 positively charged V-In₂S₃-3 and negatively charged CdTe-4.2 self-assemble and form a CdTe-4.2/V-
107 In₂S₃-3 heterostructure (**Supplementary Fig. 16**). The XRD pattern of CdTe-4.2/V-In₂S₃-3 only shows
108 the In₂S₃ characteristic peaks due to the low CdTe quantum dot concentration (**Supplementary Fig.**
109 **17**). The A_{1g}, E_g, B_{2g}, V–S peaks of V-In₂S₃ and TO and LO peaks of CdTe are observed in the Raman
110 spectrum of CdTe-4.2/V-In₂S₃-3³⁷, indicating the successful synthesis of CdTe-4.2/V-In₂S₃-3 (**Fig. 2a**).
111 The scanning and transmission electron microscopy show the resulting nanoflower morphology of
112 CdTe-4.2/V-In₂S₃-3 (**Fig. 2b and c**). The detailed atomic configuration of CdTe-4.2/V-In₂S₃-3 was
113 studied using aberration-corrected high-angle annular dark-field scanning TEM (HAADF-STEM).
114 Because the contrast in the HAADF-STEM image is proportional to the square of the atomic number,
115 the V atoms are paler than the In atoms, and the V dopant is shown in the atomically dispersed paler
116 spots (**Fig. 2d**)⁴⁰. The change in the line profile intensity in the selected area confirms the In and V
117 coexistence in the cation site of the In₂S₃ crystal lattice (**Fig. 2e**). The lattice fringes observed at 0.19

118 and 0.27 nm, which correspond to the (440) of In₂S₃ and (411) planes of CdTe, respectively, are
119 observed in the high-resolution STEM (HRTEM) image (**Fig. 2f**). This further supports that CdTe-4.2
120 has been stably anchored on the V-In₂S₃-3 surface. The energy dispersive X-ray spectroscopy patterns
121 exhibit a homogeneous dispersion of V, In, S, Cd, and Te elements on CdTe-4.2/V-In₂S₃-3 (**Fig. 2g**).

122 **Adjustment of Interfacial built-in electric fields**

123 The interfacial interaction within the CdTe/V-In₂S₃ was characterized using XPS. By increasing
124 the quantum dot size or V doping, the In 3d XPS and Cd 3d XPS curves of CdTe/V-In₂S₃ gradually
125 shift to higher and lower binding energies, respectively (**Fig. 3a, b, and Supplementary Fig. 18**). This
126 indicates an electron transfer from V-In₂S₃ to CdTe, inducing an increase in the number of the outer
127 electrons of CdTe, which results in a weaker binding energy in CdTe and higher binding energy in V-
128 In₂S₃⁴¹. The electron exchange between CdTe and V-In₂S₃ gradually increases until its maximum value
129 is obtained at a CdTe quantum dot size of 5.0 nm and V doping of 3.1%. This was further studied based
130 on the energy band structure. **Figure 3c** shows the energy band alignment of the developed CdTe
131 quantum dot and V-In₂S₃ before their contact. Because the Fermi level of V-In₂S₃ is higher than that
132 of CdTe, electron transfer takes place from V-In₂S₃ to CdTe until the Fermi level between them reaches
133 equilibrium and forms a space charge region at the CdTe/V-In₂S₃ heterojunction interface (**Fig. 3d**).
134 With the increase in the quantum dot size and V-dopant content, the Fermi level difference between V-
135 In₂S₃ and CdTe gradually increases, enhancing the interfacial electron exchange, which is consistent
136 with the XPS results (**Fig. 3a, b, and Supplementary Fig. 18**).

137 The width (W) of the space charge region of the developed CdTe/V-In₂S₃ hybrids were calculated
138 using Equations (1) and (2).

