Supplementary Materials

Carbon-based Hybrid Catalytic-Protective Overlayer for Kesterite Photocathode for for Solar Water Splitting

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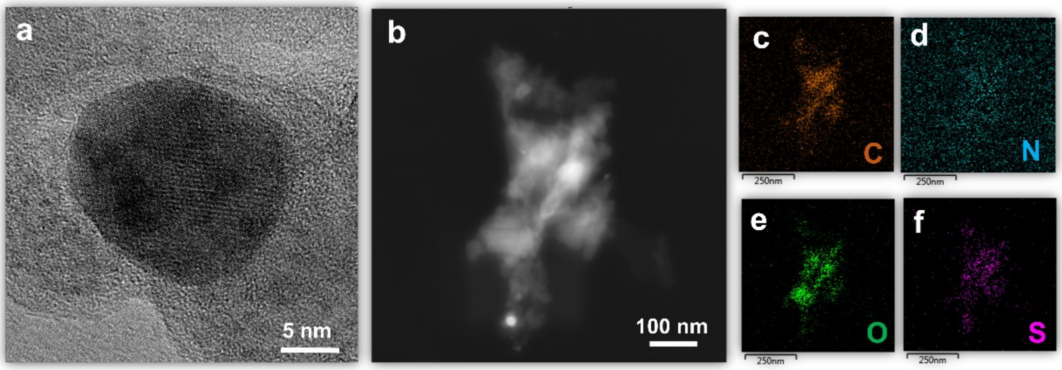

Fig. S1 (a) HR-TEM image of synthesized C_{60}-NSG nanoparticles, (b-f) STEM elemental mapping images of synthesized C_{60}-NSG nanoparticles (orange to C, blue to N, green to O, and pink to S.

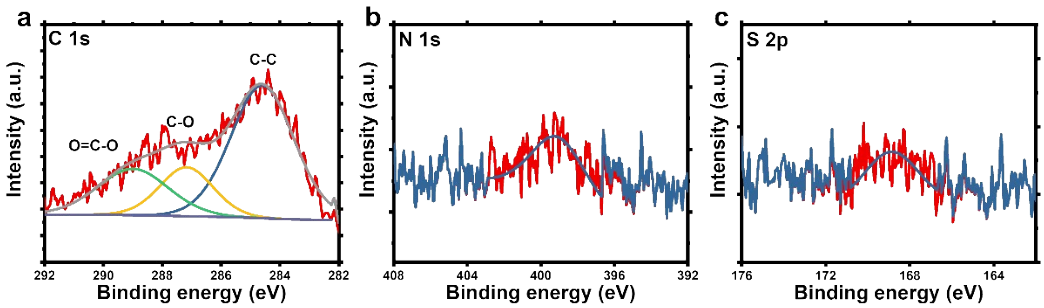

Fig. S2 Core-level XPS spectra of C_{60}-NSG nanoparticles; (a) C 1*s*, (b) N 1*s*, and (c) S 2*p*, respectively.

