Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
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MOF Derivative Porous ZnO Integrated with NiO and Colloidal QDs for Efficient Hydrogen Generation via Synergistic Photoelectrochemical and Electrochemical Process

Yi Tao,[a] Zikun Tang,[a] Yihong Zhong,[a] Dequan Bao,[a] Zhenqiu Gao,[a] Wei Zhao,[a] Zhen Wen,[a] Hao Zhang,[*a] Kanghong Wang[*ab] and Xuhui Sun[*a]

[a]Institute of Functional Nano & Soft Materials (FUNSOM), Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Jiangsu Key Laboratory of Advanced Negative Carbon Technologies, Soochow University, 199 Ren-ai Road, Suzhou, 215123, Jiangsu, China.

[b]Suzhou Institute for Advanced Research, University of Science and Technology of China, Suzhou, Jiangsu 215123, China.

∗ Corresponding authors: haozhang@suda.edu.cn (H. Zhang), kanghongwang@ustc.edu.cn (K. Wang), xhsun@suda.edu.cn (X. Sun)

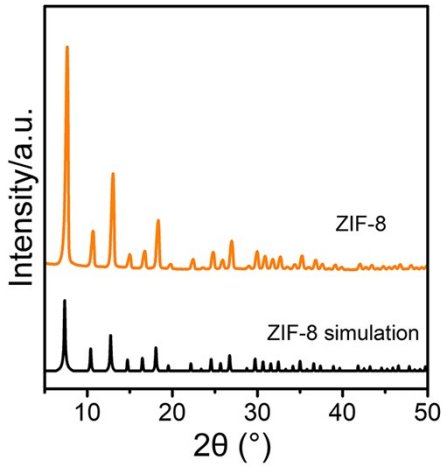

Fig. S1 XRD patterns of as-synthesized ZIF-8.

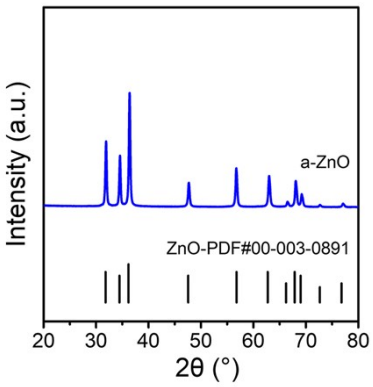

Fig. S2 XRD patterns of MOF derivative a-ZnO.

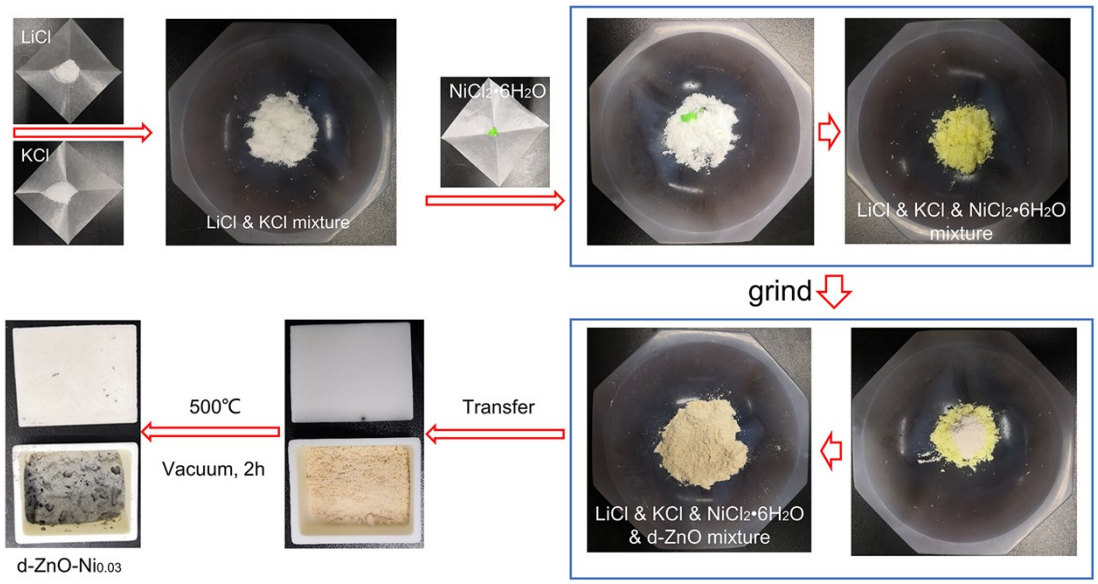

Fig. S3 The photos of the mixture of $NiCl_2 \cdot 6H_2O$, LiCl, and KCl at different stages of the MSM process.

