Supporting Information

Core@Dual-shell Nanorod Array with Cascading Band Configuration for Enhanced Photocatalytic Properties and Anti-photocorrosion

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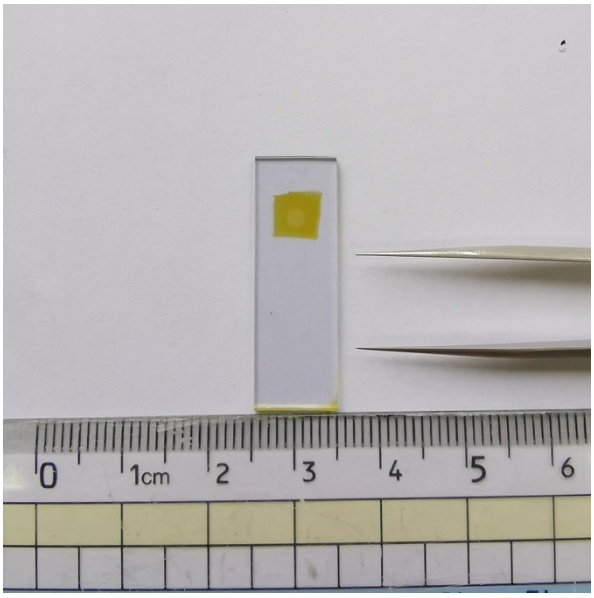

Fig. S1. The picture of the working photoelectrode.

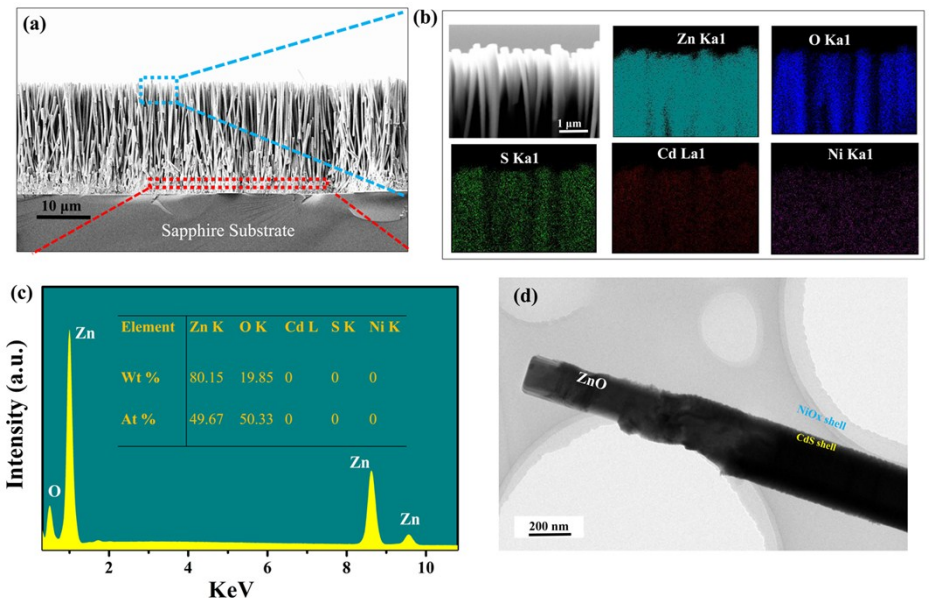

Fig. S2. (a) SEM image of the cross-section of the ZnO-CdS-NiO_x nanorod array, (b) EDS element maps of Zn, O, S, Cd and Ni collected from the top-middle part (light blue box region), and (c) EDS spectrum from the bottom of the nanorod array (red box region). (d) TEM images of an individual ZnO-CdS-NiO_x nanorod.

