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1 **Highly Porous SnO₂ Nanosheet Arrays Sandwiched within TiO₂ and CdS**
2 **Quantum Dots for Efficient Photoelectrochemical Water Splitting**

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13
14 **Abstract**

15 A porous SnO₂ nanosheets/TiO₂/CdS quantum dots (SnO₂ NSs/TiO₂/CdS QDs)
16 sandwich structure has been designed and fabricated as a “host-guest” photoanode for
17 efficient solar water splitting applications. In this novel photoanode design, the highly
18 porous SnO₂ NSs serve as the host skeleton for efficient electron collection, while
19 CdS QDs serve as efficient visible light absorbers. A thin interlayer of TiO₂ is
20 introduced for band alignment and reduction of charge recombination. Enhanced
21 photoelectrochemical performance of the as fabricated photoanode is observed with
22 introduction of the TiO₂ interlayer. The optimized host-guest SnO₂ NSs/TiO₂/CdS
23 QDs photoanode shows a photocurrent density as high as 4.7 mA cm⁻² at 0 V versus

24 Ag/AgCl, which is 7 times higher than that of the SnO₂ NSs/TiO₂ reference
25 photoanode (0.7 mA cm⁻²). Furthermore, it also shows lower charge recombination
26 rate compared to the SnO₂ NSs/CdS QDs reference photoanode. Due to the high
27 porosity and transparency of the as developed SnO₂ NSs arrays host, it has great
28 potential in various applications, such as solar energy conversion and energy storage.

29 **Keywords** photoanode, host-guest, SnO₂ nanosheet, CdS

30

31 **1. Introduction**

32 Photoelectrochemical (PEC) water splitting is an effective method to convert
33 unlimited solar energy into clean and storable chemical energy-hydrogen.[1-3]
34 Recently, the host-guest type nanostructured photoelectrodes have attracted much
35 attention due to their high charge collection ability, efficient light absorption and
36 effective charge separation.[4-7] For such structures, the host skeletons generally have
37 high conductivity and large specific surface area, while the photoactive guest
38 materials coated on the host skeleton surface would have high visible light absorption
39 efficiency. Various host-guest photoelectrodes, such as WO₃ nanorod/BiVO₄,[8]
40 antimony-doped SnO₂ macropore/Fe₂O₃-nanorod[9] and Al-doped ZnO inverse
41 opals/BiVO₄,[10] have been reported for PEC water splitting. A host with high
42 conductivity and specific surface area coupled with an efficient light-absorber guest as
43 well as having good interface band alignment are essential for fabricating efficient
44 host-guest photoelectrodes.[11-15] In PEC water splitting applications, the energy
45 conversion efficiency of the host-guest photoelectrode-based devices are usually
46 undermined by the low electron mobility of the host, inefficient light absorption as
47 well as high charge recombination rate at the interface.[16-19]

48 Due to its abundance on earth, high stability, high transparency, and potential for

49 doping with fluorine or antimony, SnO₂ has been considered an ideal host material for
50 photoelectrodes.[20-24] For example, antimony-doped SnO₂ nanorods have
51 reportedly boosted the PEC performance of BiVO₄ based photoanode.[25] A
52 fluorine-doped SnO₂/TiO₂ based composite inverse opal structure photoanode has
53 been reported with enhanced PEC performance for solar water splitting
54 applications.[26] Recently, 3D porous SnO₂ nanosheets (NSs) coated on carbon fiber
55 cloth have been reported for lithium battery and electrocatalyst applications due to
56 their high specific surface area.[27, 28] SnO₂ NSs grown on transparent conductive
57 oxide, such as fluorine-doped tin oxide (FTO), can be an ideal host skeleton for
58 host-guest type photoelectrodes because of the high stability, high specific surface
59 area as well as the excellent transparency of SnO₂. CdS quantum dots (QDs) have also
60 been extensively employed as absorber guests in various hybrid photoanodes for PEC
61 applications due to their suitable band structure and efficient visible light
62 absorption.[19, 29-32] The uniform dispersion of CdS QDs on three dimensional
63 SnO₂ host skeletons has been reported for PEC water splitting, such as screw-like
64 SnO₂ nanostructures/CdS QDs.[33] However, the energy conversion efficiency of
65 SnO₂/CdS host-guest photoanodes is greatly limited by the high charge recombination
66 rate at the host/guest interface. TiO₂ has been introduced by researchers to reduce the
67 charge recombination at the SnO₂/CdS host-guest interface.[34, 35]

68 In this work, we report a 3D SnO₂ NSs/TiO₂/CdS QDs structure as host-guest
69 photoanode for efficient PEC water splitting. Uniform and transparent SnO₂ NSs were
70 grown on the FTO substrate through a hydrothermal reaction followed by a
71 calcination process. Thin TiO₂ interlayer was conformally coated on SnO₂ NSs by
72 atomic layer deposition (ALD), while CdS QDs were assembled on SnO₂ NSs surface
73 by successive ionic layer adsorption and reaction (SILAR) method. The as-prepared

74 SnO₂ NSs/TiO₂/CdS QDs host-guest photoanode showed better PEC performance
75 than SnO₂ NSs/TiO₂ and SnO₂ NSs/CdS QDs reference photoanodes. The enhanced
76 PEC performance of the SnO₂ NSs/TiO₂/CdS QDs can be attributed to strong visible
77 light absorption from CdS guest, high specific surface area and light trapping effect of
78 the transparent host as well as the good band alignment from the ALD TiO₂ interlayer.

