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1 Influence of QD photosensitizers in the photocatalytic production
2 of hydrogen with biomimetic [FeFe]-hydrogenase. Comparative
3 performance of CdSe and CdTe

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13 *Highlights:*

- 14 - Photocatalytic hydrogen production system with [Fe-Fe]H₂-ase mimic, and
15 CdSe or CdTe QDs as photosensitizers.
16 - Comparison of CdSe and CdTe QDs performance as photosensitizers
17 - CdSe showed the best performance for hydrogen production.
18 - Electron transfer rate from ascorbic acid to QDs and from QDs to catalysts has
19 been investigated.
20 - Electron transfer rate from ascorbic acid to QDs was found as rate limiting step.

21

22 *Abstract*

23 Photocatalytic systems comprising a hydrogenase-type catalyst and CdX (X = S, Se, Te)
24 chalcogenide quantum dot (QD) photosensitizers show extraordinary hydrogen
25 production rates under visible light excitation. What remains unknown is the
26 mechanism of energy conversion in these systems. Here, we have explored this question
27 by comparing the performance of two QD sensitizers, CdSe and CdTe, in photocatalytic
28 systems featuring aqueous solutions of a [Fe₂ (μ -1,2-benzenedithiolate) CO₆] catalyst

29 and an ascorbic acid sacrificial agent. Overall, the hydrogen production yield for CdSe-
30 sensitized reactions QDs was found to be 13 times greater than that of CdTe
31 counterparts. According to emission quenching experiments, an enhanced performance
32 of CdSe sensitizers reflected a greater rate of electron transfer from the ascorbic acid
33 (k_{Asc}). The observed difference in the QD-ascorbic acid charge transfer rates between
34 the two QD materials was consistent with respective driving forces for these systems,
35 determined from cyclic voltammetry measurements.

36 *Keywords:* Photocatalytic hydrogen production, hydrogenase mimic, quantum dot,
37 CdSe, CdTe, electron transfer, hybrid systems.

38

39 1. Introduction

40 In the current global context, greenhouse gas emissions due to the combustion of fossil
41 fuels pose a threat to the global climate change (Fang et al., 2018; Hinojosa-Reyes et al.,
42 2017; Seadira et al., 2018). Therefore, research efforts have been directed towards
43 finding alternative and environmentally-friendly energy sources. In this context,
44 hydrogen appears as a clean energy vector whose combustion only produces water
45 (Chen et al., 2018; Munfarida et al., 2020; Oh et al., 2020). Nowadays, it is mainly
46 produced by steam reforming from fossil fuels (Chu et al., 2017; Corredor et al., 2020a;
47 Nikolaidis and Poullikkas, 2017). This process is energy intensive and plagued by the
48 emission of greenhouse gases (Holladay et al., 2009; Ribao et al., 2019). As a result, the
49 potential to produce hydrogen from alternative and greener technologies, where
50 electrolysis takes the leading role, is becoming increasingly important.
51 Complementarily, hydrogen can be released from residual gas or liquid effluents
52 through the use of cost-effective technologies, such as photocatalysis (Nasir et al., 2019;

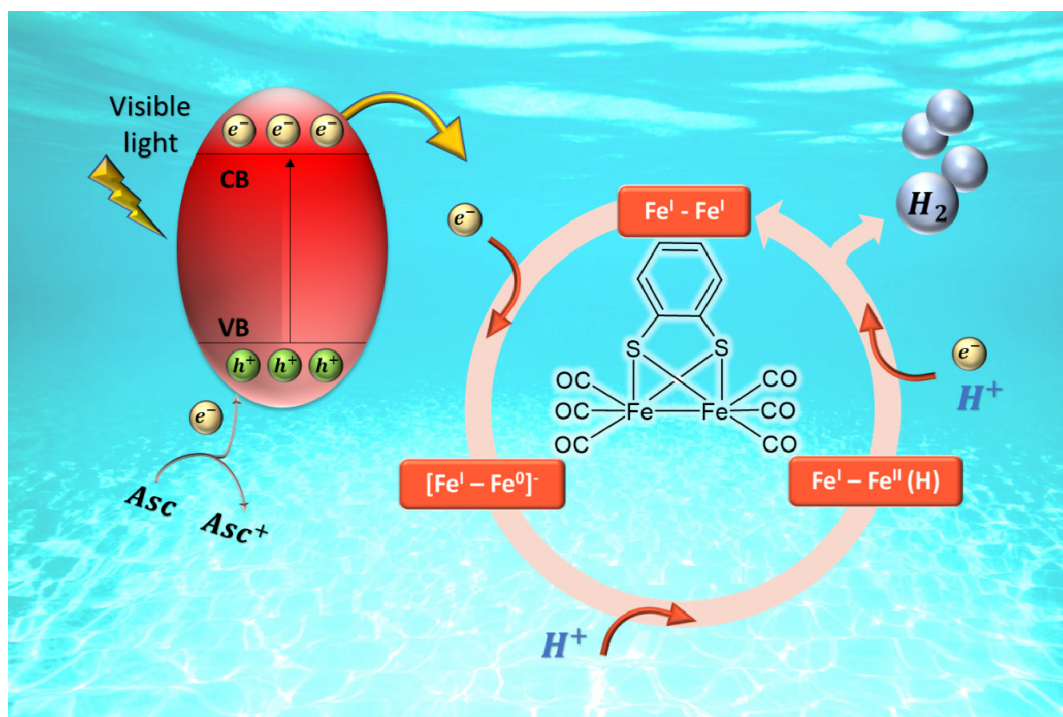
53 Rivero et al., 2019; Yue et al., 2017). Photocatalysis is a way to harvest sunlight energy
54 and store it in the form of solar fuels, just as nature has done through natural
55 photosynthesis (Christoforidis and Fornasiero, 2017; El-Khouly et al., 2017; Lewis S.
56 Nathan, 2016; Zamkov, 2017).

57 As an alternative to noble metal catalysts, (Cho et al., 2021; Lai et al., 2021; Y. Yang et
58 al., 2021), recent studies have explored heterogeneous photocatalytic systems
59 comprising hydrogenases catalysts and semiconductor quantum dot (QD)
60 photosensitizers. The hydrogen production rates for these materials approaching 2 mmol
61 $\text{H}_2 \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ were below those of homogeneous catalysts but showed an impressive long-
62 term stability (Elsayed et al., 2021; Putri et al., 2020; J. Yang et al., 2021).

63 Hydrogenase mimics is another promising noble metal-free catalyst that shows
64 compelling hydrogen production performance (Fukuzumi et al., 2018; Trincado et al.,
65 2014). Hydrogenases in nature are enzymes, which active sites are composed of Fe
66 and/or Ni, synthesized by certain bacteria and algae; these enzymes catalyze the
67 reversible redox reaction of H^+ to H_2 (Hemming et al., 2018; Li et al., 2018; Wang et al.,
68 2012). Among hydrogenases, [Fe-Fe] H_2 -ases have shown a very high production
69 activity of hydrogen, about 6000-9000 H_2 molecules per second per active site (Li et al.,
70 2018; Stripp and Happe, 2009; Wang et al., 2019; Wittkamp et al., 2018). Therefore,
71 they have been studied in the last decades and have awakened interest in the synthesis
72 of biomimetic molecules (Ahmed et al., 2018; Capon et al., 2004; Liu and Darensbourg,
73 2007; Orain et al., 2014; Quentel et al., 2012; Roy et al., 2013).

74 [Fe-Fe] H_2 -ases photocatalytic hydrogen production systems containing metal
75 complexes, such as $[\text{Ru}(\text{bpy})_3]^{2+}$ (bpy = 2,2'-bipyridine) or $[\text{Re}(4,4'$
76 dimethylbpy)(CO) $_3]^+$ (Na et al., 2008; Pullen et al., 2013; Streich et al., 2010; Wang et
77 al., 2010; Yu et al., 2013) or organic dyes such as Eosin Y or Rose Bengal as

78 photosensitizers have been extensively studied (Li et al., 2012; Orain et al., 2014;
 79 Supplis et al., 2018). Orain et al studied the photocatalytic hydrogen production in
 80 aqueous solutions with [Fe-Fe]H₂-ase mimics, and organic dyes as photosensitizers
 81 (Orain et al., 2014). Despite promising performance, their main drawback was the fast
 82 excitation decay and the spectrally-narrow absorption band of dye sensitizers. In order
 83 to overcome these issues, semiconductor QDs have been employed as photosensitizers
 84 (Jian et al., 2016; Liang et al., 2015; Song et al., 2014; Troppmann and König, 2016;
 85 Wang et al., 2013, 2011; M. Wang et al., 2015; Wen et al., 2017, 2016). Jian et al.
 86 compared the performance of [Ru(bpy)₃]²⁺ and CdSe QDs as a photosensitizer for the
 87 same aqueous system achieving a hydrogen production rate of 301 and 20840 mmol
 88 H₂·g_{cat}⁻¹·h⁻¹, respectively, duplicating the stability of the system. Hydrogen production
 89 was further enhanced by using a sacrificial agent that acted as an electron donor, such as
 90 ascorbic acid (Figure 1) (Goy et al., 2017).



