Electronic supplementary information *for*

Promising Ce single-atom-dispersed nitrogen-doped graphene catalysts for hydrogen evolution reaction

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Turnover Frequency (TOF)

The amount of oxygen/hydrogen evolved per unit of time of the catalyst can be determined by the below expression,

TOF= $j \times N_A / n \times F \times \tau$ ……………… equation 1

where, j = current density, N_A= Avogadro number, F = Faraday constant (96 485 C mol−1), n = Number of electrons (For OER, n = 4 and HER, n = 2), Γ = Surface concentration. Determination of Surface concentration from the redox feature of CV:

The calculated area associated with the reduction of Ce4+/Ce3+ of 1Ce/NGr = 0.0002764VA

Hence, the associated charge is = 0.0002764VA / 0.1 Vs-1

= 0.002764 As

= 0.002764 C

Now, the number of electron transferred is = 0.002764 C / 1.602 ×10-19 C

= 1.725×10^{16} C

Since the reduction of Ce^{4+}/Ce^{3+} is a single electron transfer reaction, the number of electrons calculated above is the same as the number of surface-active sites.

Hence, the number of Ce participate in HER is = 1.725×10^{16} C

The TOF values for 1Ce/NGr, 3Ce/NGr, and NGr were calculated from the redox feature, and the calculated values are 3.16 sec-1, 3.0 sec-1, and 0.238 sec-1.

2. Schematic for Ce/NGr

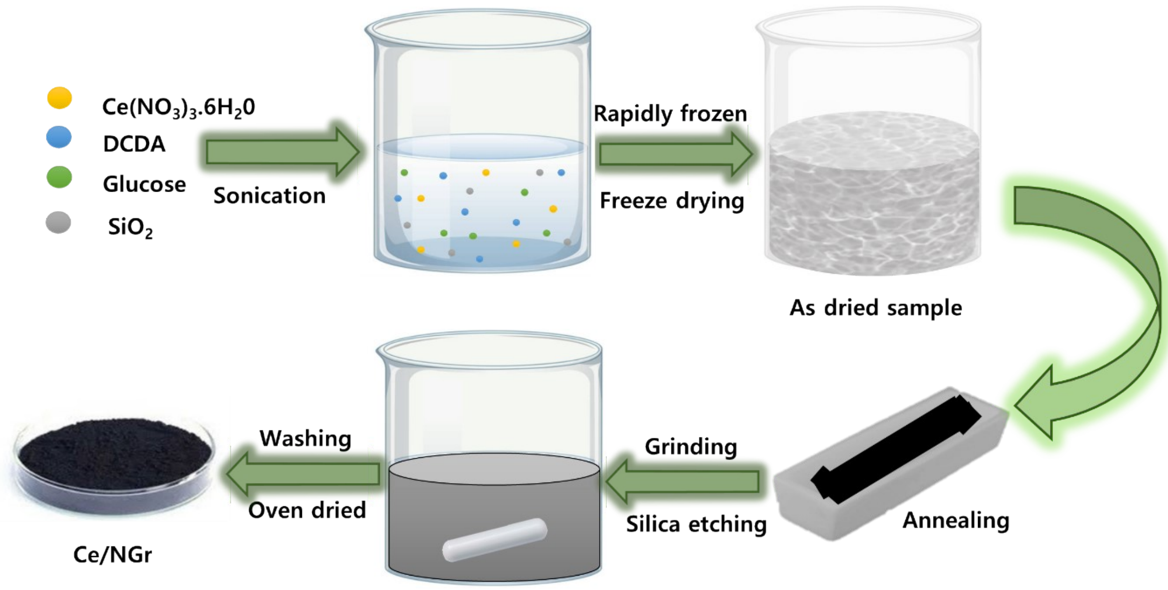

Fig. S1. Schematic of preparation process of rare-earth Ce single atom dispersed on NGr (Ce/NGr).