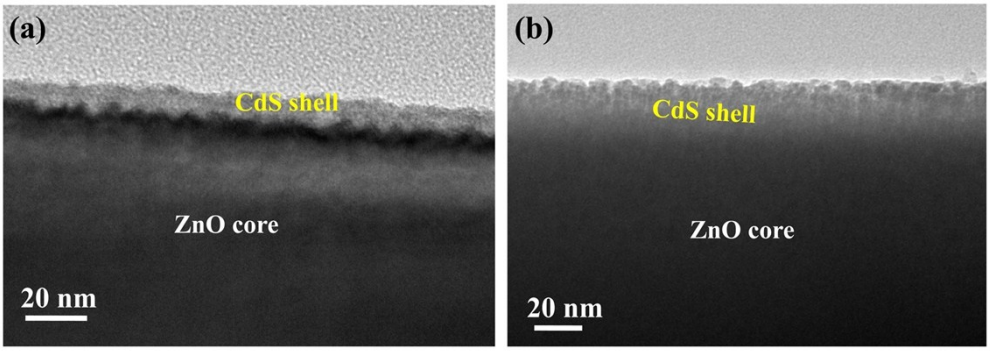

Fig. S3. TEM images of (a) ZnO-CdS-1 (sputtering for 8 min) core-shell nanorod and (b) ZnO-CdS-3 (sputtering for 15 min) core-shell nanorod.

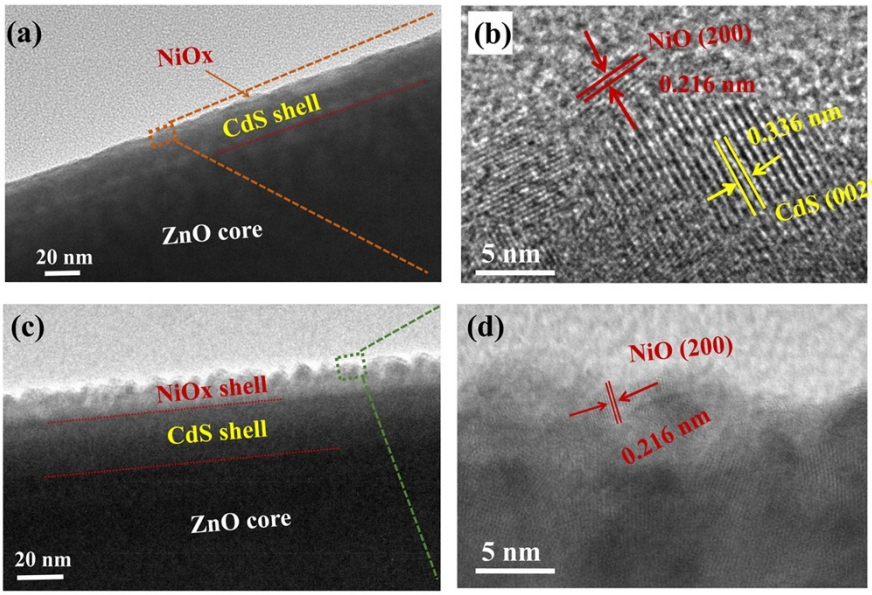

Fig. S4. TEM images and corresponding HRTEM images of (a), (b) ZnO-CdS-NiO_x-1 (sputtering for 3 min) core@dual-shell nanorod and (c), (d) ZnO-CdS-NiO_x-3 (sputtering for 8 min) core@dual-shell nanorod.

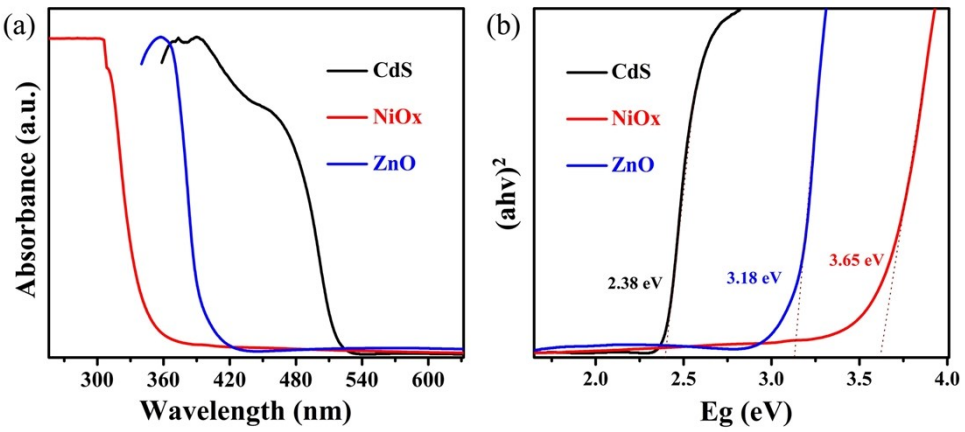

Fig. S5. (a) UV-Vis diffuse reflectance spectra of CdS, ZnO and NiO_x. (b) Tauc plots of CdS, ZnO and NiOx.

