Metal organic framework derived Se blended ZrO_2 at a nitrogen-doped carbon heterostructure for electrocatalytic overall water splitting

Krishnendu M Nair, Pavithra Shankar, Selvaraju Thangavelu*
Department of Chemistry, Bharathiar University, Coimbatore-641 046.
Email: veluselvaraju@gmail.com; selvaraju@buc.edu.in

XRD Calculations

The average crystallite size of the composite can be calculated using the Debye-Scherer equation:

$$D = \frac{K\lambda}{\beta Cos\theta} \tag{1}$$

Where D is the crystallite size, K denoted the Scherrer constant (0.98), λ represents the wavelength (1.54), and the β represents the full width at half maximum (FWHM).

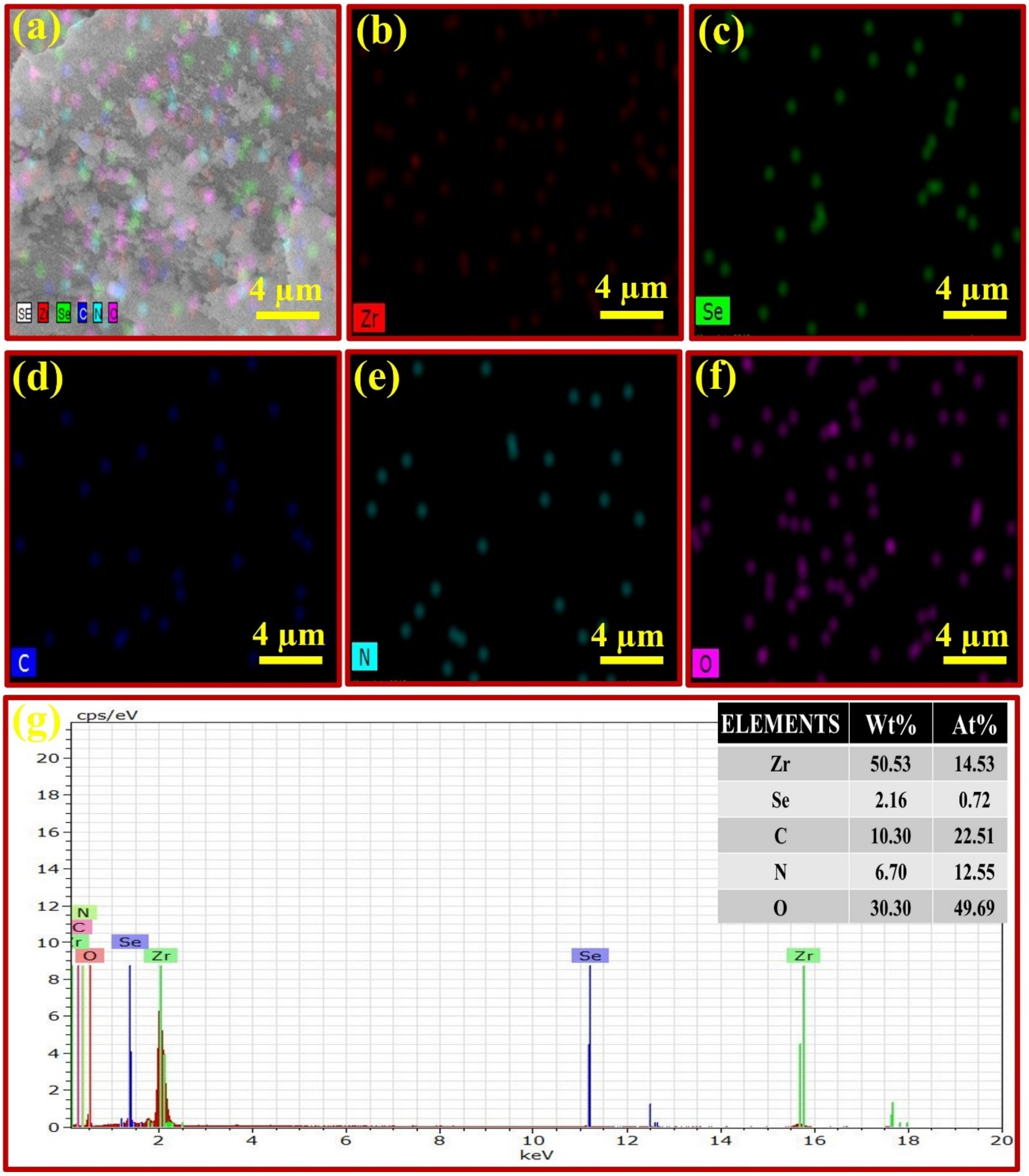

Fig. S1 (a) Elemental mapping of Se-ZrO_2@NC-500 composite; (b-f) individual elemental mapping of Zr, Se, C, N and O respectively and (g) elemental composition.