79

80 **2 Experimental section**

81 *2.1 Materials*

82 Tin (IV) chloride pentahydrate (SnCl₄·5H₂O), thiourea (C₂H₅NS), isopropanol,
83 cadmium nitrate tetrahydrate and sodium sulfide nonahydrate were purchased from
84 Sigma-Aldrich. FTO substrates with a surface resistivity of 8 Ω/sq were procured
85 from Pilkington.

86 *2.2 Synthesis of SnO₂ NSs on FTO substrates*

87 FTO substrates (1.5 cm x 5 cm) were sequentially cleaned with acetone, methanol,
88 ethanol and deionized (DI) water and dried with nitrogen flow. The precursor
89 solution was prepared based on existing literatures with SnCl₄ (100 mg), C₂H₅NS
90 (100 mg) and isopropanol (25 ml).[27, 28] Then, four pieces of clean FTO substrates
91 were placed standing at opposing walls of a 100 ml Teflon autoclave containing the
92 as-prepared precursor solution. After sealing, the autoclave was transferred to an oven
93 and kept at 200 °C for 24 h. After the hydrothermal reaction, the obtained SnS₂
94 nanosheet samples were washed with DI water and annealed at 500 °C in an
95 atmospheric environment for 2 h to convert them into SnO₂.

96 *2.3 Coating of SnO₂ NSs with TiO₂ by ALD*

97 A homebuilt ALD system was utilized to deposit a thin film of TiO₂ on the surface of
98 SnO₂ NSs at 80 °C.[36] TiCl₄ and water were used as the Ti and oxygen precursors,
99 respectively. A total of 400 ALD cycles were used to deposit ~15 nm TiO₂ conformal
100 layers on the SnO₂ NSs. After ALD of TiO₂, the as-prepared samples were annealed at
101 500 °C in air for 1 hour for the crystallization of TiO₂.

102 *2.4 Preparation of CdS QDs*

103 The CdS QDs were deposited on the surface of SnO₂ NSs/TiO₂ using the typical
104 SILAR method.[37, 38] Specifically, a SnO₂ NSs/TiO₂ sample was immersed into
105 cadmium nitrate methanol solution for 1 minute and then rinsed with methanol for
106 another minute, followed by drying with nitrogen flow. Next, the sample was
107 immersed into the sodium sulfide solution for 1 minute and rinsed with ethanol
108 solution for another minute, followed by drying with nitrogen flow. The entire
109 procedure was repeated for 15 times. Finally, the sample was annealed at 400 °C for
110 30 minutes under argon protection.

111 *2.5 Materials Characterization*

112 Field-emission scanning electron microscope (SEM), JEOL, JSM 7600F was used to
113 investigate the microstructure and morphology of the as-prepared samples. X-ray
114 diffraction (XRD) pattern was carried out on a Bruker D8 X-ray diffractometer,
115 equipped with Cu K α radiation source. UV-Vis diffuse reflectance spectra were
116 collected on a Varian, Cary 5000 spectrum system. Raman spectra were collected on a
117 Renishaw in Via Raman system using 477 and 532 nm as the excitation wavelengths.

118 *2.6 PEC measurements*

119 The PEC performance measurements of the as-prepared samples were carried out on

120 an Autolab 270 workstation with a three-electrode electrochemical system under AM
121 1.5G simulated sunlight illumination (100 mW cm^{-2}) from a solar simulator (300W
122 Xe lamp, Newport). The as-prepared photoanodes, Ag/AgCl (3M KCl) and platinum
123 mesh were used as the working electrode, reference electrode and counter electrode,
124 respectively. $0.25 \text{ M Na}_2\text{SO}_3$ and $0.35 \text{ M Na}_2\text{S}$ were used as the electrolyte during the
125 PEC water splitting test. The light intensity of the solar simulator was calibrated to
126 100 mW cm^{-2} using a standard reference silicon solar cell. The photocatalytic
127 hydrogen generation was measured by a gas chromatograph (Shimadzu GC-2014;
128 Molecular sieve 5A, TCD detector, Ar carrier gas) with $0.25 \text{ M Na}_2\text{SO}_3$ and 0.35 M
129 Na_2S as electrolyte under AM 1.5G simulated sunlight illumination. The applied
130 voltage was 0 V versus AgCl and the size of the photoanode is 1.5 cm x 4 cm.

131

132 **3 Result and discussion**

133 *3.1 Fabrication and Characterization of SnO_2 NSs/ TiO_2 /CdS QDs*

134 The fabrication process of SnO_2 NSs/ TiO_2 /CdS QDs photoanodes is schematically
135 shown in **Figure 1**. Firstly, SnS_2 nanosheet arrays are grown on the FTO substrates
136 through a hydrothermal reaction. After calcination, the as-grown SnS_2 nanosheet
137 arrays are converted into 3D vertically aligned SnO_2 NSs. Next, conformal TiO_2 films
138 are deposited on the surface of SnO_2 NSs by ALD. Finally, CdS QDs are deposited on
139 the surface of TiO_2 through SILAR method.

