Electronic Supplementary Information (ESI)

Petal-Like Hierarchical Array of Ultrathin $Ni(OH)_2$ Nanosheets Decorated with $Ni(OH)_2$ Nanoburls: An Highly Efficient OER Electrocatalyst

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Experimental Section

*(a) Reagents and Instruments***.**

Nickel(II) acetate hexahydrate, Fe free potassium hydroxide (99.99%), 5% Nafion solution and isopropyl alcohol were procured from Sigma-Aldrich. Ethanol (99.9%) was purchased from SRL, India. Hg/HgO reference electrode, Pt-foil counter electrodes were purchased from CH Intruments pvt. Ltd. Glassy carbon (GC) working electrode of 0.0732 cm^2 area was used as working electrode after modifying with the catalysts.Milli Q water (18 MΩ) was used for the entire synthesis and electrocatalysis processes. The synthesized petal-like 3D hierarchical array of β-Ni(OH)2 nanosheets and nanoburlsmicrospheres were characterized with HR-TEM, (Tecnai^{TM} G^2 TF20) working at an accelerating voltage of 200 kV.The Energy Dispersive X-ray Spectroscopy (EDS) analysis was done with the FE-SEM instrument (Oxford) with a separate EDS detector connected to that instrument. The XRD analysis was done with a scanning rate of 5° min^{-1} in the 2θ range 10-90° using a Bruker X-ray powder diffractometer (XRD) with Cu K_α radiation (λ = 0.154 nm). X-ray photoelectron spectroscopic (XPS) analysis was performed using a Theta Probe AR-XPSsystem (Thermo Fisher Scientific, UK). Electrochemical analyzer CHI6084c version 12.13 was used for the entire OER and related studies. RRDE experiments were carried out with a PINE RRDE equipment coupled with a bipotentiostat of AUTOLAB. An RRD electrode of GC disc and Pt ring electrode was used for all the RRDE related experiments. Hg/HgO reference electrode was used along with a Pt-foil counter electrode where our burl-like petal-like 3D hierarchical array of β-Ni(OH)2 nanosheets and nanoburls modified GC electrode was used as working electrode.

(b) Sample preparation for various characterizations.

As synthesized samples were directly taken for XRD and XPS analyses before cycling. TEM samples were prepared by dispersing required quantity in 1 mL of Milli Q water followed by drop casting on carbon coated copper TEM grid and dried at RT for slow evaporation of water before analyses in dark and vacuum.

(c) Determination of Surface Concentration of Ni from LSV redox peak.

Area from of Ni^{2+} to Ni^{3+} redox peak is = 5.303 ×10^{-4} V mA

Hence, Charge is = 5.303×10^{-4} V mA / 0.01 Vs^{-1}

= 5.303×10^{-2} mA s

or = 5.303×10^{-5} A s

i.e., = 5.303×10^{-5} Coulombs (since q =It)

Then, no. of electrons = 5.303×10^{-5} C/1.602×10^{-19}C

= 3.310×10^{14}

Now, divide by the number of e-transferred in the redox reaction which is 1 here.

= 3.310×10^{14} /1

= 3.310×10^{14} atoms

Area selected for surface concentration calculation from LSV is given as Figure S4.

(d) Determination of TOF value from OER current.

Turnover frequency for an electrocatalytic water splitting reactions can be done in more than one way. The surface concentration of Ni atoms at the modified GC working electrode was calculated from the Ni^{2+} to Ni^{3+} redox peak from the LSV (the first method stated in the main text).The corresponding expression is,

$$\mathbf{TOF} = \boldsymbol{i} \times \mathbf{N_A} / \mathbf{A} \times \mathbf{F} \times \mathbf{n} \times \boldsymbol{\Gamma}$$

Where,

i = current

N_A= Avogadro number

A = Geometrical surface area of the electrode

F = Faraday constant

n = Number of electrons

Γ = Surface concentration

We have taken the OER current of 1 mA/cm^2 observed at 1.47 V vs. RHE, 10 mA/cm^2 observed at 1.53 V vs. RHE and 47.8 mA/cm^2 at 1.61 V vs RHE with the loaded catalyst to calculate TOF$_{max}$.

Hence we have,

$$\mathbf{TOF_{1.47V}} = [(1\times 10^{-3})\ (6.023\times 10^{23})] / [(1)\ (96485)\ (4)\ (3.31 \times 10^{14})]$$

$$\mathbf{TOF_{1.47V}} = 4.71\ s^{-1}$$

$$\mathbf{TOF_{1.53V}} = [(10\times 10^{-3})\ (6.023\times 10^{23})] / [(1)\ (96485)\ (4)\ (3.31 \times 10^{14})]$$

$$\mathbf{TOF_{1.53V}} = 47.14\ s^{-1}$$

And the TOF$_{1.61V}$ is

$$\mathbf{TOF_{1.61V}} = [(47.8\times 10^{-3})\ (6.023\times 10^{23})] / [(1)\ (96485)\ (4)\ (3.31 \times 10^{14})]$$

$$\mathbf{TOF_{1.61V}} = 238.50\ s^{-1}$$

(e) Determination of TOF value from ORR current.

