

Supporting Information

Atomically Dispersed Ru Sites on MOF-derived NC-ZnO for Efficient Oxygen Evolution Reaction in Acid Media

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1. Experimental section

A. Chemicals and reagent

Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98%, Sigma-Aldrich), Ruthenium chloride hydrate ($\text{RuCl}_3 \cdot x\text{H}_2\text{O}$) were used as metal sources; 2- methylimidazole ($\text{C}_4\text{H}_5\text{N}_2$, 97%, Sigma-Aldrich) was employed as a ligand and methanol (99.8%, Alfa Aesar) was used to perform the experiment. All of the reagents used in this study were utilized without any additional treatment.

B. Preparation method

Preparation of ZIF-8

The ZIF-8 was prepared by a simple and facile crystallization process with slight modifications in reported in previous work.¹ Firstly, a metal precursor of Zn^{+2} , $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (10 mmol), and as a ligand 2-methylimidazole (37 mmol) were dissolved in 150 ml of CH_3OH , to form their homogenous solutions, separately. Subsequently, ligand solution 2-methylimidazole was agitatedly added into the Zn^{+2} solution. The resulting mixture solution was then stirred for 24 h; the white precipitate was obtained and then centrifuged and rinsed with CH_3OH several times to remove excess from the precipitate. At last, the catalyst was vacuum-dried at 60 °C and collected.

Preparation of NC(ZnO)

The dried ZIF-8 powder sample weighing 500 mg added into a ceramic boat and calcined at 600 °C for 3h in an N_2 atmosphere with a heating rate of 3 °C.min⁻¹. The black powder sample was further calcined at 600 °C for 2 h in air and allowed to cool at room temperature.² The collected samples was labelled as NC(ZnO).

Preparation of $\text{Ru}_x@\text{NC}(\text{ZnO})$

The pre-synthesized NC(ZnO) powder weighing 200 mg was added into 20 mL ethanol and ultrasonically dispersed for 1h. Afterward, 0.15 mL ethanol solution of ruthenium chloride hydrate (4.4 mg/mL) was added drop wise into the ZnO suspension and stirred at room temperature for 6 h. This solution was centrifuged, washed with water frequently, and vacuum-dried at 60 °C overnight. The collected sample was labelled as $\text{Ru}_{1.75}@\text{NC}(\text{ZnO})$. The sample $\text{Ru}_{1.75}@\text{NC}(\text{ZnO})$ was further calcined in a tubular furnace under an H_2 -Ar atmosphere (8.0 vol% H_2) at 250 °C for 2h.³ Similarly the samples $\text{Ru}_3@\text{NC}(\text{ZnO})$ and $\text{Ru}_{0.75}@\text{NC}(\text{ZnO})$ were prepared with 3 mmol and 0.75 mmol Ru loadings respectively.

1. Materials Characterization

The structural phase analysis of the as-synthesized photocatalysts was performed by using Powder X-ray diffraction patterns (XRD) on a Bruker AXS diffractometer (D8 advance) at a generator voltage of 40 kV and current of 30 mA using Cu-K α 1 irradiation ($\lambda = 1.5406 \text{ \AA}$). The sample was scanned in the range of $2\theta = 10\text{-}80^\circ$ with a scan rate of 1 s/step. X-ray photoelectron spectroscopy (XPS) was performed via a Kratos (axis 165) analytical instrument with Mg K α irradiation. About 10^{-9} Torr pressure was maintained in the spectrometer. The structural morphology of the photocatalysts was examined by using MIRA3 FEG-SEM (TESCAN) scanning electron microscopy (SEM) at an accelerating voltage of 5 kV. Transmission electron microscopy (TEM) image of the representative photocatalysts was obtained by using a JEOL 2010EX TEM instrument equipped with the high-resolution style objective-lens pole piece at an acceleration voltage of 200 kV fitted with a CCD camera. N₂ adsorption-desorption isotherms of the photocatalysts were obtained on a Quanta chrome Nova 2200e gas adsorption analyzer at 77 K.

2. X-ray Absorption Spectroscopy measurement

X-ray Absorption Spectroscopy (XAS) measurement of Ru_{1.75}@NC(ZnO) single atom catalyst sample has been carried out at Ru K edge in fluorescence mode at the Scanning EXAFS Beamline (BL-9) at the Indus-2 Synchrotron Source (2.5 GeV, 200 mA) at the Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India.^{4,5} The beamline uses a double crystal monochromator (DCM) which works in the photon energy range of 4-25 KeV with a resolution of 10^4 at 10 KeV. A 1.5 m horizontal pre-mirror with meridional cylindrical curvature is used prior to the DCM for collimation of the beam and higher harmonic rejection. The second crystal of the DCM is a sagittal cylinder with radius of curvature in the range of 1.28-12.91 meters which provides horizontal focusing to the beam while another Rh/Pt coated bendable post mirror facing down is used for vertical focusing of the beam at the sample position.

For fluorescence mode, the sample is placed at 45° to the incident X-ray beam, and a fluorescence detector is placed at right angle to the incident X-ray beam to collect the signal. One ionization chamber detector is placed prior to the sample to measure the incident flux (I_0) and fluorescence detector measures the fluorescence intensity (I_f). In this case the X-ray absorption co-efficient of the sample is determined by $\mu = I_f / I_0$, and the spectrum was obtained as a function of energy by scanning the monochromator over the specified range.

The EXAFS spectra have been extracted using the standard procedure⁶⁻⁸. In order to take care of the EXAFS oscillations in the absorption spectra, the energy dependent absorption coefficient $\mu(E)$ has been converted to absorption function $\chi(E)$ defined as follows:

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta\mu_0(E_0)} \quad (1)$$

where E_0 absorption edge energy, $\mu_0(E_0)$ is the bare atom background and $\Delta\mu_0(E_0)$ is the step in the $\mu(E)$ value at the absorption edge. After converting the energy scale to the photoelectron wave number scale (k) as defined by,

$$k = \sqrt{\frac{2m(E - E_0)}{\hbar^2}} \quad (2)$$

the energy dependent absorption coefficient $\chi(E)$ has been converted to the wave number dependent absorption coefficient $\chi(k)$, where m is the electron mass. Finally, $\chi(k)$ is weighted by k^2 to amplify the oscillation at high k and the functions $\chi(k)k^2$ are Fourier transformed in r space to generate the $\chi(r)$ versus r plots (or FT-EXAFS spectra) in terms of the real distances from the centre of the absorbing atom. The k range used for Fourier transform is 3-10 Å⁻¹.

Subsequently the experimentally derived $\chi(r)$ versus r data are fitted with theoretical plots simulated using the structural information of the sample provided. The $\chi(r)$ versus r plot of the Ru_{1.75}@NC(ZnO) single atom catalyst sample at Ru K edge has been fitted from 1.15-2.0 Å assuming one Ru-O shell.