140 For PEC water splitting applications, full coverage of the FTO substrate with
141 photoanode materials is required. Otherwise, the direct contact of the FTO and
142 electrolyte will cause significant dark current and depress the charge separation, hence
143 reducing the entire PEC efficiency. We have found that the amount of chemicals used

144 in the precursor solution played an important role in the coverage of as-grown SnO₂
145 NSs on FTO substrates, as shown in Figures 2(a)-(c). When 40 mg of SnCl₄ and 40
146 mg of C₂H₅NS were used for preparing the precursor solution, the SnO₂ NSs coverage
147 of the final product was very poor where a few clusters of SnO₂ NSs were sparsely
148 grown on the FTO surface as shown in Figure 2(a). Figures 2(b&c) show the SEM
149 images of the SnO₂ NSs samples grown with 80 mg of SnCl₄ and C₂H₅NS each and
150 100 mg of SnCl₄ and C₂H₅NS each, respectively. Figure 2b clearly show that the more
151 clusters of SnO₂ NSs were grown on the FTO substrate with an increased amount of
152 chemicals used in the precursor solution. Full coverage of SnO₂ NSs on FTO were
153 achieved when 100 mg of SnCl₄ and C₂H₅NS each were used in the precursor solution,
154 as shown in Figure 2(c). It should be noted that the SnS₂ NSs would partially peel off
155 from FTO substrate after rinsing with DI water when even more SnCl₄ and C₂H₅NS
156 were used. Before the thermal conversion of SnS₂ NSs to SnO₂ NSs, SnS₂ NSs were
157 adhere to the FTO, indicating that the mechanism for the increased coverage of SnS₂
158 NSs may involve heterogeneous nucleation and the following growth and
159 aggregation.[39] In the early stage of the hydrothermal reaction, some SnS₂ nuclei
160 were formed on the FTO substrate due to the heterogeneous nucleation. Through the
161 ion-by-ion process, more nuclei would form subsequently, providing sites for the
162 growth of the SnS₂ NSs. When low concentrations of precursors were used, small
163 density of nuclei with large sizes formed on the FTO substrate, thus only few clusters
164 of SnS₂ NSs were obtained. With higher concentrations of precursors, higher density
165 of nuclei of smaller sizes were formed and more SnS₂ NSs were grown on the FTO
166 substrate. Thus, full coverage of SnS₂ NSs, which would be converted to SnO₂ NSs
167 after calcination, on the FTO substrate could be achieved.

168 The as-prepared SnO₂ NSs nanosheets stand vertically on the FTO substrate,

169 instead of being randomly stacked together, which is beneficial for loading of
170 photoactive guest materials. The vertically growth of SnS₂ NSs can be ascribed to the
171 formation of metal-thiourea complex, which can decrease the amount of free metal
172 ions and sulfur ions, favoring for the oriented growth of SnS₂ NSs.[40] Figure 2(d)
173 shows the magnified SEM view of the as-grown SnO₂ NSs on FTO substrate. A large
174 number of nano-pores could be observed on the SnO₂ nanosheets, indicating high
175 porosity of the as-grown SnO₂ NSs. The high specific surface area of the as-fabricated
176 SnO₂ NSs arrays is also beneficial for loading of more photoactive guest materials
177 and for increasing the contact area of the entire photoanode to electrolytes as well.
178 This enhances the PEC performance of the photoanode.

179 Due to the self-limiting growth mechanism of ALD, it can be used for deposition
180 of nano-films over 3D nanostructures with excellent conformality. In our study, the
181 as-fabricated SnO₂ NSs were coated with a thin layer of TiO₂ using ALD. In the
182 customized ALD system, N₂ was used as the carried gas while TiCl₄ and H₂O were
183 used as precursors. In each cycle of ALD process, TiCl₄ reacted with the hydroxyl
184 groups on the surface of SnO₂ NSs and formed Cl₃Ti-O-SnO₂. After the purge of
185 excess TiCl₄ and byproduct HCl by N₂, H₂O gas was introduced into the chamber to
186 react with Cl₃Ti-O-SnO₂. Thus, one layer of TiO₂ film was conformally coated on the
187 SnO₂ NSs while excess H₂O and the byproduct HCl gas were purged by N₂. The
188 thickness of TiO₂ films can be controlled by varying the number of ALD cycles. From
189 Figures 2(e), it could be clearly seen that the sheet-like structure remains unchanged,
190 indicating the conformal coating of TiO₂ films over SnO₂ NSs. The average thickness
191 of the SnO₂ NSs increases from a few nanometers to around 30 nm after 400 cycles of
192 ALD TiO₂ films. The uniform coating of TiO₂ films over SnO₂ NSs could also be
193 observed from the smooth surface. After loading of CdS QDs, the smooth surface

194 becomes coarse and the thickness of the nanosheet further increases to around 40 nm,
195 as shown in Figure 2(f). During the SILAR process, Cd^{2+} ions were first adsorbed
196 onto the TiO_2 surface and then reacted with S^{2-} ions to form CdS particles.
197 Energy-dispersive X-ray spectroscopy study further confirmed the existence of Cd, S,
198 Ti, O and Sn elements in the SnO_2 NSs/ TiO_2 /CdS QDs photoanode, as shown in
199 Figure S1.

