Electronic Supplementary Information

A 3d-printed composite electrode for sustained electrocatalytic oxygen evolution

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1. Instrumentation and Chemicals

3D printing: The 3D models were designed using the Autodesk Fusion360 software and sliced by Ultimaker Cura. The infill density was set to 70% using a line infill pattern. The mesh structure was achieved by removing the top and bottom layers in the slicing program. The samples were printed on a Prusa I3 Mk3S printer. The temperatures of extrusion and build plate were 200 °C and 80 °C, respectively. Yellow ABS filament was purchased from SainSmart, diameter 1.75 mm and it was used without modification. The printed samples were washed with water and ethanol and dried for several hours.

Scanning electron microscopy (SEM): SEM images were obtained using a Hitachi 5200 SEM.
X-ray diffraction: patterns were recorded on a Rigaku XRD-6000 diffractometer using the following conditions: 40 kV, 40 mA, Cu Kα radiation (λ = 0.154 nm).
Inductively coupled plasma optical emission spectroscopy (ICP-OES) was performed on a Spectro Arcos FHS12.
X-ray photoelectron spectroscopy (XPS): XPS measurements were performed using monochromatized Al Kα radiation on a PHI Quantera SXM system.
Electrochemical Characterization： All electrochemical experiments were performed on a CHI 760E electrochemical system (CH Instruments Inc.). 1 M aqueous KOH solution was used as the electrolyte. **Electrode 1** or **Electrode 2** were used as the working electrode, Pt wire as counter electrode and Hg/HgO (1 M KOH) as reference electrode. Linear sweep voltammetry was recorded at a scan rate of 2 mV/s with iR-correction. Chronopotentiometry was performed at constant current densities of 10 and 100 mA/cm^2. Tafel slopes were derived from LSV curves. Electrochemically active surface area analyses (ESCA) were examined from 10 mV/s to 70 mV/s and calculated in a reported method.[1] OER Faradic efficiency was measured by bulk electrolysis. An optical fluorescence O_2 sensing probe (PyroScience FireSting) was used to obtain O_2 concentration.
Chemicals: Tin chloride ($SnCl_2 \cdot 2H_2O$, Alfa Aesar), Palladium chloride ($PdCl_2$), trisodium citrate ($Na_3C_6H_5O_7$ Merck), ammonium chloride (NH_4Cl, Sigma-Aldrich), sodium hypophosphite monohydrate $NaH_2PO_2 \cdot H_2O$, Acros Organics), aqueous ammonia solution ($NH_3 \cdot H_2O$, VWR), nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$ Sigma-Aldrich), iron nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$, VWR), potassium hydroxide (KOH, Sigma-Aldrich), Nickel (II) sulfate hexahydrate (Fluka), ethanol (CH_3CH_2OH), chloride acid (HCl, Acros Organics), sulfate acid (H_2SO_4, Sigma-Aldrich), Phosphoric acid (H_3PO_4, VWR), Manganese oxide (MnO_2,

MERCK).

2. Synthetic section

2.1 Chemical etching of the printed ABS meshes.

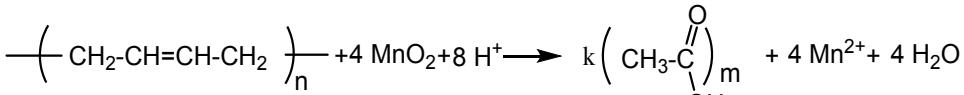
A modified literature procedure was used[2]: 60 mL H_2SO_4（96%）, 28 mL （85%） H_3PO_4 ,12 mL H_2O and 3.0 g MnO_2 were mixed and stirred for 4 h at 70 °C to prepare the etching solution (which can be re-used). The ABS mesh was immersed into 25 mL of the mixture at 60 °C for 40 min without stirring. Then, the ABS mesh was removed, washed with water and ethanol for several times and air-dried overnight.

