

Spherical Ni/NiO Nanoparticles decorated on Nanoporous Carbon (NNC) as an Active Electrode Material for Urea and Water Oxidation Reactions

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S.1 Thermogravimetric (DT) Analysis

The TGA of NNC has been demonstrated in SI Fig.S1, from which first weight loss up to 100 °C is due to water molecules and other species. Another weight loss is due to the decomposition of carbon species. After the 600 °C complete removals and formation of NiO. DTA shows that at 78 °C due to endothermic reaction which removes hygroscopic moieties. Above, the 400 °C reaction is exothermic and shows the composite's good thermal stability.

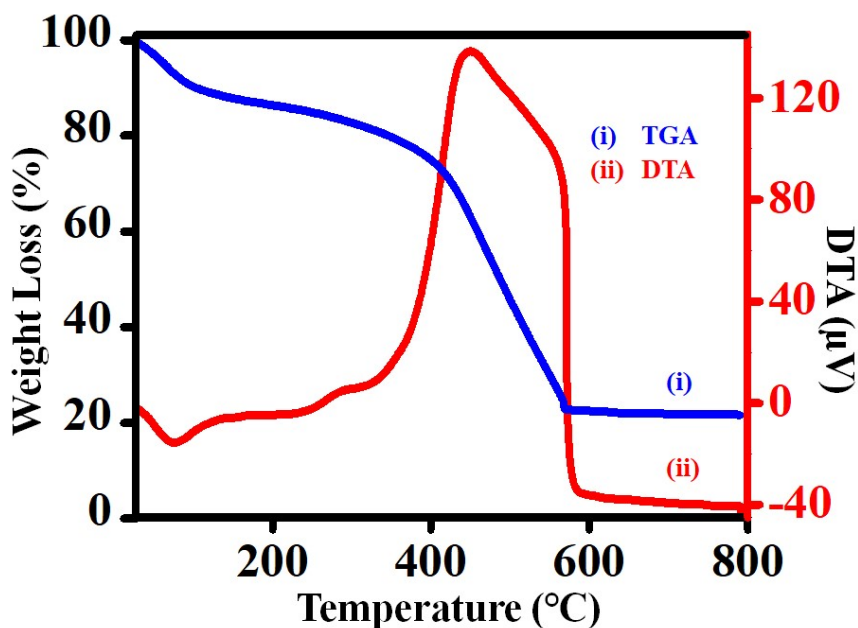


Fig. S1 Plot of Thermogravimetric Analysis (TGA & DTA) for NNC Electro catalyst.

S.2 Calculations for Enhancement Factor

The electrocatalytic Enhancement Factor is calculated by using the following formula:

$$E. F. = \frac{\text{Current density of electrocatalyst}}{\text{Current density of bare electrode}} \times 10$$

Table S 1. Comparison of electrochemical Urea oxidation reaction on GCE, NC, and NNC Electro catalytic systems in 0.5 M KOH + 0.3 M Urea electrolytes based on parameters current density and enhancement factor at a fixed potential of NC and NNC.

Sr. No	Electrocatalyst	Current density (mA/cm ²)	Enhancement Factor
1	GCE	0.05	-
2	NC	0.15	300
3	NiO-NPs	1	1500
3	NNC	1.52	3040

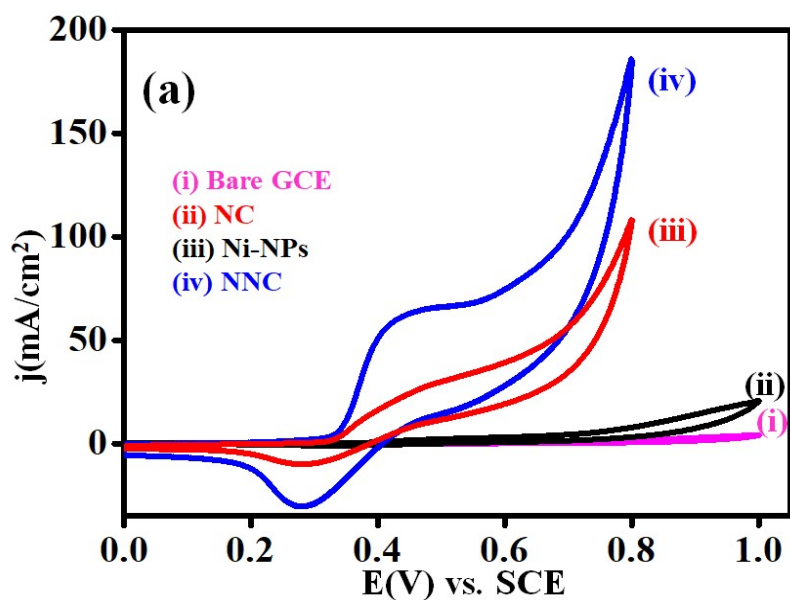


Fig. S2: Represents superimposable CV scans for UOR in 0.5 M KOH+ 0.3M Urea.

