

## ***Supporting Information***

# **Ni/NiO@NC as a high efficiency and durable HER electrocatalyst**

## **derivated from Nickel( II ) complexe: the importance of polydentate amino acid ligand**

**Xu Yang<sup>a,1</sup>, Mengxue Liu<sup>a,1</sup>, Fang Cui<sup>\*a</sup>, Qinghai Ma<sup>a</sup>, Tieyu Cui<sup>\*a</sup>**

*School of Chemistry and Chemical Engineering, Harbin Institute of Technology,  
Harbin, 150001, P.R. China.*

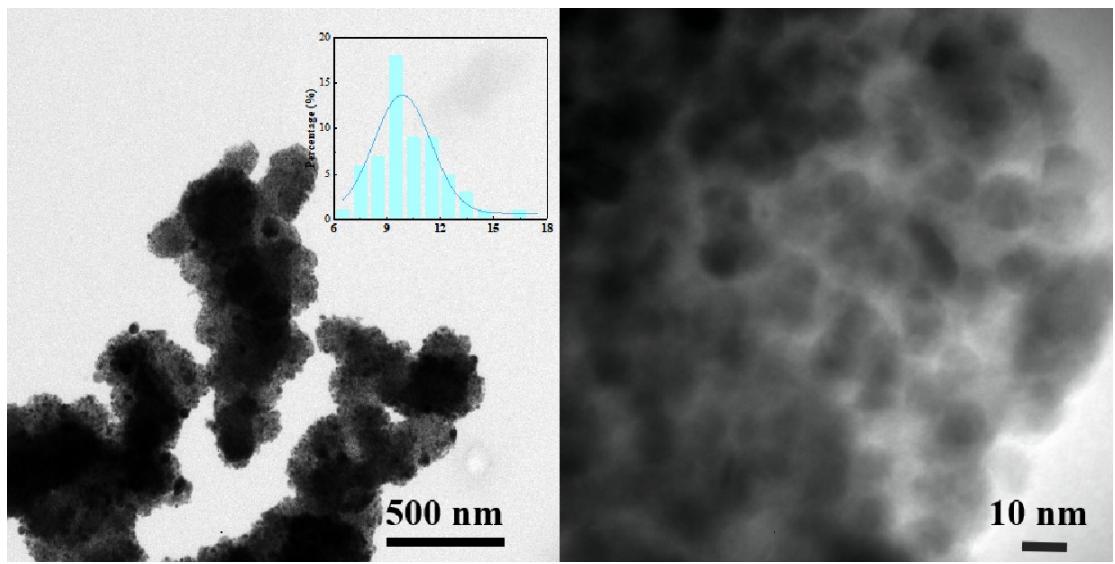
These authors contributed equally.