2.2 Preparation of Electrode 1

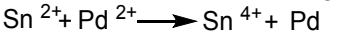
The modified ABS substrate was immersed for 10 min in 20 mL aqueous HCl solution (0.24 M) containing 10 g/L (0.04 M) $SnCl_2 \cdot 2H_2O$. After washing with water, the substrate was dipped in 10 mL aqueous HCl solution (0.24 M) containing 0.5 g/L $PdCl_2$ (3 mM). After 10 min, the mesh was removed from above solution and washed with water and ethanol and air-dried. The aqueous plating solution containing 32 g/L (0.122 M) $NiSO_4 \cdot 6H_2O$, 20 g/L (0.068 M) trisodium citrate, 20 g/L (0.374 M) NH_4Cl and 33 g/L (0.375 M) NaH_2PO_2 was prepared. The pH was adjusted to pH 9.0 using aqueous ammonia solution. The ABS substrate was immersed in the plating solution without stirring for 40 min. The mesh was then removed, rinsed with water and ethanol and air-dried, giving **Electrode 1**.

2.3 Preparation of Electrode 2

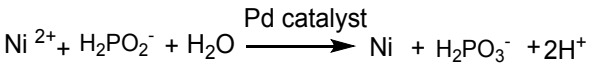
The aqueous electrodeposition solution contains 3 mM $Ni(NO_3)_2 \cdot 6H_2O$ and 3 mM $Fe(NO_3)_3 \cdot 9H_2O$.[3] The electrodeposition was performed in a three-electrode system, **Electrode 1** was used as the working electrode, Pt wire as the counter electrode and Ag/AgCl (3 M KCl) as reference electrode. The electrodeposition was carried out in 25 mL electrodeposition solution at a constant potential of -1.7 V for 300 s at room temperature. After deposition, the working electrode was removed, rinsed with water and ethanol and air-dried. The average catalyst amount was 1.3 mg per electrode (based on the weight difference of **Electrode 1** and **2**, based on three electrode measurements).



eq. S1



eq. S2



eq. S3

Scheme S1: Proposed oxidative etching of ABS by MnO_2.