3. EDS Spectrum for free-standing NGr

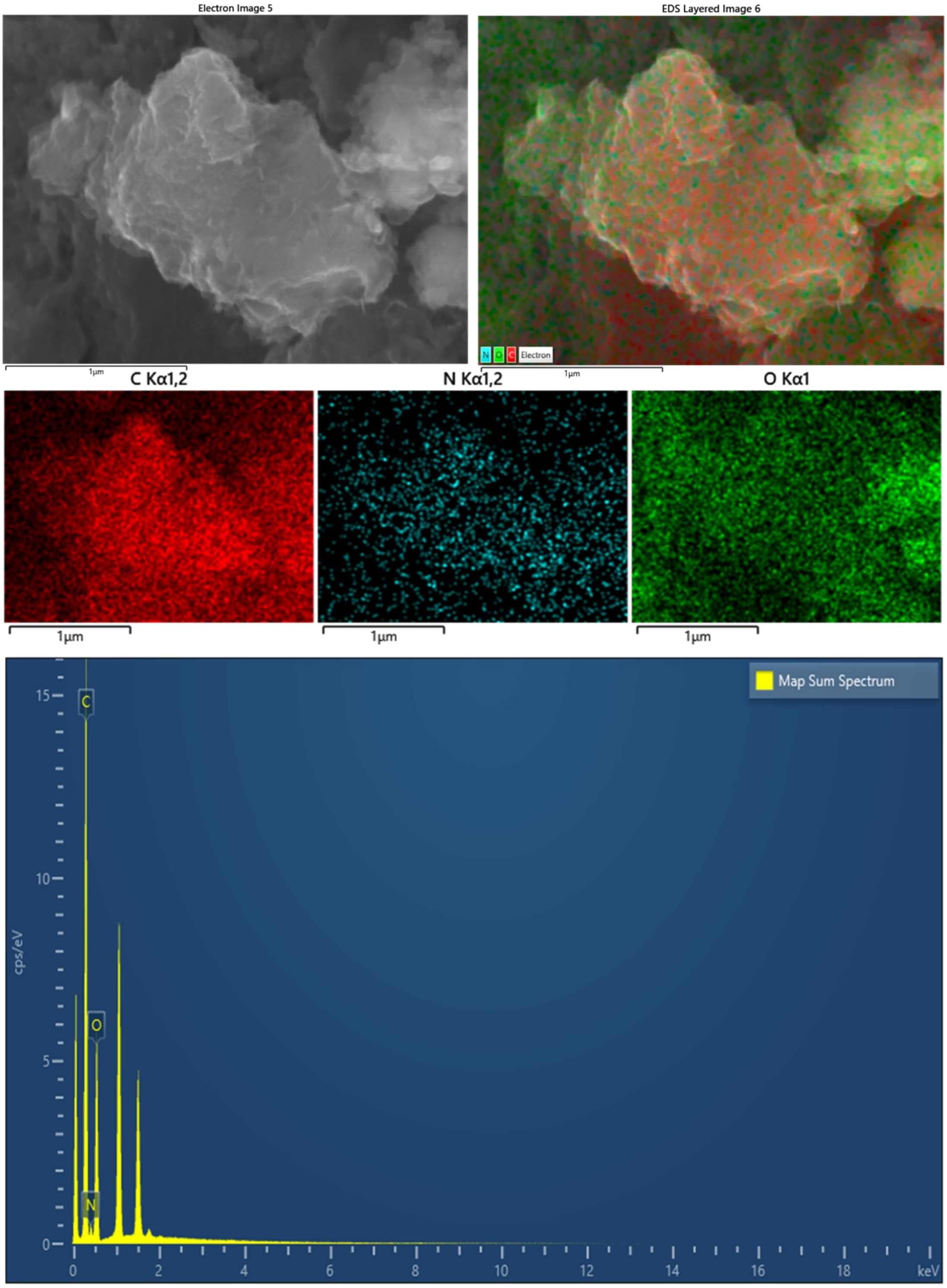

Fig. S2. EDS Spectrum for free standing NGr showing presence of C, N, O.