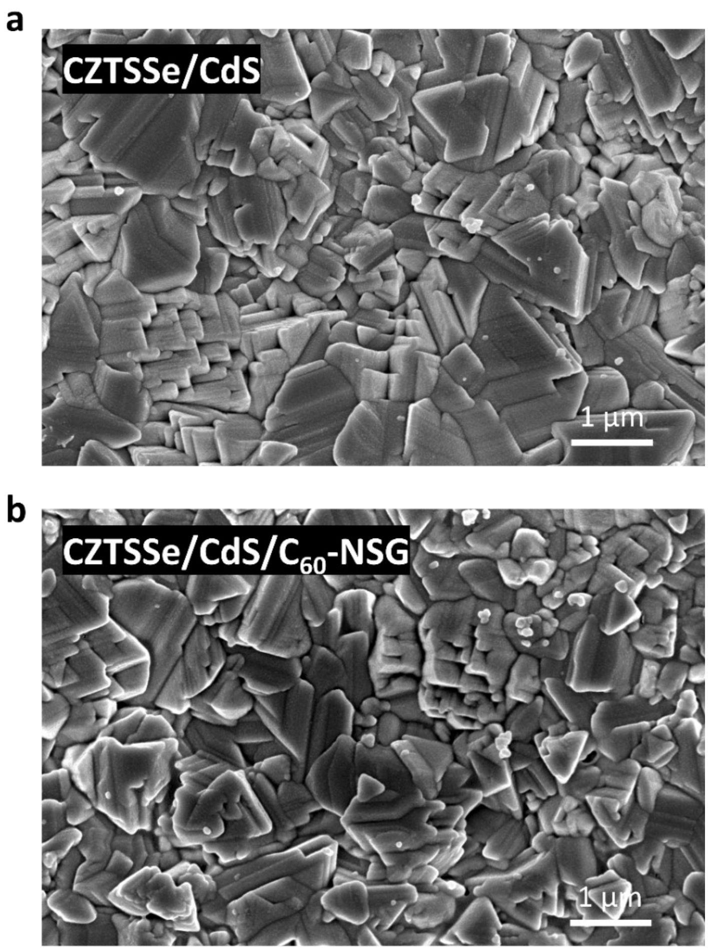

Fig. S3 The surface SEM images of photocathodes with a configuration of **(a)** CZTSSe/CdS and **(b)** CZTSSe/CdS/C_{60}-NSG. The C_{60}-NSG hybrid layer was deposited by spin coating for 1 cycle.

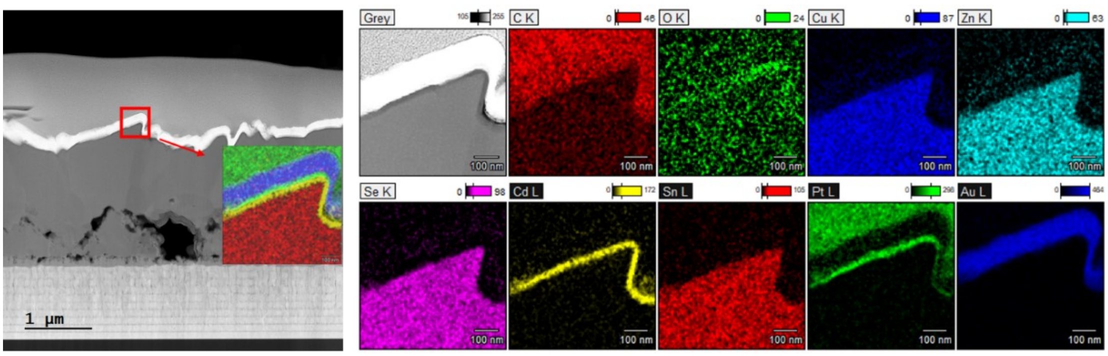

Fig. S4 STEM image and elemental mapping including C, O, Cu, Zn, Se, Cd, Sn and Pt of CZTSSe/CdS/C_{60}-NSG/Pt photocathodes before stability test. Au coating is for conductivity improvement while STEM mapping.

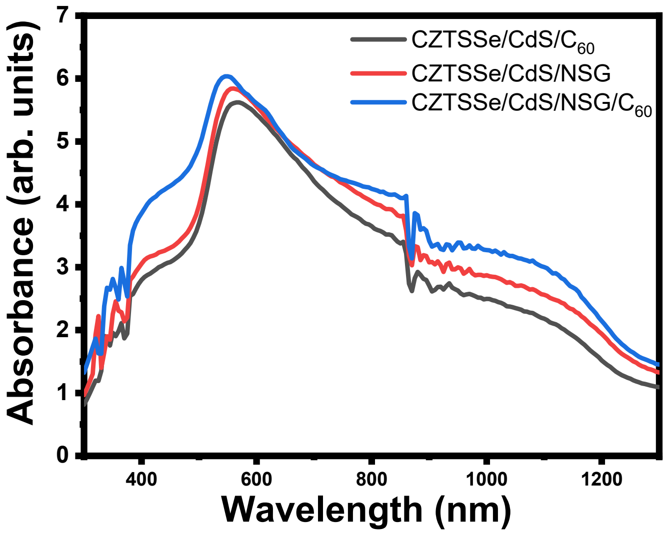

Fig. S5 The absorption spectra of CZTSSe/CdS/NSG, CZTSSe/CdS/C_{60}, and CZTSSe/CdS/C_{60}-NSG, respectively