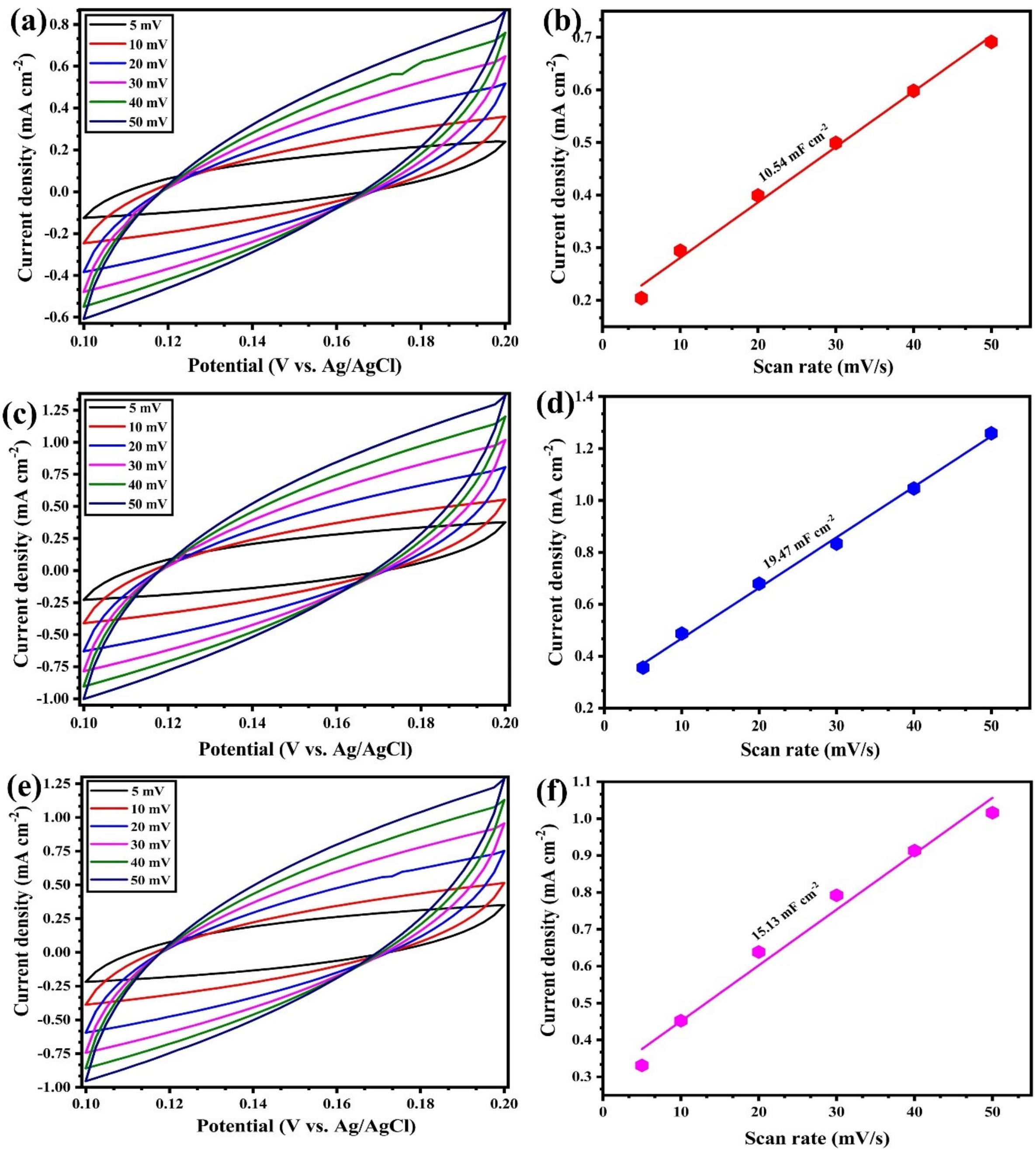

Fig. S2 CV profile of (a) Zr-MOF; (c) Se-ZrO_2@NC-300 and (e) Se-ZrO_2@NC-400 at non-faradic region at different scan rates (5 to 50 mV/s) in 1 M KOH, plot of current density as a function of scan rate of (b) Zr-MOF; (d) Se-ZrO_2@NC-300 and (f) Se-ZrO_2@NC-400.