91

92 *Figure 1. Hydrogen production by a [FeFe]H₂-ase mimic from ascorbic acid aqueous solution*
 93 *with QDs as photosensitizer.*

95 The selection of the QD material for sensitizing hydrogen production is still a challenge.
96 Cadmium chalcogenides, CdS, CdSe and CdTe, are good candidates due to their visible-
97 range absorbance and energetically favorable positions of band edges for driving the
98 hydrogen production processes. Since CdS absorbs the smallest fraction of the solar
99 energy, CdSe and CdTe QDs, exhibiting absorption in the visible and near-IR, are
100 usually preferred. For instance, CdSe has been used as photosensitizer for hydrogen
101 generation in combination with hydrogenases, hydrogenase mimics, and even with
102 bacteria that produce hydrogenases (Chica et al., 2017; Ding et al., 2019; Hamon et al.,
103 2014; Jian et al., 2016; Li et al., 2013, 2020; Liang et al., 2015; Sanchez et al., 2019a,
104 2019b; Shen et al., 2013; Troppmann and König, 2016; Wang et al., 2013; Wen et al.,
105 2016). CdTe has been also used for this purpose (Brown et al., 2014, 2010; Greene et
106 al., 2012; Jian et al., 2013; Wang et al., 2011; Wroblewska-Wolna et al., 2020). Overall,
107 the two QD sensitizers appeared to perform differently in the presence of the same
108 scavenger and catalyst components (Acharya et al., 2011; JACS 2012, 134 (12) , 5627-
109 5636.), which makes this pair of QDs a promising model system for interrogating
110 energy conversion processes in sacrificial hydrogen production reactions.

111 The present study offers a comprehensive analysis of the hydrogen production
112 performance for CdSe and CdTe QD photosensitizers under visible light irradiation.
113 The photocatalytic systems in present experiments featured a bio-mimetic hydrogenase
114 catalyst and ascorbic acid as a sacrificial agent. By drawing a comparison between the
115 two sensitizer QDs, we were able to infer that the primary rate-limiting step in these
116 systems is an electron transfer between the sacrificial agent and semiconductor QDs.
117 This conclusion was supported by cyclic voltammetry measurements showing a larger

118 difference between the oxidation potential of ascorbic acid and the valence band of
119 CdSe, as compared to CdTe.

120

121 2. Materials and methods

122 2.1. Materials

123 Oleic acid (OA) 90%, 1-octadene (ODE) 90%, trioctylphosphine oxide (TOPO),
124 cadmium oxide (CdO) 99.5%, tellurium powder 99.8% and tributylphosphine 97%
125 (TBP) were purchased from Sigma Aldrich. Chloroform and acetone were purchased
126 from ChemPure Chemicals. L-Ascorbic acid 98+% and methanol were provided by
127 Alfa Aesar. N-octadecylphosphonic acid (ODPA) was supplied by PCI.
128 Trioctylphosphine (TOP) was purchased from Strem Chemicals Inc. Selenium powder
129 99.99% was supplied by Beantown Chemicals. 3-mercaptopropionic acid (MPA) was
130 acquired from Acros Organics. Sodium dodecyl sulfate (SDS) 10% was provided by
131 LifeTechnologies.

132 2.2. Hydrogenase synthesis

133 $[\text{Fe}_2(\mu\text{-}1,2\text{-benzenedithiolate})(\text{CO})_6]$, the $[\text{Fe-Fe}]\text{H}_2\text{-ase}$ mimic, was synthesized as
134 previously described in the literature (Cabeza et al., 1998).

135 2.3. Synthesis of CdSe and CdTe quantum dots

136 OA-capped CdSe QDs were synthesized according to a procedure adapted from the
137 literature (Mongin et al., 2018). Briefly, OA-capped CdSe QDs were synthesized from
138 cadmium and selenium solutions. To prepare cadmium solution, 180 mg of CdO were
139 dissolved with 75 mg of ODPA, 9 g of TOPO and 6 mL of OA in a flask at 300 °C
140 under Ar atmosphere. When the solution turned clear, 5.4 mL of TOP were added.
141 Selenium solutions were prepared with 180 mg of Se powder and 3 mL of TOP at 140

142 °C under Ar atmosphere. When selenium was dissolved, the solution was cooled down
143 to 80°C and it was injected into the cadmium solution. The reaction time was 2 min.
144 Every step was performed under magnetic stirring.

145 To synthesize ODP A-capped CdTe QDs, the cadmium solution was prepared with 25.6
146 mg of CdO, 147.2 mg of ODP A and 8 mL of ODE at 300 °C under Ar atmosphere.
147 Tellurium solution was prepared from 51 mg of tellurium powder, 4 mL of ODE, and
148 0.46 mL of TBP at 80 °C under Ar atmosphere. Tellurium solution was injected into the
149 cadmium solution and the reaction was carried out for 4.75 min.

150 Both CdTe and CdSe solutions were centrifuged for 4.5 min at 6500 rpm after adding
151 ethanol:acetone solution, with a volume ratio 2:1, to cause precipitation of the crystals.
152 The ratio between the crystals solution and the ethanol-acetone mixture was 1:3 in
153 volume. The precipitated crystals were re-dissolved in chloroform.

154 The ligand exchange process was carried out according to a procedure adapted from the
155 literature (Chang et al., 2016). Briefly, 0.5 mL of MPA were dissolved in 10 mL of a
156 1:1 methanol:chloroform solution at basic pH. 1.5 mL of crystals solution were added
157 under constant stirring. QDs precipitated after centrifugation in acetone. They were
158 dissolved in water and re-precipitated in acetone. Finally, the QDs were dissolved and
159 stored in water.

160 2.4. Materials characterization

161 ¹H NMR spectra of [Fe₂(μ-1,2-benzenedithiolate)(CO)₆] in deuterated acetone were
162 recorded on a Bruker AC-300 FT-NMR spectrometer and were referenced against
163 SiMe₄. The infrared spectra of [Fe₂(μ-1,2-benzenedithiolate)(CO)₆] in hexane were
164 recorded on a Nicolet Nexus FT-IR spectrometer.

165 The materials absorbance spectra were recorded in a UV-Vis spectrophotometer Cary
166 60 (Agilent). Photoluminescence spectra and excitation decay lifetime (τ_0) of CdSe and
167 CdTe QDs were obtained, exciting them with 405 nm PicoQuant PDL 800-D pulsed
168 laser and measuring their emission with an AndornewtonEM SR-303i-A spectrograph.

169 2.5. Hydrogen production

170 Hydrogen production experiments were carried out in an 8 mL reactor under magnetic
171 stirring. The reaction medium consisted of 4 mL of aqueous solution with ascorbic acid
172 200 mM (excess of the sacrificial agent was used to avoid its influence on the kinetics
173 of hydrogen production), 0.1 mM of [Fe-Fe] H_2 -ase mimic, QDs in a concentration
174 between 0.001 mM and 0.1 mM, and 10 mM SDS sodium dodecyl sulfate (SDS) to
175 solubilize the [Fe-Fe] H_2 -ase mimic (Orain et al., 2014; Supplis et al., 2018). The light
176 source consisted of a 150 W halogen lamp, provided with a filter which allowed only
177 visible light to pass ($400 \text{ nm} < \lambda < 800 \text{ nm}$). The irradiance on the reactor wall was 31
178 $\text{mW}\cdot\text{cm}^{-2}$. It was measured with a Compact Power and Energy Meter Console PM100D
179 from Thorlabs. The concentration of hydrogen was measured with a Shimadzu 8A gas
180 chromatograph, equipped with a thermal conductivity detector and a molecular sieve
181 column 80/100 using argon as a carrier gas. Hydrogen production experiments were
182 performed at pH 4.5, which is close to the ascorbic acid pK_a (4.2) (Tu et al., 2017); it
183 has been reported that working close to the sacrificial agent pK_a enhances hydrogen
184 production (Corredor et al., 2019).

185

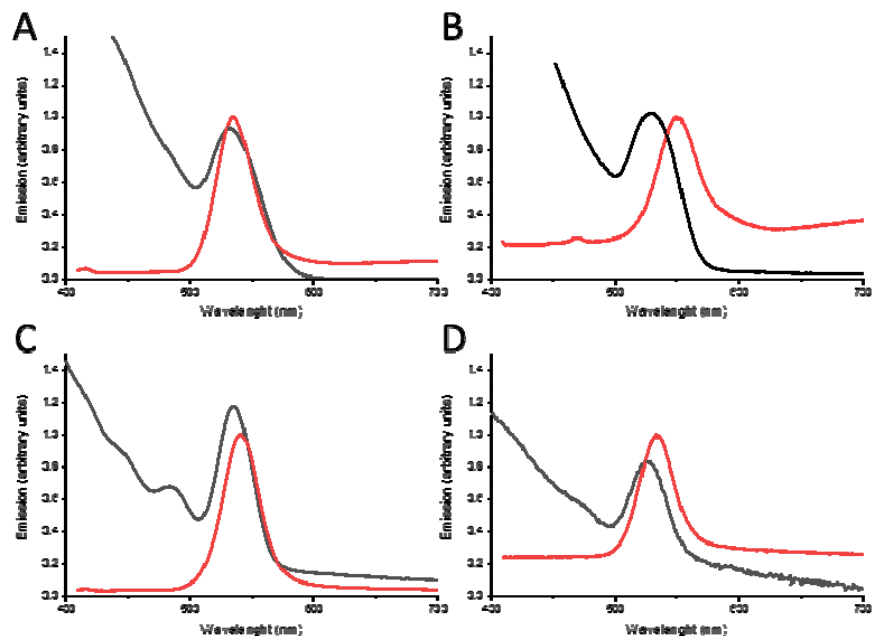
186 3. Results

187 The [Fe-Fe] H_2 -ase mimic $[\text{Fe}_2(\mu\text{-}1,2\text{-benzenedithiolate})(\text{CO})_6]$ was characterized by
188 FTIR and $^1\text{H-NMR}$ spectroscopy. Three bands were displayed in the infrared spectra in

189 the ν_{CO} region: 2006, 2045 and 2079 cm^{-1} . $^1\text{H-NMR}$ (300 MHz, $(\text{CD}_3)_2\text{CO}$): δ 7.24 (m,
190 2H), 7.46 (m, 2H). These data are in good agreement with those reported by Cabeza et
191 al. (Cabeza et al., 1998). The $[\text{Fe-Fe}]\text{H}_2\text{-ase}$ mimic absorbance spectra (Figure S1)
192 showed an absorption peak at 330 nm and absorption at wavelengths lower than 300
193 nm. Therefore, the catalyst did not absorb radiation during hydrogen production
194 experiments, which were carried out using visible light excitation (400-800 nm).

