CSIR-KIER workshop
12-13 August 2019

Ultrasonic exfoliation of NiFe LDH/CB nanosheets/few layered sheets for enhanced oxygen evolution electrocatalysis

Munonde Tshimangadzo

tmunonde@csir.co.za

Dr H Zheng (CSIR)
Prof PN Nomngongo (UJ)

our future through science

Background: Oxygen evolution reaction

- An important reaction for energy conversion and storage processes.

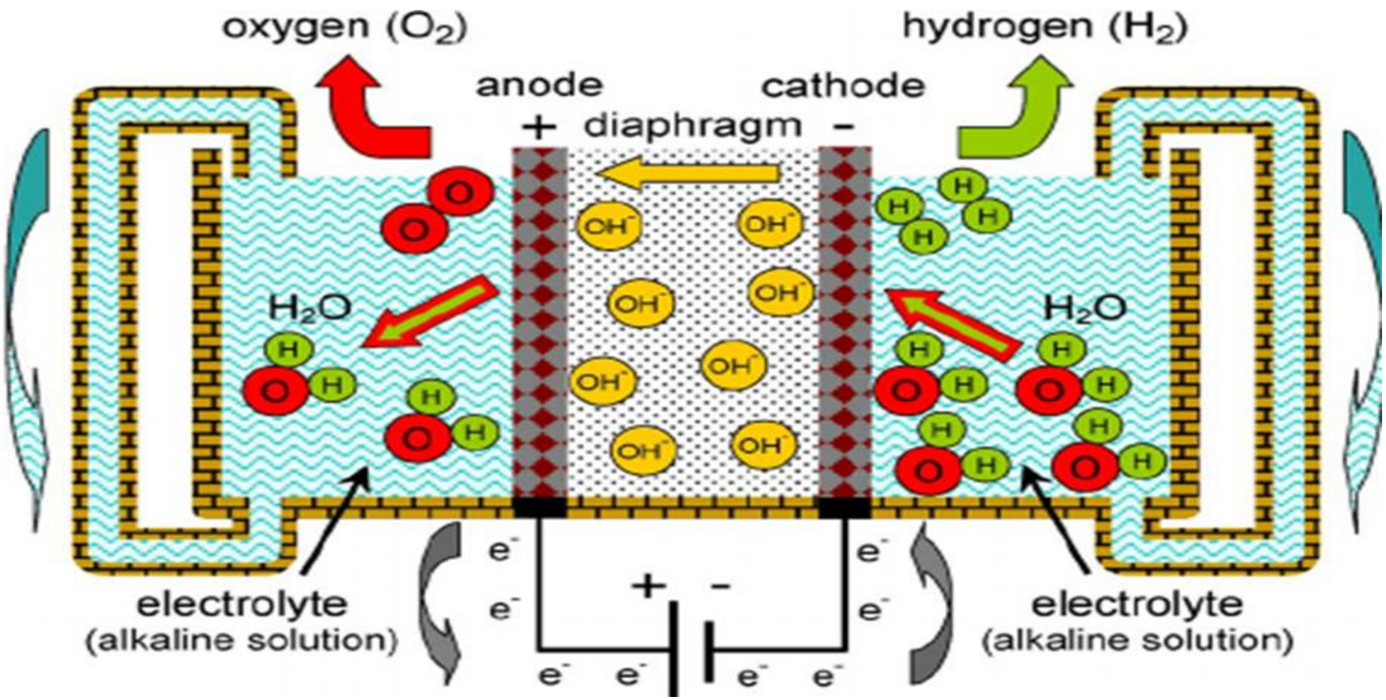


Fig. 1 Basic alkaline water electrolyzer

Anode: $4OH^{-}(aq) \rightarrow O_2(g) + 2H_2O(aq) + 4e^{-}$ **E° = 1.23 V** **(1)**

Ursua, A., Gandia, L.M., Sanchis, P. (2012). *Proceedings of the IEEE*, 100(2), 410-426.

Background: Layered double hydroxides

- LDH's are a class of synthetic layered materials with highly tunable, chemically versatile and flexible open structures.

