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Electronic Supplementary Information (ESI)

Sensibilization of p-NiO with ZnSe/CdS and CdS/ZnSe Quantum Dots for Photoelectrochemical Water Reduction

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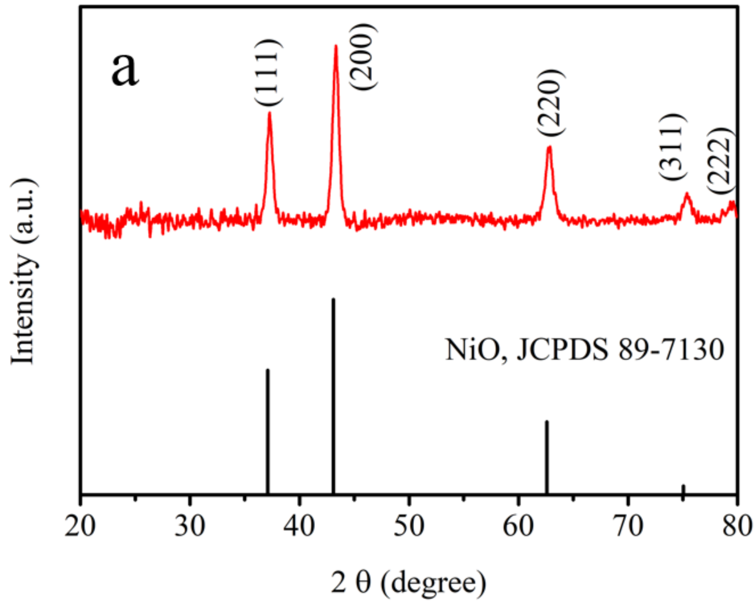

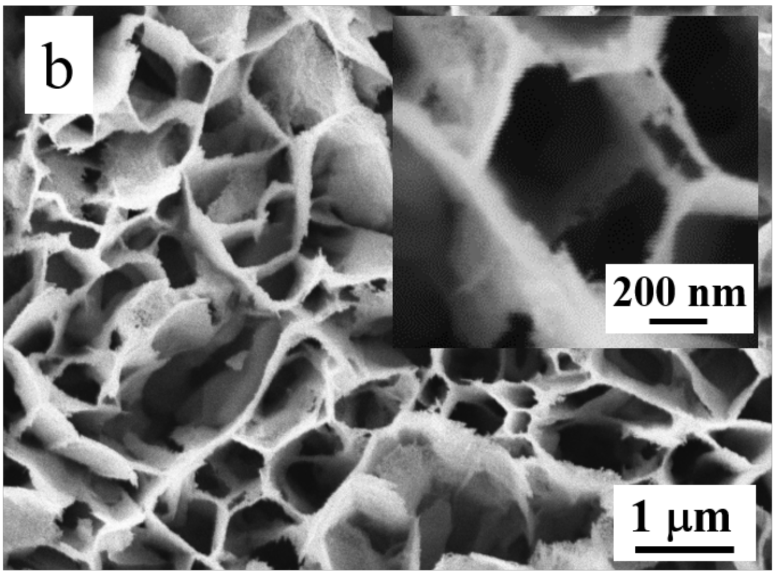

Fig. S1 (a) PXRD patterns and (b) SEM image of NiO.

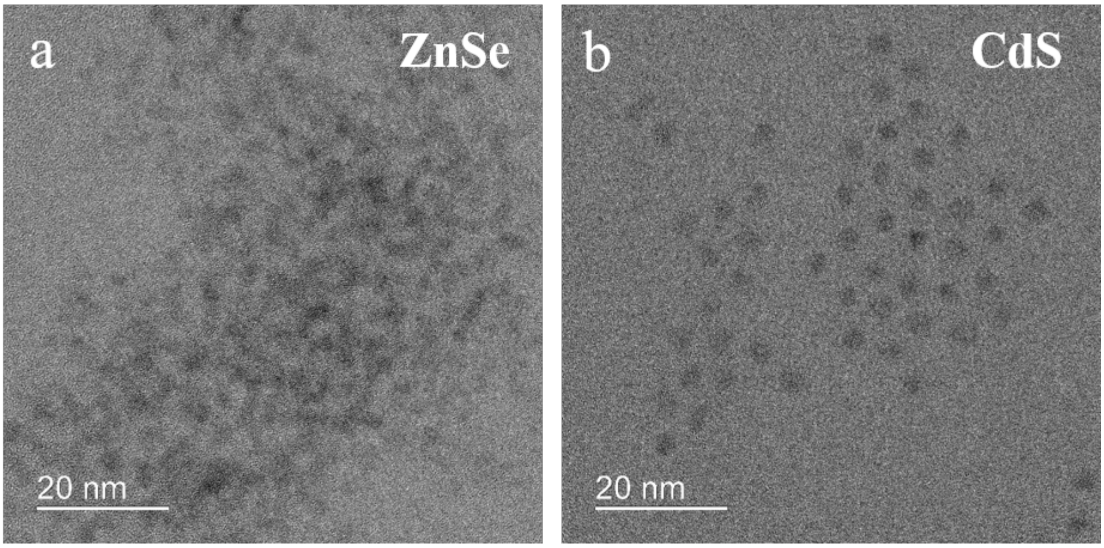

Fig. S2 TEM micrographs of the (a) ZnSe and (b) CdS core particles with average sizes of 4.10 and 3.52 nm, respectively. Due to the low contrast of the material the diameter is hard to determine exactly and the measurement is likely biased towards too low values.

