Electronic Supplementary Information for

A phosphorus modified mesoporous AuRh film as an efficient bifunctional electrocatalyst for urea-assisted energy-saving hydrogen production

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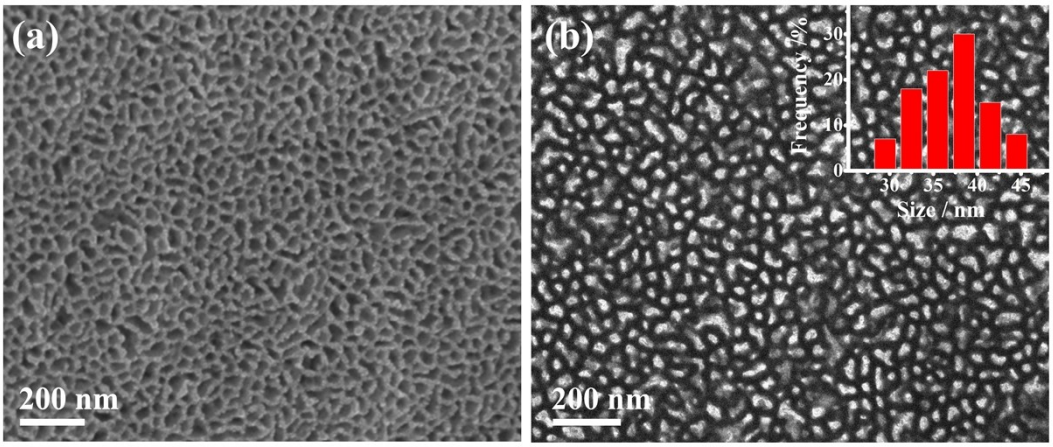

Fig. S1 (a) SEM image of the mAuRh film/NF and (b) TEM image of the mAuRh film. The inset of (b) represents the pore-size distribution histogram of mAuRh film.

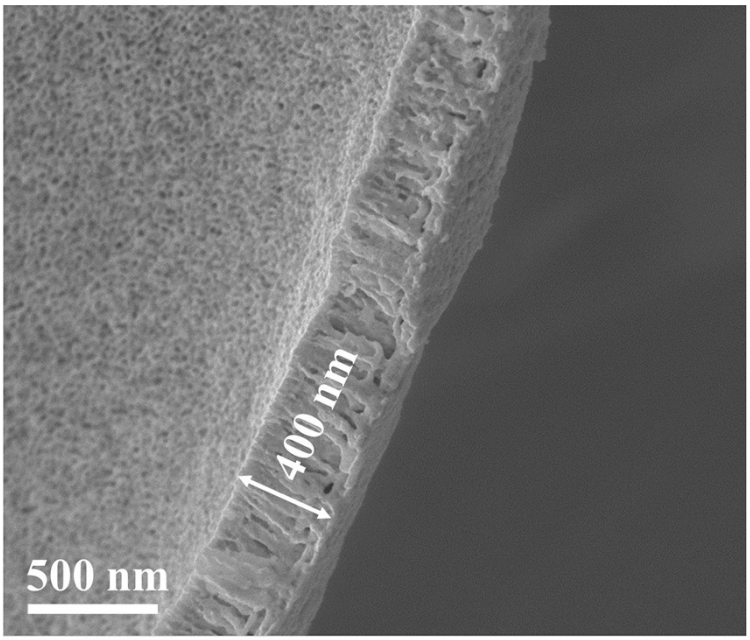

Fig. S2 Cross-sectional SEM image of P-mAuRh film/NF.