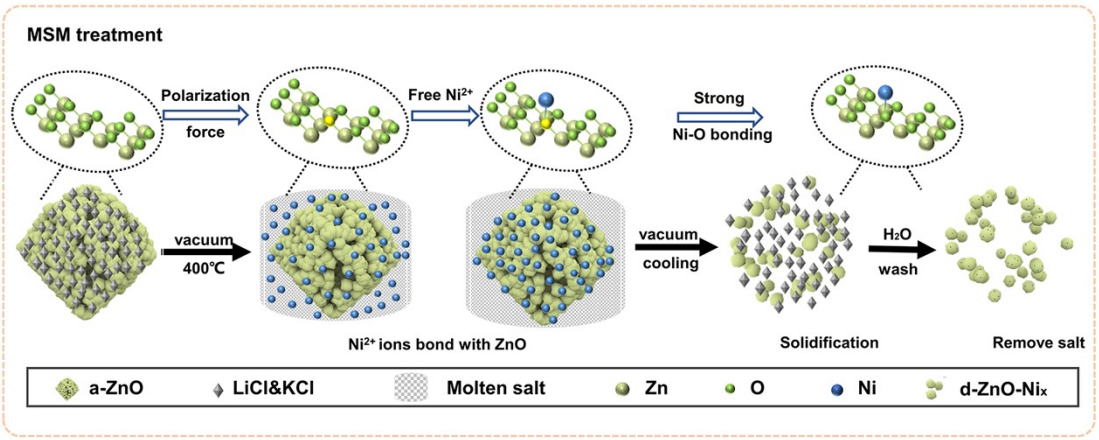

Fig. S4 Illustration of molten-salt-mediated (MSM) preparation of d-ZnO-Ni.

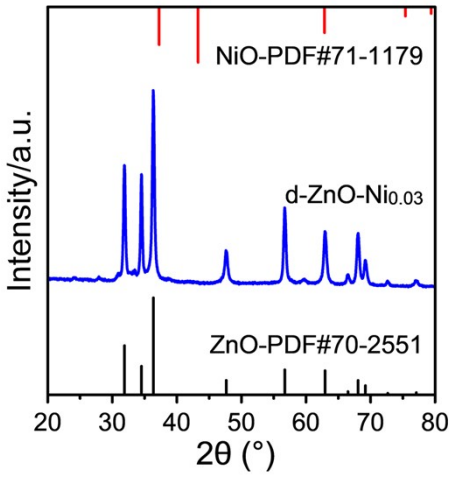

Fig. S5 XRD patterns of MOF derivative d-ZnO-$Ni_{0.03}$.

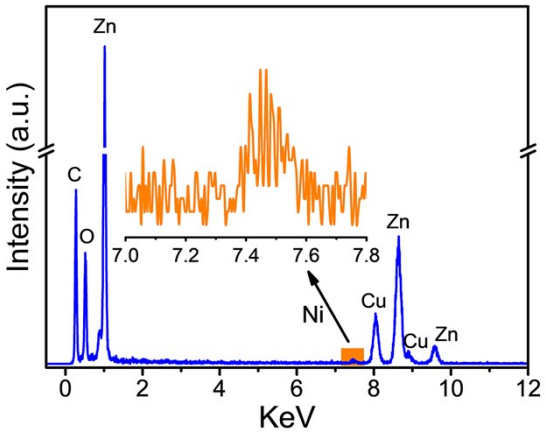

Fig. S6 EDX spectrum of d-ZnO@$NiO_{0.03}$.