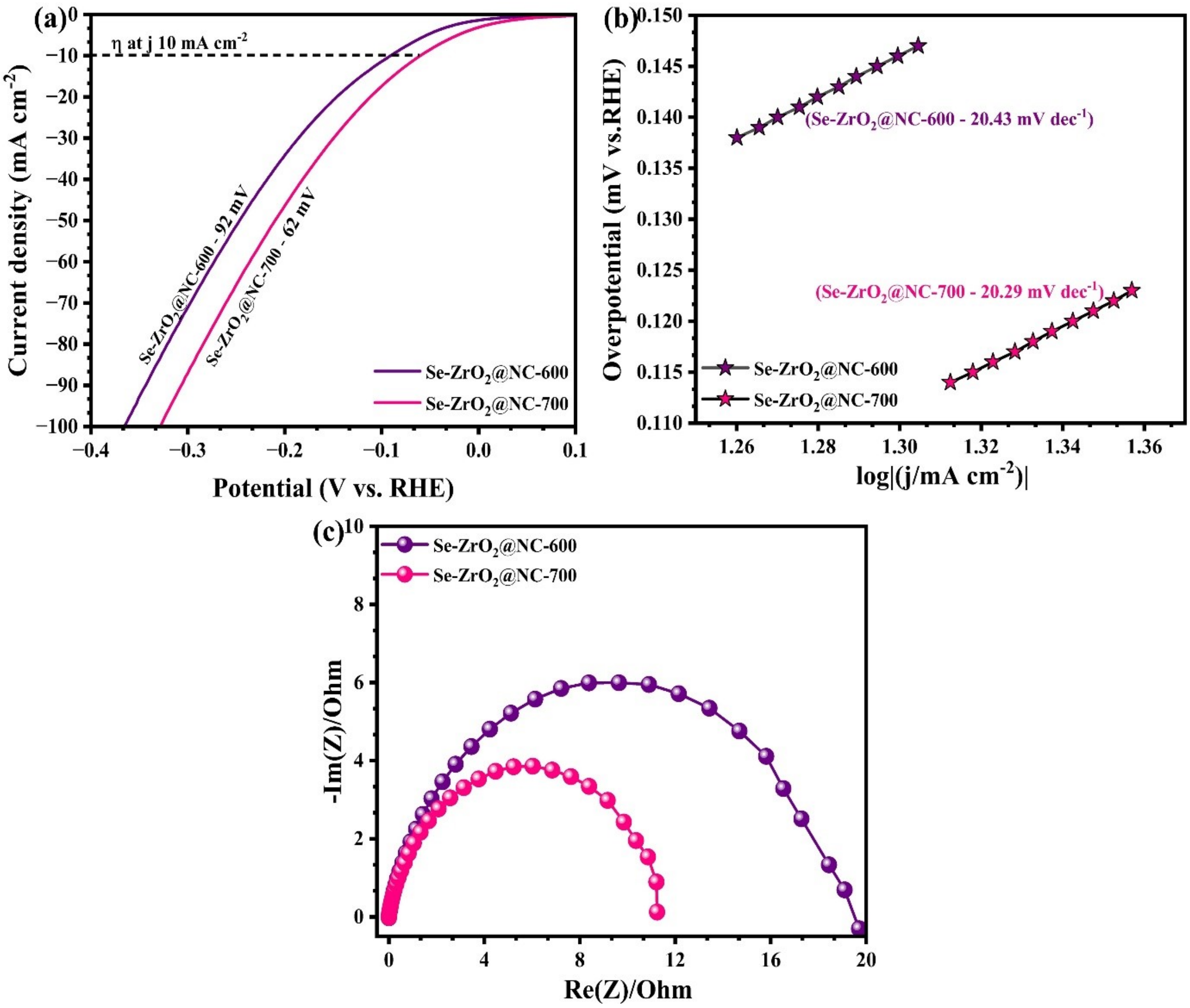

Fig. S3 HER activity of Se-ZrO_2@NC-600 and Se-ZrO_2@NC-700 loaded electrode in 1.0 M KOH. (a) LSV polarization curves at 2 mV/s; (b) the corresponding Tafel plot and (c) Nyquist plots.

