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Supporting Information

Unraveling the evolution of exsolved Fe-Ni alloy nanoparticles in Ni-doped $La_{0.3}Ca_{0.7}Fe_{0.7}Cr_{0.3}O_{3-\delta}$ and their role in enhancing CO_2-CO electrocatalysis

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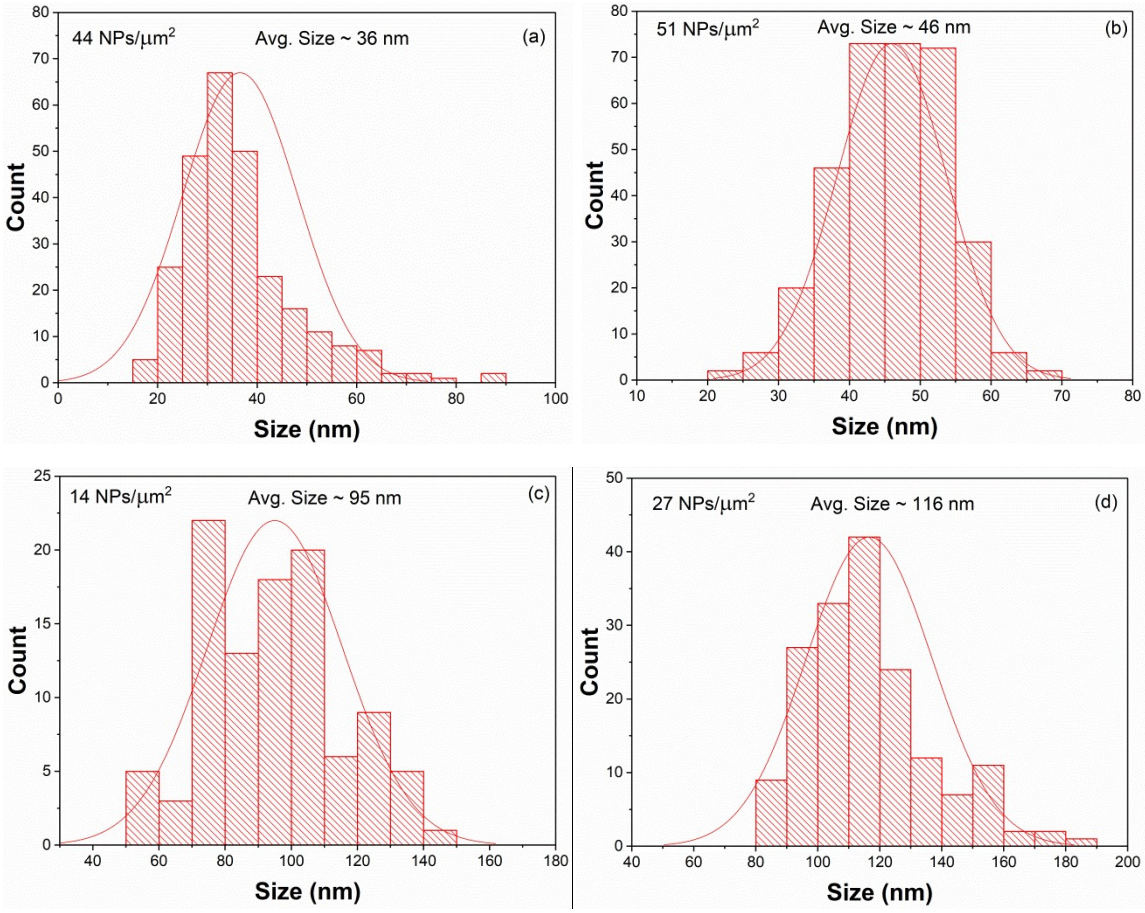

Fig. S1 Histograms depicting the size distribution and areal densities of the NPs grown in 5:95 H_2:N_2 at (a) 750 °C for 5 hr, (b) 750 °C for 25 hr, (c) 800 °C for 5 hr, and (d) 800 °C for 25 hr, respectively.