$$139 \quad W = \sqrt{2\varepsilon_0\varepsilon_r V_{bi}/qN_d} \quad (1)$$

140
$$N_d = (2/e\epsilon_0\epsilon_r)[d(1/C^2)/dV]^{-1} \quad (2)$$

141 where V_{bi} is the built-in potential, which is calculated by subtracting the flat-band potential from the
142 applied potential; q is the elementary charge; N_d is the charge density; e is the electron charge; ϵ is the
143 dielectric constant of the material; ϵ_0 is the permittivity of vacuum; and $d(1/C^2)/dV$ is the slope of the
144 obtained Mott-Schottky (M-S) plot^{42,43}. The enhanced interfacial electron exchange generates an
145 extended space charge region within the CdTe/V-In₂S₃ heterojunction, which increases the built-in
146 electric field intensity (**Fig. 3e and Supplementary Fig. 19**). The interfacial built-in electric field
147 intensity of CdTe/V-In₂S₃ is calculated **via surface voltage and surface accumulated electrons density**
148 ⁴⁴ (**Fig. 3f and Supplementary Figs. 20–23**). When the quantum dot size changes from 2.8 to 4.2 nm
149 and the V-dopant content increases from 0% to 3.1%, the built-in electric field intensity exhibits an
150 increasing trend similar to that of the space charge region width. CdTe-4.2/V-In₂S₃-3 exhibits a
151 maximum built-in electric field intensity that is 14.14 times higher than that of CdTe-2.8/V-In₂S₃-0.
152 With further increase of the quantum dot size, the built-in electric field intensity decreases because of
153 the mismatch between the energy band structures of V-In₂S₃-3 and CdTe-5.0.

154 The change in the interfacial built-in electric field intensity was further confirmed by density
155 functional theory. We constructed CdTe adsorption models on V-In₂S₃ with different V dopant contents
156 (from 0% to 3%) for simulating CdTe/V-In₂S₃-0, CdTe/V-In₂S₃-1, CdTe/V-In₂S₃-2 and CdTe/V-In₂S₃-
157 3. The V-In₂S₃ Fermi level gradually increases with the V-dopant content, which is consistent with the
158 experimental results (**Supplementary Figs. 24, 25**). The In-Te distance on CdTe/V-In₂S₃ gradually
159 decreases with increasing V doping, confirming the enhanced interfacial interaction between CdTe and
160 V-In₂S₃. The built-in electric field intensity was simulated based on the surface potential plot^{44,45}. The
161 surface electric potential difference within CdTe/V-In₂S₃ is proportional to the Fermi level difference

162 between CdTe and V-In₂S₃. This similar increasing trends of built-in electric field and Fermi level
163 difference further proves that the enhanced Fermi level difference significantly increases the built-in
164 electric field intensity (**Fig. 3g**). Meanwhile, at the interface of CdTe and V-In₂S₃, an interfacial state
165 contributed by In 5s and S 3p orbitals is formed near the conduction band (CB) edge, which could act
166 as electron traps and is favorable for effective utilization of MEG effect⁴⁶ (further discussion later)
167 (**Supplementary Fig. 26**).

168 **Kinetics of interfacial carrier transport and MEG effect**

169 The kinetics of the carrier transport within CdTe/In₂S₃ were significantly improved because of
170 the enhanced interfacial interaction and built-in electric field intensity. *In situ* electrochemical
171 impedance spectroscopy (EIS) was used to evaluate the charge transfer resistance in the proposed
172 hybrids. The carrier transport activation energy of CdTe/V-In₂S₃ was calculated using Arrhenius
173 equation based on the *in situ* EIS plots at different temperatures⁴⁷ (**Supplementary Figs. 27-29 and**
174 **Supplementary Table 3**). By controlling the quantum dot size and V doping, CdTe-4.2/V-In₂S₃-3
175 exhibited the smallest carrier transport activation energy (0.12 eV), promoting charge separation and
176 transfer. The photoluminescence (PL) and time-resolved photoluminescence (TRPL) results further
177 verified the excellent charge separation efficiency of CdTe-4.2/V-In₂S₃-3. CdTe-4.2/V-In₂S₃-3 showed
178 the lowest fluorescence intensity and longest average carrier lifetime (35.3 ns) among all hybrids
179 (**Supplementary Figs. 30–31, and Supplementary Table 4**). More striking, the robust built-in electric
180 field at CdTe/V-In₂S₃ interface drives the exciton transport from CdTe to V-In₂S₃, which significantly
181 suppresses Auger recombination of CdTe quantum dot (**Supplementary Fig. 32**).