The band gap energy (E_g) for the samples were determined through following formula: $(\alpha h\upsilon)^{1/n} = A(h\upsilon - E_g)$, where A, E_g, h, α and υ are proportionality constant, band gap, Planck constant, absorption coefficient and light frequency, respectively. The n value is determined by the type of optical transition of semiconductors (the n values of direct-gap semiconductor and indirect-gap semiconductor are 1 and 4).[1,2] The corresponding of E_g values of CdS, ZnO and NiO_x were estimated to be 2.38 eV, 3.18 eV and 3.65 eV, respectively.

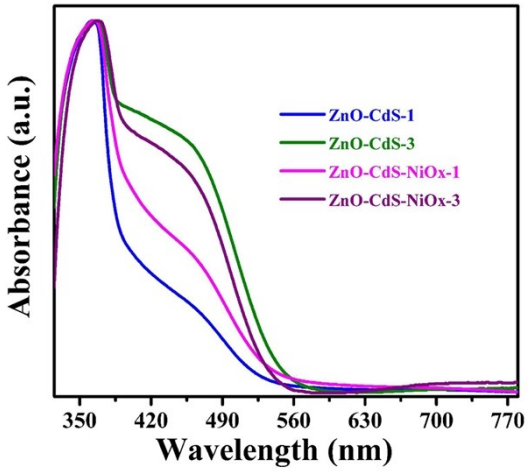

Fig. S6. The optical absorption spectra of samples.

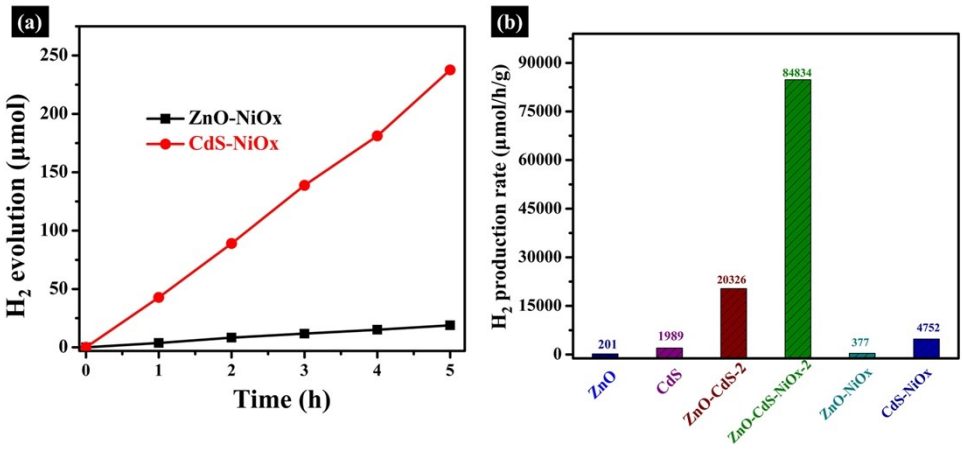

Fig. S7. (a) Time courses of ZnO-NiO_x and CdS-NiOx H_2 evolution, and (b) the compared H_2 evolution rates of ZnO, CdS, ZnO-CdS-2, ZnO-CdS-NiO_x-2, ZnO-NiO_x and CdS-NiO_x under simulated sunlight irradiation.

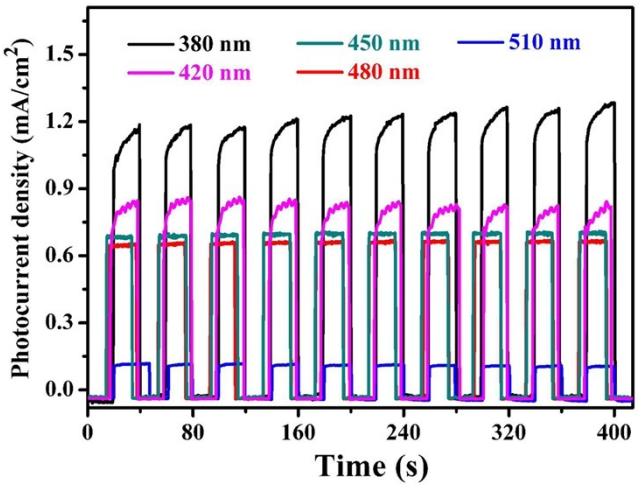

Fig. S8. Photocurrent responses of ZnO-CdS-NiO_x-2 measured at λ = 380, 420, 450, 480 and 510 nm, respectively.

