

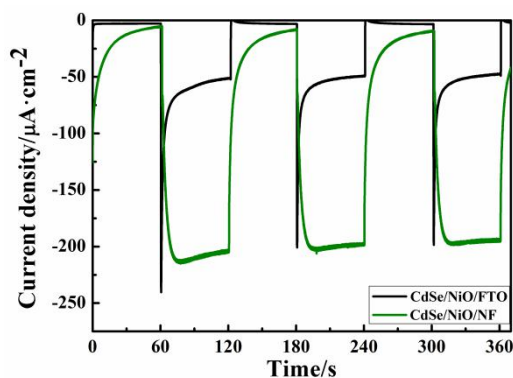
## Supplementary Information

### NiO nanowires as hole-transfer layer for drastic enhancement of CdSe-sensitized photocathodes

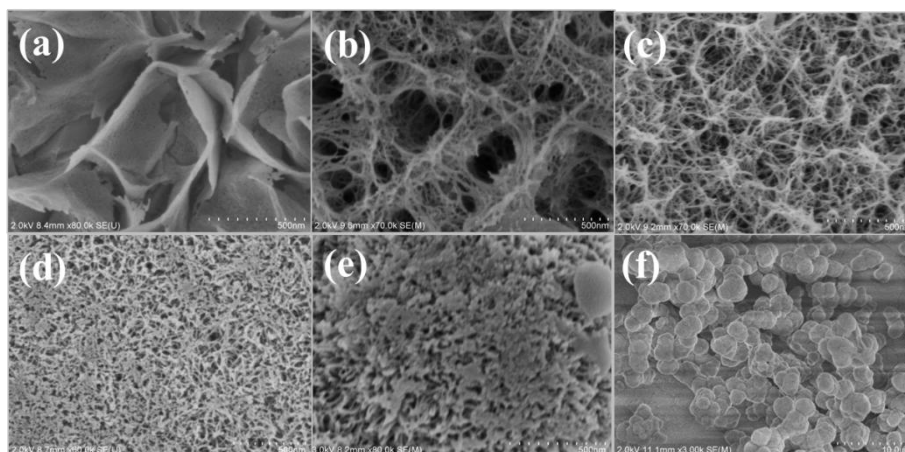
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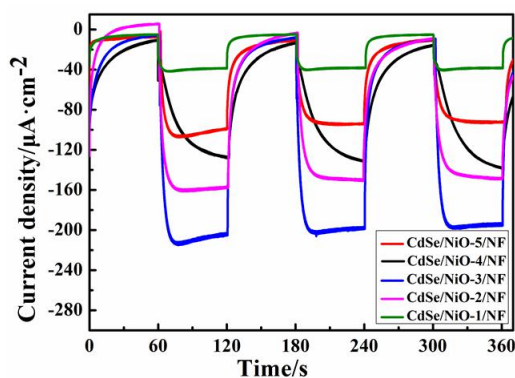
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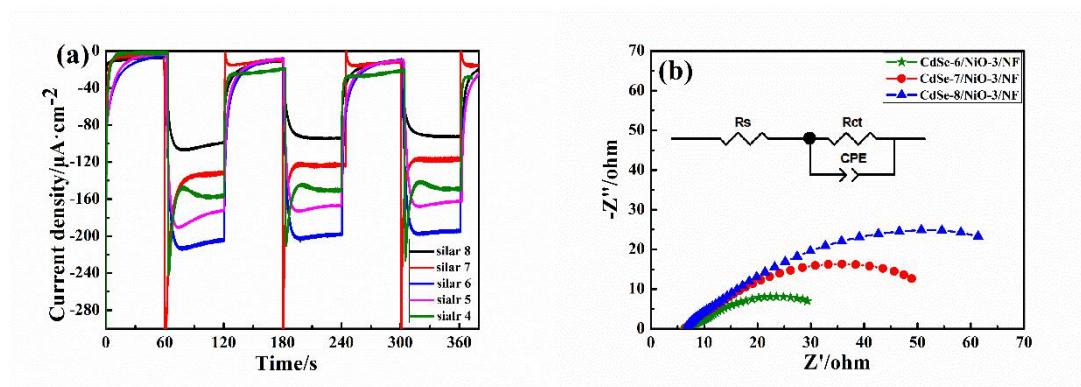
**Figure S1.** Photocurrent responses to on-off illumination of CdSe/NiO/FTO and CdSe/NiO/NF in air-saturated buffer solution (pH 6) at -0.222 V vs. Ag/AgCl. The NiO/NF(FTO) was prepared with 0.056 M  $\text{Ni}(\text{NO}_3)_2$  and 0.112 M  $\text{CO}(\text{NH}_2)_2$  precursor solution, and the SILAR cycle of CdSe was 6.



