Electronic Supplementary Information (ESI)

Activating Bulk Nickel Foam for Electrochemical Oxidization of Ethanol by Anchoring MnO_2@Au nanorods

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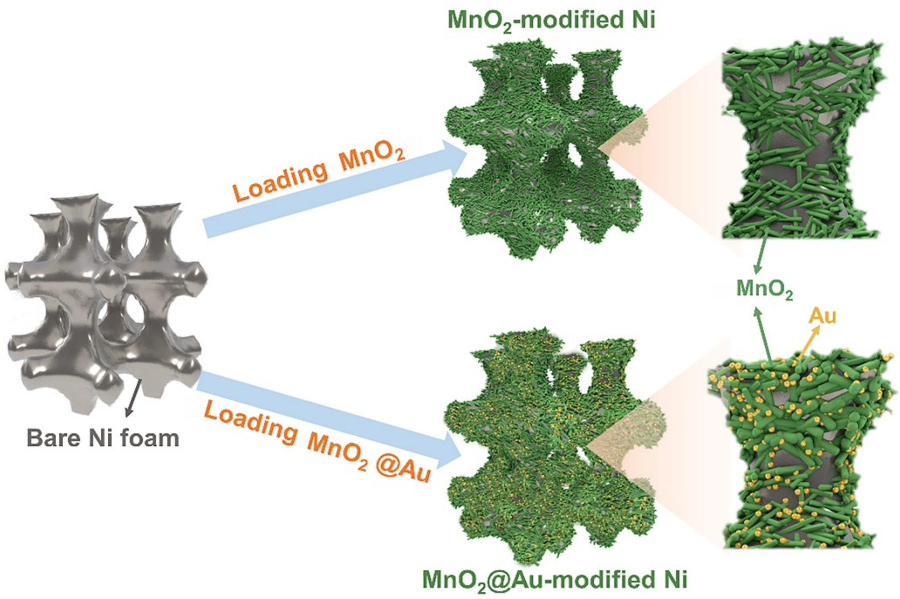

Fig. S1 Illustration for the electrodes of bare Ni foam, Ni-MnO_2, and Ni-MnO_2@Au

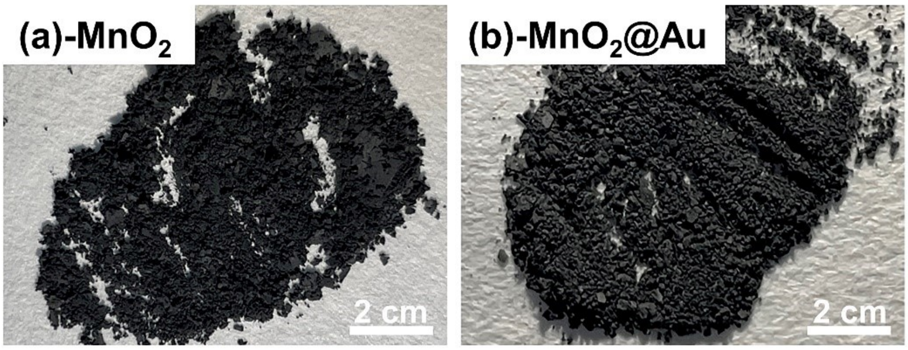

Fig. S2 The optical images of MnO_2 (a) and MnO_2@Au

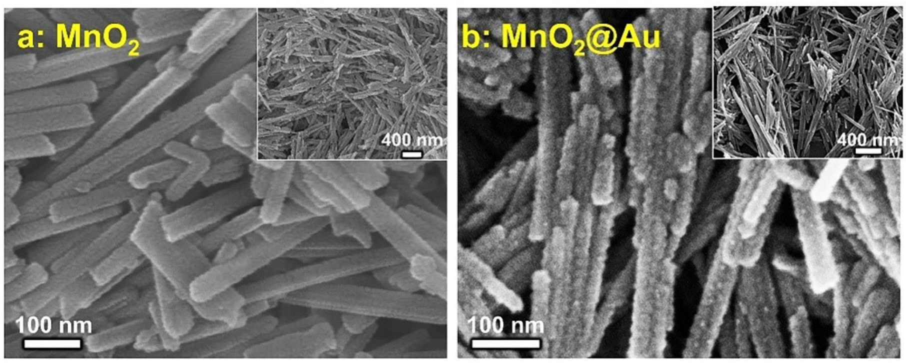

Fig. S3 SEM images of MnO_2 (a) and MnO_2@Au (b)