195 The influence of the QD diameter on the effectiveness of hydrogen production with
196 hydrogenase enzymes has been investigated previously (Brown et al., 2014). In this
197 work, we only focus on single sizes of CdTe and CdSe QDs (2.95 nm and 2.68 nm,
198 respectively, see Figure S2. Yu et al., 2003), which were chosen to enable similar
199 extinction values for the two sensitizers in the visible range. In this size range, the rate
200 of electron transfer to a catalysis was not expected to be influenced by the particle size
201 (Brown et al., 2014).

202 The UV-Vis absorbance and the emission spectra of the synthesized CdSe and CdTe
203 QDs before and after the ligand exchange process are shown in Figure 2. A slight blue-
204 shift was observed in the absorbance peak of both materials when the hydrophobic
205 ligands were exchanged with MPA.

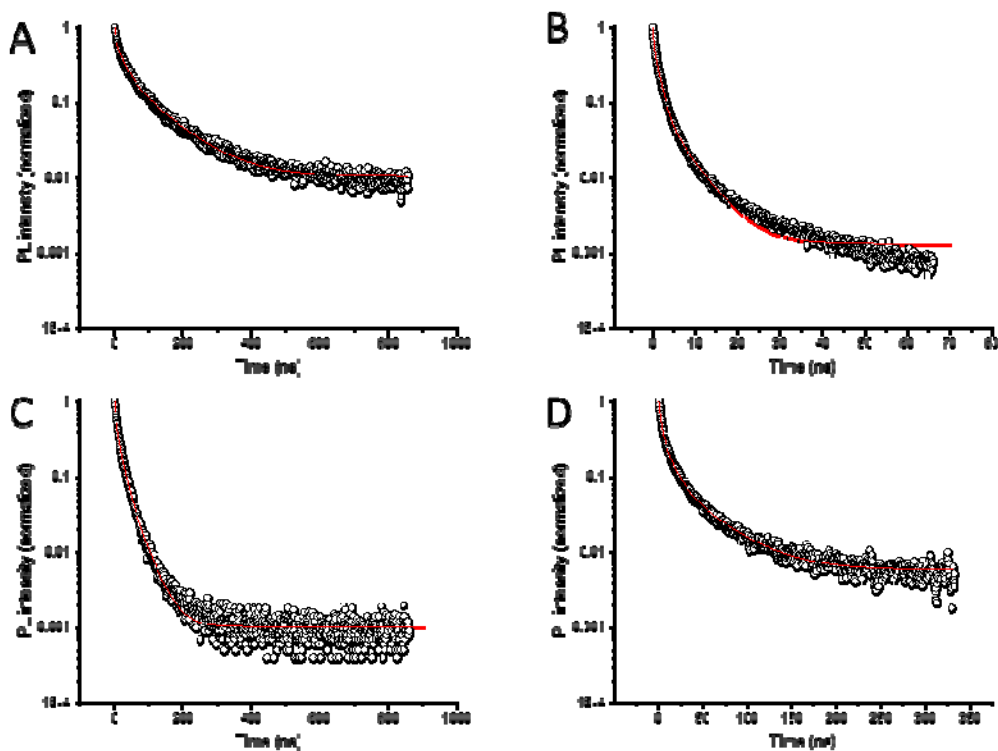


206

207 *Figure 2. CdSe and CdTe absorption (black) and emission (red) spectra of: (A) CdSe-OA; (B)*
 208 *CdSe-MPA; (C) CdTe-ODPA; (D) CdTe-MPA.*

209

210 Figure 3 shows the time-resolved luminescence decay curves of excited CdSe-OA,
 211 CdSe-MPA, CdTe-ODPA and CdTe-MPA. The fluorescence intensity decay lifetime
 212 (τ_0) was calculated by fitting the data to a three-phase exponential decay function (Gong
 213 et al., 2013). The τ_0 values for CdSe-OA, CdSe-MPA, CdTe-ODPA and CdTe-MPA
 214 were determined to be 38.4, 2.6, 14.7 and 9.6 ns, respectively. The value of τ_0 decreases
 215 upon the ligand exchange with MPA for both materials. This decrease was previously
 216 explained by the photoinduced hole transfer from a nanocrystal to MPA, which exhibits
 217 a more negative energy relative to the semiconductor valence band (Ben-Shahar et al.,
 218 2015; P. Wang et al., 2015).



219

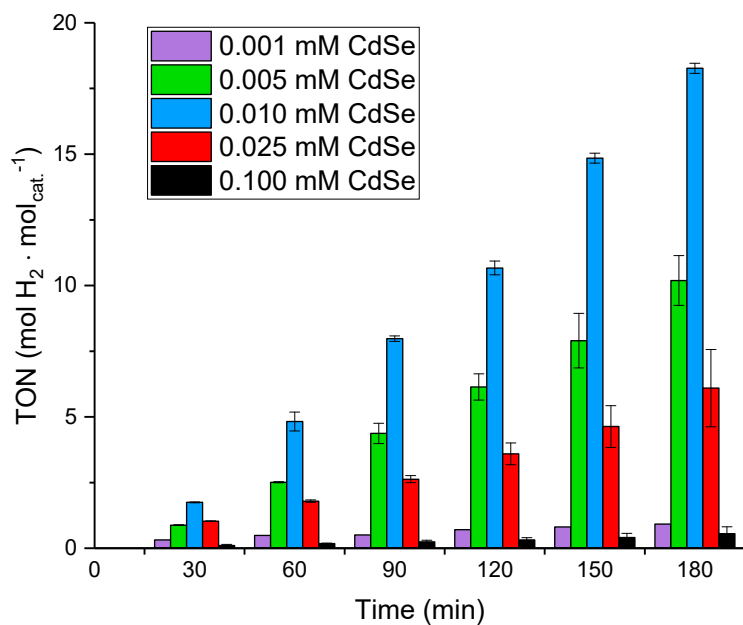
220 *Figure 3. Time-resolved photoluminescence decay spectra for (A) CdSe-OA, (B) CdSe-MPA, (C)*
 221 *CdTe-ODPA and (D) CdTe-MPA.*

222

223 3.2. Influence of Photosensitizer concentration on hydrogen production

224 Control tests were carried out in the dark and in the absence of a catalyst and
 225 photosensitizers successfully confirming the absence of hydrogen production. In the
 226 next step, the influence of the CdSe QD concentration on hydrogen production was
 227 investigated in the 0.001 mM to 0.1 mM range. The pH of the solution was the natural
 228 pH of the ascorbic acid (pKa 4.2) (Tu et al., 2017), as the optimal pH for these systems
 229 has a value close to the pKa of the sacrificial agent. In addition, Gloaguen and
 230 coworkers reported that a pH between 3 and 6 favored the protonation of the
 231 electrochemically reduced [Fe-Fe]H₂-ase mimic leading to higher hydrogen production
 232 (Quentel et al., 2012). The selected concentration of ascorbic acid was 200 mM

233 following previous reports (Jian et al., 2016). Figure 4 shows that the highest amount of
234 hydrogen was produced using $[CdSe] = 0.01$ mM, giving a turnover number (TON) of
235 18.3 mol of H_2 produced per mol of $[Fe_2(\mu-1,2-benzenedithiolate)(CO)_6]$ during 3 h.
236 The corresponding turnover number frequency (TOF), measured in mol of produced H_2
237 per mol of catalyst per unit of time, was $6.5\ h^{-1}$. Under the conditions of this study, the
238 generated hydrogen increased with the QD concentration up to a maximum value
239 obtained at a concentration of CdSe 0.01M, and after that it decreased as the
240 concentration of the QD increased.



241

242 *Figure 4. Hydrogen production for different CdSe-MPA concentrations. [Ascorbic acid]: 200*
243 *mM, $[Fe_2(\mu-1,2-benzenedithiolate)(CO)_6]$: 0.1 mM, pH: 4.5.*

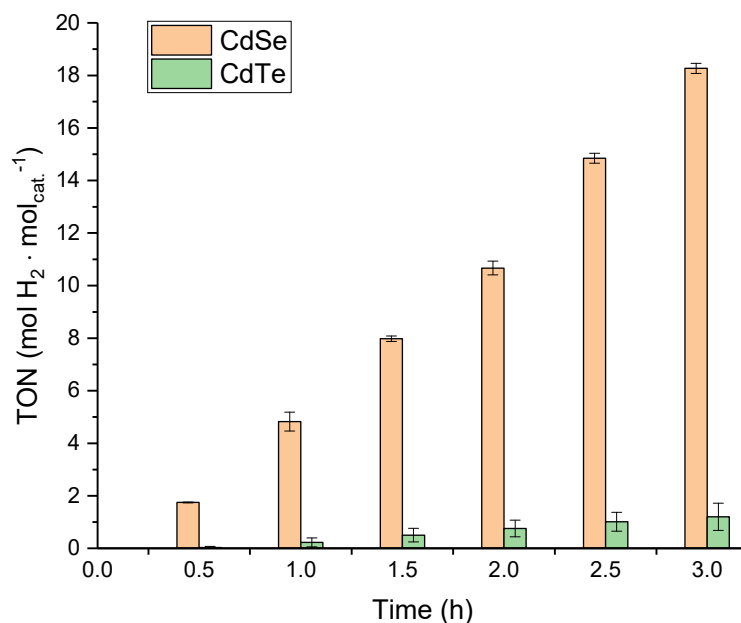
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245 Further insights into the influence of the CdSe QD concentration on hydrogen
246 generation are provided in Figure S3, which shows the number of excited CdSe
247 particles per second versus the total number of CdSe nanoparticles in the solution. The
248 procedure for estimating the number of excited QDs is given in SI, together with the

249 absorption spectra of QD solutions (Figure S4) and the excitation spectrum (Figure S5).
250 The dashed line in Figure S3 shows an ideal case in which the average number of
251 excited nanoparticles approaches that of the nanoparticles in solution. These conditions
252 are observed when the concentration of the photosensitizer is less than 0.01 mM.
253 However, only about 75% and 20% of the total particles were excited for QD
254 concentrations of 0.025 mM and 0.1 mM, respectively. Therefore, the decrease in
255 hydrogen production for concentrations of CdSe greater than 0.01 mM was attributed to
256 the inefficient activation of the photosensitizer particles. This is clarified by equation
257 S6, which shows that the irradiation of the light source strongly influences the optimal
258 concentration of the photosensitizer because the number of excited particles depends on
259 the number of accessible photons.

