Electronic Supplementary Information

One-pot "shielding-to-etching" strategy to synthesize amorphous MoS_2 modified $CoS/Co_{0.85}Se$ heterostructured nanotube arrays for boosted energy-saving H_2 generation

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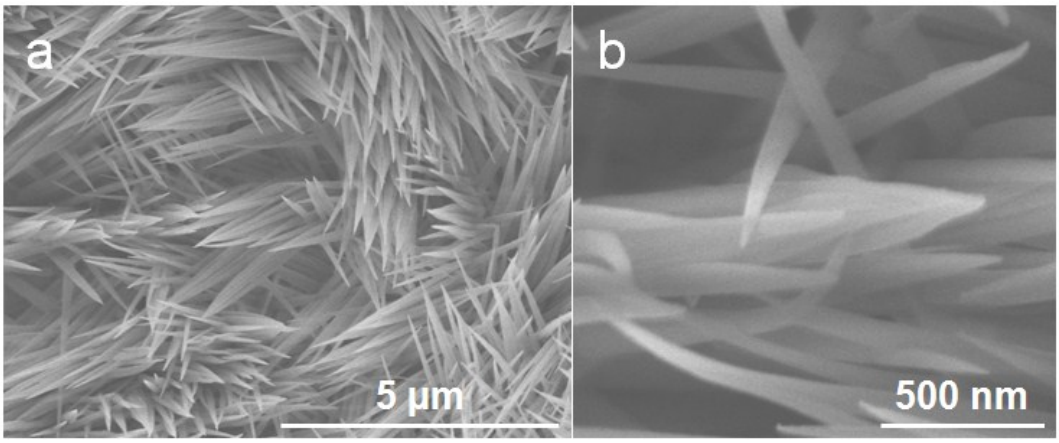


Fig. S1 SEM images of the as-prepared CCH NRs.

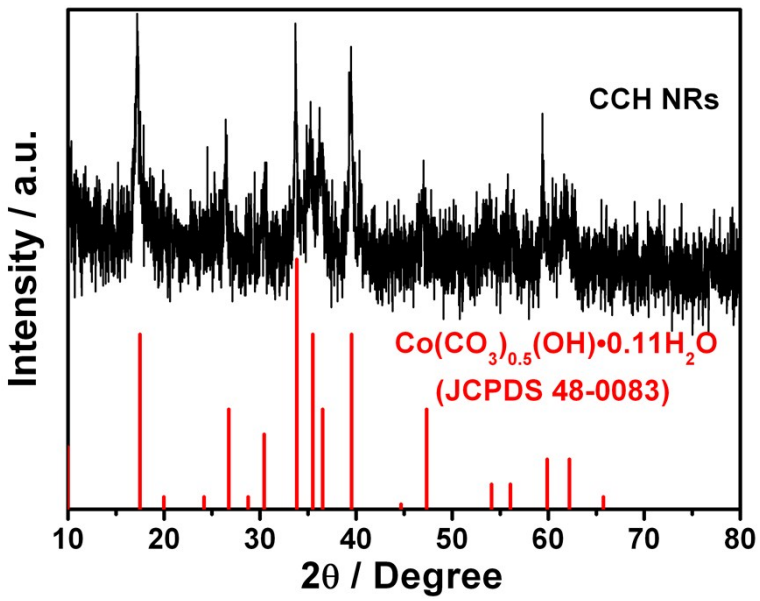


Fig. S2 XRD pattern of the as-prepared CCH NRs.

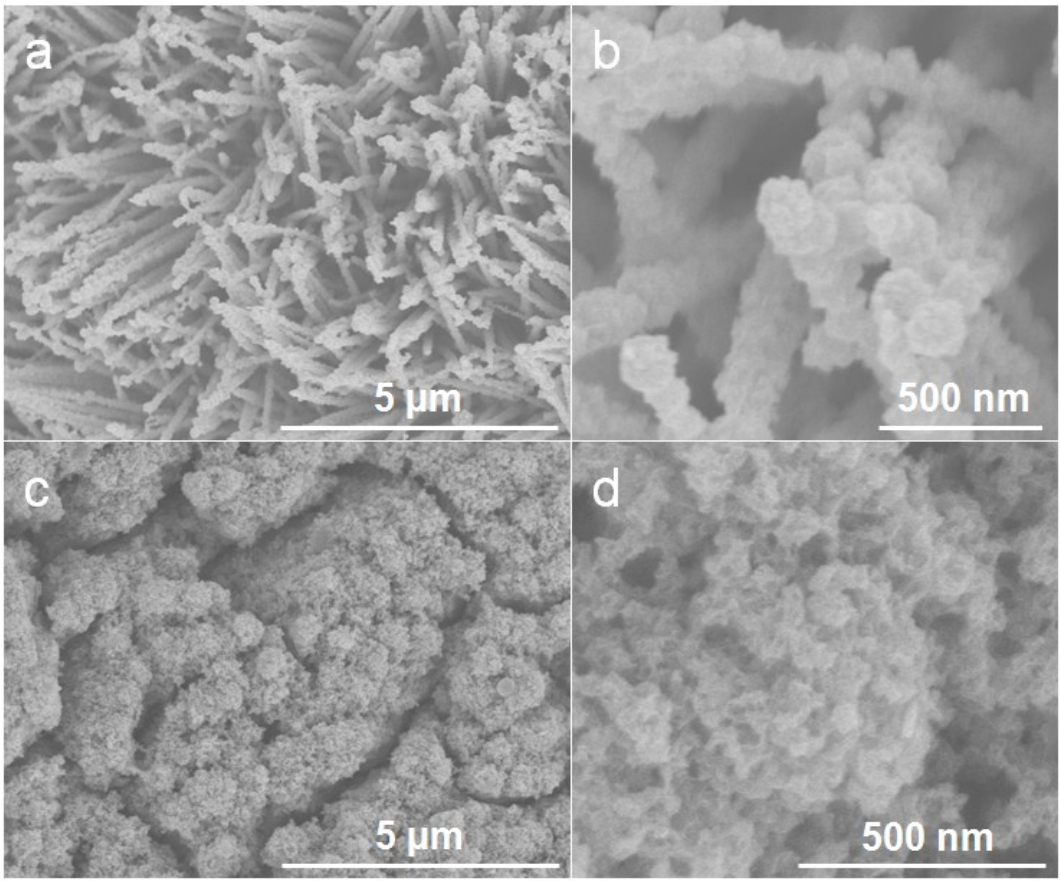


Fig. S3 SEM images of the as-prepared (a, b) $Co_{0.85}Se$ NRs and (c, d) a-MoS_2/CoS HNSs.