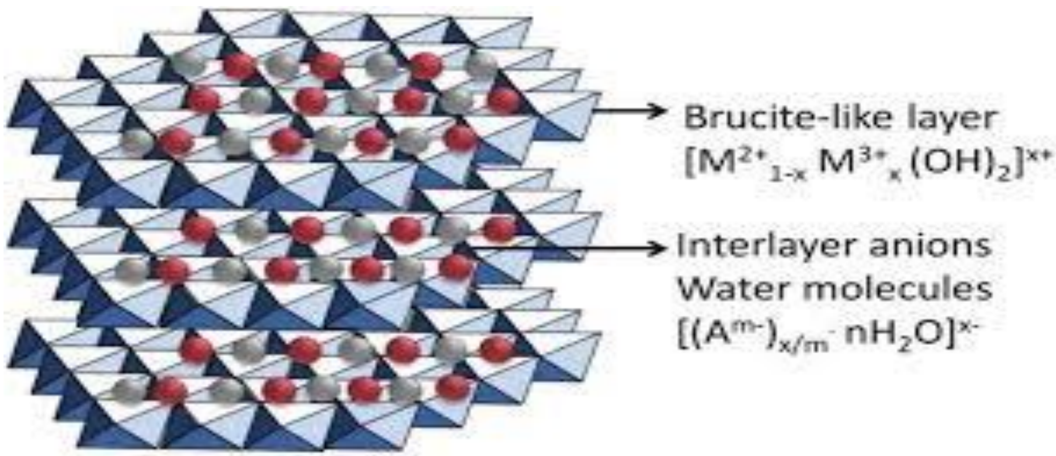


Fig. 2 Layered double hydroxides structure

- $[M^{II}_{1-x} M^{III}_{x} (OH)_2]^{x+} (A^{n-})_{x/n}.mH_2O$ consists of divalent (M^{II}) and substituted trivalent (M^{III}) cations that are balanced with intercalated A^{n-} anions and solvation H_2O molecules within their space regions.