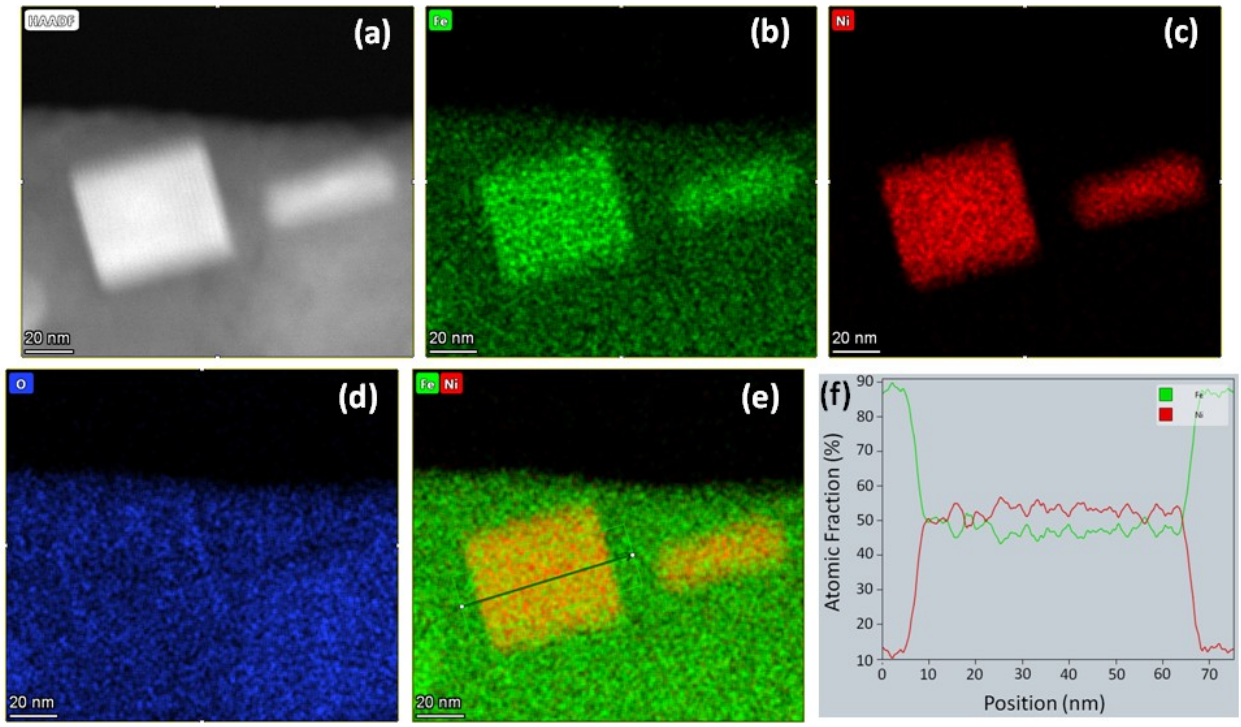

Fig. S2 (a) HAADF STEM image of a faceted NP with a square base. EDS elemental maps of (b) Fe, (c) Ni, and (d) O, and (e) Fe and Ni overlayed, for the NP in (a). (f) EDS line scan across the middle of the NP in (d) showing a stoichiometry close to FeNi. The LCFCrN powder was reduced at 750 ^{o}C for 5 hr in 5:95 H_2:N_2.