The turnover frequency (TOF) of the catalyst, defined as a electron transfer per second and a catalytic site active for a paricular reaction, can be calculated from the oxygen reduction (ORR) current at the ring (I_R) electrode using the equation (1) where n is the number of electrons transferred per oxygen molecule at the ring electrode (n = 4), F is Faraday's constant (96485 C), A is the area of the disk electrode, Γ is the surface concentration in moles/cm^2 (5.49×10^{-10}) of the catalyst as determined earlier using the peak of Ni^{2+} to Ni^{3+} oxidation and N_{CL} is the collection efficiency (0.3684).

$$TOF_{1.55\ V} = I_R / n \times F \times A \times N_{CL} \times \Gamma \qquad (1)$$

The calculated TOF of the our catalyst is 69.05 s^{-1}, which is in closer agreement with the one calculated using the OER current at the same potential and with the earlier report which followed similar calculation methods for the determination TOF value for Ni-Fe monoliths.[11] Both the faradaic efficiency and the corresponding TOF value of our catalyst are clearly implying that the observed current is mainly due to the O_2 evolution at OER region rather than the redox reaction that occurs just before the O_2 evolution on our catalyst. Moreover, the highest TOF values obtained from both OER current and the ORR current (from RRDE experiment) at the same potential of 1.55 V have undoubtedly confirmed that our catalyst is highly efficient and active in electrocatalytic OER at such a lower overpotential (0.032 V). This further entails; though the potential for the redox reaction of the catalyst is closer to that of OER region, at this overpotential OER have ultimately dominated the redox reaction and also witnesses that the observed current is only due to O_2 evolution.

Determination of electrochemically active surface area (ECSA):

Though there are more than one method is available for the determination of ECSA of an electrocatalyst, we have chosen the double layer capacitance method as per the existing literature reports (ref. 1 & 37 in main text). In this method a set CVs are acquired by varying the scan rate lower to higher (e.g., 1 to 200 mV/s) on the catalyst modified GC. Then the double layer charging current at potential where both anodic and cathodic portion of CV is parallel to one another is measured and plotted against the corresponding scan rate. The double layer charging current is expressed as given in the following equation.

$$\boldsymbol{I_c = vC_{DL}}$$

where I_c is the double layer charging current, v is the scan rate and C_{DL} is the double capacitance associated with it. Hence, the slope of the linear plot of I_c *vs* v will yield the corresponding C_{DL}

of the catalyst. From the C_{DL}, one can easily find out the ECSA of an electrocatalyst using the following equation, in case when the specific capacitance (C_S) of the same material is known or determined under similar experimental conditions.

$$\boldsymbol{ECSA = C_{DL} / C_S}$$

In our case, it becomes easier, as there are many reports available stating the C_S of both $Ni(OH))_2$ and RuO_2. For $Ni(OH)_2$ the reported value of C_S varies from 0.033 mF to 0.056 mF in alkaline conditions. Hence we have chosen an average of 0.040 mF to get the ECSA of our catalyst as done earlier reports (ref. 1& 37 in main text). Similarly, for RuO_2, the C_S values reported in alkali are ranging from 0.013 mF to 0.019 mF. Hence we have chosen a value of 0.016 mF to get the ECSA of the commercial RuO_2-Sigma catalyst. The figures related to this are given as Figure S3, a-d. The ECSA values obtained by this method for our catalyst is 0.1515 cm^2 and for RuO_2-Sigma is 0.1136 cm^2. This ECSA is used to normalize the electrochemical data to obtain other significant activity parameters of both the catalysts.