- NiFe LDH need to be exfoliated to reach its full potential and has shown better OER activity than Ir and Ru based electrocatalysts.

Hunter, B. M., Hieringer, W., Winkler, J. R., Gray, H. B., & Müller, A. M. (2016), Energy & Environmental Science, 9(5), 1734-1743.

Background: Sonication assisted exfoliation

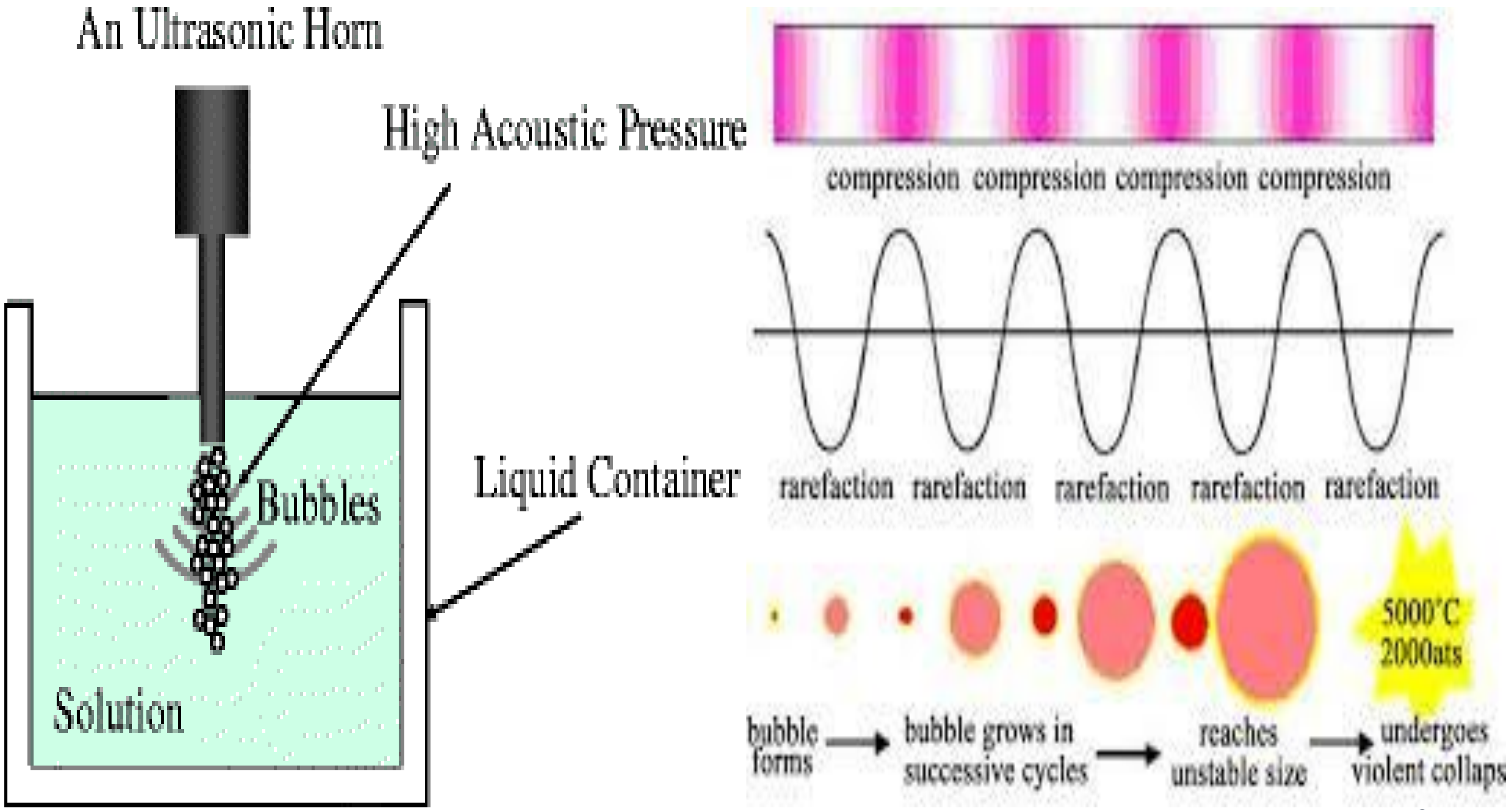
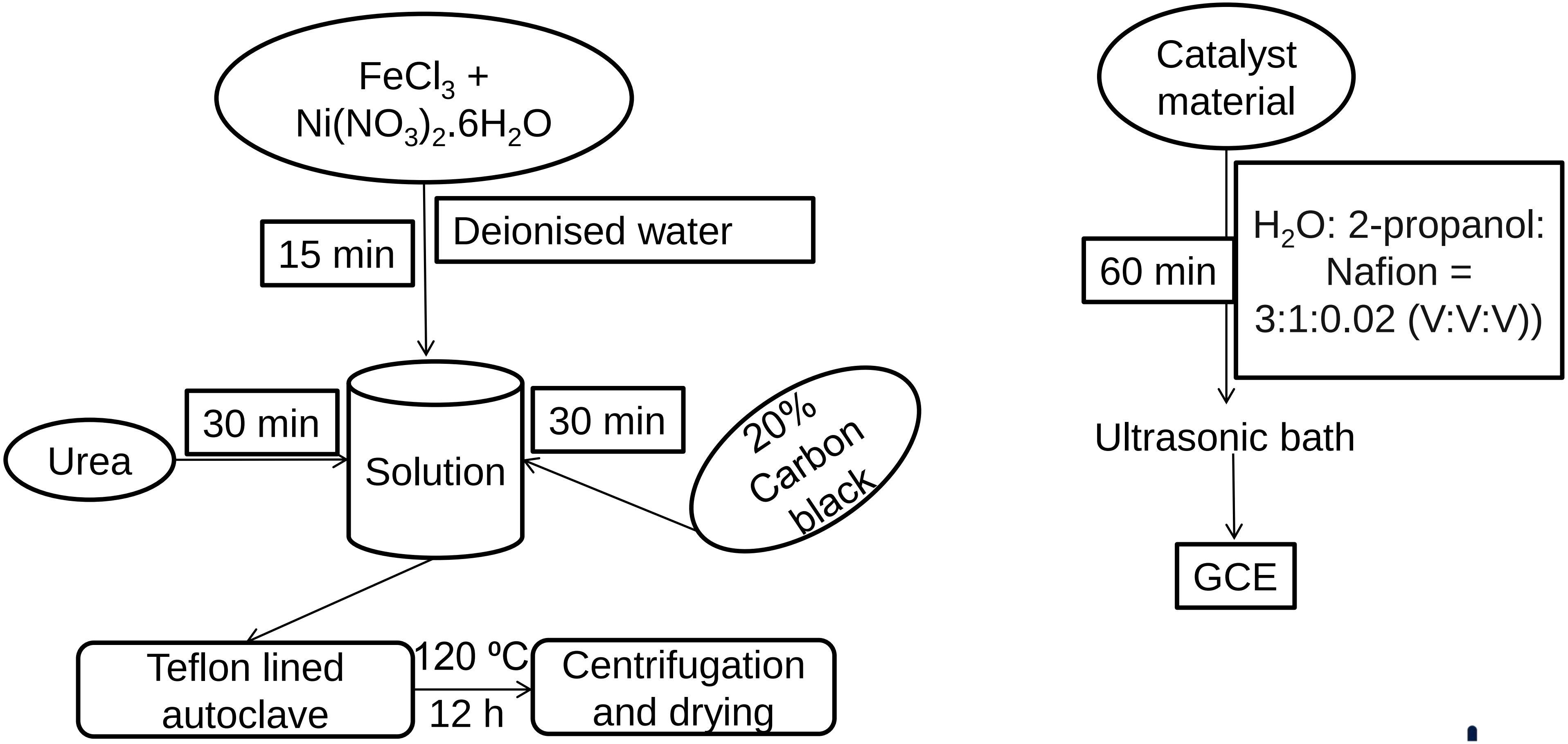