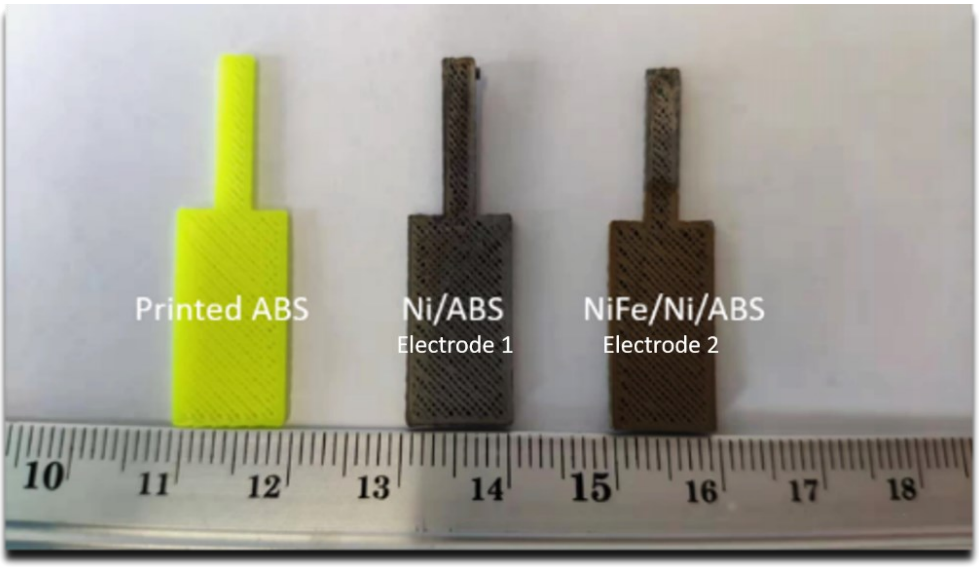


Fig. S1: photograph of as-printed ABS mesh, **Electrode 1** and **Electrode 2**

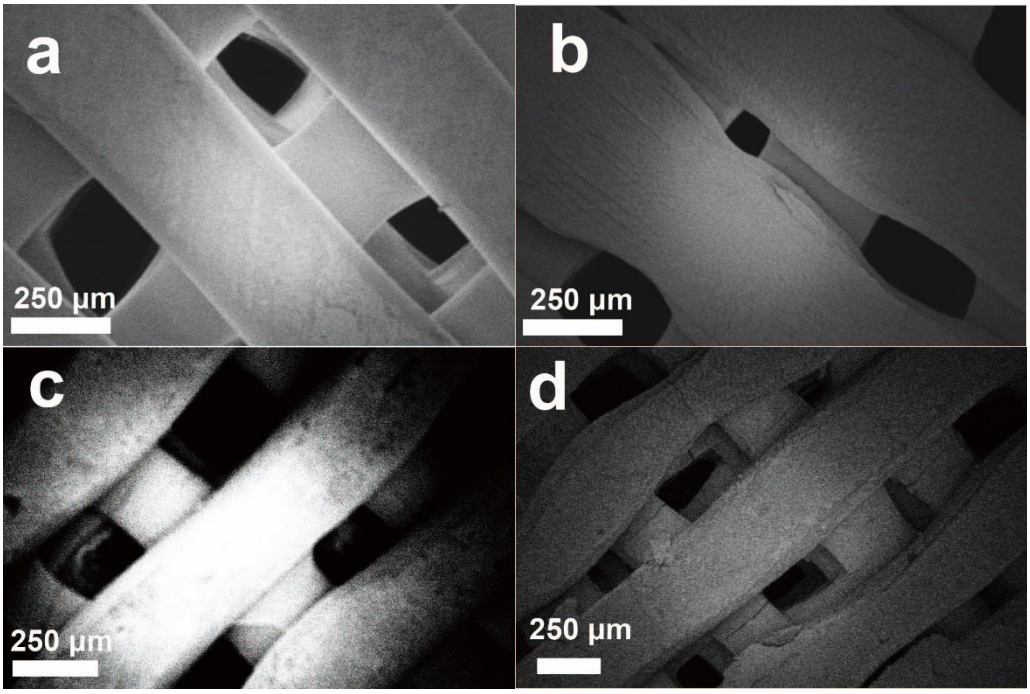


Fig.S2: SEM image of Printed ABS mesh (a), etched ABS (b), **Electrode 1**(c) and **Electrode 2** (d),