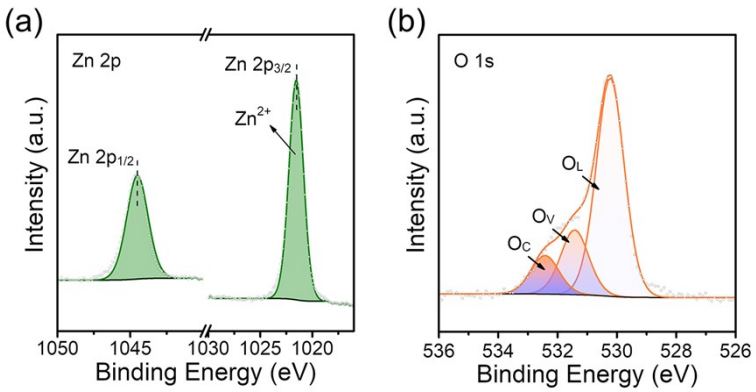

Fig. S7 High-resolution XPS spectra of d-ZnO@$NiO_{0.03}$: (a) Zn 2p, (b) O 1s.

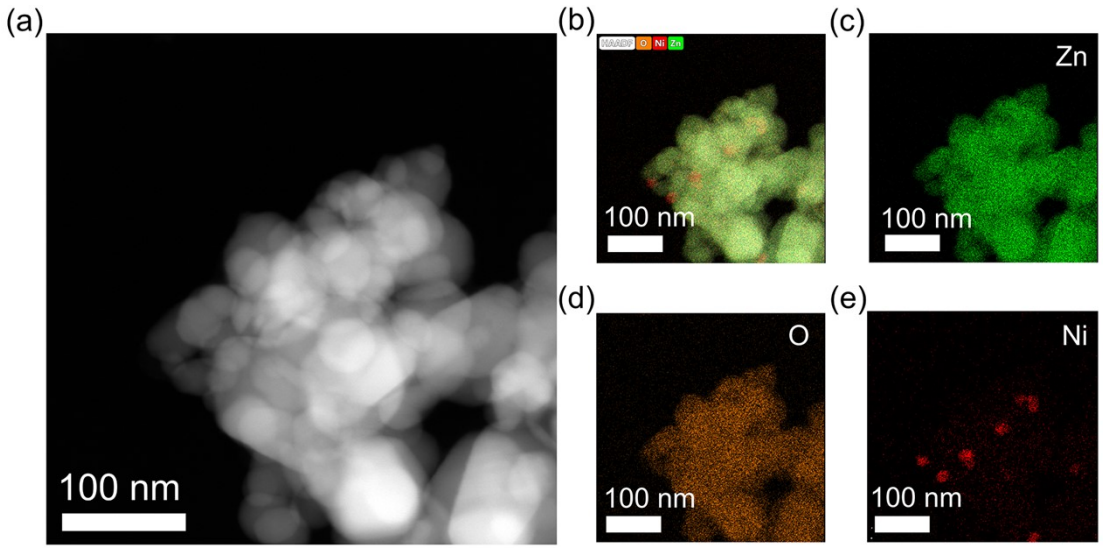

Fig. S8 Representative HAADF image (a) of d-ZnO@$NiO_{0.06}$ and related EDX mapping of (b) comprehensive image, (c) Zn, (d) O, (e) Ni.

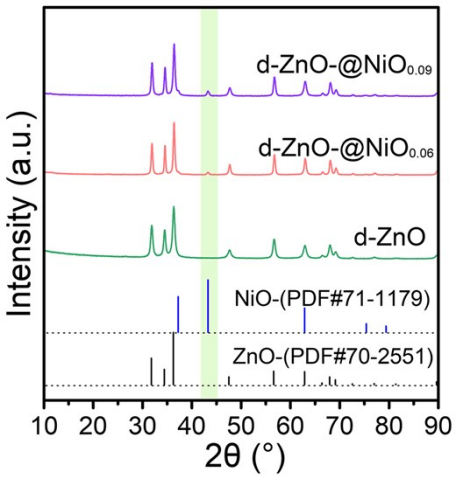

Fig. S9 XRD patterns of d-ZnO, d-ZnO@$NiO_{0.06}$, and d-ZnO@$NiO_{0.09}$.