In the fitting process the atom to atom bond distance (R) between the respective atomic pairs and the disorder factor (Debye –Waller factor) (σ^2), which gives the mean square fluctuation in the atomic bond lengths and the thermal disorder in the system, have been used as fitting parameters while the coordination no. (N) has been kept fixed at nominal values. **Fig. 3f** shows the experimental $\chi(r)$ versus r plots of the Ru_{1.75}@NC(ZnO) single atom catalyst sample at Ru K edge along with the best fit theoretical simulations and the best fit parameters have been

shown in **Table S4**. The goodness of fit has been determined by the value of the R_{factor} defined by:

$$R_{factor} = \sum \frac{[\text{Im}(\chi_{dat}(r_i) - \chi_{th}(r_i))]^2 + [\text{Re}(\chi_{dat}(r_i) - \chi_{th}(r_i))]^2}{[\text{Im}(\chi_{dat}(r_i))]^2 + [\text{Re}(\chi_{dat}(r_i))]^2} \quad (3)$$

where, χ_{dat} and χ_{th} refer to the experimental and theoretical $\chi(r)$ values respectively and Im and Re refer to the imaginary and real parts of the respective quantities.

It should be mentioned here that a set of EXAFS data analysis program available within the Demeter software package⁹ have been used for reduction and fitting of the experimental EXAFS data. This includes data reduction and Fourier transform to derive the $\chi(r)$ versus r plots from the absorption spectra, generation of the theoretical EXAFS spectra starting from an assumed crystallographic structure and finally fitting of the experimental $\chi(r)$ versus r data with the theoretical ones using the FEFF 6.0 code.

3. Computational details

The Vienna Ab initio Simulation Package¹⁰ is employed for quantum mechanics calculations utilizing density functional theory (DFT), integrating the van der Waals interaction through the empirical correction DFT-D3 approach¹¹. The projector augmented wave method¹², with a kinetic energy cutoff for plane wave expansions set at 520 eV, was employed to consider core-valence interactions. Utilizing the Perdew–Burke–Ernzerhof (PBE)¹³ functional under the generalized gradient approximations (GGA), DFT calculations were conducted to describe electron exchange-correlation interactions. Convergence of the self-consistent electronic steps was achieved when the differences in total energy and eigenvalues between successive steps fell below the threshold of 1×10^{-5} eV. Atomic relaxations as per the Hellmann-Feynman criteria continued until the forces on the atoms were below 0.01 eV/Å. For geometry relaxation, the Brillouin zone integration utilized a Monkhorst–Pack¹⁴ k-point sampling of $7 \times 7 \times 1$, while maintaining a minimum vacuum layer of 15 Å in the z direction to reduce potential interactions among replicated cells. To address the incomplete self-interaction cancellation leading to localization deficiency in transition metals, we implemented the DFT+U approach with a U value of 3.5 eV. Convergence was achieved by optimizing the

adsorption behavior of *O, *OH, and *OOH intermediates, with ΔG for each OER step calculated using the computational hydrogen electrode model using the following equation:

$$\Delta G = \Delta E_{\text{DFT}} + \Delta \text{ZPE} - T\Delta S \quad (4)$$

In standard conditions (pH = 0, pressure, $p_{\text{H}_2} = 1$ bar, and $T = 298.15$ K), ΔE_{DFT} , ΔZPE and ΔS indicates the changes in DFT computed total energies, zero-point energy, and entropy, respectively.

4. Electrochemical measurements

The electrochemical properties were measured using a Metrohm AUTOLAB-M240 instrument with techniques like CV, LSV, and chronoamperometry. All the electrochemical experiments were carried out by employing a conventional three-electrode set-up. (Saturated calomel electrode (SCE)-reference, graphite rod-counter and carbon cloth (CC)-working electrode). The working electrodes were fabricated using 1 mg of polyvinylidene fluoride (PVDF) as a binder and N-Methyl-2-pyrrolidone (NMP) as a slurry preparation agent. Typically, the $\approx 4:1$ (with respect to overall catalyst loading over the electrode surface) ratio of powder catalyst and PVDF had taken into a mortar, followed by the addition of NMP solvent with continuous mixing by a pestle. Then a certain amount of catalyst ink was fabricated over the $1 \times 1 \text{ cm}^2$ area of the carbon cloth (CC). The amount of loaded catalyst was calculated by measuring the difference in weight of coated and uncoated carbon cloth (CC). Then, EIS analysis of all the catalyst were done at an applied potential of 1.55 V (vs RCE) for pH=0.3 (0.5 M H_2SO_4) respectively. Likewise, chronopotentiometric analysis also carried out at a 10 mA cm^{-2} current density for pH=0.3.

All the potential data were converted into an RHE scale according to the following equation:

For OER in 0.5 M H_2SO_4 solution, the commercial SCE and graphite were used as a reference and counter electrodes, respectively.

$$E_{\text{RHE}} = E_{\text{ref}} + 0.241 + 0.059 \text{ pH} \quad (5)$$

All the polarization results have normalized with respect to geometrical surface area and mass. The ECSA and mass normalization of all the LSV data were done by using the following relations:

$$\text{ECSA normalization} = \text{Current density} / \text{ECSA} \quad (6)$$

$$\text{Mass normalization} = \text{Current density} / \text{Loading} \quad (7)$$

Overpotential

The overpotential values of all the catalysts were calculated at a benchmarking current density of 10 mA cm^{-2} by employing the following relation:

$$\eta_{10}(\text{HER}) = (0 - E_{\text{obs}}) \text{ V versus RHE} \quad (8)$$

The Tafel Slope

The Tafel slope was calculated by fitting the overpotential versus $\log(j)$ using the Tafel equation as given below:

$$\eta = b \times \log(j/j_0) \quad (9)$$

where “ b ” signifies the Tafel slope value, “ j ” implies the current density value, and “ j_0 ” is the exchange current density. Electrochemical impedance spectroscopy (EIS) measurements were done on the frequency ranges from 10^5 to 0.1 Hz .

Electrochemical Active Surface Area (ECSA)

The electrochemical active surface areas (ECSA) were measured by determining the electrochemical C_{dl} using the following equations:

$$i_c = v \times C_{\text{dl}} \quad (10)$$

$$\text{ECSA} = C_{\text{dl}} / C_s \quad (11)$$

where “ i_c ” indicates the double-layer charging current resulting from scan-rates (v) dependent CVs at non-faradic potential, and “ C_s ” denotes a specific capacitance value of 0.040 mF cm^{-2} depending on the typical reported values.

Turnover Frequency (TOF)

The amount of oxygen/hydrogen that is evolved per unit of time is known as the TOF. The TOF of the catalyst can be determined by the below expression,

$$\text{TOF} = \frac{j \times N_A}{n \times F \times \tau} \quad (12)$$

where, j = current density, N_A = Avogadro number, F = Faraday constant ($96\,485\text{ C mol}^{-1}$), n = Number of electrons (For OER, $n = 4$ and HER, $n = 2$), Γ = Surface concentration.

Faradaic efficiency calculation:

The Faradaic efficiency (FE) information the catalyst is calculated by using the Faraday's second law of electrolysis as given below:

$$m = \frac{M \times I \times t}{N \times F} \quad (13)$$

m = faradaic efficiency; M = molecular weight of O_2 ; I = Current density at certain applied potential; t = time in hour; N = number of electron transfer (here $N = 4$) and F = Faraday constant = 96485 C/mol . The amount of gas evolved was measured by GC-MS at an applied potential of 1.6 V vs RHE . The experimentally obtained amount of gas with different time interval were measured and compared with theoretical amount of O_2 that can be produced.