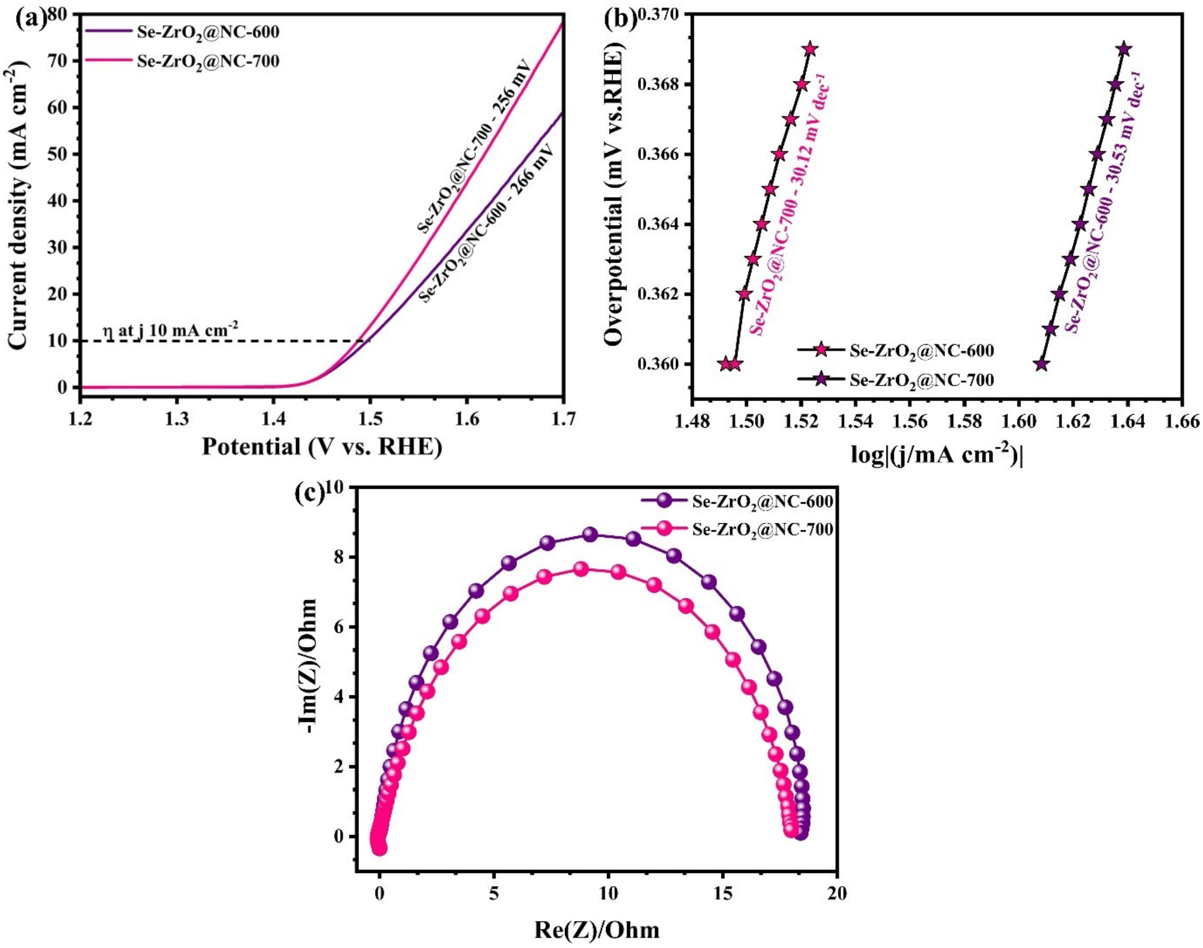

Fig. S4 OER activity of Se-ZrO_2@NC-600 and Se-ZrO_2@NC-700 loaded electrode in 1.0 M KOH. (a) LSV polarization curves at 2 mV/s; (b) the corresponding Tafel plot and (c) Nyquist plots.