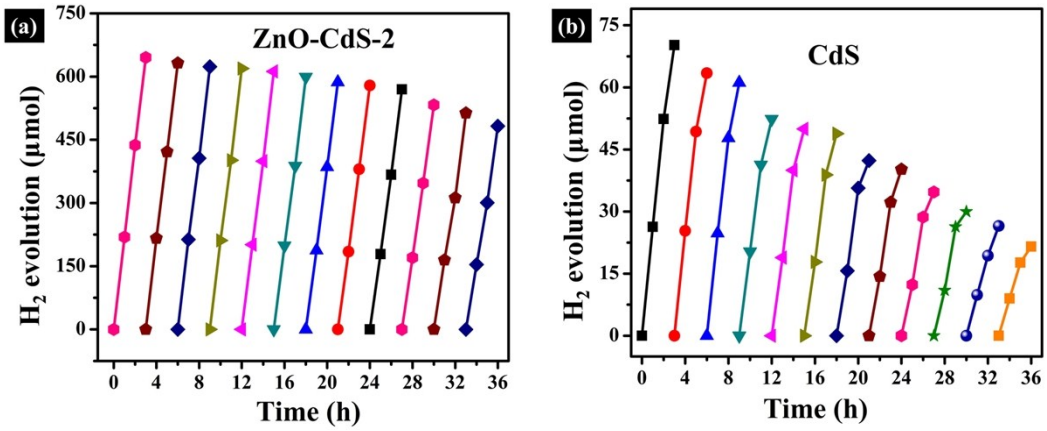

Fig. S9. Cycling runs for the photocatalytic hydrogen evolution activity under simulated sunlight of (a) ZnO-CdS-2 and (b) CdS.

Table S1. Comparison with previous ZnO-CdS heterostructure photocatalysts on H_2 evolution activity.

Photocatalyst	Light source	Sacrificing agent	Activity [mmol/h g]	Stability	AQE (%)	Photocurrent (mA/cm^2)	Ref
ZnO-CdS-NiO_x core@dual-shell nanorod	300W Xe lamp	Na_2S/Na_2SO_3	84.83	36 h	33.89	8.44@0.1 V	This work
CdS/ZnO nanofibers	500W Xe lamp（$\lambda \geq 420$ nm)	Na_2S/Na_2SO_3	0.35	24 h	-	-	3
ZnO/CdS microspheres	350W Xe lamp	Na_2S/Na_2SO_3	4.13	12 h	-	0.06	4
CdSQDs/ZnO nanosheets	300W Xe lamp（$\lambda \geq 420$ nm）	Na_2S/Na_2SO_3	22.12	25 h	-	0.5@0.5 V	5
NiO@Ni-ZnO/RGO/CdS	300W Xe lamp	Na_2S/Na_2SO_3	8.2	15 h	-	-	6
Pt/CdS/ZnO	300W Xe lamp	Na_2S/Na_2SO_3	4.41	-	-	-	7
CdS@ZnO	225W Xe lamp	Na_2S/Na_2SO_3	11.13	20 h	7.18	0.6@0.5 V	8
CdS-ZnO nanowires	300W Xe lamp	ascorbic Acid	9.61	-	-	-	9
CdS/ZnO	500W Xe lamp	Na_2S/Na_2SO_3	0.85	15 h	-	-	10
ZnO/NiO/$Cd_{1-x}Zn_xS$	450W Xe lamp	Na_2S/Na_2SO_3	17	12 h	15	-	11
NiO-ZnO–CdS	150W Xe lamp	Na_2S/Na_2SO_3	-	-	-	2.15@1.23V	12
NiO/CdS@ZnO	300W Xe lamp	Na_2S/Na_2SO_3	-	-	-	0.96@-0.6 V	13

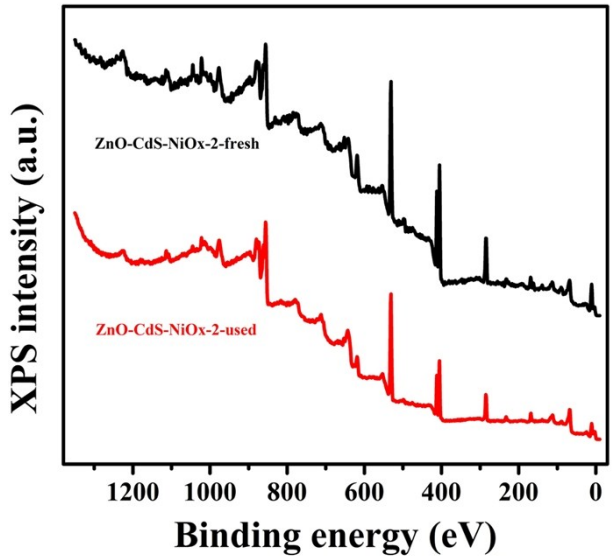

Fig. S10. XPS survey spectra of ZnO-CdS-NiO_x-2 before and after 12 cyclic usages.

