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Synergistic Effect of Ceria on the Structure and Hydrogen Evolution Activity of Nickel Nanoparticles Grown on the Reduced Graphene Oxide

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Synthesis of GO:

Graphite powder added to the sulfuric acid and phosphoric acid mixture (9/1, V/V). Then potassium permanganate was gradually added to the sample in the ice bath. The procedure was followed by stirring at 50 °C for 12 h and then adding the ice water and hydrogen peroxide. The resulted yellow sample was centrifuged and washed with hydrochloric acid/ water solution, then with water and absolute ethanol repeatedly to reach the natural pH.

Electrochemical calculations:

The obtained data from LSV measurement were fitted to the Tafel equation as follows:

$$\eta = a + b \log j \qquad (1)$$

Where η is the cathode overpotential obtained by eq. 2. a is the experimental coefficient, b the tafel slope and j is current density. The overpotential (η) was calculated using eq. 2:

$$\eta = E_{applied} + E_{ref} - E^0 \qquad (2)$$

Where $E_{applied}$ is the obtained experimental potential, E_{ref} is the reference electrode potential (0.197 V for Ag/AgCl) and E^0 is the equilibrium HER potential (-0.828 V for pH=14, 298 K).

Table S1. Description of prepared catalysts samples

Sample name	Preparation method	GO wt% at int. dispersion	Ceria wt% at int. dispersion	Theo. Ni wt%	Actual Ni wt% (by ICP result)
Ni/rGO	SBH reduction	100	0	20	24.6
Ni/Ceria-rGO (1,3)	SBH reduction	75	25	20	19.8
Ni/Ceria-rGO (1,1)	SBH reduction	50	50	20	22.7
Ni/Ceria-rGO (3,1)	SBH reduction	25	75	20	14.2*
Ni/Ceria	Wet impregnation	0	100	20	20.8

* Too much deviation from the theoretical value for the Ni/Ceria-rGO (3,1) can be attributed to the lacking of adequate functional groups for involving the Ni^{2+} ions at the synthesis procedure.

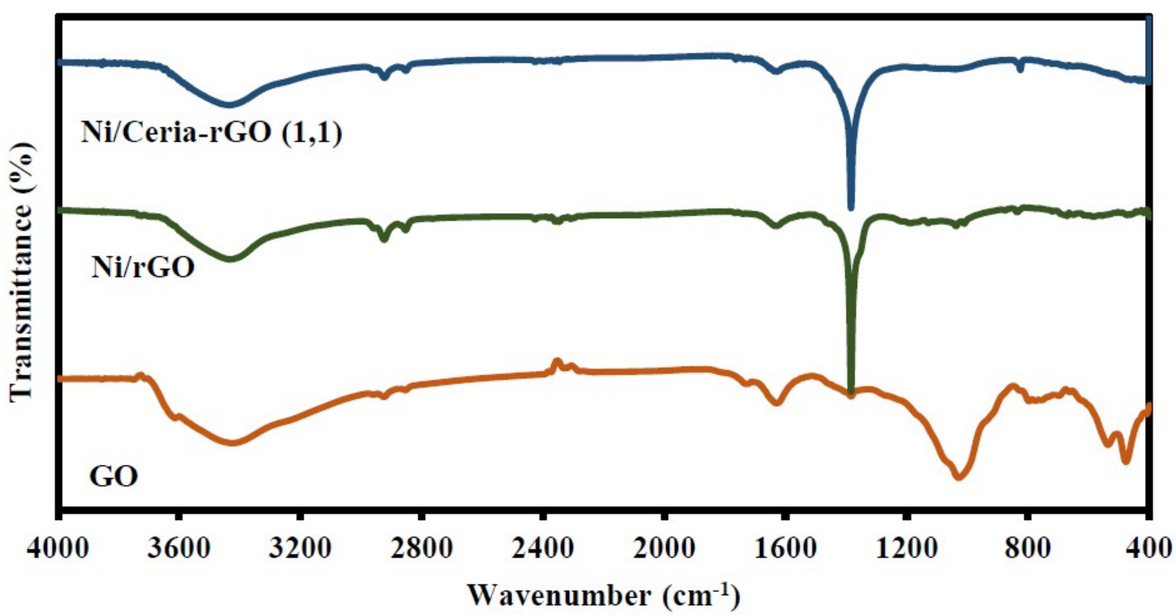

Figure S1. FT-IR spectra of GO, Ni/rGO and Ni/Ceria-rGO (1,1)