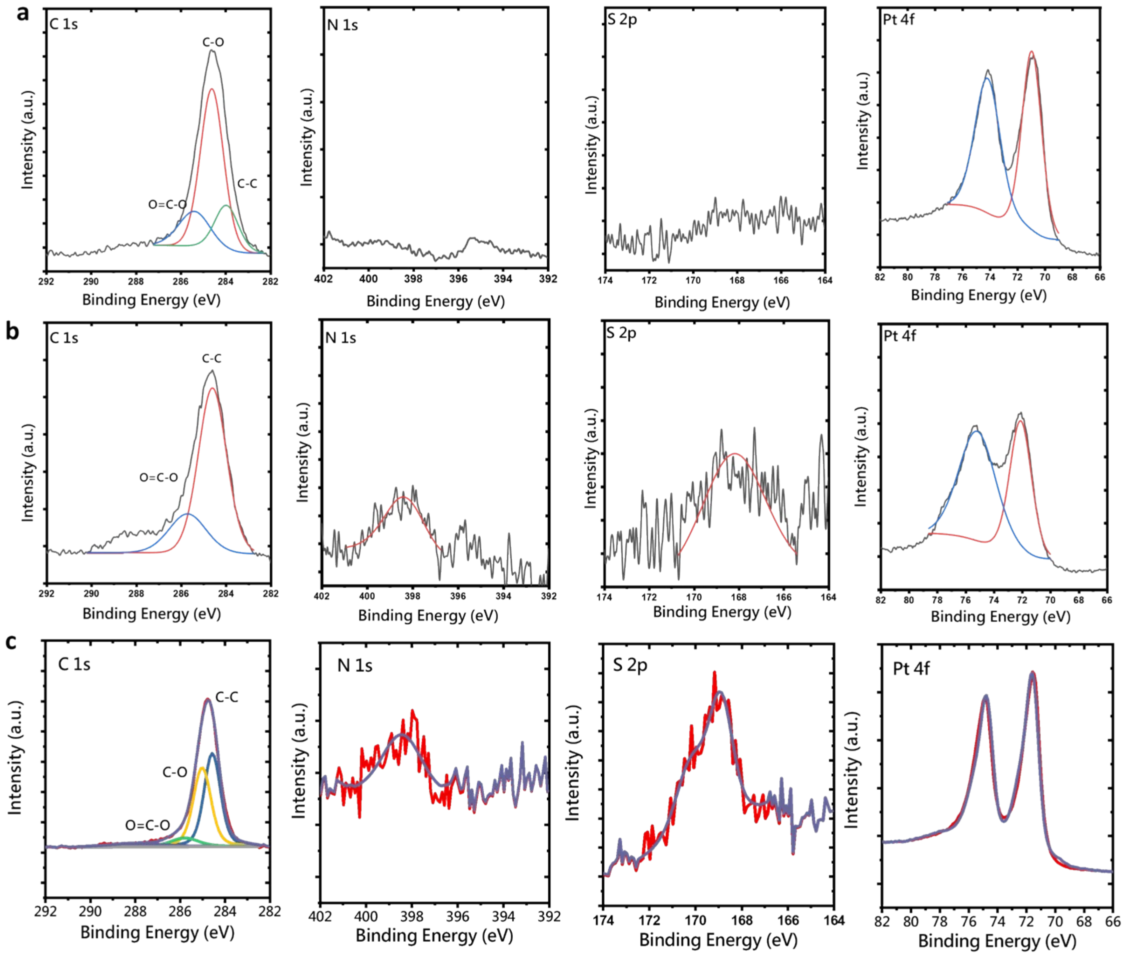

Fig. S6 XPS spectra of (a) CZTSSe/CdS/C_{60} (b) CZTSSe/CdS/ NSG (c) CZTSSe/CdS/C_{60}-NSG photocathode; C 1*s*, N 1*s*, S 2*p*, and Pt 4*f*, respectively.