### **Corresponding Authors:**

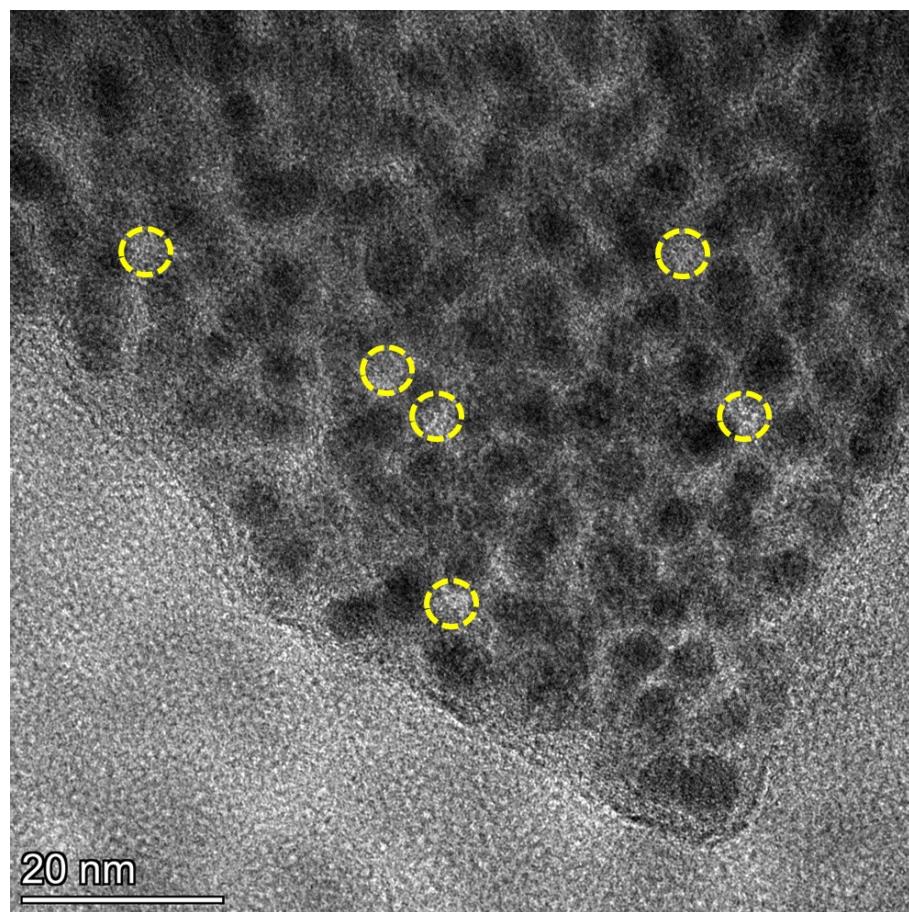
Fang Cui, Tieyu Cui

Fax: (+86) 0451-86403646

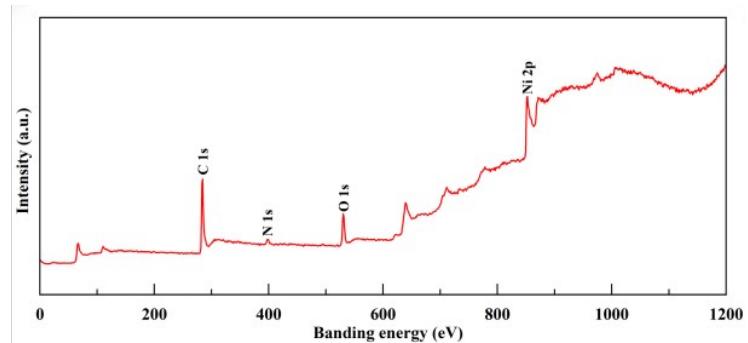
Email: [cufang@hit.edu.cn](mailto:cufang@hit.edu.cn) (F. Cui), [cuit@hit.edu.cn](mailto:cuit@hit.edu.cn) (T. Y. Cui)



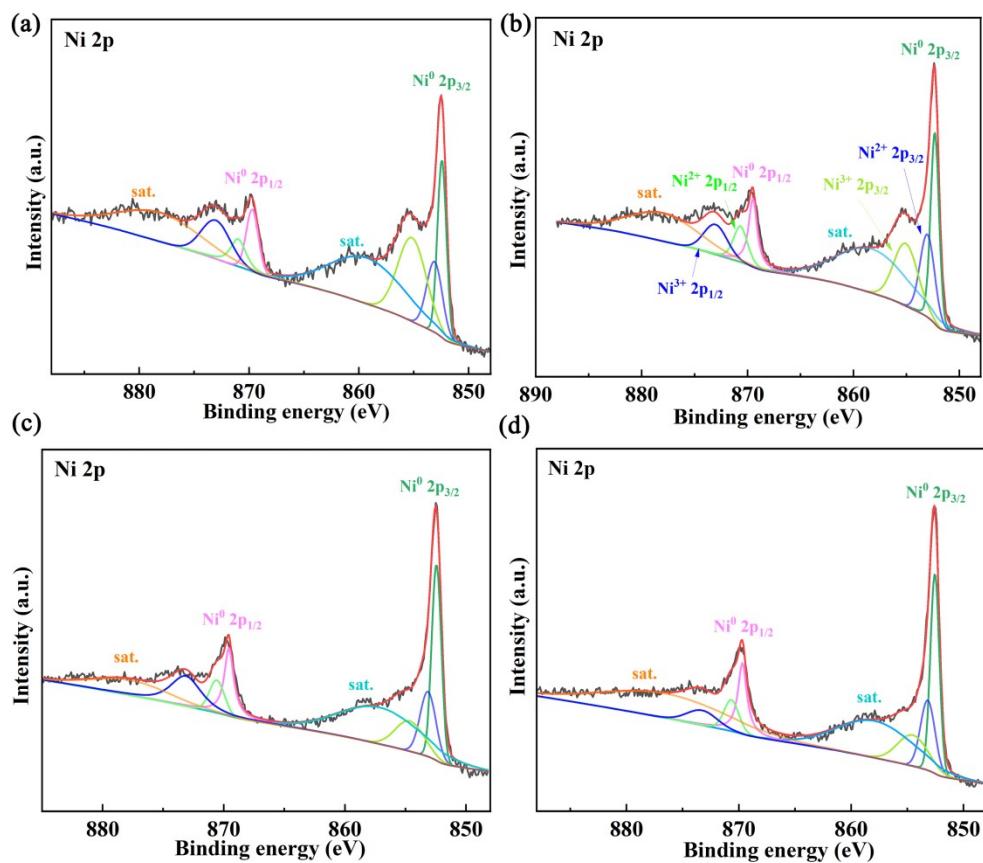
**Fig. S1 (a) TEM images of Ni/NiO/C-Acrylic acid**



