

Supplementary Material for New Journal of Chemistry

Unravelling the Potential of Disposable and modifiable Pencils as Catalyst Supports for Hydrogen Evolution Reaction

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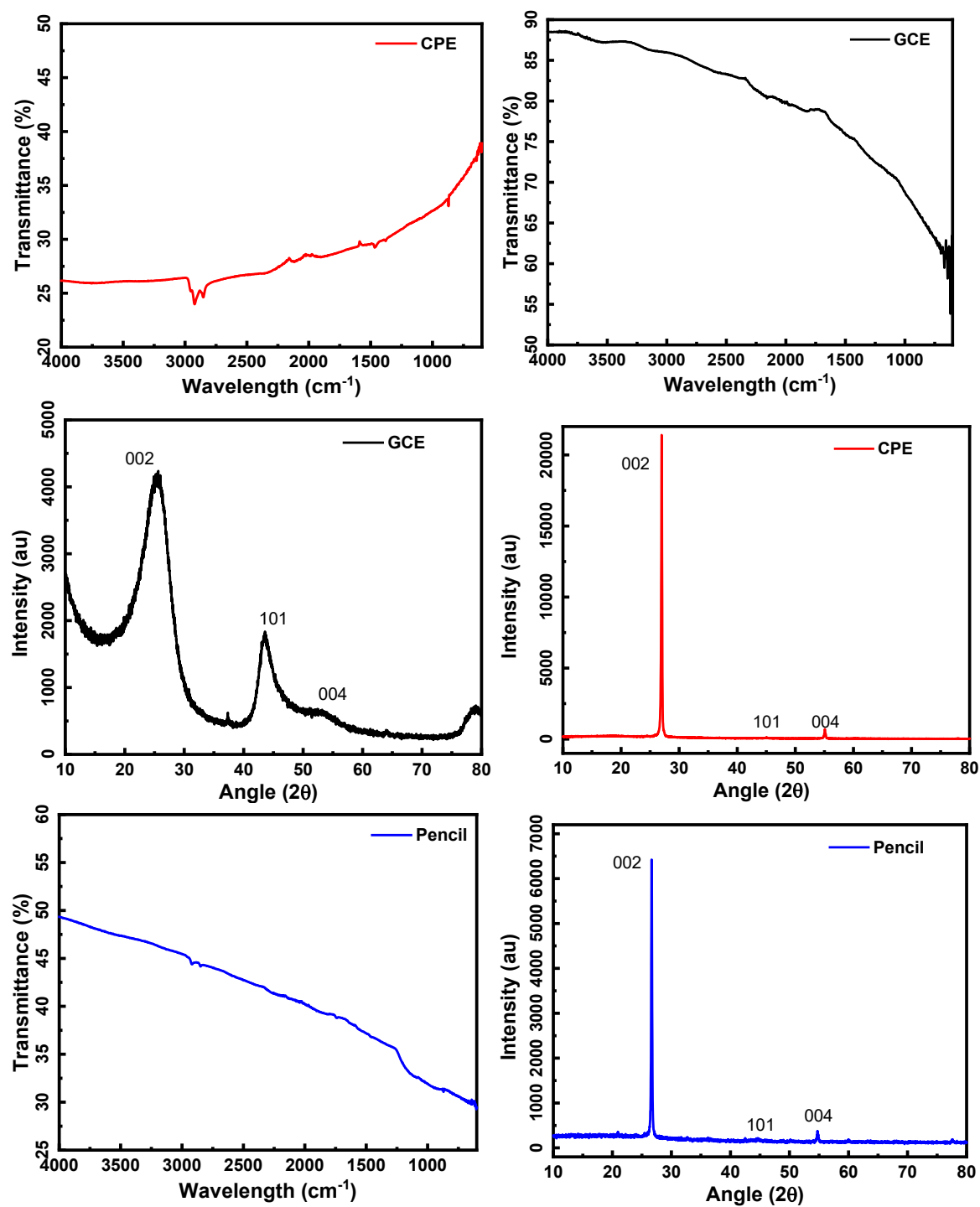


Figure S1. FT-IR spectra (left) and XRD (right) of different carbon electrodes.