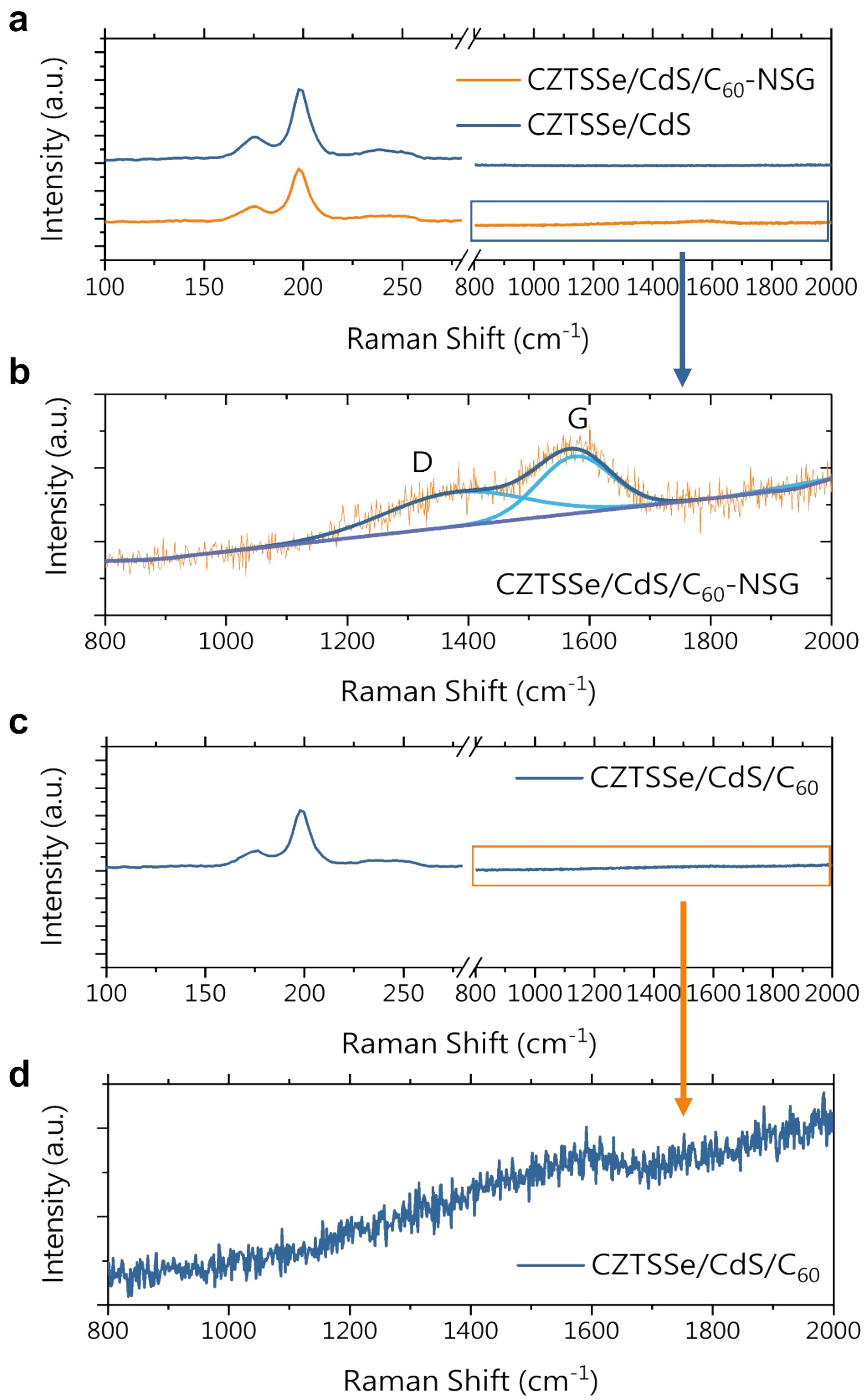

Fig. S7 (a) Raman spectra of the CZTSSe/CdS/C_{60}-NSG and CZTSSe/CdS photocathode. (b) The fitted Raman spectrum of CZTSSe/CdS/C_{60}-NSG in the Raman shift range from 800 to 2000 cm^{-1}. (c) Raman spectrum of the CZTSSe/CdS/C_{60} and CZTSSe/CdS photocathode. (d) Raman spectrum of CZTSSe/CdS/C_{60} in the Raman shift range from 800 to 2000 cm^{-1}.