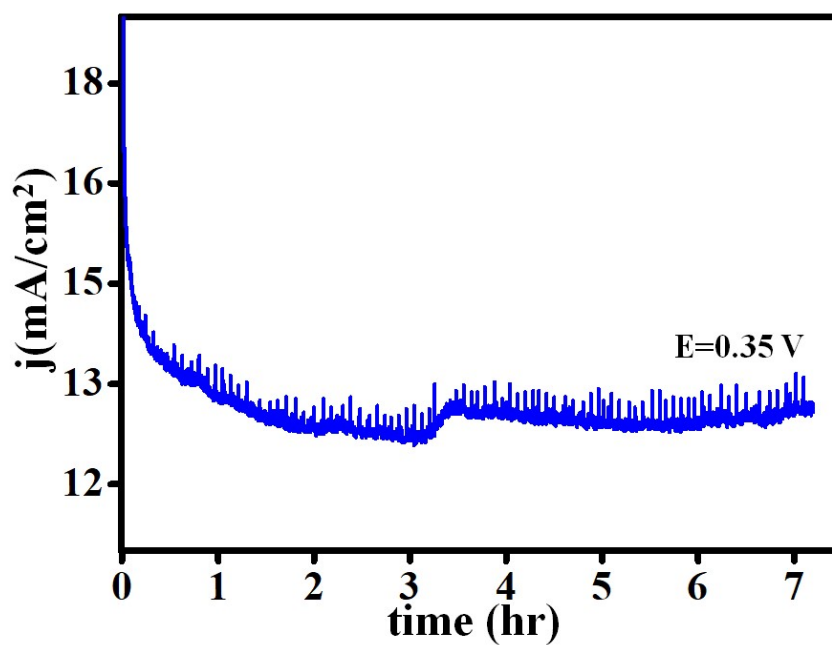


Fig. S3: Represents chronoamperometric i-t stability of NNC Electro-catalyst for 0.3M Urea in 0.5 M KOH solution.

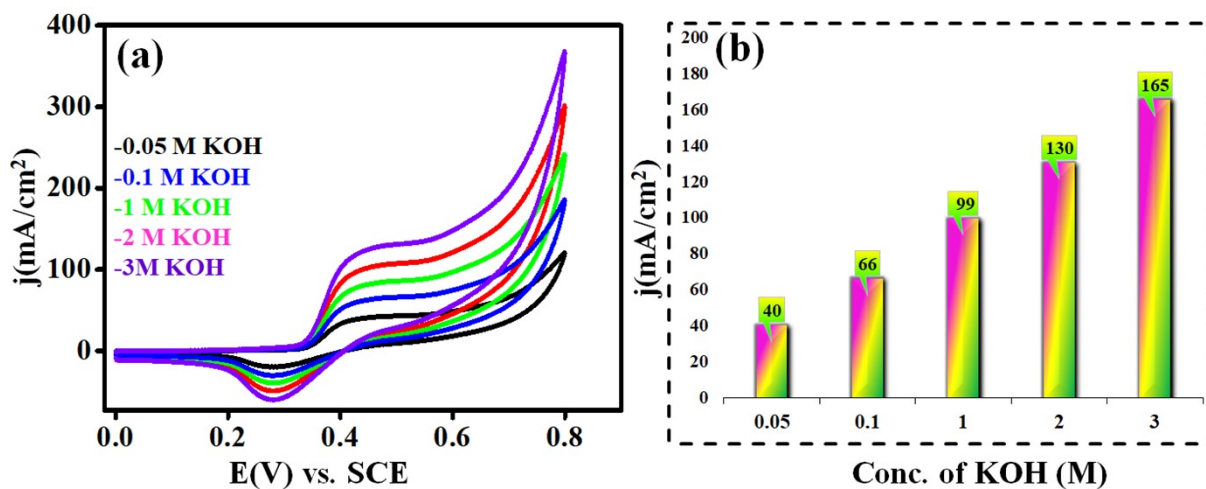


Fig. S4. Represents the CV plot of the NNC Electro catalyst for KOH concentration dependent UOR at 0.3 M Urea(a) and linear plot for Increment with KOH concentration.