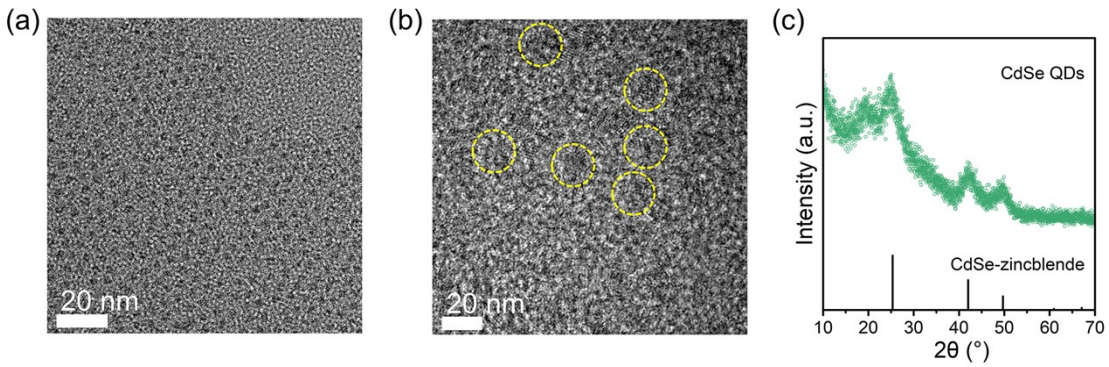

Fig. S10 (a) Representative TEM image of CdSe QDs. (b) HRTEM of CdSe QDs. (c) XRD patterns of CdSe QDs.

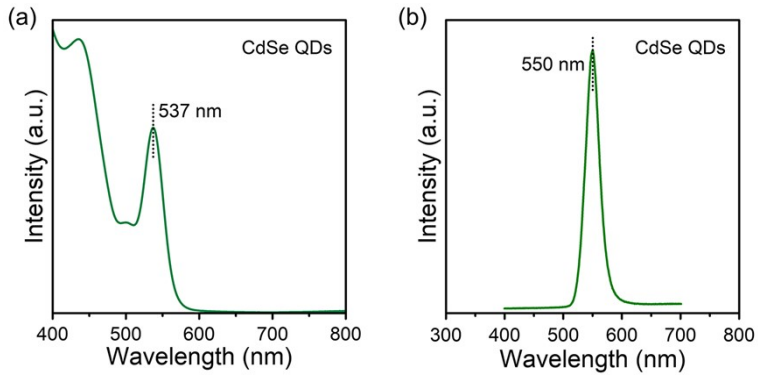

Fig. S11 (a) UV-Vis absorption spectum and (b) PL spectrum of CdSe QDs in toluene.

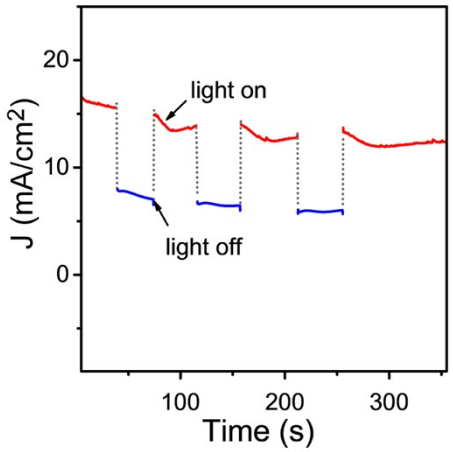

Fig. S12 Current density-time under chopped illumination.