260 3.3. Comparative performance of the photosensitizers CdSe and CdTe

261 In order to compare the performance of photosensitizers MPA-CdSe and MPA-CdTe,
262 experiments were carried out with a concentration 0.01 mM of each photosensitizer.
263 Figure 6 shows the data of hydrogen production expressed as TON with CdSe and CdTe
264 during 3 h. Under similar experimental conditions, a TOF of 6.5 h^{-1} was observed with
265 CdSe, which is 13-fold higher than with CdTe (TOF = 0.5 h^{-1}). Table S1 collects the
266 values of the total hydrogen production and the production rate.



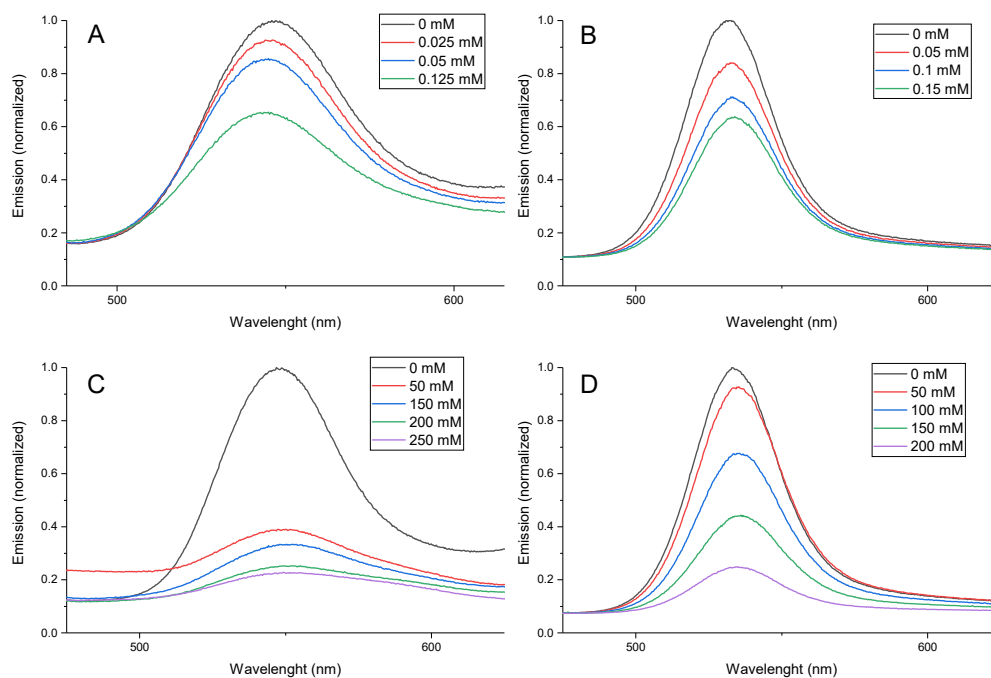
267

268 *Figure 6. Hydrogen production with CdSe and CdTe as photosensitizers. [Photosensitizer]: 0.01*
 269 *mM [Ascorbic acid]: 200 mM and [Fe₂(μ-1,2-benzenedithiolate)(CO)₆]: 0.1 mM, pH 4.5.*

270

271 Emission quenching spectra with progressive addition of catalyst and ascorbic acid to
 272 CdSe-MPA and CdTe-MPA solutions are shown in Figure 7. According to Figures 7A
 273 and 7B, addition of a catalyst causes a decrease in the fluorescence intensity, which is
 274 consistent with the transfer of photoexcited electrons from CdSe/CdTe to the catalyst.
 275 The comparison of the UV-Vis spectrum of [Fe₂(μ-1,2-benzenedithiolate)(CO)₆]
 276 (Figure S1), which shows an absorption peak around 340 nm, with the emission spectra
 277 of CdSe and CdTe showing maxima around 545 and 540 nm, respectively (Figure 2),
 278 leads to the conclusion that the catalyst does not absorb the fluorescence emitted by the
 279 photosensitizer. Thus, the loss of fluorescence intensity is due to the transfer of
 280 electrons from the conduction band of the photosensitizer to the catalyst. Consequently,
 281 the quenching constant (k_q), calculated using the Stern-Volmer equation (Figure S7)
 282 (Stern and Volmer, 1919), is equal to the rate constant of electron transfer from the

283 photosensitizer to the catalyst (k_{ET}), $k_q=k_{ET}$, with values of $1.55 \cdot 10^{12} \text{ M}^{-1} \cdot \text{s}^{-1}$ and
 284 $4.02 \cdot 10^{11} \text{ M}^{-1} \cdot \text{s}^{-1}$ for CdSe and CdTe, respectively. Similarly, quenching of fluorescence
 285 was also observed with increasing concentration of the ascorbic acid (scavenger) in
 286 solution (see Figures 7C and 7D). Since there is no overlap between the ascorbic acid
 287 absorption (Figure S6) and the photosensitizer emission (Figure 2), it was concluded
 288 that the quenching effect is due to the transfer of electrons from ascorbic acid to the
 289 photosensitizer valence band. In this case, the rate constant of electron transfer from
 290 ascorbic acid to the photosensitizer (k_{asc}), was found to be $5.42 \cdot 10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$ and $4.31 \cdot 10^8$
 291 $\text{M}^{-1} \cdot \text{s}^{-1}$ for CdSe and CdTe, respectively.

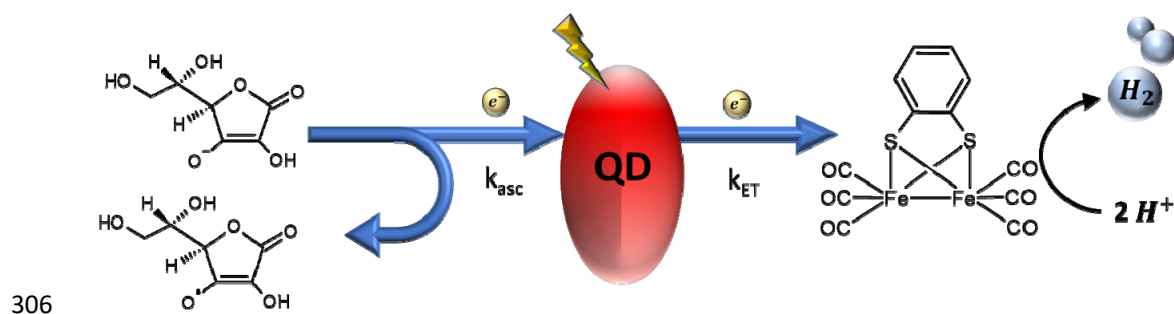


292

293 *Figure 7. Emission spectra at different concentrations of (A) catalyst in CdSe-MPA solution; (B)*
 294 *catalyst in CdTe-MPA solution; (C) ascorbic acid in CdSe-MPA solution; (D) ascorbic acid in*
 295 *CdTe-MPA solution.*

296

297 A difference of 2-3 orders of magnitude was observed between k_{ET} and k_{asc} in both
 298 materials. This difference agrees with previous reports (Jian et al., 2016; Wen et al.,
 299 2016). Figure 8 depicts the proposed mechanism where the electron transfer from
 300 ascorbic acid to the valence band of the QDs is the rate-limiting step as k_{asc} is two
 301 orders of magnitude smaller than k_{ET} . Furthermore, CdSe sensitizer showed a greater
 302 k_{asc} which was nearly 13 times higher than for CdTe. This fact is consistent with the 13
 303 times greater hydrogen production rate obtained with CdSe than with CdTe. Therefore,
 304 it was concluded that the electron transfer from the ascorbic acid to the QD was the
 305 primary rate-limiting step in hydrogen production reactions.