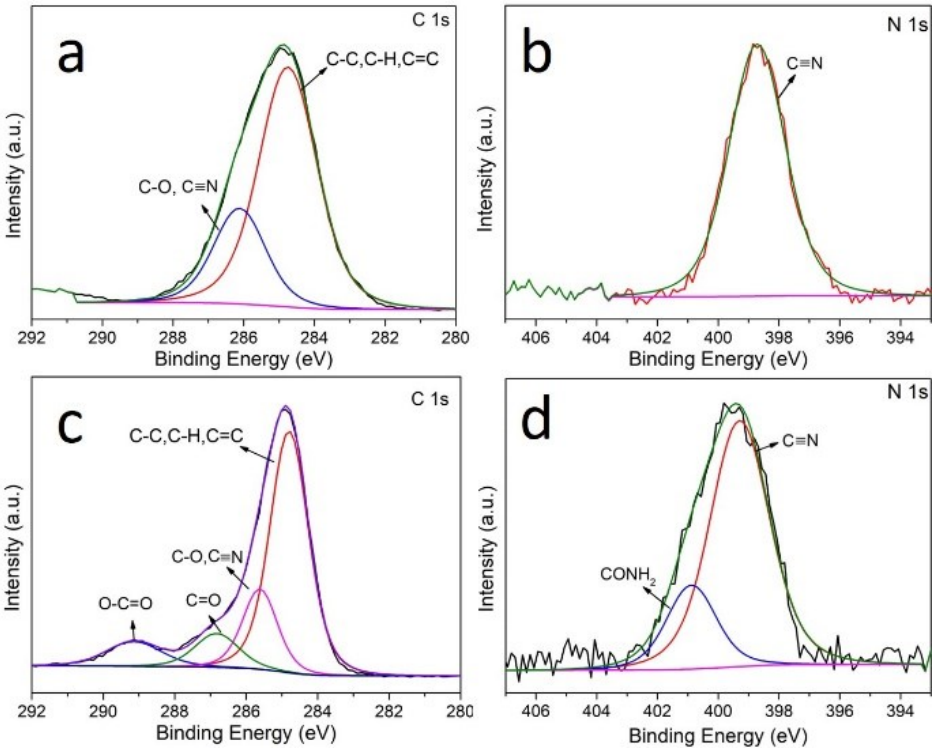


Fig. S3: XPS spectra of printed ABS (a, b) and etched ABS (c, d)

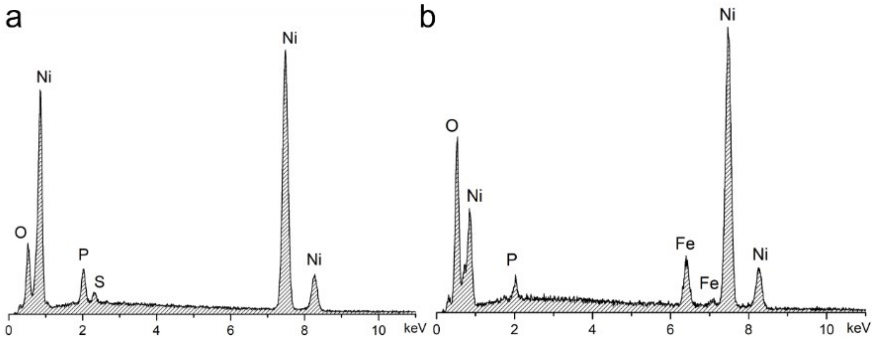


Fig. S4 EDX spectra of **Electrode 1** (a) and **Electrode 2**(b)