The infrared spectrum (Figure S1a) shows a sharp N-H stretch at 3343 cm^{-1} and C=N stretch at 1574 cm^{-1} , consistent with previously reported literature values. Two distinct absorption bands are observed in UV-visible spectrum of the catalyst (Figure S1b), one intense ligand-to-ligand charge transfer band at 257 nm and another ligand-to-metal charge transfer band at 398 nm . Figure S2 shows the ^1H NMR spectrum of Ni-ATSM in DMSO- D_6 . The spectrum shows three characteristic peaks at 7.68 ppm , 2.78 ppm and 1.94 ppm for NH protons, pendant methyl protons and the backbone methyl protons, respectively.

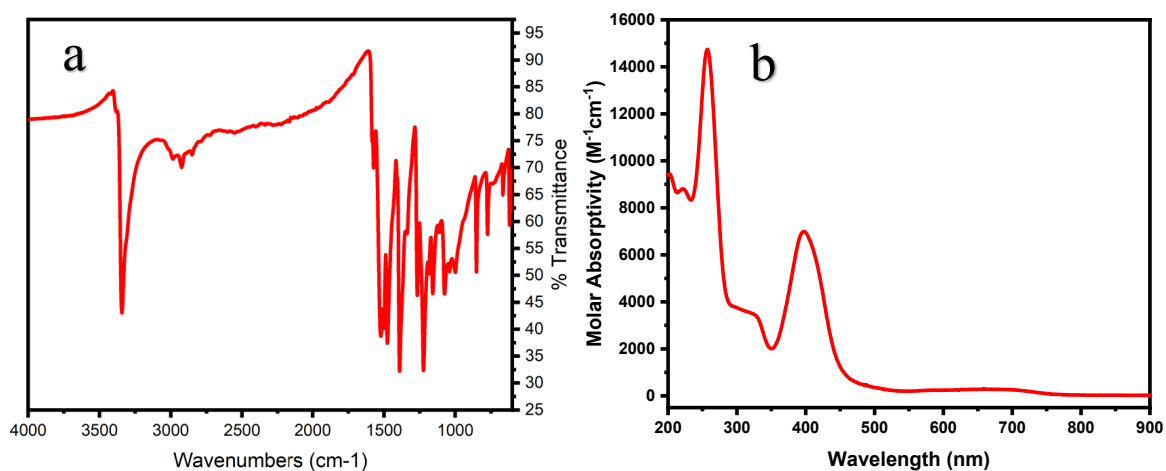


Figure S2. a) FT-IR spectrum of Ni-ATSM b) UV-visible spectra of Ni-ATSM in acetonitrile.