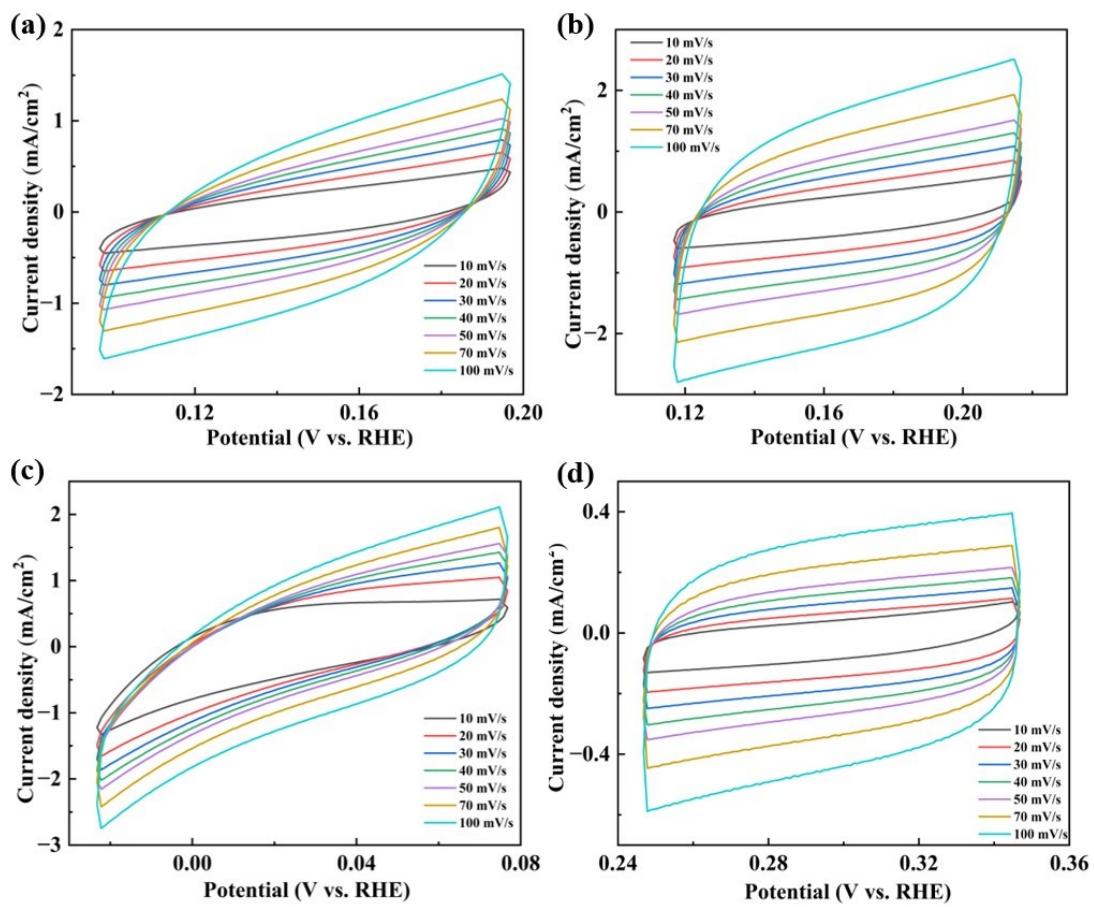
**Fig. S2 TEM image of Ni/NiO@NC-540 .**