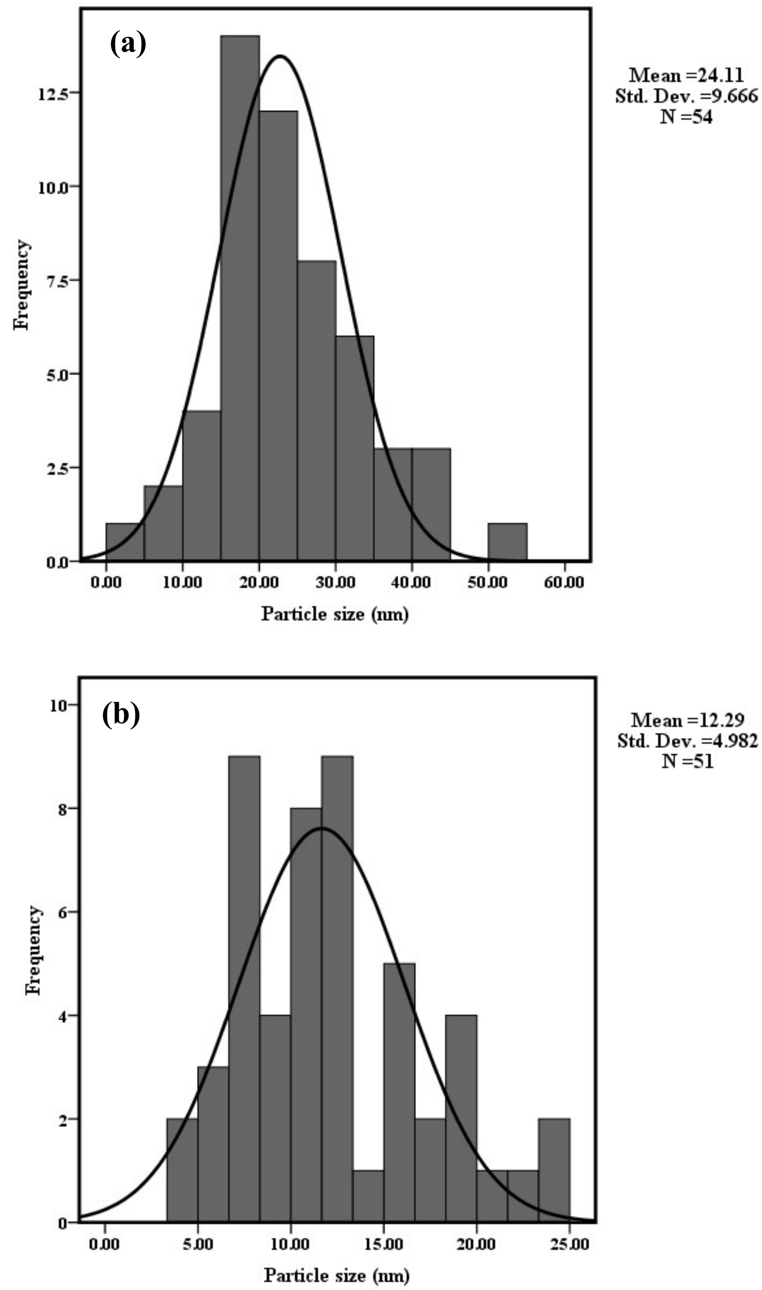

Figure S2. Size distribution histogram of Ni nanoparticles for (a) Ni/rGO and (b) Ni/Ceria-rGO (1,1)