Ni-ATSM

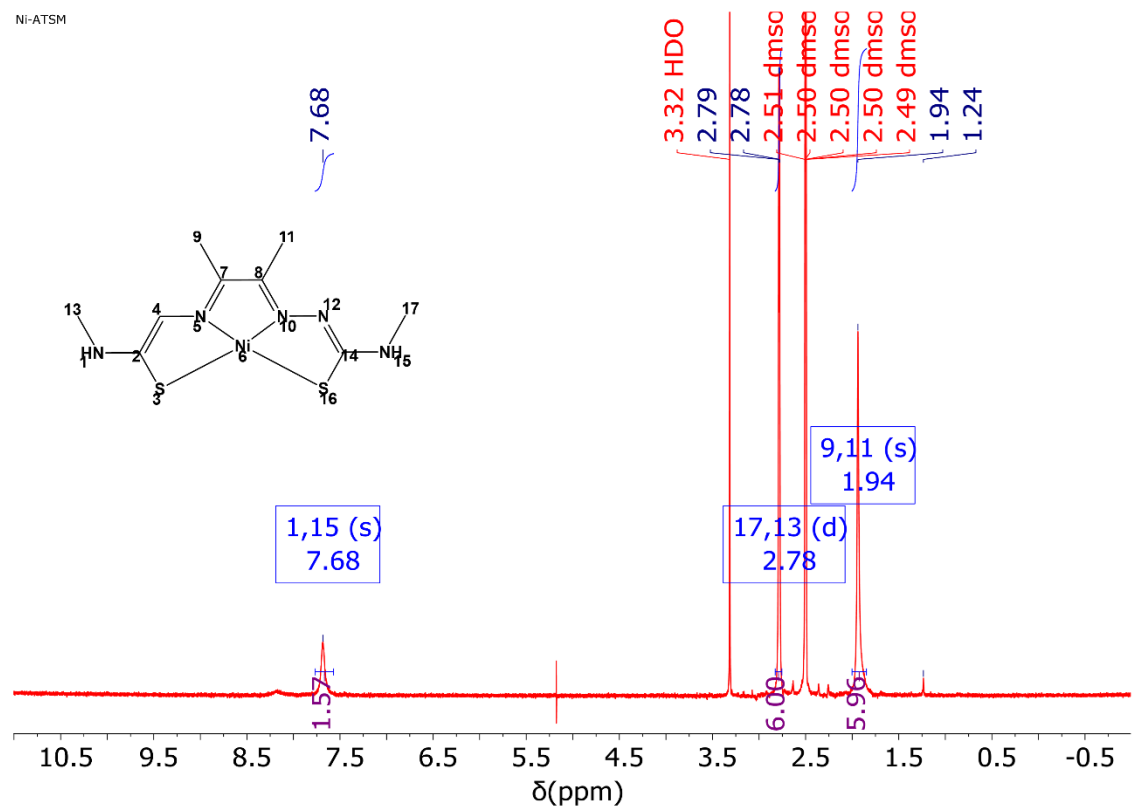


Figure S3. ^1H NMR of Ni-ATSM in DMSO- D_6 (500MHz, δ 7.68 (s, 2H), δ 2.78 (d, $J = 4.8$ Hz, 6H), δ 1.94(s, 6H)).

Table S1. Tafel slope and overpotential of different carbon substrates at -10 mA/cm 2 .

	Overpotential	Tafel slope mV/decade
Blank GCE	>900	140
Blank CPE	>900	130
Blank HB	730	190
Blank 2B	743	192
Blank 4B	751	220
Blank 8B	748	186

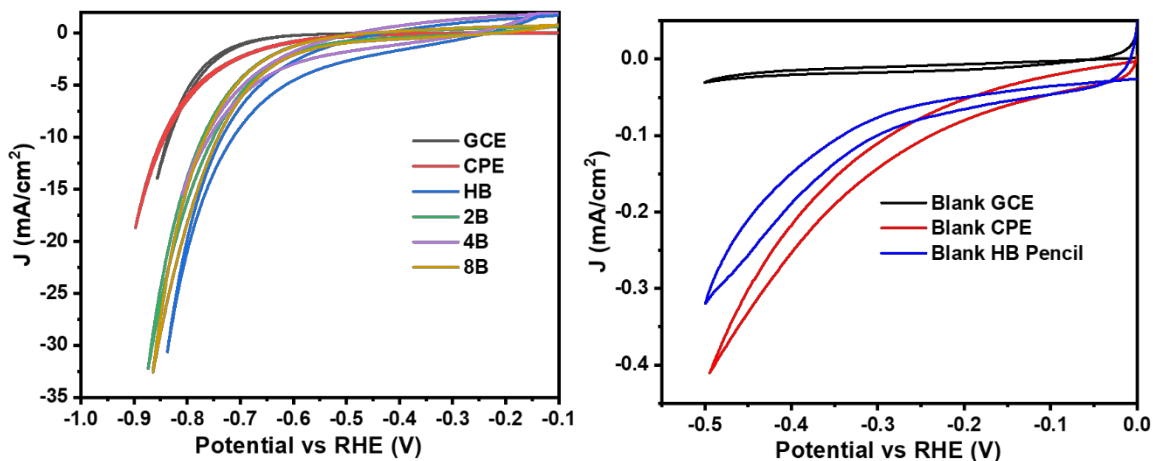


Figure S4. Cyclic voltammograms for carbon supports in 0.5 M H₂SO₄ from -0.1 to -1.0 V vs RHE (left) and for GCE, CPE, and HB pencil from 0 to -0.5 V in 0.5 M H₂SO₄ (right) (Scan rate 100 mV/s).