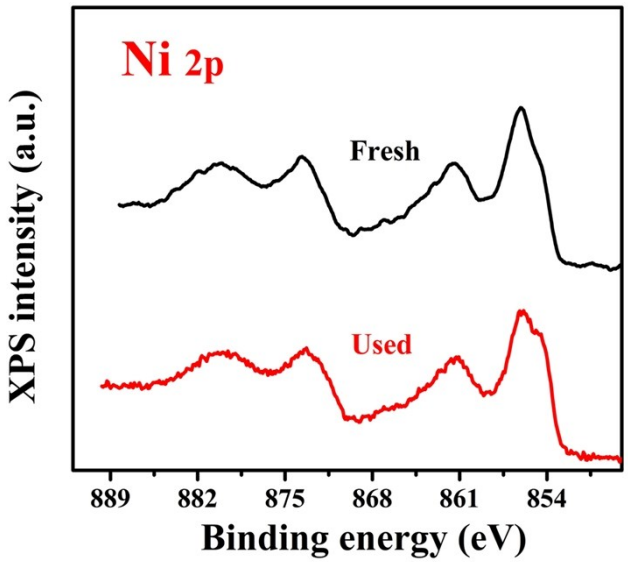

Fig. S11. High-resolution Ni 2p XPS spectra of ZnO-CdS-NiO_x-2 before and after 12 cyclic usages.

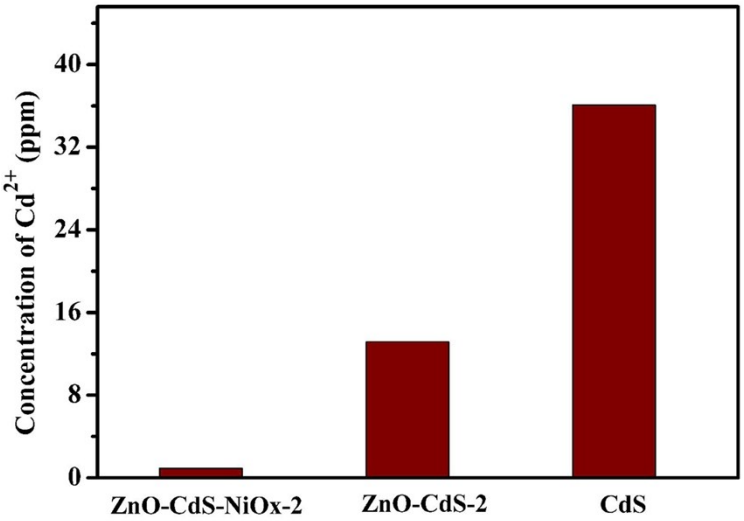

Fig. S12. The concentration of $Cd^{2+}$of CdS, ZnO-CdS-2 and ZnO-CdS-NiO_x-2 after 12 cyclic usages.

Table S2. The average fluorescence lifetimes of ZnO, ZnO-CdS-2 and ZnO-CdS-NiO_x-2, respectively.

Sample	**Lifetime, τ (ps)**	**Pre-exponential factors B (%)**	**Average lifetime τ (ps)**
ZnO	$\tau_1 = 257.55$ $\tau_2 = 257.55$	$B_1 = 52$ $B_2 = 48$	257.55
ZnO-CdS-2	$\tau_1 = 378.72$ $\tau_2 = 575.34$	$B_1 = 63.25$ $B_2 = 36.75$	450.98
ZnO-CdS-NiO_x-2	$\tau_1 = 492.23$ $\tau_2 = 691.41$	$B_1 = 71.38$ $B_2 = 28.62$	549.23

The biexponential function: $I(t) = B_1\exp(-t/\tau_1) + B_2\exp(-t/\tau_2)$ [14]

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