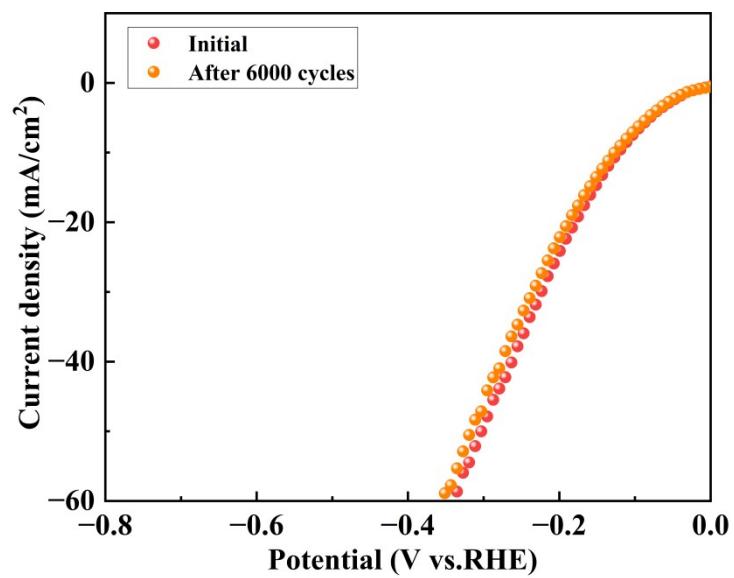
**Fig. S3** The full scan of the XPS spectrum of Ni/NiO@NC-540



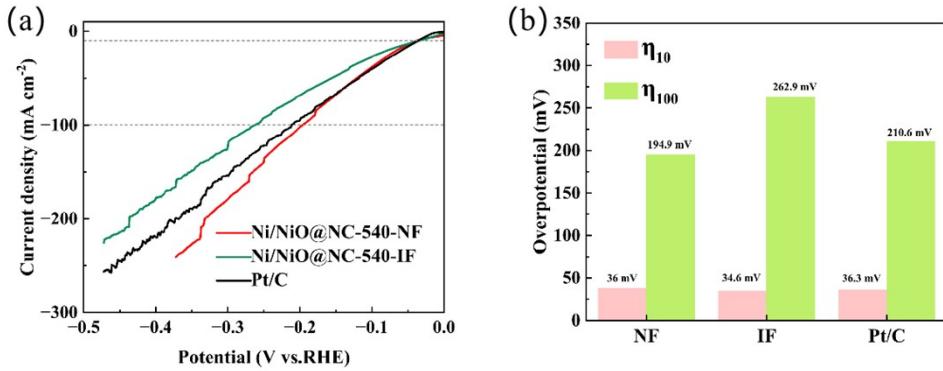
**Fig. S4** The Ni 2p spectrum of Ni/NiOx@NC-AA-T : (a) 480°C, (b) 540°C, (c) 600°C, (d) 660°C.



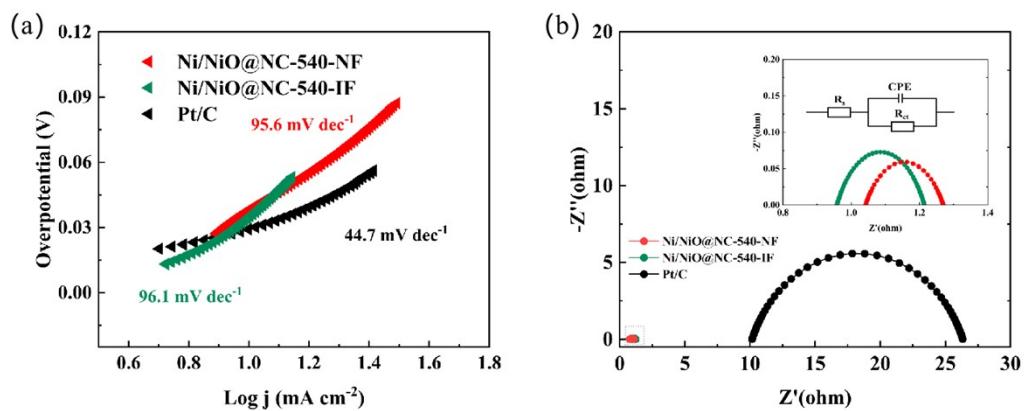
**Fig. S5 Cyclic voltametric curves of Ni/NiO@NC-480(a), -540(b), -600(c) and -660(d) at different scan rates where no faradaic reactions occurred.**