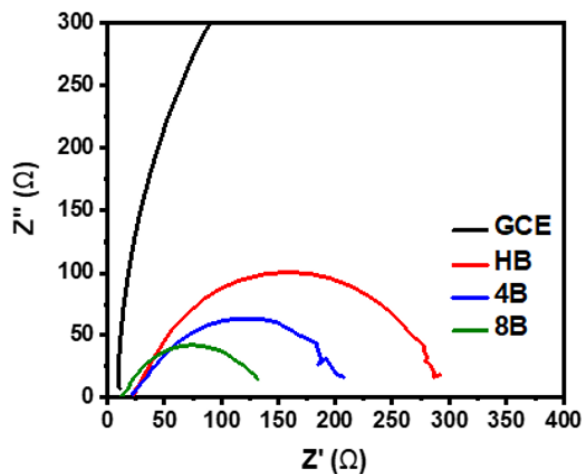


Figure S5. Nyquist plot of different grade of pencils in comparison with glassy carbon electrode.

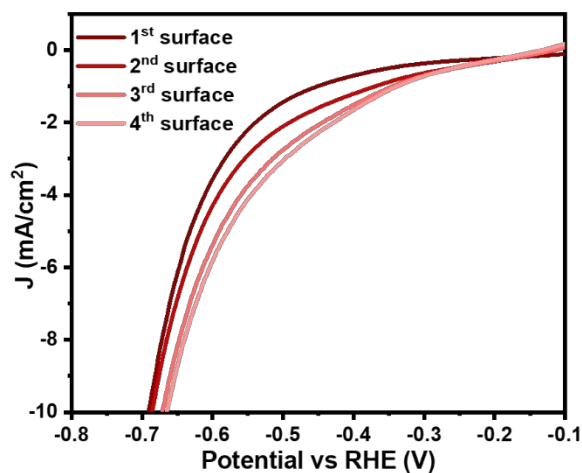


Figure S6. LSV plot of different surface of pencils generated using table saw in 0.5 M H₂SO₄ from -0.1 to -0.8 V vs RHE.

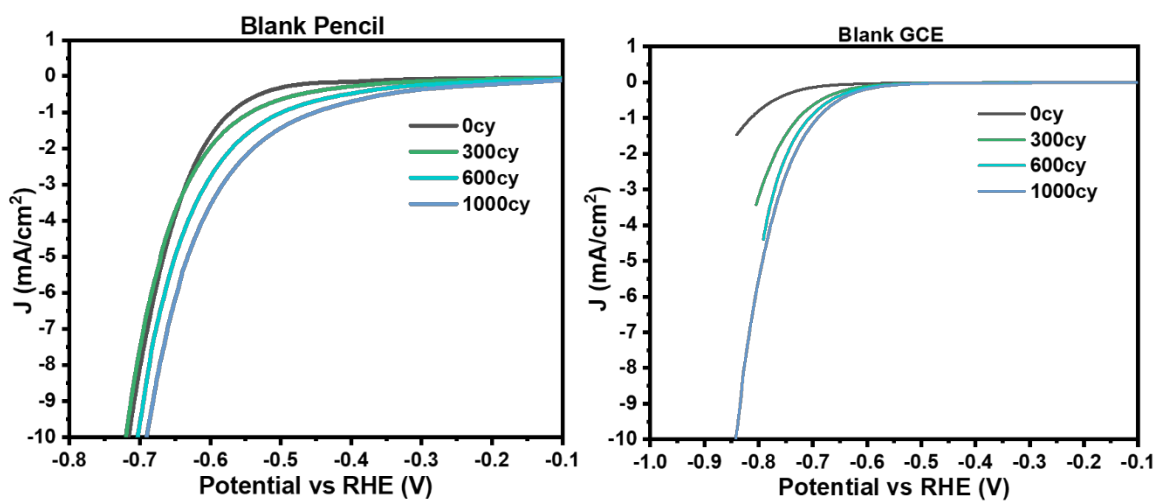


Figure S7. LSV of pencil surface (left) and GCE surface (right) after each 300 reductive cycling.