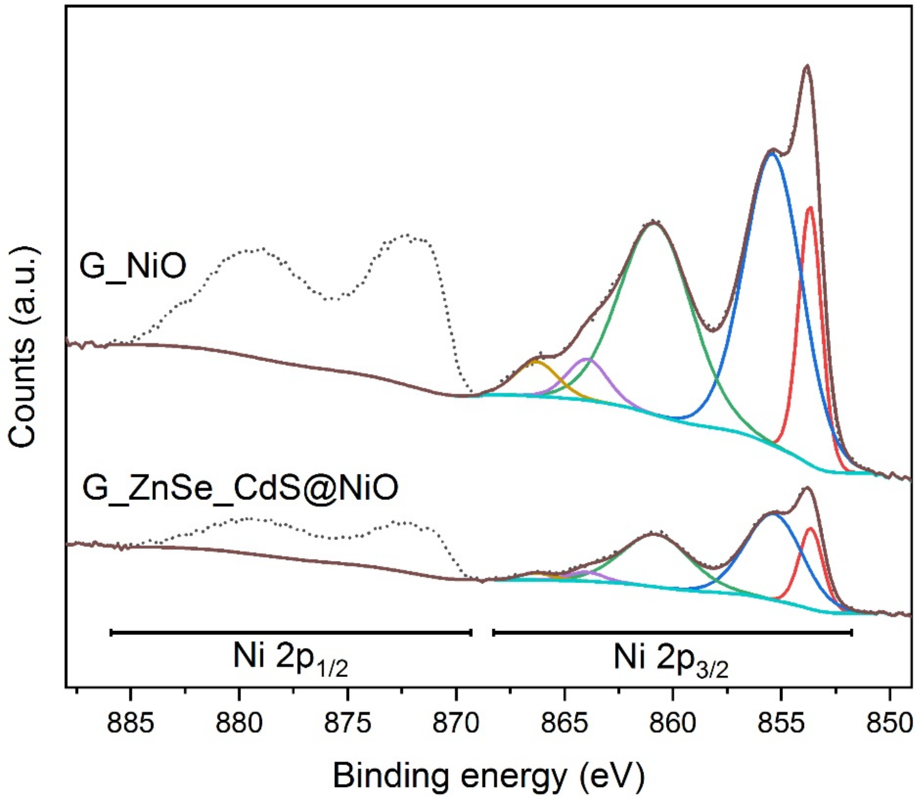

Fig. S3 XPS core level analysis of Ni 2p for bare NiO and ZnSe/CdS@NiO.

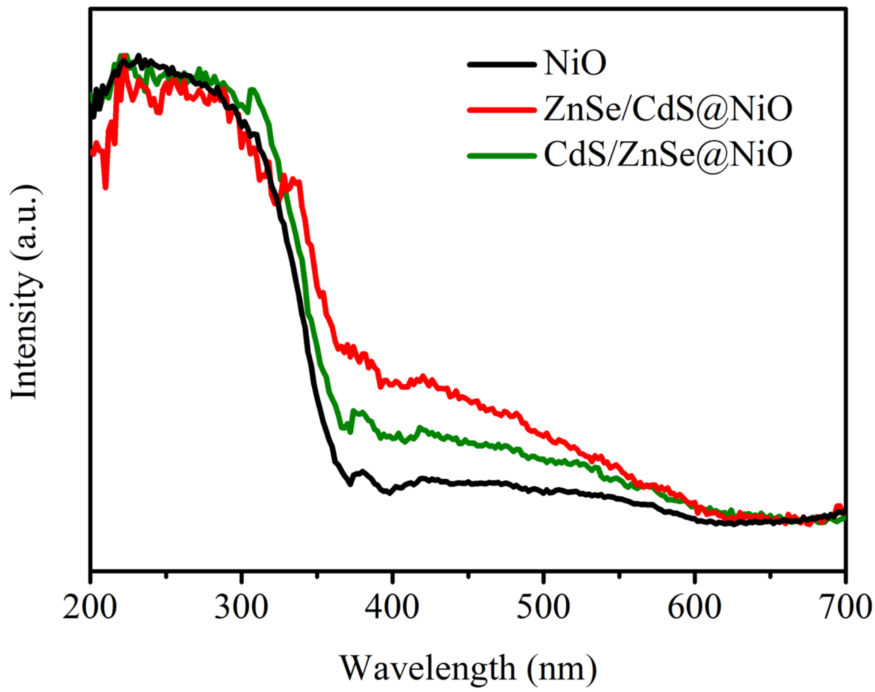

Fig. S4 Absorption spectra of NiO, ZnSe/CdS@NiO and CdS/ZnSe@NiO.