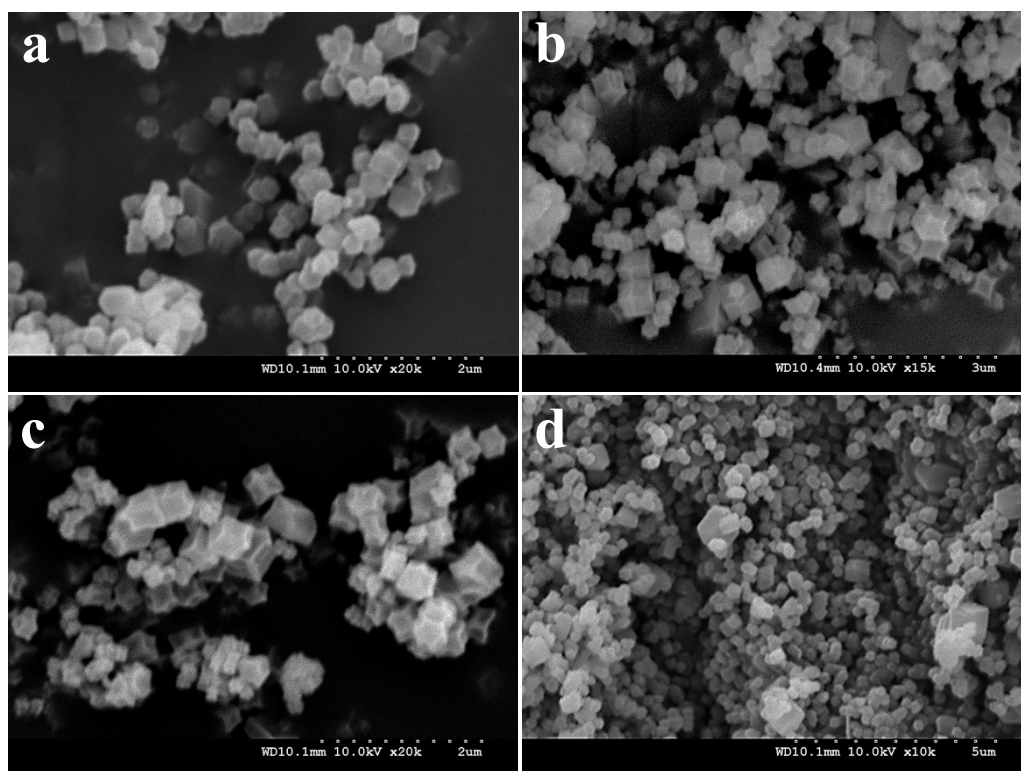


Fig. S1 SEM images of (a-d) ZIF-8, NC(ZnO), $Ru_{1.75}@NC(ZnO)$, and $Ru_{0.75}@NC(ZnO)$.

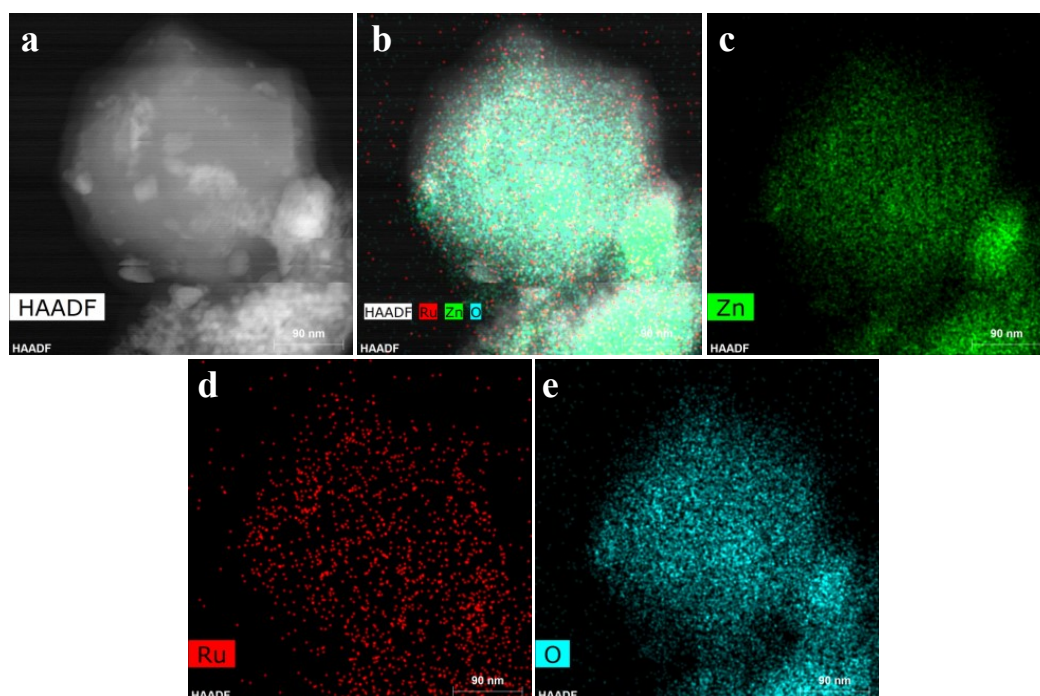


Fig. S2 (a, b) HAADF image and (c-e) elemental mapping images of Zn, Ru and O for $\text{Ru}_{1.75}@\text{NC}(\text{ZnO})$.