182 The incident photon-to-current efficiency (IPCE) and corresponding internal quantum efficiency
183 (IQE_{pc}) were measured based on the photocurrent density under monochromatic light irradiation to

184 directly evaluate the photoelectric conversion efficiency of CdTe/V-In₂S₃. The IPCE plots of CdTe/V-
185 In₂S₃ at different wavelengths were consistent with the optical absorption results (**Fig. 4a**,
186 **Supplementary Figs. 33, 34 and Supplementary Table 5**). The IPCE value gradually increased with
187 V doping (from 0% to 3.1%) or quantum dot size (from 2.8 to 4.2 nm). An IPCE of 73.74% is achieved
188 on CdTe-4.2/V-In₂S₃-3 at 350 nm, implying an excellent carrier transfer and separation. By further
189 increasing the quantum dot size, the mismatch in the energy band structure between CdTe and V-In₂S₃
190 significantly hinders the charge transfer and separation at the CdTe/V-In₂S₃ interface, dramatically
191 decreasing IPCE. The IQE_{pc} was assessed by normalizing the IPCE values to the measured absorption
192 curve of CdTe/V-In₂S₃ (the detail measurement and calculation process seen in **Supplementary Note**
193 **1**). Along with the increase of V doping content, the IQE_{pc} curves of CdTe-2.8/V-In₂S₃ held flat
194 (**Supplementary Fig. 35a**). By increasing the CdTe quantum dot size, the IQE_{pc} curves of CdTe/V-
195 In₂S₃-3 kept flat around the total wavelength when the quantum dot sizes are 2.8 and 3.9 nm, while the
196 IQE_{pc} curves of CdTe/V-In₂S₃-3 exhibits an upward trend when the quantum dot sizes are 4.2 and 5.0
197 nm (**Fig. 4b**). This phenomenon implies the CdTe quantum dot induces MEG effect under high-energy
198 photon irradiation when the quantum dot size exceeding 4.2 nm³¹. More striking, the CdTe-4.2/V-
199 In₂S₃-3 displayed the maximum IQE_{pc} value of 118% at 350 nm, implying an efficiently utilization of
200 the generated multiple excitons from MEG effect *via* the enhanced exciton extraction force driven by
201 robust built-in electric field at interface of CdTe/V-In₂S₃ hybrids.

202 We further plotted the IQE_{pc} curves versus the bandgap of the CdTe and V-In₂S₃ to elucidate the
203 MEG effect in the CdTe/V-In₂S₃ system (**Fig. 4c and Supplementary Fig. 35b**). The IQE_{pc} of CdTe/V-
204 In₂S₃ with different V doping remained unchanged and gradually increased when the incident photon
205 energy exceeded a value 2.75 times of CdTe bandgap energy. With consideration of the relationship

206 between the CdTe quantum dot size and bandgap (**Fig. 1f**), we can conclude that the MEG effect of
207 CdTe quantum dot generates when the incident photon energy exceeding 2.75 times CdTe bandgap by
208 increasing quantum dot size, then significantly facilitating the charge transport and separation within
209 the hybrids^{29,31}. Moreover, CdTe-5.0/V-In₂S₃-3 exhibited a lower IQE_{pc} than CdTe-4.2/V-In₂S₃-3,
210 which is attributed to the poor exciton extraction due to the mismatched energy band structures. We
211 probed the dynamics of ground state bleaching (GSB) through transient absorption (TA) spectroscopy
212 with different pump energy under low pump intensity ($\langle N_0 \rangle = 0.20$) to evaluate the MEG process of
213 CdTe-4.2/V-In₂S₃-3 and its yield. The emergence of fast decay with increased amplitudes for CdTe-
214 4.2/V-In₂S₃-3 at higher photoexcitation energies (2.81, 2.97 and 3.14 folds E_g of CdTe-4.2) further
215 indicated the existence of MEG effect²⁸ (**Fig. 4d**). Meanwhile, the QY_{MEG}, i.e., average number of
216 excitons generated per absorbed photon is 1.69 (at $h\nu = 3.14E_g$) in CdTe-4.2/V-In₂S₃-3, which can
217 provide sufficient carriers for photocatalytic overall water splitting (**Fig. 36**).