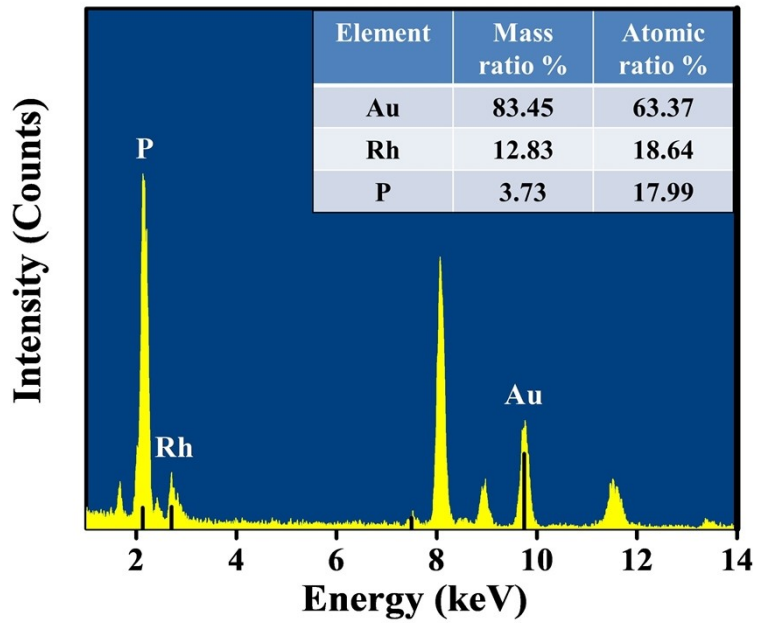

Fig. S3 EDX spectrum of P-mAuRh film.

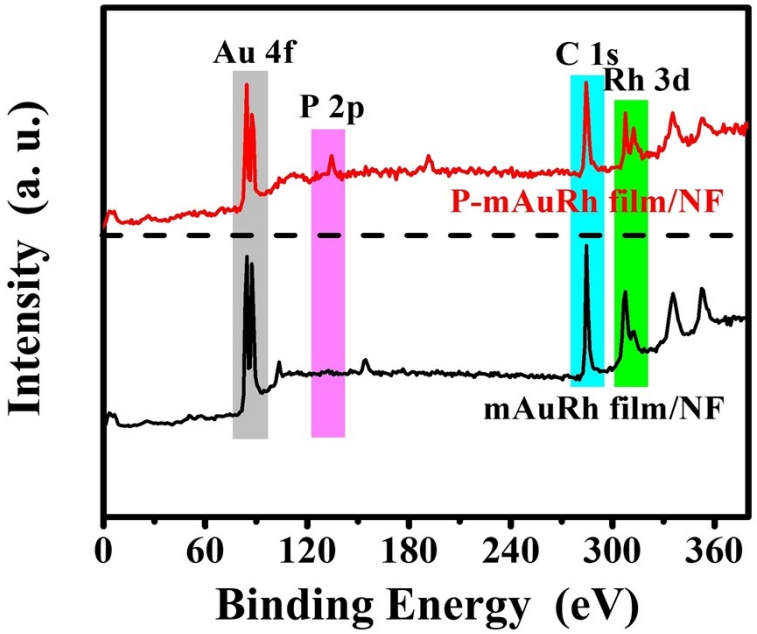

Fig. S4 XPS survey spectra of P-mAuRh film and mAuRh film.

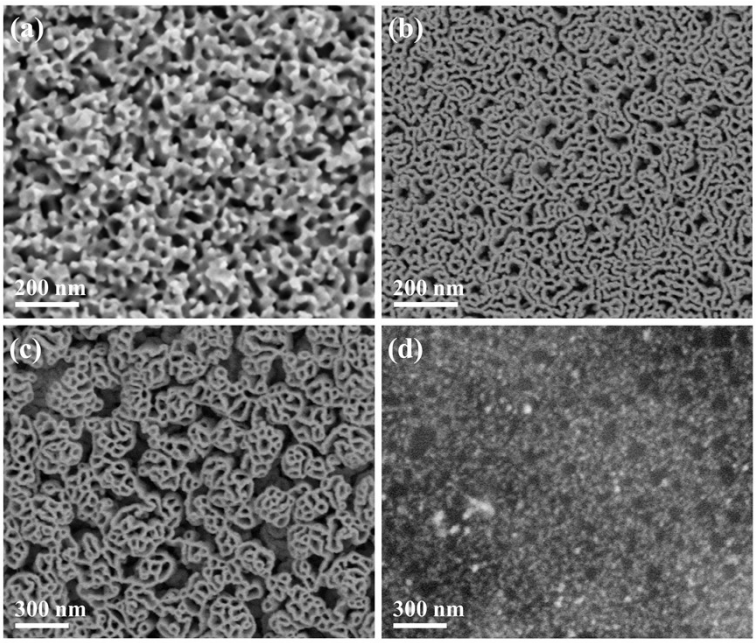

Fig. S5 SEM images of mAuRh film/NF obtained with different molar rations of metal precursors: (a) Au_4Rh_0, (b) Au_1Rh_1, (c) Au_1Rh_3 and (d) Au_0Rh_4.