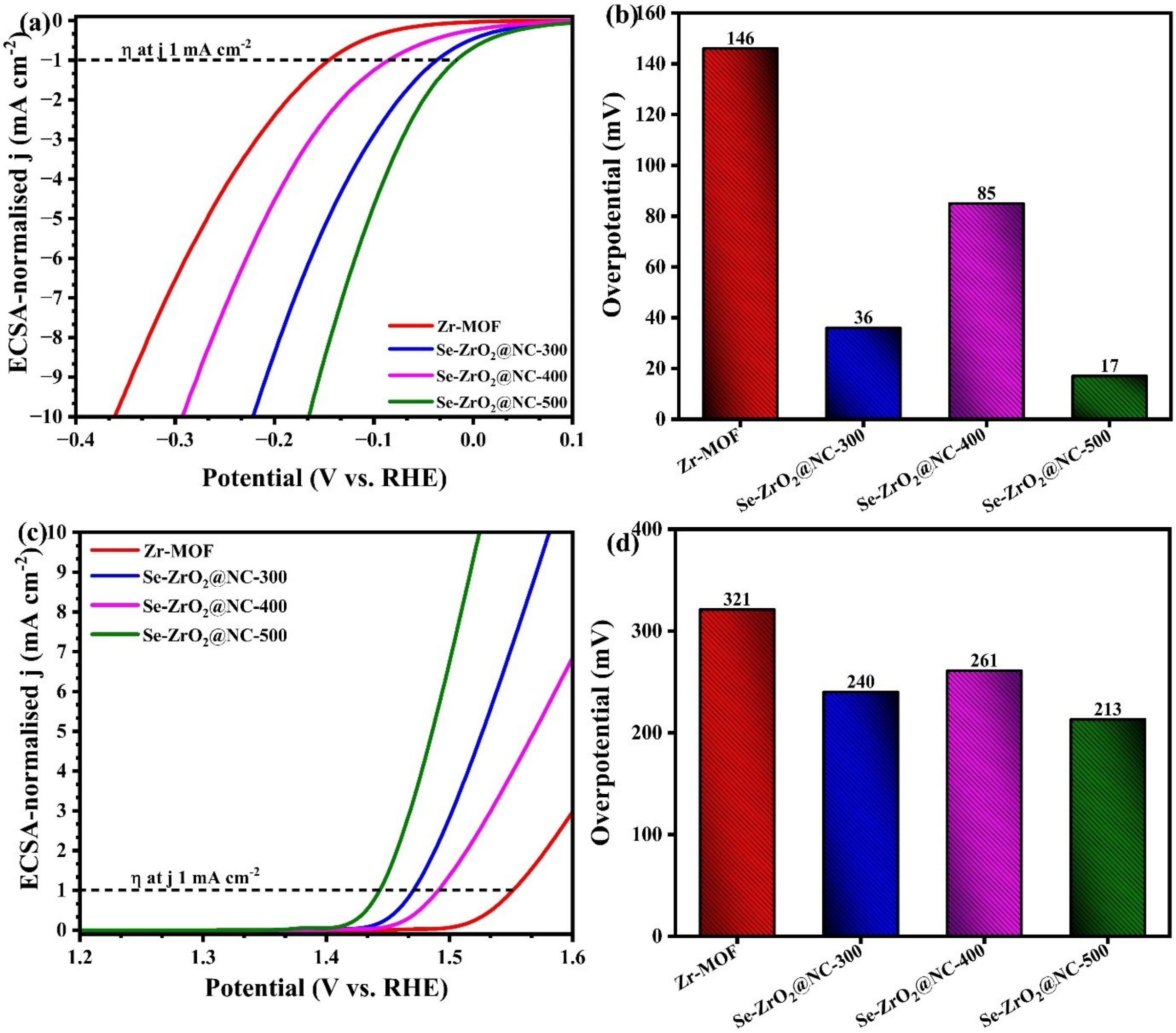

Fig. S5 ECSA normalized LSV curve and corresponding overpotential at 1 mA cm^{-2} current density of Zr-MOF, Se-ZrO_2@NC-300, Se-ZrO_2@NC-400 and Se-ZrO_2@NC-500 for (a, b) HER and (c, d) OER activity.