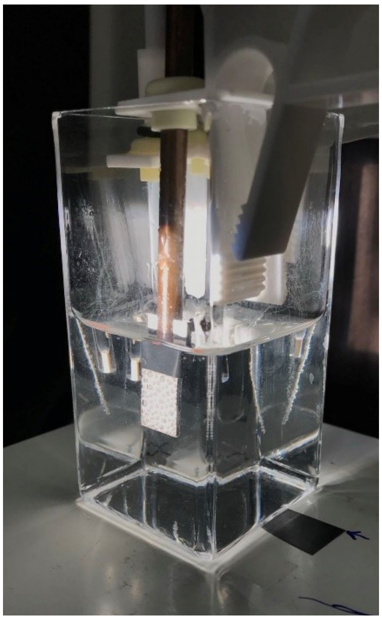

Fig. S8 Photograph of the CZTSSe/CdS/C_{60}-NSG/Pt photocathode during operation

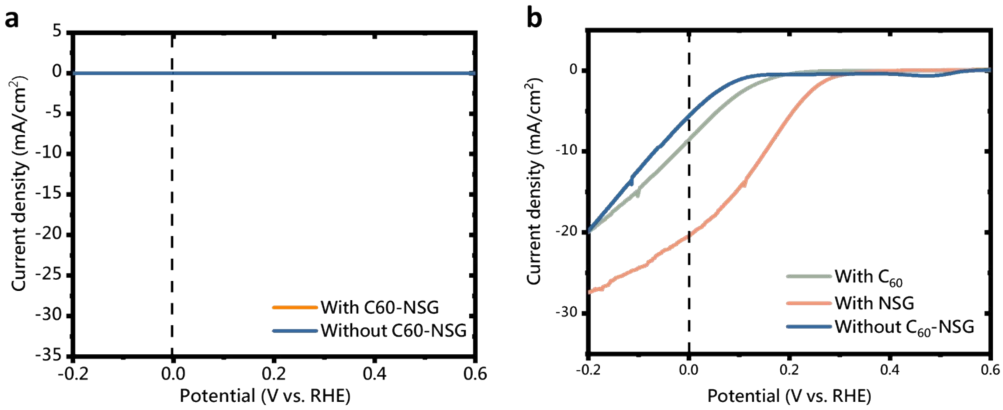

Fig. S9 (a) Linear sweep voltammetry of CZTSSe/CdS/Pt without and with C_{60}-NSG under dark. (b) Linear sweep voltammetry of CZTSSe/CdS/Pt with C_{60}, NSG and without C_{60}-NSG under AM 1.5G illumination.