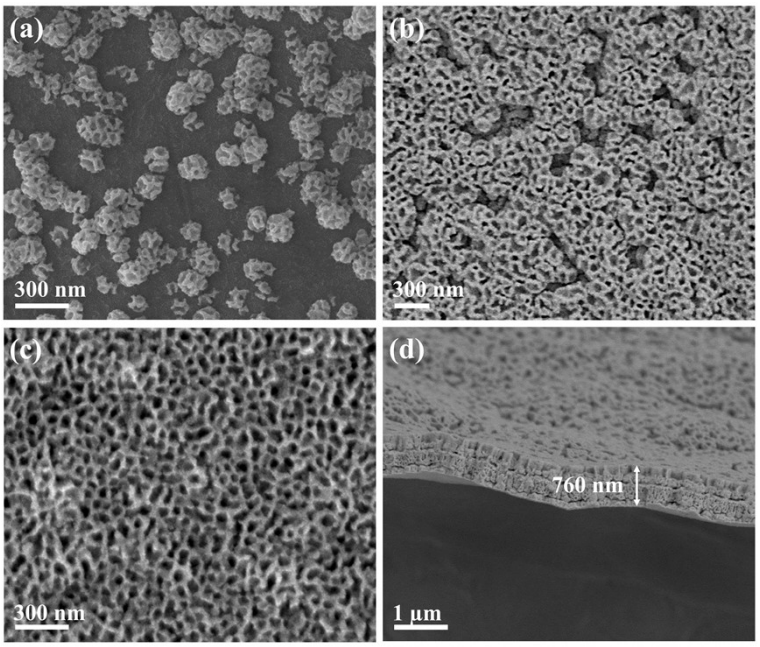

Fig. S6 SEM images of mAuRh film/NF taken from different soaking times: (a) 20 min, (b) 60 min, (c) 180 min, respectively, and (d) the cross-section image of mAuRh film/NF taken from 180 min.

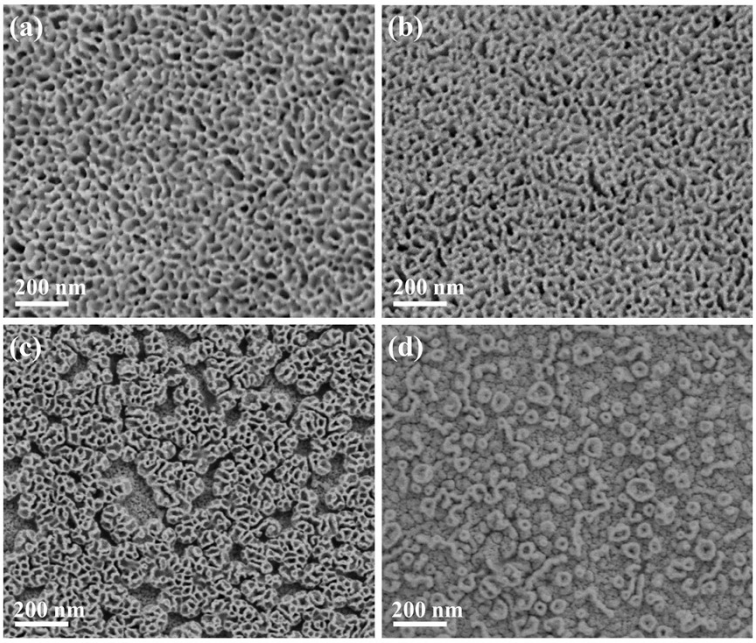

Fig. S7 SEM images of P-mAuRh film/NF under different heating treatment times: (a) 3 h, (b) 4 h, (c) 6 h and (d) 8 h.