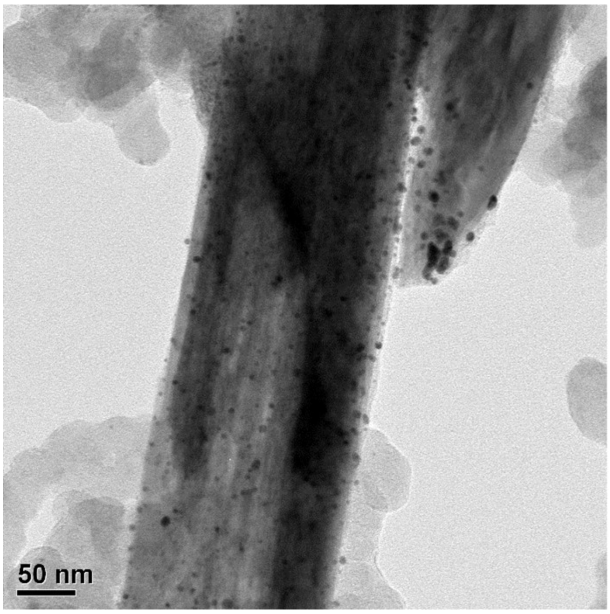

Fig. S4 TEM images of MnO_2@Au scraped from the nickel foam after long-term electrolysis at 1.8 V *vs*. RHE

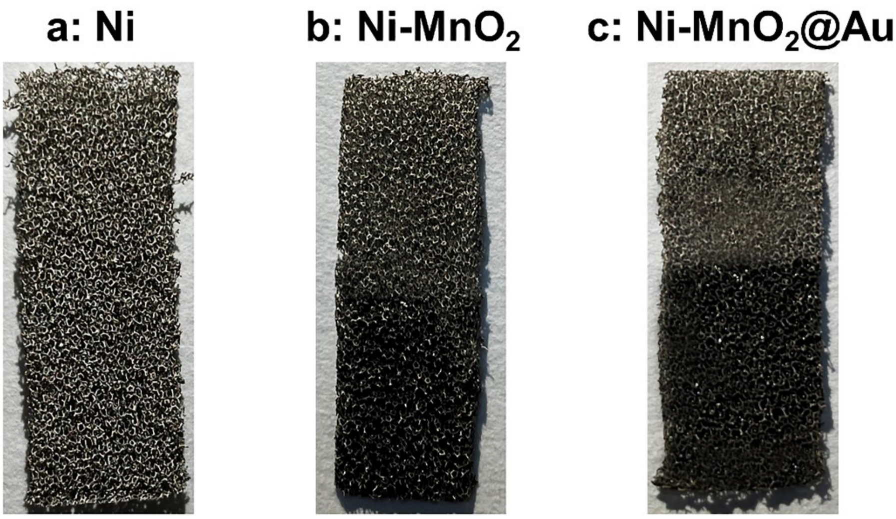

Fig. S5 The optical image of Ni (a), Ni-MnO_2(b), and Ni-MnO_2@ Au(c)

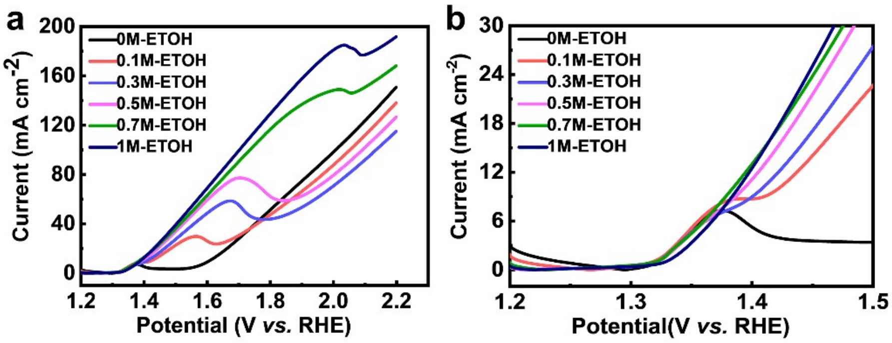

Fig. S6 LSV curves of different ETOH concentrations at 50 mV s^{-1} in Ni foam electrode:1.2 ~2.2 V *vs*. RHE (a); 1.2 ~1.5 V *vs*. RHE (b)