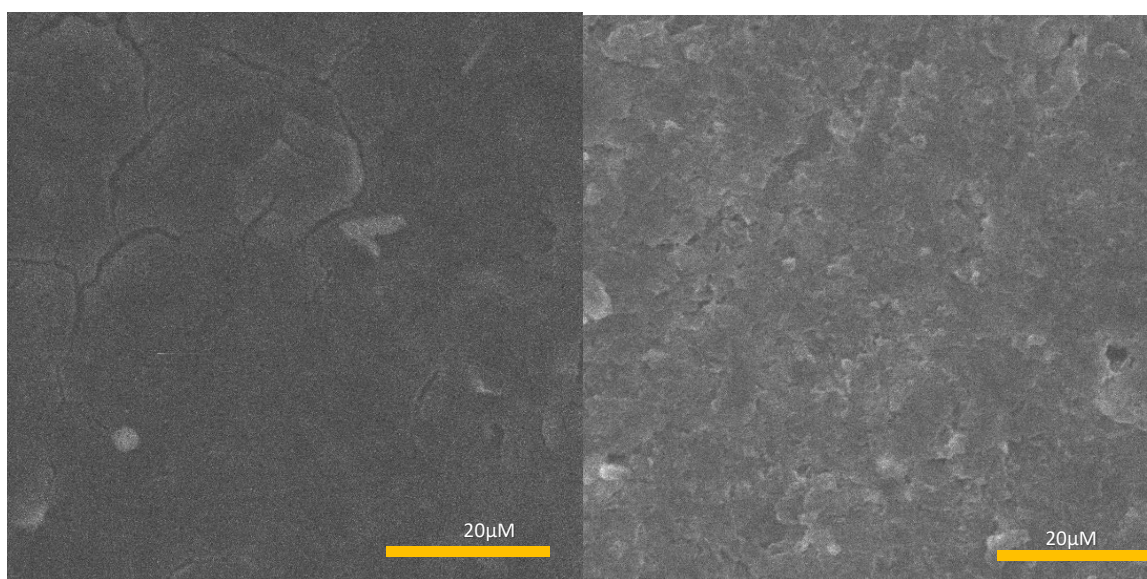


Figure S8. SEM image of pencil before (left) and after (right) 1000 reductive cycling.