200 XRD was utilized to determine the crystallinity and constituent of the as-prepared
201 samples. Figure 3(a) shows the XRD patterns of bare FTO substrate, SnO_2 NSs, SnO_2
202 NSs/ TiO_2 and SnO_2 NSs/ TiO_2 /CdS QDs. The diffraction peaks of SnO_2 NSs at 27° ,
203 34° , 38° , 52° and 55° correspond to (110), (101), (200), (211) and (220) planes of the
204 rutile structure of SnO_2 . As both SnO_2 NSs and FTO are comprised of rutile SnO_2 , the
205 XRD peaks of SnO_2 NSs and FTO overlap. However, the XRD peaks can be
206 distinguished by their different full width at half maximum (FWHM). The FWHM of
207 the XRD peaks for SnO_2 NSs are much broader than that for FTO substrate,
208 indicating that SnO_2 NSs are composed by nanosized SnO_2 crystals, which is
209 consistent with our SEM study, as shown in Figure 2(d). After coating of ALD TiO_2 ,
210 small but obvious diffraction peaks located at 28° , 36° and 41° could be observed,
211 which can be ascribed to the (110), (101) and (200) planes of rutile phase TiO_2 .
212 Through the comparison of the XRD patterns of SnO_2 NSs/ TiO_2 and SnO_2 NSs
213 / TiO_2 /CdS QDs, two new obvious diffraction peaks located at 29° and 44° could be
214 observed after deposition of CdS QDs, and they can be ascribed to the (101) and (110)
215 planes of hexagonal phase CdS. Raman spectroscopy was further utilized to determine
216 the compositions and crystal structures of the as-prepared hybrid nanostructures.
217 Figure 3(b) shows the Raman spectra of FTO substrate and SnO_2 NSs. Due to the high
218 transparency of SnO_2 NSs, the incident light is able to penetrate through the SnO_2

219 NSs array and reach the FTO substrate, which causes unavoidably strong background
220 signals of FTO substrate. The pure FTO substrate has one obvious peak located at 557
221 cm^{-1} , which is consistent with previous reports.[41] After growth of SnO_2 NSs,
222 another weak but obvious peak located at 632 cm^{-1} could be observed, which can be
223 ascribed to A_{1g} mode of SnO_2 . As compared to XRD, Raman could clearly indicate
224 the successful fabrication of SnO_2 NSs on FTO substrate. Figure 3(c) presents the
225 Raman spectra of SnO_2 NSs/ TiO_2 and SnO_2 NSs/ TiO_2 /CdS QDs. For the spectrum of
226 SnO_2 NSs/ TiO_2 (red curve in Figure 3c), the peaks located at 236 cm^{-1} (broad band),
227 443 cm^{-1} (E_g) and 610 cm^{-1} (A_{1g}) can be ascribed to rutile phase of TiO_2 ,[41] which is
228 consistent with our XRD study. The new peak located at 304 cm^{-1} observed in the
229 Raman spectrum of SnO_2 NSs/ TiO_2 /CdS QDs corresponds to the 1LO optical phonons
230 of CdS.[35] Thus, both Raman peaks of TiO_2 and CdS can be observed. The
231 disappearance of Raman peaks of SnO_2 at 632 cm^{-1} might be caused by the limited
232 penetration depth of laser used in the Raman testing or the relative weak signals of
233 SnO_2 . The step by step Raman testing as well as XRD characterization indicate the
234 successful fabrication of the composite SnO_2 NSs/ TiO_2 /CdS QDs.

235 Figure 3(d) shows the UV-Vis absorption spectra of SnO_2 NSs/ TiO_2 and SnO_2
236 NSs/ TiO_2 /CdS QDs. The SnO_2 NSs/ TiO_2 sample has light absorption merely in the
237 UV range due to the wide bandgaps of SnO_2 (3.6 eV) and TiO_2 (3.2 eV). However, the
238 light absorption spectrum edge of SnO_2 NSs/ TiO_2 extends to the visible area of up to
239 around 550 nm. This is due to the introduction of CdS QDs which have a smaller
240 bandgap of 2.4 eV. Since visible light accounts for a large part of solar energy,
241 photoanodes with strong visible light absorption should have higher PEC performance
242 for water splitting application.

243 *3.2 PEC performance of SnO_2 NSs/ TiO_2 /CdS QDs photoanode*

244 The PEC performance of the as-prepared samples was evaluated by linear sweep
245 voltammetry with a three-electrodes system. The as-prepared samples, platinum sheet,
246 Ag/AgCl were used as the photoanode, cathode and reference electrode respectively.
247 A 0.25 M Na₂S and 0.35 M Na₂SO₃ aqueous solution was used as the electrolyte. As
248 counter electrode platinum sheet has little effect on the generated photocurrent, the
249 photocurrent density-potential characteristics can be used to determine the
250 performance and nature of the photoanode. With higher photocurrent, larger amount
251 of photogenerated electrons can be involved in the hydrogen evolution on the counter
252 electrode platinum sheet.[42] Figure 4(a) shows the comparison of linear sweep
253 curves of the SnO₂ NSs/TiO₂, SnO₂ NSs/CdS-QDs, and SnO₂ NSs/TiO₂/CdS QDs
254 photoanodes collected under both dark and illumination conditions. It can be clearly
255 observed that the SnO₂ NSs/TiO₂/CdS QDs photoanodes show much better PEC
256 performance than the SnO₂ NSs/TiO₂ and SnO₂ NSs/CdS QDs photoanodes. The
257 photocurrent density of the SnO₂ NSs /TiO₂/CdS QDs photoanode reaches 4.7 mA
258 cm⁻² at 0 V versus AgCl, which is almost 7 times higher than that of the SnO₂
259 NSs/TiO₂ photoanode (0.7 mA cm⁻²). The reason behind this is due to the introduction
260 of CdS QDs which increases the light absorption in the visible range. This is
261 consistent with our UV-Vis study, as shown in Figure 3(d). Besides the increase in
262 photocurrent density, the onset potential of SnO₂ NSs/TiO₂/CdS-QDs photoanode has
263 also dropped from -0.75 V for SnO₂ NSs/TiO₂ photoanode to -1 V and that could also
264 be due to the introduction of CdS QDs in the photoanode. To further determine the
265 role of TiO₂ interlayer, the linear sweep curve of SnO₂ NSs/CdS QDs photoanode was
266 also collected, as seen in the black curve in Figure 4(a). It could be clearly seen that
267 the photocurrent density of SnO₂ NSs/CdS QDs photoanode is much smaller than that
268 of the SnO₂ NSs/TiO₂/CdS QDs photoanode with the applied voltage near the onset