218 The charge transport path also affects the photoelectric conversion efficiency and utilization of
219 MEG effect. *In situ* XPS was used to study the charge transport path²³. **Figure 4e and Supplementary**
220 **Fig. 37** indicated a shift in the In 3d XPS curve of CdTe-4.2/V-In₂S₃-3 toward a lower binding energy
221 under light irradiation, whereas the Cd 3d curve shifted to a higher binding energy, indicating the
222 transport of the photoinduced electrons from CdTe to V-In₂S₃ and resulting in a weaker binding energy.
223 Electron spin resonance analysis was used to verify the charge transfer direction (**Fig. 38**). CdTe-4.2/V-
224 In₂S₃-3 showed a more intense $\cdot O_2^-$ peaks than V-In₂S₃-3 under light irradiation, implying that more
225 electrons accumulated on the CB of V-In₂S₃-3²². Thus, the charge transfer path in CdTe-4.2/V-In₂S₃-3
226 follows a Z-scheme transfer path. Based on above results, the exciton generation and transfer process
227 of CdTe/V-In₂S₃ hybrids can be described as shown in **Figure 4f**. Firstly, the CdTe was excited by a

228 high-energy photon and generated a hot electron and hole. Then, the hot electron transported from
229 CdTe to V-In₂S₃ driven by the robust built-in electric field (**Fig. 3f**) and trapped at CdTe/V-In₂S₃
230 interface via the interfacial state contributed by In 5s and S 3p orbitals traps (**Supplementary Fig. 26**),
231 thus slowing the hot electrons relaxation rate⁴⁶ and facilitating the hot electrons with sufficient excess
232 energy to undergo MGE. Finally, the CdTe/V-In₂S₃ hybrids realize effective utilization of MEG effect
233 of CdTe quantum dot via the trapping state and robust built-in electric field at CdTe/V-In₂S₃ interface,
234 resulting in a promising photoelectric conversion efficiency with an IQE_{pc} of 118% at 350 nm.

235 **Photocatalytic overall water splitting**

236 A photocatalytic overall water splitting test was conducted using CdTe/V-In₂S₃, V-In₂S₃ and CdTe
237 act as H₂ and O₂-evolving components, respectively, which is ascribed to their energy band structures
238 (**Fig. 1f and Supplementary Fig. 39**). Pt and CoOx have been used as cocatalyst. Thus, CdTe/V-In₂S₃
239 can simultaneously evolve H₂ and O₂ at a molar ratio close to 2:1 in pure water under simulated solar
240 illumination. (**Fig. 5a, b and Supplementary Figs. 40-42**). The gas evolution rate of CdTe/V-In₂S₃
241 exhibited a similar trend to the internal electric field intensity. CdTe-4.2/V-In₂S₃-3 exhibits a maximum
242 H₂ and O₂ evolution rates of 101.15 and 47.38 μmol h⁻¹, respectively. No gas evolution occurs without
243 irradiation, proving the water splitting process is driven by light (**Supplementary Fig. 43**). The
244 isotopic measurement further confirms that the water splitting into H₂ and O₂⁴⁸ (**Supplementary Figs.**
245 **44, 45**). We also conducted the photocatalytic stability test for CdTe/V-In₂S₃ hybrids. The CdTe-4.2/V-
246 In₂S₃-3 with CoOx as co-catalyst shows the highest photocatalytic stability with a value of 90.31%
247 after 100 h photocatalytic test (**Fig. 46**). The CoOx co-catalyst loading and internal electric field
248 intensity play significant roles for the photocatalytic stability of CdTe/V-In₂S₃. The enhancement of
249 photocatalytic stability for CdTe/V-In₂S₃ hybrids can be ascribed to the synergistic effect of cascade

250 energy band structure of CdTe/V-In₂S₃-CoOx and robust interfacial built-in electric field, which
251 effectively extracts the photogenerated holes at valence band (VB) of CdTe to CoOx and prevents the
252 oxidation of CdTe (**Supplementary Fig. 47**).

253 The solar to hydrogen (STH) efficiency and apparent quantum yield (AQY) of CdTe-4.2/V-In₂S₃-
254 3 were calculated to evaluate the photocatalytic overall water splitting activity. The CdTe-4.2/V-In₂S₃-
255 3 exhibits an average STH value as high as 1.31% (**Fig. 5c and Supplementary Table 6**). The
256 theoretical STH value is close to the experimental STH value³, which further verifies the outstanding
257 photocatalytic water splitting activity (**Fig. 5d and Supplementary Fig. 48**). Moreover, CdTe-4.2/V-
258 In₂S₃-3 shows the highest AQY (73.25%) at 350 nm, which is higher than most reported values (**Fig.**
259 **5d, e, Supplementary Fig. 49 and Supplementary Tables 7, 8**). Assisted by the robust built-in
260 electric field and cascade energy band structure of CdTe/V-In₂S₃, the MEG charge separation is
261 significantly facilitated and it exhibits an internal quantum efficiency calculated via photocatalytic
262 hydrogen evolution (IQE_{hy}) of 114% at 350 nm. This phenomenon further proves the effective
263 utilization of MEG effect and breakthrough in IQE in our system (the detail measurement and
264 calculation process seen in **Supplementary Note 2**).