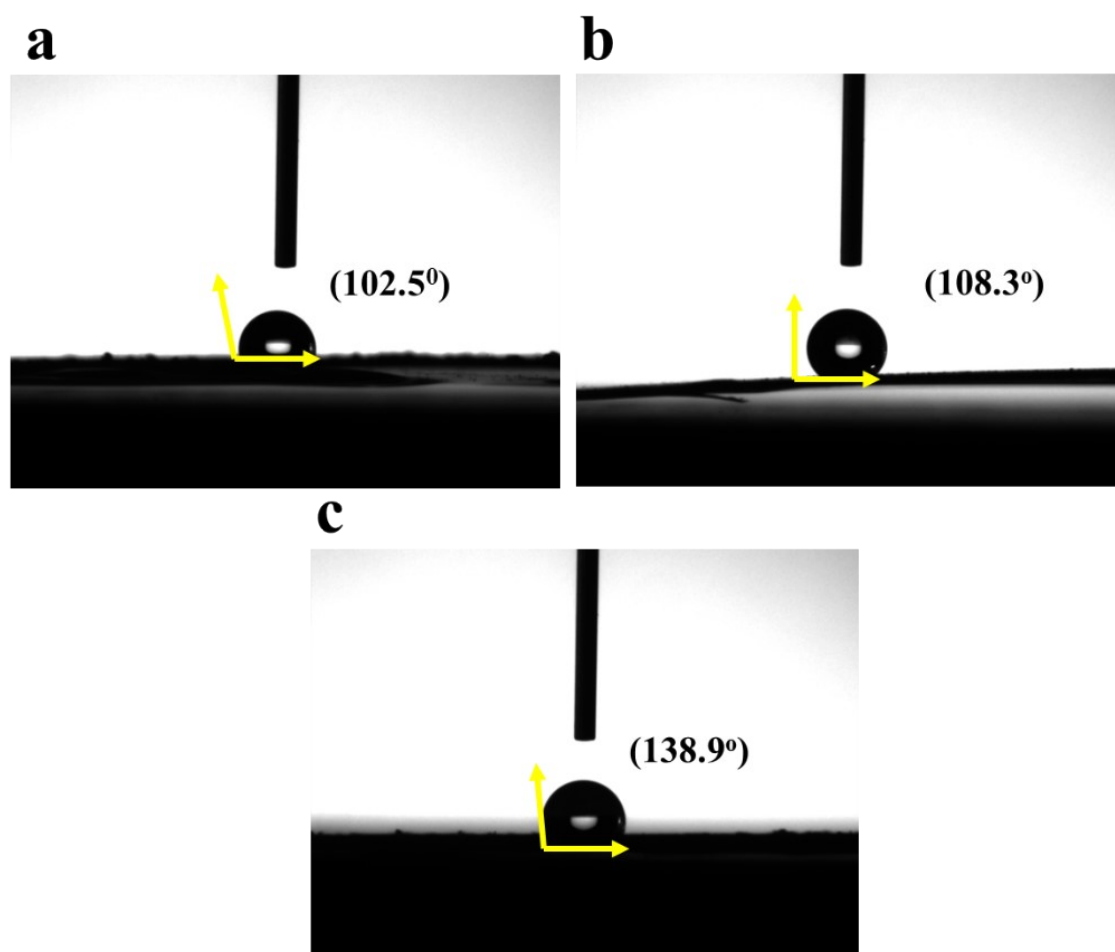


Fig. S3 Contact angles of (a) $\text{Ru}_{1.75}\text{@NC}(\text{ZnO})$, (b) ZIF-8, and, (c) $\text{NC}(\text{ZnO})$.

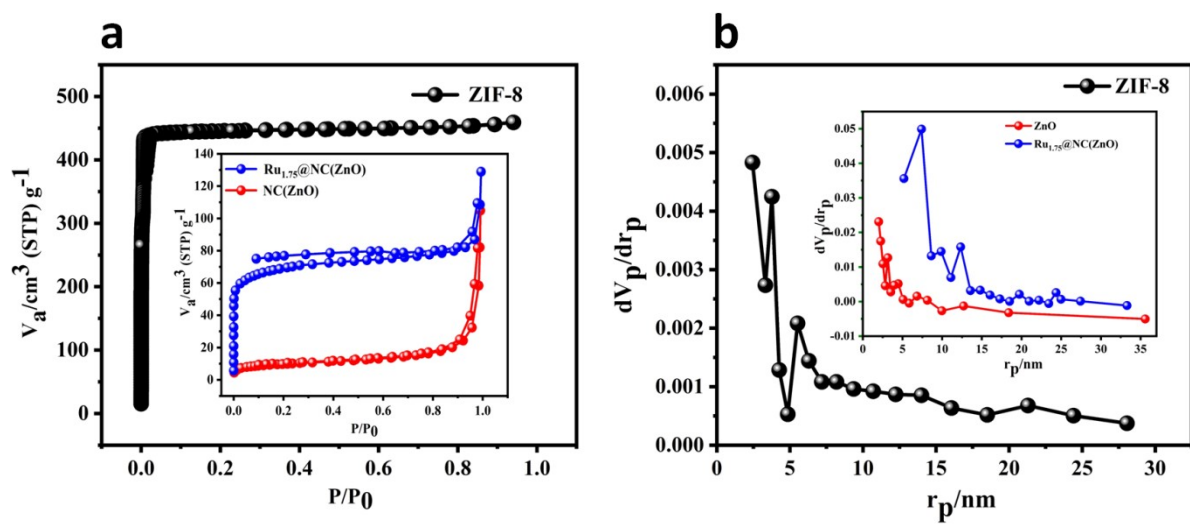


Fig. S4 (a) N_2 adsorption-desorption isotherms and (b) Barrett-Joyner-Halenda (BJH) Pore size distribution curves of ZIF-8, inset $\text{Ru}_{1.75}\text{@NC}(\text{ZnO})$, and $\text{NC}(\text{ZnO})$.