269 potential of SnO₂ NSs/CdS QDs photoanode at around -0.8 V versus Ag/AgCl. This
270 could be due to the charge recombination rate of SnO₂ NSs/CdS QDs photoanode
271 being much higher than that of the photoanode with TiO₂ interlayer.[43] With
272 increased applied voltage, the photocurrent difference between the SnO₂ NSs/CdS
273 QDs and SnO₂ NSs/TiO₂/CdS QDs photoanodes becomes smaller, which is
274 understandable as the increased applied voltage can depress the charge recombination
275 process. Figure 4(b) shows the linear sweep curves of the SnO₂ NSs/TiO₂, SnO₂
276 NSs/CdS QDs and SnO₂ NSs/TiO₂/CdS QDs electrodes under chopped light
277 illumination, which agrees well with the difference between their photocurrent and
278 dark current showed in Figure 4(a).

279 The measurement of actual hydrogen evolution of SnO₂ NSs/TiO₂/CdS QDs was
280 performed at 0 V versus Ag/AgCl in a 0.25 M Na₂S and 0.35 M Na₂SO₃ mixture
281 electrolyte solution. The amount of produced hydrogen gas in the sealed PEC cell was
282 determined by a gas chromatograph. As shown in Fig. S2, the overall hydrogen
283 generated increases with the illumination time with almost constant hydrogen
284 generation rate, indicating the high stability of the as-prepared photoanode. The
285 hydrogen generation rate of SnO₂ NSs/TiO₂/CdS QDs is 7.6 μmol mA⁻¹ h⁻¹, which is
286 comparable to hydrogen generation rate reported for another CdS-based photoanode
287 in the literature.[44]

288 The band alignment and charge transfer process of SnO₂ NSs/TiO₂/CdS QDs
289 photoanode are schematically shown in Figure 5(a). The band edge position of SnO₂,
290 TiO₂ and CdS are favorable for charge transfer.[34, 35] Under light illumination,
291 photo-generated electrons of CdS are sequentially transported from its conductive
292 band (CB) level to lower CB of TiO₂ and then to even lower CB of SnO₂. These
293 photogenerated electrons would then to the conductive FTO substrate and finally to

294 the counter Pt electrode for hydrogen evolution. The holes transfer conversely from
295 valence band (VB) of SnO₂ to higher VB of TiO₂ and even higher VB of CdS for
296 oxidation of S₂²⁻ to 2S²⁻. The enhancement in the photocurrent of SnO₂ NSs/TiO₂/CdS
297 QDs photoanode compared to that of SnO₂ NSs/TiO₂ can be ascribed to the visible
298 light absorption of CdS QDs with a band gap of 2.4 eV, while TiO₂ (3.2 eV) and SnO₂
299 (3.6 eV) can only absorb UV light. As visible light accounts for a larger part in the
300 sunlight as compared to UV light, with the same light illumination, more absorption
301 of visible light means there will be more photogenerated electron-hole pairs in the
302 photoanode. In addition, the good band alignment between CdS QDs, TiO₂ and SnO₂
303 provides fast and direct electron pathways, hence enhancing charge separation and
304 reducing the charge recombination rate. Furthermore, the vertically aligned sheet-like
305 and porous structures provide high specific surface area for loading of CdS QDs
306 without stacking. Transparent SnO₂ NSs also ensure effective light transmission
307 inside the hybrid nanostructures, as schematically shown in Figure 5(b). The light
308 illuminated on one side of a single hybrid nanosheet can penetrate through the
309 transparent SnO₂ NSs and reach the CdS and TiO₂, and even the adjacent dwarf
310 nanosheets, on the other side. This means that the incident light can be absorbed for
311 multiple times by CdS QDs.

312 The photocurrent of some SnO₂/CdS based hybrid photoanodes collected at 0.9 V
313 versus RHE with AM 1.5 illumination (100 mW cm⁻²) is summarized in the Table 1. It
314 can be seen that the nanostructure and composition have a great impact on the PEC
315 performance. Although the photocurrent of the as-prepared SnO₂ NSs/TiO₂/CdS QDs
316 is not the highest, the improved PEC performance due to the introduction of TiO₂
317 layer points out a possible solution to enhance PEC performance of CdS and other
318 existing semiconductors. The PEC performance of the SnO₂ NSs/TiO₂/CdS QDs