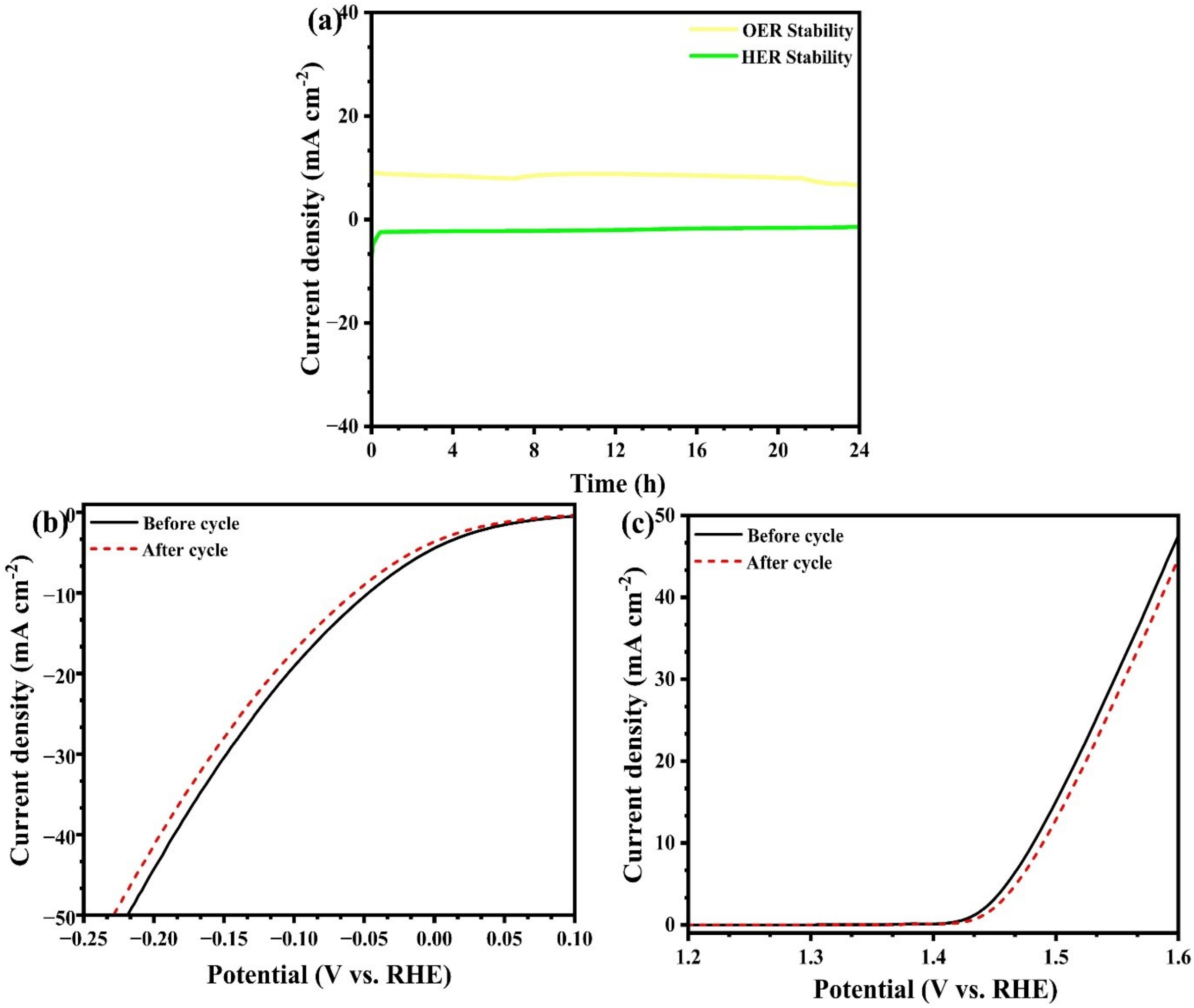

Fig. S6 (a) Chronoamperometric i–t curves for Se-ZrO_2@NC-500 loaded electrode showing HER and OER stability for 24 h; LSV curves for before and after chronoamperometric studies (b) HER and (c) OER activity.

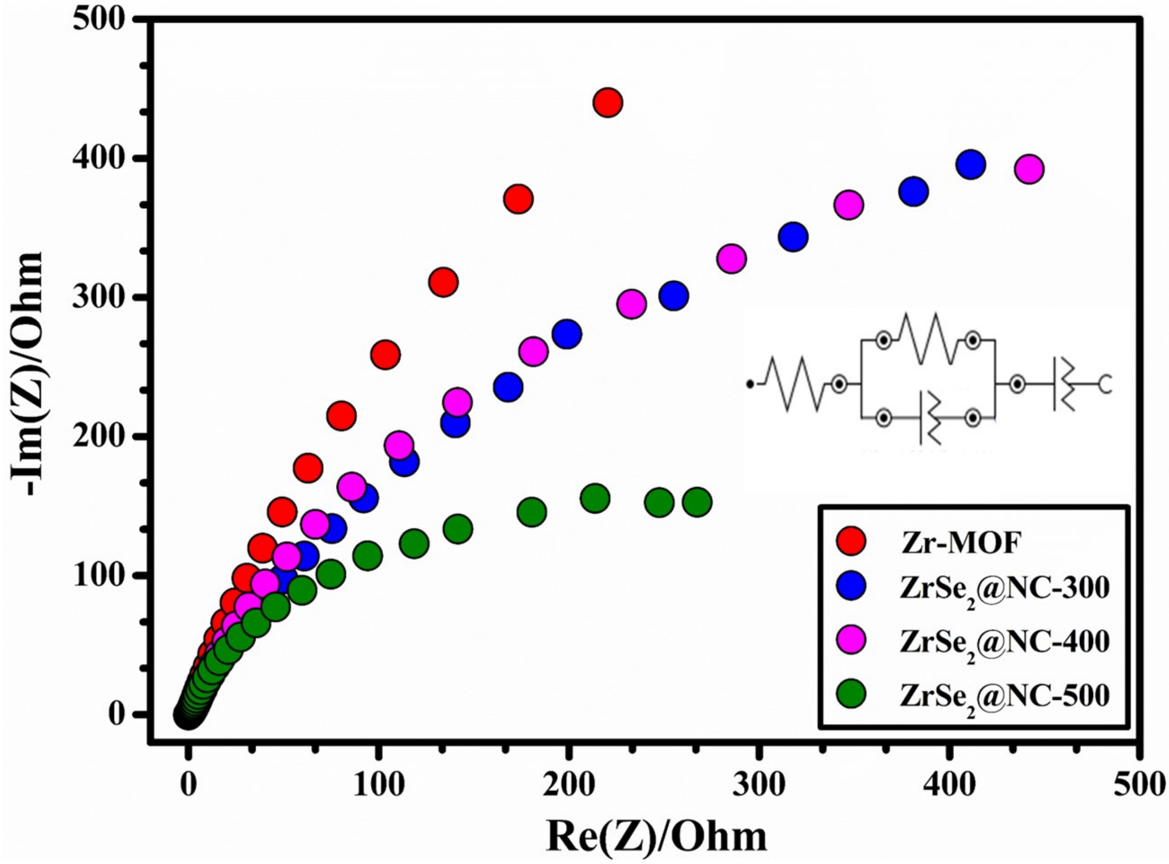

Fig. S7 Nyquist plots for overall water splitting reactions of Zr-MOF, Se-ZrO_2@NC-300, Se-ZrO_2@NC-400 and Se-ZrO_2@NC-500 in 1 M KOH. Inset shows the equivalent circuit fitted for loaded electrode.