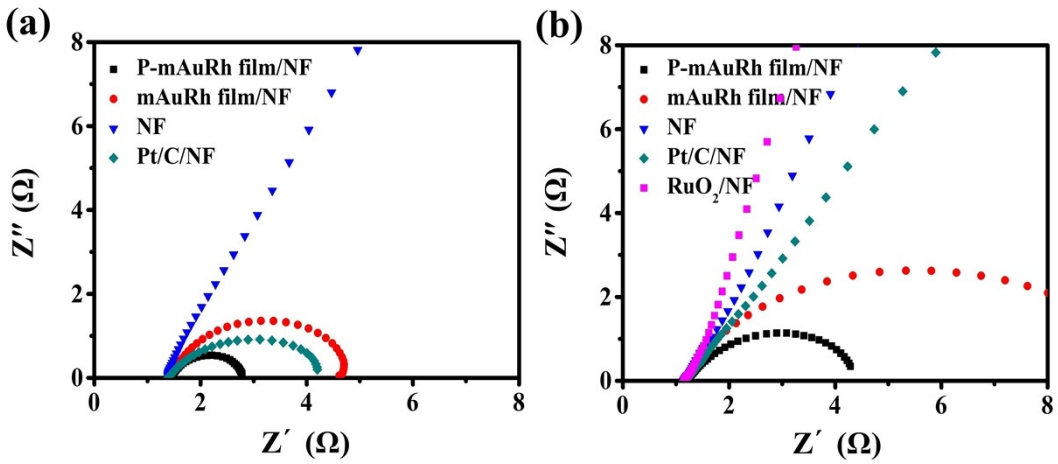

Fig. S8 EIS curves of different catalysts for (a) HER at -0.12 V (*vs*. RHE) and (b) UOR at 1.35 V (*vs*. RHE).

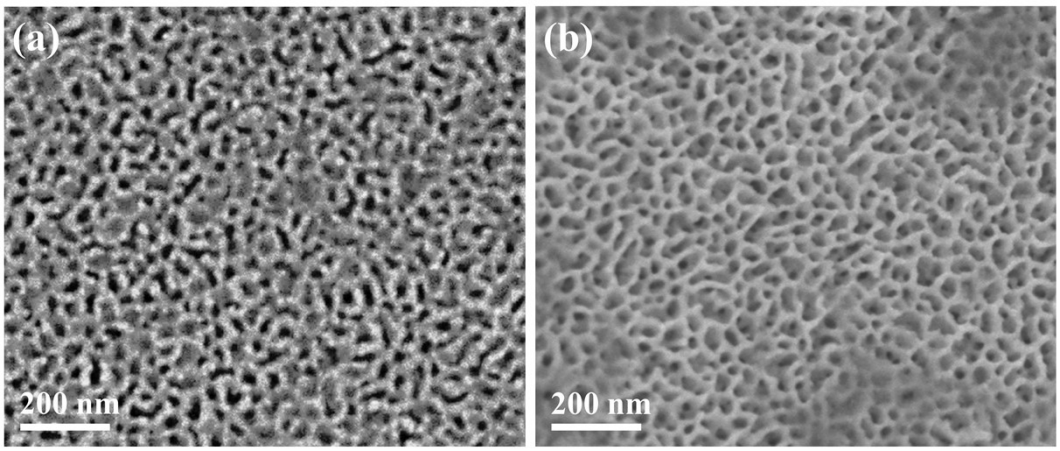

Fig. S9 SEM images of P-mAuRh film/NF after long-term durability tests for (a) HER and (b) UOR.

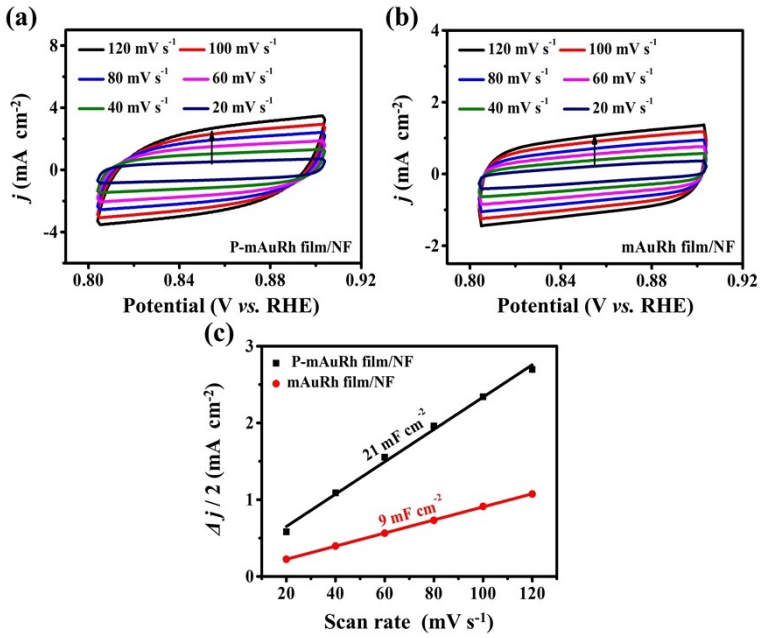

Fig. S10 CV curves of (a) P-mAuRh film/NF, (b) mAuRh film/NF from 0.804 to 0.904 V (*vs*. RHE).