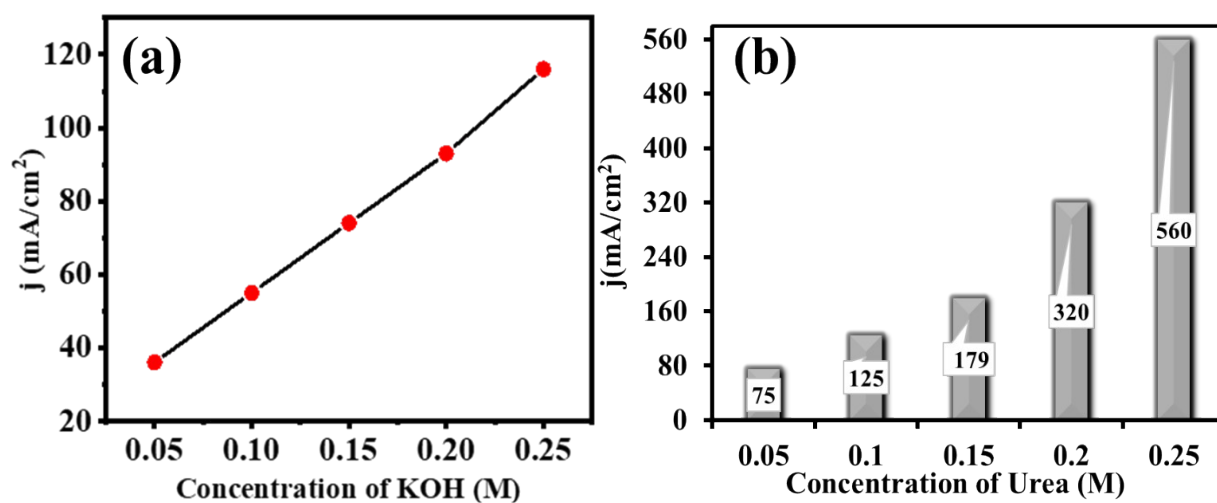


Fig. S5: Linear increment of the anodic peak of CV vs. concentration added (all urea solutions were prepared in 0.5 M KOH solution).

Table S2. Comparative studies of the previously reported electrocatalysts for UOR studies.

Sr. no	Electrocatalyst	Electrolyte	Potential (RHE) At 10mA/ cm ²	Ref.
1	β -Ni(OH) ₂	1M KOH+0.33 M Urea	1.43 V	1
2	KNiAlF ₆	1 M KOH+0.33 M Urea	1.35 V	2
3	Ni-Bi	1M KOH+ 0.33 M Urea	1.42 V	3
4	Ni ₂ P/C YS	1M KOH +0.33 M Urea	1.36 V	4
5	NiOx/CuOx/PANI/GC	0.5M NaOH+0.33 M Urea	1.44 V	5
6	Ni-Cu-CNFs	1M KOH+1 M Urea	1.32 V	6
7	CuCo ₂ O ₄	1 M KOH+ 0.33 M Urea	1.45 V	7
8	C@NiO	1 M KOH+0.33 M Urea	1.4 V	8
9	Ni-Cu-CNFs	1M KOH+1 M Urea	1.32 V	6
10	NiMoO ₄	1 M KOH+0.33 M Urea	1.34 V	9
11	NNC	0.5 M KOH +0.3 M Urea	1.33 V	This work

The calculation for electrochemical surface area.

It is generally known that; the electrochemical active surface area (ECSA) plays a significant role in electrocatalytic reactions. Fig. SI. 5 shows the CV of NNC electrocatalysts at various scan rates in a non-Faradaic potential range.^{10,11}

The equation that can be used to determine ECSA is;

$$Cs = \frac{A}{2mk(V2 - V1)} \quad \dots(1)$$

Cs= Specific Capacitance in mF.cm⁻¹

A= Area inside the CV

m=Mass of active materials

k = Scan rate mV/s

(V2-V1) = Potential window

Table SI 3. Parameters of specific capacitance

Reaction	Area(A)	Scan rate (mV/s)	Mass (mg)	Potential window (ΔV)	Specific Capacitance (Cs)
UOR	5.32×10^{-5}	10	0.03	0.05	0.0399

The result is shown in Fig. SI.5 CV of UOR scans of NNC electrodes were recorded in non-Faradic regions (0.23 to 0.28 V vs. SCE) at the different scan rates (10, 20, 30, 40, 50, 60, 70, and 80 mV/s) in 1 M KOH + 0.3 M Urea. Their anodic densities were measured at the central point potential from UOR. In Figure SI.5 Capacitive currents are plotted as a function of the scan rate.