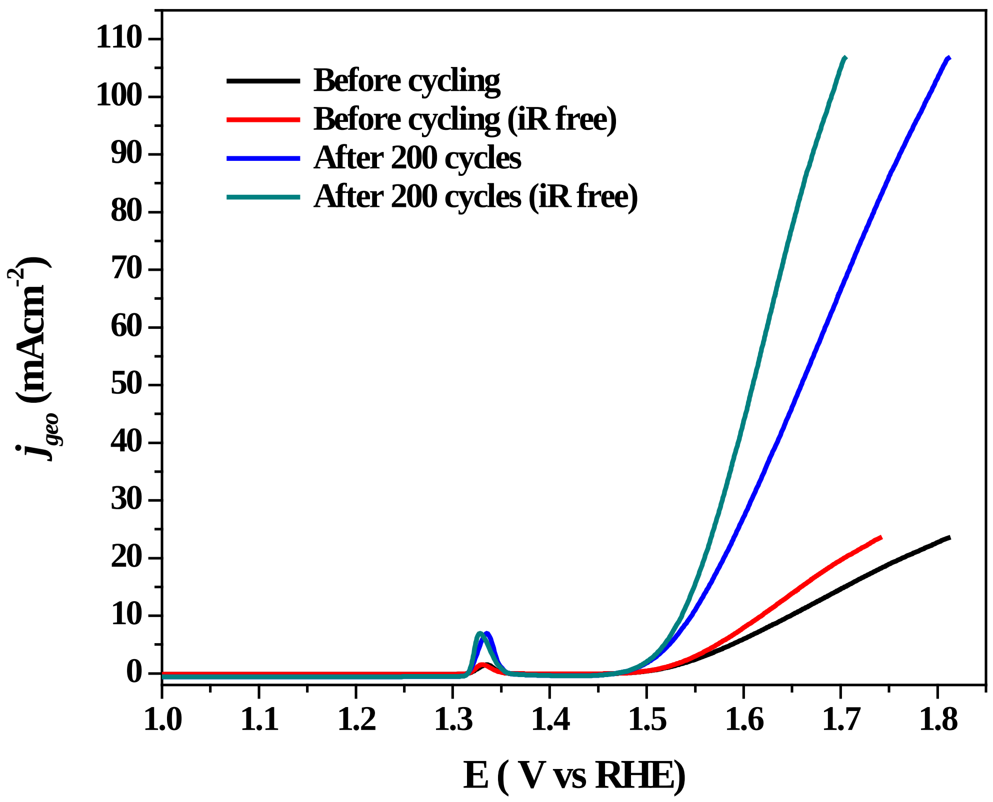

Figure S1: LSVsof burl-like petal-like 3D hierarchical array of β-Ni(OH)$_2$ nanosheets and nanoburls modified GC before and after cycling with and without ohmic drop as indicated above in different colors.

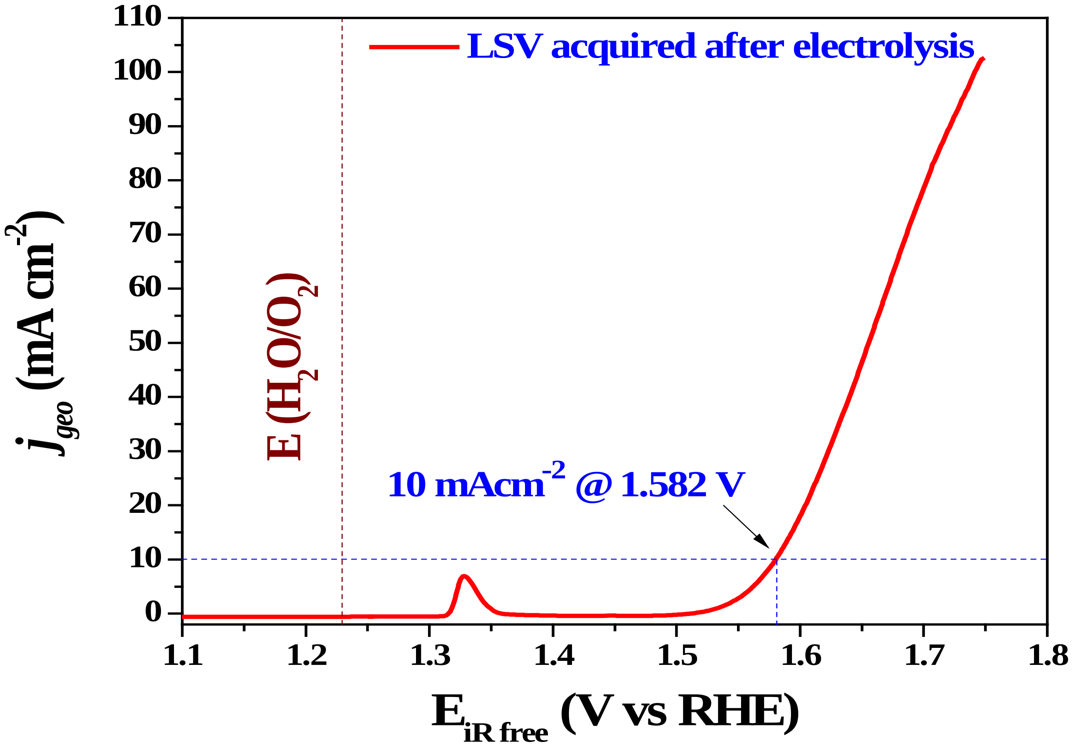

Figure S2: Post-Chronopotentiometric LSV acquired on the cycled petal-like 3D hierarchical array of β-$Ni(OH)_2$ nanosheets and nanoburls after 24 h of chronopotentiometry at 10 $mAcm^{-2}$.