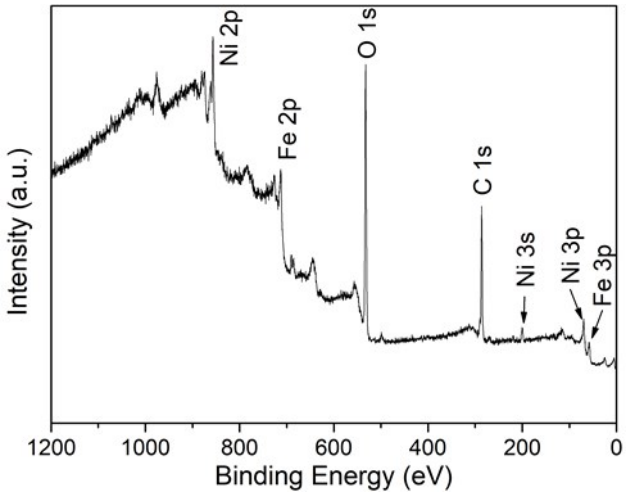


Fig. S5 XPS survey spectrum for **Electrode 2**

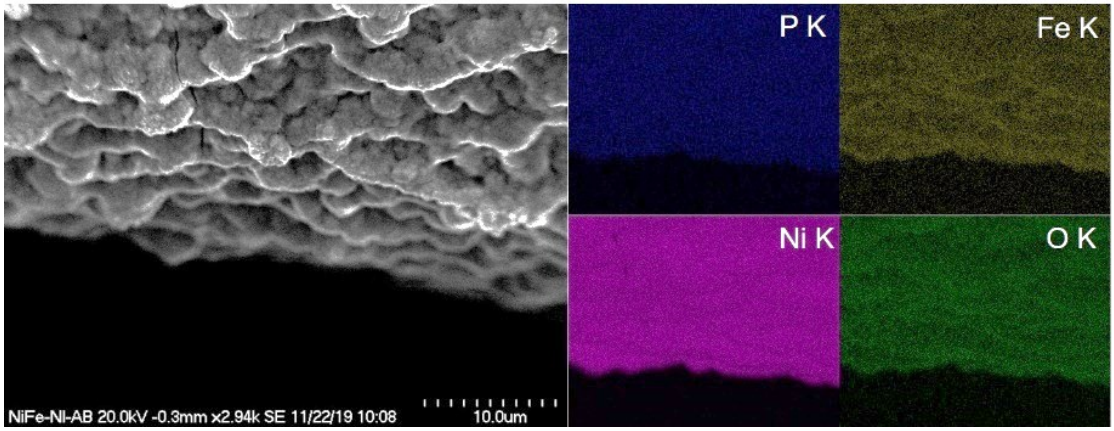


Fig. S6 SEM-EDX mapping images of **Electrode 2**

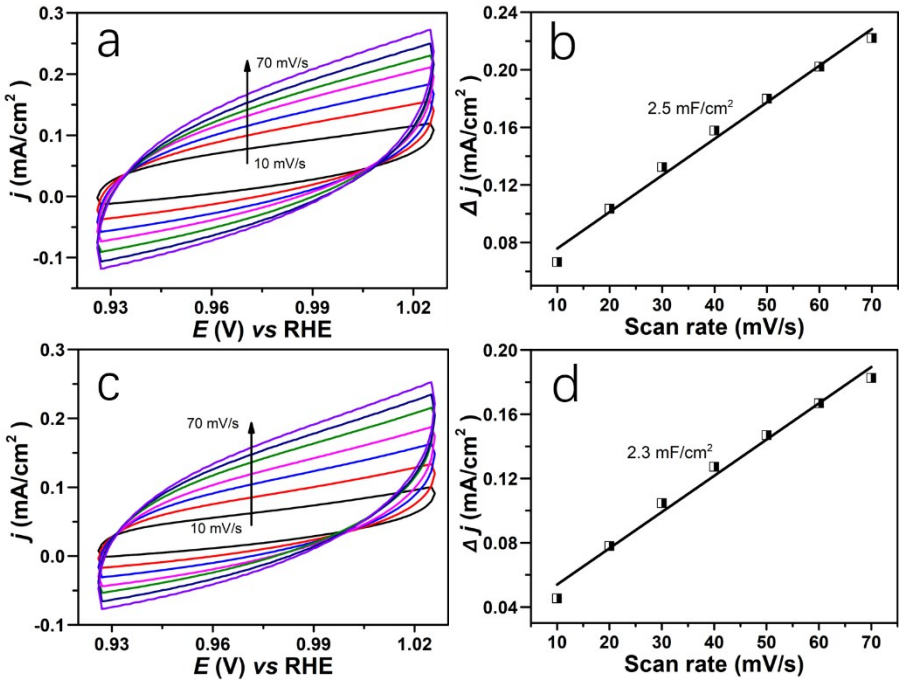


Fig. S7 (a) CV curves of **Electrode 1** measured at scan rates from 10 to 70 mV/s, (b) The corresponding linear fitting plots of differences in current density ($\Delta j = j_a - j_c$) at 0.98 V vs scan rate for **Electrode 1**, (c) CV curves of **Electrode 2** measured at different scan rates and (d) The corresponding linear fitting plots of differences in current density ($\Delta j = j_a - j_c$) at 0.98 V vs scan rate for **Electrode 2.** J_a: anodic current density; J_c: cathodic current density.

