

Electronic Supplementary Information

A comparative study of electrocatalytic oxidation of glucose on conductive Ni-MOF nanosheet arrays with different ligands

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Experimental section

Materials

Nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), Nickel acetate tetrahydrate ($\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$), 2,3,6,7,10,11-hexaaminotriphenylene hexahydrochloride ($\text{HATP} \cdot 6\text{HCl}$), 3-amino-1, 2, 4-triazole (Hatz), 2-aminoterephthalic acid (ATA), tannin (TA), 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP), guanine (G), cytosine (C), fructose (Fru), ascorbic acid (AA), uric acid (UA), chloride ion (Cl^-) and sulfate ion (SO_4^{2-}) were purchased from Aladdin Ltd. (Shanghai, China). N,N-Dimethylformamide (DMF), Ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$) (28-30%) is purchased from Tianjin Guangfu Technology Development Co. Ltd. (Tianjin, China). Glucose (Glu) were purchased from Beijing Chemical Works. Carbon cloth (CC) was purchased from Cetech Co. Ltd. All reagents were used as received without further purification. The water use throughout all experiments was purified through a Millipore system. Human blood samples were kindly provided by the Shuozhou Modern Hospital (Gubei Street, Shuocheng District, Shuozhou, Shanxi, China). The human serum was separated from the blood samples by centrifugation. Human serum samples were diluted to different concentrations with NaOH solution, and each sample was analyzed for three times.

Instruments

Powder X-ray diffraction (XRD) data were acquired on a RigakuD/MAX 2550 diffractometer with Cu $K\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$). Scanning electron microscopy

(SEM) measurements were performed on a Hitachi S-4800 field emission scanning electron microscope at an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) measurements were made on a Hitachi H-8100 electron microscope (Hitachi, Tokyo, Japan) with an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source. The Brunauer-Emmett-Teller (BET) surface area and pore volume were measured on a Quantachrome NOVA 1000 system at liquid N₂ temperature. Fourier Transform Infrared spectroscopy (FT-IR) measurements were made on a FT-IR Spectrometer TENSOR 27 (Bruker Optik GmbH, Ettlingen, Germany). Electrochemical measurements were performed with a CHI 660E electrochemical analyzer (CH Instruments Ins., Shanghai).

Preparation of various Ni-MOF/CC

1. Preparation of conductive Ni-MOF NSAs/CC

Prior to synthesis, a piece of CC (2 cm × 3 cm) was cleaned by sonication sequentially in acetone, water, and ethanol for 10 min, respectively. In a typical procedure, 11.2 mg of nickel chloride hexahydrate (NiCl₂·6H₂O) in 10 mL of water and 0.7 mL of NH₃·H₂O was added to a solution of 20 mg of HATP·6HCl in 10 mL of water. Then the solution was transferred into a clear Teflon-lined stainless-steel autoclave with carbon cloth. Then, reaction underwent in an electric oven at 120 °C for 6 h. After cooling down to room temperature, the reaction product was centrifuged and the solid precipitate was washed with ultrapure water. The resulting black powder

was dried overnight at 65 °C.

2. Preparation of Ni-Hatz (3-amino-1, 2, 4-triazole)/CC¹

A mixture of NiCl₂ · 6H₂O (0.20 mmol), Hatz (0.20 mmol) in DMF (2 mL) and H₂O (8 mL) with clean CC was sealed in a Teflon-lined stainless steel (25 mL) container and heated at 180 °C for 3 days, then cooled to room temperature.

3. Preparation of Ni-ATA (2-aminoterephthalic acid)/CC²

In a typical synthetic procedure, 0.3 mmol NiCl₂ · 6H₂O and 0.2 mmol ATA were dissolved in DMF (2 mL) and H₂O (8 mL). Subsequently, the solution with clean CC was transferred into a 100mL Teflon-lined stainless-steel autoclave and maintained at 160 °C for 12 h in an oven. After the autoclave was automatically cooled down.

4. Preparation of Ni-TA (tannin)/CC³

In a typical synthesis, 8 mL of 3 mg mL⁻¹ TA, 4 mL of 0.1 M NiCl₂ · 6H₂O aqueous solution in 10 mL of water and 10 mL of DMF while stirring. Then the mixture was transferred into a 30 mL teflon-lined autoclave with clean CC and heated at 100 °C for 3 h.