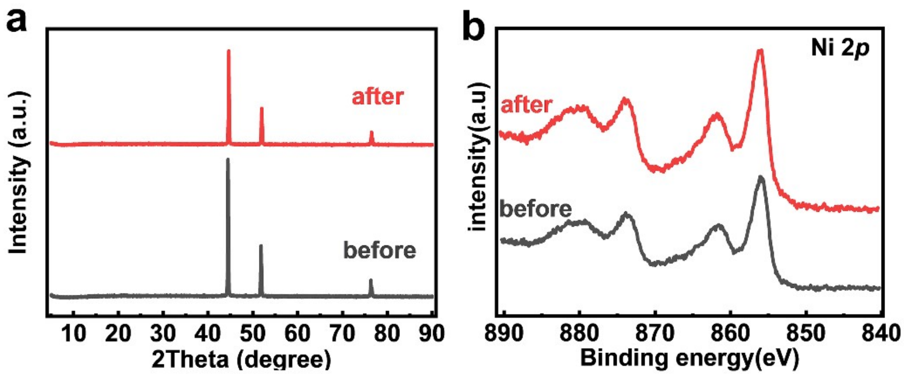

Fig. S7 Ni-MnO_2@Au before and after electrolysis at 1.8 V *vs*. RHE for 7200 s: (a) XRD; (b) XPS spectrum of Ni 2*p*

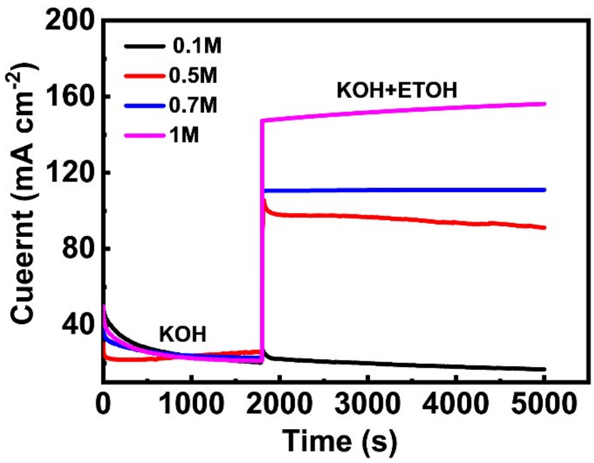

Fig. S8 Potentiostatic electrolysis at 1.8 V *vs*. RHE for Ni-MnO_2@Au electrode

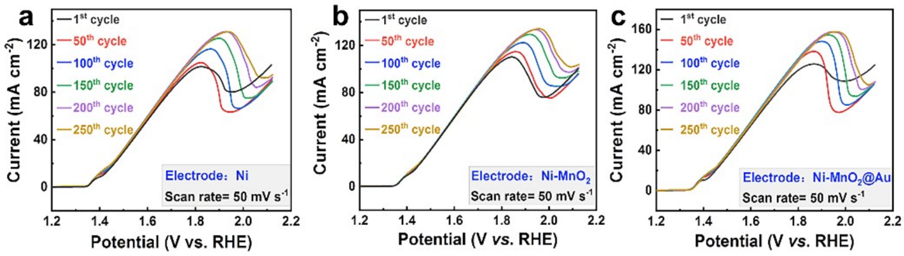

Fig. S9 LSV curves of different cycles at 50 mV s^{-1}: (a) Ni; (b) Ni-MnO_2; (c) Ni-MnO_2@Au