265 According to above results, a photocatalytic overall water splitting mechanism is proposed (**Fig.**
266 **5f**). First, CdTe and V-In₂S₃ are excited by photons or the MEG effect and generate sufficient
267 photoinduced electrons and holes in the CB and VB, respectively, of V-In₂S₃ and CdTe. The
268 photogenerated electrons on the CB of CdTe then recombine with the photogenerated holes on the VB
269 of V-In₂S₃, while the photoinduced electrons on the CB of V-In₂S₃ and the photoinduced holes on the
270 VB of CdTe are separated to Pt and CoOx site, respectively, then participating in the redox reaction.
271 Under the synergistic effect of the large internal electric field intensity, MEG effect, and cascade energy

272 band structure, the photoinduced electrons and holes are efficiently separated and achieving a 114%
273 $\text{IQE}_{\text{hy}}/118\% \text{IQE}_{\text{pc}}$ at 350 nm, thus indicating a promising photocatalytic overall water splitting activity
274 and stability.

275 **Conclusion**

276 In summary, we achieved an IQE that exceeded 100% (118% IQE_{pc} derived by photocurrent
277 measurement and 114% IQE_{hy} derived by photocatalytic H_2 evolution) at 350 nm in the CdTe-4.2/V-
278 In_2S_3 -3 hybrids, which provides sufficient photoinduced carriers for a water redox reaction to
279 simultaneously generate H_2 and O_2 . By adjusting the V doping content and quantum dot size, the Fermi
280 level difference between the CdTe and V- In_2S_3 exhibits a monotone and linear change, thus inducing
281 a robust built-in electric field and achieving an effective utilization of MEG effect. Under the
282 synergistic effect of the robust built-in electric field, MEG effect, and cascade energy band structure,
283 the charge separation kinetics of CdTe-4.2/V- In_2S_3 -3 is dramatically facilitated, resulting in an
284 excellent photocatalytic activity with a STH efficiency of 1.31%. This approach opens a promising
285 design for the development of photocatalytic devices operated in a MEG regime for achieving efficient
286 charge separation and solar-to-fuel conversion.

287 With consideration of MEG photocatalysis development, designing a bigger built-in electric field
288 intensity (e.g., using anion exchange method⁴⁴) and a better interfacial electronic state (e.g.,
289 constructing Janus structure⁴⁶) at non-MEG/MEG heterojunction interface might be a future direction.
290 In terms of competition of light absorption between In_2S_3 and CdTe, constructing a non-MEG/MEG
291 heterojunction with broadband absorption range by combining wavelength-complementary MEG
292 component and non-MEG component may be a feasible approach to further improve performance.

293 **Methods**

294 All the chemicals were obtained via Sigma-Aldrich without further purification.

295 **Synthesis of Vanadium doped In₂S₃ (V-In₂S₃) with different V doping:** The synthetic procedure of
296 V-In₂S₃ was followed as follow: 0.1 mmol of NH₄VO₃, 1 mmol of In(NO₃)₃ and 2 mmol of
297 thioacetamide are dissolved in 35 mL of distilled (DI) water. After being stirring evenly, the precursor
298 solution is transferred into a 50 mL Teflon-lined cup stainless autoclave for hydrothermal treatment at
299 90 °C for 12 h. After washing with ethanol and DI water, the orange suspension is collected and dried
300 at 60 °C under vacuum overnight and denoted as V-In₂S₃-1 for further use. The V-In₂S₃ with different
301 V doping is synthesized via the changing the NH₄VO₃ content in precursor and denoted as V-In₂S₃-0⁴⁹
302 (without NH₄VO₃), V-In₂S₃-2 (NH₄VO₃ content of 30 mg), V-In₂S₃-3 (NH₄VO₃ content of 50 mg) and
303 V-In₂S₃-4 (NH₄VO₃ content of 60 mg).

