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Supporting Information

Two-dimensional metal−organic frameworks with high oxidation state for efficient electrocatalytic urea oxidation

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1. Experimental Section

1.1 Materials

All chemicals, including N, N-Dimethylformamide (DMF), 1,4-benzenedicarboxylic acid (BDC), anhydrous ethanol, Triethylamine (TEA), Nickel(II) chloride hexahydrate ($NiCl_2 \cdot 6H_2O$), hexamethylenetetramine, Pt/C (20 wt% of Pt on Vulcan XC72), Nafion (15 wt%) were purchased from Sigma-Aldrich and used without further purification. Milli-Q water with a resistance of 18.2 MΩ was used in all experiments.

1.2 Synthesis of Ni-MOF nanosheets

32 mL DMF, 2 mL ethanol, and 2 mL water were firstly mixed in a 100mL glass bottle (Duran Schott). Then 0.75 mmol BDC and 0.75 mmol $NiCl_2 \cdot 6H_2O$ were added in the bottle, respectively. After the solution was stirred for 5 mins, 0.8 mL TEA was injected into the solution. Afterwards, the glass bottle was continuously ultrasonicated for 8 hours under ambient conditions. The resulting product was collected via centrifugation, washed with ethanol for 4 times, and dried by vacuum freeze-drying.

1.3 Synthesis of $Ni(OH)_2$ nanosheets

0.5 mmol $NiCl_2 \cdot 6H_2O$ and 168 mg hexamethylenetetramine were dissolved in 27 mL water and 3 mL ethanol under vigorous stirring. Then the solution was transferred into a 40 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and heated at 120 °C for 12 h. After the autoclave was naturally cooled down to room temperature, the product was collected via centrifugation, washed with water for 4 times, and dried by vacuum freeze-drying.

1.4 Characterizations

The morphology of the samples was characterized by field emission scanning electron microscopy (SEM, QUANTA 450), transmission electron microscopy (TEM, Tecnai G2 Spirit, which operates at an accelerating voltage of 200 KV) and scanning transmission electron microscopy (STEM, JEOL JEM-ARM200F, which operates at an accelerating voltage of 80 KV) equipped with energy dispersive spectrometer (EDS), and atomic force microscopy (AFM, Asylum Research MFP-3D). The structure, and chemical composition of the samples were characterized by powder X-ray diffractometer (PXRD, Cu-target Bruker D8 Advance), X-ray photoelectron spectroscopy (XPS, ESCALab250) and Synchrotron-based X-ray absorption near edge spectra (XANES).The XANES measurements were carried out on the soft X-ray spectroscopy beamline at the Australian Synchrotron, which is equipped with a hemispherical electron analyser and a microchannel plate detector that enables a simultaneous recording of the total and partial electron yields.

1.5 Electrochemical Measurements

Electrocatalyst inks were prepared by mixing active material with carbon black and Nafion. Specifically, 5 mg Ni-MOF was dispersed in 1 mL H_2O, then 300 µL carbon black (3mg ml^{-1}) and 35 µL Nafion (5%) were added in the solution and sonicated over 1 h. Glassy carbon electrodes with an area of 0.196 cm^2 were polished to a mirror finish before use. Then, 10 µL of the electrocatalyst ink was drop-cast onto the electrode, and the electrocatalyst layer was dried overnight. For comparison, $Ni(OH)_2$, Pt/C were prepared by using same method on glassy carbon electrode, except that no carbon black was added for Pt/C. Ni-MOF/Ni foam was obtained by dropping 50 µL ink of Ni-MOF on 1cm^2 Ni foam.

Electrochemical tests were carried out in a three-electrode system on a workstation (CHI 760D Instruments, Inc., USA). Ag/AgCl (4 M KCl) electrode and carbon rod were used as the reference and counter electrodes, respectively. The reversible hydrogen electrode (RHE) potentials were obtained by the following equation: $E(RHE) = E(Ag/AgCl) + 0.205 + 0.059 \times pH$. 1 M KOH and 0.33 M urea solution was used as the electrolyte for urea oxidation reaction test. A flow of N_2 (ultra-high-grade purity, Airgas) was maintained in the electrolyte during the test.