(c) C_{dl} curves of different catalysts at 0.854 V (*vs*. RHE) in 1.0 M KOH solution.

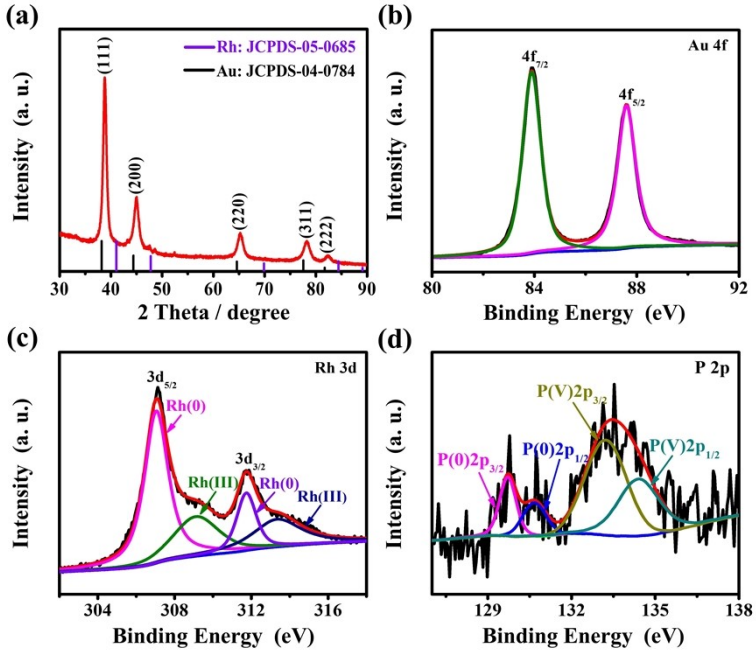

Fig. S11 (a) XRD pattern, (b) Au 4f, (c) Rh 3d and (d) P 2p XPS spectra of P-mAuRh film/NF after long-term durability test for UOR.

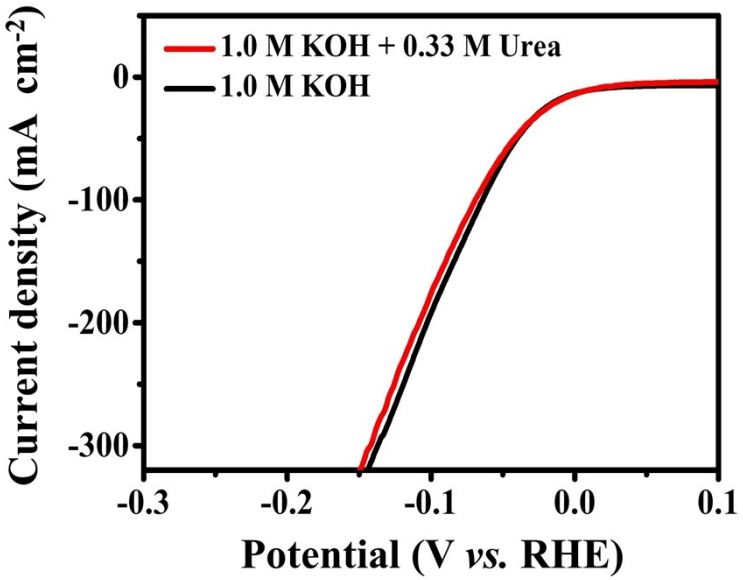

Fig. S12 LSV curves of P-mAuRh film/NF in 1.0 M KOH with and without 0.33 M urea for HER.

Table S1 HER performance comparison between the P-mAuRh film/NF and some other reported electrocatalysts.

Electrocatalysts	Electrolytes	substrate	Current density (mA cm^{-2})	Overpotential (mV *vs*. RHE)	Ref.
P-mAuRh film/NF	**1.0 M KOH**	**NF**	**50**	**45**	**This work**
			100	**73**	
Co-NCNTFs/NF	1.0 M KOH	NF	10	141	[1]
Ni_2P-UNMs/NF	1.0 M KOH	NF	10	75	[2]
Mo/Mn-Ni_xS_y/NF	1.0 M KOH	NF	10	144	[3]
$Ni_{1.8}Cu_{0.2}$-P/NF	1.0 M KOH	NF	10	78	[4]
Co-NT/NF	1.0 M KOH	NF	10	178	[5]
Mn-doped NiS_2/NF	1.0 M KOH	NF	10	71	[6]
NiSe/NF	1.0 M KOH	NF	10	96	[7]
N-NiS/MoS_2-NF	1.0 M KOH	NF	10	71	[8]
NiCoP-CoP/NF	1.0 M KOH	NF	10	73	[9]
Ni_xP-400	1.0 M KOH	NF	10	71	[10]

Table S2 UOR performance comparison between the P-mAuRh film/NF and some other reported electrocatalysts.