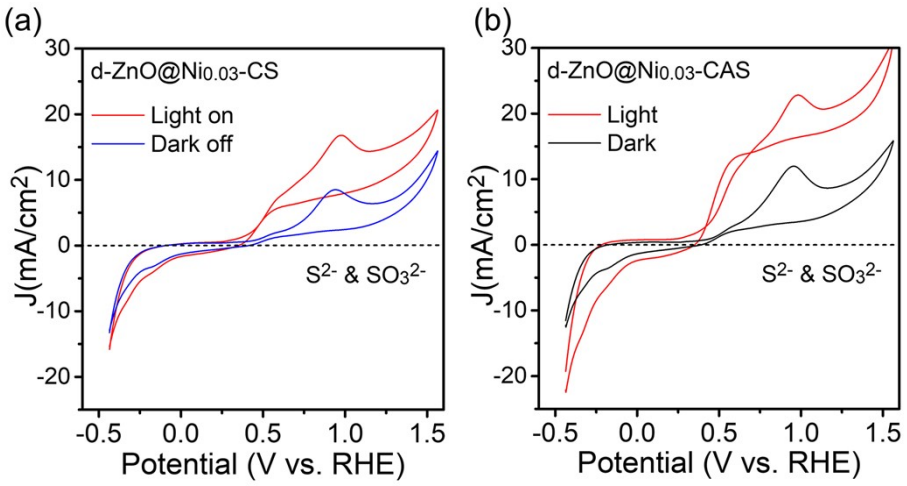

Fig. S13 Cyclic voltammetry (CV) curves of (a) d-ZnO@$NiO_{0.03}$-CS and (b) d-ZnO@$NiO_{0.03}$-CAS in the S^{2-} & SO_3^{2-} electrolyte (pH ~ 13).

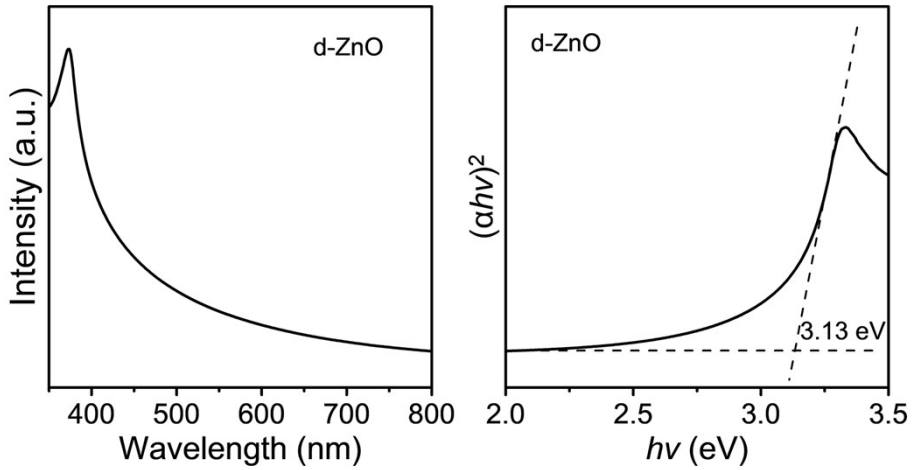

Fig. S14 The UV-vis spectroscopy measurement and the related Tauc plot for d-ZnO.

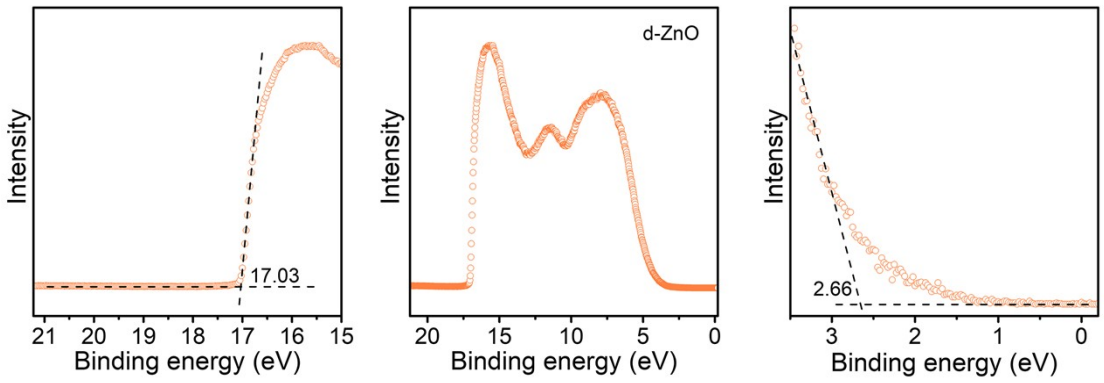

Fig. S15 UPS measurement of d-ZnO: high binding energy cut-off (left); overall UPS spectrum (middle); low binding energy cut-off (right).