5. Preparation of Ni-HHTP (2,3,6,7,10,11-hexahydroxytriphenylene)/CC⁴

In a typical procedure, HHTP (0.02 mmol) and Ni(OAc)₂ · 4H₂O (0.04 mmol) were added were added in 1 mL solvent mixture of water/DMF (v: v = 1:1) under sonication for 20 min in a 20 mL glass vial. The reaction mixture was then heated in an oven with clean CC at 120 °C for 15 h.

Preparation of human blood serum

The human blood was put into 45 °C water bath for 10 minutes and then centrifuged at 4000 r/min for 5 minutes. Human blood serum was obtained by

collected the supernate. The disposed serum is kept in $-5\text{ }^{\circ}\text{C}$ to $-20\text{ }^{\circ}\text{C}$.

Electrochemical measurements

All electrochemical measurements were performed with a CHI 660E electrochemical workstation at room temperature. The electrochemical measurements were performed in 0.1 M NaOH using traditional three-electrode configuration: conductive Ni-MOF NSAs/CC ($0.25\text{ cm} \times 0.3\text{ cm}$) as the working electrode, Ag/AgCl (saturated KCl) and Pt wire as the reference electrode and the counter electrode, respectively. For amperometric tests, the solution was stirred to facilitate mixing.

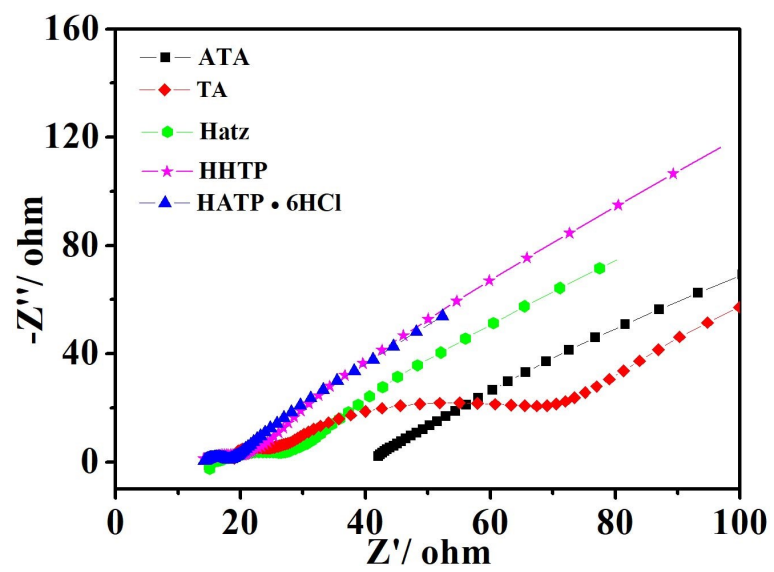


Fig. S1. The Nyquist electrochemical impedance spectra on a small scale.

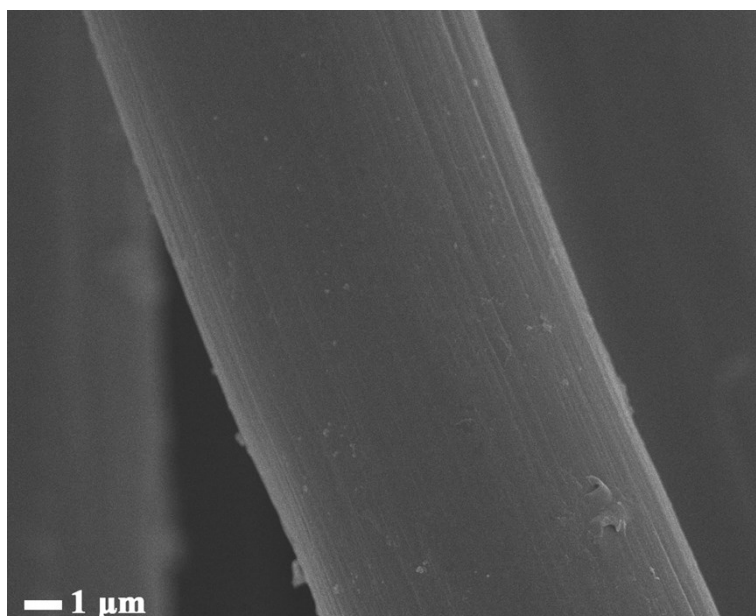


Fig. S2. SEM of bare carbon cloth with 1 μm .