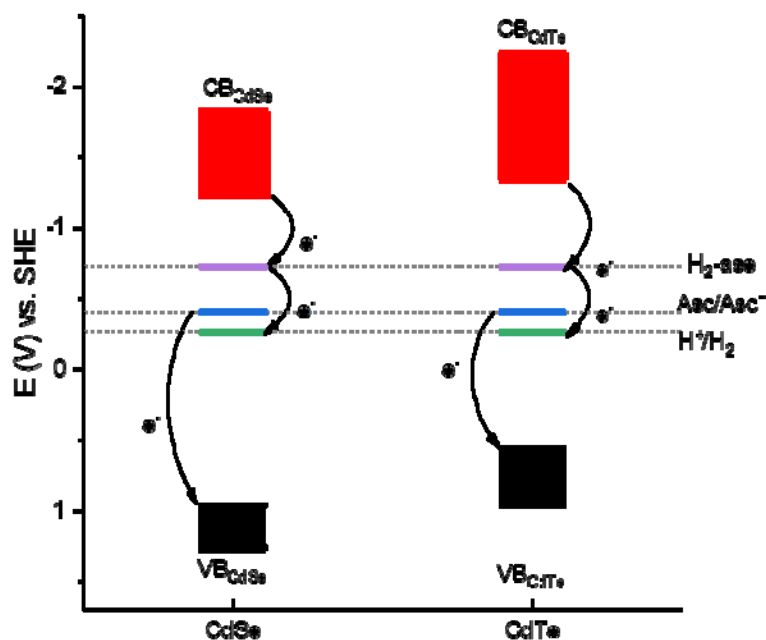


307 *Figure 8. Mechanism of photocatalytic hydrogen production.*

308

309 Figure 9 represents the energy diagram of both systems at pH 4.5. The reduction
 310 potential of the [Fe-Fe]H₂-ase mimic was determined by cyclic voltammetry as $E_{1/2} \sim$
 311 0.68 V at pH 4.5 (Quentel et al., 2012) and for ascorbic acid the corresponding value
 312 was -0.41 V (Tu et al., 2017). Although it is energetically favorable for the ascorbic acid
 313 to produce hydrogen directly, it was confirmed experimentally that this redox reaction
 314 did not occur. For both semiconductors, Figure 9 illustrates the conduction and valence
 315 band edge energies for CdSe and CdTe QDs adjusted for present particle diameters
 316 considering the variability range found in literature. (Jasieniak et al., 2011). Notably, the
 317 energy difference between the oxidation potential of ascorbic acid and the valence band

318 of the QD is greater for CdSe than for CdTe, which is consistent with the higher value
 319 of k_{Asc} of CdSe with respect to CdTe. This causes a comparatively greater driving force
 320 for the photoinduced electron transfer from sacrificial agent to the CdSe.



321

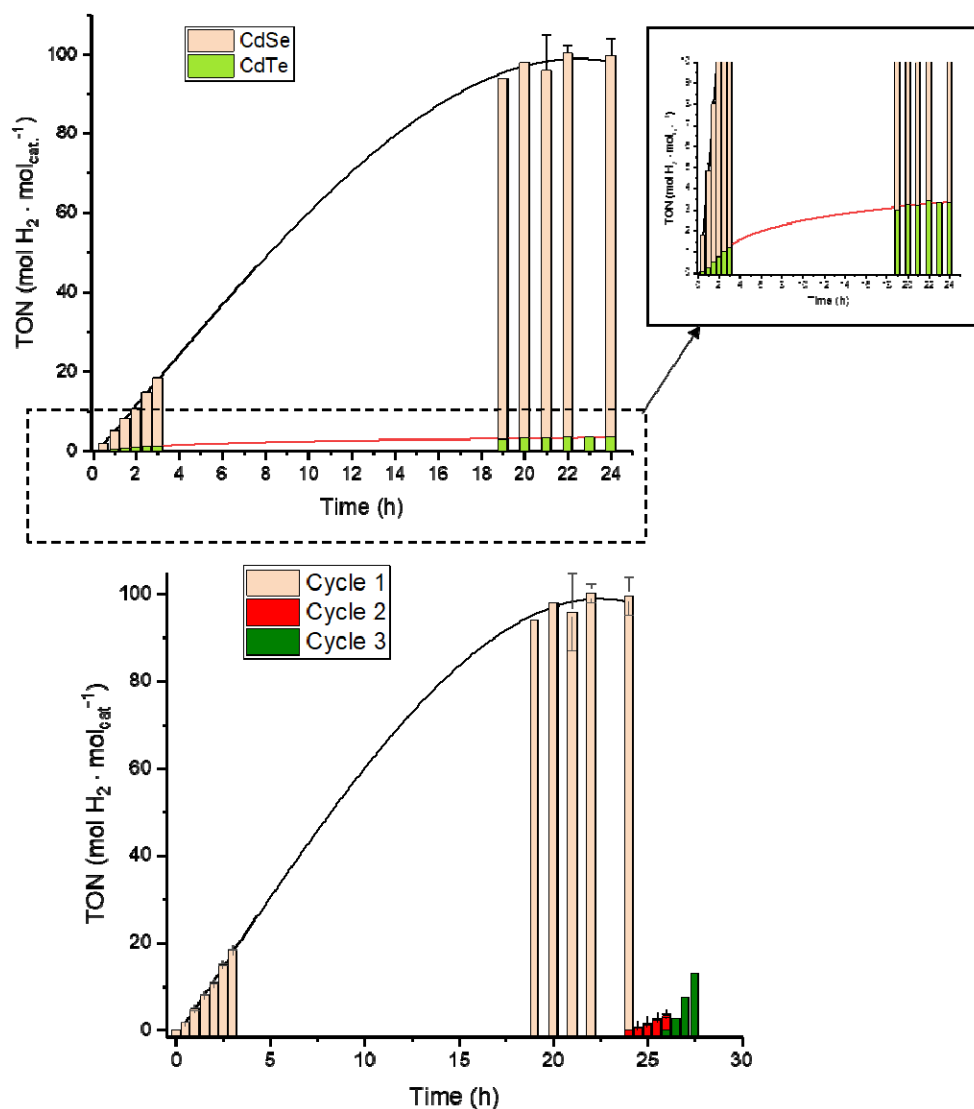
322 *Figure 9. Energy levels at pH 4.5 of CdSe, CdTe, [FeFe]H₂-ase mimic and ascorbic acid.*

323

324 Overall, the above experiments demonstrate that the rate-limiting step for the hydrogen
 325 production in the QD-([FeFe]H₂-ase mimic)-(ascorbic acid) system is the electron
 326 transfer from the ascorbic acid (sacrificial agent) to the valence band of the
 327 photosensitizer characterized by the kinetic constant k_{Asc} .

328 In an effort to assess the stability of the investigated catalytic system, several selected
 329 experiments were carried out for the duration of 24 h. According to Figure 10A, CdSe
 330 reached a TON value of 100 while CdTe achieved a TON value of 3.5 after 24 h. The
 331 initial TOF with CdSe was 6.5 h⁻¹ decreasing to 1.8 h⁻¹ after 18 h while the initial TOF
 332 with CdTe was 0.5 h⁻¹ decreasing to 0.1 h⁻¹ after 18 h. Therefore, hydrogen production

333 rate decreased about 75% for both materials in this period of time. Figure 10B shows
334 hydrogen production with CdSe operating in different cycles. Cycle 1 shows hydrogen
335 production with a fresh catalyst. Hydrogen production rate decreased to 1.8 h^{-1} after 18 h
336 of reaction. Before starting cycle 2, a purge with argon was carried out in the
337 photoreactor to eliminate any possible inhibitory effect of the product, as has been
338 previously reported (Corredor et al., 2020b). After this purge, the TOF was 1.7 h^{-1} ,
339 similar to the value at the end of cycle 1. Therefore, the decrease in hydrogen
340 production was not attributed to the hydrogen inhibitory effect. Next, catalyst
341 deactivation was examined by addition of $7.5 \cdot 10^{-3} \text{ mM}$ of fresh catalyst at the beginning
342 of cycle 3; hydrogen production recovered similar values to the initial experimental
343 conditions. Therefore, the decline and stop of hydrogen production is attributed to the
344 loss of catalyst activity.



345

346 *Figure 10. Hydrogen production with (A) CdSe and CdTe for longer operation times, and (B)*
 347 *catalyst reuse with CdSe.*

348

349 4. Conclusions

350 In this work, we compare the photocatalytic performance of two QD photosensitizers,

351 CdSe and CdTe, in hydrogen production systems composed of a hydrogenase mimic

352 catalyst and ascorbic acid as sacrificial agent. CdSe QDs showed an overall better

353 performance. For these materials, the highest hydrogen production rate was observed

354 using 0.01 mM nanoparticle concentration, 200 mM of ascorbic acid, and 0.1 mM of
355 [Fe-Fe]H₂-ase mimic (excitation intensity = 31 mW·cm⁻² of, 400 nm < λ < 800 nm).

356 Quenching experiments revealed that the rate of electron transfer from photosensitizer
357 to the catalyst, k_{ET} , is of 2-3 orders of magnitude higher than that of scavenger →
358 photosensitizer transfer process, k_{Asc} . In particular, we found that k_{asc} for CdSe was 13
359 times greater than that of CdTe. The ratio of hydrogen production rates for the two
360 materials, CdSe and CdTe, exhibited roughly the same ratio (13:1), suggesting that the
361 photoinduced hole transfer from a QD to a scavenger was the rate limiting step. A
362 relatively greater value of k_{asc} for CdSe was attributed to the larger difference between
363 the oxidation potential of ascorbic acid and the valence band energy of CdSe in
364 comparison with CdTe. This conclusion suggests that photosensitizers that enable faster
365 sacrificial regenerations may hold the key to improving the hydrogen production rate.
366 Another important area to be addressed by the future research is the long-term stability
367 of hydrogenase mimic catalysts, which lost 25% of catalytic activity after 18 h in
368 present measurements.

369

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376

377 6. References

378 Acharya, K.P., Khnayzer, R.S., O'Connor, T., Diederich, G., Kirsanova, M., Klinkova,
379 A., Roth, D., Kinder, E., Imboden, M., Zamkov, M., 2011. The role of hole
380 localization in sacrificial hydrogen production by semiconductor-metal
381 heterostructured nanocrystals. *Nano Lett.* 11, 2919–2926.
382 <https://doi.org/10.1021/nl201388c>

383 Ahmed, M.E., Dey, S., Darensbourg, M.Y., Dey, A., 2018. Oxygen-Tolerant H₂
384 Production by [FeFe]-H₂ase Active Site Mimics Aided by Second Sphere Proton
385 Shuttle. *J. Am. Chem. Soc.* 140, 12457–12468.
386 <https://doi.org/10.1021/jacs.8b05983>

387 Baker, D.R., Kamat, P. V., 2010. Tuning the emission of CdSe Quantum Dots by
388 Controlled Deep-Trap Enhancement. *Langmuir* 26, 11272–11276.