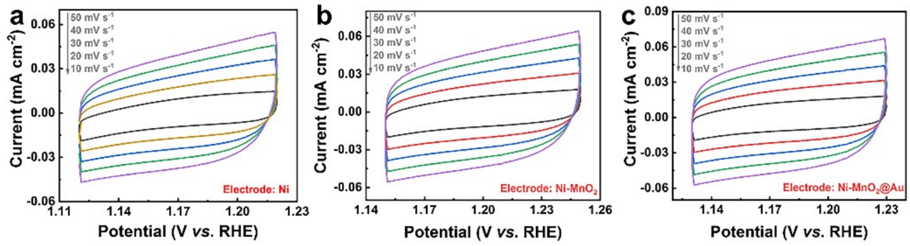

Fig. S10 CV curves at different scanning rate in the non-faradic regions: (a) Ni; (b) Ni-MnO_2; (c) Ni-MnO_2@Au

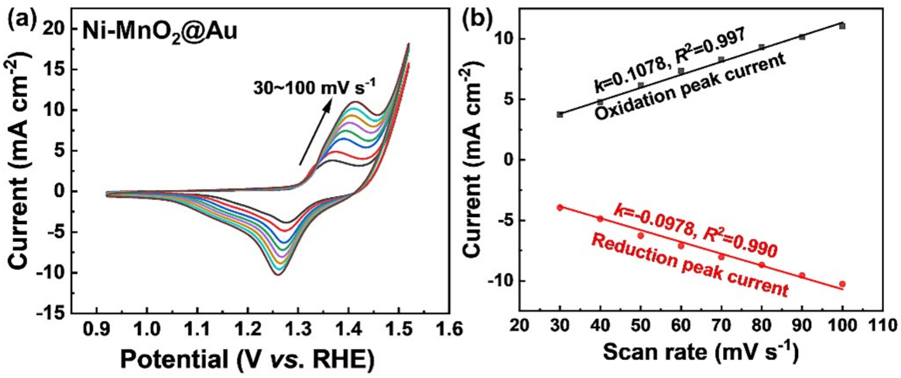

Fig. S11 (a) Cyclic voltammogram curves for bare foam Ni-MnO_2@Au in 0.5 M KOH solution and (b) the corresponding linear simulation of redox peak currents

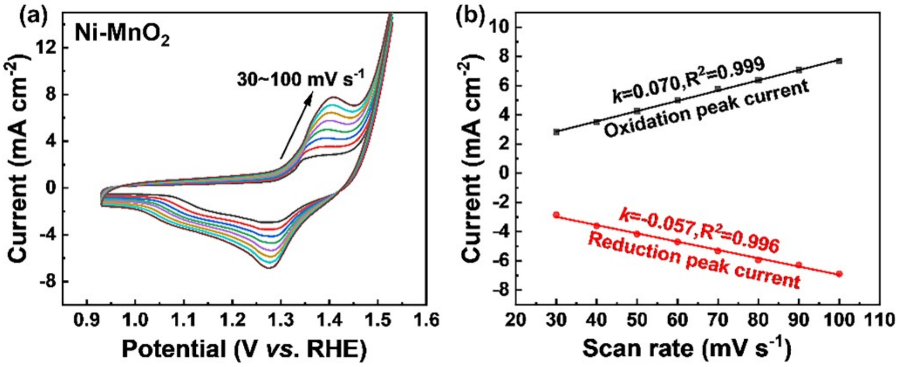

Fig. S12 (a) Cyclic voltammogram curves for bare foam Ni-MnO_2 in 0.5 M KOH solution and (b) the corresponding linear simulation of redox peak currents