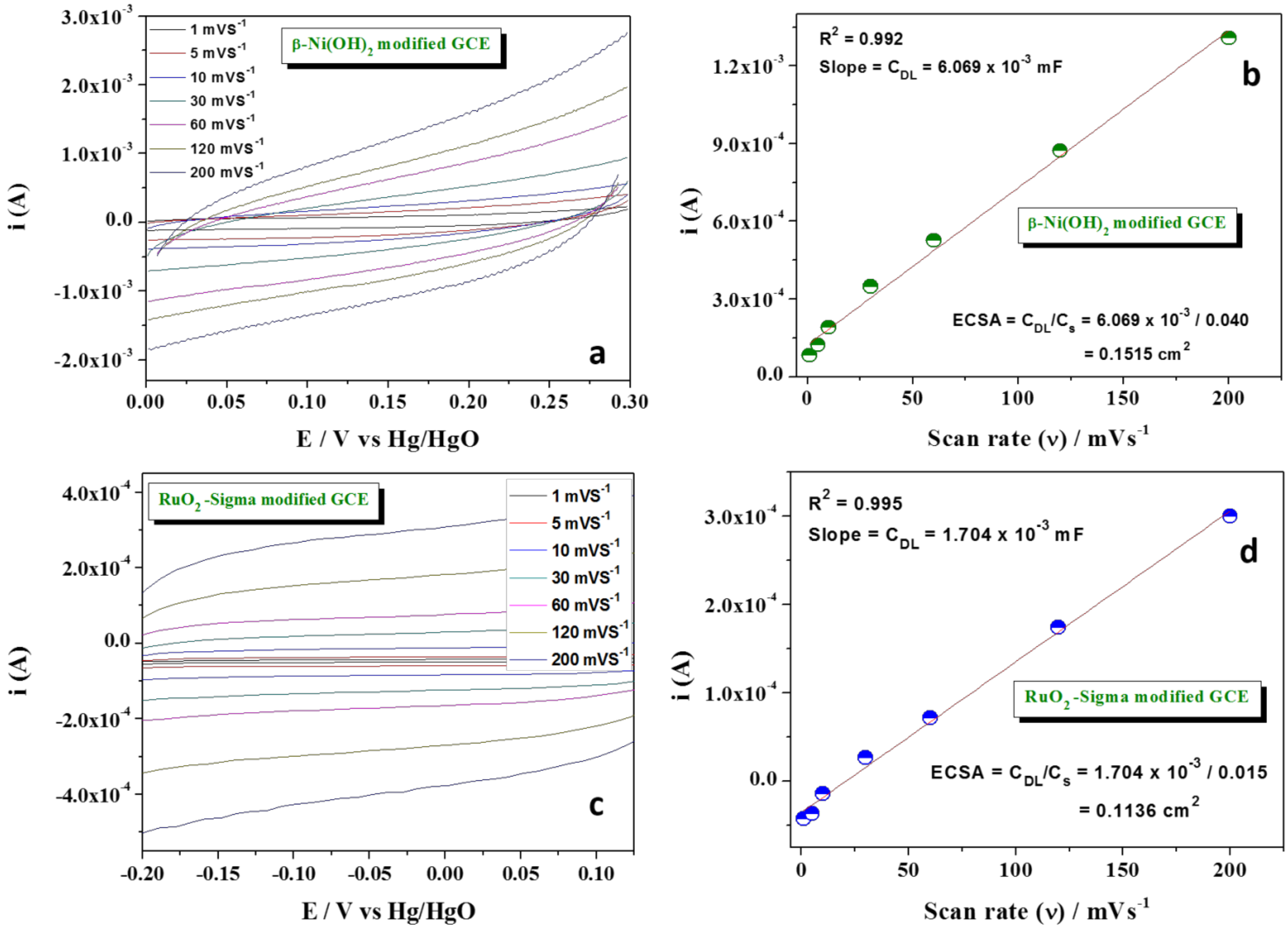

Figure S3: (a) CVs of cycled petal-like 3D hierarchical array of β-$Ni(OH)_2$ nanosheets and nanoburls at various scan rates. (b) plot of double layer charging current vs the scan rate of cycled petal-like 3D hierarchical array of β-$Ni(OH)_2$ nanosheets and nanoburls. (c) CVs of RuO_2-Sigma at various scan rates. (d) plot of double layer charging current vs the scan rate of RuO_2-Sigma