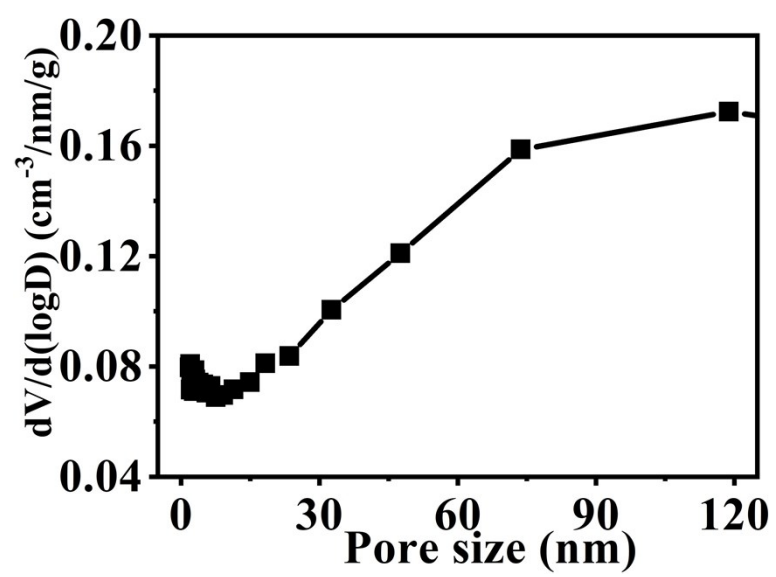


Fig. S3. The pore size distribution of the conductive Ni-MOF.

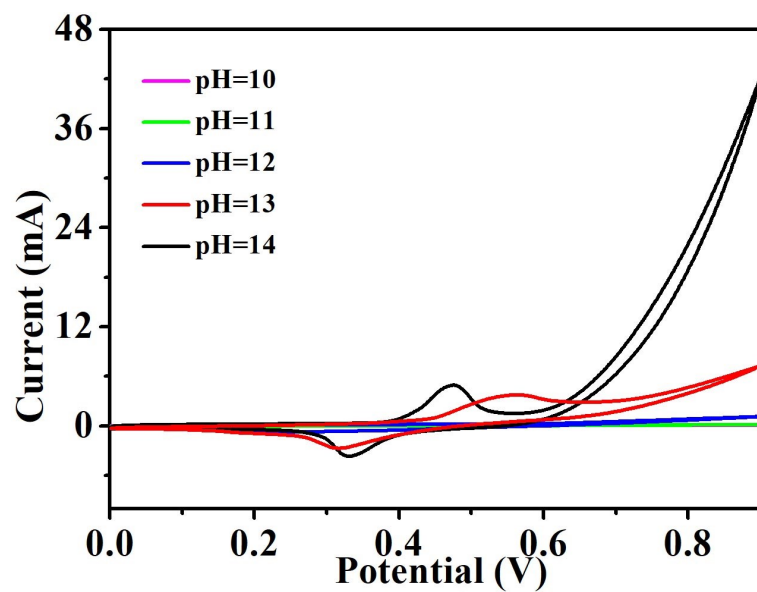


Fig. S4. The CV curves of influence of different pH on the current response of Ni-MOF NSAs/CC with 2 mM glucose (scan rate: 30 mv/s).