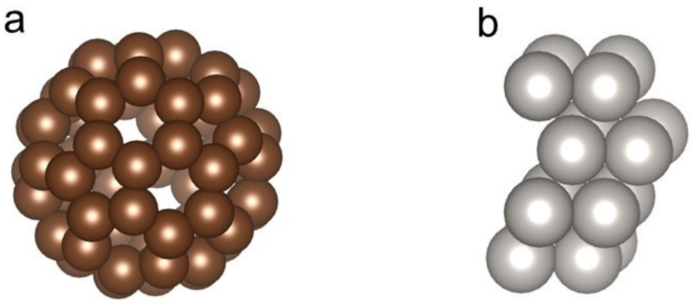

Fig. S10 (a) Structural model of fullerene (C_{60}), and (b) a 2 x 2 periodic slab model of Pt (111) containing four layers used in our DFT calculations.

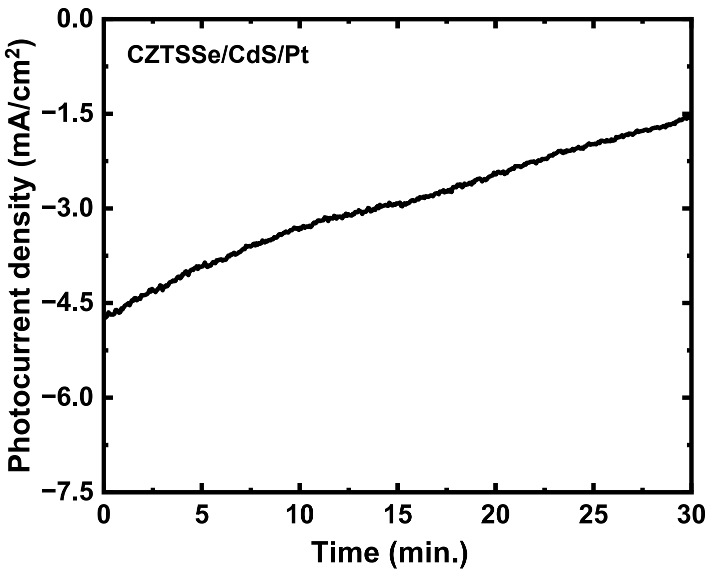

Fig. S11 The stability of CZTSSe/CdS- structured photocathodes under AM 1.5G illumination in a 0.5 M H_2SO_4 electrolyte (pH ~ 0.3) at 0 V_{RHE} condition.

Table S1 PEC performance of the typical emerging photocathodes. CZTS: Cu_2ZnSnS_4; CZTSe: $Cu_2ZnSnSe_4$; ACZTS: $(Ag,Cu)_2ZnSnSe_4$; CZCTS: $Cu_2(Zn,Cd)SnS_4$; CZTGS: $Cu_2Zn(Sn,Ge)S_4$; CBTS: Cu_2BaSnS_4; CBTSSe: $Cu_2BaSn(S,Se)_4$; CBiS: Cu_3BiS_3.

Photocathode	Electrolyte	pH	J_{sc} (mA/cm^2)	Onset potential (V_{RHE})	Stability
This work: CZTSSe/CdS/C_{60}-NSG-Pt	**0.5 M H_2SO_4**	**0.3**	**24.5**	**0.51**	**96% of initial PEC after 1.3 h and 80% of initial PEC after 10 h**
CZTSe/CdS/ZnO/ITO/ALD TiO_2-Pt[10]	0.5 M H_2SO_4	0.3	27.0	0.60	91% of initial PEC after 1.3 h
CZTS/CdS/sputtered TiO_2-Pt[1]	0.1 M Na_2SO_4	9.5	9.0	0.60	-
CZTS/CdS/solution In_2S_3-Pt[2]	0.2 M Na_2HPO_4/NaH_2PO_4	6.5	9.3	0.63	-
CZTS/CdS/ALD TiO_2-Pt[3]	Phosphate buffered solution	6.8	12.5	0.85	75% of initial PEC after 1 h
CZTS/CdS/AZO/ALD TiO_2-Pt[4]	0.5 M Phosphate buffered solution	7	1.0	0.2	55% of initial PEC after 900 s
CZTS/CdS/TiO_2-NB-Pt_{np}[5]	0.2 M Na_2HPO_4/NaH_2PO_4	6.8	14.6	0.7	80% of initial PEC after 3 h
CZTS/CdS/ZnO/drop cast GO/ALD Al_2O_3[6]	0.5 M Na_2SO_4	6.5	8.0	0.7	100% of initial PEC after 16 h
CZTS/CdS/ALD HfO_2-Pt[7]	0.2 M Na_2HPO_4/NaH_2PO_4	6.5	11.9	0.7	100% of initial PEC after 10 h
CZTS/ALD HfO_2/CdS/ALD HfO_2-Pt[8]	0.2 M Na_2HPO_4/NaH_2PO_4	6.5	14.6	0.72	100% of initial PEC after 24 h