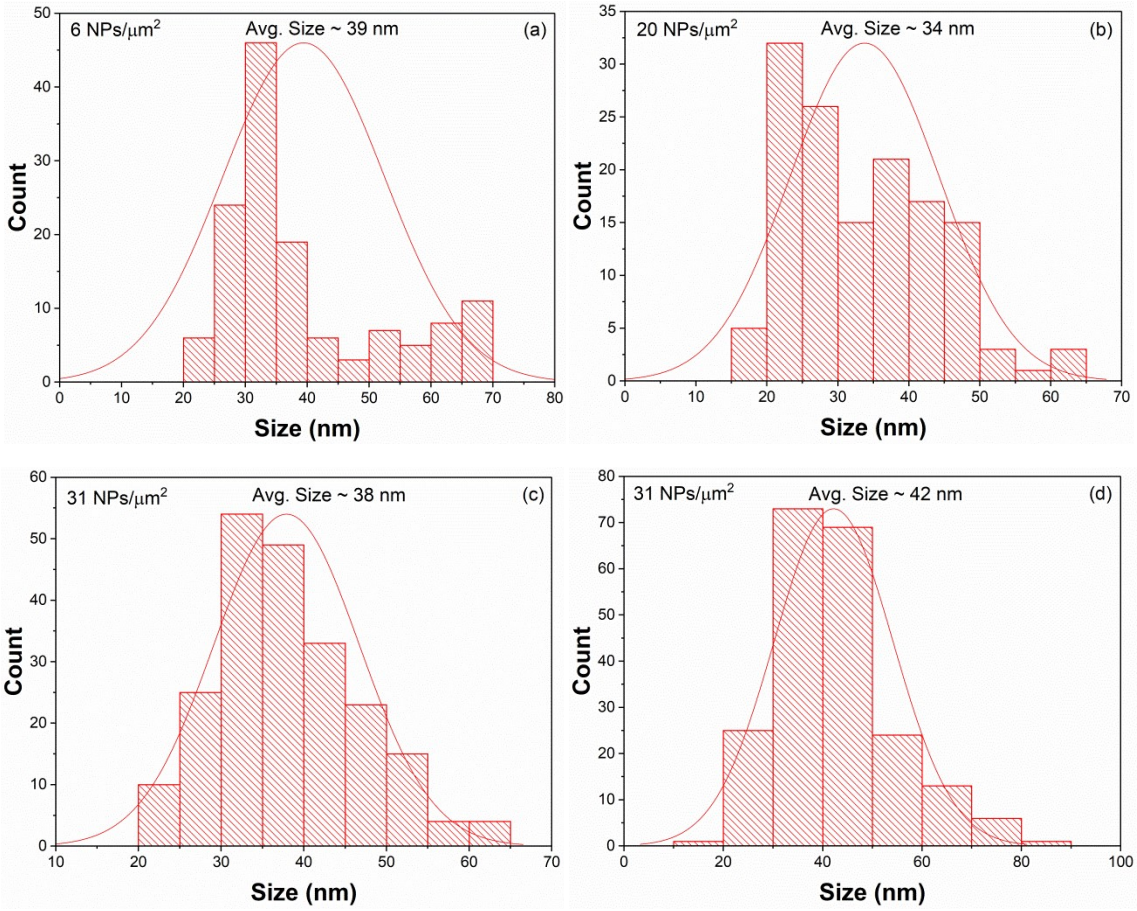

Fig. S3 Histograms depicting the size distribution and areal densities of the NPs grown at 800 °C for 5 hr for CO:CO_2 gas compositions of (a) 10:90, (b) 30:70, (c) 70:30, and (d) 90:10, respectively.