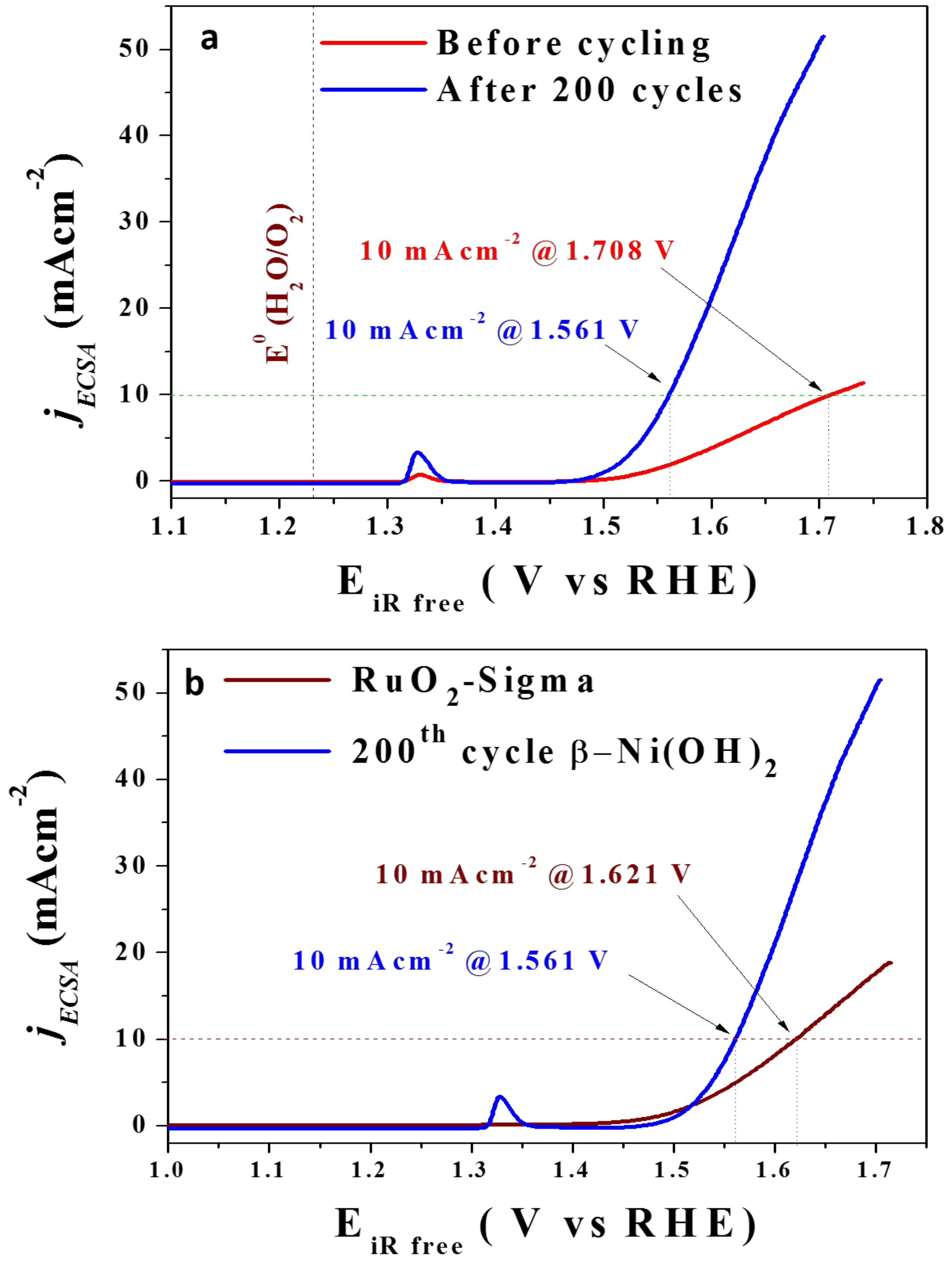

Figure S4: (a-b) LSVs of RuO_2-Sigma and the cycled petal-like 3D hierarchical array of β-$Ni(OH)_2$ nanosheets and nanoburls normalized with ECSA calculated from the double layer capacitance.