4. EDS Spectrum for Ce/NGr

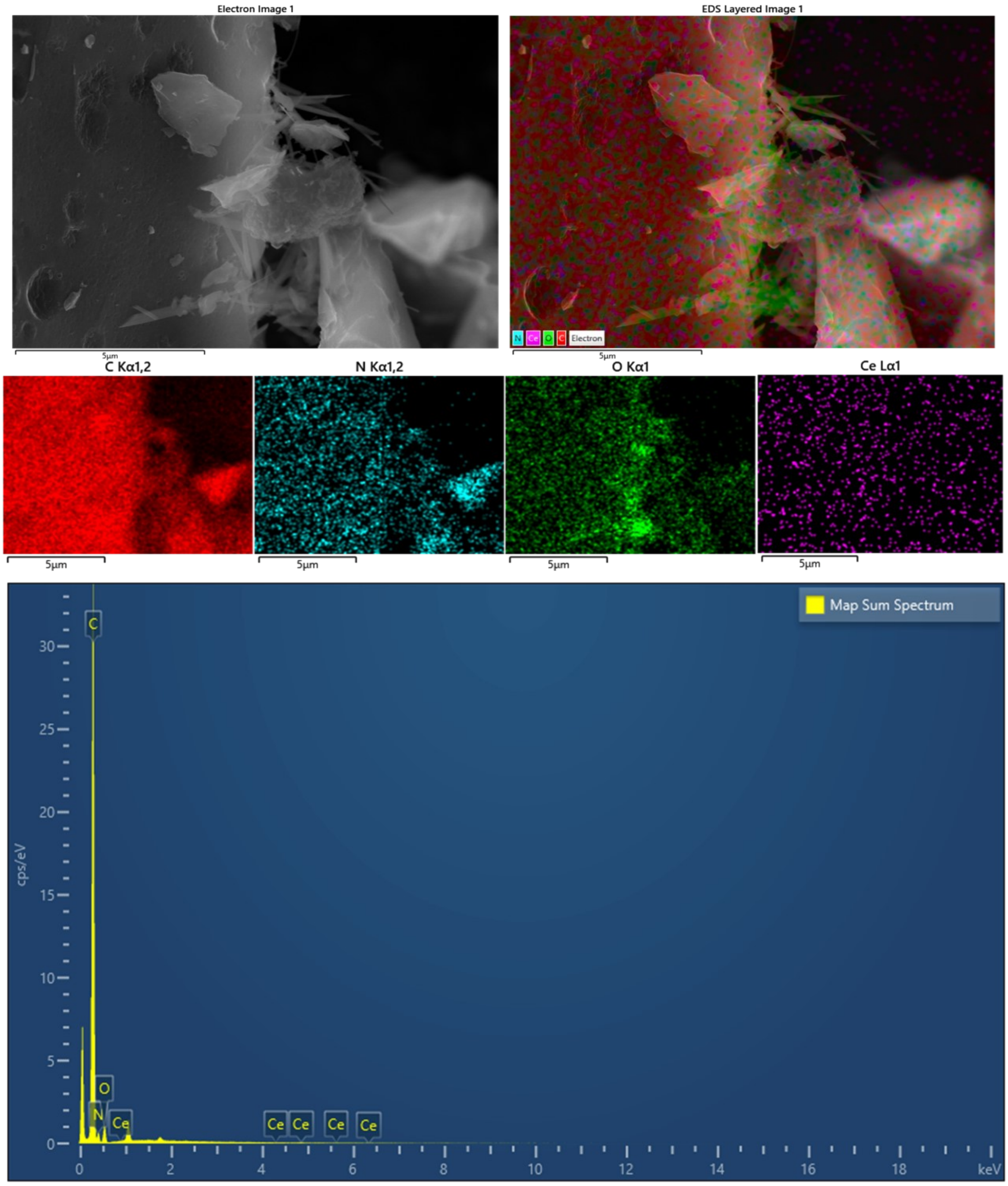

Fig. S3. EDS Spectrum for Ce/NGr showing presence of Ce, C, N and O

5. HR-TEM images

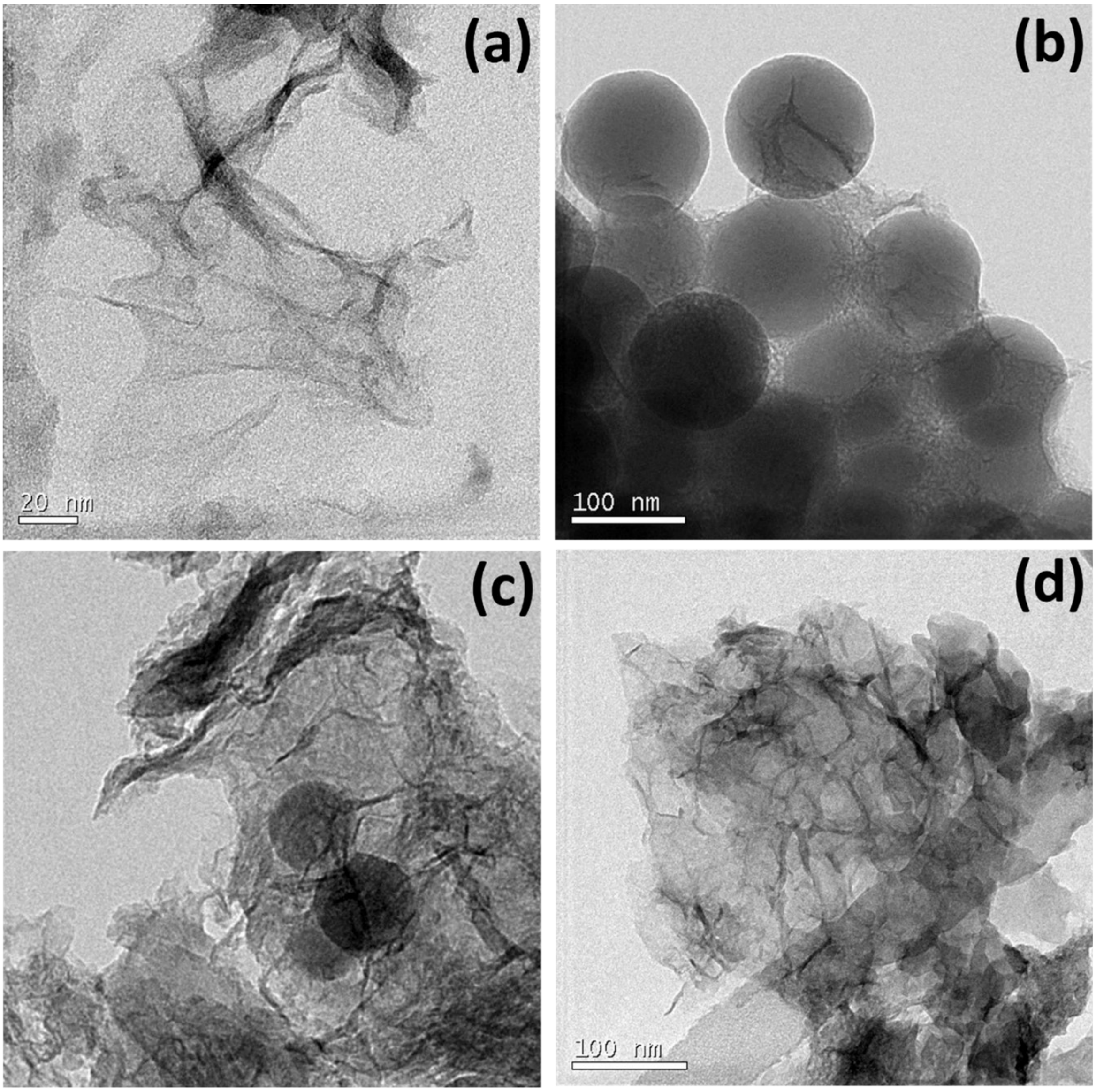

Fig. S4. (a) High-resolution TEM images showing (a) Free-standing nitrogen-doped graphe ne (NGr) (b) Free-standing nitrogen-doped graphene (NGr) with Silica doping (c) Silica co vered with layered NGr (d) Cavities after removal of silica.

6. STEM images of NGR and Ce/NGr

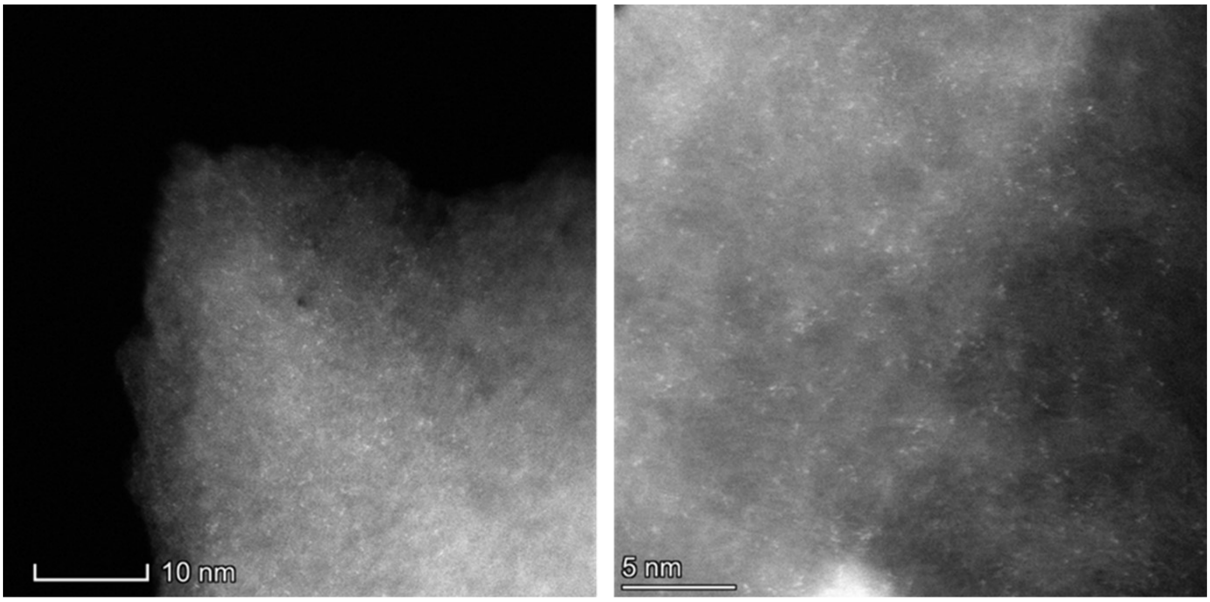

Fig. S5. STEM Images showing densely distributed Ce single atoms on NGr in 1Ce/NGr.

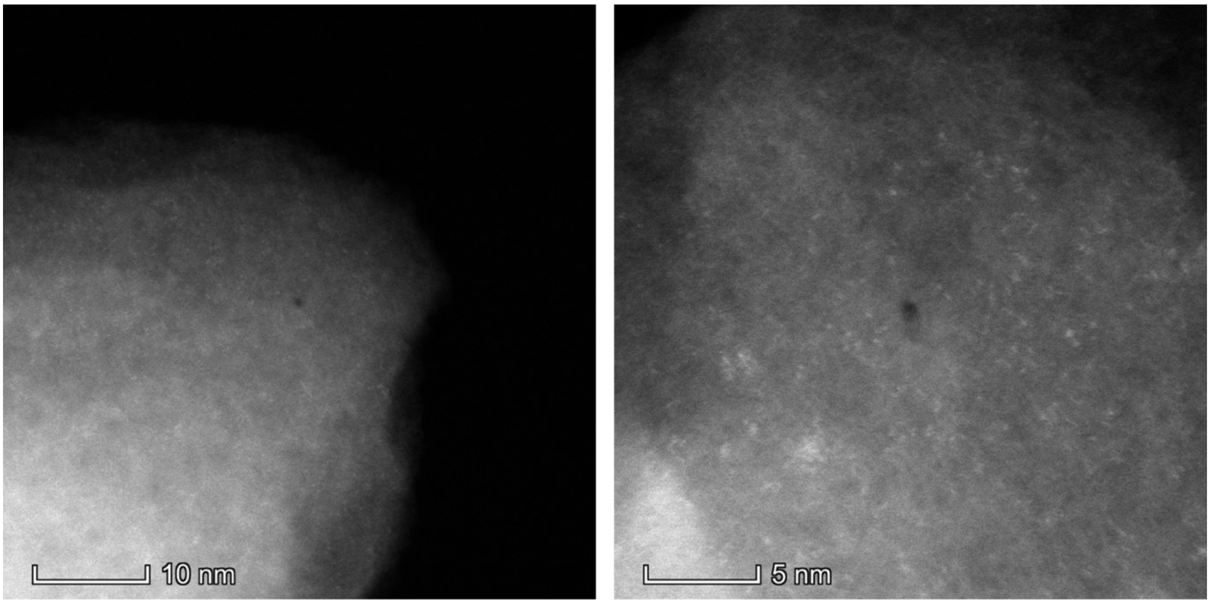

Fig. S6. STEM Images showing densely distributed Ce single atoms on NGr in 3Ce/NGr.