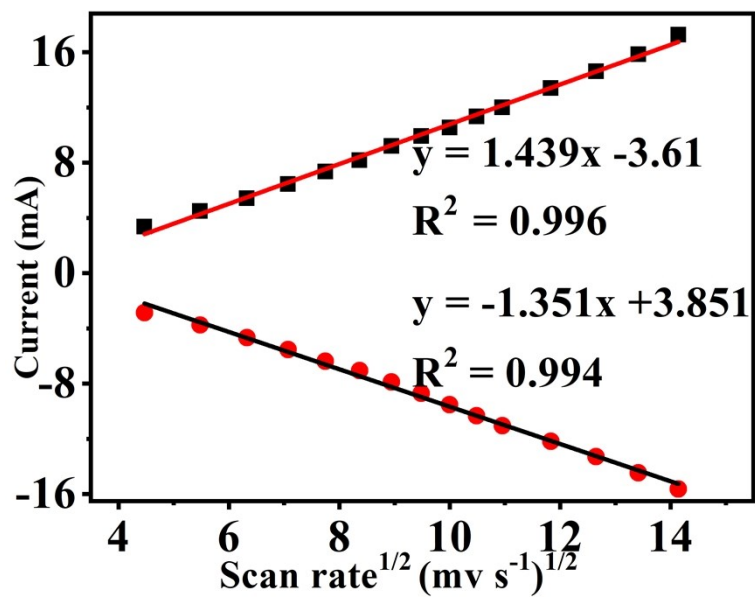


Fig. S5. The calibration curves of peak currents vs. square root of scan rates.

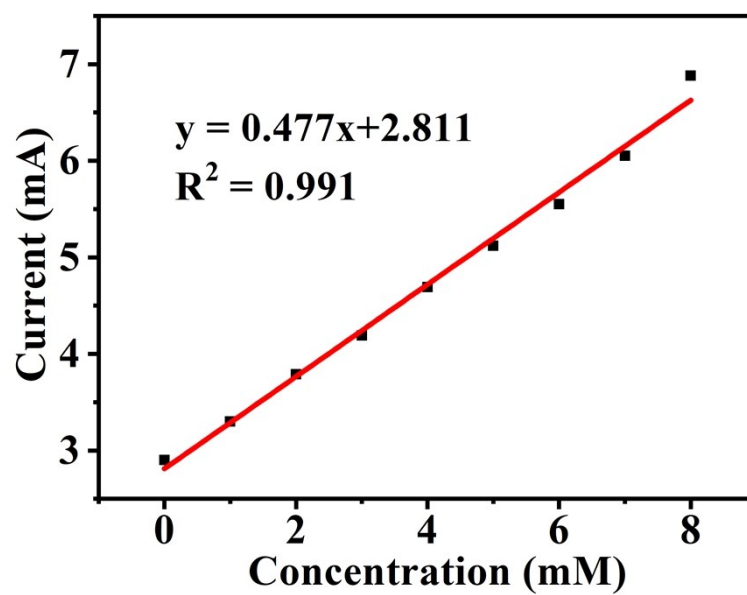


Fig. S6. The calibration curve of peak currents vs. glucose concentration.

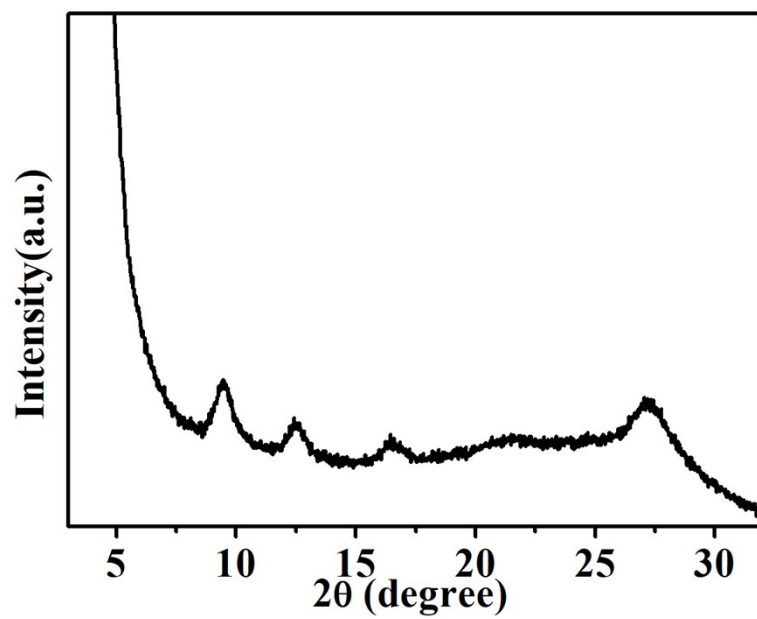


Fig. S7. XRD pattern for the conductive Ni-MOF after long term stability tests.