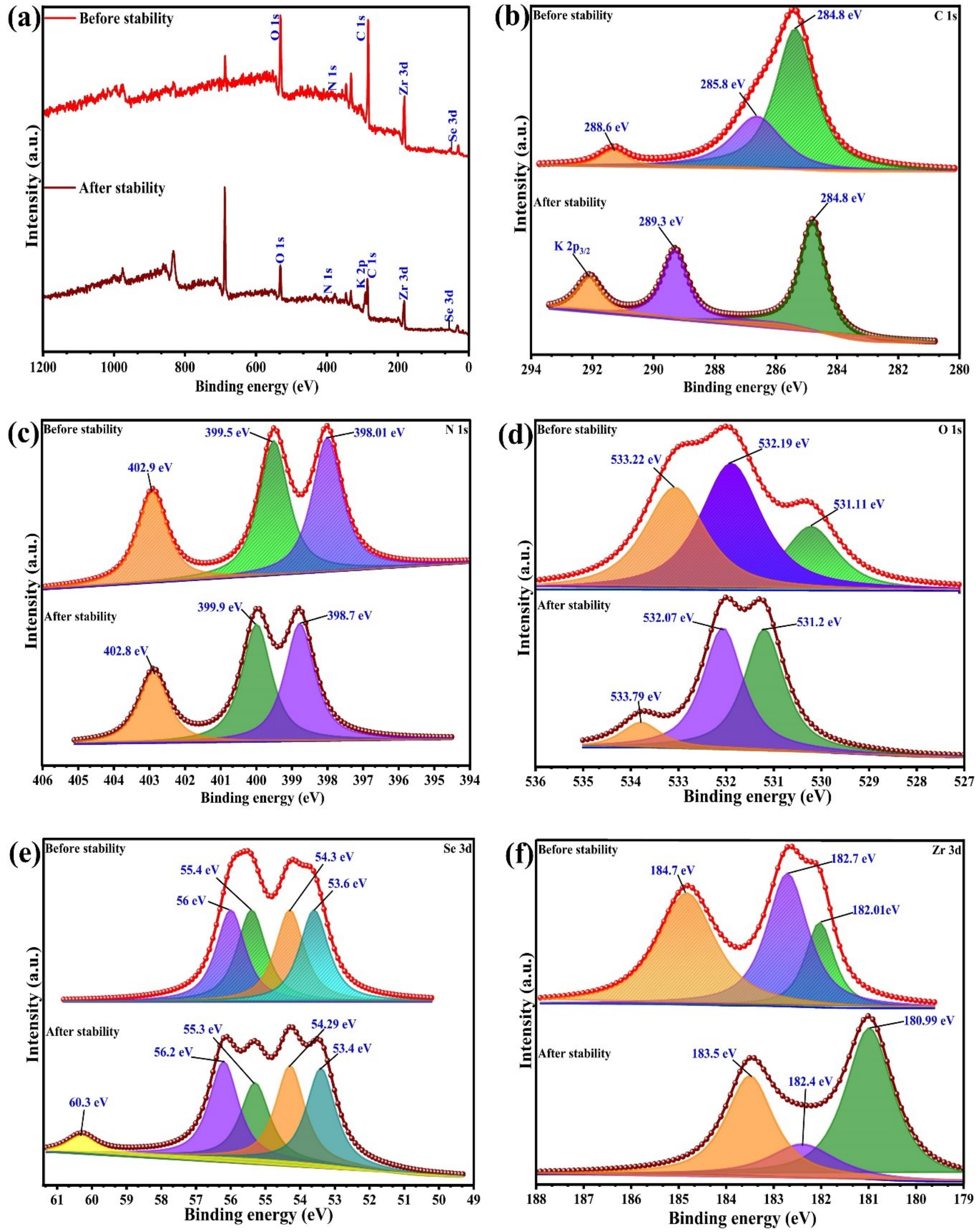

Fig. S8 (a) XPS survey spectra studied before and after stability for Se-ZrO_2@NC-500 composite and (b–f) the corresponding high-resolution XPS of C 1s, N 1s, O 1s, Se 3d and Zr 3d, respectively.

Table S1. Chemical composition of Se-ZrO_2@NC-500 obtained from XPS spectra

Elements	Atomic weight %
Zr	15.1
Se	6.3
C	41.2
N	4.4
O	33.0

Table S2. Electrochemical impedance spectroscopy for HER, OER and overall water splitting of different composites as electrocatalyst.

S.No.	Electrocatalyst	HER		OER		Overall water splitting	
		Rs (Ω)	Rct (Ω)	Rs (Ω)	Rct (Ω)	Rs (Ω)	Rct (Ω)
1	Zr-MOF	1.03	73.59	1.65	60.50	2.80	5.84
2	Se-ZrO_2@NC-300	0.90	31.98	1.18	24.53	1.20	3.63
3	Se-ZrO_2@NC-400	0.94	49.29	1.35	28.50	1.63	4.13
4	Se-ZrO_2@NC-600	0.84	19.69	1.13	18.69	-	-
5	Se-ZrO_2@NC-700	0. 71	11.3	1.13	17.31	-	-
6	Se-ZrO_2@NC-500	0.59	10.61	1.12	17.12	1.20	1.30

Table S3. Chemical composition of Se-ZrO_2@N-500 composites at the electrode surface for before and after the chronoamperometric stability study obtained from XPS spectra.