389 Ben-Shahar, Y., Scotognella, F., Waiskopf, N., Kriegel, I., Dal Conte, S., Cerullo, G.,
390 Banin, U., 2015. Effect of surface coating on the photocatalytic function of hybrid
391 CdS-Au nanorods. *Small* 11, 462–471. <https://doi.org/10.1002/smll.201402262>

392 Brown, K.A., Dayal, S., Ai, X., Rumbles, G., King, P.W., 2010. Controlled assembly of
393 hydrogenase-CdTe nanocrystal hybrids for solar hydrogen production. *J. Am.*
394 *Chem. Soc.* 132, 9672–9680. <https://doi.org/10.1021/ja101031r>

395 Brown, K.A., Song, Q., Mulder, D.W., King, P.W., 2014. Diameter dependent electron
396 transfer kinetics in semiconductor-enzyme complexes. *ACS Nano* 8, 10790–10798.
397 <https://doi.org/10.1021/nn504561v>

398 Cabeza, J.A., Martínez-García, M.A., Riera, V., Ardura, D., García-Granda, S., 1998.
399 Binuclear iron(I), ruthenium(I), and osmium(I) hexacarbonyl complexes containing
400 a bridging benzene-1,2-dithiolate ligand. Synthesis, X-ray structures, protonation
401 reactions, and EHMO calculations. *Organometallics* 17, 1471–1477.

402 <https://doi.org/10.1021/om970922j>

403 Capon, J.F., Gloaguen, F., Schollhammer, P., Talarmin, J., 2004. Electrochemical
404 proton reduction by thiolate-bridged hexacarbonyldiiron clusters. *J. Electroanal.*
405 *Chem.* 566, 241–247. <https://doi.org/10.1016/j.jelechem.2003.11.032>

406 Chang, C.M., Orchard, K.L., Martindale, B.C.M., Reisner, E., 2016. Ligand removal
407 from CdS quantum dots for enhanced photocatalytic H₂ generation in pH neutral
408 water. *J. Mater. Chem. A* 4, 2856–2862. <https://doi.org/10.1039/c5ta04136h>

409 Chen, Y., Xiao, K., Shen, N., Zeng, R.J., Zhou, Y., 2018. Hydrogen production from a
410 thermophilic alkaline waste activated sludge fermenter: Effects of solid retention
411 time (SRT). *Chemosphere* 206, 101–106.
412 <https://doi.org/10.1016/j.chemosphere.2018.04.170>

413 Chica, B., Wu, C.H., Liu, Y., Adams, M.W.W., Lian, T., Dyer, R.B., 2017. Balancing
414 electron transfer rate and driving force for efficient photocatalytic hydrogen
415 production in CdSe/CdS nanorod-[NiFe] hydrogenase assemblies. *Energy Environ.*
416 *Sci.* 10, 2245–2255. <https://doi.org/10.1039/c7ee01738c>

417 Cho, H., Joo, H., Kim, H., Kim, J.E., Kang, K.S., Yoon, J., 2021. Improved
418 photoelectrochemical properties of TiO₂ nanotubes doped with Er and effects on
419 hydrogen production from water splitting. *Chemosphere* 267, 129289.
420 <https://doi.org/10.1016/j.chemosphere.2020.129289>

421 Christoforidis, K.C., Fornasiero, P., 2017. Photocatalytic Hydrogen production: A rift
422 into the future energy supply. *ChemCatChem* 9, 1523–1544.
423 <https://doi.org/10.1002/cctc.201601659>

424 Chu, K.H., Ye, L., Wang, W., Wu, D., Chan, D.K.L., Zeng, C., Yip, H.Y., Yu, J.C.,

425 Wong, P.K., 2017. Enhanced photocatalytic hydrogen production from aqueous
426 sulfide/sulfite solution by ZnO_{0.6}S_{0.4} with simultaneous dye degradation under
427 visible-light irradiation. *Chemosphere* 183, 219–228.
428 <https://doi.org/10.1016/j.chemosphere.2017.05.112>

429 Corredor, J., Perez-Peña, E., Rivero, M.J., Ortiz, I., 2020a. Performance of rGO/TiO₂
430 photocatalytic membranes for hydrogen production. *Membranes* 10, 1–13.
431 <https://doi.org/10.3390/membranes10090218>

432 Corredor, J., Rivero, M.J., Ortiz, I., 2020b. New insights in the performance and reuse
433 of rGO/TiO₂ composites for the photocatalytic hydrogen production. *Int. J.*
434 *Hydrogen Energy* (In press). <https://doi.org/10.1016/j.ijhydene.2020.01.181>

435 Corredor, J., Rivero, M.J., Rangel, C.M., Gloaguen, F., Ortiz, I., 2019. Comprehensive
436 review and future perspectives on the photocatalytic hydrogen production. *J.*
437 *Chem. Technol. Biotechnol.* 94, 3049–3063. <https://doi.org/10.1002/jctb.6123>

438 Ding, Y., Bertram, J.R., Eckert, C., Bommarreddy, R.R., Patel, R., Conradie, A., Bryan,
439 S., Nagpal, P., 2019. Nanorg Microbial Factories: Light-Driven Renewable
440 Biochemical Synthesis Using Quantum Dot-Bacteria Nanobiohybrids. *J. Am.*
441 *Chem. Soc.* 141, 10272–10282. <https://doi.org/10.1021/jacs.9b02549>

442 El-Khouly, M.E., El-Mohsnawy, E., Fukuzumi, S., 2017. Solar energy conversion:
443 From natural to artificial photosynthesis. *J. Photochem. Photobiol. C Photochem.*
444 *Rev.* 31, 36–83. <https://doi.org/10.1016/j.jphotochemrev.2017.02.001>

445 Elsayed, M.H., Jayakumar, J., Abdellah, M., Mansoure, T.H., Zheng, K., Elewa, A.M.,
446 Chang, C.-L., Ting, L.-Y., Lin, W.-C., Yu, H., Wang, W.-H., Chung, C.-C., Chou,
447 H.-H., 2021. Visible-light-driven hydrogen evolution using nitrogen-doped carbon
448 quantum dot-implanted polymer dots as metal-free photocatalysts. *Appl. Catal. B*

449 Environ. 283, 119659. <https://doi.org/10.1016/j.apcatb.2020.119659>

450 Fang, X., Cui, L., Pu, T., Song, J., Zhang, X., 2018. Core-shell CdS@MnS nanorods as
451 highly efficient photocatalysts for visible light driven hydrogen evolution. Appl.
452 Surf. Sci. 457, 863–869. <https://doi.org/10.1016/j.apsusc.2018.07.012>

453 Fukuzumi, S., Lee, Y.M., Nam, W., 2018. Thermal and photocatalytic production of
454 hydrogen with earth-abundant metal complexes. Coord. Chem. Rev. 355, 54–73.
455 <https://doi.org/10.1016/j.ccr.2017.07.014>

456 Gong, K., Zeng, Y., Kelley, D.F., 2013. Extinction coefficients, oscillator strengths, and
457 radiative lifetimes of CdSe, CdTe, and CdTe/CdSe nanocrystals. J. Phys. Chem. C
458 117, 20268–20279. <https://doi.org/10.1021/jp4065449>

459 Goy, R., Bertini, L., Rudolph, T., Lin, S., Schulz, M., Zampella, G., Dietzek, B.,
460 Schacher, F.H., De Gioia, L., Sakai, K., Weigand, W., 2017. Photocatalytic
461 Hydrogen Evolution Driven by [FeFe] Hydrogenase Models Tethered to Fluorene
462 and Silafluorene Sensitizers. Chem. Eur. J. 23, 334–345.
463 <https://doi.org/10.1002/chem.201603140>

464 Greene, B.L., Joseph, C.A., Maroney, M.J., Dyer, R.B., 2012. Direct evidence of active-
465 site reduction and photodriven catalysis in sensitized hydrogenase assemblies. J.
466 Am. Chem. Soc. 134, 11108–11111. <https://doi.org/10.1021/ja3042367>

467 Hamon, C., Ciaccafava, A., Infossi, P., Puppo, R., Even-Hernandez, P., Lojou, E.,
468 Marchi, V., 2014. Synthesis and enzymatic photo-activity of an O₂tolerant
469 hydrogenase-CdSe@CdS quantum rod bioconjugate. Chem. Commun. 50, 4989–
470 4992. <https://doi.org/10.1039/c3cc49368g>

471 Hemming, E.B., Chan, B., Turner, P., Corcilius, L., Price, J.R., Gardiner, M.G.,

472 Masters, A.F., Maschmeyer, T., 2018. $[\text{Fe}(\text{C}_5\text{Ar}_5)(\text{CO})_2\text{Br}]$ complexes as
473 hydrogenase mimics for the catalytic hydrogen evolution reaction. *Appl. Catal. B*
474 *Environ.* 223, 234–241. <https://doi.org/10.1016/j.apcatb.2017.04.053>

475 Hinojosa-Reyes, M., Camposeco-Solís, R., Zanella, R., Rodríguez González, V., 2017.
476 Hydrogen production by tailoring the brookite and Cu_2O ratio of sol-gel Cu-TiO_2
477 photocatalysts. *Chemosphere* 184, 992–1002.
478 <https://doi.org/10.1016/j.chemosphere.2017.06.066>

479 Holladay, J.D., Hu, J., King, D.L., Wang, Y., 2009. An overview of hydrogen
480 production technologies. *Catal. Today* 139, 244–260.
481 <https://doi.org/10.1016/j.cattod.2008.08.039>

482 Jasieniak, J., Califano, M., Watkins, S.E., 2011. Size-dependent valence and conduction
483 band-edge energies of semiconductor nanocrystals. *ACS Nano* 5, 5888–5902.
484 <https://doi.org/10.1021/nn201681s>

485 Jian, J.-X., Ye, C., Wang, X.-Z., Wen, M., Li, Z.-J., Li, X.-B., Chen, B., Tung, C.-H.,
486 Wu, L.-Z., 2016. Comparison of H_2 photogeneration by $[\text{FeFe}]$ -hydrogenase
487 mimics with CdSe QDs and $\text{Ru}(\text{bpy})_3\text{Cl}_2$ in aqueous solution. *Energy Environ. Sci.*
488 9, 2083–2089. <https://doi.org/10.1039/C6EE00629A>

489 Jian, J.X., Liu, Q., Li, Z.J., Wang, F., Li, X.B., Li, C.B., Liu, B., Meng, Q.Y., Chen, B.,
490 Feng, K., Tung, C.H., Wu, L.Z., 2013. Chitosan confinement enhances hydrogen
491 photogeneration from a mimic of the diiron subsite of $[\text{FeFe}]$ -hydrogenase. *Nat.*
492 *Commun.* 4, 2695. <https://doi.org/10.1038/ncomms3695>

493 Lai, G.J., Lyu, L.M., Huang, Y.S., Lee, G.C., Lu, M.P., Perng, T.P., Lu, M.Y., Chen,
494 L.J., 2021. Few-layer WS_2 – MoS_2 in-plane heterostructures for efficient
495 photocatalytic hydrogen evolution. *Nano Energy* 81, 105608.