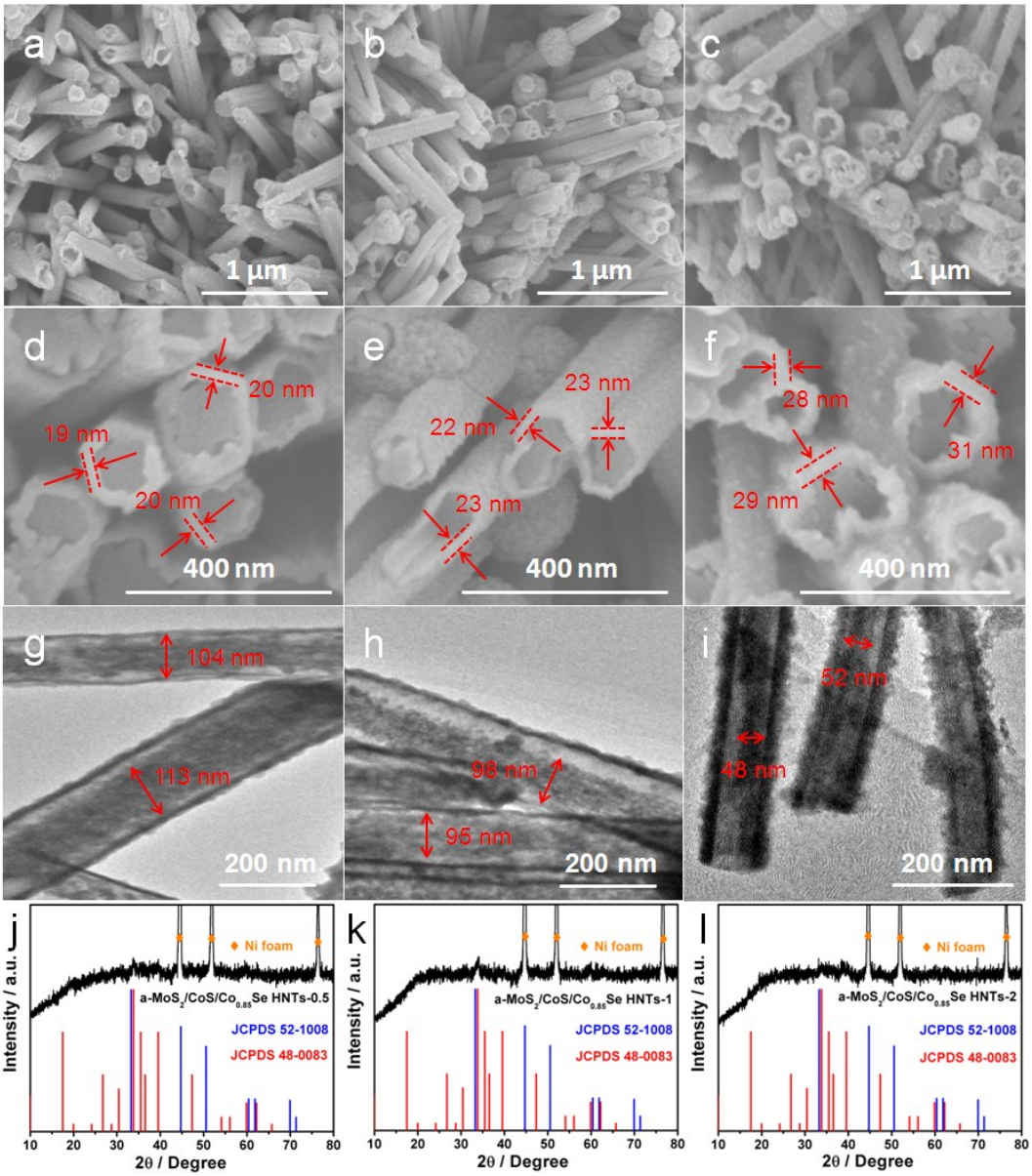


Fig. S4 SEM images of the as-prepared (a, d) a-MoS_2/CoS/$Co_{0.85}$Se HNTs-0.5, (b, e) a-MoS_2/CoS/$Co_{0.85}$Se HNTs-1 and (c, f) a-MoS_2/CoS/$Co_{0.85}$Se HNTs-2. TEM images of the as-prepared (g) a-MoS_2/CoS/$Co_{0.85}$Se HNTs-0.5, (h) a-MoS_2/CoS/$Co_{0.85}$Se HNTs-1, (i) a-MoS_2/CoS/$Co_{0.85}$Se HNTs-2. XRD patterns of the as-prepared (j) a-MoS_2/CoS/$Co_{0.85}$Se HNTs-0.5, (k) a-MoS_2/CoS/$Co_{0.85}$Se HNTs-1 and (l) a-MoS_2/CoS/$Co_{0.85}$Se HNTs-2.

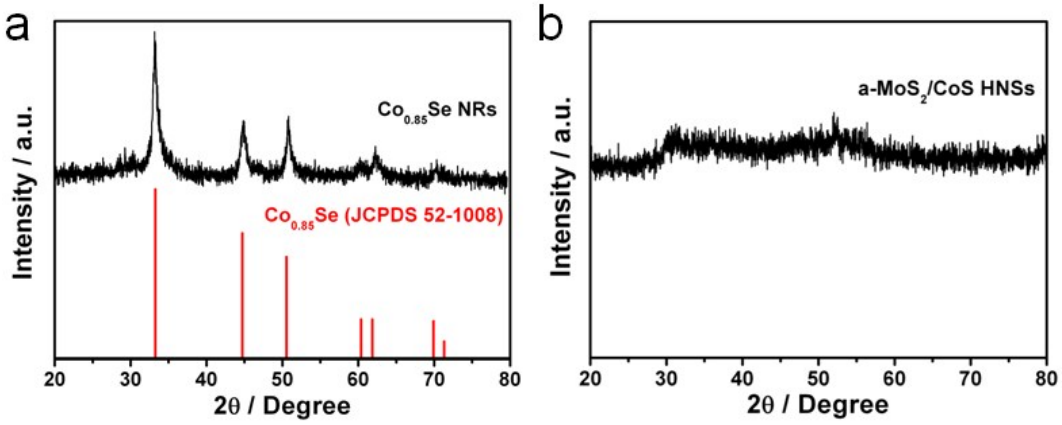


Fig. S5 XRD patterns of the as-prepared (a) $Co_{0.85}Se$ NRs and (b) a-MoS_2/CoS HNSs.