Fig. 3 Sonication-assisted liquid exfoliation process.

Sana, S., Rajanna, K. C., et al., (2012). *Green and Sustainable Chemistry*, 2(03), 97.

Experimental section

(a) Hydrothermal synthesis of NiFe LDH/CB **(b) Ink preparation**



Scheme 1: (a) Hydrothermal synthesis of NiFe LDH/CB; and (b) Ink preparation

Sebastián, D., Baglio, V., Aricò, A.S., Serov, A., Atanassov, P. (2016). *Applied Catalysis B: Environmental*, 182, 297-305.

Results and Discussion: X-ray Diffraction (XRD)

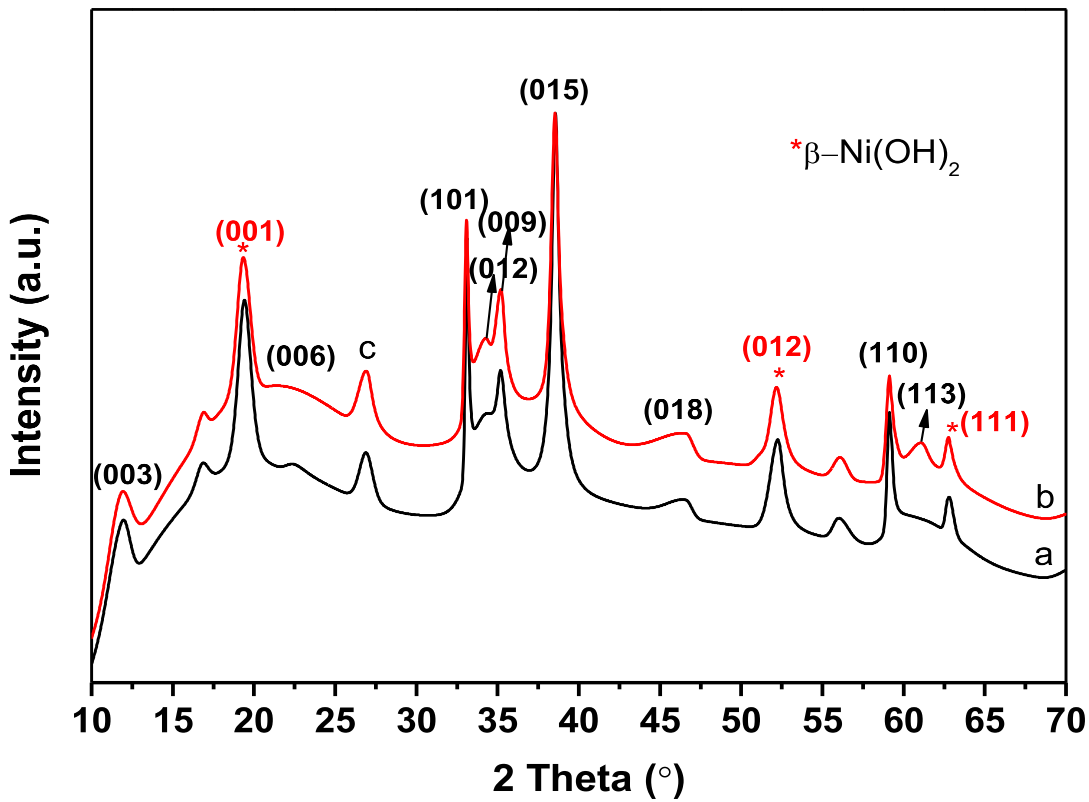
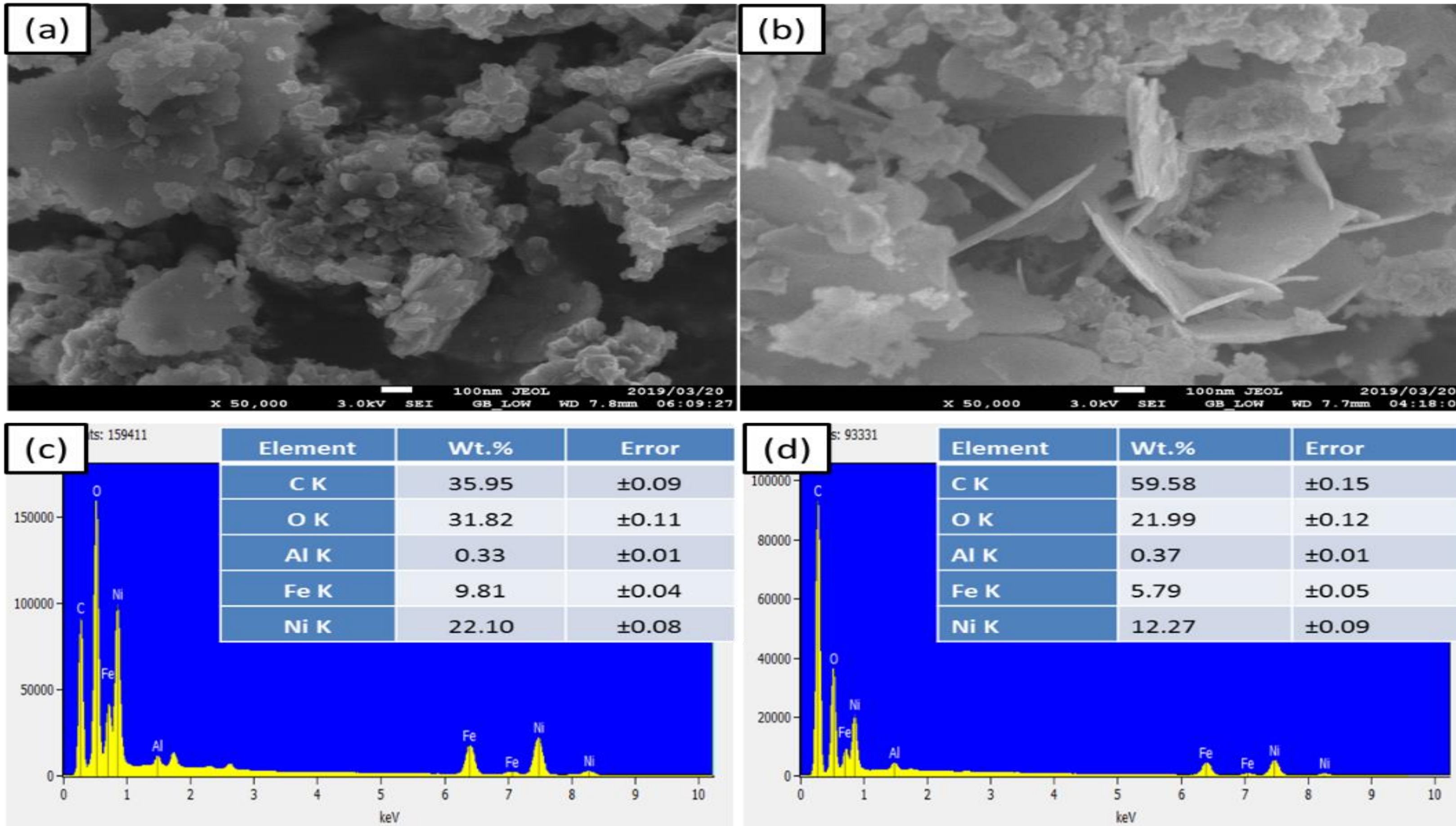


Fig. 4 XRD patterns of NiFe LDH/CB (a) and Exf NiFe LDH/CB (b).