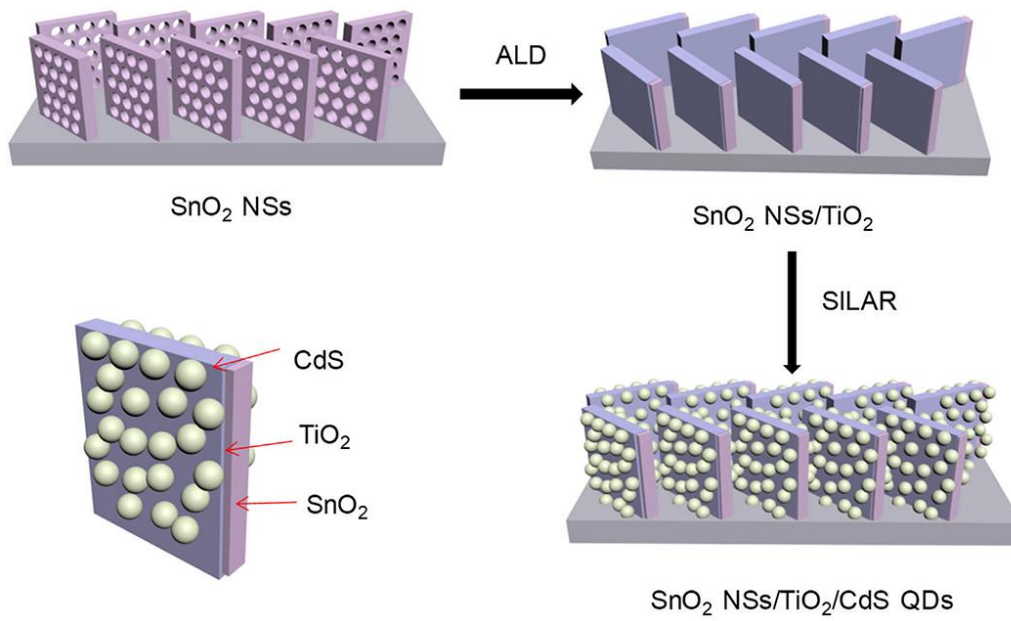
319 photoanode could be further improved by increasing the conductivity of SnO₂ NSs
320 host via doping with antimony or fluorine, which will be part of our future work.

321

322 **4. Conclusion**

323 In summary, a SnO₂ NSs/TiO₂/CdS QDs host-guest type photoanode has been
324 designed and fabricated for solar water splitting application through a combination of
325 hydrothermal method, ALD technique and typical SILAR method. The density of the
326 as-grown SnO₂ NSs can be tuned by the amount of chemicals used in the precursor
327 solution for the hydrothermal reaction. To reduce the charge recombination rate
328 between CdS guest and SnO₂ host, a thin TiO₂ interlayer has been introduced for band
329 alignment of the host-guest photoanode. The optimized SnO₂ NSs/TiO₂/CdS QDs
330 guest-host photoanode shows better PEC performance compared to SnO₂ NSs/CdS
331 QDs and SnO₂ NSs/TiO₂ reference photoanodes. This enhanced PEC performance is
332 attributed to the high visible light absorption of the CdS guest, large specific surface
333 area and effective light trapping effect from the SnO₂ NSs host as well as the good
334 band alignment from the ALD TiO₂ interlayer. Due to the high porosity and
335 transparency of the as-developed SnO₂ NSs array host, it has great potential in
336 applications in various fields, such as photoelectrodes for solar hydrogen generation,
337 energy storage and smart windows.

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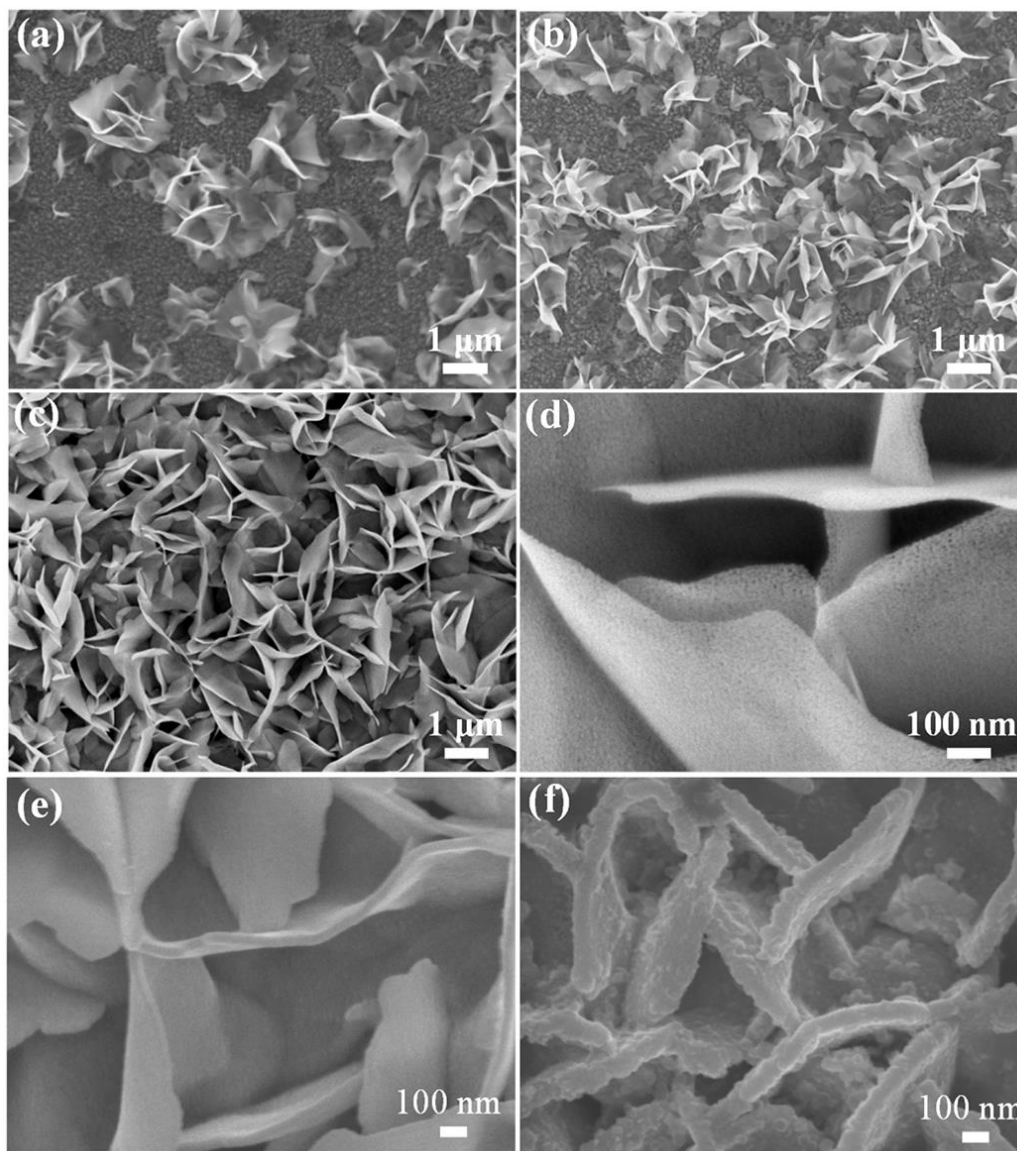
340 **Figure 1** Schematic illustration for the fabrication process of the SnO_2 NSs/ TiO_2 /CdS