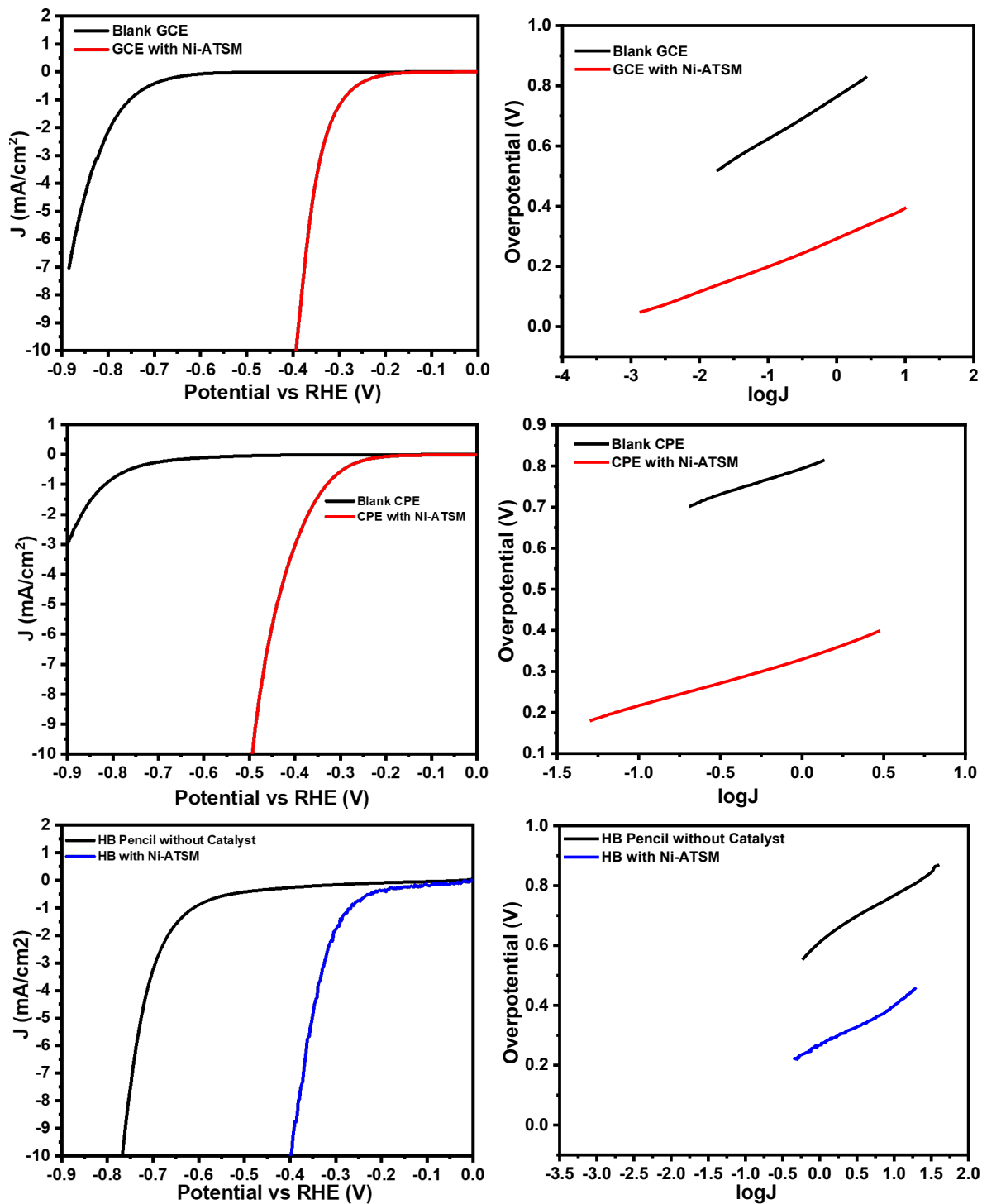


Figure S9. LSV and Tafel plots of the the carbon supports GCE, CPE, and HB, with and without catalyst.

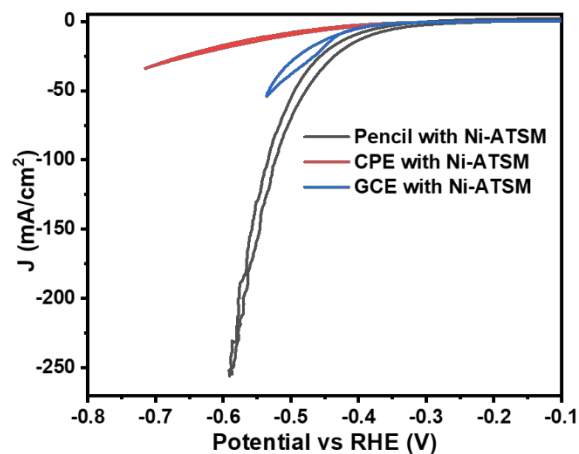


Figure S10. Cyclic voltammograms for Ni-ATSM on GCE, CPE, and HB pencil in 0.5 M H₂SO₄ from -0.1 to -0.8 V vs RHE at a scan rate of 100 mV/s.

Table S2. Tafel slope and overpotential (at -10 mA/cm₂) of catalyst loaded carbon surfaces.