CZTS/CdS/solution ZnS-Pt[9]	0.2 M Na_2HPO_4/NaH_2PO_4	6.5	8.0	0.63	100% of initial PEC after 2 h
ACZTS/CdS-Pt[11]	0.2 M Na_2HPO_4	10.0	3.7	0.33	30% of initial PEC after 7 h
ACZTS/CdS-Pt[12]	1 M K_2HPO_4/KH_2PO_4	7.0	17.7	0.85	85% of initial PEC after 1 h
ACZTS/CdS/solution In_2S_3-Pt[13]	0.2 M Na_2HPO_4/NaH_2PO_4	6.5	15.0	0.7	-
CZCTS/CdS/Sputtered TiMo-Pt[14]	1 M K_2HPO_4/KH_2PO_4	7.0	17.0	0.6	80% of initial PEC after 1 h
CZTGS/CdS/solution In_2S_3-Pt[15]	0.2 M Na_2HPO_4/NaH_2PO_4	6.5	11.1	0.6	91% of initial PEC after ~ 2 h
CBTS/CdS/ZnO/ALD TiO_2-Pt[16]	0.5 M Na_2SO_4	7.0	7.5	0.51	-
CBTSSe/CdS/ALD TiO_2-Pt[17]	0.5 M Na_2SO_4/KH_2PO_4	4.3	12.0	0.5	100% of initial PEC after 1 h
CBiS/CdS/ALD-TiO_2-Pt[18]	0.2 M Na_2HPO_4/NaH_2PO_4	6.5	7	0.9	90% of initial PEC after 10 h
Sb_2Se_3/CdZnS-Pt[19]	0.2 M Na_2HPO_4/NaH_2PO_4	6.5	17.5	0.8	80% of initial PEC after 2 h
Sb_2Se_3/CdS/ALD-TiO_2-RuO_x[20]	H_2SO_4	1.0	20	0.5	-
GeSe/C_{60pat}-TiO_{2ball}-Pt[21]	0.2 M Na_2HPO_4/NaH_2PO_4	6.8	11.3	0.6	98% of initial PEC after 20 h
SnS/Ga_2O_3/ALD-TiO_2-Pt[22]	0.5 M H_2SO_4	1.0	28	0.4	100% of initial PEC after 6 h
Cu_2O/Ga_2O_3/TiO-RuO_x[23]	0.5 M Na_2SO_4 and	5	10	1.0	80% of

	0.1 M phosphate solution	initial PEC after 120 h

Reference

1 D. Yokoyama, T. Minegishi, K. Jimbo, T. Hisatomi, G. Ma, M. Katayama, J. Kubota, H. Katagiri and K. Domen, *Applied Physics Express*.

2 F. Jiang, Gunawan, T. Harada, Y. Kuang, T. Minegishi, K. Domen and S. Ikeda, *J Am Chem Soc*, 2015, **137**, 13691–13697.

3 W. Yang, Y. Oh, J. Kim, M. J. Jeong, J. H. Park and J. Moon, *ACS Energy Lett*, 2016, **1**, 1127–1136.

4 L. Rovelli, S. D. Tilley and K. Sivula, *ACS Appl Mater Interfaces*, 2013, **5**, 8018–8024.

5 L. Li, K. Feng, D. Huang, K. Wang, Y. Li, Z. Guo, Y. H. Ng and F. Jiang, *Chemical Engineering Journal*.

6 M. Vishwakarma, Y. Batra, J. Hadermann, A. Singh, A. Ghosh and B. R. Mehta, *ACS Appl Energy Mater*, DOI:10.1021/acsaem.2c01011.