304 **Synthesis of size-tailored CdTe quantum dot:** The cadmium (Cd) foil was washed with (1:1 v/v)
305 HNO₃: H₂O solution to remove the oxide layer. In a typical procedure, the Cd foil and Na₂TeO₃ (1
306 mmol) are added to an N₂-saturated vessel with 10 mL DI water. The vessel undergoes continuous
307 ultrasonication with an Nd:YAG laser fluence of 570 mJ pulse⁻¹ cm⁻². CdTe quantum dots of various
308 sizes are obtained under irradiation treatment times.

309 **Synthesis of CdTe quantum dot/V-In₂S₃ (CdTe/V-In₂S₃):** The synthesis procedure of CdTe/V-In₂S₃
310 hybrids with different V doping and CdTe quantum dot sizes is similar to the preparation of V-In₂S₃.
311 The prepared CdTe quantum dots of different sizes are added into the precursor solutions for further
312 hydrothermal treatment.

313 **Characterization of the photocatalysts:** SEM (Quanta 600 FEG), TEM (FEI Tecnai F30G2) and
314 HAADF-STEM (Nion Ultra STEM U100) were used to examine the morphology of prepared
315 photocatalysts. The crystal structure of prepared photocatalysts was recorded by a PANalytical X'pert
316 XRD system via using Cu K α radiation at 0.154 nm. The Raman spectrometer (Renishaw inVia) was
317 used to characterize the Raman spectrum of the samples with a 532 nm laser. The optical performance
318 was evaluated by Perkin-Elmer Lambda 35 UV-vis-NIR spectrophotometer. The detailed electronic
319 structure of prepared photocatalysts was measured by Kratos Axis supra XPS spectrometer. All the
320 binding energy values were subjected to carbon correction referring to the C 1s peak at 284.8 eV. PL
321 spectrum was measured by a PL spectrometer (FLS 980) at the excitation wavelength of 325 nm.
322 TRPL spectrum was collected via a FLS920 fluorescence spectrometer (Edinburgh Instruments). Zeta-

323 sizer Nano ZS (Malvern Instruments) was used to record the surface Zeta potential. TA measurement
324 was conducted using a femtosecond laser formed by a Ti:sapphire femtosecond regenerative amplifier
325 with 800 nm wavelength (Coherent Libra) and a Helios pump/probe setup (Ultrafast Systems). The
326 tested sample was spin coated on FTO glass (1 cm×1 cm) with a thickness of ~100 nm.

327 The photoelectrochemical measurements were performed on an electrochemical workstation
328 (CHI760). The light source was a PLS-SCE300 Xe lamp (100 mW cm⁻²). The applied potential for
329 electrochemical impedance spectroscopy (EIS) measurement was 0.2 V Ag/AgCl (sinusoidal wave: 5
330 mV, frequency range: 10 kHz-0.05 Hz). The *in-situ* EIS test at different temperatures was carried out
331 using a thermostatic water bath (Precision TSGP02). The Mott-Schottky (M-S) plots were conducted
332 at a frequency of 4 kHz and the amplitude of the sinusoidal wave was 5 mV. The surface voltage could
333 be evaluated by applying the open-circuit potential measurements. The sample was placed under
334 the 100 mW cm⁻² light irradiation until the potential reached to a constant. As for the calculation of
335 surface voltage, we recorded the change of potential when the light was removed. When the potential
336 of sample achieved an equilibrium under dark conditions, the difference between the potential under
337 light irradiation and dark conditions is the value of surface voltage.

338 **Co-catalyst loading:** Pt was loaded on the surface of V-In₂S₃ to act as the H₂-evolving component via
339 a photo-deposition method. The as-prepared V-In₂S₃ powder (50 mg) was dispersed in 100 mL (25
340 vol.%) lactic acid aqueous containing H₂PtCl₆ (1.5 mL, 1 mg/mL). N₂ was purged into the solution for
341 30 min to remove O₂. A 500 W mercury lamp (XPA-7 photochemical reactor) was used to achieve the
342 photo-deposition of Pt. The Pt-V-In₂S₃ solution was collected, washed, and dried at 60 °C overnight.
343 CoO_x was mixed with CdTe quantum dot to act as the O₂-evolving component via an impregnation
344 method. In detail, Co(NO₃)₂·6H₂O (1 mg) and CdTe quantum dot (10 mL) solution was mixed under
345 continuous stirring. 1 mL NH₃·H₂O was introduced to the solution. Finally, the products were collected
346 by lyophilized.