7. HER, Mass density, and EIS measurements of NGr, 1Ce/NGr, and 3Ce/NGr

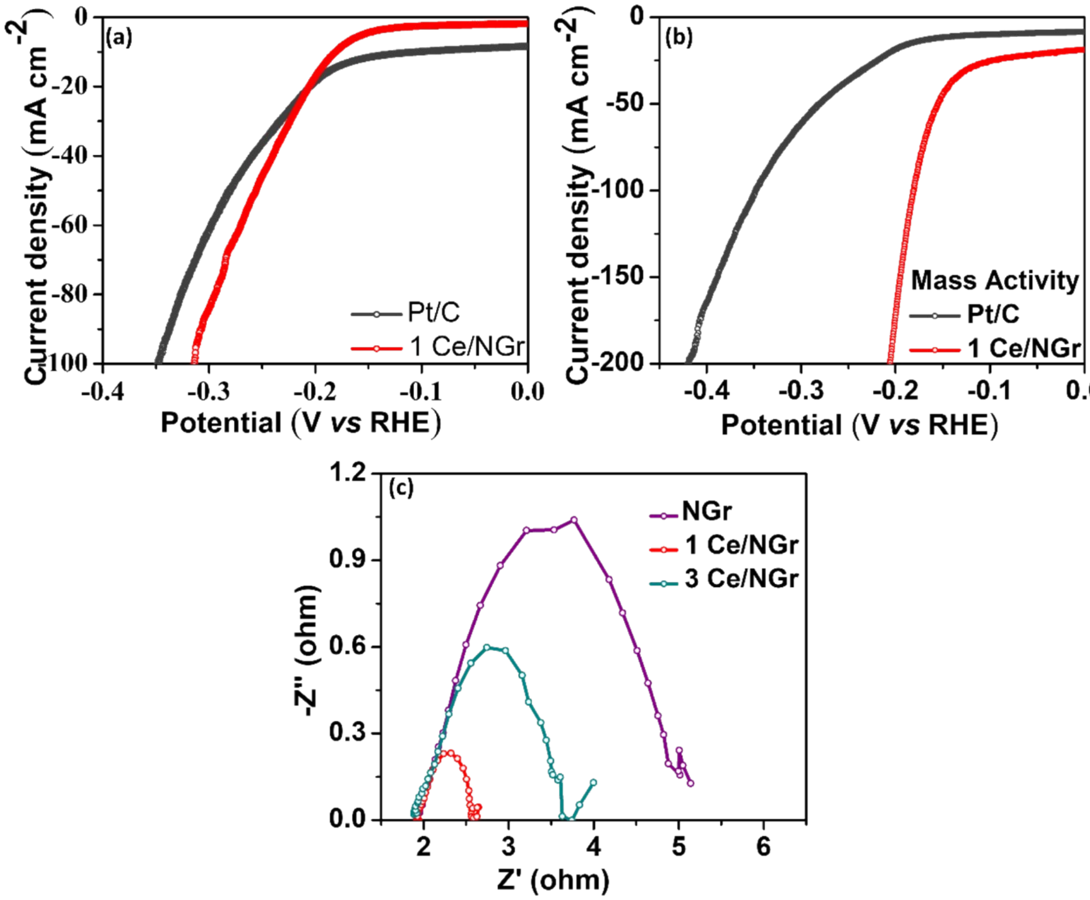

Fig. S7. (a) HER polarization curve for Pt/C and 1Ce/NGr, (b) mass density of Pt/C and 1Ce