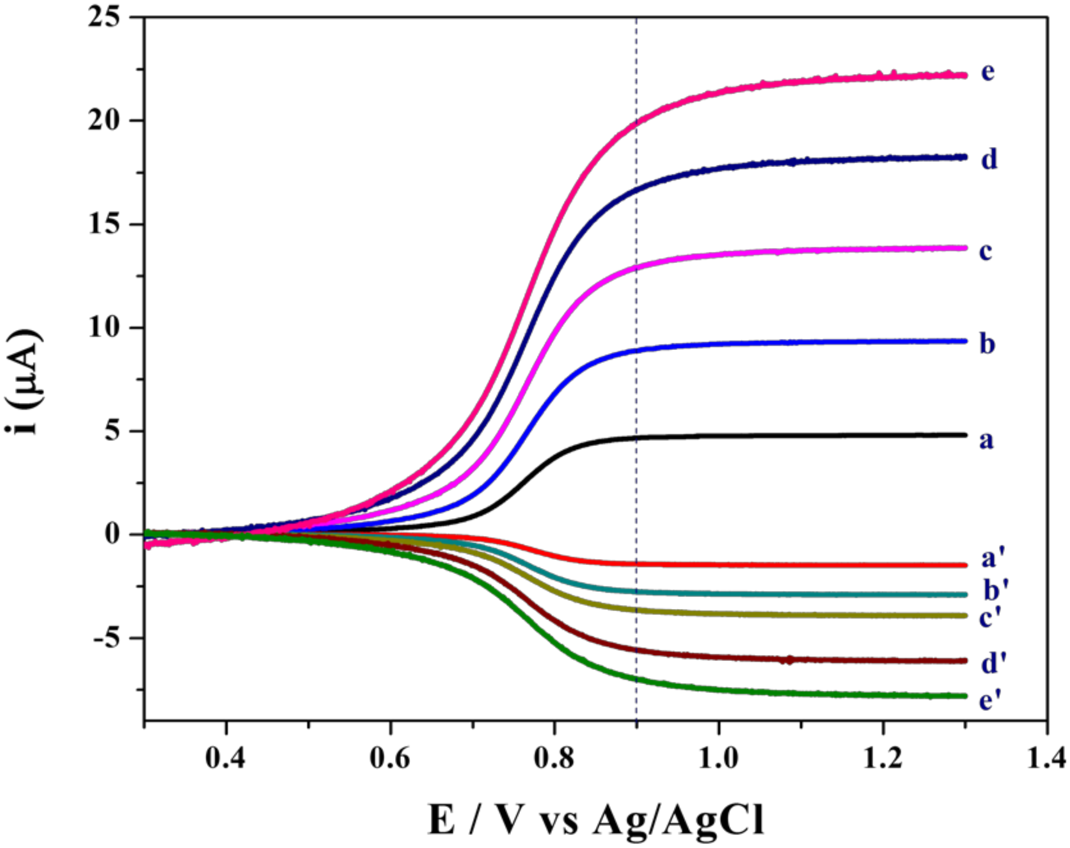

Figure S5: LSV responses of the taken RRD electrode for the redox reaction of ferro-ferri in 0.5 M H_2SO_4 at various rpm.

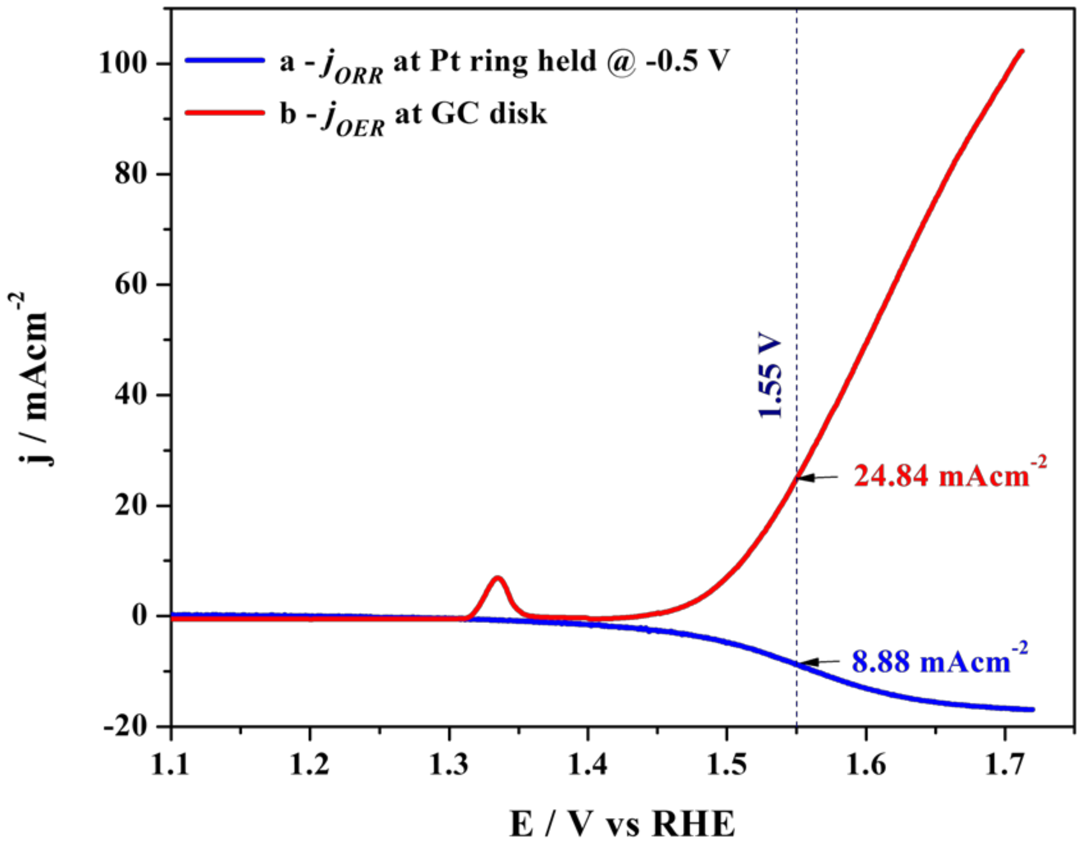

Figure S6: LSV obtained at 1600 rpm faceting cycled petal-like 3D hierarchical array of β-$Ni(OH)_2$ nanosheets and nanoburls on RRDE of GC disk and Pt ring with the corresponding ORR LSV curve.