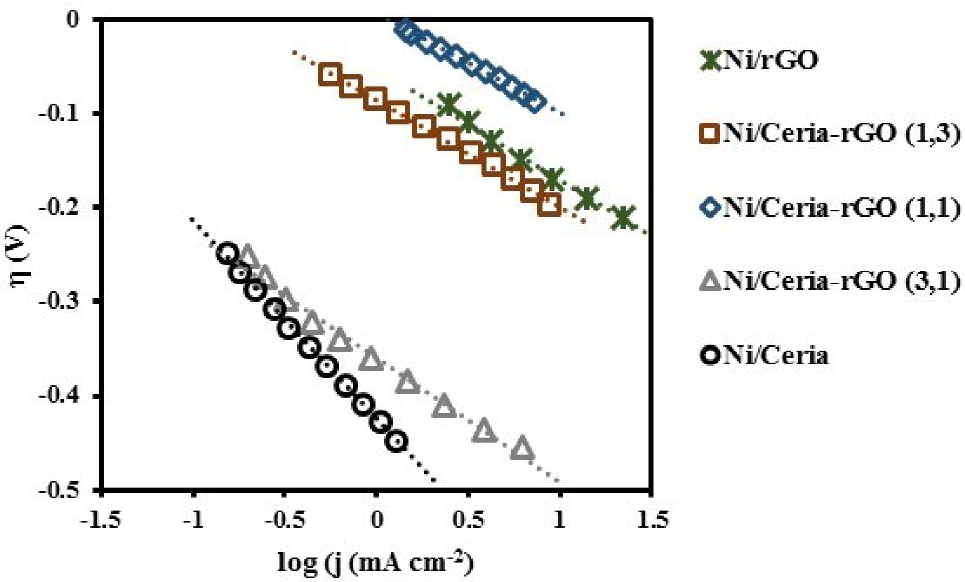

Figure S3. Tafel plots of the electrodes

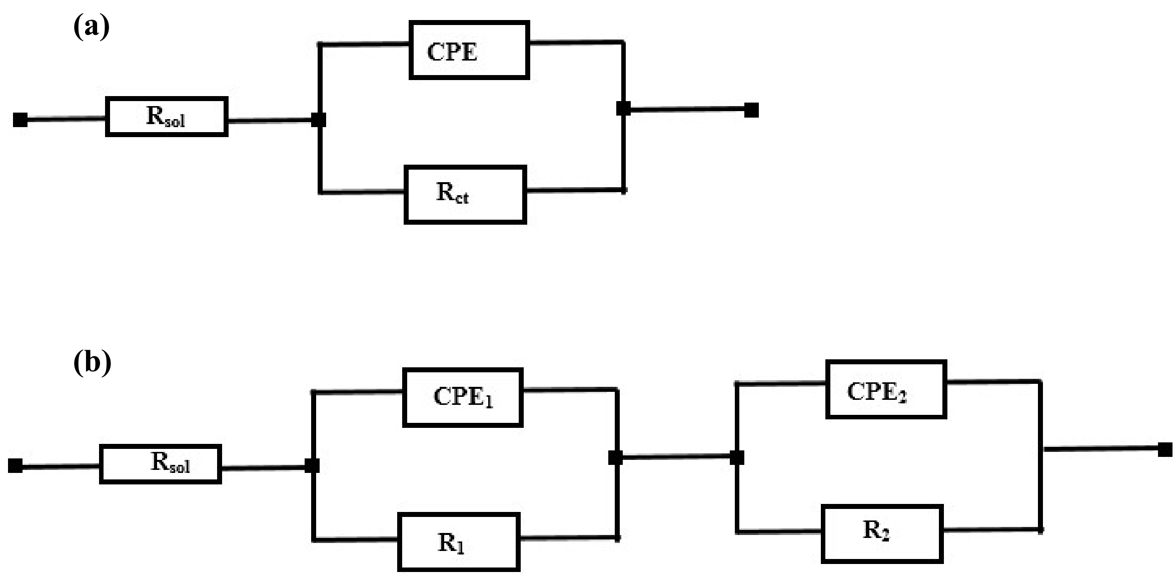

Figure S4. Equivalent circuit models used to fit the EIS response of HER on the (a) Ni/rGO and Ni/Ceria-rGO (1,3 and 1,1) and (b) Ni/Ceria-rGO (3,1) and Ni/Ceria

Table S2. An overview of the reported HER parameters for some non-noble electrocatalysts in the literatures in comparison to the current study

sample	Electrolyte	η/ mV (Current Density which η measured in)	-b/ mV. dec^{-1}	[ref.]
Fe_2P/NGr	1 M KOH	-355 (10)	-	[1]
Ni_2P–G@NF	1 M KOH	-7 (onset)	30	[2]
Fe–Ni-graphene	6 M KOH	-111 (onset)	92.6	[3]
N–C@Ni–Al_2O_3@GO	1 M NaOH	-75 (onset)	115.1	[4]
RGO–Ni foam	1 M KOH	-	130	[5]
Ni_3S_2/MWCNT-NC	1 M KOH	-340 (10)	102	[6]
Cu/NiCu	1 M KOH	-269 (100)	149	[7]
Ni–P + TiO2 + Ti	5 M KOH	-288 (100)	152	[8]
Ni-Mo	6 M KOH	-	116	[9]
Ni–S–Mn	30 wt.% KOH	-107 (200)	282	[10]
Ni-S-Co	30 wt.% KOH	-	195.6	[11]
NiFe nanosheets	1 M KOH	-139 (10)	112	[12]
Ni-G/304 SS	0.1 M KOH	-75 (onset)	182.04	[13]
NiCo	30 wt.% KOH	- 166 (100)	117.7	[14]
Ni-NiO/N-rGO/ Ni foam	1 M KOH	-160 (20)	46	[15]
Co-CoO/N-rGO/ Ni foam	1 M KOH	-170 (20)	51	[15]
nitrogen-rich holey graphene monoliths	0.1 M KOH	-300 (onset)	157	[16]
Graphene/N-doped amorphous carbon	1 M KOH	-370 (10)	169	[17]
nickel-phosphorus-graphite composite	1 M NaOH	-242.4 (250)	90.9	[18]
Ni−Sn@C	1 M NaOH	-192 (onset)	145	[19]
CoMn-S@NiO/CC	1 M KOH	-232 (100)	147.3	[20]
Ni/Ceria-rGO (50)	1 M KOH	-15 (onset) -111 (10) -170 (20)	107.3	Current Study

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