- The Interlayer spacing on (003) was 0.745 (a) and 0.750 nm (b)

Results and Discussion: SEM/EDX



Element	Wt.%	Error
C K	35.95	±0.09
O K	31.82	±0.11
Al K	0.33	±0.01
Fe K	9.81	±0.04
Ni K	22.10	±0.08

Element	Wt.%	Error
C K	59.58	±0.15
O K	21.99	±0.12
Al K	0.37	±0.01
Fe K	5.79	±0.05
Ni K	12.27	±0.09

Fig. 5 FE-SEM of NiFe LDH/CB (a), Exf NiFe LDH/CB (b); and their corresponding EDX spectra in (c) and (d), respectively.

- Ni/Fe = 2.15 (a) and 2.05 (b), but 2.62 from the synthesis

CSIR
our future through science

Results and Discussion: TEM (1)

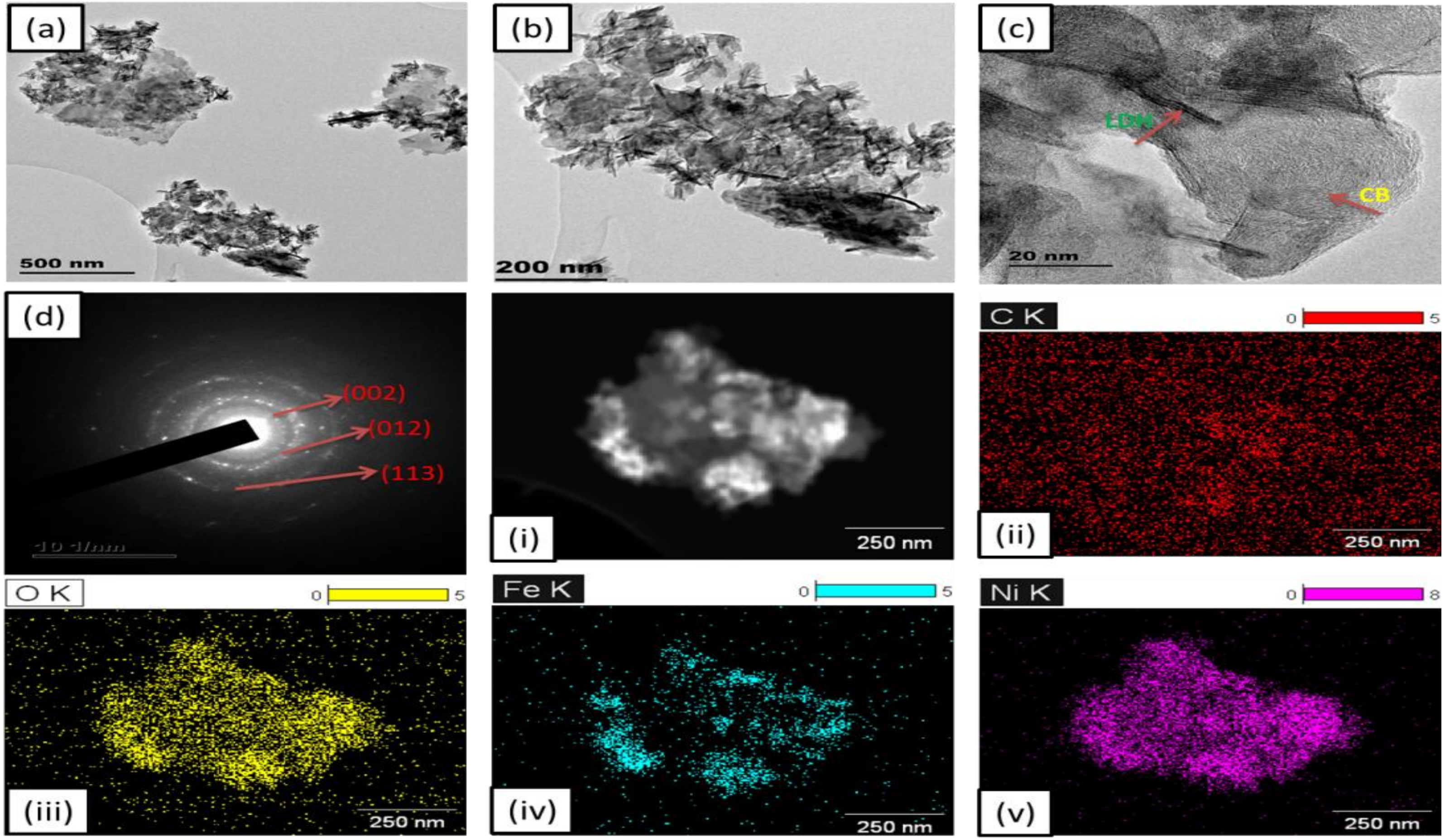


Fig. 6 TEM (a); HR-TEM (b, c); SAED (d); Elemental Mappings from (i-v) of NiFe LDH/CB.