8. CV cycle of Pt/C, NGr, 1Ce/NGr, and 3Ce/NGr

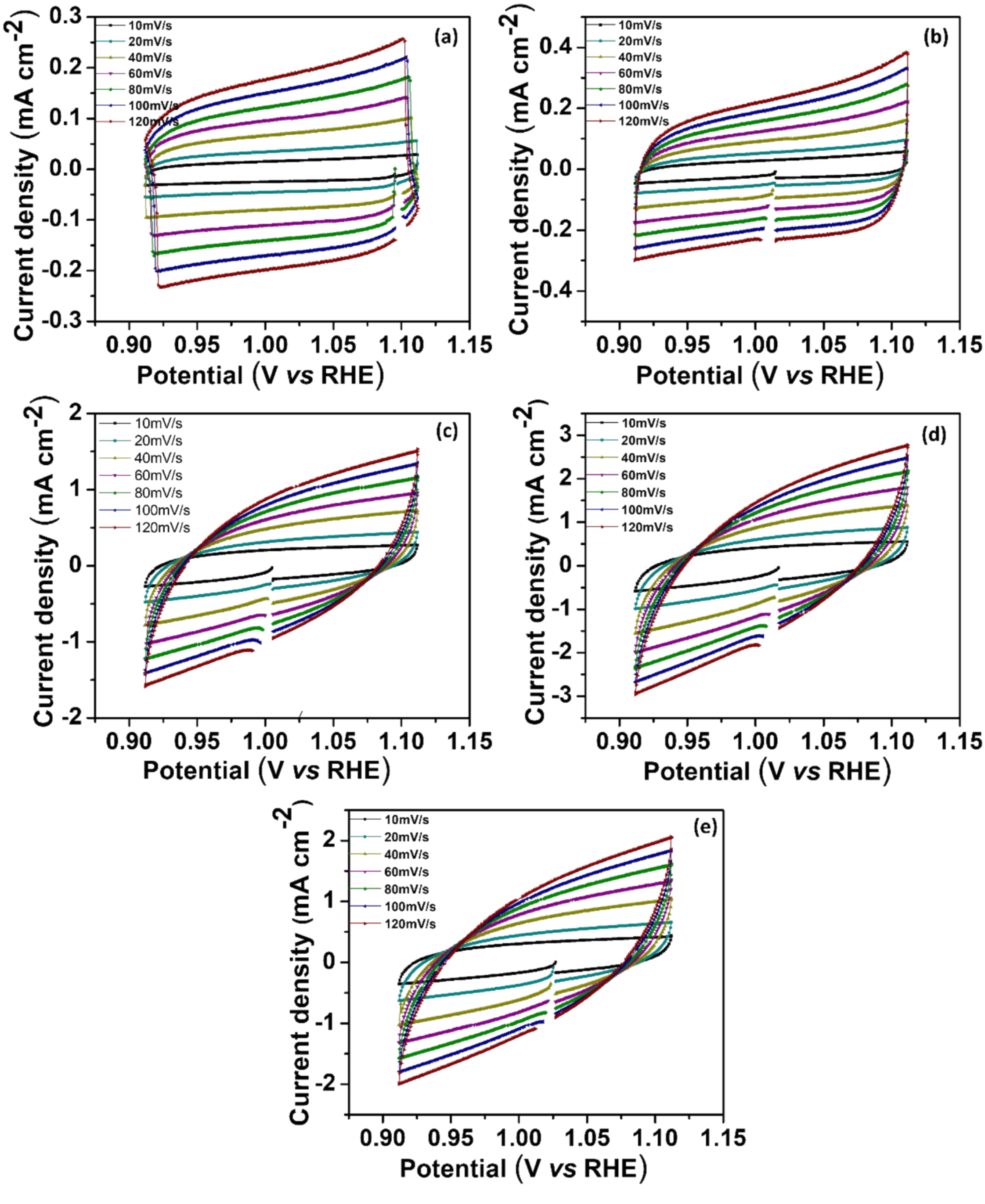

Fig. S8. CV cycle at different scan rates (a) Pt/C, (b) Ni foam, (c) NGr, (d) 1Ce/NGr, and (e)

9. I-t graph of NGr and 3Ce/NGr

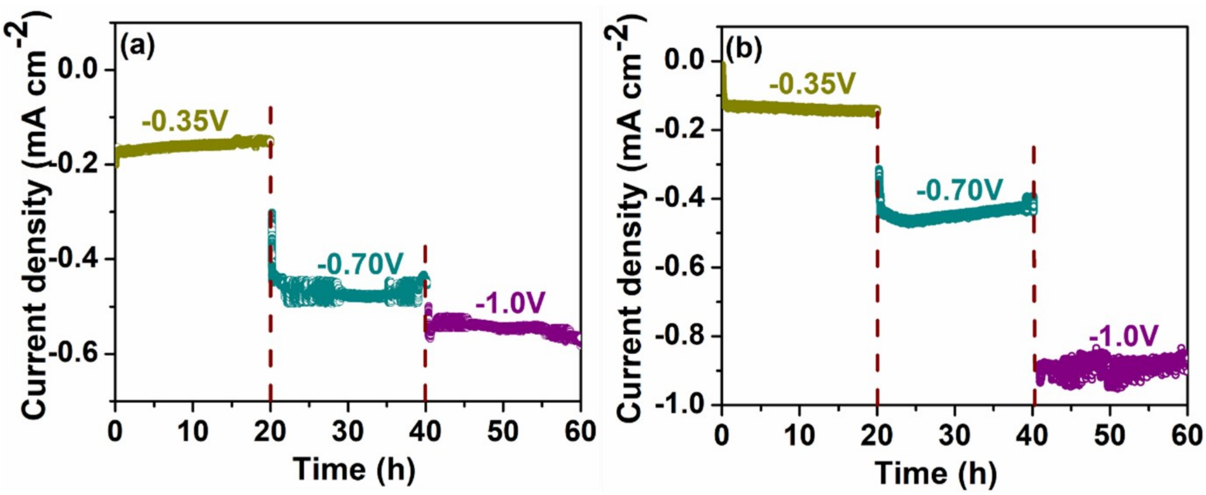

Fig. S9. (a) I-t graph of NGr, and (b) 3Ce/NGr at different potentials.