496 <https://doi.org/10.1016/j.nanoen.2020.105608>

497 Lewis S. Nathan, 2016. Research opportunities to advance solar energy utilization.
498 Science 351, aad1920. <https://doi.org/10.1126/science.aad1920.22>

499 Li, C.B., Li, Z.J., Yu, S., Wang, G.X., Wang, F., Meng, Q.Y., Chen, B., Feng, K., Tung,
500 C.H., Wu, L.Z., 2013. Interface-directed assembly of a simple precursor of [FeFe]-
501 H₂ase mimics on CdSe QDs for photosynthetic hydrogen evolution in water.
502 Energy Environ. Sci. 6, 2597–2602. <https://doi.org/10.1039/c3ee40992a>

503 Li, R.X., Ren, X.T., Tang, M.Y., Chen, M.X., Huang, G.B., Fang, C.H., Liu, T., Feng,
504 Z.H., Yin, Y.B., Guo, Y.M., Mei, S.K., Yan, J., 2018. Fabrication of covalently
505 linked graphene-mediated [FeFe]-hydrogenases biomimetic photocatalytic
506 hydrogen evolution system in aqueous solution. Appl. Catal. B Environ. 224, 772–
507 782. <https://doi.org/10.1016/j.apcatb.2017.09.062>

508 Li, X., Wang, M., Chen, L., Wang, X., Dong, J., Sun, L., 2012. Photocatalytic water
509 reduction and study of the formation of Fe^IFe⁰ species in diiron catalyst systems.
510 ChemSusChem 5, 913–919. <https://doi.org/10.1002/cssc.201100490>

511 Li, X.B., Jian, J.X., Wang, X.Z., Wang, Y., Xia, S.G., Tung, C.H., Wu, L.Z., 2020. Per-
512 6-Thiol-Cyclodextrin Engineered [FeFe]-Hydrogenase Mimic/CdSe Quantum Dot
513 Assembly for Photocatalytic Hydrogen Production. Sol. RRL (In press).
514 <https://doi.org/10.1002/solr.202000474>

515 Liang, W.J., Wang, F., Wen, M., Jian, J.X., Wang, X.Z., Chen, B., Tung, C.H., Wu,
516 L.Z., 2015. Branched polyethylenimine improves hydrogen photoproduction from
517 a CdSe quantum dot/[FeFe]-hydrogenase mimic system in neutral aqueous
518 solutions. Chem. Eur. J. 21, 3187–3192. <https://doi.org/10.1002/chem.201406361>

519 Liu, T., Darensbourg, M.Y., 2007. A mixed-valent, Fe(II)Fe(I), diiron complex
520 reproduces the unique rotated state of the [FeFe]hydrogenase active site. *J. Am.*
521 *Chem. Soc.* 129, 7008–7009. <https://doi.org/10.1021/ja071851a>

522 Lyon, E.J., Georgakaki, I.P., Reibenspies, J.H., Darensbourg, M.Y., 2001. Coordination
523 sphere flexibility of active-site models for Fe-only hydrogenase: Studies in intra-
524 and intermolecular diatomic ligand exchange. *J. Am. Chem. Soc.* 123, 3268–3278.
525 <https://doi.org/10.1021/ja003147z>

526 Mongin, C., Moroz, P., Zamkov, M., Castellano, F.N., 2018. Thermally activated
527 delayed photoluminescence from pyrenyl-functionalized CdSe quantum dots. *Nat.*
528 *Chem.* 10, 225–230. <https://doi.org/10.1038/nchem.2906>

529 Munfarida, S., Widayat, Satriadi, H., Cahyono, B., Hadiyanto, Philia, J., Prameswari, J.,
530 2020. Geothermal industry waste-derived catalyst for enhanced biohydrogen
531 production. *Chemosphere* 258, 127274.
532 <https://doi.org/10.1016/j.chemosphere.2020.127274>

533 Na, Y., Wang, M., Pan, J., Zhang, P., Åkermark, B., Sun, L., 2008. Visible light-driven
534 electron transfer and hydrogen generation catalyzed by bioinspired [2Fe2S]
535 complexes. *Inorg. Chem.* 47, 2805–2810. <https://doi.org/10.1021/ic702010w>

536 Nasir, M.S., Yang, G., Ayub, I., Wang, S., Wang, L., Wang, X., Yan, W., Peng, S.,
537 Ramakarishna, S., 2019. Recent development in graphitic carbon nitride based
538 photocatalysis for hydrogen generation. *Appl. Catal. B Environ.* 257, 117855.
539 <https://doi.org/10.1016/j.apcatb.2019.117855>

540 Nikolaidis, P., Poullikkas, A., 2017. A comparative overview of hydrogen production
541 processes. *Renew. Sustain. Energy Rev.* 67, 597–611.
542 <https://doi.org/10.1016/j.rser.2016.09.044>

543 Oh, W.C., Nguyen, D.C.T., Areerob, Y., 2020. Novel cadmium oxide-graphene
544 nanocomposite grown on mesoporous silica for simultaneous photocatalytic H₂-
545 evolution. *Chemosphere* 239, 124825.
546 <https://doi.org/10.1016/j.chemosphere.2019.124825>

547 Orain, C., Quentel, F., Gloaguen, F., 2014. Photocatalytic Hydrogen Production Using
548 Models of the Iron-Iron Hydrogenase Active Site Dispersed in Micellar Solution.
549 *ChemSusChem* 7, 638–643. <https://doi.org/10.1002/cssc.201300631>

550 Pullen, S., Fei, H., Orthaber, A., Cohen, S.M., Ott, S., 2013. Enhanced photochemical
551 hydrogen production by a molecular diiron catalyst incorporated into a metal-
552 organic framework. *J. Am. Chem. Soc.* 135, 16997–17003.
553 <https://doi.org/10.1021/ja407176p>

554 Putri, L.K., Ng, B.J., Ong, W.J., Lee, H.W., Chang, W.S., Mohamed, A.R., Chai, S.P.,
555 2020. Energy level tuning of CdSe colloidal quantum dots in ternary 0D-2D-2D
556 CdSe QD/B-rGO/O-gC₃N₄ as photocatalysts for enhanced hydrogen generation.
557 *Appl. Catal. B Environ.* 265, 118592. <https://doi.org/10.1016/j.apcatb.2020.118592>

558 Quentel, F., Passard, G., Gloaguen, F., 2012. Electrochemical hydrogen production in
559 aqueous micellar solution by a diiron benzenedithiolate complex relevant to [FeFe]
560 hydrogenases. *Energy Environ. Sci.* 5, 7757–7761.
561 <https://doi.org/10.1039/c2ee21531d>

562 Ribao, P., Alexandra Esteves, M., Fernandes, V.R., Rivero, M.J., Rangel, C.M., Ortiz,
563 I., 2019. Challenges arising from the use of TiO₂/rGO/Pt photocatalysts to produce
564 hydrogen from crude glycerol compared to synthetic glycerol. *Int. J. Hydrogen*
565 *Energy* 44, 28494–28506.
566 <https://doi.org/https://doi.org/10.1016/j.ijhydene.2018.09.148>

- 577 Rivero, M.J., Iglesias, O., Ribao, P., Ortiz, I., 2019. Kinetic performance of
578 TiO₂/Pt/reduced graphene oxide composites in the photocatalytic hydrogen
579 production. *Int. J. Hydrogen Energy* 44, 101–109.
570 <https://doi.org/10.1016/j.ijhydene.2018.02.115>
- 571 Roy, S., Groy, T.L., Jones, A.K., 2013. Biomimetic model for [FeFe]-hydrogenase:
572 asymmetrically disubstituted diiron complex with a redox-active 2,2'-bipyridyl
573 ligand. *Dalt. Trans.* 42, 3843–3853. <https://doi.org/10.1039/c2dt32457a>
- 574 Sanchez, M.L.K., Sommer, C., Reijerse, E., Birrell, J.A., Lubitz, W., Dyer, R.B., 2019a.
575 Investigating the Kinetic Competency of CrHydA1 [FeFe] Hydrogenase
576 Intermediate States via Time-Resolved Infrared Spectroscopy. *J. Am. Chem. Soc.*
577 141, 16064–16070. <https://doi.org/10.1021/jacs.9b08348>
- 578 Sanchez, M.L.K., Wu, C.H., Adams, M.W.W., Dyer, R.B., 2019b. Optimizing electron
579 transfer from CdSe QDs to hydrogenase for photocatalytic H₂ production. *Chem.*
580 *Commun.* 55, 5579–5582. <https://doi.org/10.1039/c9cc01150a>
- 581 Seadira, T.W.P., Sadanandam, G., Ntho, T., Masuku, C.M., Scurrrell, M.S., 2018.
582 Preparation and characterization of metals supported on nanostructured TiO₂
583 hollow spheres for production of hydrogen via photocatalytic reforming of
584 glycerol. *Appl. Catal. B Environ.* 222, 133–145.
585 <https://doi.org/10.1016/j.apcatb.2017.09.072>
- 586 Shen, M., Jia, W., You, Y., Hu, Y., Li, F., Tian, S., Li, J., Jin, Y., Han, D., 2013.
587 Luminescent properties of CdTe quantum dots synthesized using 3-
588 mercaptopropionic acid reduction of tellurium dioxide directly. *Nanoscale Res.*
589 *Lett.* 8, 1–6. <https://doi.org/10.1186/1556-276x-8-253>
- 590 Song, X.W., Wen, H.M., Ma, C.B., Hu, M.Q., Chen, H., Cui, H.H., Chen, C.N., 2014.