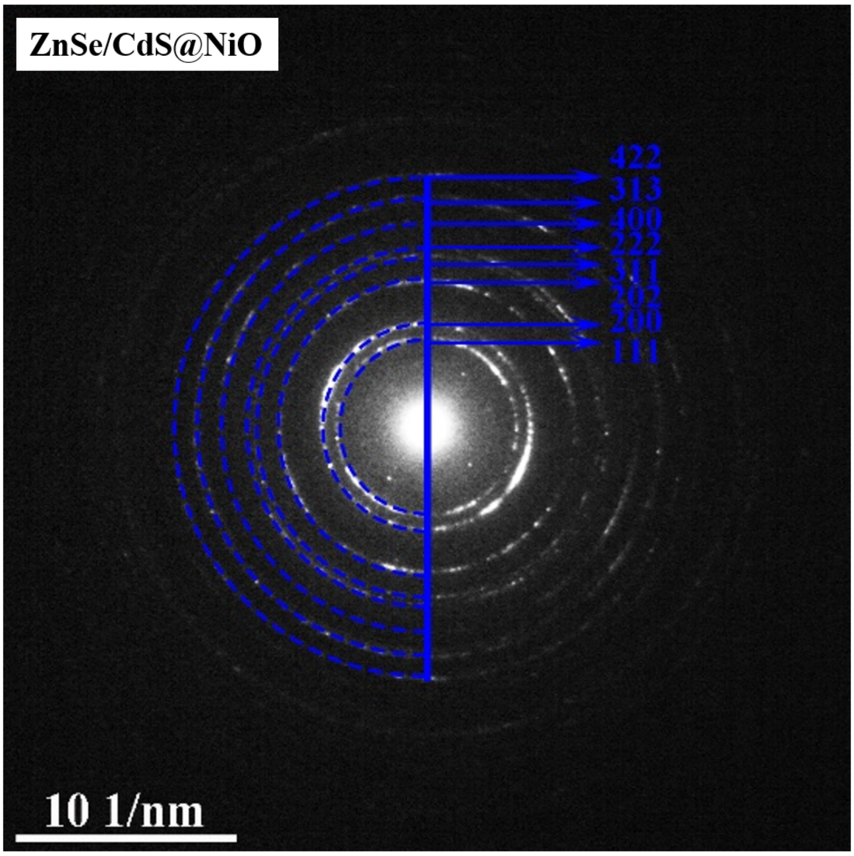

Fig. S5 Selected area electron diffraction (SAED) analysis of ZnSe/CdS@NiO.

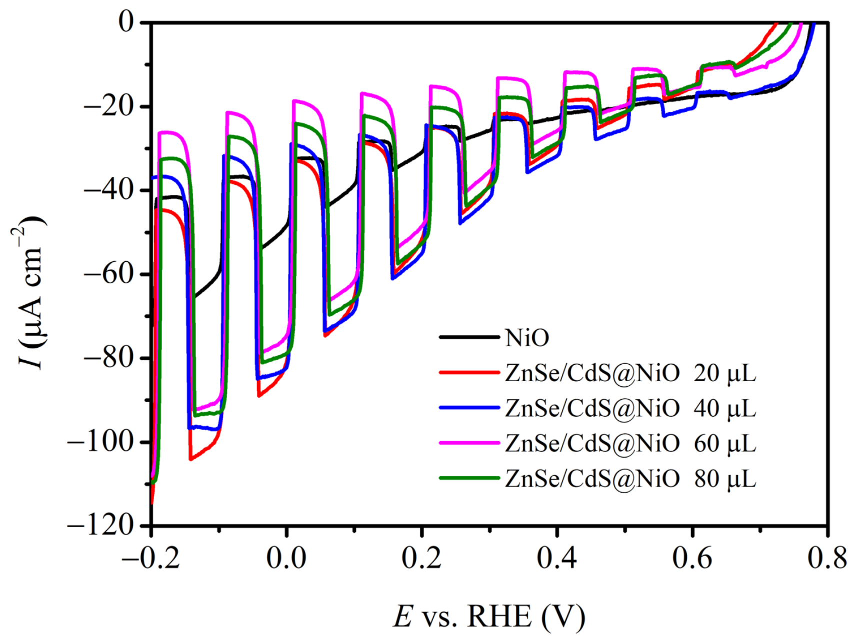

Fig. S6 LSV curves on the optimization of the loading amount of ZnSe/CdS QDs, recorded under back-side AM 1.5G illumination. 60 μL was then selected as the optimized content to modify NiO photocathode.