10. Electrochemical measurement of Ni foam, NGr, 1Ce/NGr, and 3Ce/NGr using a graphite rod

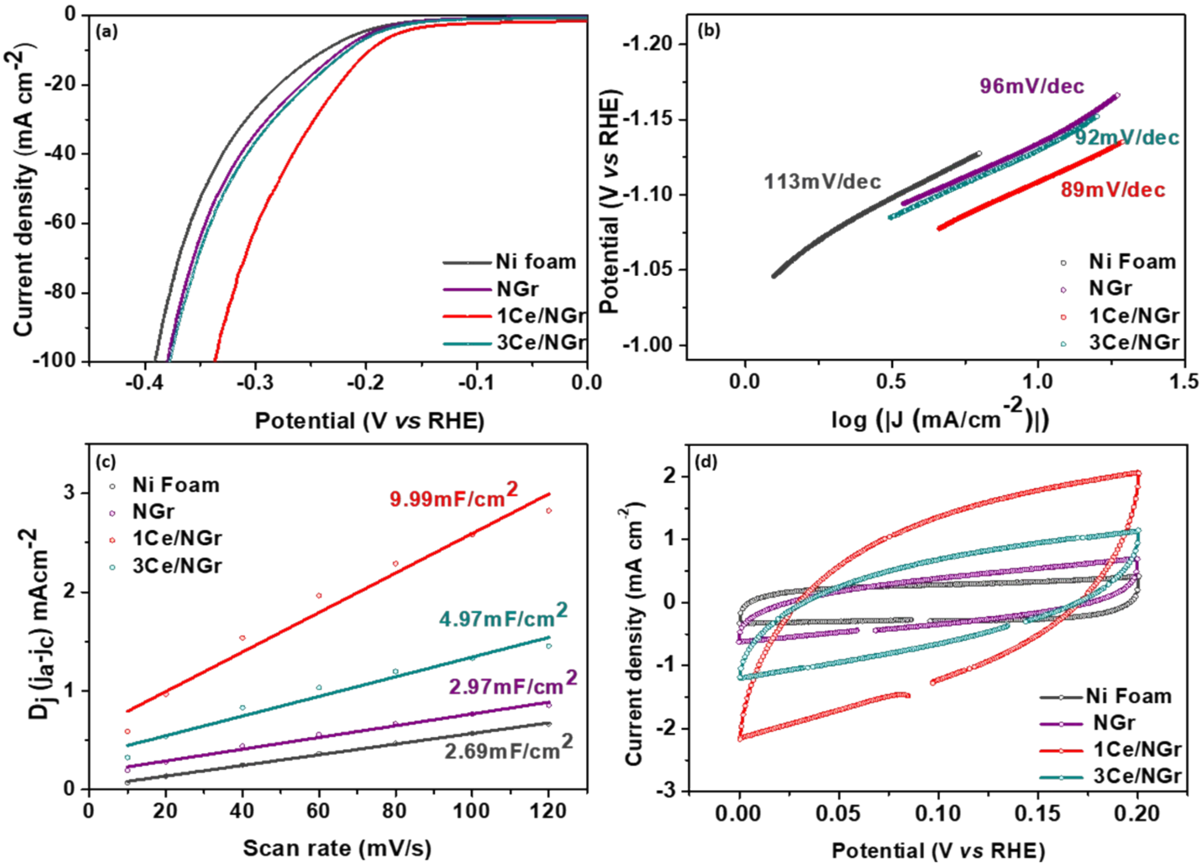

Fig. S10. (a) HER polarization curves for Ni foam, NGr, 1Ce/NGr and 3Ce/NGr, (b) tafel plot of Ni foam, NGr, 1Ce/NGr and 3Ce/NGr, (c) extraction of the double layer capacitance (C_{dl}) of Ni foam, NGr, 1Ce/NGr and 3Ce/NGr, (d) CV cycle of Ni foam, NGr, 1Ce/NGr and 3Ce/NGr at 100mV/s us

11. CV cycle of NGr, 1Ce/NGr, and 3Ce/NGr

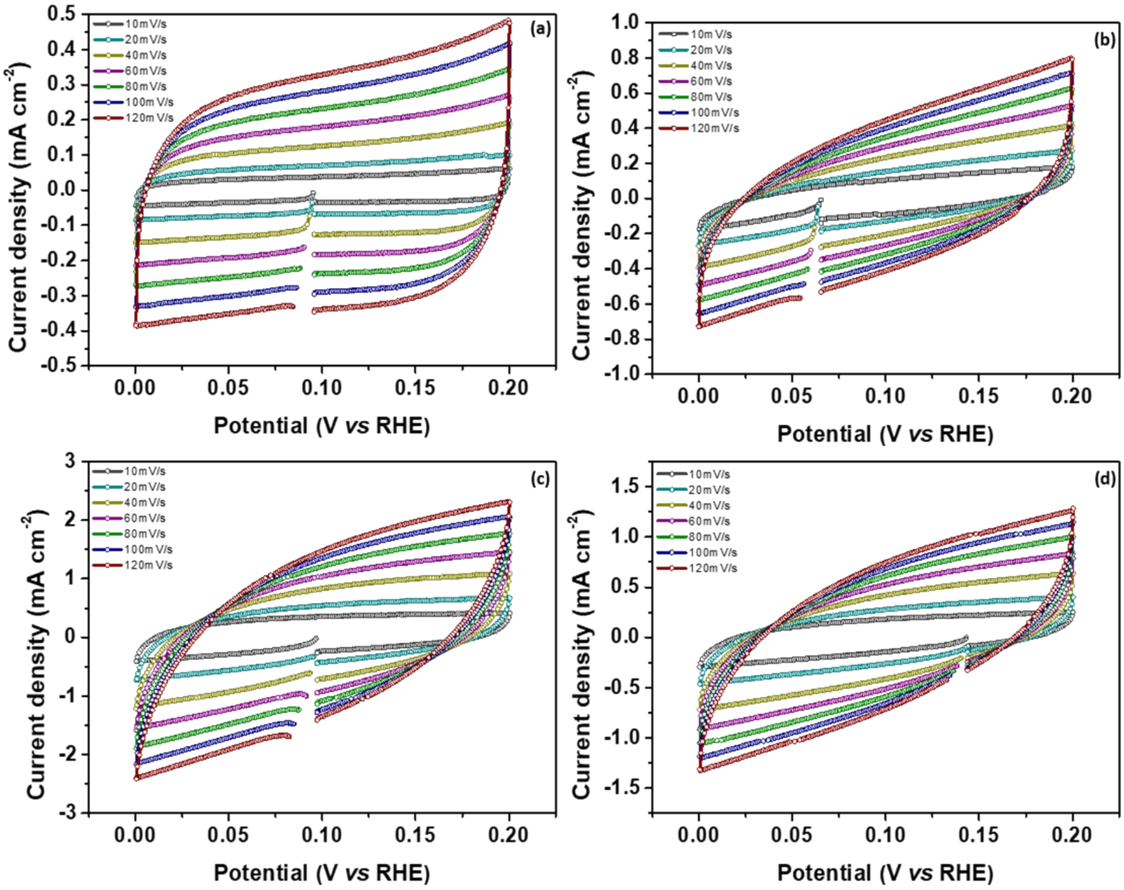

Fig. S11. CV cycle at different scan rates (a) Ni foam, (b) NGr, (c) 1Ce/NGr, and (d) 3Ce/NGr.