347 **Measurement of Photocatalytic activity:** Photocatalytic water splitting test was conducted in a Pyrex
348 reaction vessel under light irradiation ($\lambda \geq 300$ nm, 300 W Xe lamp, light intensity 100 mW cm⁻²) with
349 a stationary temperature at 5 °C. Photocatalyst (50.0 mg) was dispersed into 50.0 mL of pure water.
350 The residual air in the reactor was removed via purging argon. The evolved gases (H₂ and O₂) generated
351 from the reactor were analyzed at given time intervals *via* a Shimadzu GC-2014c gas chromatographer.

352 The NaX zeolite column and nitrogen (20 mL/min) were used as gas chromatograph and carrier gas,
353 respectively. Photocatalytic half-reactions (H₂ or O₂ evolution) were measured following a similar
354 procedure by using 0.5M Na₂S-Na₂SO₃ or AgNO₃ as the sacrificial agent. No appreciable gas evolved
355 without photocatalysts or light irradiation. Gas chromatograph-mass spectrometer (Agilent 7890A-
356 5975C) was used for detecting photocatalytic H₂¹⁸O (99%) splitting.

357 **Computational method:** All calculations were conducted using the density functional theory, as
358 implemented in the Vienna ab initio simulation package (VASP)⁵⁰. The PBE exchange-correlation
359 functional and the dispersion interaction were corrected by the D3 scheme in all the calculations within
360 the framework of DFT^{51,52}. The PAW pseudopotentials were used with a plane-wave cutoff energy of
361 400 eV. A gamma k-point mesh and dipole correction along the z-direction was used in DFT
362 calculation⁵³. The In₂S₃ (001) combining with CdTe (001) surface was used to build the heterojunction.
363 For V doping in In₂S₃ study, In₂S₃ (001) was used. The experimental lattice constant value of In₂S₃ and
364 CdTe was 10.77 Å and 6.477 Å, respectively. The slab model was separated from adjacent layers by a
365 vacuum thickness of 15 Å.

366 **Data Availability**

367 All data generated in this study are provided in the article, its Supplementary Information and Source
368 Data.

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376 **Author contributions**

377 X. L. and Y. Z. proposed the experimental concepts, designed the experiments, and prepared the

378 manuscript; X. L. supervised the project; Y. Z., X.X., Y.W., P.G., R.W. and B.W. carried out the
379 experiments and conducted the material characterization; W.H. and A.S. revised the manuscript; Y. L.
380 finished the computation. All authors discussed the results and approved the final version of the
381 manuscript.

382 **Competing Interests**

383 The authors declare no competing interests.

384

385 **Figure Legends**

386 **Figure 1. Energy band structures of CdTe quantum dot and V-In₂S₃.** (a) XRD patterns, the (440) plane of In₂S₃
387 is magnified and shown in right; (b) V 2p XPS lines, and (c) Heat map of Raman spectra of V-In₂S₃ with different V
388 contents, the V-S and In-S Raman peaks are marked by yellow rectangle; (d) Absorption spectra and fluorescence
389 (PL) spectra of CdTe-2.8, CdTe-3.9, CdTe-4.2 and CdTe-5.0; (e) UPS spectra of secondary electron cut-off plots for
390 V-In₂S₃ with different V doping (V-In₂S₃-0, V-In₂S₃-1, V-In₂S₃-2 and V-In₂S₃-3) and CdTe with different quantum
391 dot sizes (CdTe-2.8, CdTe-3.9, CdTe-4.2 and CdTe-5.0); (f) Schematic illustration the energy band structure change
392 via doping engineering and quantum effect.

393

394 **Figure 2. Morphology and structure of CdTe/V-In₂S₃ photocatalysts.** (a) Raman spectra, (b) scanning electron
395 microscopy image, the scale bars are 1 μm , (c) transmission electron microscopy image, the scale bars are 500 nm,
396 and (d) HAADF-STEM image of CdTe-4.2/V-In₂S₃-3, the scale bars are 0.5 nm; (e) The line profiles measuring the
397 atom intensity variations on the selected area of **Figure 2d**; (f) HR-STEM image to determine the lattice fringe of
398 CdTe-4.2/V-In₂S₃-3, the scale bars are 2 nm; (g) Elemental mapping of V (cyan), In (green), S (blue), Cd (red) and
399 Te (yellow) for CdTe-4.2/V-In₂S₃-3, the scale bars are 500 nm.