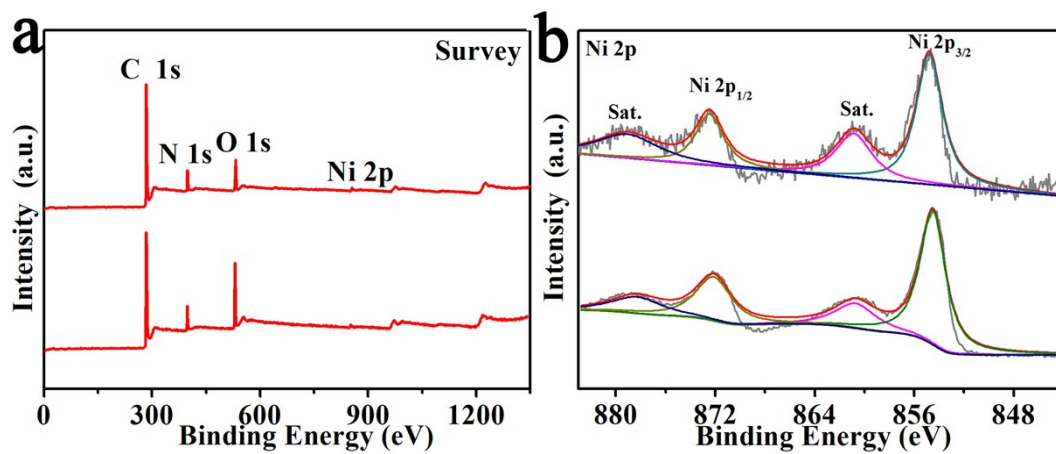


Fig. S8. (a) XPS survey spectrum for the conductive Ni-MOF NSAs after long-term stability tests. XPS spectra of the conductive Ni-MOF NSAs in the (b) Ni 2p regions.

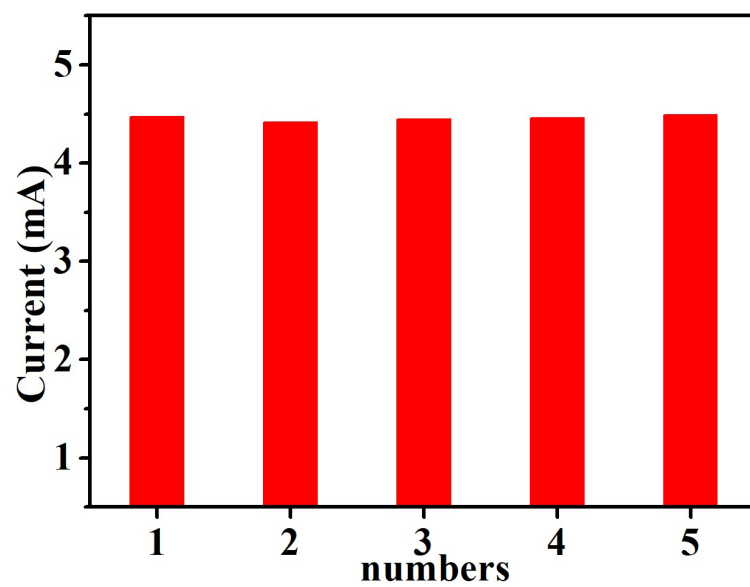


Fig. S9. Reproducibility of 5 sensors towards 2 mM glucose in 0.1 M NaOH.