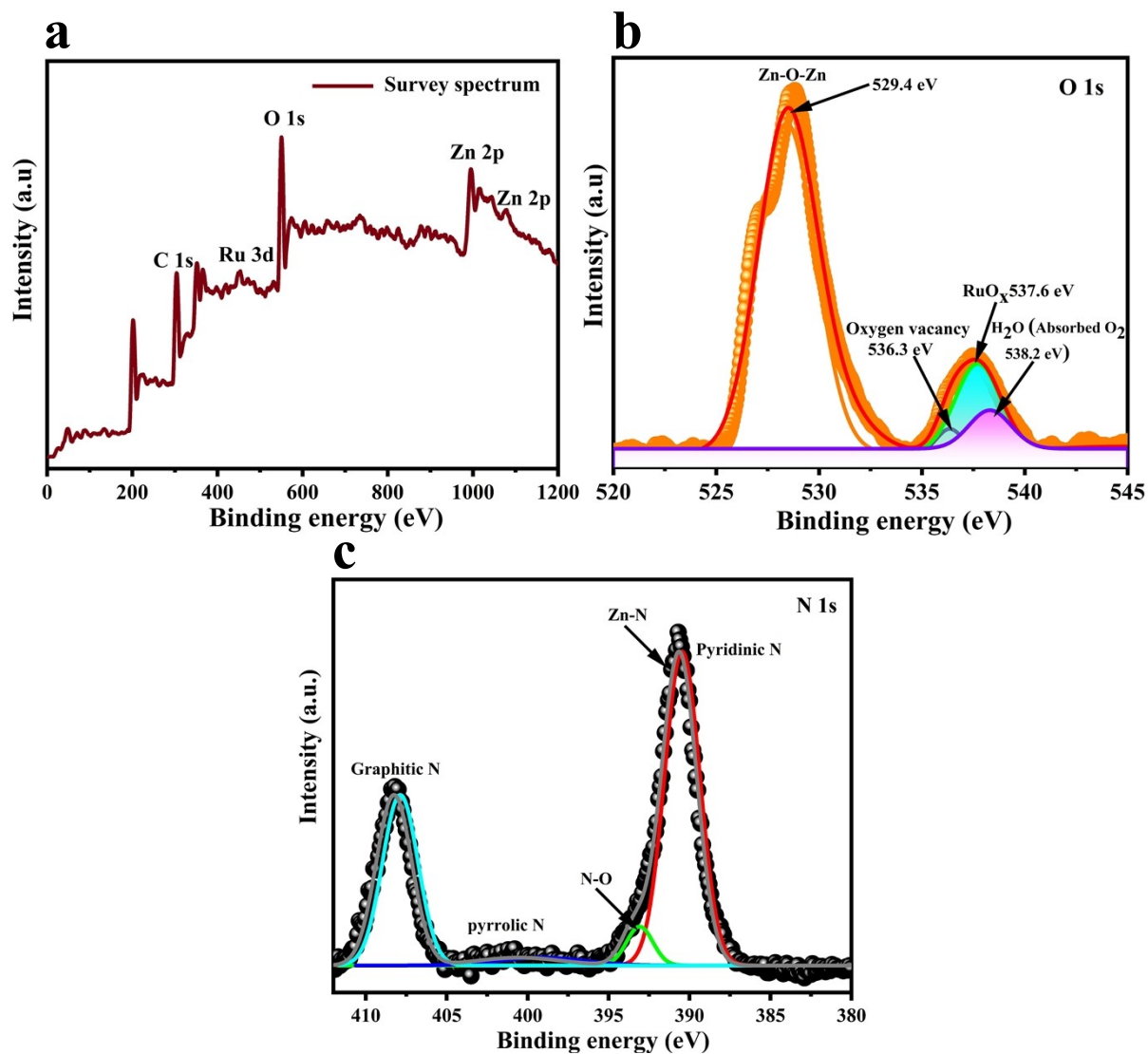


Fig. S5 (a) XPS full survey spectra, (b, c) high resolution images XPS spectrum of O 1s, N 1s in Ru_{1.75}@NC(ZnO) sample.

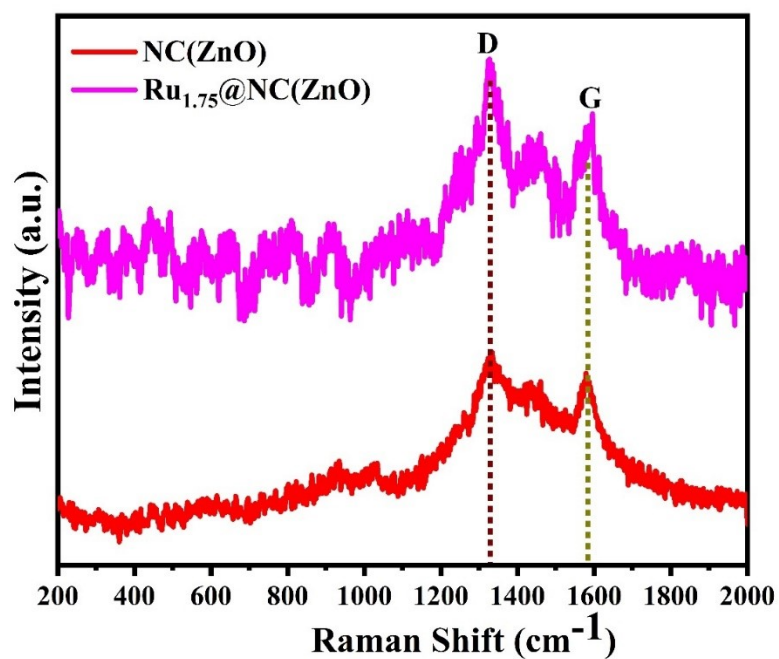


Fig. S6 Raman spectra of NC(ZnO) and Ru_{1.75}@NC(ZnO) composites.

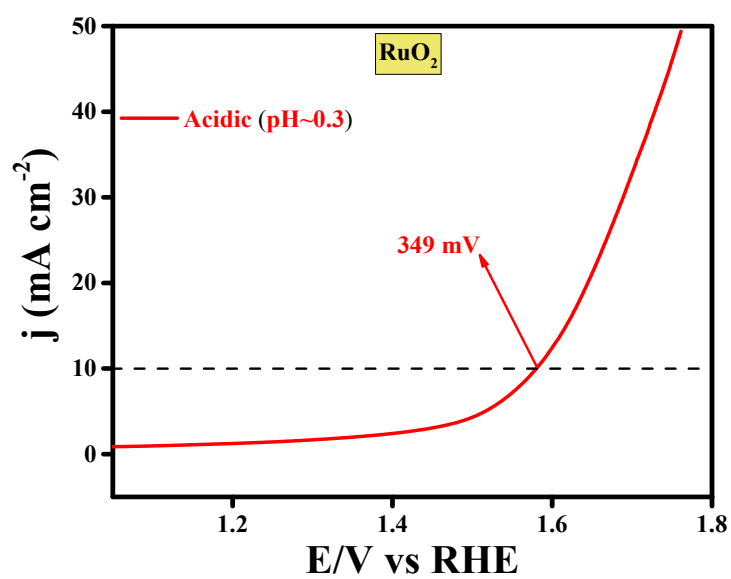


Fig. S7 LSV polarization results of commercial RuO₂ in 0.5 M H₂SO₄.