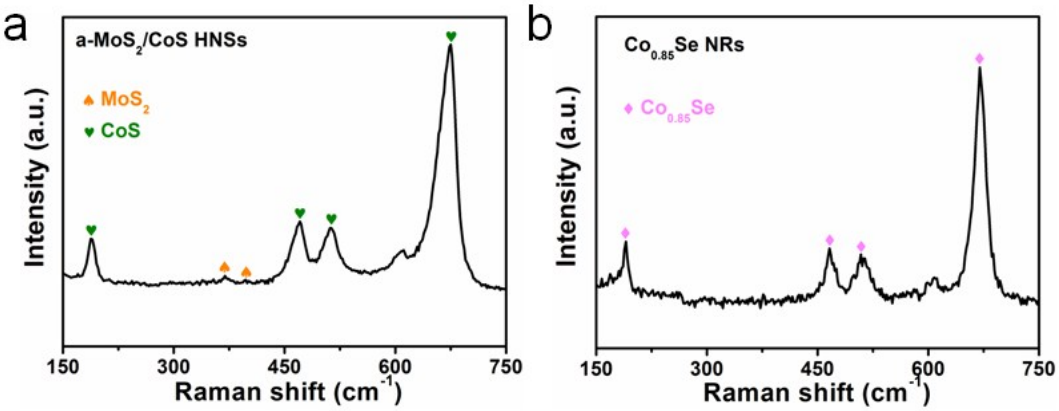


Fig. S6 Raman spectra of the as-prepared (a) a-MoS_2/CoS HNSs and (b) $Co_{0.85}Se$ NRs.

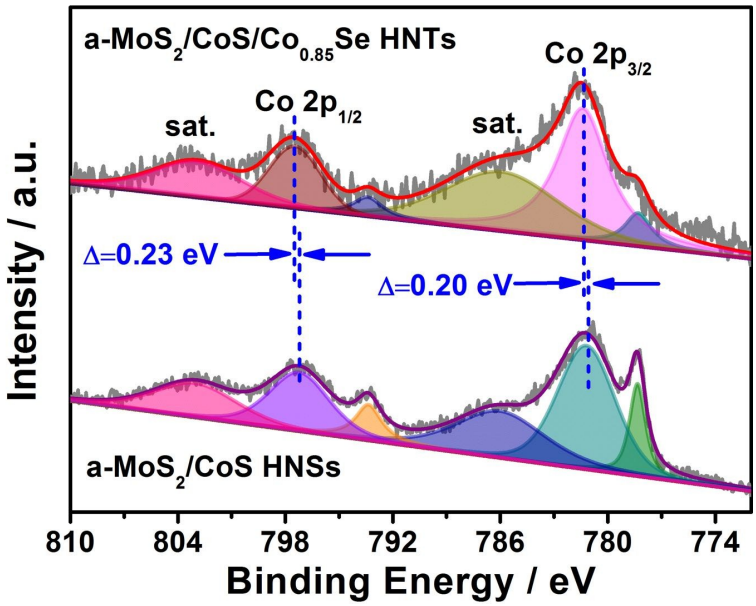


Fig. S7 High-resolution XPS spectra of Co 2p for the a-MoS_2/CoS/$Co_{0.85}$Se HNTs and a-MoS_2/CoS HNSs.

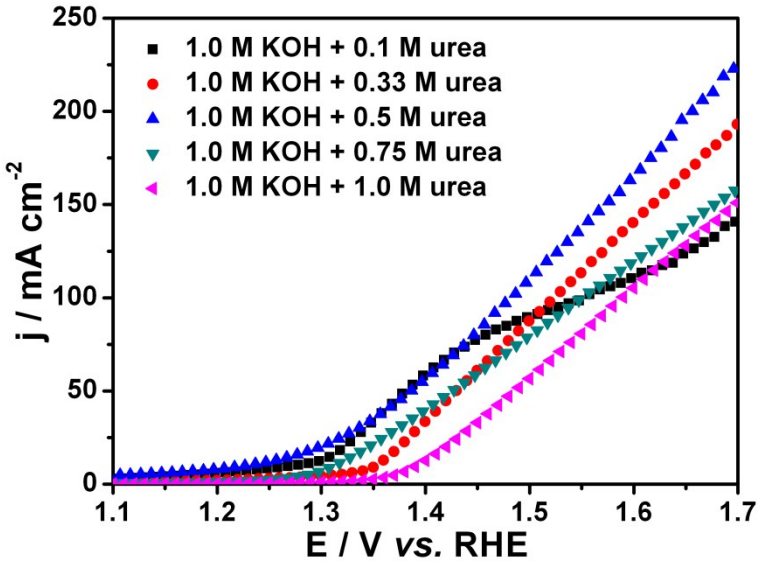


Fig. S8 Polarization curves of the a-MoS_2/CoS/$Co_{0.85}$Se HNTs in 1.0 M KOH with different urea concentration.

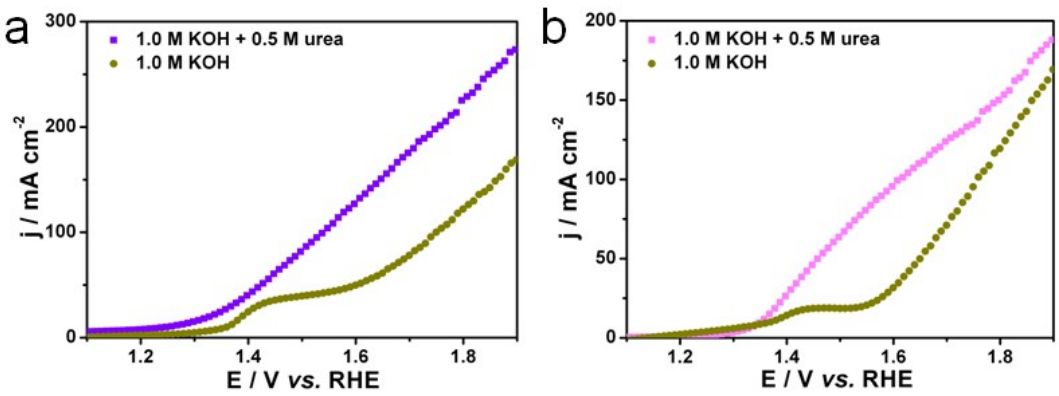


Fig. S9 Polarization curves for UOR and OER of the as-prepared (a) a-MoS_2/CoS HNSs and (b) $Co_{0.85}Se$ NRs.