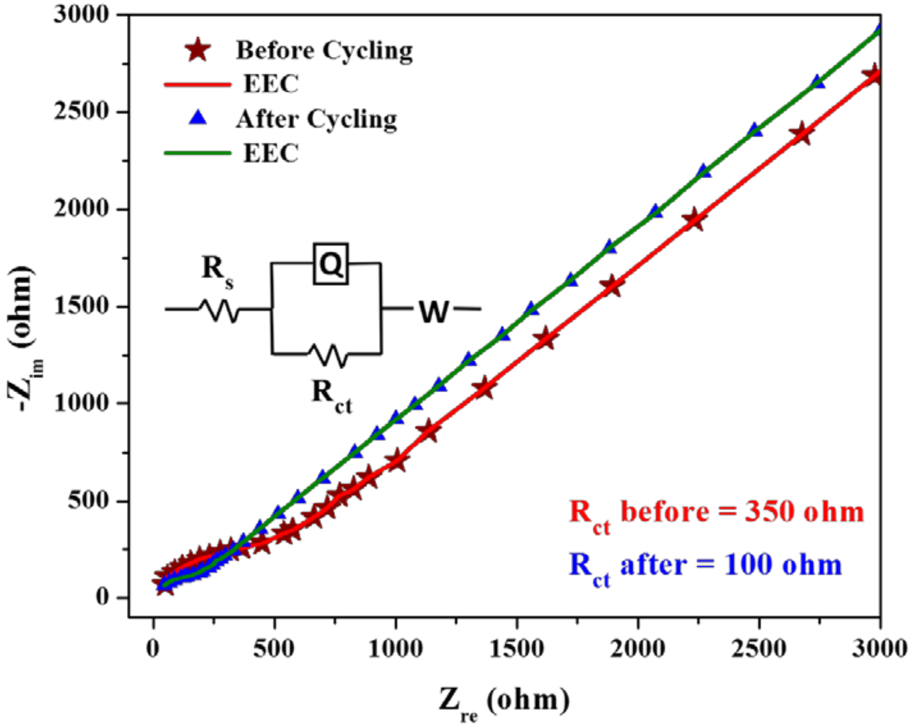

Figure S7: EIS spectra before and after 200 cycles of potential sweeping with corresponding EEC fit as inset.

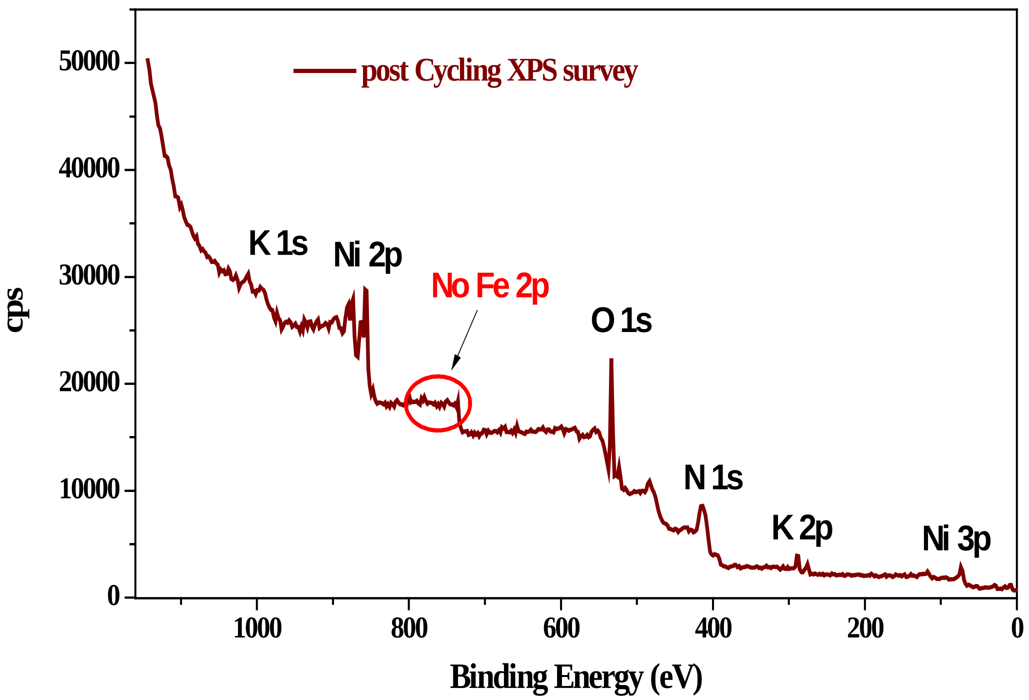

Figure S8: XPS Survey spectrum after 200 cycles of potential sweeping that shows the absence of Fe on the surface of our catalyst surface.