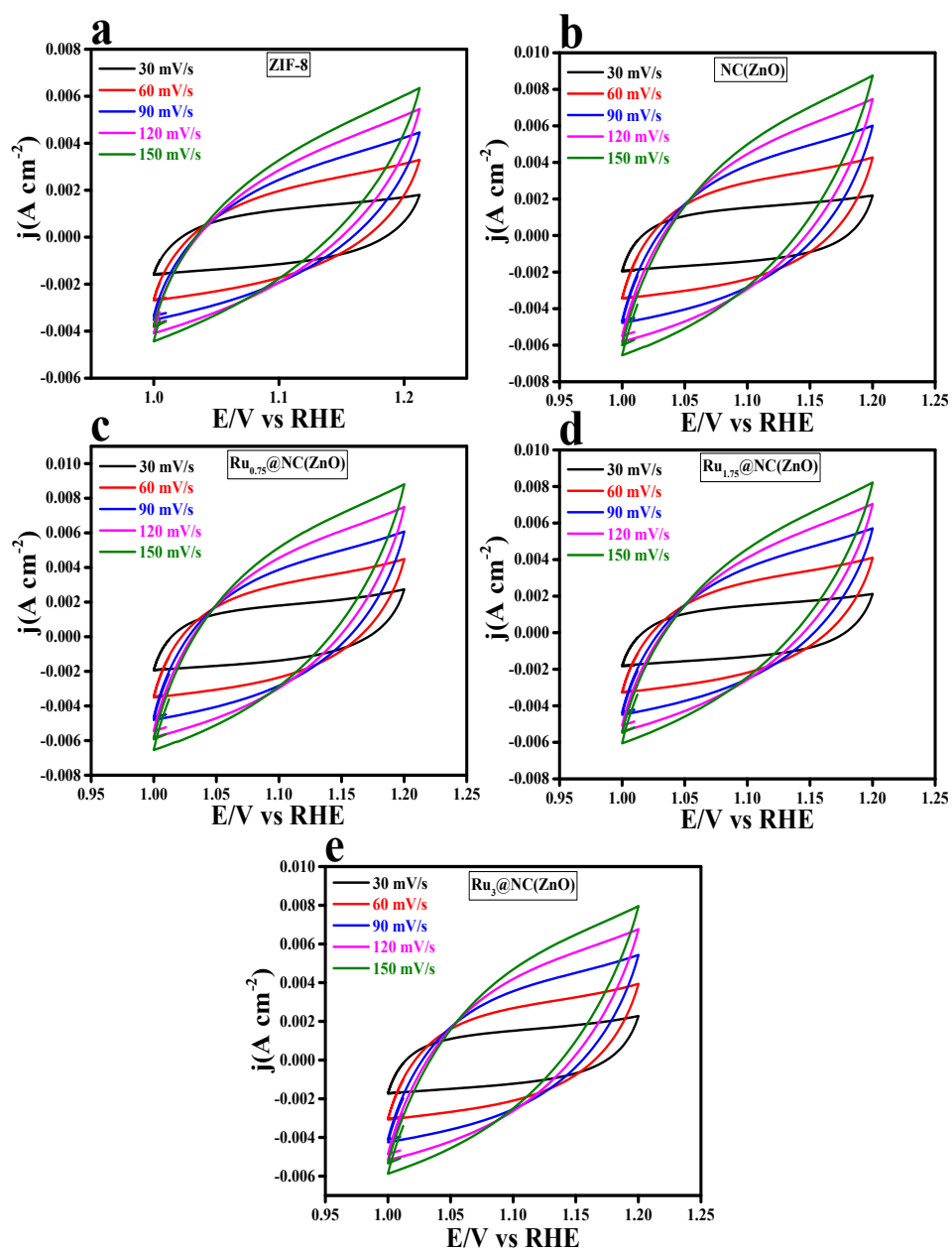


Fig. S8 (a-e) Shows the CV recorded at different scan rates at a non-faradic region of NC(ZnO), $\text{Ru}_{0.75}\text{@NC}(\text{ZnO})$, $\text{Ru}_{1.75}\text{@NC}(\text{ZnO})$ and $\text{Ru}_3\text{@NC}(\text{ZnO})$ respectively.

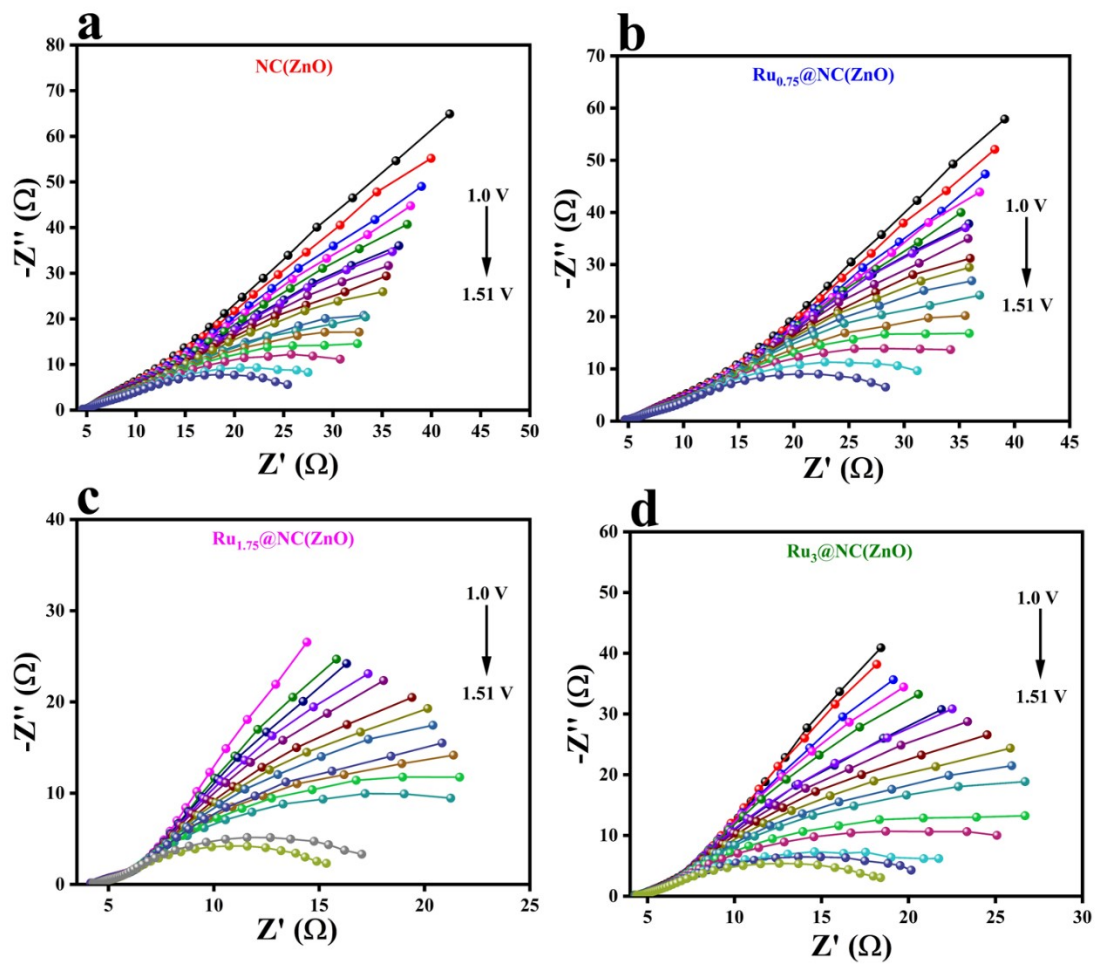


Fig. S9 (a-d) Operando Nyquist plot of Ru_{1.75}@NC(ZnO) after 500 CV cycles in 0.5 M H₂SO₄ solution respectively.

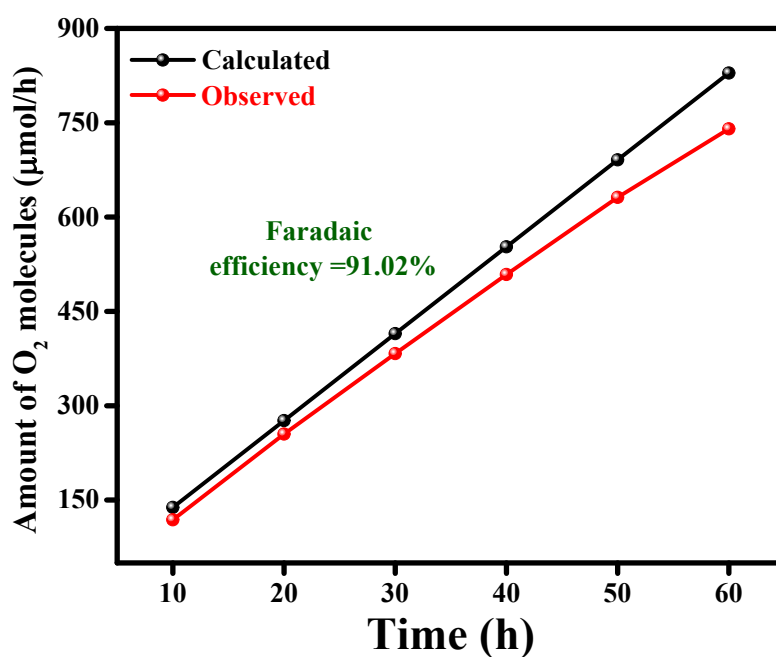


Fig. S10 Faradaic efficiency calculated for catalyst $\text{Ru}_{1.75}\text{@NC}(\text{ZnO})$ in 0.5 M H_2SO_4 solution.