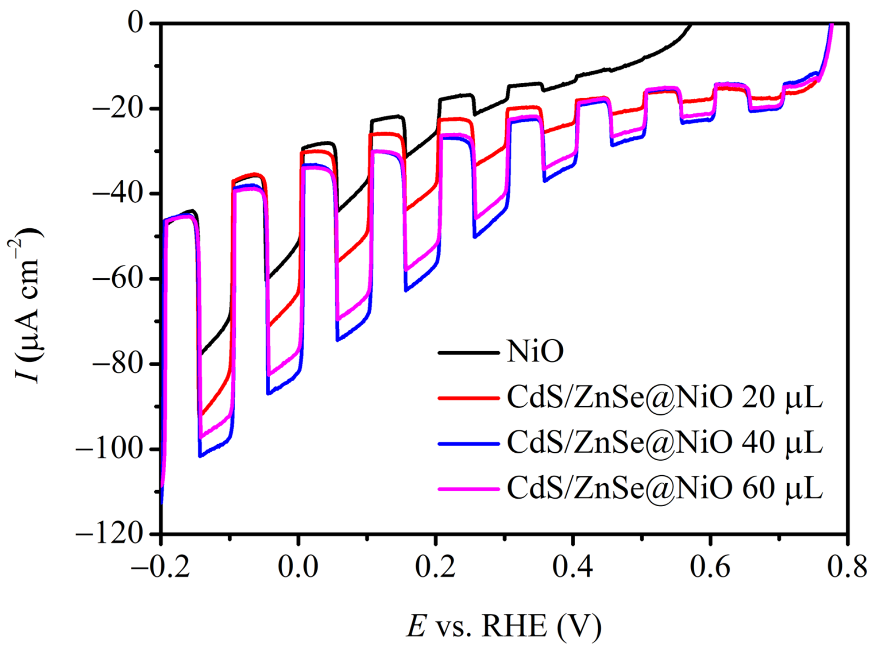

Fig. S7 LSV curves on the optimization of the loading amount of CdS/ZnSe QDs, recorded under back-side AM 1.5G illumination. 40 μL was then selected as the optimized content to decorate NiO photocathode.

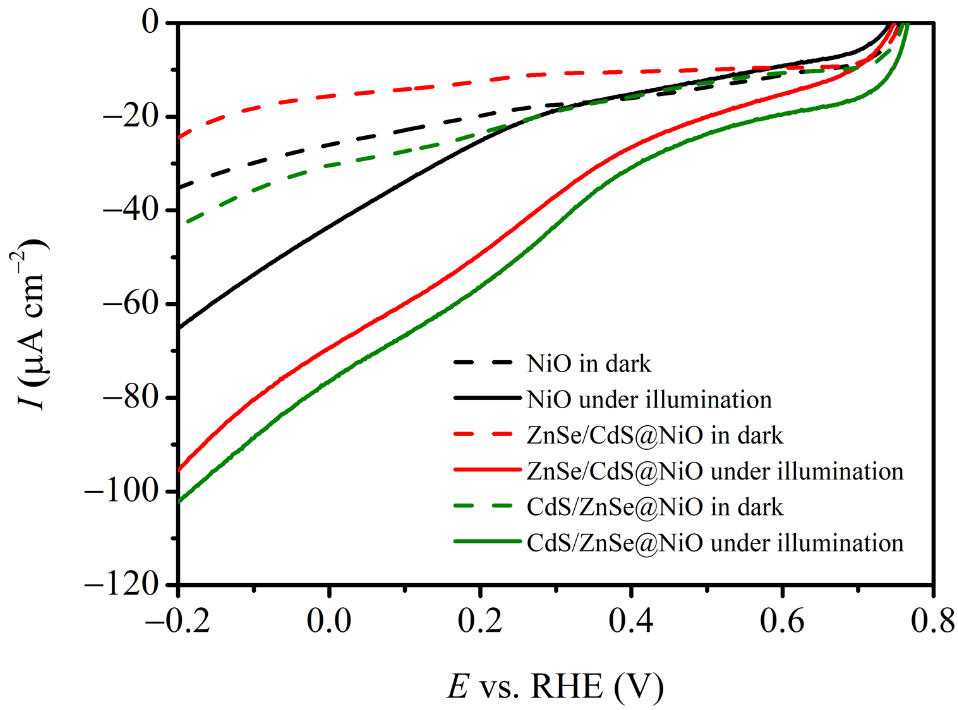

Fig. S8 LSV curves of NiO, ZnSe/CdS@NiO, and CdS/ZnSe@NiO photocathodes recorded in 0.1 M KP_i with (solid lines) or without (dash lines) AM 1.5G illumination.