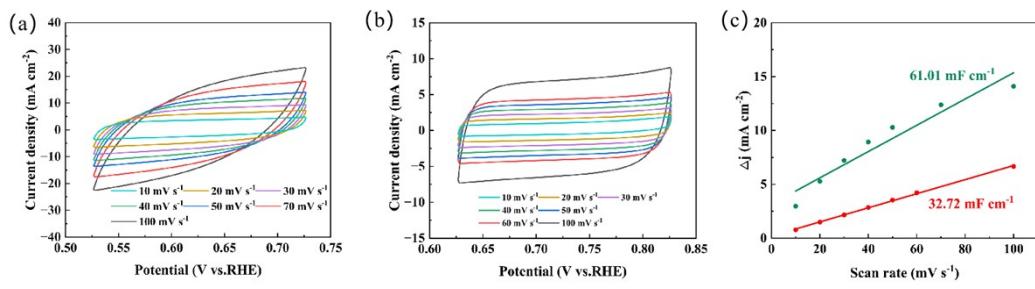
**Fig. S6** Polarization curves before and after 6000 CV cycles (-0.9 V ~ -1.4 V)



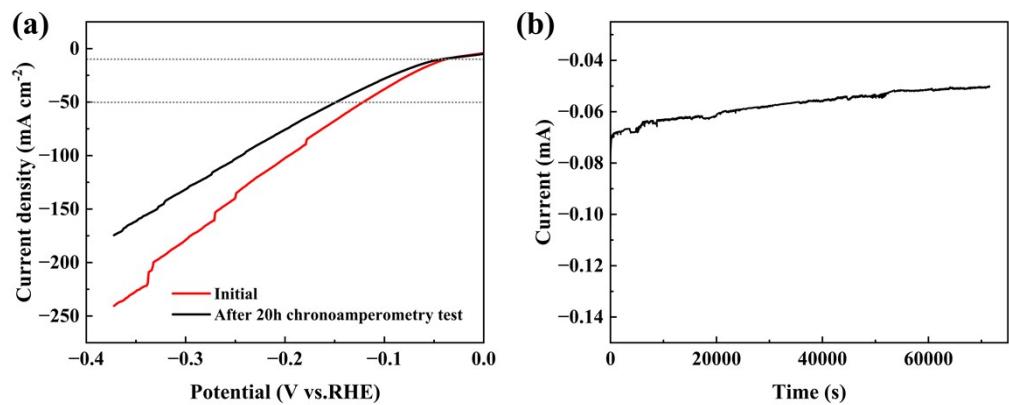
**Fig. S7 (a) LSVs of Ni/NiO@NC-540-NF, -IF and 20w% Pt/C for HER. (b) Overpotentials of different catalysts at current densities of  $10 \text{ mA cm}^{-2}$  and  $100 \text{ mA cm}^{-2}$ .**