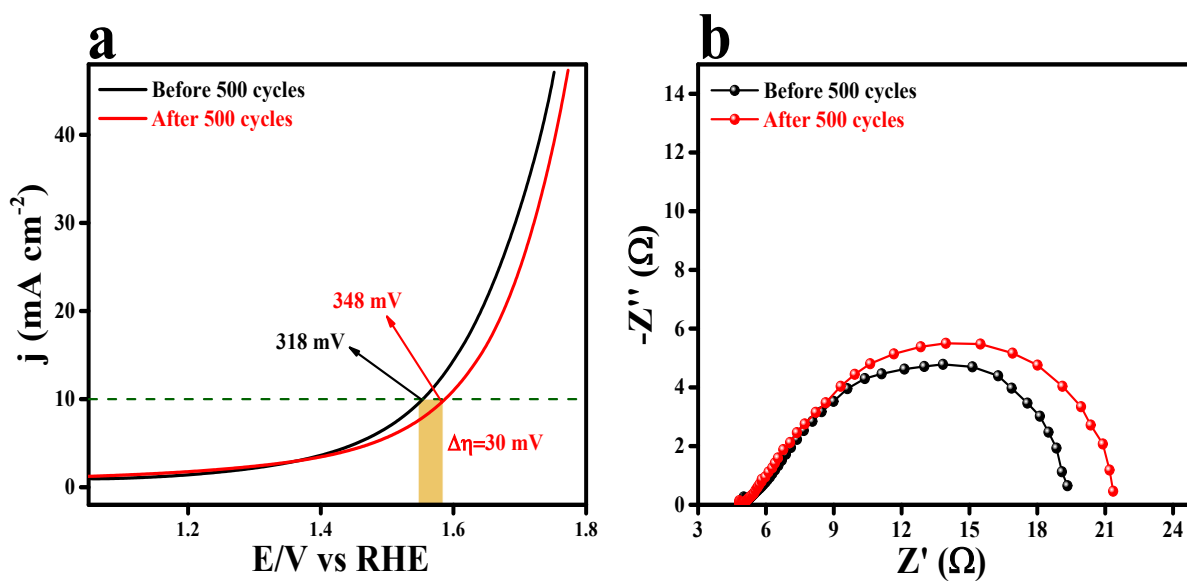


Fig. S11 (a) LSV polarization results of $\text{Ru}_{1.75}\text{@NC}(\text{ZnO})$ after 500 CV cycles in 0.5 M H_2SO_4 solution; (b) corresponding EIS spectra.

Electrochemical impedance spectroscopy

The fitted equivalent circuit diagram exhibits R_s (uncompensated solution resistance), R_{ct} (charge transfer resistance), R_p (resistance), C_{dl} (double layered capacitance), CPE (constant phase element) was employed owing to frequency dispersion of capacitance at the electrode/electrolyte interface. The comparison of R_{ct} implies that $Ru_{1.75}@NC(ZnO)$ exhibits less resistance and suggest faster electron transfer kinetics. Further, the double layered capacitance (C_{dl}) value also exhibited similar type of capacitive behavior. The higher C_{dl} value indicates that the concentration of surface charge over the electrode surface is increased and facilitate the OER. Further, R_p relates the formation of surface intermediates. With the increase of potential, R_p decreases with increase in intermediates (OOH^-). C_p is related to fluctuating concentration of charged intermediate species on the electrode surface during the OER. With the increase in potential, C_p is shifted to faradaic process, inferring the charging and formation of intermediate step in the RDS step.

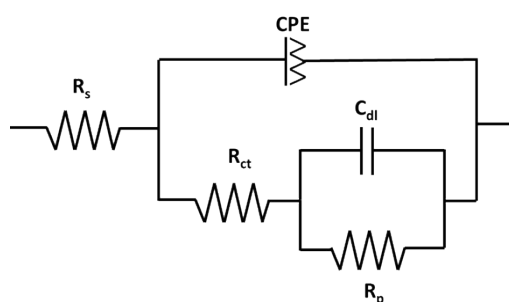


Fig. S12 Equivalent circuit diagram used for fitting the impedance data.

Parameter			
R_s	4.391	4.391	0.4695
Q-Yo (CPE)	0.02552	0.02552	6.233
R_{ct}	7.455	7.455	8.009
C_{dl}	0.01002	0.01003	12.96
R_p	10.89	10.88	5.133

Table S1 Impedance parameters obtained from the fitted equivalent circuit diagram

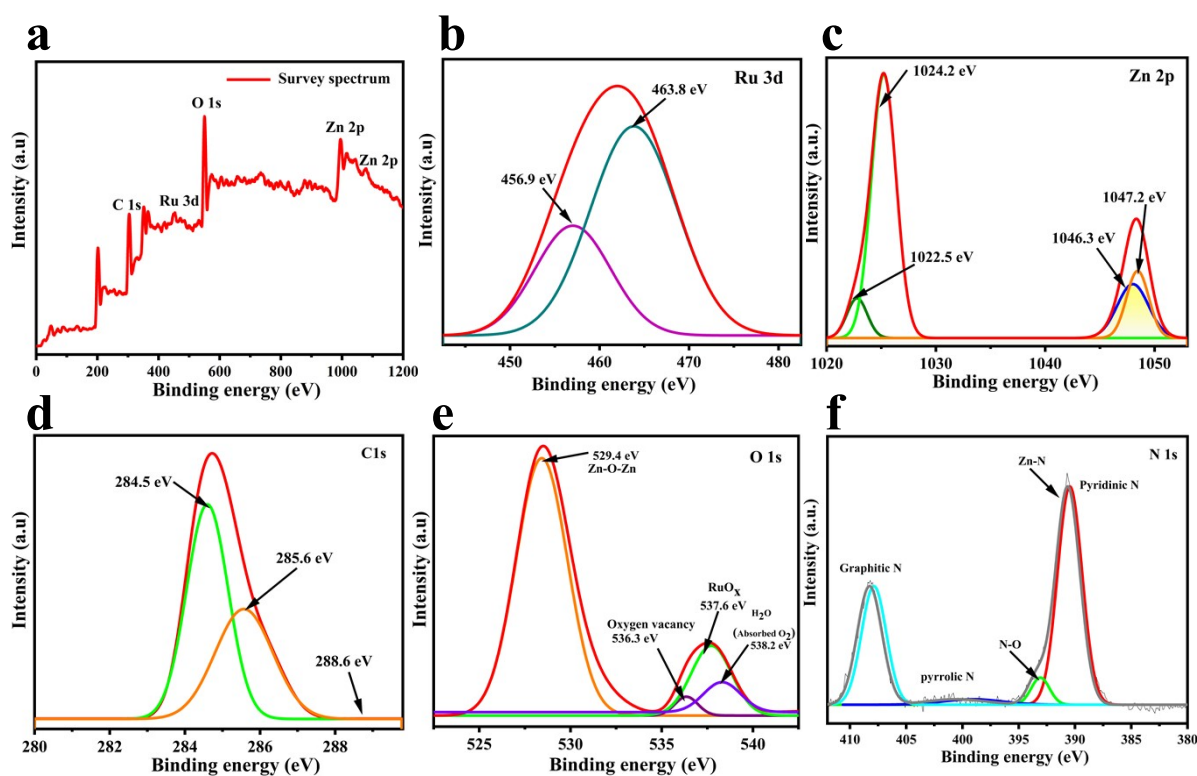


Fig. S13. (a) XPS spectrum, XPS spectra of (b) Ru 3d, (c) Zn 2p, (d) C 1s, (e) O 1s, and (f) N 1s in $\text{Ru}_{1.75}\text{@NC}(\text{ZnO})$ after OER studies in 0.5 M H_2SO_4 .