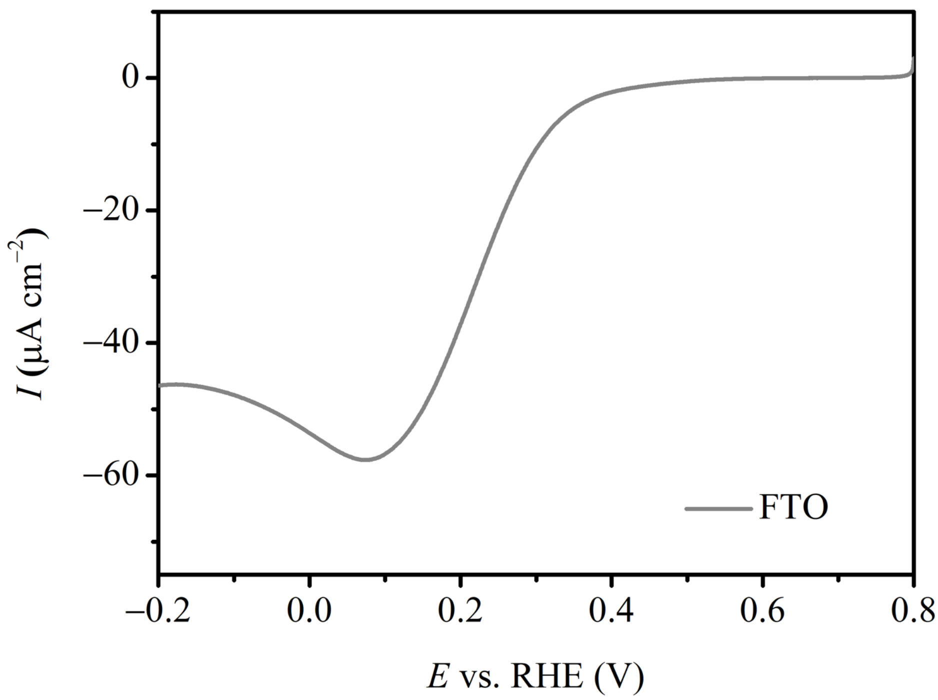

Fig. S9 LSV curve of bare FTO recorded in 0.1 M KP_i without AM 1.5G illumination.

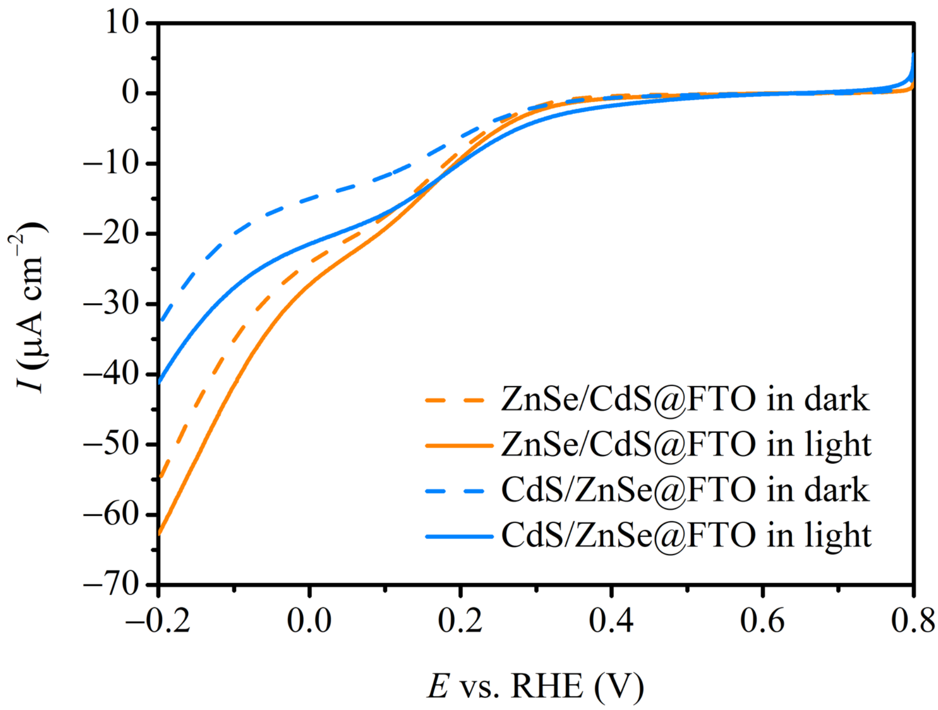

Fig. S10 LSV curves of ZnSe/CdS@FTO and CdS/ZnSe@FTO electrodes recorded in dark (dash lines) and under AM 1.5G illumination (Solid lines).