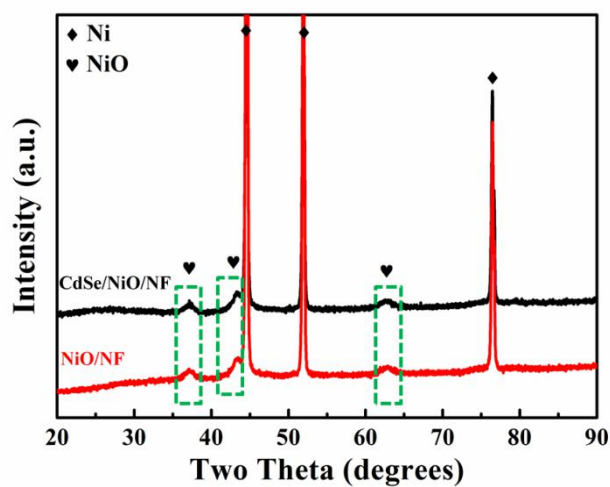
**Figure S2.** SEM images of (a) NiO-1/NF (b) NiO-2/NF(c) NiO-3/NF (d) NiO-4/NF (f) NiO-5/NF. (e) is the enlargement of (f). The NiO/NF prepared with 0.014 M  $\text{Ni}(\text{NO}_3)_2$  and 0.028 M  $\text{CO}(\text{NH}_2)_2$  precursor solution were signed as NiO-1/NF, and the electrode was signed as NiO-2/NF, NiO-3/NF, NiO-4/NF and NiO-5/NF when the concentrations of precursor solution is 2, 4, 6, 10 times of NiO-1/NF.)



**Figure S3.** Photocurrent responses to on-off illumination of CdSe/NiO/NF in air-saturated buffer solution (pH 6) at -0.222 V vs. Ag/AgCl. (The NiO/NF prepared with 0.014 M  $\text{Ni}(\text{NO}_3)_2$  and 0.028 M  $\text{CO}(\text{NH}_2)_2$  precursor solution were signed as NiO-1/NF, and the electrode was signed as NiO-2/NF, NiO-3/NF, NiO-4/NF and NiO-5/NF when the concentrations of precursor solution is 2, 4, 6, 10 times of NiO-1/NF, and the SILAR cycle of CdSe was 6).



**Figure S4.** (a) Photocurrent responses to on-off illumination of CdSe/NiO/NF with different CdSe-SILAR cycle numbers (4-8) in air-saturated buffer solution (pH 6) at -0.222 V vs. Ag/AgCl. (b) Nyquist plots of CdSe/NiO/NF with different CdSe-SILAR cycle numbers (6-8) in nitrogen-saturated buffer solution (pH 6) with an equivalent circuit model in the inset. (The NiO/NF was prepared with 0.056 M Ni(NO<sub>3</sub>)<sub>2</sub> and 0.112 M CO(NH<sub>2</sub>)<sub>2</sub> precursor solution.)



**Figure S5.** XRD patterns of NiO/NF and CdSe/NiO/NF photocathode. (The NiO/NF was prepared with 0.056 M Ni(NO<sub>3</sub>)<sub>2</sub> and 0.112 M CO(NH<sub>2</sub>)<sub>2</sub> precursor solution, and the SILAR cycle of CdSe was 6.)

**Table S1.** The results of EIS fitting into equivalent circuit model for CdSe/NiO/NF with different prepare conditions

Sample	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O (M)	CO(NH) <sub>2</sub> (M)	SILAR cycles of CdSe	R <sub>ct</sub> (Ω)	CPE (μF)
CdSe-6/NiO/NF	0.056	0.112	6	49.05	10.64
CdSe-7/NiO/NF	0.056	0.112	7	61.94	6.11
CdSe-8/NiO/NF	0.056	0.112	8	98.83	2.99

**Table S2.** Comparison of different NiO-based photocathodes in a three-electrode PEC cell for the HER

Photocathode	conditions	Cocatalysist	Photocurrent density at an applied potential (V vs. NHE)	Ref.
CdSe(SILAR)/NiO NWs/NF	buffer solution (pH=6); λ >400 nm	No	50 μA cm <sup>-2</sup> at -0.014 V	Present work
MoS <sub>2</sub> /CdSe (SILAR) /porous NiO/FTO	buffer solution (pH=6); λ >400 nm	MoS <sub>2</sub>	22 μA cm <sup>-2</sup> at -0.014 V	1
CdSe(SILAR)/ NiO/FTO	0.1 M LiClO <sub>4</sub> , 0.01 M PBS(pH= 6.8); λ > 420 nm	No	<20 μA cm <sup>-2</sup> at 0 to 0.5 V	2
CdS/NiO/ FTO	0.05 M Na <sub>2</sub> SO <sub>4</sub>	Cobaloxime	25 μA cm <sup>-2</sup> at 0 V	3
CdSe/NiO/FTO linker-engineered CdSe/NiO/FTO	0.1 M Na <sub>2</sub> SO <sub>4</sub> , (pH=6.8); λ >400 nm	No	8 μA cm <sup>-2</sup> 55 μA cm <sup>-2</sup> at -0.1 V	4 4
CdSe/NiO/FTO	0.1 M Na <sub>2</sub> SO <sub>4</sub> , (pH=6.8); λ >400 nm	CoP Co	102 μA cm <sup>-2</sup> 100 μA cm <sup>-2</sup> at 0 V	5 5

**Table S3.** The results of EIS fitting into equivalent circuit model for CdSe/NiO/NF with different prepare conditions

Sample	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O (M)	CO(NH) <sub>2</sub> (M)	SILAR cycles of CdSe	R <sub>ct</sub> (Ω)	CPE (μF)
CdSe/NiO-1/NF	0.014	0.028	6	202.2	0.57
CdSe/NiO-2/NF	0.028	0.056	6	117.4	2.50
CdSe/NiO-3/NF	0.056	0.112	6	49.05	10.64
CdSe/NiO-4/NF	0.084	0.168	6	71.77	3.49
CdSe/NiO-5/NF	0.14	0.28	6	161.4	0.72

### Notes and references

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- 2 M. A. Par, S. Y. Lee, J. H. Kim, S. H. Kang, H. Kim, C. J. Choi and K. S. Ahu, *Phys. Status Solidi A*, 2014, 211, 1868-1872.
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