our future through science

Results and Discussion: TEM (2)

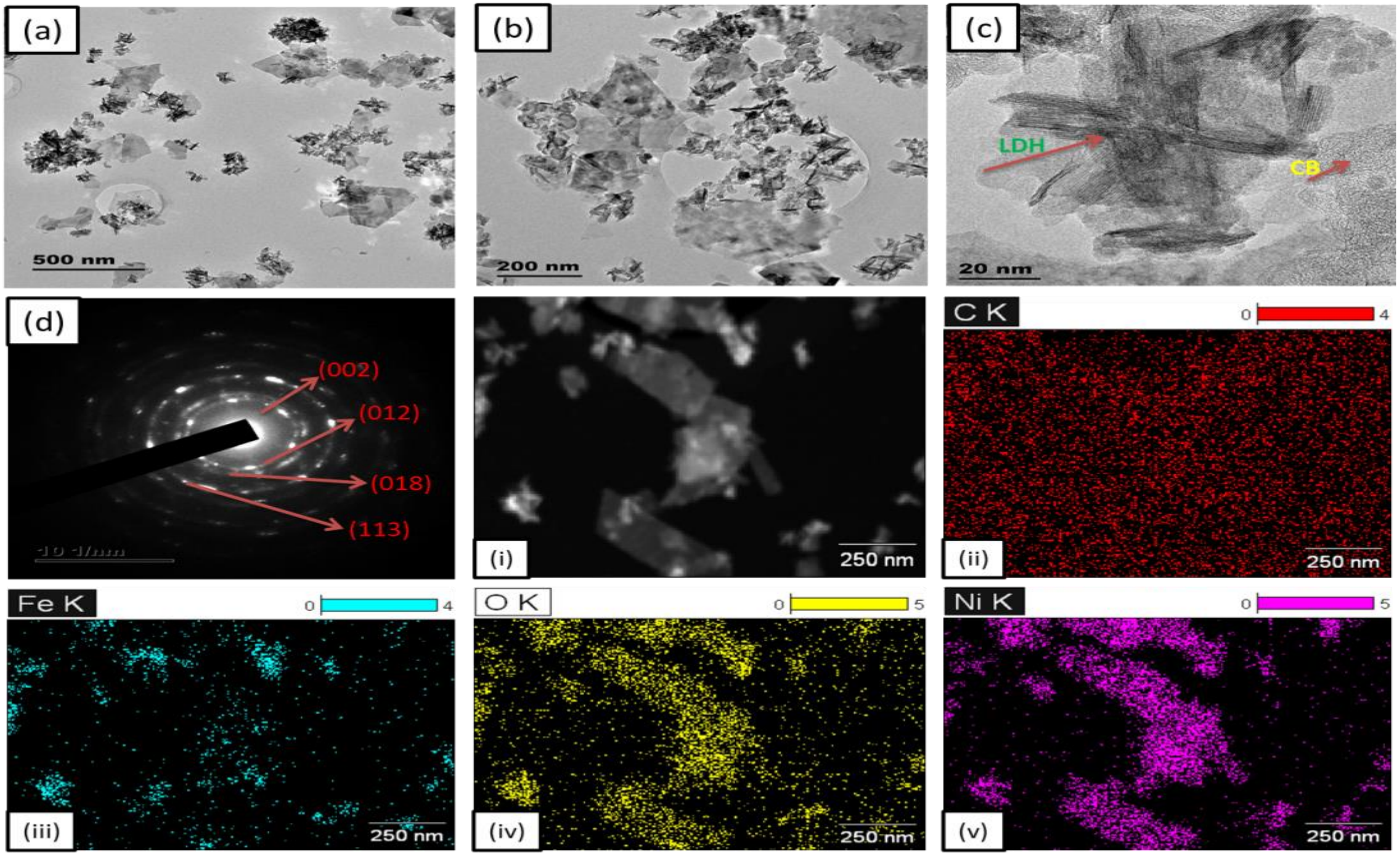


Fig. 7 TEM (a); HR-TEM (b, c); SAED (d); Elemental Mappings from (i-v) of Exf NiFe LDH/CB.

Results and Discussion: X-ray photoelectron spectroscopy (XPS)