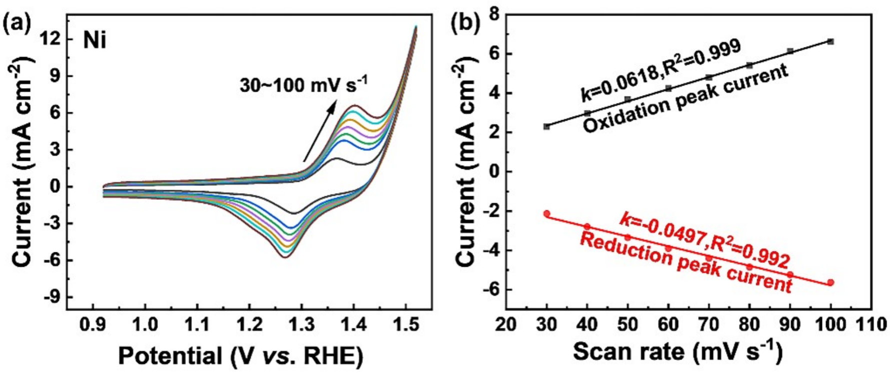

Fig. S13 (a) Cyclic voltammogram curves for bare foam Ni in 0.5 M KOH solution and (b) the corresponding linear simulation of redox peak currents

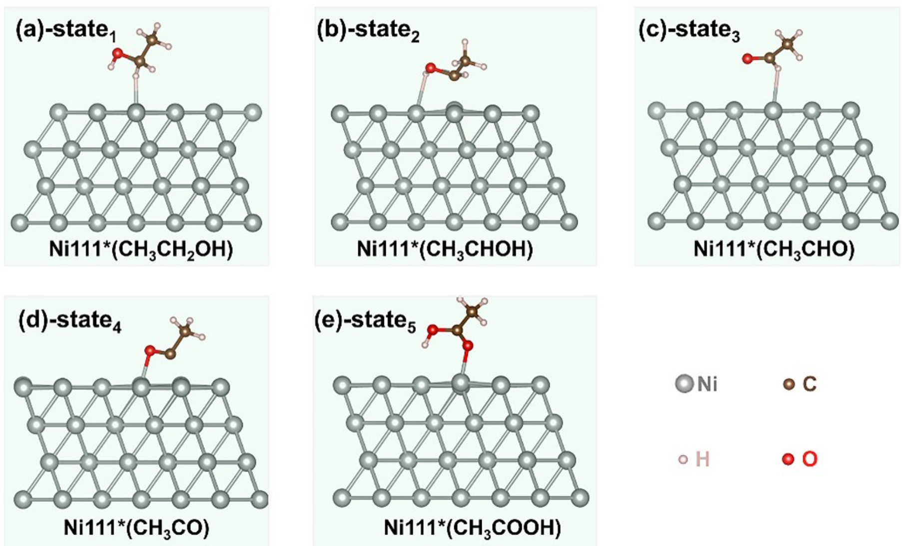

Fig. S14 Optimized structures for different reaction intermediates on Ni: (a) Ni_{111}* CH_3CH_2OH; (b) Ni_{111}*CH_3CHOH; (c) Ni_{111}*CH_3CHO; (d) Ni_{111}*CH_3CO; (e) Ni_{111}*CH_3COOH