12. Fe-SEM, STEM, and XPS data after stability test of 1Ce/NGr and 3Ce/NGr

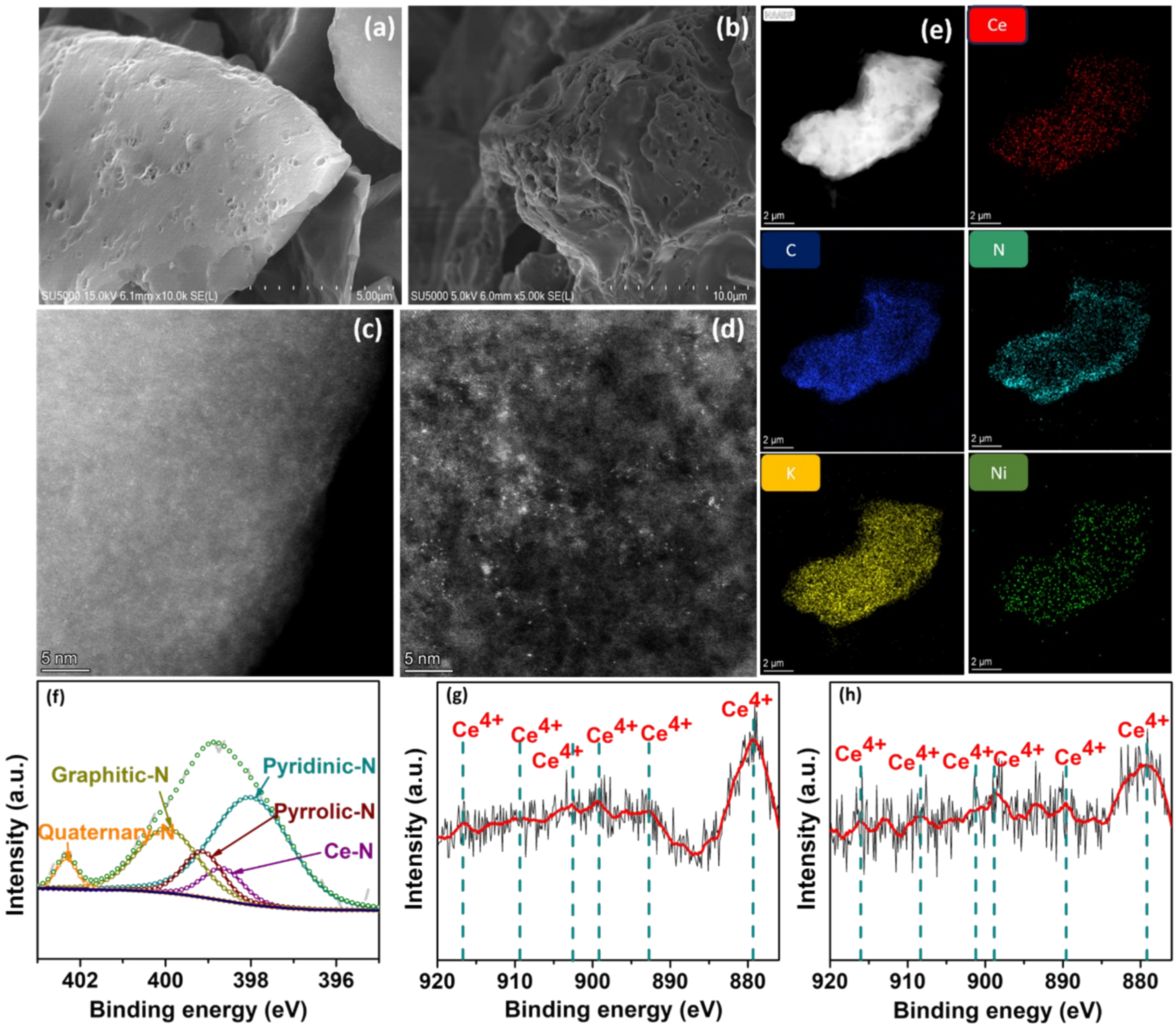

Fig. S12. (a) FE-SEM images of NGr after stability test, (b) porous structure of Ce/NGr af ter stability test, (c) aberration-corrected HAADF-STEM image after stability test for 1Ce/ NGr, and (d) 3Ce/NGr, (e) elemental mapping of Ce, C and N after stability test, (f) N 1s f

13. FE-SEM images of Ce/NGr after stability test

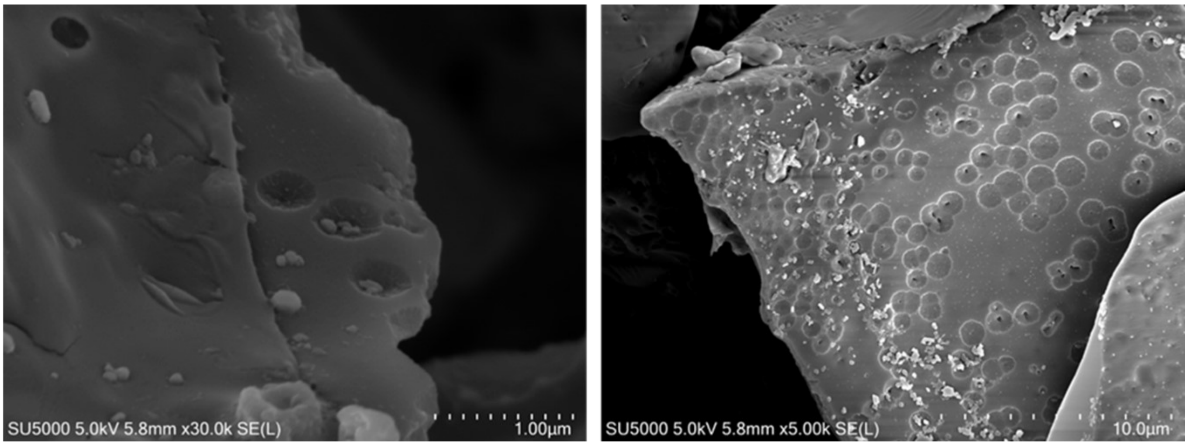

Fig. S13. FE-SEM images of Ce/NGr after stability test.