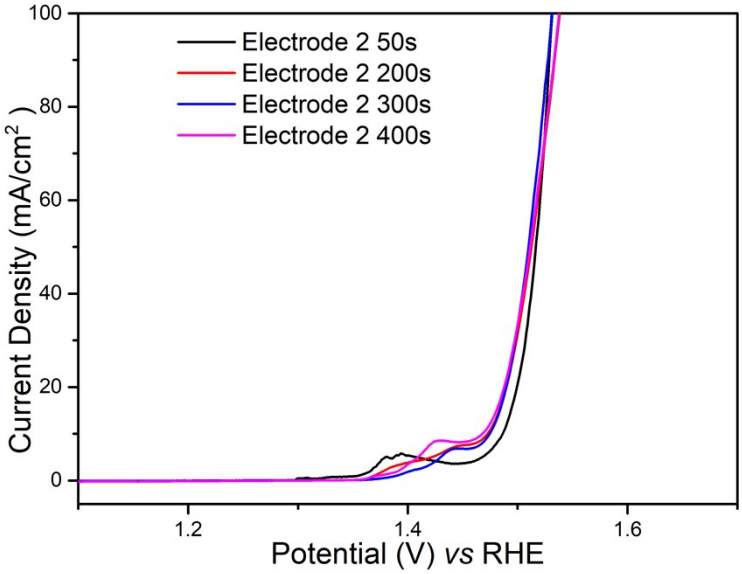


Fig. S8: LSV curves of **Electrode 2** with different electrodeposition time (50 – 400 s).