341 QDs.

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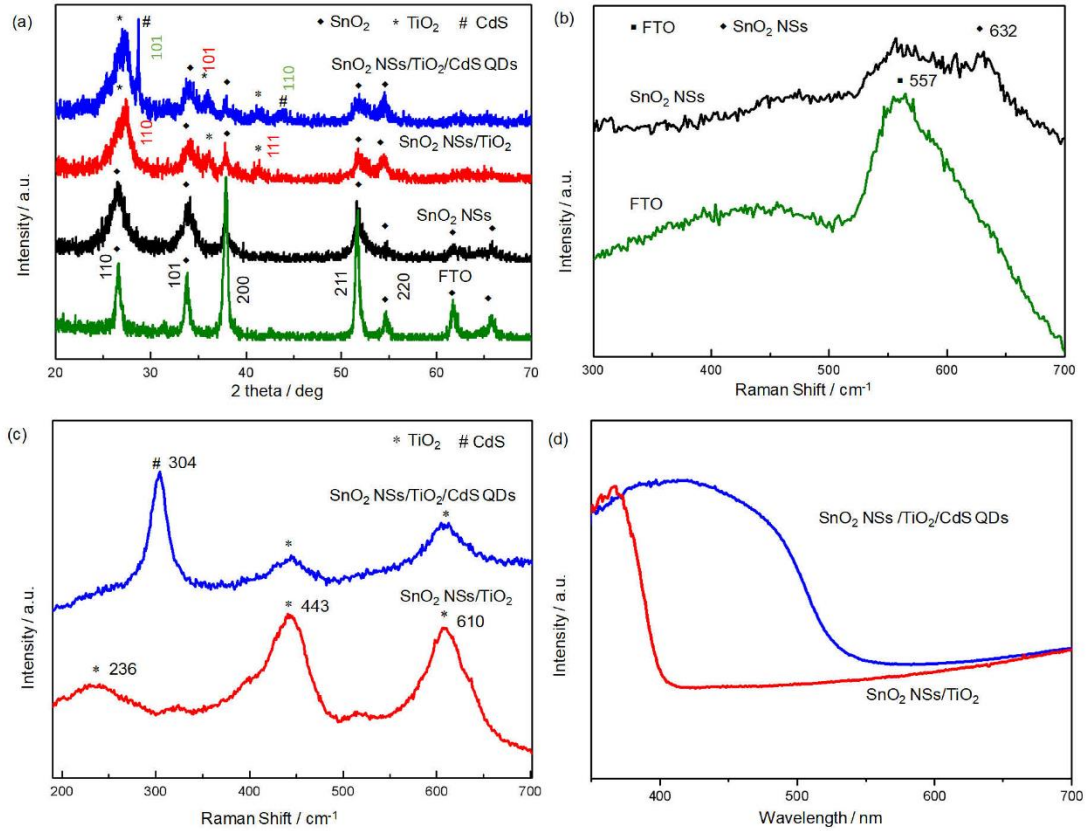
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346 **Figure 2** SEM images of: (a) SnO₂ NSs prepared with SnCl₄ (40 mg) and C₂H₅NS
 347 (40 mg), (b) SnO₂ NSs prepared with SnCl₄ (80 mg) and C₂H₅NS (80 mg), (c) SnO₂
 348 NSs prepared with SnCl₄ (100 mg) and C₂H₅NS (100 mg), (d) SnO₂ NSs with high
 349 magnification. (e) SnO₂ NSs/TiO₂, (f) SnO₂ NSs/TiO₂/CdS QDs.