7 D. Huang, K. Wang, L. Yu, T. H. Nguyen, S. Ikeda and F. Jiang, *ACS Energy Lett*, 2018, **3**, 1875–1881.

8 D. Huang, K. Wang, L. Li, K. Feng, N. An, S. Ikeda, Y. Kuang, Y. Ng and F. Jiang, *Energy Environ Sci*, 2021, **14**, 1480–1489.

9 K. Wang, D. Huang, L. Yu, H. Gu, S. Ikeda and F. Jiang, *J Colloid Interface Sci*, 2019, **536**, 9–16.

10 C. Ros, T. Andreu, S. Giraldo, V. Izquierdo-Roca, E. Saucedo and J. R. Morante, *ACS Appl Mater Interfaces*, 2018, **10**, 13425–13433.

11 Z. Xu, Z. Guan, J. Yang and Q. Li, *ACS Appl Energy Mater*, 2019, **2**, 2779–2785.

12 Y. F. Tay, S. S. Hadke, M. Zhang, N. Lim, S. Y. Chiam and L. H. Wong, *J Mater Chem A Mater*, 2020, **8**, 8862–8867.

13 S. Ikeda, T. H. Nguyen, R. Okamoto, M. Remeika, I. Abdellaoui, M. M. Islam, T. Harada, R. Abe and T. Sakurai, *Physical Chemistry Chemical Physics*, 2022, **24**, 468–476.

14 Y. F. Tay, H. Kaneko, S. Y. Chiam, S. Lie, Q. Zheng, B. Wu, S. S. Hadke, Z. Su, P. S. Bassi, D. Bishop, T. C. Sum, T. Minegishi, J. Barber, K. Domen and L. H. Wong, *Joule*, 2018, **2**, 537–548.

15 X. Wen, W. Luo, Z. Guan, W. Huang and Z. Zou, *Nano Energy*, 2017, **41**, 18–26.

16 J. Ge, P. J. Roland, P. Koirala, W. Meng, J. L. Young, R. Petersen, T. G. Deutsch, G. Teeter, R. J. Ellingson, R. W. Collins and Y. Yan, *Chemistry of Materials*, 2017, **29**, 916–920.

17 Y. Zhou, D. Shin, E. Ngaboyamahina, Q. Han, C. B. Parker, D. B. Mitzi and J. T. Glass, *ACS Energy Lett*, 2018, **3**, 177–183.

18 D. Huang, L. Li, K. Wang, Y. Li, K. Feng and F. Jiang, *Nat Commun*, 2021, **12**, 1–10.

19 Y. Li, K. Wang, D. Huang, L. Li, J. Tao, N. A. A. Ghany and F. Jiang, *Appl Catal B*, 2021, **286**, 119872.

20 W. Yang, J. H. Kim, O. S. Hutter, L. J. Phillips, J. Tan, J. Park, H. Lee, J. D. Major, J. S. Lee and J. Moon, *Nat Commun*.

21 K. Wang, Y. Li, L. Li, C. Wang, Y. Fang, W. Zhao, H. Cai, F. Sun and F. Jiang, *Appl Catal B*, 2021, **297**, 120437.

22 H. Lee, J. W. Yang, J. Tan, J. Park, S. G. Shim, Y. S. Park, J. Yun, K. Kim, H. W. Jang and J. Moon, *Advanced Science*, 2021, **8**, 1–11.

23 L. Pan, J. H. Kim, M. T. Mayer, M. K. Son, A. Ummadisingu, J. S. Lee, A. Hagfeldt, J. Luo and M. Grätzel, *Nat Catal*, 2018, **1**, 412–420.