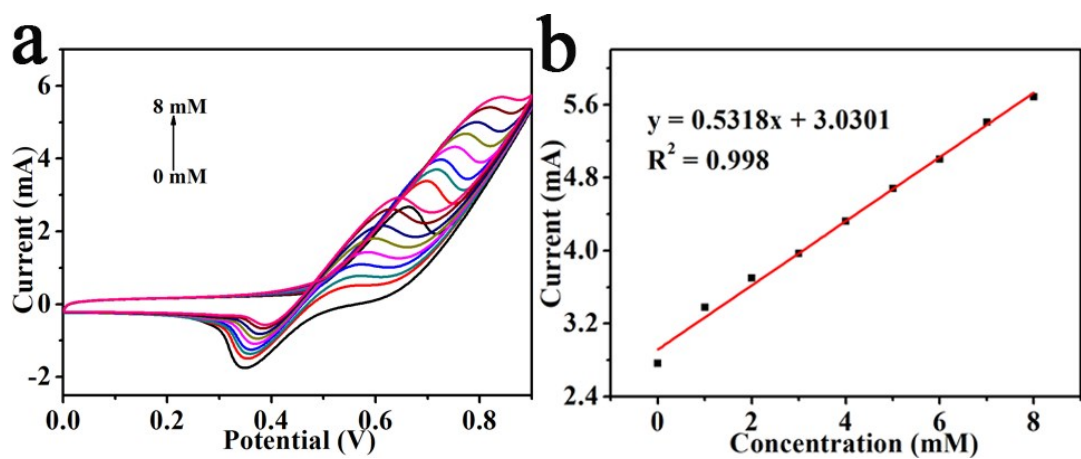


Fig. S10. (a) CV curves of samples where different glucose concentrations from 0 to 8mM added into 0.1 M NaOH solution containing 2 % of pulsating drink (scan rate: 30 mV/s). (b) Calibration curve of oxidation peak current response to the concentration of glucose.

Table S1. The conductivity of MOFs with different ligands.

MOFs	Ligands	Electrical conductivity (S/cm²)
HHTP	2,3,6,7,10,11- hexahydroxytriphenylene	0.006
TA	tannin	6.8×10^{-8}
Hatz	3-amino-1, 2, 4-triazole	1.5×10^{-10}
ATA	2-aminoterephthalic acid	2.5×10^{-10}
HATP·6HCl	2,3,6,7,10,11-hexaaminotriphenylene hexahydrochloride	0.2

The characteristic current–voltage curves are obtained using a semiconductor characterization system (4200-SCS, Keithley) in a probe station (CGS-MT Mini Multi-Functional Probe Station & supply Beijing Zhongju High-tech Technology Co., Ltd.) under an air conditioner to detect the change in the current signal. The conductivity is calculated by the resistance value. We have listed the conductivity of MOFs in the Table S2.

Table S2. The pore size distribution with different Ni-MOFs.

Number	Ni-MOFs	Ligands	Pore size (nm)	Ref.
1	Ni-BTC-1 m	H ₃ BTC (Benzene-1,3,5-tricarboxylic acid)	4.6	5
	Ni-BTC-5 m			
	Ni-BTC-30 m			
	Ni-BTC-60 m			
	Ni-BTC-180 m		4.1	
2	Ni-MOF-60	MeIM (2-methylimidazole)	1.06	6
	Ni-MOF-80		1.07	
	Ni-MOF-100			
3	Ni-MOF 1-1	Trimesic acid	5.4	7
	Ni-MOF 1-2		13.22	
	Ni-MOF 1-4		23.62	
	Ni-MOF 1-6		19.03	
4	Ni-ZIF	MeIM (2-methylimidazole)	2-10	8
	Ni-BTC			
5	Ni-MOF	MeIM (2-methylimidazole)	111.6	9
	Ni-MOF/Ni		111.8	
6	Ni-MOF	2,3,6,7,10,11-hexahydroxytriphenylene	2-9	4
7	Ni-MOF	2,3,6,7,10,11-hexaaminotriphenylene hexahydrochloride	2-9	this work

Table S3. Performance comparison of non-enzymatic glucose electrochemical sensors using different catalyst materials.

Catalysts	Sensitivity ($\mu\text{A mM}^{-1} \text{cm}^{-2}$)	Linear range (mM)	Detection limit (μM)	Ref.
Ni-MOF NSAs/CC	13428.89	0.001-7	0.57	This work
Ni-MOF/Ni/Ni/C	367.45	0.004-5.664	0.8	10
Ni Nanowire	367	0.001-5	1	11
CPO-27-Ni ^{II}	40.95	0.04-6	1.46	12
NiCo-MOF NSAs	684.4	0.001-8	0.29	13
Ni foam	-	0.05-7.35	2.2	14
Ni ₅ P ₄ GCE	-	0.002-5.3	0.7	15
AuNPs/Ni(OH) ₂ NS/GCE	-	0.002-6	0.66	16
Ni-B/NF	8500	0.005-2.66	5	17
Ni(OH) ₂ &NiOOH film/Ni foam	5758.4	0.001-0.130	-	18
RGO-Ni(OH) ₂	-	0.003-3.1	0.6	19
NiO-BP	2701	0.1-9	-	20
Ni-MIL-77	118.77	0.1-7	2.23	21

Note: NSAs = nanosheet array; NF = Ni foam; BP = buckypaper

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