Electrocatalysts	Electrolytes	substrate	Current density (mA cm^{-2})	Potential (V *vs*. RHE)	Ref.
P-mAuRh film/NF	**1.0 M KOH/ 0.33 M urea**	**NF**	**50**	**1.35**	**This work**
			100	**1.358**	
MoS_2/Ni_3S_2/NF	1.0 M KOH/ 0.33 M urea	NF	200	1.35	[11]
α- $Ni(OH)_2$/NF	1.0 M KOH/ 0.33 M urea	NF	10	1.44	[12]
			100	1.73	
$NiCo_2S_4$ NS/CC	1.0 M KOH/ 0.33 M urea	CC	10	1.45	[13]
Ni/C-1	1.0 M KOH/ 0.33 M urea	-	10	1.36	[14]
$Ni_{(10\%)}Pd_{(10\%)}$/OMC	1.0 M KOH/ 0.33 M urea	OMC	30	1.346	[15]
$Ni(OH)_2$//F-Ni_3S_2/NF (NF-20)	1.0 M KOH/ 0.33 M urea	NF	50	1.36	[16]
Fe doped α- $Ni(OH)_2$/NF	1.0 M KOH/ 0.33 M urea	NF	100	1.408	[17]
$Ni(OH)_2$ NS@NW/NF	1.0 M KOH/ 0.33 M urea	NF	10	1.408	[18]
Ni-Co_9S_8/CC	1.0 M KOH/ 0.33 M urea	CC	100	1.43	[19]
$Ni_{1.5}Mn_{1.5}O_4$	1.0 M KOH/ 0.33 M urea	-	6.9	1.338	[20]
Ni MOF	1.0 M KOH/ 0.33 M urea	-	10	1.36	[21]

Table S3. The overall urea-assistant water splitting performance comparison between the P-mAuRh film/NF and some other reported electrocatalysts.

Electrocatalysts		**Electrolytes**	**Current density (mA cm^{-2})**	**Voltage (V)**	**Ref.**
Anode	**Cathode**				
P-mAuRh film/NF	**P-mAuRh film/NF**	**1.0 M KOH/ 0.33 M urea**	**10**	**1.33**	**This work**
			50	**1.415**	
			100	**1.47**	
MoS_2/Ni_3S_2/NF	MoS_2/Ni_3S_2/NF	1.0 M KOH/ 0.33 M urea	20	1.45	[11]
$NiCo_2S_4$ NS/CC	$NiCo_2S_4$ NS/CC	1.0 M KOH/ 0.33 M urea	10	1.45	[13]
Ni/C-1/CC	Ni/C-1/CC	1.0 M KOH/ 0.33 M urea	10	1.6	[14]
$N_{i(10\%)}Pd_{(10\%)}$/ OMC	$N_{i(10\%)}Pd_{(10\%)}$/ OMC	1.0 M KOH/ 0.33 M urea	30	1.35	[15]
$Ni(OH)_2$ NS@NW/NF	Co_2P NW/NF	1.0 M KOH/ 0.33 M urea	5	1.58	[18]
Ni-Co_9S_8/CC	Ni-Co_9S_8/CC	1.0 M KOH/ 0.33 M urea	10	1.52	[19]
$NiSe_2$-NiO	commercial Pt/C	1.0 M KOH/ 0.33 M urea	10	1.39	[22]
MoS_2/Ni_3S_2/NiFe -LDH	MoS_2/Ni_3S_2/NiFe -LDH	1.0 M KOH/ 0.5 M urea	50	1.343	[23]
Ni-MOF-0.5	Ni-MOF-0.5	1.0 M KOH/ 0.5 M urea	10	1.52	[24]
Ni_3N-350/NF	Ni_3N-350/NF	1.0 M KOH/ 0.5 M urea	100	1.51	[25]

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