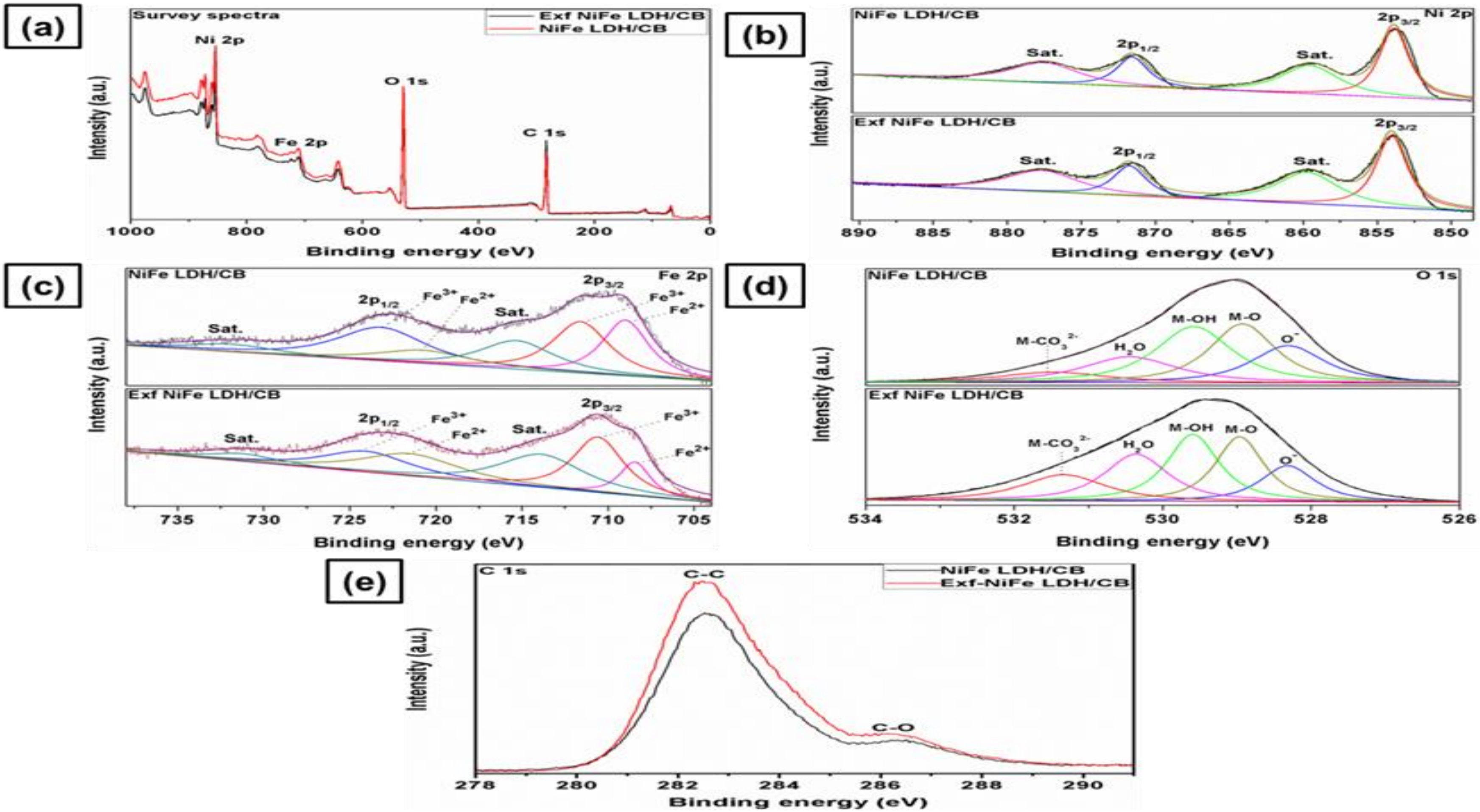


Fig. 8 XPS survey spectra (a); Ni 2p spectra (b); Fe 2p spectra (c); O 1s spectra (d); C 1s spectra (e), of NiFe LDH/CB and Exf NiFe LDH/CB.