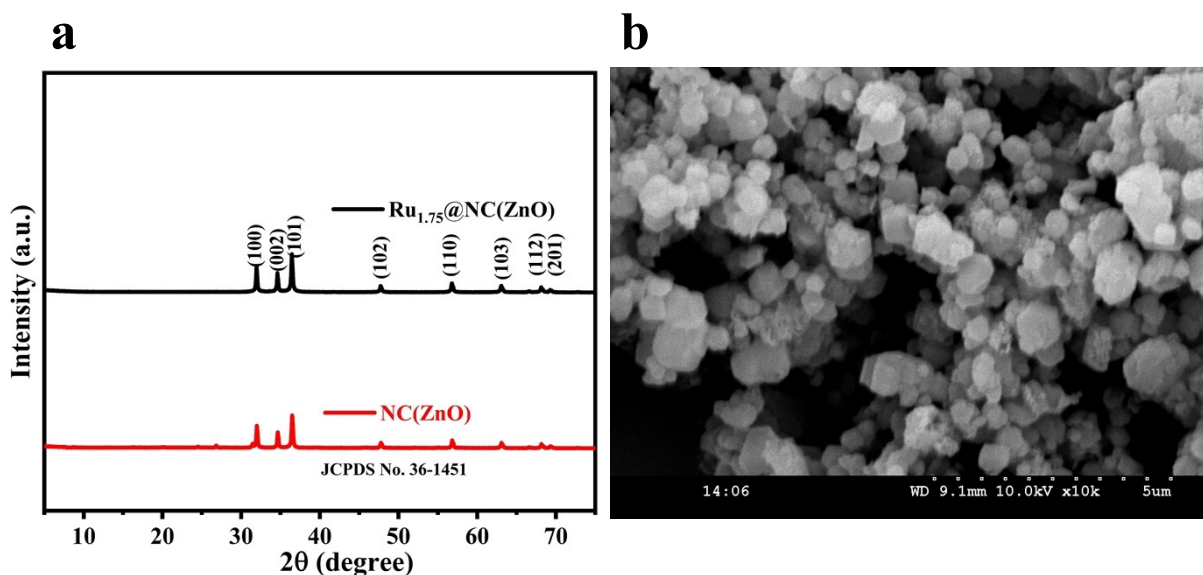


Fig. S14 (a) P-XRD and (b) SEM images of recovered $\text{Ru}_{1.75}\text{@NC}(\text{ZnO})$ sample after catalytic performance.

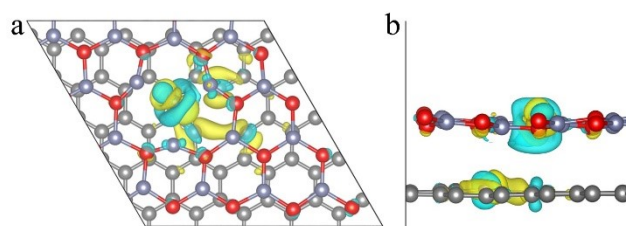


Fig. S15: Charge density difference for $\text{Ru}_x@\text{NC}(\text{ZnO})$ complex. Here, blue and yellow isosurfaces indicate charge depletion and accumulation, respectively. The balls in red, purple, blue, grey and green represent O, Zn, N, C and Ru atoms, respectively.

Table S2 ICP-OES analysis of composites.

Sl. No	Samples	Ru (ppm)	Zn (ppm)
1	NC(ZnO)	-	74.43
2	$\text{Ru}_{1.75}@\text{NC}(\text{ZnO})$	0.8043	52.20

Table S3 Surface area analyses of ae prepared electrocatalyst.

S. No	Samples	Surface area (m^2g^{-1})	Pore volume (Cm^3g^{-1})	Average pore diameter (nm)
1.	ZIF-8	1968.7	0.7102	1.443
2.	NC(ZnO)	33.99	0.1478	17.39
3.	$\text{Ru}_{1.75}@\text{NC}(\text{ZnO})$	285.55	0.13	2.6

Table S4 Ru K edge EXAFS fitting results.

Compound					
Ru _{1.75} @NC(ZnO)	Ru Edge				
		N	σ^2	R (Å)	R_{factor}
	Ru-O	2.6±0.3	0.0010 ±0.0009	1.97±0.02	0.0076857

Table S5 Comparison of electrocatalytic performance of as-prepared NC(ZnO) with the similar reported electrocatalyst in acidic medium.

Sl. No	Electrocatalyst	Substrate	Overpotential (mV)	Electrolyte (M)	Current density (mA cm ⁻²)	Ref.
1.	Ru-N-C	GCE	267	0.5 M H ₂ SO ₄	10 mA cm ⁻²	15
2.	Ru/Co-N-C	Three-electrode system	232	0.5 M H ₂ SO ₄	10 mA cm ⁻²	16
3.	Ru ₁ -Pt ₃ Cu	active carbon	280	0.1M HClO ₄	10 mA cm ⁻²	17

4.	Ru-SA/Ti ₃ C ₂ T _x	RDE	290	0.1 M HClO ₄	10 mA cm ⁻²	18
5.	Pt ₁ -C ₂ N ₂	CP	405	0.5 M H ₂ SO ₄	10 mA cm ⁻²	19
6.	Rutile RuO ₂	RDE	≈255	0.1 M HClO ₄	10 mA cm ⁻²	20
7.	Rutile RuO ₂ nanoparticles	RRDE	~440	0.1 M HClO ₄	10 mA cm ⁻²	21
8.	Co-RuO ₂	CC	328	0.5 M H ₂ SO ₄	10 mA cm ⁻²	22
9.	RuO ₂ /TiO ₂	GCE	239	0.5 M H ₂ SO ₄	10 mA cm ⁻²	23
10.	NC(ZnO)	CC	400	0.5 M H ₂ SO ₄	10 mA cm ⁻²	This work
11.	Ru _{0.75} @NC(ZnO)	CC	366			
12.	Ru _{1.75} @NC(ZnO)	CC	320			
13.	Ru ₃ @NC(ZnO)	CC	348			

Note: GCE-Glassy carbon electrode, RDE- rotating disk electrode; RRDE-Rotating ring disk electrode, CP-Carbon paper, CC- Carbon Cloth.

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