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351 **Figure 3** (a) XRD patterns of FTO substrate, SnO₂ NSs, SnO₂ NSs/TiO₂ and SnO₂

352 NSs/TiO₂/CdS QDs. (b) Raman spectra of FTO substrate, SnO₂ NSs. (c) Raman

353 spectra of SnO₂ NSs/TiO₂ and SnO₂ NSs/TiO₂/CdS QDs. (d) UV-Vis absorbance of

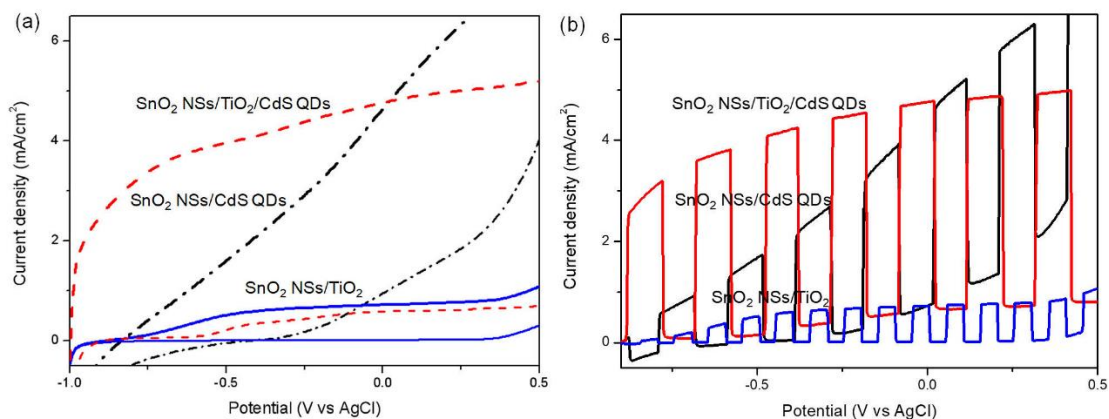
354 SnO₂ NSs/TiO₂ and SnO₂ NSs/TiO₂/CdS QDs.

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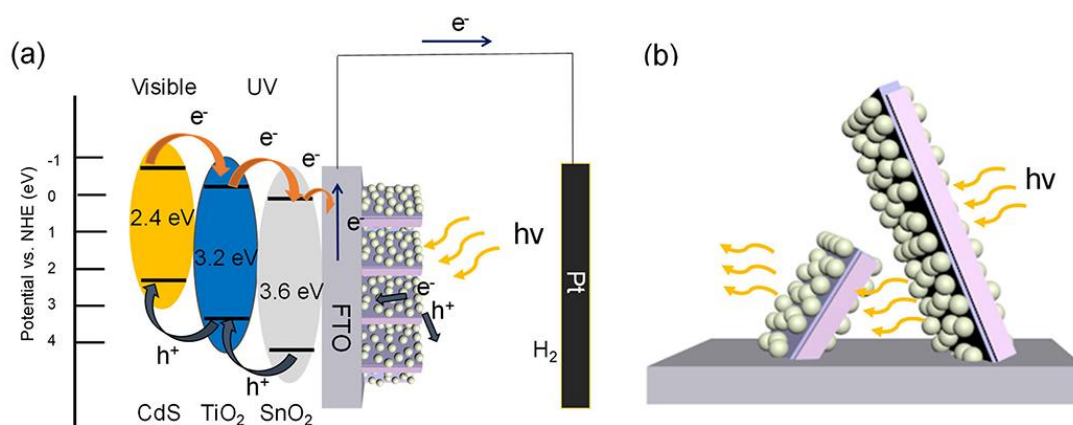
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360 **Figure 4** (a) Linear sweep voltammetry measurement of SnO₂ NSs/TiO₂, SnO₂
 361 NSs/CdS QDs and SnO₂ NSs/TiO₂/CdS QDs. (b) Linear sweep voltammetry
 362 measurement of SnO₂ NSs/TiO₂, SnO₂ NSs/CdS QDs and SnO₂ NSs/TiO₂/CdS QDs
 363 under chopped light illumination.

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366 **Figure 5** (a) Scheme of band alignment and charge transfer process in the SnO₂
 367 NSs/TiO₂/CdS QDs photoanode. The bandgap of CdS, TiO₂ and SnO₂ are 2.4 eV, 3.2
 368 eV and 3.6 eV, respectively. (b) Scheme of light transmission inside the hybrid SnO₂
 369 NSs/TiO₂/CdS QDs photoanode.

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373 **Table 1** Comparison of PEC performance of reported SnO₂/CdS based nanostructured
374 photoanodes.

SnO ₂ /CdS based photoanodes	Electrolyte	Photocurrent density [mA cm ⁻²] ^{a)}	Remarks
SnO ₂ NSs/TiO ₂ /CdS QD		4.7	This work
SnO ₂ nanorods/CdS films		1.38	[45]
SnO ₂ /TiO ₂ sea urchinlike nanotube arrays/CdS QDs	a mixture of 0.25 M Na ₂ S	2.8	[34]
SnO ₂ nanobowl arrays/CdS-NRs	and 0.35 M Na ₂ SO ₃ aqueous	3.5	[46]
SnO ₂ nanowires/TiO ₂ nanoneedles/CdS QDs	solution	9	[35]
Screw-like SnO ₂ nanostructures/CdS QDs		10	[33]

375 ^{a)}The photocurrent density was collected at 0.9 V vs. reversible hydrogen electrode under AM 1.5
376 illumination (100 mW cm⁻²).

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378

379 **Conflicts of interest**

380 There are no conflicts of interest to declare.

381

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386 hydrogen evolution.

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