Before data collection, the working electrodes were scanned by cyclic voltammetry (CV) plots until the signals were stabilized. The linear sweep voltammetry (LSV) curves were recorded with a scan rate of 10 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) was measured in the frequency range from 0.1 Hz to 100 kHz with an initial potential of 1.6 V (vs. RHE). The electrical double layer capacitor (C_{dl}) of the samples were obtained from CV plots in a small potential range of 0.06−0.16 V (vs. Ag/AgCl). The electrode durability was tested by Galvanostatic method, which was conducted at 20 mA cm^{-2} for 36000 s.

2. Supplementary Figures and Tables

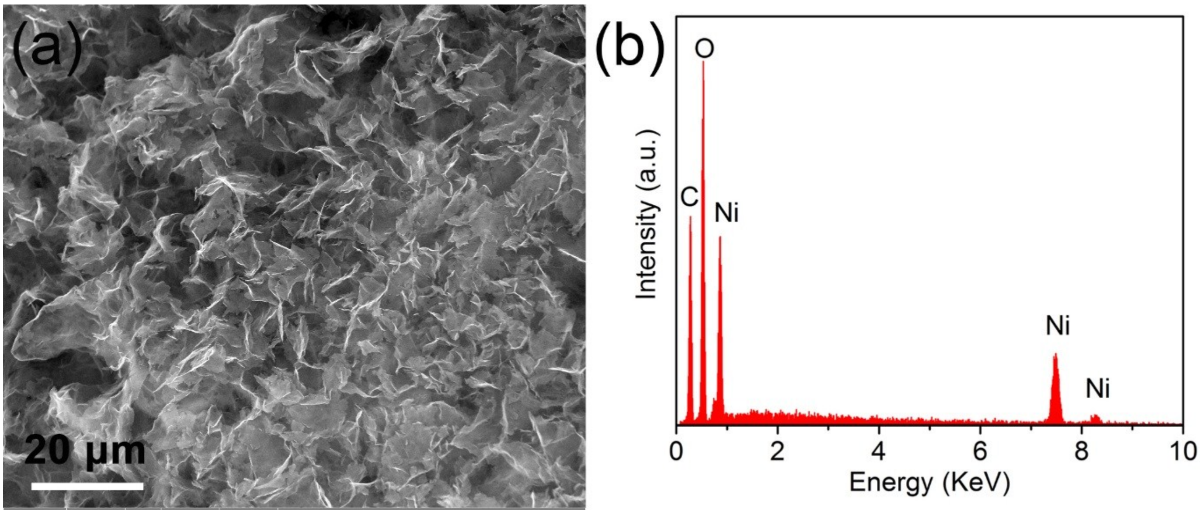


Fig. S1 (a) SEM image of Ni-MOF. (b) EDS spectrum of Ni-MOF.