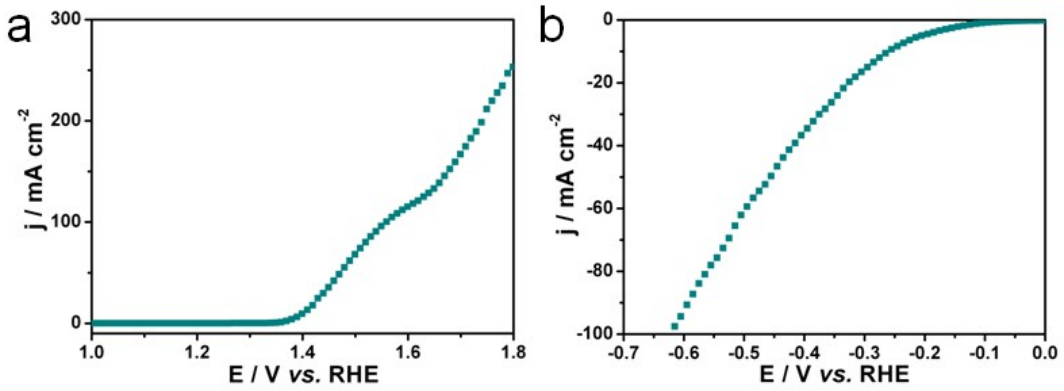
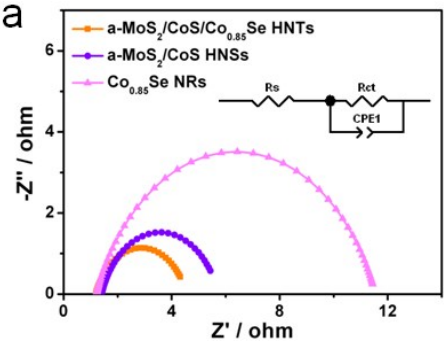


Fig. S10 Polarization curves of NF towards (a) UOR and (b) HER in 1.0 M KOH with 0.5 M urea.

a



b

	a-MoS_2/CoS /$Co_{0.85}$Se HNTs	a-MoS_2/CoS HNSs	$Co_{0.85}$Se NRs
R_s/Ω	1.20	1.41	1.21
R_{ct}/Ω	3.35	4.33	10.34
CPE1-T	0.38	0.32	0.12
CPE1-P	0.76	0.78	0.76

Fig. S11 (a) Nyquist plots of the a-MoS_2/CoS/$Co_{0.85}$Se HNTs, a-MoS_2/CoS HNSs and $Co_{0.85}$Se NRs and (b) the corresponding EIS data for UOR.