14. EDS Spectrum for free-standing NGr after stability test

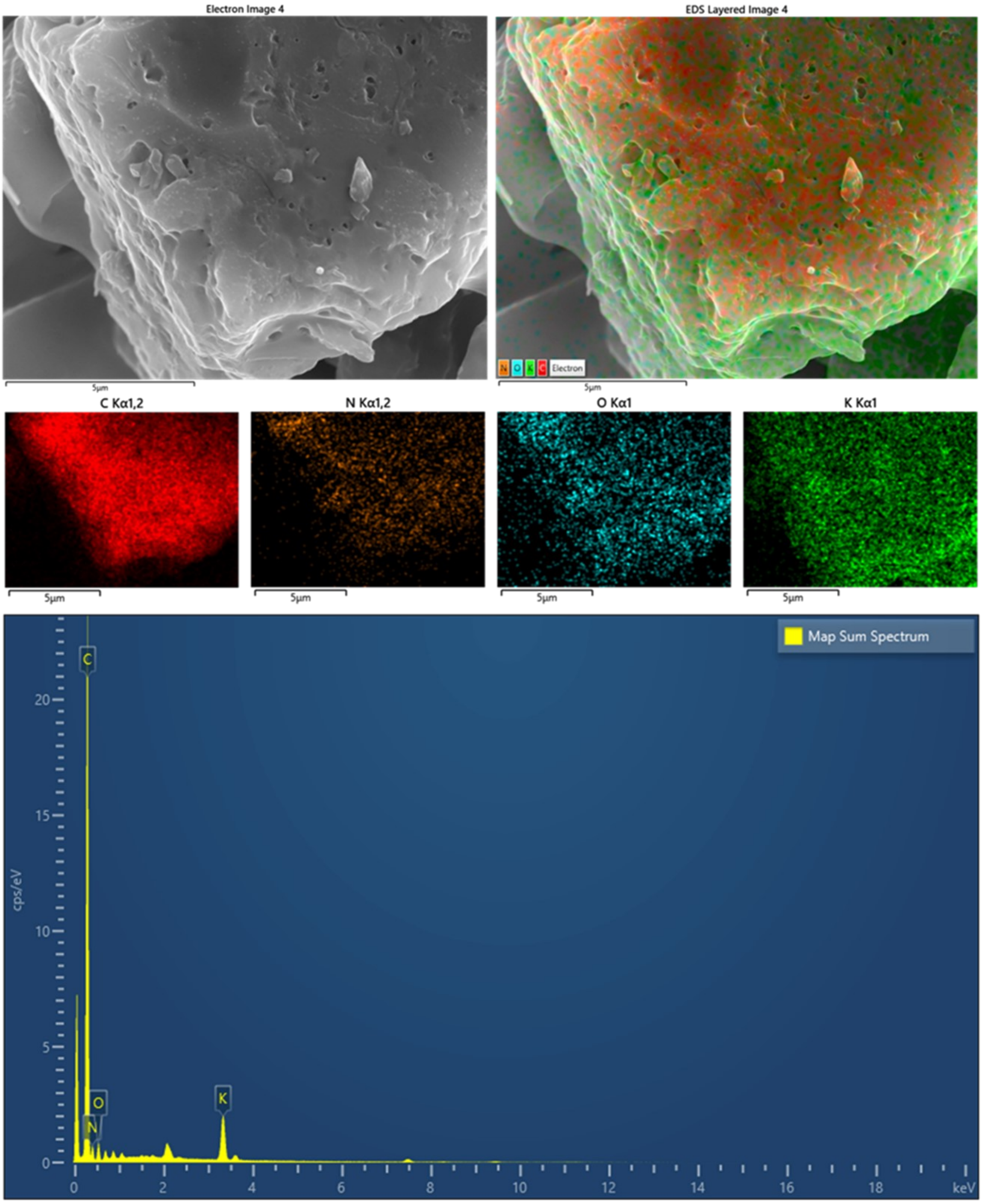

Fig. S14. EDS Spectrum for free standing NGr after stability test showing presence of

15. EDS Spectrum for free standing Ce/NGr after stability test

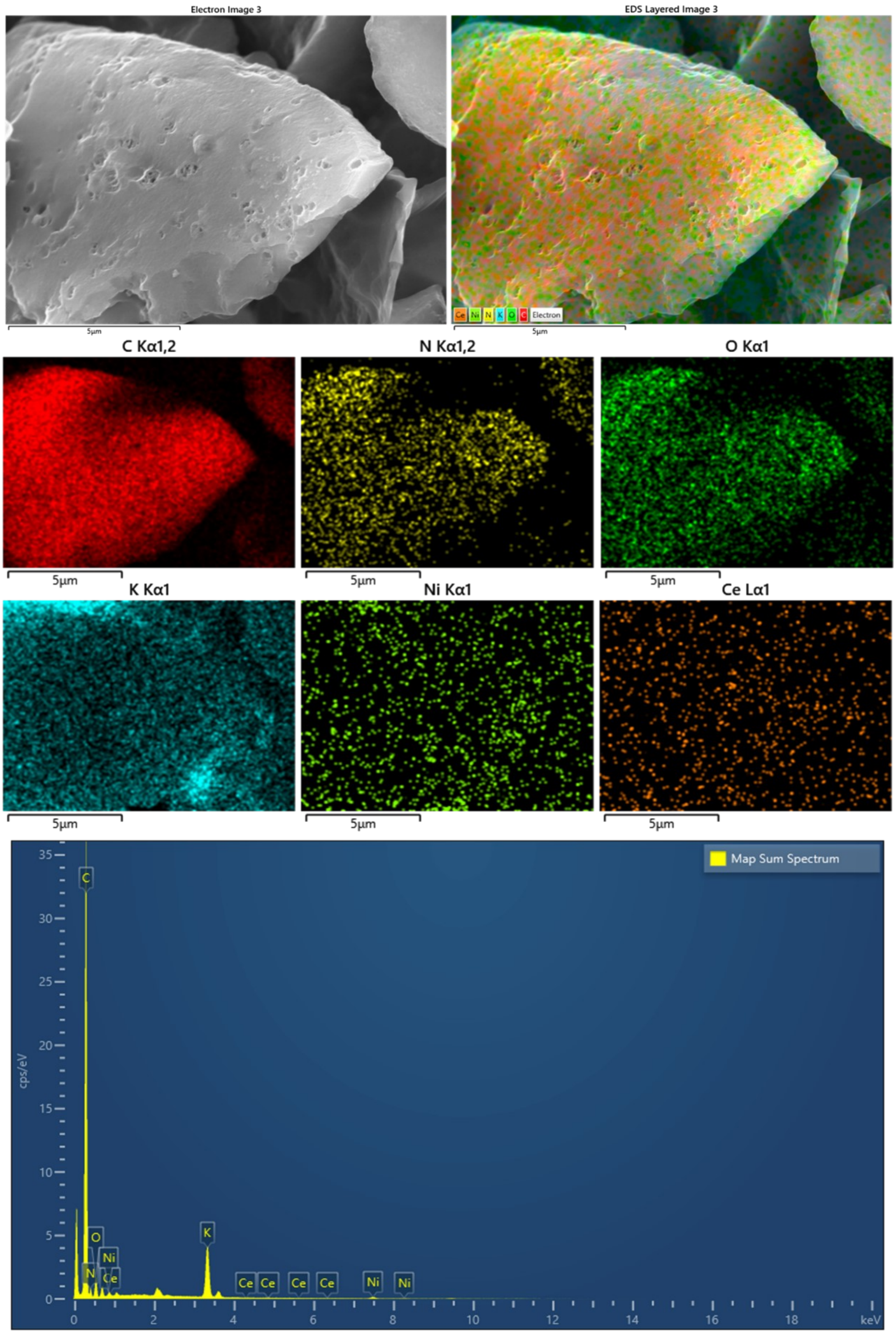

Fig. S15. EDS Spectrum for free standing Ce/NGr after stability test.

16. Comparison of HER active catalysts

Table S1. Comparison of HER active catalysts

Catalysts	Overpotential (mV, at 10 mA/ cm^2)	Tafel slope (mV/dec)	electrolyte	Ref.
Ce/NGr	180	83	1 M KOH	This work
Co@CNT/CeO_2	181	118	1 M KOH	Int. J. Hydrog. Energy, 2020, 45, 3948-3958. [S1]
3D-rGO-CeO_2	192	112.8	1 M KOH	Eur. J. Inorg. Chem., 2018, 3952-3959. [S2]
$Co_{NC\text{-}SA}$/N*–C	194	91.9	1 M KOH	ACS Catal., 2022, 12, 10771-10780. [S3]
Co/CeO_2/Co_2P/CoP@NC	195	66	1 M KOH	Int. J. Hydrog. Energy, 2020, 45, 30559-30570. [S4]
Ni-1T MoS_2	199	52.7	1 M KOH	Small, 2022, 18, 2107238. [S5]
Co-1T-MoS_2	261	88.5	1 M KOH	Small, 2022, 18, 2107238 [S5]
Fe-1T-MoS_2	269	168	1 M KOH	Small, 2022, 18, 2107238. [S5]
g-C_3N_4/CeO_2/Fe_3O_4	310	102	1 M KOH	Chem Cat Chem, 2018, 10, 5587. [S6]
Pr2CeO3	374	110	1 M KOH	Ceram. Int., 48, 13, 2022. [S7]

References

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