Cdl was calculated by the equation;(2)

$$C_{dl} = (\text{Slope anodic} - \text{Slope cathodic})/2 \quad \dots\dots (2)$$

$$(\text{Slope Anodic} = 5.364 \times 10^{-3})$$

$$(\text{Slope Cathodic} = -4.457 \times 10^{-3})$$

$$C_{dl} = 5.364 - (-4.457)/2$$

$$C_{dl} = 9.821/2$$

$$C_{dl} = 7.5925 \text{ mF}$$

ECSA was then calculated by dividing the CDL using the specific capacitance (Cs) of the electrode surface equation (3):

$$ECSA(C_p) = C_{dl}/C_s \quad (3)$$

The ESCA value ($\sim 42.89 \text{ mF cm}^{-1}$) for the NNC electrode. Cdl of NNC electrodes is $\sim 7.5925 \text{ mF}$, calculated all parameters are summarized in Table SI.1

The equations (I) and (II) were used to determine double-layer capacitance (Cdl) and specific capacitance (Cs). Therefore, the electrocatalyst electrode surface area increases with increasing Cdl value.

We also calculated the roughness factor (RF) and the ECSA of the NNC catalyst. The following equation was applied to calculate RF:

$$RF = ECSA / A_g$$

Where A_g is the geometric area of the glassy carbon electrode.

RF value of 142.89 and a maximum ECSA of 42.89 cm^2 .

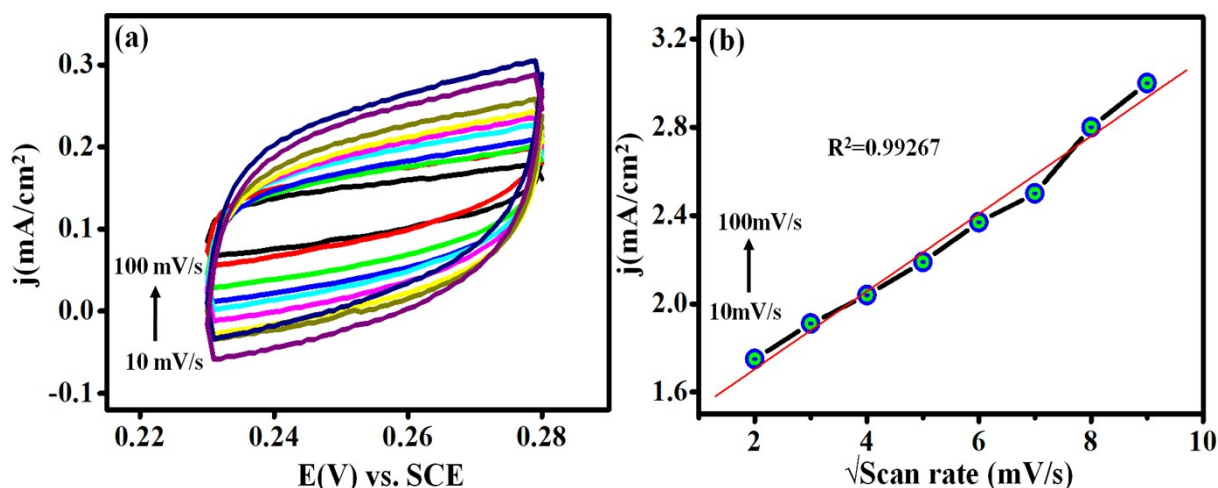


Fig. S6: (a) superimposed CV of UOR scans of NNC electrodes were recorded in non-Faradic regions (0.23 to 0.28 V vs. SCE) at the different scan rates (10, 20, 30, 40, 50, 60, 70, and 80 mV/s in 1 M KOH+ 0.3 M urea. (b) linear relationship between scan rate vs current density for I_{pa} .

S.4 Calculation for No. of active catalytic sites:

The NNC oxidation peak has a peak area of 7.75×10^{-8} AV and an associated charge is 155 mC from the production of NiOOH. Similar to the NiO-NPs, and NC these materials exhibit peak areas 1.03×10^{-6} , and 5.49×10^{-6} AV with respective charges of 20.6, and 10.98, mC due to single-electron oxidation of Ni^{2+} to NiOOH for NiO-NPs than NC. The following equation (4) could be used to determine the total number of active sites created on the electrocatalytic surface,

$$Number\ of\ Active\ Sites\ (\Gamma) = \frac{Charge\ Associated\ with\ Oxidation\ Peak}{N \times Charge\ of\ Electron} \quad (4)$$

Where Γ is the number of active sites, and N is the number of electrons transferred for the respective oxidation process.¹²

According to equation (4), the NNC has a larger oxidation peak region displaying 1.14×10^{12} for Ni/Ni-OOH sites on the electrocatalytic interface. The oxidation peaks of the NNC, NiO-NPs, and NC demonstrate that the electrode surface contains active catalytic NiOOH sites at concentrations of 1.14×10^{14} , 2.14×10^{16} , and 1.61×10^{12} respectively. It is evident from the findings that NNC performs more electrochemically stable for CO poisoning tolerance than other Ni-based comparable systems described in the literature.¹³ As a result, the UOR, indicates that, a higher electrocatalytic performance from NNC.