our future through science

Results and discussion: Electrocatalytic activity and stability

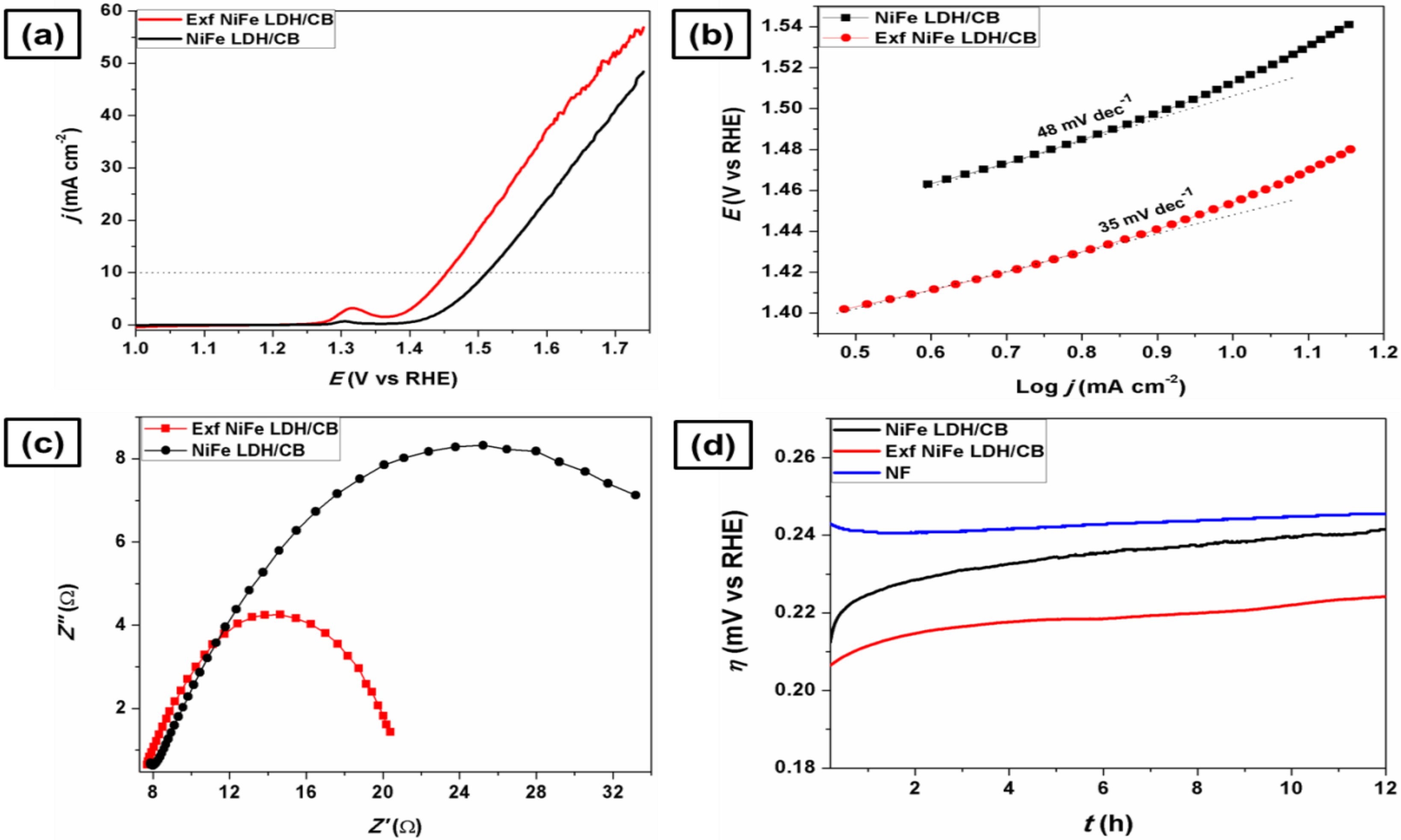


Fig. 9 OER polarization curves (a); Tafel plots (b); Nyquists plots (c); Chronopotentiometric curves (d), of Exf NiFe LDH/CB and NiFe LDH/CB

Results and discussion: Electrocatalytic activity comparison

Table 1 Comparison of the OER activity with other related materials.

Catalyst	Method	Electrolyte	Loading (mg cm^{-2})	Onset overpotential (mV)	$\eta^{10\ mA\ cm-2}$ (mV)	Tafel slope (mV dec^{-1})	Ref
NiFe-LDH nanosheet	Coprecipitation	0.1 M NaOH	0.2	-	350	47	Gong et al.
NiFe LDH Nanosheet	Hydrothermal	1 M KOH	0.07	~ 250	325	40	Qi et al.
CQD/NiFe-LDH nanoplates	Solvothermal	1 M KOH	0.2	210	235	30	Han et al.
NiFe LDH/CB	Hydrothermal	1 M KOH	0.2	170	280	48	This work
Exf NiFe LDH/CB nanosheets	Hydrothermal	1 M KOH	0.2	150	220	35	This work

M. Gong, Y. Li, et al., *J. Am. Chem. Soc.* 135 (2013) 8452-8455.
X. Qi, B. Blizanac, et al., *Physical Chemistry Chemical Physics.* 16 (2014) 25306-25313.
Y. Han, P. Li, et al., *Scientific reports*. 8 (2018) 1359.

Conclusion

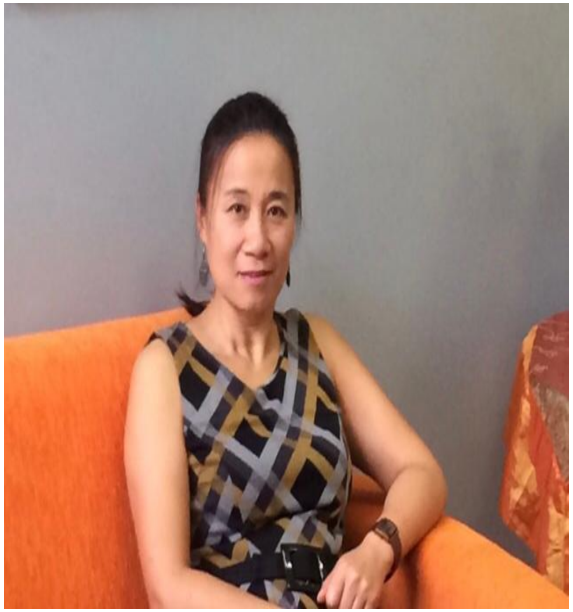
- The ultrasonic exfoliation process has exfoliated the NiFe LDH/CB stacked layers into single/few-layer nanosheets.
- XRD, FESEM, HRTEM and XPS was used to confirm and support the success of the exfoliation process adopted.
- The exfoliated NiFe LDH/CB has shown better catalytic activity for OER with an overpotential of 220 mV at a current density of 10 mA cm^{-2}, compared to the 280 mV of the bulk NiFe LDH/CB nanosheets.
- The higher durability was also achieved on Exf NiFe LDH/CB with nearly a constant potential during the 12 hours OER electrolysis at 10 mA cm^{-2}.
- The ultrasonic process provides an effective method to exfoliate layered materials in a green approach.

Acknowledgements

UNIVERSITY OF JOHANNESBURG

CSIR
our future through science

NRF
National Research Foundation



Thank you

our future through science