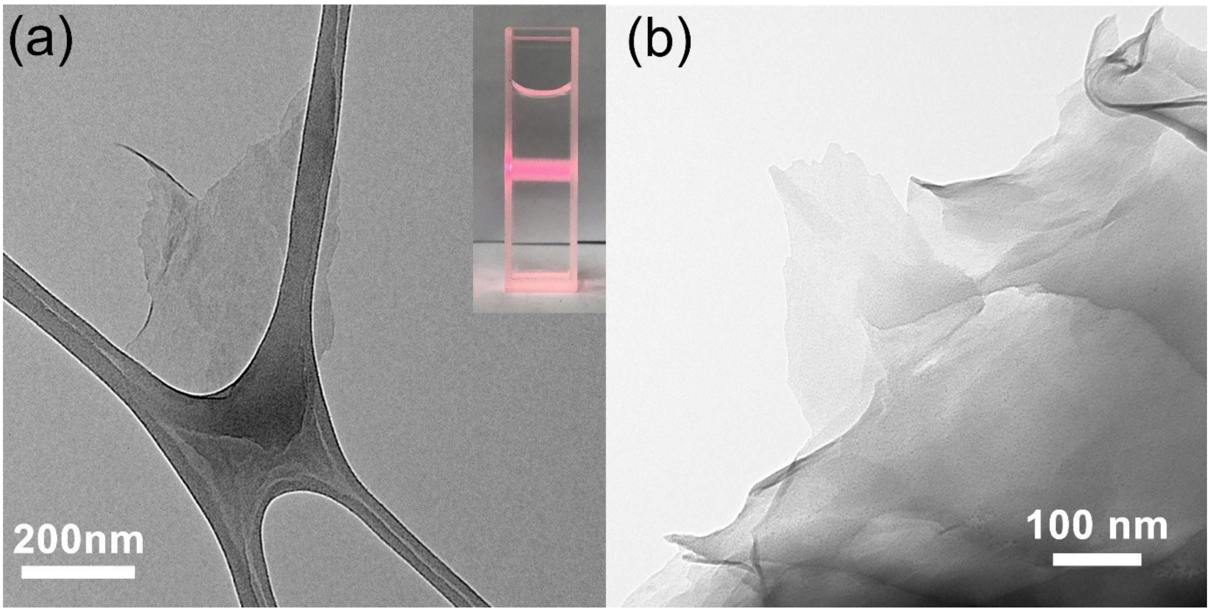


Fig. S2 (a, b) TEM images of Ni-MOF. The inset in S2a shows the Tyndall effect of the 2D Ni-MOF colloidal solution in water.

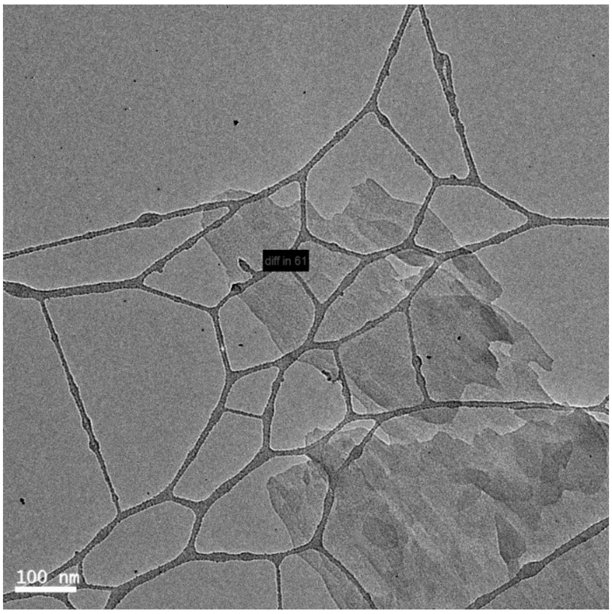


Fig. S3 The black square shows the area for SAED.