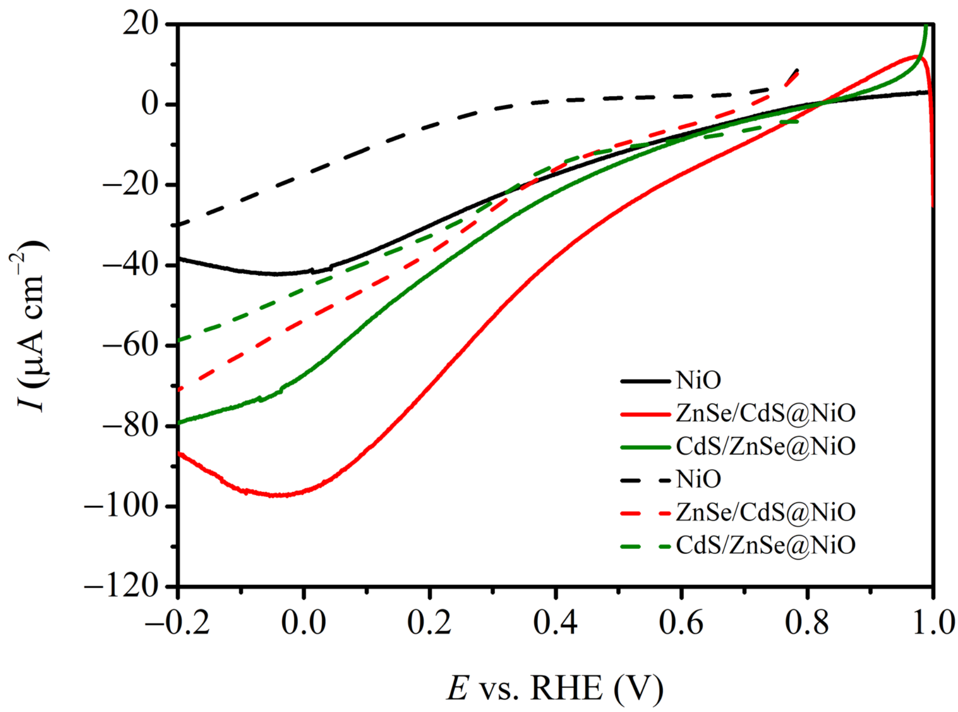

Fig. S11 Net photocurrent density of NiO, ZnSe/CdS@NiO and CdS/ZnSe@NiO photocathodes documented in the electrolyte with (solid lines) and without (dash lines) the addition of $K_2S_2O_8$ as electron scavenger. The net photocurrent density is acquired by deducting corresponding dark current density.

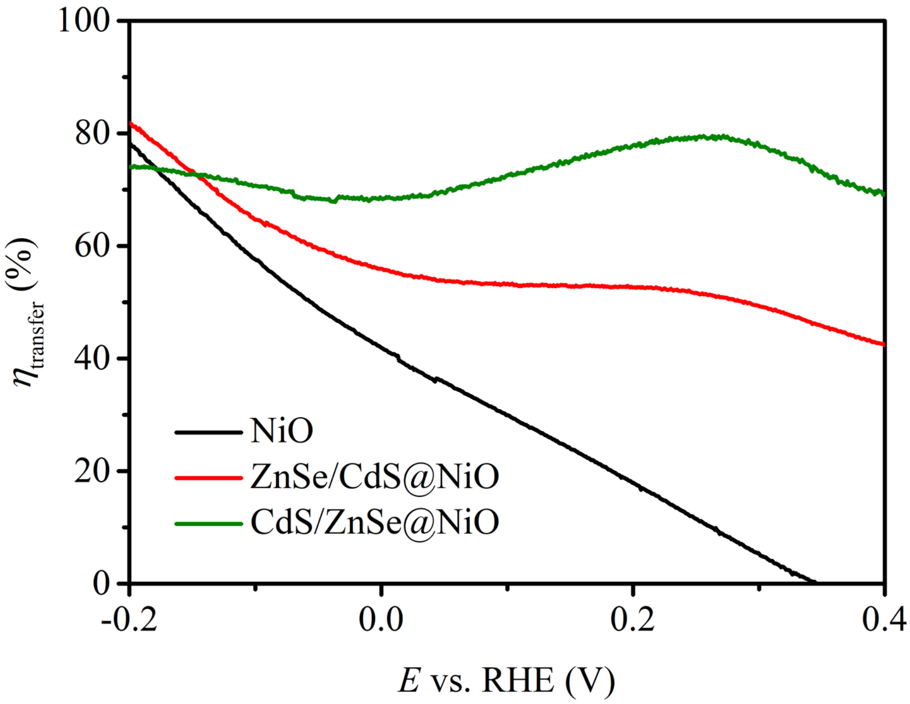

Fig. S12 Surface charge-transfer efficiency of the photocathodes.

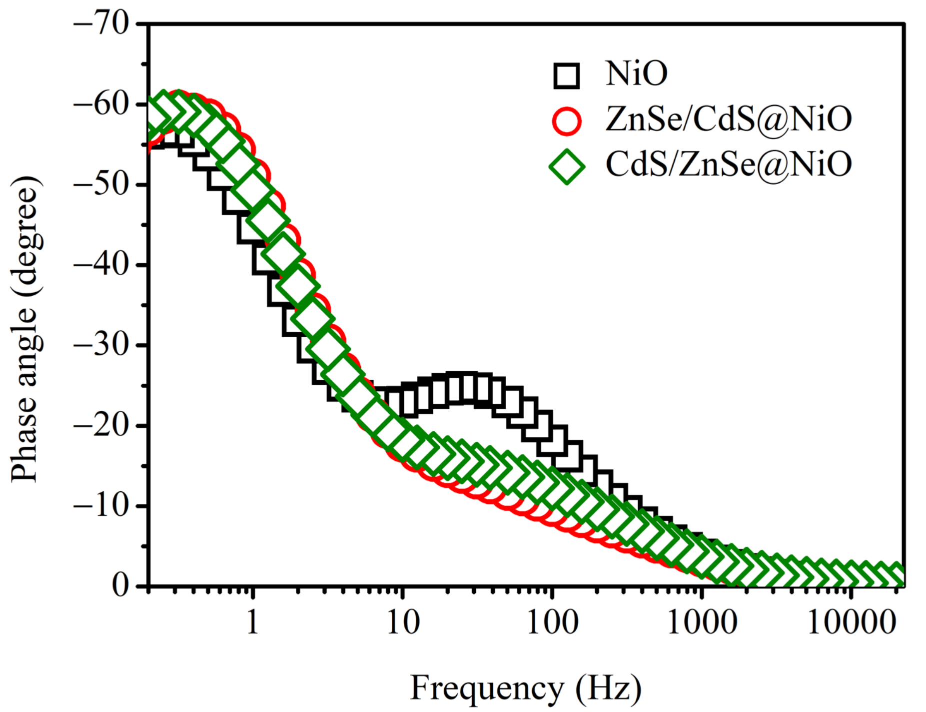

Fig. S13 Bode phase plots of NiO, ZnSe/CdS@NiO, CdS/ZnSe@NiO photocathodes.