	Over potential (mV)	Tafel slope
PGE with catalyst	400	137
GCE with catalyst	393	90
CPE with catalyst	493	118
Etched PGE with catalyst	354	116
Platinum	61	29

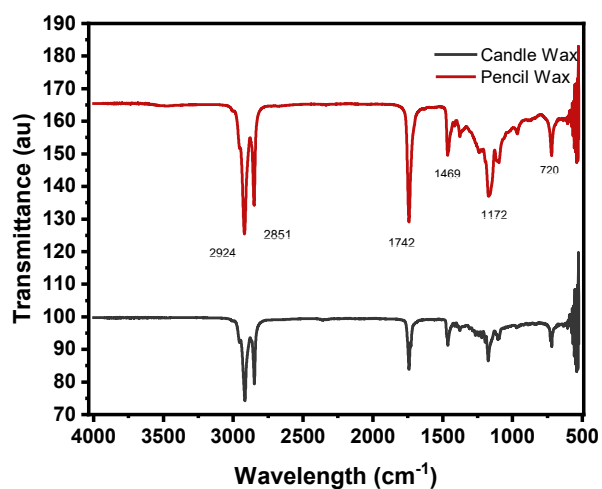


Figure S11. IR spectra of wax obtained from HB pencil by acetone extraction compared to candle wax.

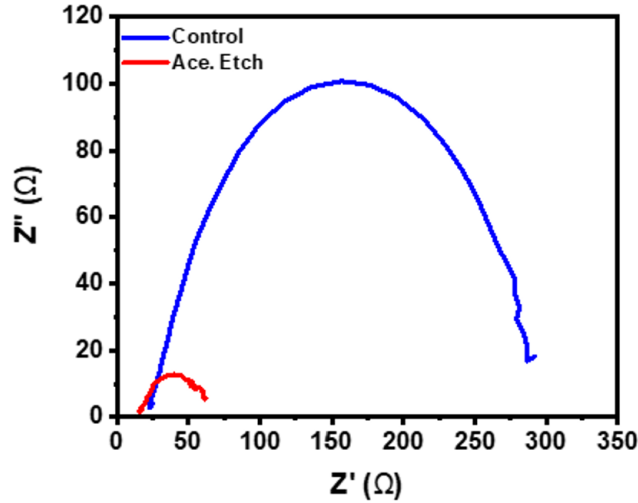


Figure S12. Nyquist plots for the HB Pencil Before and after etching.

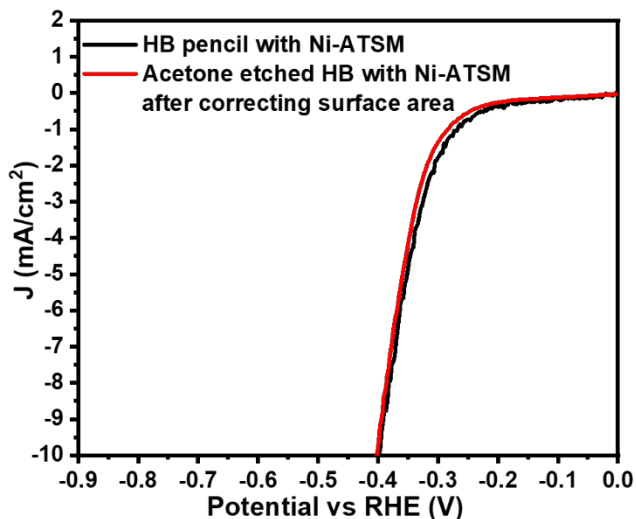
Measurement of relative electrochemically active surface area

$$|I_p| = 0.4463nAF C_{bulk} \left(\frac{nF_s D_A}{RT} \right)^{1/2}$$

Capacitance measurement method was used to determine the relative increase in electrochemically active surface area of the pencil after etching with acetone. For this cyclic voltammetry (CV) was utilized. Ag/Ag⁺ was used as reference electrode, graphite rod as counter and pencil graphite before or after etching as working electrode. CV of the unetched pencil and the same pencil after etching with acetone was taken in 0.5 M H₂SO₄ in small constant potential window in non-faradaic region using different scan rates (10, 20, 30, 40, 50 mV/s). CV was plotted and the area under the curve of CV was determined which can be correlated to the current used for charging the electrical double layer. This integrated current can be correlated to the surface area of electrode using following equation. When potential window is same and scan rate is same, increase in current can be related to increase in surface area of the electrode. Therefore, ratio of the current after and before etching with acetone will give the relative increase in the surface area after etching. Table S3 below shows the calculated values of ratio of capacitance after and before etching which can be correlated to the relative increase in surface area after etching.