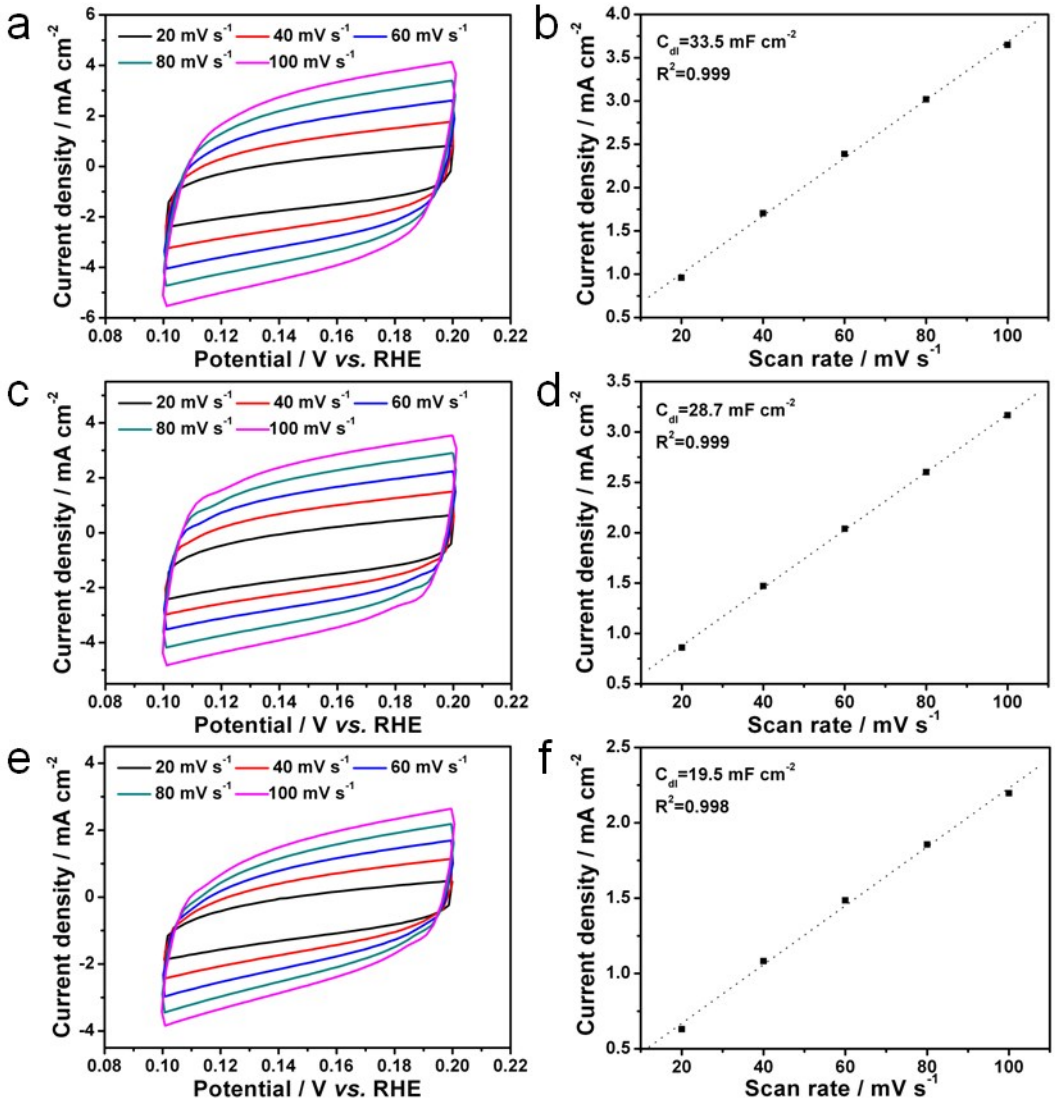


Fig. S12 CV curves and the plots of current density as a function of scan rate: (a, b) a-MoS_2/CoS/$Co_{0.85}$Se HNTs, (c, d) a-MoS_2/CoS HNSs and (e, f) $Co_{0.85}$Se NRs electrodes in the double layer region at scan rates of 20, 40, 60, 80 and 100 mV s^{-1} in 1.0 M KOH with 0.5 M urea.

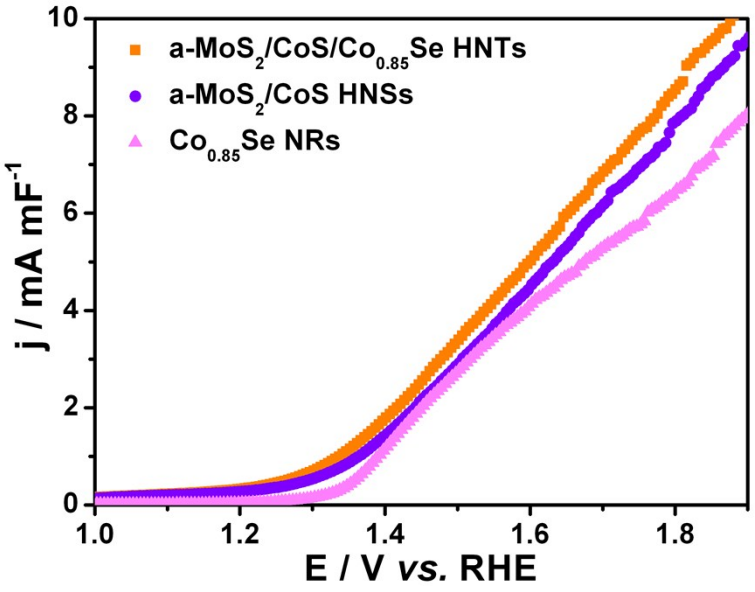


Fig. S13 UOR polarization curves of the different samples normalized by ECSA.

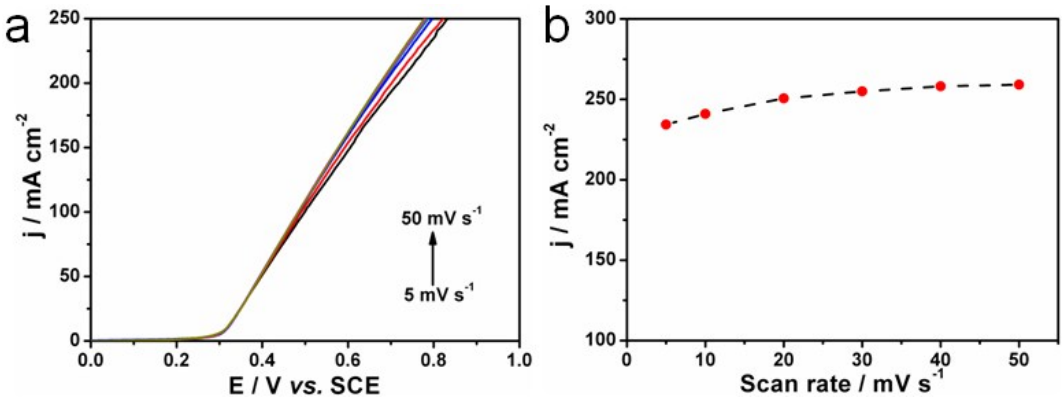


Fig. S14 (a) UOR polarization curves of the a-MoS_2/CoS/$Co_{0.85}$Se HNTs electrode at different scan rates. (b) The corresponding current densities at 0.8 V versus SCE with different scan rates.

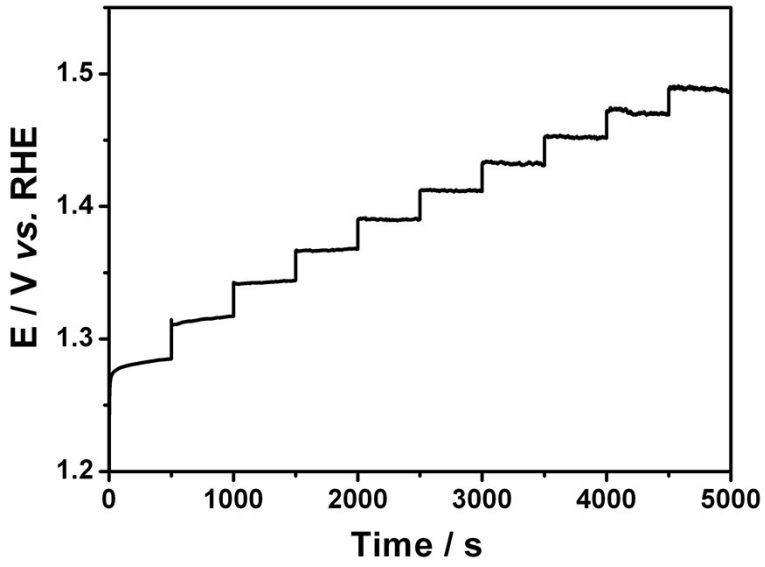


Fig. S15 Multi-current process of a-MoS_2/CoS/$Co_{0.85}$Se HNTs electrode. The current density started at 10 mA cm^{-2} and ended at 110 mA cm^{-2} with an increment of 10 mA cm^{-2} per 500 s.