591 Photocatalytic hydrogen evolution by two comparable [FeFe]-hydrogenase mimics
592 assembled to the surface of ZnS. *Appl. Organomet. Chem.* 28, 267–273.
593 <https://doi.org/10.1002/aoc.3119>

594 Stern, O., Volmer, M., 1919. Über die Abklingzeit der Fluoreszenz. *Z. Phys.* 20, 183–
595 188.

596 Streich, D., Astuti, Y., Orlandi, M., Schwartz, L., Lomoth, R., Hammarström, L., Ott,
597 S., 2010. High-turnover photochemical hydrogen production catalyzed by a model
598 complex of the [FeFe]-hydrogenase active site. *Chem. Eur. J.* 16, 60–63.
599 <https://doi.org/10.1002/chem.200902489>

600 Stripp, S.T., Happe, T., 2009. How algae produce hydrogen—news from the
601 photosynthetic hydrogenase. *Dalt. Trans.* 9960–9969.
602 <https://doi.org/10.1039/b916246a>

603 Supplis, C., Gros, F., Dahi, G., Dauchet, J., Roudet, M., Gloaguen, F., Cornet, J.F.,
604 2018. Spectral radiative analysis of bio-inspired H₂ production in a benchmark
605 photoreactor: A first investigation using spatial photonic balance. *Int. J. Hydrogen*
606 *Energy* 43, 8221–8231. <https://doi.org/10.1016/j.ijhydene.2018.03.097>

607 Trincado, M., Banerjee, D., Grützmacher, H., 2014. Molecular catalysts for hydrogen
608 production from alcohols. *Energy Environ. Sci.* 7, 2464–2503.
609 <https://doi.org/10.1039/c4ee00389f>

610 Troppmann, S., König, B., 2016. Functionalized Vesicles with Co-Embedded CdSe
611 Quantum Dots and [FeFe]-Hydrogenase Mimic for Light-Driven Hydrogen
612 Production. *ChemistrySelect* 1, 1405–1409. <https://doi.org/10.1002/slct.201600032>

613 Tu, Y.J., Njus, D., Schlegel, H.B., 2017. A theoretical study of ascorbic acid oxidation

614 and $\text{HOO}^{\bullet}/\text{O}_2^{\bullet-}$ Radical scavenging. *Org. Biomol. Chem.* 15, 4417–4431.
615 <https://doi.org/10.1039/c7ob00791d>

616 Wang, F., Liang, W.J., Jian, J.X., Li, C.B., Chen, B., Tung, C.H., Wu, L.Z., 2013.
617 Exceptional poly(acrylic acid)-based artificial [FeFe]-hydrogenases for
618 photocatalytic H_2 production in water. *Angew. Chemie Int. Ed.* 52, 8134–8138.
619 <https://doi.org/10.1002/anie.201303110>

620 Wang, F., Wang, W.G., Wang, H.Y., Si, G., Tung, C.H., Wu, L.Z., 2012. Artificial
621 photosynthetic systems based on [FeFe]-hydrogenase mimics: The road to high
622 efficiency for light-driven hydrogen evolution. *ACS Catal.* 2, 407–416.
623 <https://doi.org/10.1021/cs200458b>

624 Wang, F., Wang, W.G., Wang, X.J., Wang, H.Y., Tung, C.H., Wu, L.Z., 2011. A highly
625 efficient photocatalytic system for hydrogen production by a robust hydrogenase
626 mimic in an aqueous solution. *Angew. Chemie Int. Ed.* 50, 3193–3197.
627 <https://doi.org/10.1002/anie.201006352>

628 Wang, H.-Y., Wang, W.-G., Si, G., Wang, F., Tung, C.-H., Wu, L.-Z., 2010.
629 Photocatalytic Hydrogen Evolution from Rhenium(I) Complexes to [FeFe]
630 Hydrogenase Mimics in Aqueous SDS Micellar Systems: A Biomimetic Pathway.
631 *Langmuir* 26, 9766–9771. <https://doi.org/10.1021/la101322s>

632 Wang, M., Han, K., Zhang, S., Sun, L., 2015. Integration of organometallic complexes
633 with semiconductors and other nanomaterials for photocatalytic H_2 production.
634 *Coord. Chem. Rev.* <https://doi.org/10.1016/j.ccr.2014.12.005>

635 Wang, P., Zhang, J., He, H., Xu, X., Jin, Y., 2015. The important role of surface ligand
636 on CdSe/CdS core/shell nanocrystals in affecting the efficiency of H_2
637 photogeneration from water. *Nanoscale* 7, 5767–5775.

638 <https://doi.org/10.1039/c4nr07343f>

639 Wang, W., Song, X.W., Hong, Z., Li, B., Si, Y., Ji, C., Su, K., Tan, Y., Ju, Z., Huang,
640 Y., Chen, C.N., Yuan, D., 2019. Incorporation of iron hydrogenase active sites into
641 a stable photosensitizing metal-organic framework for enhanced hydrogen
642 production. *Appl. Catal. B Environ.* 258, 117979.
643 <https://doi.org/10.1016/j.apcatb.2019.117979>

644 Wen, M., Li, X.B., Jian, J.X., Wang, X.Z., Wu, H.L., Chen, B., Tung, C.H., Wu, L.Z.,
645 2016. Secondary coordination sphere accelerates hole transfer for enhanced
646 hydrogen photogeneration from [FeFe]-hydrogenase mimic and CdSe QDs in
647 water. *Sci. Rep.* 6, 29851. <https://doi.org/10.1038/srep29851>

648 Wen, M., Wu, H.-L., Jian, J.-X., Wang, X.-Z., Li, X.-B., Chen, B., Tung, C.-H., Wu, L.-
649 Z., 2017. Integrating CdSe Quantum Dots with a [FeFe]-Hydrogenase Mimic into
650 a Photocathode for Hydrogen Evolution at a Low Bias Voltage. *ChemPhotoChem*
651 1, 260–264. <https://doi.org/10.1002/cptc.201700041>

652 Wittkamp, F., Senger, M., Stripp, S.T., Apfel, U.P., 2018. [FeFe]-Hydrogenases: Recent
653 developments and future perspectives. *Chem. Commun.* 54, 5934–5942.
654 <https://doi.org/10.1039/c8cc01275j>

655 Wroblewska-Wolna, A.M., Harvie, A.J., Rowe, S.F., Critchley, K., Butt, J.N., Jeuken,
656 L.J.C., 2020. Quantum dot interactions with and toxicity to *Shewanella oneidensis*
657 MR-1. *Nanotechnology* 31, 134005. <https://doi.org/10.1088/1361-6528/ab5f78>

658 Yang, J., Miao, H., Jing, J., Zhu, Y., Choi, W., 2021. Photocatalytic activity
659 enhancement of PDI supermolecular via π - π action and energy level adjusting with
660 graphene quantum dots. *Appl. Catal. B Environ.* 281, 119547.
661 <https://doi.org/10.1016/j.apcatb.2020.119547>

662 Yang, Y., Zhou, C., Wang, W., Xiong, W., Zeng, G., Huang, D., Zhang, C., Song, B.,
663 Xue, W., Li, X., Wang, Z., He, D., Luo, H., Ouyang, Z., 2021. Recent advances in
664 application of transition metal phosphides for photocatalytic hydrogen production.
665 Chem. Eng. J. 405, 126547. <https://doi.org/10.1016/j.cej.2020.126547>

666 Yu, T., Zeng, Y., Chen, J., Li, Y.Y., Yang, G., Li, Y., 2013. Exceptional dendrimer-
667 based mimics of diiron hydrogenase for the photochemical production of
668 hydrogen. Angew. Chemie Int. Ed. 52, 5631–5635.
669 <https://doi.org/10.1002/anie.201301289>

670 Yu, W.W., Qu, L., Guo, W., Peng, X., 2003. Experimental determination of the
671 extinction coefficient of CdTe, CdSe, and CdS nanocrystals. Chem. Mater. 15,
672 2854–2860. <https://doi.org/10.1021/cm034081k>

673 Yue, D., Qian, X., Kan, M., Ren, M., Zhu, Y., Jiang, L., Zhao, Y., 2017. Sulfurated
674 [NiFe]-based layered double hydroxides nanoparticles as efficient co-catalysts for
675 photocatalytic hydrogen evolution using CdTe/CdS quantum dots. Appl. Catal. B
676 Environ. 209, 155–160. <https://doi.org/10.1016/j.apcatb.2017.02.075>

677 Zamkov, M., 2017. Solar hydrogen generation: Exceeding 100% efficiency. Nat.
678 Energy 2, 17072. <https://doi.org/10.1038/nenergy.2017.72>

679