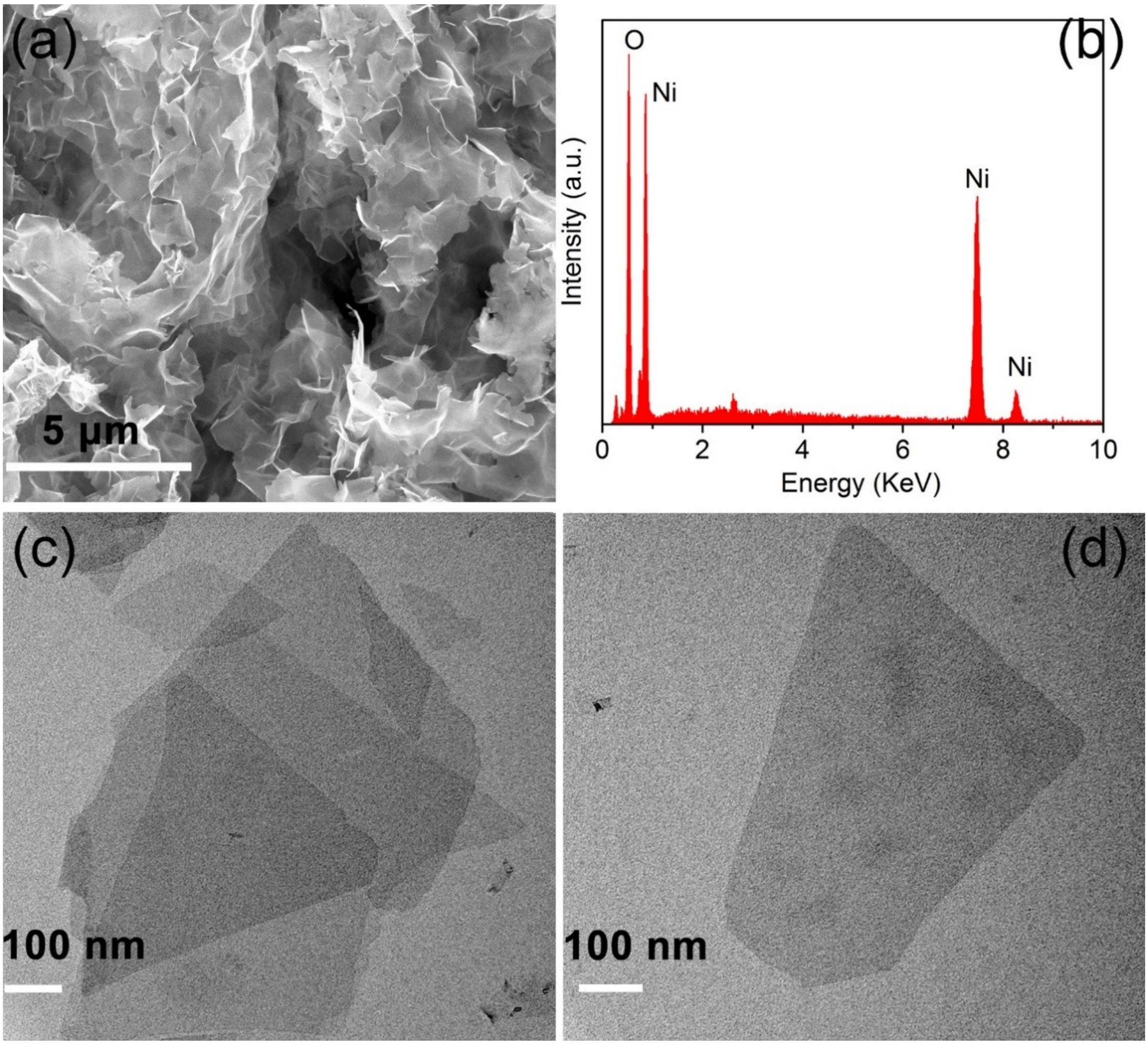
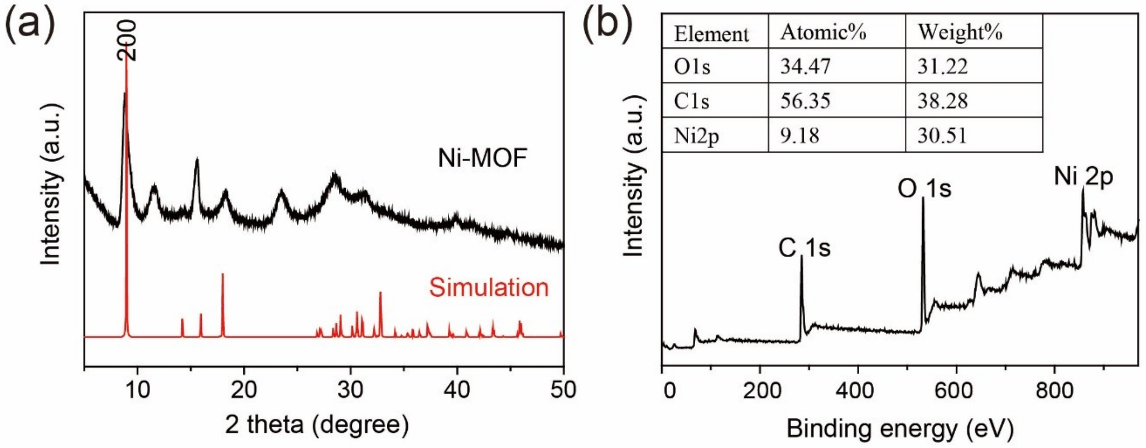


Fig. S4 (a) SEM, (b) EDS and (c,d) TEM images of $Ni(OH)_2$ nanosheets.



Element	Atomic%	Weight%
O1s	34.47	31.22
C1s	56.35	38.28
Ni2p	9.18	30.51

Fig. S5 (a) PXRD pattern of Ni-MOF and the simulated diffraction pattern based on the crystal structure. Two peaks with 2θ at 11.6 and 23.3° correspond to d-spacing of 7.6 and 3.8 Å, which should be related to layered materials. The similar results have been observed in previous works.[1-3] (b) XPS survey spectrum of Ni-MOF.