400

401 **Figure 3. Interfacial built-in electric field of CdTe/V-In₂S₃ photocatalysts.** (a) In 3d XPS lines for CdTe/V-In₂S₃-
402 0 hybrids with different CdTe quantum dot sizes; (b) In 3d XPS lines for V-In₂S₃ and CdTe-5.0/V-In₂S₃ hybrids with
403 different V doping; (c) Schematic illustration of the energy band structure of CdTe and V-In₂S₃ before contact; (d)
404 Schematic illustration of the energy band structure of CdTe and V-In₂S₃ hybrids in contact, W represents the depletion
405 layer of CdTe and V-In₂S₃; (e) Depletion layer width for CdTe/V-In₂S₃ hybrids with different V doping and CdTe
406 quantum dot sizes in the unit of CdTe-2.8/V-In₂S₃-0; (f) Built-in electric field intensity for CdTe/V-In₂S₃ hybrids with
407 different V doping and CdTe quantum dot sizes in the unit of CdTe-2.8/V-In₂S₃-0; (g) Calculated electrostatic
408 potential difference for CdTe/V-In₂S₃ hybrids with different V doping, the inset images are the configuration of
409 CdTe/V-In₂S₃ hybrids.
410

411 **Figure 4. Kinetics of interfacial carrier transport and MEG effect of CdTe/V-In₂S₃ photocatalysts.** (a) IPCE
412 plots and absorption spectra of CdTe/V-In₂S₃-3 hybrids with different quantum dot sizes; (b) IQE_{pc} as a function of
413 illumination photon energy (eV) of CdTe/V-In₂S₃-3 hybrids with different CdTe quantum dot sizes, **data are presented**
414 **as mean values, and** error bars indicated standard deviation for 10 measurements, the applied bias used in the
415 photocurrent measurement is 0.24V (CdTe-2.8/V-In₂S₃-3), 0.21V (CdTe-3.9/V-In₂S₃-3), 0.16V (CdTe-4.2/V-In₂S₃-3),
416 0.23V (CdTe-5.0/V-In₂S₃-3), respectively; (c) IQE_{pc} as a function of multiples of the bandgap (hν/E_g) of CdTe
417 quantum dot for CdTe/V-In₂S₃-3 hybrids with different CdTe quantum dot sizes, **data are presented as mean values,**
418 **and** error bars indicated standard deviation for 10 measurements, **the inset represent CdTe quantum dot with different**
419 **size, and the shadings region represented the incident photon energy exceeded 2.75 times of CdTe bandgap;** (d) GSB
420 dynamics normalized at the long decay tail under different pump photon energies in CdTe-4.2/V-In₂S₃ (E_g of CdTe-
421 4.2 is 1.13 eV). The solid lines are exponential decay fittings; (e) Cd 3d XPS lines for CdTe-4.2/V-In₂S₃-3 under dark
422 and light conditions; (f) Schematic illustration of multiple excitons generation process in CdTe-4.2/V-In₂S₃-3.
423

424 **Figure 5. Photocatalytic performance of CdTe/V-In₂S₃ photocatalysts.** (a) The overall water splitting performance
425 of CdTe/V-In₂S₃-0 and CdTe/V-In₂S₃-3 hybrids with different CdTe quantum dot sizes under standard AM 1.5
426 illumination (100 mW cm⁻²), the mass of photocatalysts is 70 mg, Pt and CoOx as cocatalyst and CdTe:V-In₂S₃ equal
427 to 1:1; (b) Time-dependent photocatalytic overall water splitting profiles of CdTe-4.2/V-In₂S₃-3 hybrids; (c) The STH
428 value of CdTe-4.2/V-In₂S₃-3 hybrids of 10 separated photocatalytic test, the center line represented median, and the
429 top and bottom box limits represented the upper and lower quartiles, respectively, the small rectangle represented the
430 mean value, the maximum/minimum values are represented by the top/bottom bars; (d) The AQY, IQE_{hy} and
431 absorption spectrum of CdTe-4.2/V-In₂S₃-3 hybrids, data are presented as mean values, and error bars indicated
432 standard deviation for 10 measurements; (e) The STH and AQY values of previous reported photocatalysts^[1-8,10,18-21],
433 the detail value summarized in **Table S8**; (f) Schematic illustration of photoinduced carrier transfer and photocatalytic
434 H₂ and O₂ evolution process.
435

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