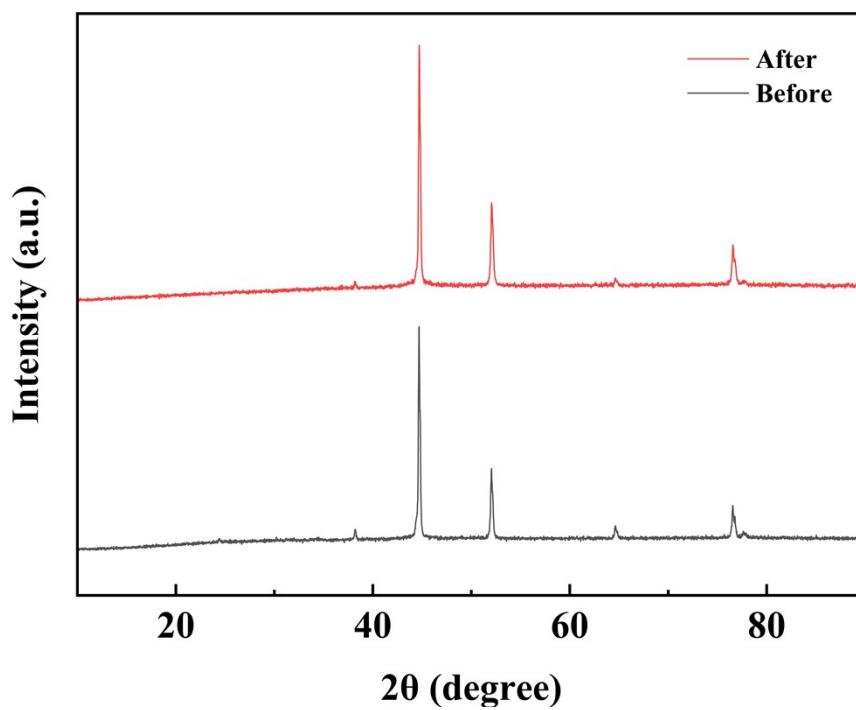
**Fig. S8 (a)** The Tafel slope of Ni/NiO@NC-540-NF, -IF and 20w% Pt/C for HER.  
**(b)** The relevant EIS plot.



**Fig. S9 Cyclic voltametric curves of Ni/NiO@NC-540-IF(a) and -NF(b) at different scan rates where no faradaic reactions occurred. at different scan rates where no faradaic reactions occurred, the relevant Cdl plot (c).**



**Fig. S10** Polarization curves before and after 20 h chronoamperometry test(a),  
(b)Chronoamperometry test of Ni/NiO/C-500-NF (50 mV vs. RHE).



**Fig. S11 XRD plots before and after 20 h chronoamperometry test**

**Table. S1 Content ratio of Ni with different valence states in Ni/NiO<sub>x</sub>@NC-AA at different synthesis temperatures.**

Catalysts	Ni <sup>0</sup> 2p <sub>3/2</sub> (%)	Ni <sup>2+</sup> 2p3/2 (%)	Ni <sup>3+</sup> 2p3/2 (%)	Ni <sup>0</sup> /(Ni <sup>2+</sup> +Ni <sup>3+</sup> )
Ni/NiO <sub>x</sub> @NC-480	18.7	13.0	28.0	0.46
Ni/NiO <sub>x</sub> @NC-540	21.4	15.6	19.4	0.61
Ni/NiO <sub>x</sub> @NC-600	27.5	15.0	12.8	0.99
Ni/NiO <sub>x</sub> @NC-660	27.6	15.4	14.3	0.93

**Table S2. Overpotential comparison of Ni/NiO@NC-540 and Ni/NiO@NC-540-NF with state-of-the-art Ni-based HER catalysts.**

Catalyst	$\eta @ 10 \text{ mA cm}^{-2}$ [mV]	Reference
Ni/NiO-NC	179 (1 M KOH)	1
Sr-NiO	164 (4.24 M KOH)	2
NiOx-AC-500	180 (0.1 M KOH)	3
Ni-NiO/Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	72 (1 M KOH)	4
Ni-NiO@3DHPG	310 (1 M KOH)	5
H-Ni/NiO/C	87 (1 M KOH)	6
CNO@NSG	109.6 (1 M KOH)	7
CNN-500	127 (1 M KOH)	8
CoP/P-NiO/NF	52 (1 M KOH)	9
Mo-NiCoP/NF	64 (1M KOH)	10
P-Ni/Mo-TEC@NF	22 (1 M KOH)	11
Ni <sub>2</sub> P/FeP-FF	42 (1M KOH)	12
CoS/Ni <sub>x</sub> P <sub>y</sub> /Fe-Ni <sub>3</sub> S <sub>2</sub> @NF	49 (1 M KOH)	13
NiWO <sub>4</sub> -Ni <sub>3</sub> S <sub>2</sub> @NiO/NF-3	89 (1 M KOH)	14
Co <sub>2</sub> P-x/Ni <sub>2</sub> P-y @ NF	79 (1 M KOH)	15
Ni/NiO <sub>x</sub> @NC-AA-540	100 (1 M KOH)	This work
Ni/NiO <sub>x</sub> @NC-AA-540-NF	36 (1 M KOH)	This work

## References

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