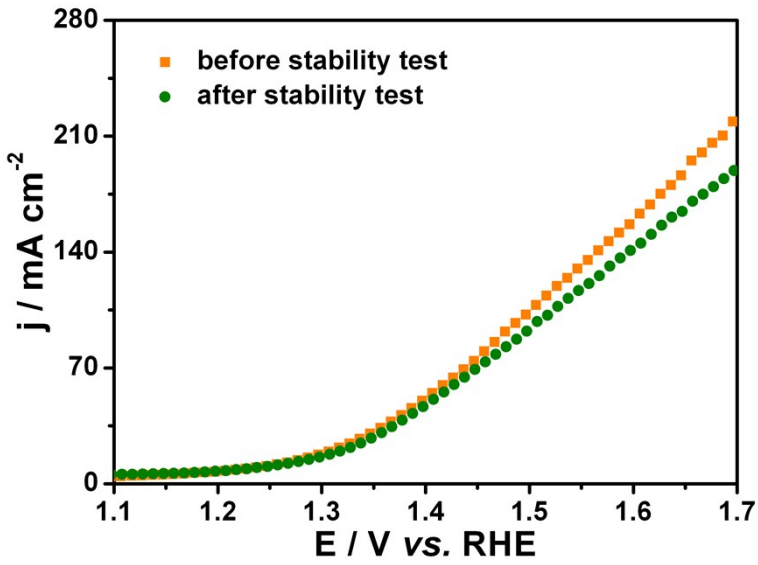


Fig. S16 Polarization curves of the as-prepared a-MoS_2/CoS/$Co_{0.85}$Se HNTs electrode before and after long-term stability test.

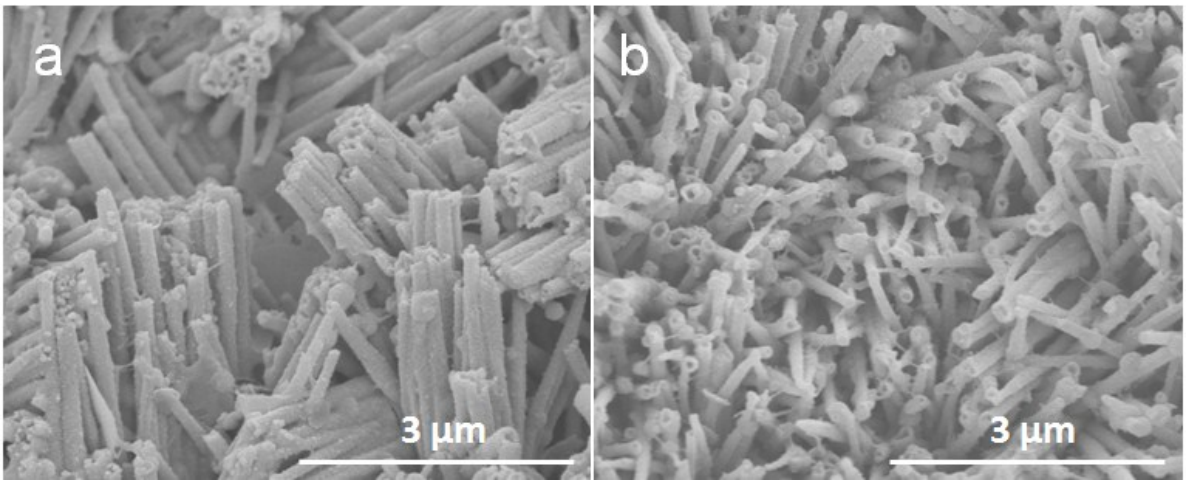
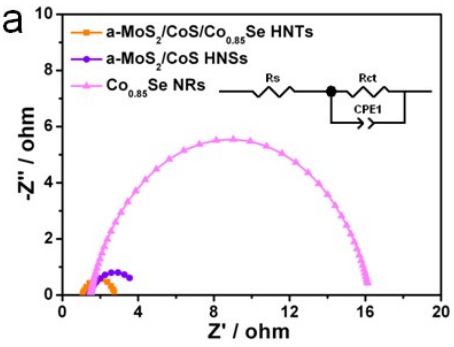


Fig. S17 SEM images of the a-MoS_2/CoS/$Co_{0.85}$Se HNTs electrode after long-term stability test for (a) UOR and (b) HER.

a



b

	a-MoS_2/CoS /$Co_{0.85}$Se HNTs	a-MoS_2/CoS HNSs	$Co_{0.85}$Se NRs
R_s/Ω	1.07	1.41	1.48
R_{ct}/Ω	1.72	2.74	14.78
CPE1-T	0.28	0.92	0.02
CPE1-P	0.75	0.68	0.82

Fig. S18 (a) Nyquist plots of the a-MoS_2/CoS/$Co_{0.85}$Se HNTs, a-MoS_2/CoS HNSs and $Co_{0.85}$Se NRs electrodes and (b) the corresponding EIS data for HER.

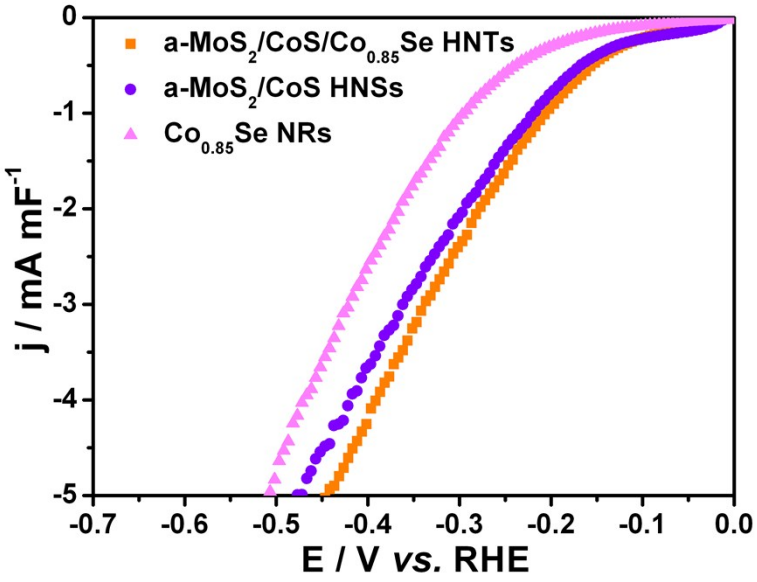


Fig. S19 HER polarization curves of the different samples normalized by ECSA.