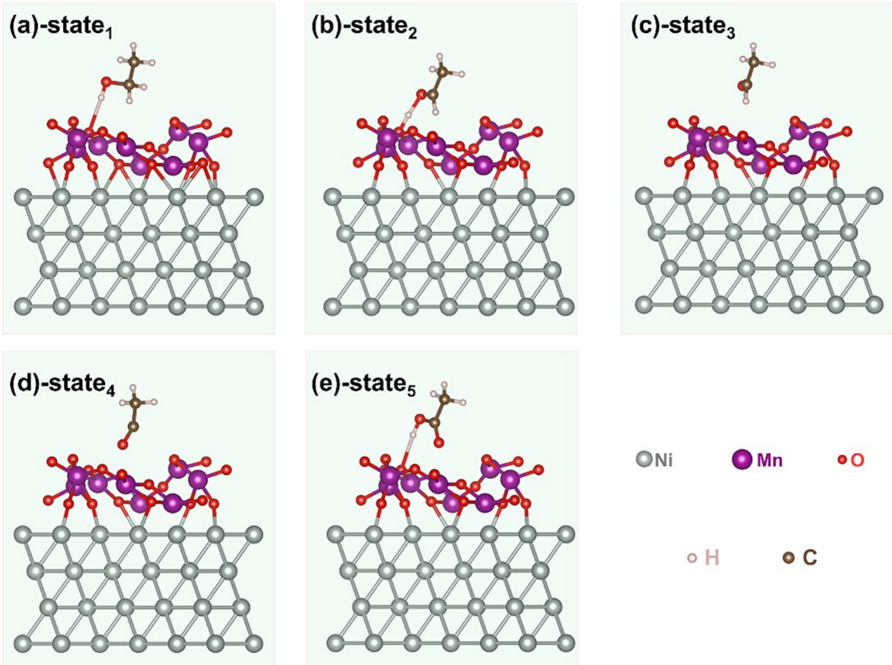

Fig. S15 Optimized structures for different reaction intermediates on Ni-MnO_2: (a) (Ni-MnO_2)*CH_3CH_2OH; (b) (Ni-MnO_2)*CH_3CHOH; (c) (Ni-MnO_2)*CH_3CHO; (d) (Ni-MnO_2)*CH_3CO; (e) (Ni-MnO_2)*CH_3COOH

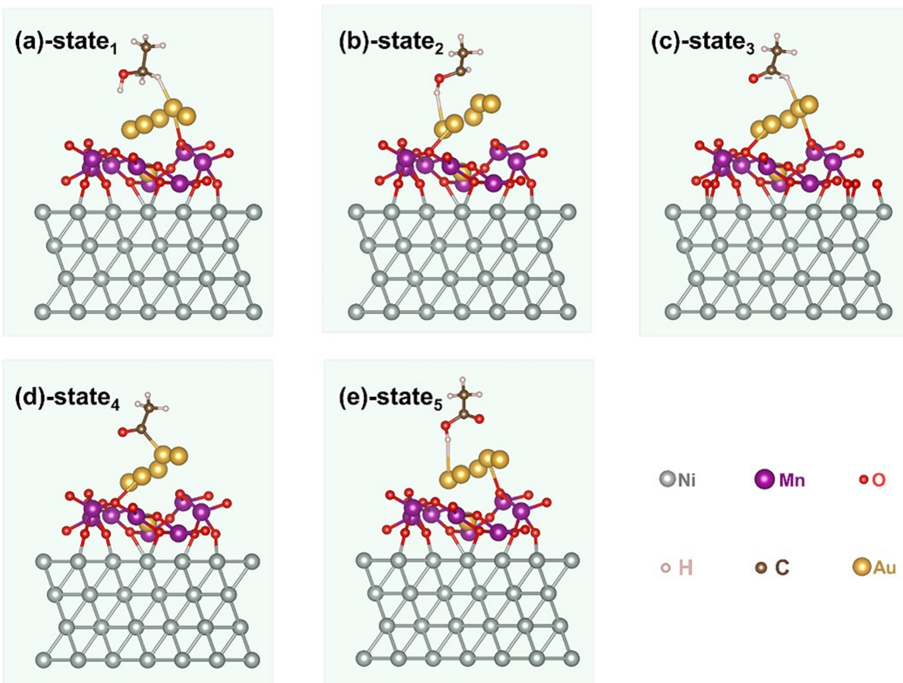

Fig. S16 Optimized structures for different reaction intermediates on Ni-MnO_2@Au: (a) (Ni-MnO_2@Au)*CH_3CH_2OH; (b) (Ni-MnO_2@Au)*CH_3CHOH; (c) (Ni-MnO_2@Au)*CH_3CHO; (d) (Ni-MnO_2@Au)*CH_3CO; (e) (Ni-MnO_2@Au)*CH_3COOH