Elements	Atomic weight %	
	Before stability	After stability
Zr	3.5	3.2
Se	1.2	1.1
C	69.8	72.8
N	5.1	4.0
O	20.4	19.0

Table S4. Comparative electrocatalytic performances of as-prepared electrocatalysts with similar state-of-the-art materials.

S. No.	Electrocatalyst	Electrolyte	OER, η(mV)@10 mA cm^{-2}	HER, η(mV)@10 mA cm^{-2}	Cell voltage (V)	Reference
1	NiCoSe/C	1 M KOH	249.00	143.00	1.68	1
2	$CoWSe_2$@PANI	1 M KOH	360.00	308.00	1.87	2
3	CC/MOF-$CoSe_2$@$MoSe_2$	1 M KOH	183.81	109.87	1.53	3
4	MZU-$Co_{2.5}Zr_1$	1 M KOH	252.00	172.00	1.56	4
5	$Co_{0.9}Fe_{0.1}$-Se/NF	1 M KOH	246.00	125.00	1.55	5
6	Mo2C/UiO-66 hybrid	1 M KOH	180 @20 mA cm^{-2}	174.00	1.33	6
7	$Zn_{0.1}Co_{0.9}Se_2$	1 M KOH	340.00	140.00 in 0.5 M KOH	-	7
8	Se:CoS_{2-X} core-shell nanotubes	1 M KOH	1.32 V	0.28 V	-	8
9	MOF-D $CoSe_2$	1 M KOH	320.00	195.00 in 0.5 M KOH	-	9
10	$Zr_{0.8}Ni_{0.2}B_2$	1 M KOH	350.00	420.00	-	10
11	CoSe/$MoSe_{2-1}$	1 M KOH	240.00	110.00	1.56	11
12	Co-Ni-Se/C/NF	1 M KOH	275.00 @10 mA cm^{-2}	90.00	1.60	12
13	$Fe_{0.2}Ni_{0.8}Se$	1 M KOH	255.00	124.00	-	13
14	MnS_XSe_{1-X}@N,F-CQDs	1 M KOH	209.00	87.00	1.55	14
15	Se-ZrO_2@NC-500	1 M KOH	251.00	48 in 0.5 M H_2SO_4	1.58	This work

References

1 Z. Chen, B. Xu, X. Yang, H. Zhang and C. Li, *Int. J. Hydrogen Energy*, 2019, **44**, 5983–5989.

2 S. Cogal, G. Celik Cogal, M. Mičušík, M. Kotlár and M. Omastová, *Int. J. Hydrogen Energy*, 2024, **49**, 689–700.

3 S. J. Patil, N. R. Chodankar, S. K. Hwang, P. A. Shinde, G. Seeta Rama Raju, K. Shanmugam Ranjith, Y. S. Huh and Y. K. Han, *Chem. Eng. J.,* 2022, **429**, 132379.

4 P. Chen, M. Wang, G. Li, H. Jiang, A. Rezaeifard, M. Jafarpour, G. Wu and B. Rao, *Inorg. Chem.*, 2022, **61**, 18424–18433.

5 H. Ren, L. Yu, L. Yang, Z. H. Huang, F. Kang and R. Lv, *J. Energy Chem.*, 2021, **60**, 194–201.

6 M. Ali, E. Pervaiz and O. Rabi, *ACS Omega*, 2021, **6**, 34219–34228.

7 X. Wang, F. Li, W. Li, W. Gao, Y. Tang and R. Li, *J. Mater. Chem. A*, 2017, **5**, 17982–17989.

8 Z. Shi, X. Qi, Z. Zhang, Y. Song, J. Zhang, C. Guo, W. Xu, K. Liu and Z. Zhu, *Nanoscale*, 2021, **13**, 6890–6901.

9 N. Sahu, J. K. Das and J. N. Behera, *Sustain. Energy Fuels*, 2021, **5**, 4992–5000.

10 B. Mete, N. S. Peighambardoust, S. Aydin, E. Sadeghi and U. Aydemir, *Electrochim. Acta*, 2021, **389**, 138789.

11 M. Hassan, M. M. Baig, K. H. Shah, A. Hussain, S. A. Hassan and A. Ali, *J. Phys. Chem. Solids*, 2022, **167**, 110780.

12 F. Ming, H. Liang, H. Shi, X. Xu, G. Mei and Z. Wang, *J. Mater. Chem. A*, 2016, **4**,

15148–15155.

13 J. He, T. Qian, C. Cai, X. Xiang, S. Li and X. Zu, *Nanomaterials*, 2022, **12**, 1–11.

14 B. Sun, G. Dong, J. Ye, D. feng Chai, X. Yang, S. Fu, M. Zhao, W. Zhang and J. Li, *Chem. Eng. J.*, 2023, **459**, 141610.