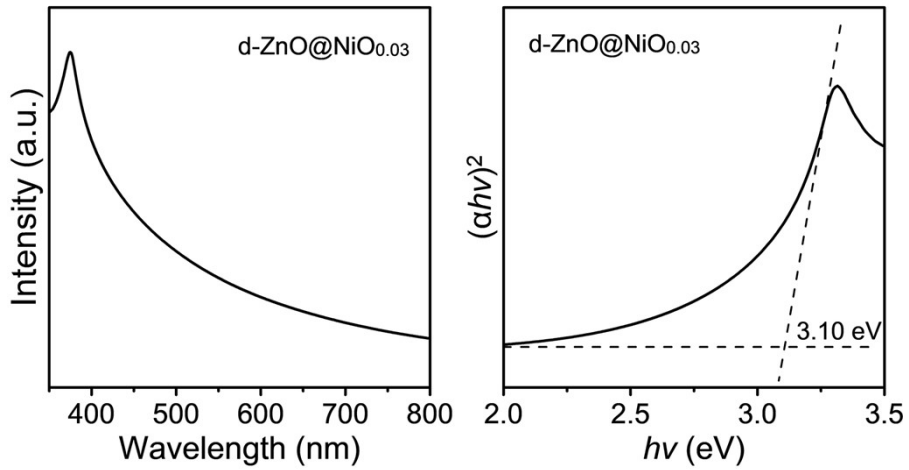

Fig. S16 The UV-vis spectroscopy measurement and the related Tauc plot for d-ZnO@$NiO_{0.03}$.

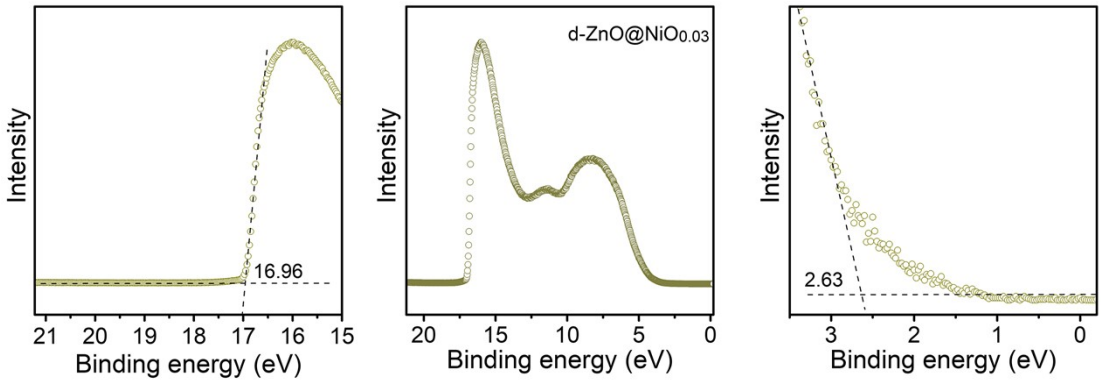

Fig. S17 UPS measurement of d-ZnO@$Ni_{0.03}$: high binding energy cut-off (left); overall UPS spectrum (middle); low binding energy cut-off (right).