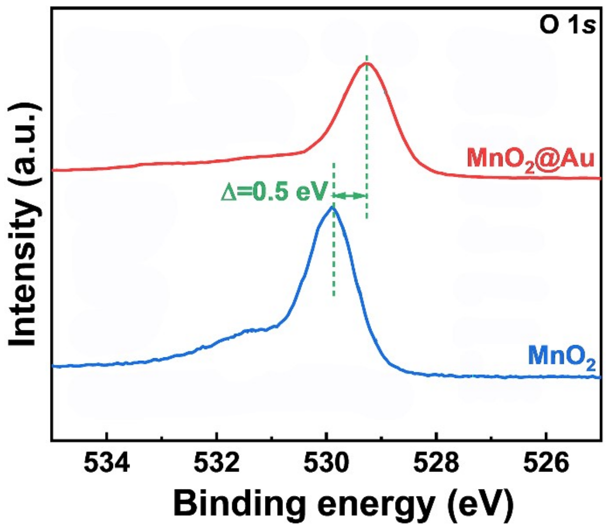

Fig. S17 The XPS O 1*s* spectra of MnO_2 and MnO_2@Au

Table S1 Performance comparison for EOR in alkaline solution

Catalysts	Peak current in LSV or CV ($mA\ cm^{-2}$)	Current retention after long-term chronopotentiometry	Ref.
Ni-MnO_2@Au	148	38 mA cm^{-2} after 5000s at 1.8 V vs. RHE	This work
Pd/B-N-Ti_3C_2	149	18.5 mA cm^{-2} at 0.72 V *vs*. RHE after 3600s	*ACS Appl. Mater. Inter.* 2022, 14, 12223-12233
Nanographitic flakes/NiO nanoparticles	1.51	2.9 mA cm^{-2} @ 1.5 V vs. RHE after 3000 s	*ACS appl. mater. Inter.* 8, 2016, 8(25):15975-15984
PdZn/NC@ZnO	2.83	0.81 mA cm^{-2} @ 0.61 V vs. RHE after 3600s	*Nat. Commun.*, 2021, 12: 5273
Pd_7Ag NSs	14	22.4 mA cm^{-2} @ 0.8 V vs. RHE after 3600s	*Adv. Funct. Mater.* 2020, 30, 2000255
Au-MnO_2	-	17mA cm^{-2} @ 1.5 V vs. RHE after 7200s	J. Mater. Chem. A,2020,8:16902-16907
Pd-Ni-MnO_2	1.46	0.3 mA cm^{-2} @ 0.72 V vs. RHE after 250 s	*Int. J. Hydrogen Energ*, 2019, 44: 28194-28205
Pd-Ag nanowires	71	14.5 mA cm^{-2}@ 0.7 V vs. RHE after 2000s	*Appl. Catal. B-Environ.*, 2019, 249: 116–125

Note: some data are recalculated from the values in the figures of the references

Table S2 Ni-MnO_2: Bader charge analysis for the specific charge of a single atom

Serial number	Element name	Number of initial valence electrons	Actual number of electrons	Total number of electrons gained or Lost
1	Ni		9.98705	
2	Ni		9.94865	
3	Ni		9.97943	
4	Ni		9.86284	
5	Ni		10.04622	
6	Ni		9.93377	
7	Ni		10.00553	
8	Ni		9.86056	
9	Ni		10.02437	
10	Ni	10	10.01496	1.5611e$^-$
11	Ni	(exist as Ni^0)	9.99196	
12	Ni		9.93761	
13	Ni		10.04355	
14	Ni		9.96716	
15	Ni		10.01214	
16	Ni		9.94918	
17	Ni		10.0305	
18	Ni		9.93817	
19	Ni		9.94732	
20	Ni		10.02606	
21	Ni		9.99524	
22	Ni		9.96066	
23	Ni		9.99758	
24	Ni		9.90331	
25	Ni		10.01099	
26	Ni		9.9721	
27	Ni		9.96631	
28	Ni		9.98035	
29	Ni		10.03386	
30	Ni		9.99057	
31	Ni		10.02024	
32	Ni		9.97811	
33	Ni		10.0411	
34	Ni		9.95696	
35	Ni		9.99168	
36	Ni		9.86598	
37	Ni		10.04776	
38	Ni		10.01717	
39	Ni		9.95001	
40	Ni		9.86136	
41	Ni		10.04189	