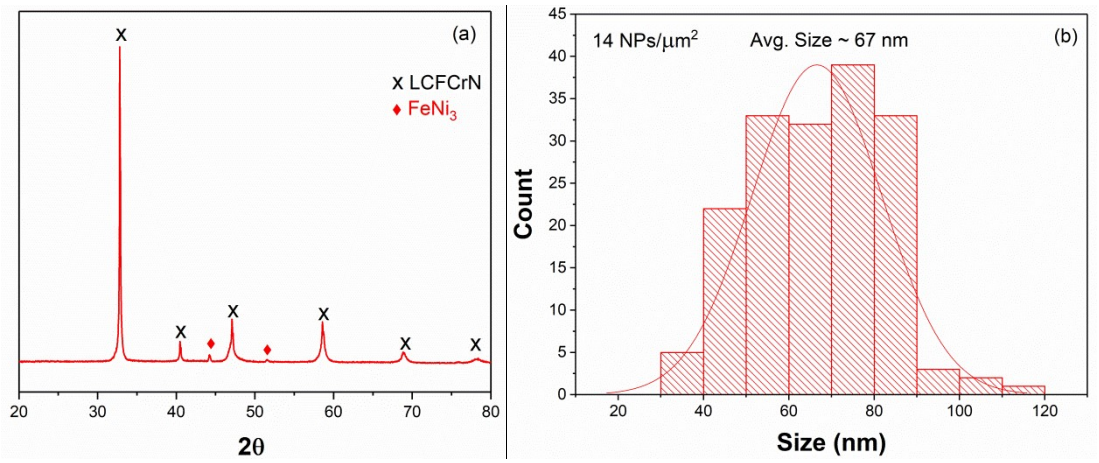

Fig. S4 (a) Room temperature x-ray diffraction pattern, and (b) a histogram depicting the size distribution and areal density of the NPs in LCFCrN exposed to humidified 7.5%H_2:92.5%N_2 at 800 ^oC for 5 hr.

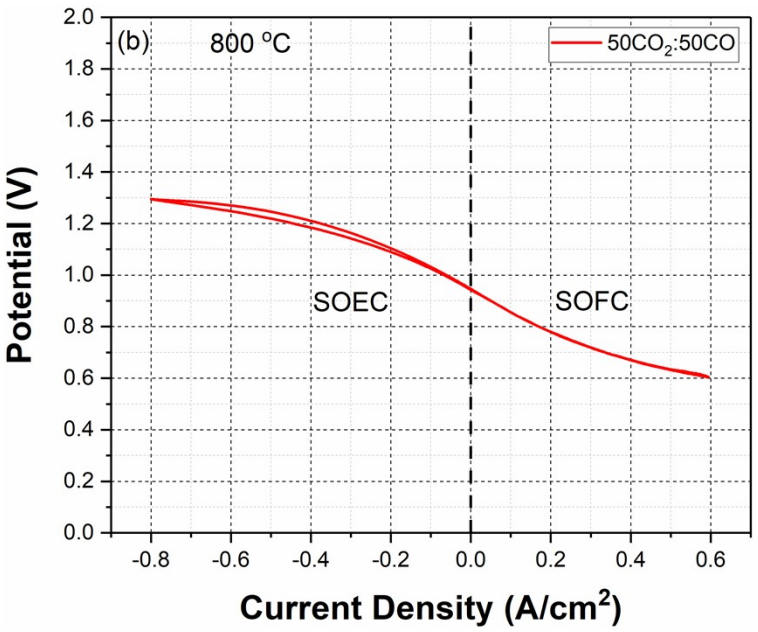

Fig. S5 (a) *iR* corrected CV acquired at 800 °C in a 50:50 CO_2:CO gas mixture.

Table S1. pO_2 of the gas compositions used in this work

Gas Composition	p_{O_2} (atm)
5:95 H_2:N_2	$< 10^{-23}$
Humidified 7.5:92.5 H_2:N_2	7.0×10^{-20}
5:95 CO:CO_2	1.4×10^{-16}
10:90 CO:CO_2	3.1×10^{-17}
30:70 CO:CO_2	2.1×10^{-18}
50:50 CO:CO_2	3.8×10^{-19}
70:30 CO:CO_2	6.9×10^{-20}
90:10 CO:CO_2	4.7×10^{-21}
95:5 CO:CO_2	1.0×10^{-21}

Table S2. Performance comparison of various electrocatalysts for CO_2 reduction at 800 °C.

Fuel Electrode	Electrolyte/Oxygen Electrode	Cell Voltage (V)	Gas Atmosphere	Current Density (A/cm^2)	Ref.
Fe-Ni@LCFCrN	SSZ/LCFCrN	1.6	CO_2	-0.65	This work
$FeNi_3$@SFMN-GDC	LSGM/LSCF-GDC	1.6	CO_2	-0.93	[1]
SFMN-GDC	LSGM/LSCF-GDC	1.6	CO_2	-0.63	[1]
LSFV-GDC	YSZ/ LSM-YSZ	1.6	CO_2	-0.62	[2]
Ni@LSTMN-SDC	YSZ/LSM	1.6	CO_2	-0.54	[3]
Fe-Ni@LSFN-GDC	YSZ/LSCF-GDC	1.6	70:30 CO_2:CO	-0.66	[4]

Note that our perovskite material (LCFCrN) is the only one that has not been composited with GDC or SDC, done by others to increase the ionic conductivity.

References

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