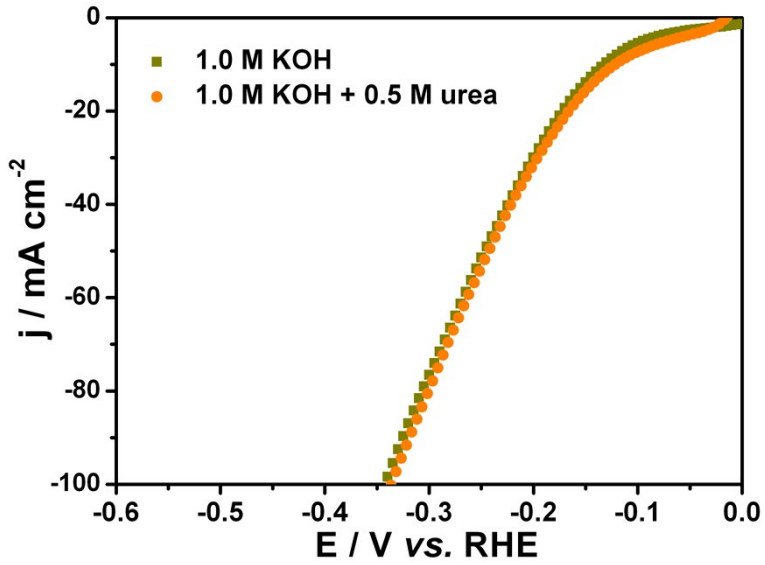


Fig. S20 Polarization curves of the as-prepared a-MoS_2/CoS/$Co_{0.85}$Se HNTs in 1.0 M KOH with and without 0.5 M urea.

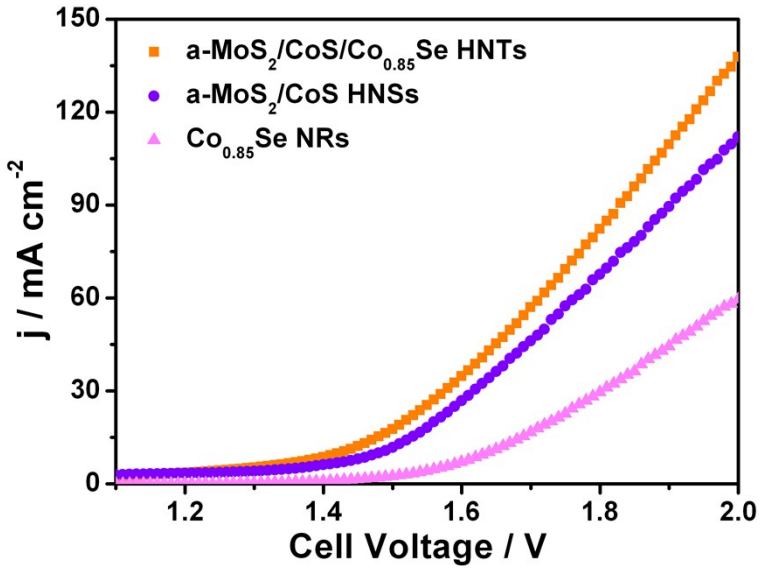


Fig. S21 Polarization curves for the as-prepared a-MoS_2/CoS/$Co_{0.85}$Se HNTs, a-MoS_2/CoS HNSs and $Co_{0.85}$Se NRs electrodes in 1.0 M KOH with 0.5 M urea.

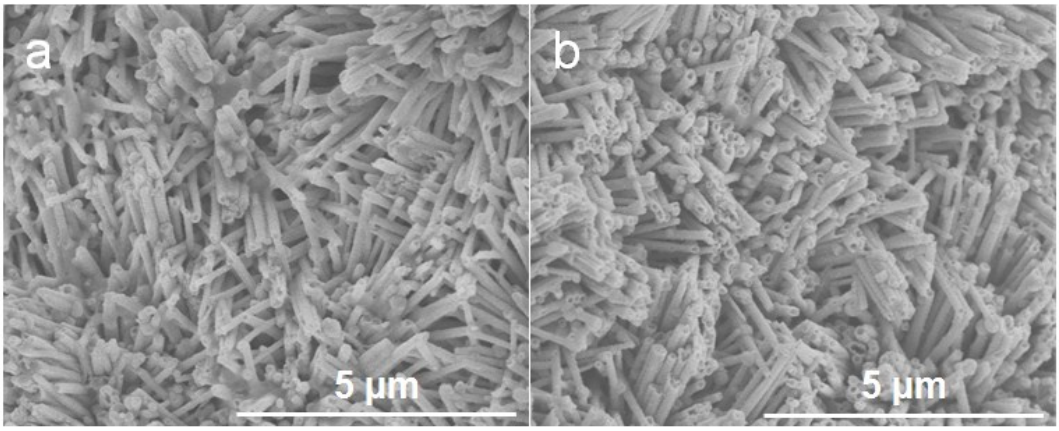


Fig. S22 SEM images of the as-prepared a-MoS_2/CoS/$Co_{0.85}$Se HNTs electrode after (a) UOR and (b)HER.