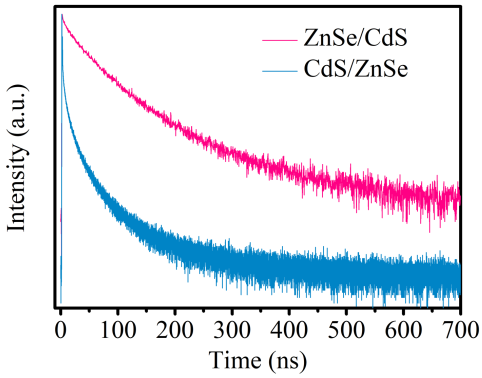

Fig. S14 PL decay curves of the ZnSe/CdS and CdS/ZnSe particles, excited at 404 nm and monitored at 605 nm.

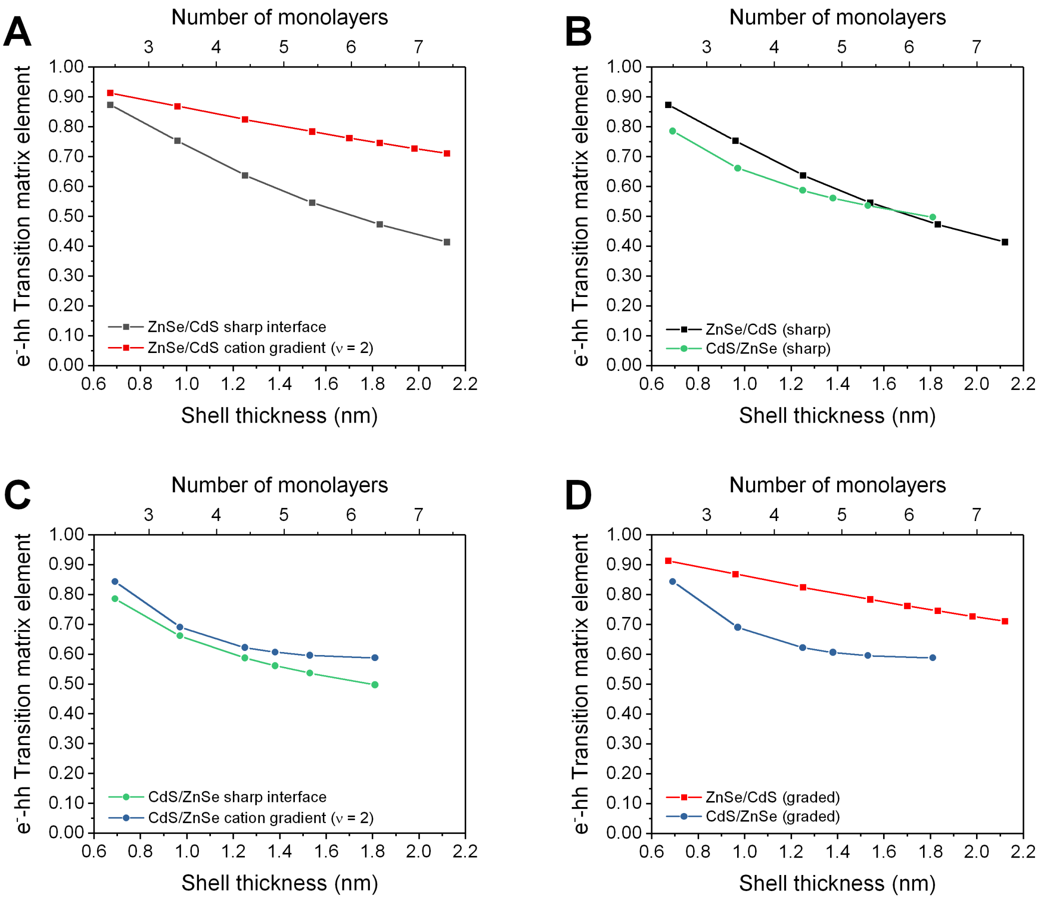

Fig. S15 Comparison plots of the calculated transition matrix element between the lowest conduction (e^-) and valence (heavy hole) band state for ZnSe/CdS and CdS/ZnSe nanocrystals, both with sharp and graded interfaces, as a function of shell thickness. The core diameter was fixed at 4.1 nm for ZnSe and 3.52 nm for CdS. The shell thickness of the particles in this study were H = 1.25 nm for ZnSe/CdS and H = 1.38 nm for CdS/ZnSe. The gradient slope for the cations was set to v = 2 (see Reference 1 for details on the gradient function).