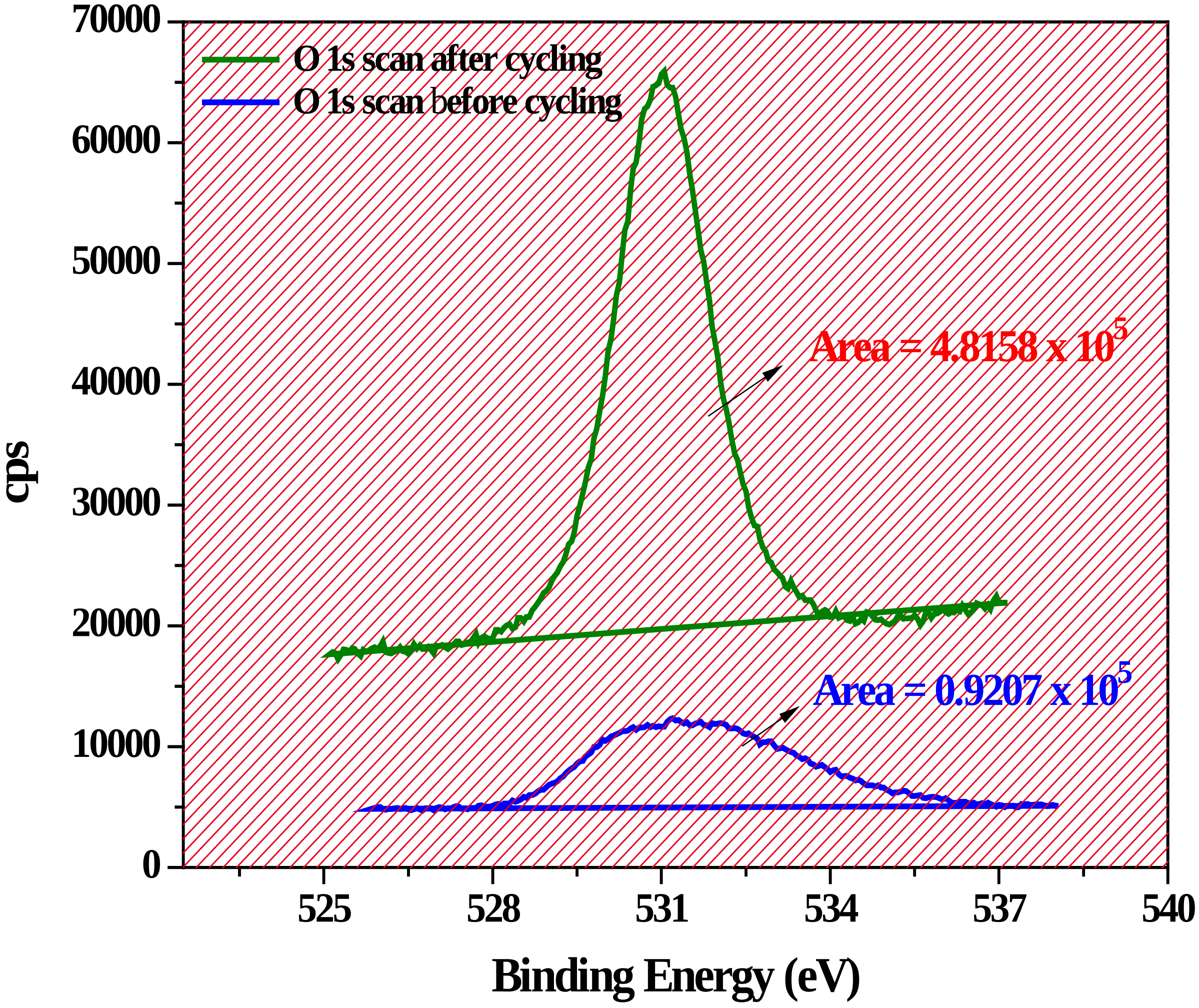

Figure S9: O 1s high resolution XPS spectra before and after 200 cycles of potential sweeping with corresponding area.

Table S1: Collection efficiency (N_{CL}) at various rotation rates (rpm).

Rotation rate (rpm)	**Ring current (i_R μA @ 0.9 V)**	**Disk current (i_D μA @ 0.9 V)**	**Collection Efficiency (N_{CL})**
100	1.77	4.7	0.3765
400	2.95	8.81	0.3606
900	3.96	11.54	0.3509
1600	5.9	15.55	0.3806
2500	7.1	19.1	0.3734
	Average collection efficiency (N_{CL})		**0.3684**