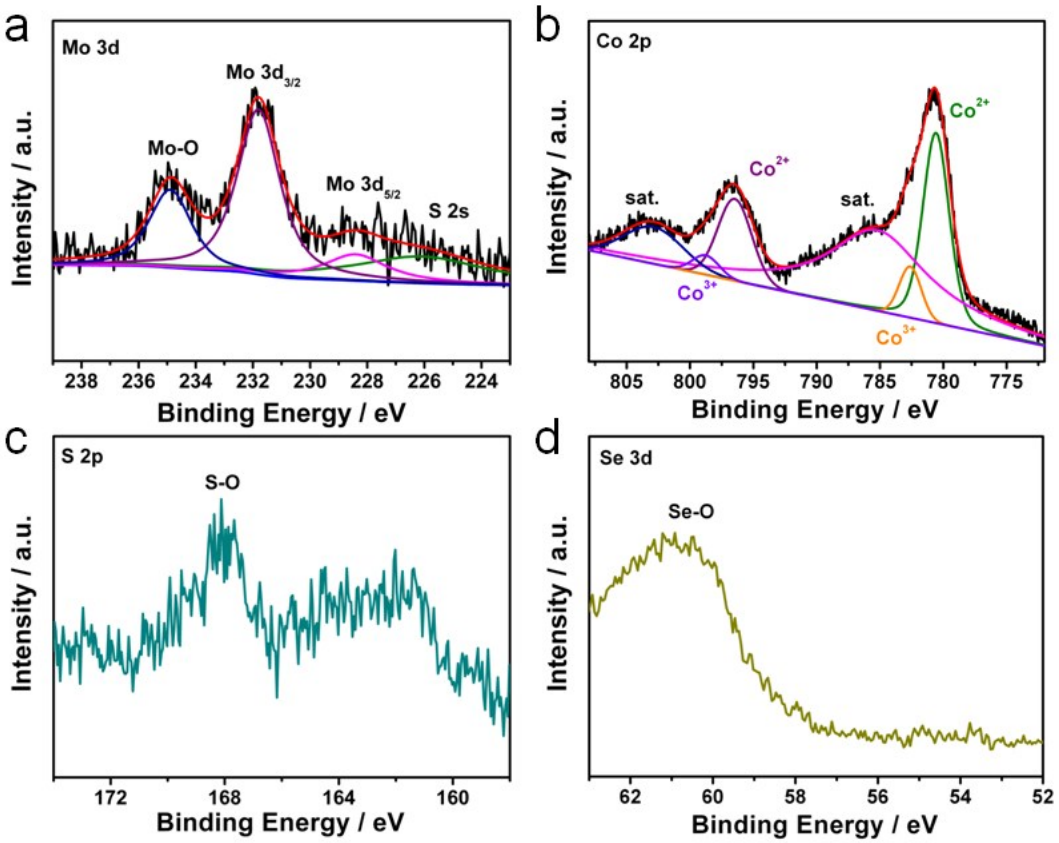


Fig. S23 High-resolution XPS spectra of a) Mo 3d, b) Co 2s, c) S 2p and e) Se 3d for the as-prepared a-MoS_2/CoS/$Co_{0.85}Se$ HNTs electrode after UOR.

Table S1. Comparison of the UOR electrocatalytic performance of the as-prepared a-MoS_2/CoS/$Co_{0.85}$Se HNTs with other report electrocatalysts in 1.0 M KOH and a certain concentration of urea.

Catalyst	The concentration of Urea	Potential (V)	References
a-MoS_2/CoS/$Co_{0.85}$Se HNTs	**0.5 M urea**	**$E_{(50\ mA\ cm-2)}$=1.38**	**This work**
HC-NiMoS/Ti	0.5 M urea	$E_{(60\ mA\ cm-2)}$=1.38	1
CoS_2 NA/Ti	0.3 M urea	$E_{(10\ mA\ cm-2)}$=1.40	2
Ni_3Se_4 nanorod	0.1 M urea	$E_{(10\ mA\ cm-2)}$=1.38	3
MnO_2/$MnCo_2O_4$@Ni	0.5 M urea	$E_{(10\ mA\ cm-2)}$=1.43	4
Ni-Mo nanotube	0.1 M urea	$E_{(50\ mA\ cm-2)}$=1.39	5
NF/NiMoO-Ar	0.5 M urea	$E_{(10\ mA\ cm-2)}$=1.37	6
$Fe_{11.1\%}$-Ni_3S_2/NF	0.33 M urea	$E_{(10\ mA\ cm-2)}$= 1.44	7
L-MnO_2	0.5 M urea	$E_{(10\ mA\ cm-2)}$=1.37	8

Table S2. Comparison of the HER electrocatalytic performance of the as-prepared a-MoS_2/CoS/$Co_{0.85}$Se HNTs with other report electrocatalysts.

Catalyst	electrolyte	Overpotential (mV) at 10 mA cm^{-2}	References
a-MoS_2/CoS/$Co_{0.85}$Se HNTs	**1.0 M KOH**	**127**	**This work**
Co_3S_4/MoS_2/Ni_2P NTs	1.0 M KOH	178	9
MoS_2/$Fe_5Ni_4S_8$/FeNi foam	1.0 M KOH	122	10
Co_9S_8/MoS_x NTs	0.5 M H_2SO_4	161	11
Ni-Co-MoS_2 NBs	0.5 M H_2SO_4	155	12
$CoMoS_4$ NS/CC	1.0 M PBi	183	13
Co-BDC/MoS_2	1.0 M KOH	155	14
(Ni, Fe)S_2@MoS_2	1.0 M KOH	130	15
Co_9S_8@MoS_2/CNFs	0.5 M H_2SO_4	190	16

Table S3. Comparison of the performance of the as-prepared a-MoS_2/CoS/$Co_{0.85}Se$ HNTs with other report electrocatalysts for overall urea electrolysis in 1.0 M KOH and a certain concentration of urea.

Catalyst	The concentration of Urea	Potential (V)	References
a-MoS_2/CoS/$Co_{0.85}Se$/NF NTs	**0.5 M urea**	**$E_{(10\ mA\ cm-2)}$=1.42**	**This work**
HC-NiMoS/Ti	0.5 M urea	$E_{(10\ mA\ cm-2)}$= 1.59	1
NF/NiMoO-Ar ‖ NF/NiMoO-H_2	0.5 M urea	$E_{(10\ mA\ cm-2)}$= 1.38	6
MnO_2/$MnCo_2O_4$/Ni	0.5 M urea	$E_{(10\ mA\ cm-2)}$= 1.55	4
$Fe_{11.1\%}$-Ni_3S_2/NF	0.33 M urea	$E_{(10\ mA\ cm-2)}$= 1.46	7
MoS_2/Ni_3S_2	0.33 M urea	$E_{(20\ mA\ cm-2)}$= 1.45	17
NiCoP/CC	0.5 M urea	$E_{(10\ mA\ cm-2)}$= 1.42	18
Ni_2P/CFC	0.33 M urea	$E_{(10\ mA\ cm-2)}$= 1.44	19
Ni-Mo nanotube	0.1 M urea	$E_{(10\ mA\ cm-2)}$= 1.43	5
Ni/C	0.33 M urea	$E_{(10\ mA\ cm-2)}$= 1.60	20

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