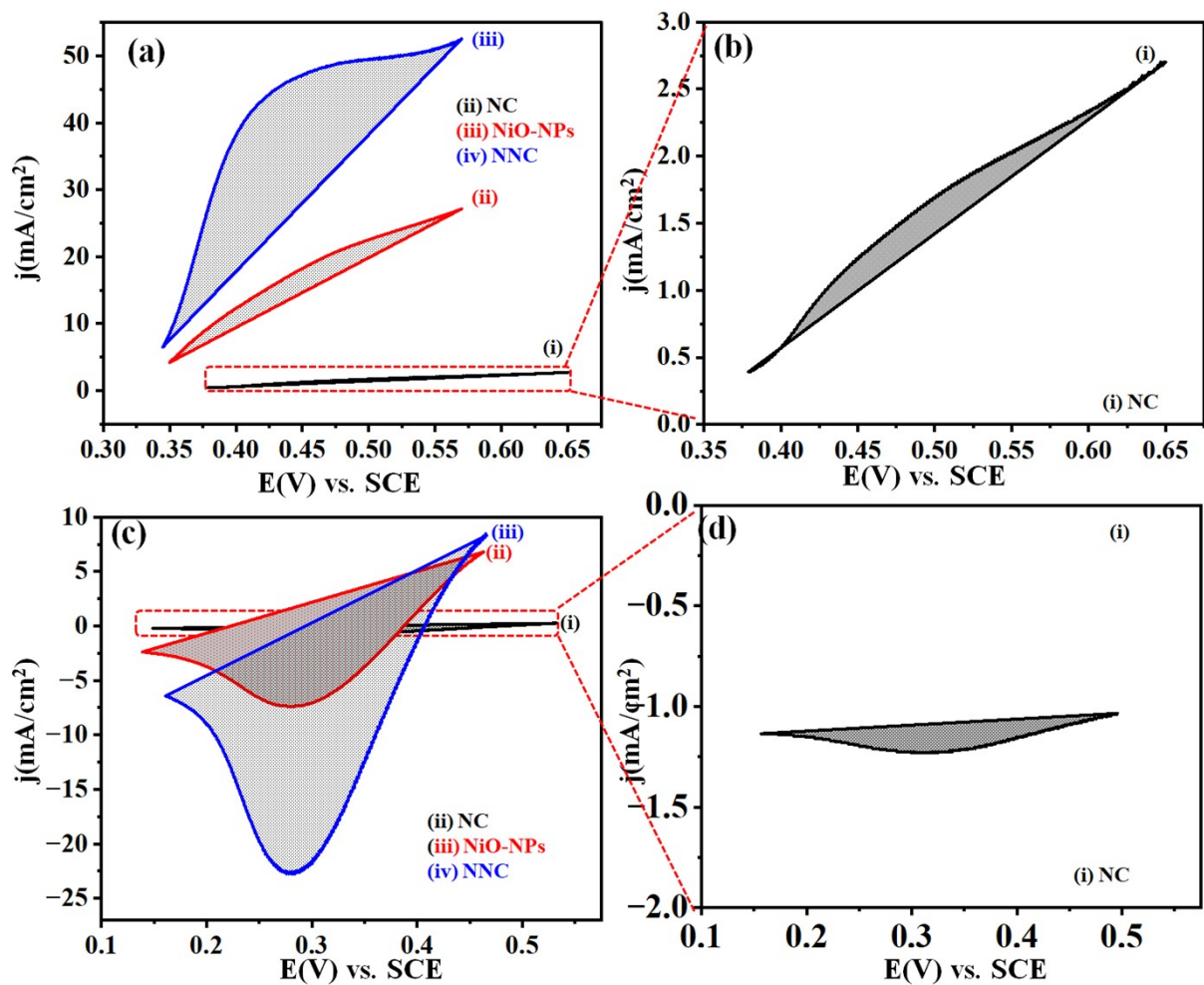


Fig. S7: (a) superimposed CV of UOR scans represents the oxidation peak areas for NC, NiO-NPs, and NNC while (b) shows the zoom-in part of NC, (c) represents the reduction peak areas for NC, NiO-NPs, NNC while (d) shows the zoom-in part of NC.

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