42	Ni		9.95392	
43	Ni		9.99271	
44	Ni		9.91248	
45	Ni		9.98808	
46	Ni		9.97025	
47	Ni		9.95959	
48	Ni		9.90671	
49	Ni		10.05901	
50	Ni		9.99997	
51	Ni		10.00939	
52	Ni		9.93751	
53	Ni		10.03938	
54	Ni		10.00746	
55	Ni		9.97868	
56	Ni		9.97543	
57	Ni		10.02899	
58	Ni		10.00331	
59	Ni		9.97969	
60	Ni		9.8019	
61	Ni		10.0209	
62	Ni		9.96722	
63	Ni		9.96441	
64	Ni		9.89163	
65	Mn	3 (exist as Mn^{4+})	5.71331	21.52719e^{-}
66	Mn		5.55049	
67	Mn		5.6563	
68	Mn		5.85397	
69	Mn		5.59477	
70	Mn		5.63158	
71	Mn		5.68492	
72	Mn		5.84184	
73	O	8 (exist as O^{2-})	6.16006	19.9663e^{-}
74	O		6.68239	
75	O		6.88214	
76	O		6.90285	
77	O		6.93831	
78	O		6.78205	
79	O		6.75954	
80	O		6.9154	
81	O		6.87742	
82	O		6.71935	
83	O		6.82462	
84	O		6.73912	
85	O		6.38664	

86	O		6.77598	
87	O		6.91053	
88	O		6.77731	

Table S3 Ni- MnO_2@Au: Bader charge analysis for the specific charge of a single atom

Serial number	Element name	Number of initial valence electrons	Actual number of electrons	Total number of electrons gained or lost
1	Ni		9.98989	
2	Ni		9.94333	
3	Ni		9.98008	
4	Ni		9.85336	
5	Ni		10.04746	
6	Ni		9.97855	
7	Ni		10.00632	
8	Ni		9.85914	
9	Ni		10.02199	
10	Ni		10.00824	
11	Ni		9.9946	
12	Ni		9.92076	
13	Ni		10.04532	
14	Ni		9.93697	
15	Ni		10.01676	
16	Ni		9.95013	
17	Ni		10.01356	
18	Ni	10	9.93896	$1.51597e^-$
19	Ni	(exist as Ni^0)	9.94373	
20	Ni		10.02452	
21	Ni		10.0147	
22	Ni		9.95557	
23	Ni		9.99823	
24	Ni		9.89227	
25	Ni		10.02726	
26	Ni		9.9975	
27	Ni		9.97424	
28	Ni		9.97892	
29	Ni		10.03484	
30	Ni		9.99114	
31	Ni		10.02407	
32	Ni		9.98035	
33	Ni		10.04033	
34	Ni		9.94044	
35	Ni		9.99091	
36	Ni		9.86807	

37	Ni		10.05216	
38	Ni		10.01227	
39	Ni		9.95708	
40	Ni		9.86302	
41	Ni		10.04678	
42	Ni		9.9533	
43	Ni		10.00498	
44	Ni		9.91197	
45	Ni		9.99023	
46	Ni		9.9701	
47	Ni		9.96231	
48	Ni		9.8977	
49	Ni		10.05633	
50	Ni		9.98177	
51	Ni		9.99898	
52	Ni		9.98871	
53	Ni		10.03765	
54	Ni		9.99996	
55	Ni		9.97625	
56	Ni		9.97144	
57	Ni		10.02359	
58	Ni		9.99957	
59	Ni		9.98797	
60	Ni		9.80971	
61	Ni		9.99837	
62	Ni		9.99861	
63	Ni		9.96337	
64	Ni		9.88736	
65	Mn	3 (exist as Mn^{4+})	5.85314	22.75323e$^-$
66	Mn		5.77433	
67	Mn		5.77872	
68	Mn		5.96497	
69	Mn		5.82729	
70	Mn		5.75506	
71	Mn		5.8483	
72	Mn		5.95144	
73	O	8 (exist as O^{2-})	6.16086	19.64906e$^-$
74	O		6.74836	
75	O		6.8953	
76	O		6.9067	
77	O		6.94731	
78	O		6.81432	
79	O		6.81432	
80	O		6.92825	

81	O		6.88294	
82	O		6.77565	
83	O		6.81441	
84	O		6.79869	
85	O		6.38963	
86	O		6.78147	
87	O		6.90928	
88	O		6.79431	
89	Au		10.96211	
90	Au		10.96321	
91	Au	11	10.58945	1.59142e$^-$
92	Au	(exist as Au^0)	10.64632	
93	Au		10.58861	
94	Au		10.65887	