Table S3. Calculation of relative surface area of acetone etched pencil

Blank Pencil		Acetone Etched Pencil		Ratio of Charge
Scan rate	Area under curve (Charge)	Scan rate	Area under curve (Charge)	
20	6.84E-08	20	1.31E-07	1.91
30	8.03E-08	30	1.99E-07	2.48
40	1.53E-07	40	2.95E-07	1.93
50	1.85E-07	50	4.91E-07	2.65

**Figure S13.** LSV catalyst modified pencil and surface area corrected acetone etched pencil with catalyst.

A reproducibility test was done with acetone etched pencil. In this test acetone etched pencil was used to drop cast catalyst and study HER activity. Catalyst modified etched pencil was cleaned by sonicating in acetone for half an hour and catalyst was drop casted on the surface again to study the HER activity. Figure S8 shows that there is not any substantial change in the overpotential of the catalyst modified etched pencil or etched pencil substrate when used again after cleaning.

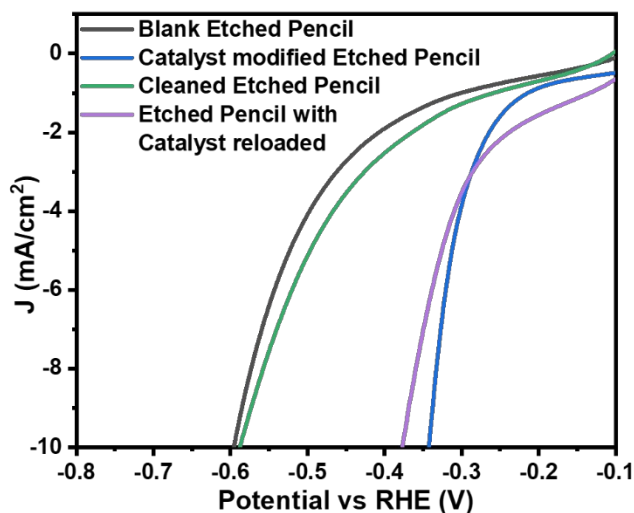


Figure S14. Reproducibility test of acetone etched pencil.

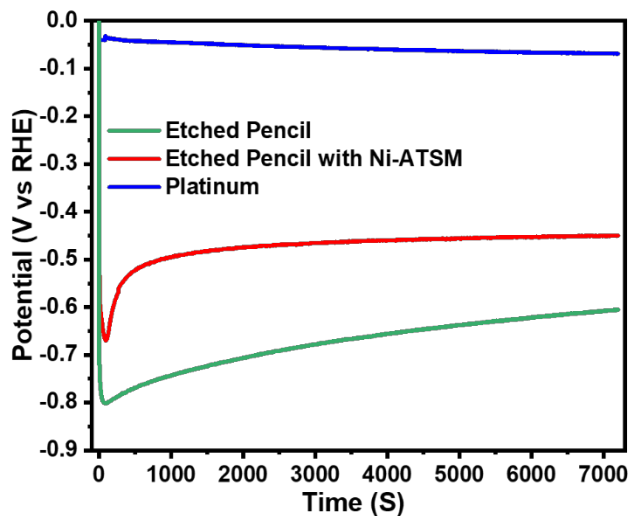


Figure S15. Chronopotentiometry at -10 mA/cm^2 of etched pencil, catalyst modified etched pencil, and platinum.

Table S4. Faradaic efficiency of platinum, acetone etched pencil and catalyst modified acetone etched pencil for HER

S.N.	Surface	Faradaic Efficiency for HER (%)
1	Platinum	100 ± 4
2	Acetone etched pencil	93 ± 3
3	Acetone etched pencil with Ni-ATSM	96 ± 6