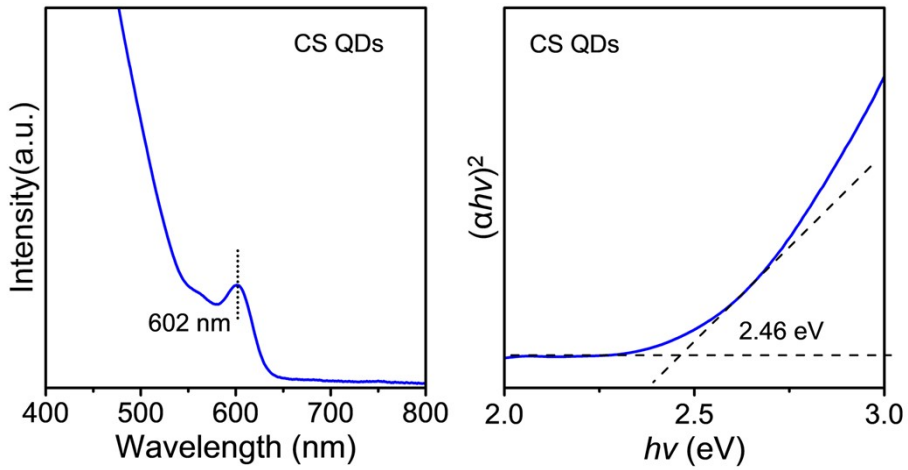

Fig. S18 The UV-vis spectroscopy measurement and the related Tauc plot for CS QDs.

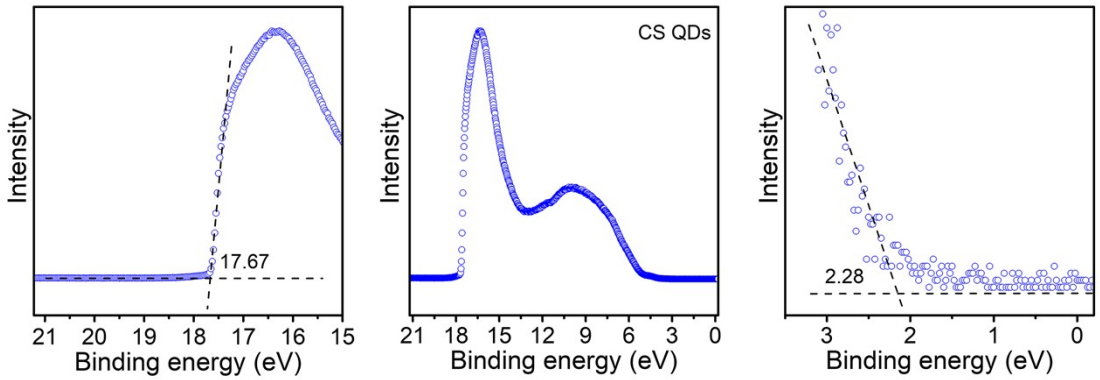

Fig. S19 UPS measurement of CS QDs: high binding energy cut-off (left); overall UPS spectrum (middle); low binding energy cut-off (right).

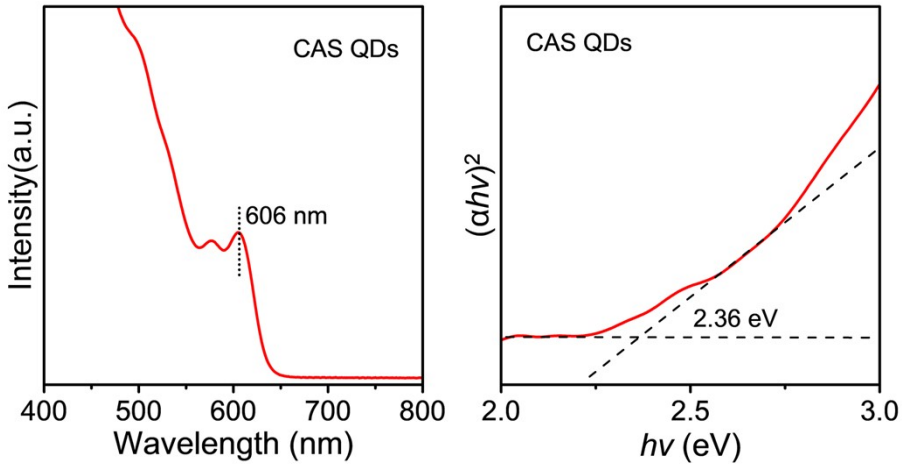

Fig. S20 The UV-vis spectroscopy measurement and the related Tauc plot for CAS QDs.