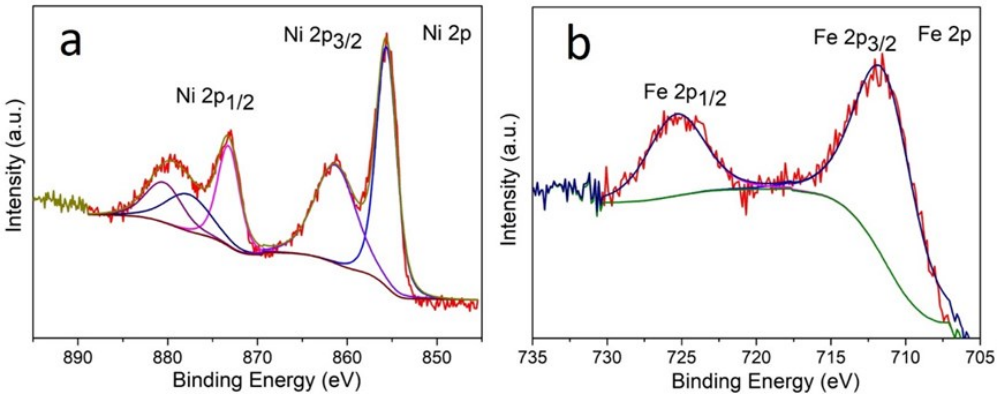


Fig. S9 XPS spectra of **Electrode 2** after 10 h electrolysis at 100 mA/cm^2

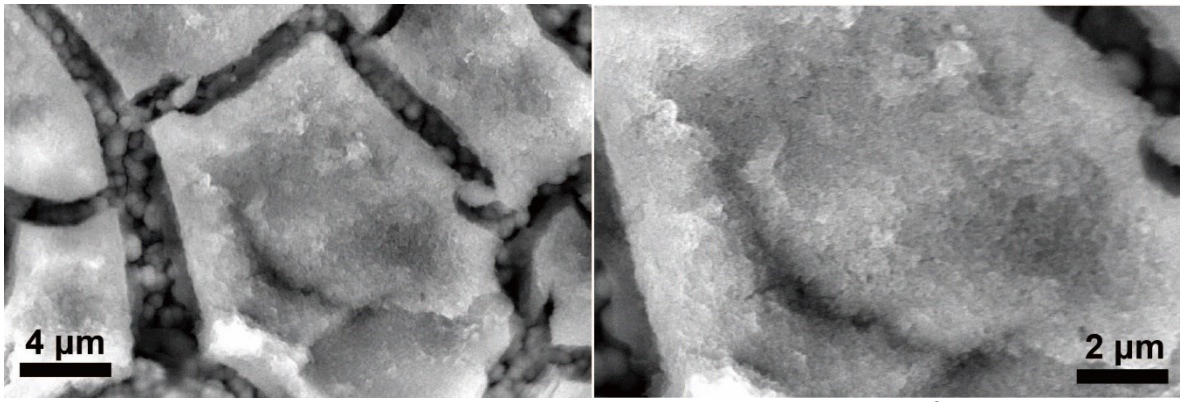


Fig. S10 SEM analysis of **Electrode 2** after 10 h electrolysis at 100 mA/cm^2

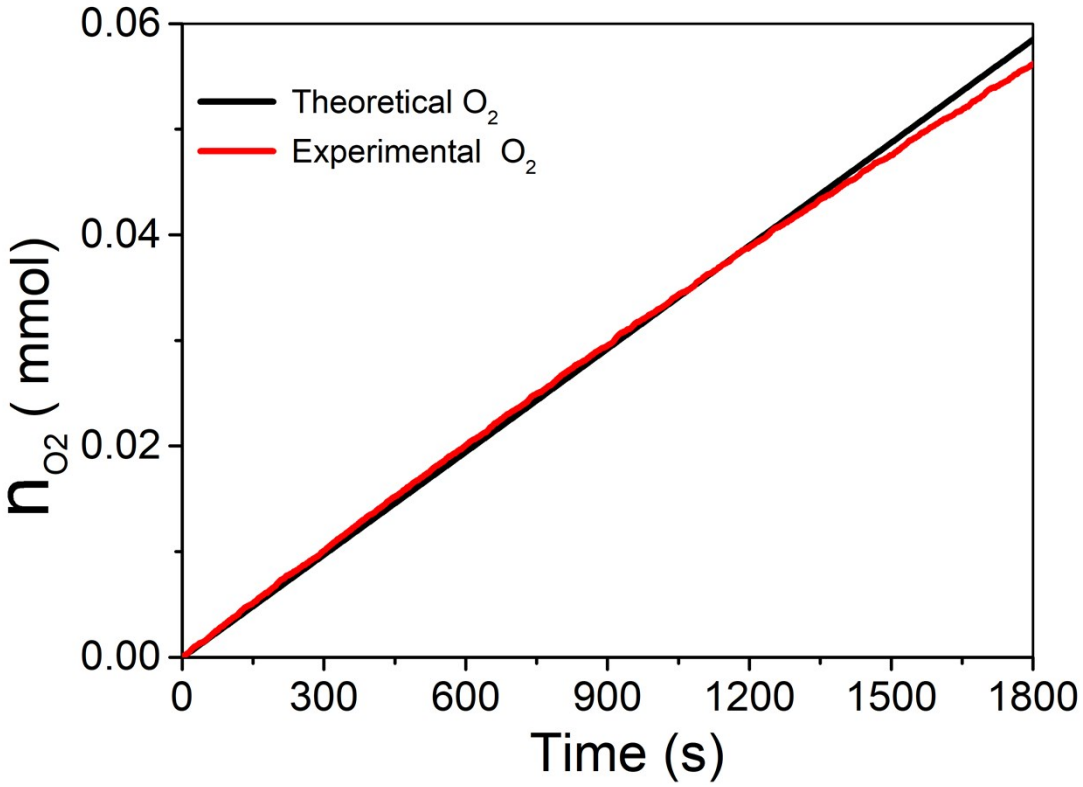


Fig. S11 Faradic efficiency of oxygen production using **Electrode 2**

Table S1: Comparison of OER performances of 3D printed electrode in in 1M aqueous KOH

Catalyst	Support	3D printing technology	Overpotential (mV) at		Tafel slope mV/dec	Ref
			10 mA/ cm^2	100 mA/ cm^2		
$NiCo_2S_4$	stainless steel	SLM	226	277	38.7	[4]
-	stainless steel	SLM	470	-	53	[5]
IrO_2	stainless stee	SLM	320	~400	92	
NiFe	stainless steel	SLM	290[a]	-	37/76	[6]
NiFe	Polymer	SLA	197	~210	51	[7]
NiFe	ABS	FDM	250	300	53	This work

a: at 20 mA /cm^2
SLM: selective laser melting
SLA: stereolithography apparatus
FDM: fused deposition modeling

3. References

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