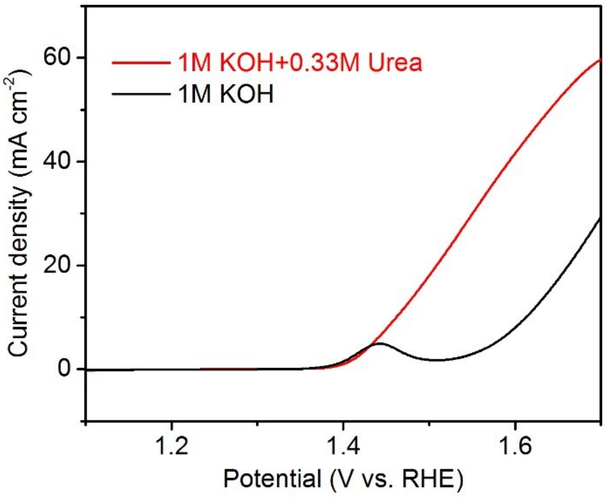


Fig. S6 LSV curves of $Ni(OH)_2$ in 1 M KOH electrolyte with and without 0.33M urea at a scan rate of 10mV s^{-1}.

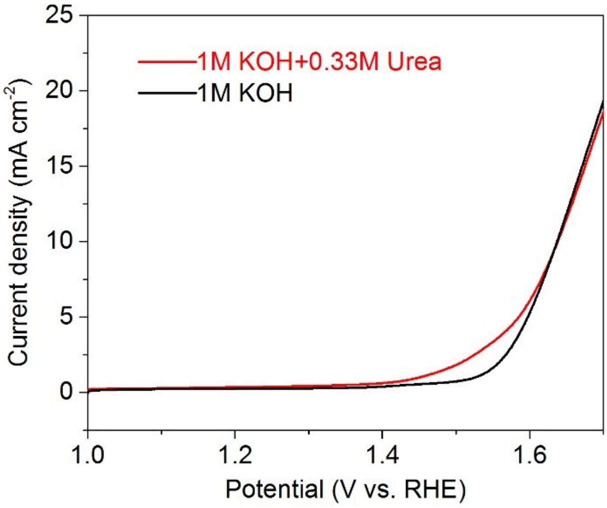


Fig. S7 LSV curves of 20% Pt/C in 1 M KOH electrolyte with and without 0.33M urea at a scan rate of 10mV s^{-1}.

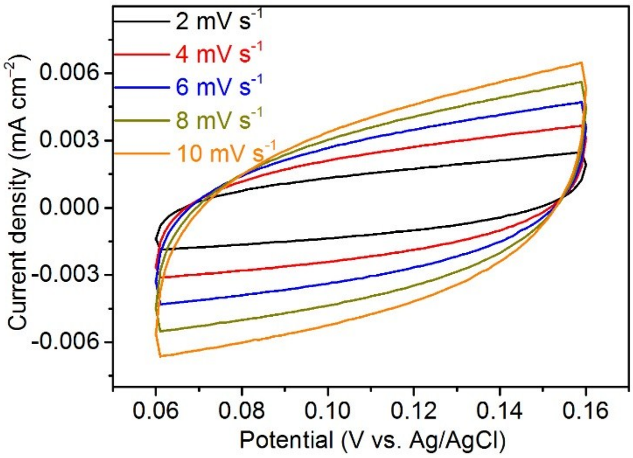


Fig. S8 CV curves recorded for Ni-MOF in a potential window (0.06 to 0.16 V vs Ag/AgCl) without faradaic processes.

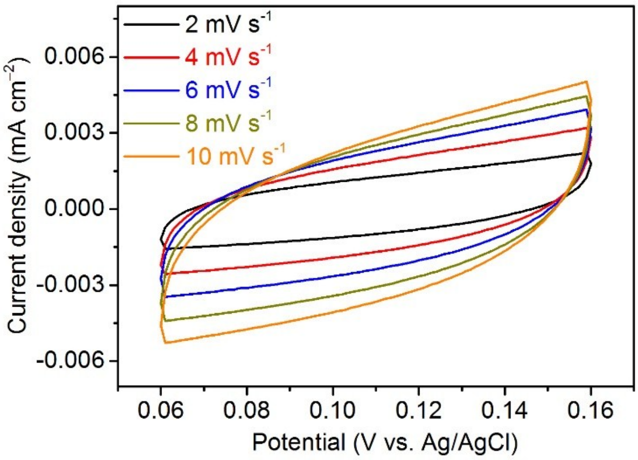


Fig. S9 CV curves recorded for $Ni(OH)_2$ in a potential window (0.06 to 0.16 V vs Ag/AgCl) without faradaic processes.