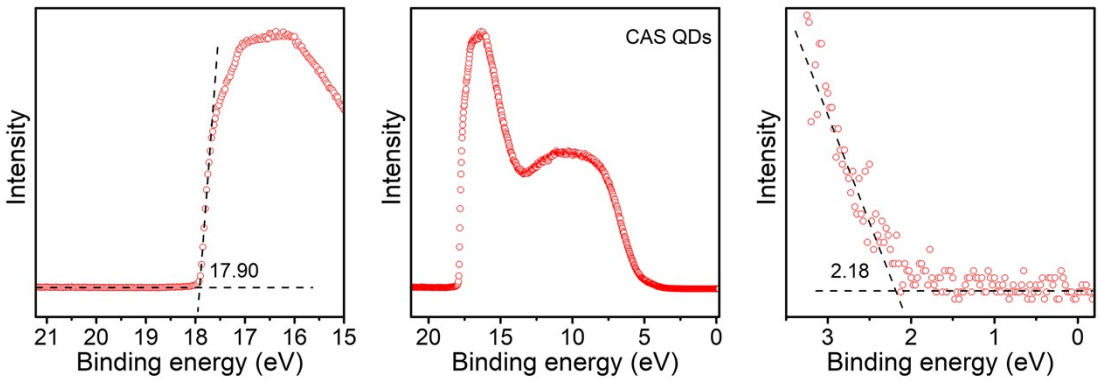

Fig. S21 UPS measurement of CAS QDs: high binding energy cut-off (left); overall UPS spectrum (middle); low binding energy cut-off (right).

Table S1 The feeding ratio of Ni/Zn and ICP tests of d-ZnO@NiO_x.

Sample	Feeding ratio	ICP	
	Ni/Zn(at%)	Ni/Zn(at%)	Ni(wt%)
d-ZnO@$NiO_{0.03}$	3	0.62	0.45
d-ZnO@$NiO_{0.06}$	6	1.28	0.91
d-ZnO@$NiO_{0.09}$	9	2.09	1.48

Table S2 Comparison of saturated photocurrent density of PEC devices based on QDs in this work and the reported literature. The configuration of PEC cell is identical in all of devices.

Photoanode structure	QDs types	*J* (mA.cm^{-2})	Ref.
d-ZnO@$Ni_{0.03}$-CAS	Colloidal	21.7	This work
d-ZnO@CAS	Colloidal	15.6	This work
d-ZnO@$Ni_{0.03}$-CS	Colloidal	14.9	This work
d-ZnO@CS	Colloidal	8.8	This work
ZnO/CdSe/CdS/IrO_x	Non-colloidal	13.9	1
CdS/$Ni(OH)_2$&$Co(OH)_2$	Non-colloidal	1.2	2
TiO_2/CdSe/$5CdSe_{0.5}S_{0.5}$/CdS	Colloidal	12.0	3
m-TiO2/CdSe/$(CdS)_6$	Colloidal	10.7	4
TiO_2/CdSe/CdS	Colloidal	10.0	5
H-TiO_2-CdSe	Non-colloidal	16.2	6
TiO_2/CdS/$Zn_yCd_{1-y}S$/ZnS	Colloidal	20.5	7
TiO_2/PbS/CdS	Colloidal	5.3	8
TiO_2/CdSe/$3Pb_xCd_{1-x}S$/3CdS	Colloidal	6.0	9
TiO_2/CdSe/$5CdSe_xS_{1-x}$/2CdS	Colloidal	11.3	10
TiO_2/CdSe/$5CdSe_xS_{1-x}$/CdS	Colloidal	17.5	11
TiO_2/CdS/$(CdSe)_6$	Colloidal	16.0	12

Table S3 The R_s and R_{ct} for the d-ZnO-QDs, d-ZnO@$NiO_{0.03}$-CS and d-ZnO@$NiO_{0.03}$-CAS photoanodes.

Sample	$R_s(\Omega)$	$R_{ct}(\Omega)$
d-ZnO@CS	41	776
d-ZnO@$NiO_{0.03}$-CS	39	367
d-ZnO@$NiO_{0.03}$-CAS	42	272

Table S4 Ratio of Se/S in the shell as a function of SILAR cycle.

	Shell	1	2	3	4	5	6
CS QD	S	0/10	0/10	0/10	0/10	0/10	0/10
CAS QDs	Se/S	8/2	6/4	4/6	2/8	0/10	0/10

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