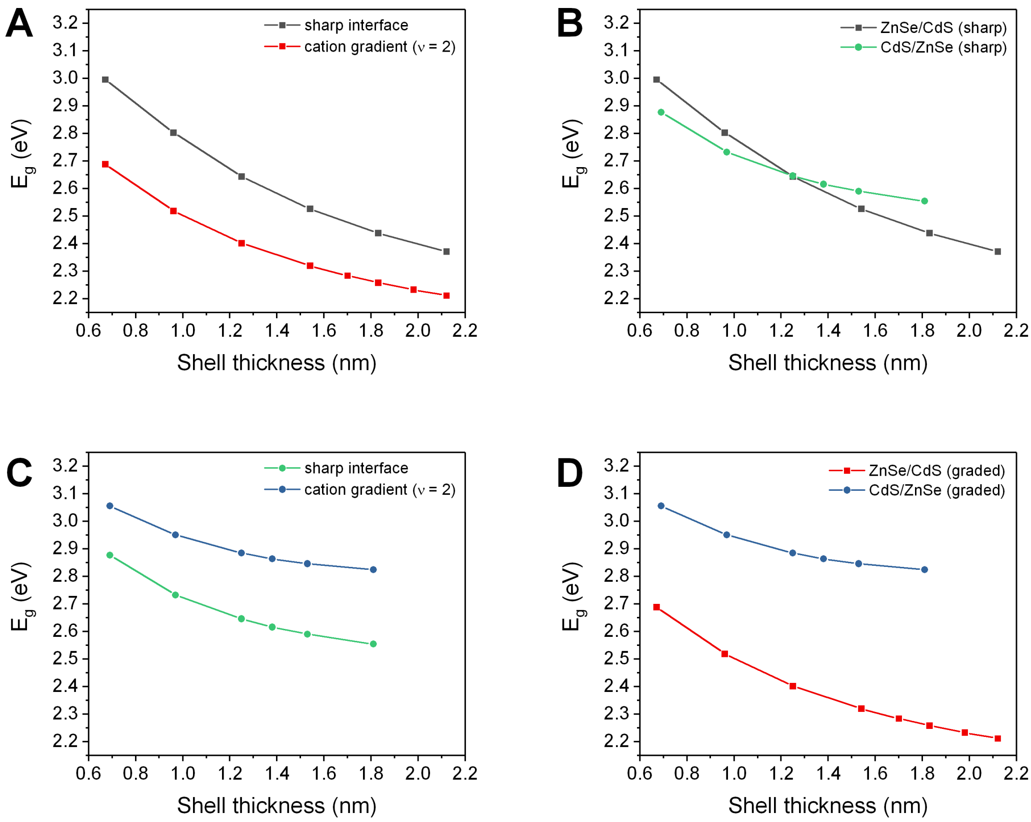

Fig. S16 Calculated optical band gaps for ZnSe/CdS and CdS/ZnSe nanocrystals, both with sharp and graded interfaces, as a function of shell thickness.

Table S1. Lattice parameter a, dielectric constants ε for the static (0) and optic (∞) limit, elastic stiffness constant C_{ij}, piezoelectric stress constant e_{14}, band gap E_g, valence band offset E_{VB} relative to ZnS, effective masses m^* for electron and holes in units of the electron rest mass, spin-orbit Δ_{so} splitting, deformation potentials a_0^Γ for the conduction band and a, b, d for the valence band, and Varshni parameters α and β. All parameters were taken from reference 2,[2] except relative band offsets, which were taken from reference 3.[3]

	CdS	ZnSe	Unit
a	5.825	5.6692	Å
ε_0	9.8	8.9	
ε_∞	5.4	5.9	
C_{11}	77.0	85.7	GPa
C_{12}	53.9	50.7	GPa
C_{44}	23.6	40.5	GPa
e_{14}	0.333	0.049	
E_g	2.445	2.721	eV
E_{VB}	0.18	0.53	eV
m_e^*	0.14	0.137	m_0
m_{hh}^*	0.39	0.52	m_0
m_{lh}^*	0.18	0.168	m_0
m_{so}^*	0.24	0.24	m_0
Δ_{so}	0.070	0.424	eV
a_0^Γ	–0.43	–5.1	eV
a	0.92	1.65	eV
b	–4.7	–1.8	eV
d	–4.4	–5.0	eV
α	3.451×10^{-4}	5.58×10^{-4}	eV/K
β	208	187	K

Table S2. Fitting results of resistance elements (R) from Nyquist plots for NiO, ZnSe/CdS@NiO, and CdS/ZnSe@NiO.

	R_S (Ω cm^{-2})	$R_{ct,\ bulk}$ (Ω cm^{-2})	$R_{ct,\ surface}$ (Ω cm^{-2})
NiO	155.8	273.2	6.885e3
NiO/(ZnSe/CdS)	154.5	118.8	5.198e3
NiO/(CdS/ZnSe)	153.5	137.3	6.410e3

References

1 K. Boldt, S. Bartlett, N. Kirkwood and B. Johannessen, *Nano Lett.*, 2020, **20**, 1009–1017.

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