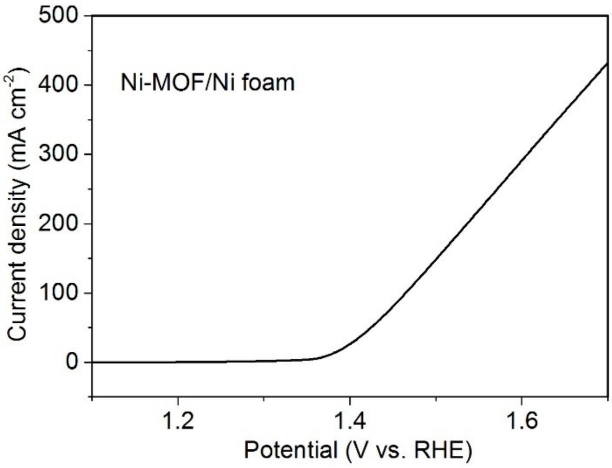


Fig. S10 LSV curve of Ni-MOF deposited on nickel foam.

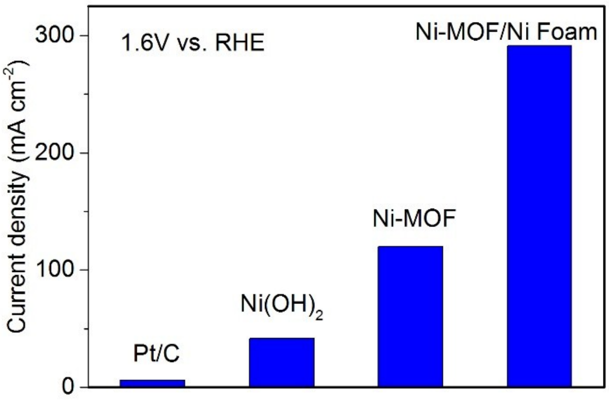


Fig. S11 (a) Current densities of Ni-MOF, Ni(OH)$_2$, Pt/C and Ni-MOF/Ni foam at 1.6V vs. RHE.

Table S1. Comparison of peak positions of Ni 2P for Ni-MOF and Ni(OH)$_2$ in XPS spectrum.

	Ni 2P$_{3/2}$ (eV)	**Ni 2P$_{3/2}$ (S) (eV)**	**Ni 2P$_{1/2}$ (eV)**	**Ni 2P$_{1/2}$ (S) (eV)**
Ni-MOF	857.6	862.6	875.1	881.4
Ni(OH)$_2$	856.1	861.7	873.6	880.6

Table S2. Comparison of the UOR activity between recently reported electrode materials.

Catalyst	**Potential @ 10 mA cm^{-2} (V vs. RHE)**	**Current density @ 1.6V (vs. RHE) (mA cm^{-2})**	**Substrate**	**Reference**
Ni-MOF	1.36	120	Glassy carbon	This work
Ni(OH)$_2$	1.46	41	Glassy carbon	This work
Ni-MOF	1.37	292	Nickel foam	This work
Metallic Ni(OH)$_2$	1.39	36 (peak current)	Glassy carbon	Angew. Chem. Int. Ed., **2016**, 55, 12465
Ni$_2$P	1.38	180	Carbon cloth	J. Mater. Chem. A, **2017**, 5, 3208
Ni$_3$N	1.35	130	Carbon cloth	Inorg. Chem. Front., **2017**, 4, 1120
Carbon/Ni-Fe	1.39	80	nickel foam	Electrochem. Acta, **2017**, 227, 210

Ni-Cr	1.38	90	Glassy carbon	ChemCatChem, 10.1002/cctc.201700451
NiO-Fe_2O_3	1.40	50	Graphene aerogel	Electrochem. Acta, **2017**, 237, 171
$LaNiO_3$	1.39	NA	Glassy carbon	ACS Catal., **2016**, 6, 5044
Ni-Co	1.53	20	Glassy carbon	Sci. Rep., **2014**, 4, 5863
Graphene-$Ni(OH)_2$	1.52	20	Glassy carbon	Electrochim. Acta, **2013**, 89, 732
L-MnO_2	1.37	170	Graphene–nickel foam	Angew. Chem. Int. Ed., **2016**, 55, 3804
S-MnO_2	1.33	260	Graphene–nickel foam	Angew. Chem. Int. Ed., **2016**, 55, 3804
$MnO_2/MnCo_2O_4$	1.33	270	Nickel foam	J. Mater. Chem. A, **2017**, 5, 7825

References

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