

# Electronic supplementary Material (ESI) for New Journal of Chemistry

## Expanding interlamellar spacing of biomass-derived hydrides with intercalated nanotubes for enhanced oxygen reduction reaction

*Junting Sun\*, Jiaxiang Jin, Yukan Yang, Jing Wang and Junjie Guo\**

Key Laboratory of Novel Materials for Sensor of Zhejiang Province, Institute of  
Advanced Magnetic Materials, College of Materials & Environmental Engineering,  
Hangzhou Dianzi University, Xiasha higher education Zone, Hangzhou 310018,  
Zhejiang Province, People's Republic of China..

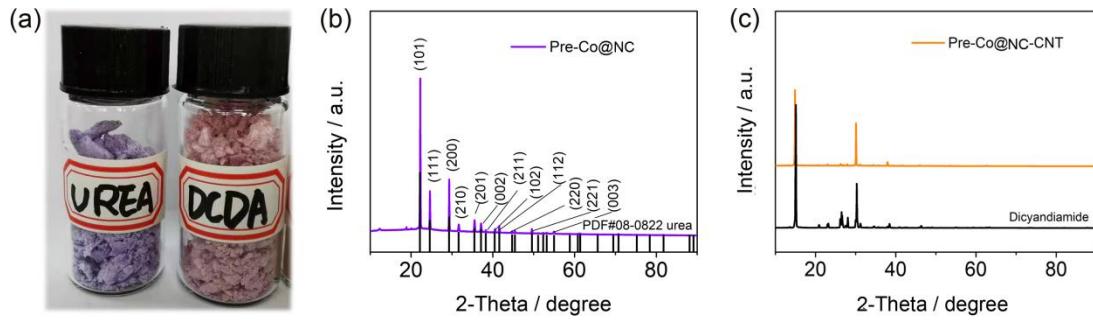
### **Corresponding Author**

E-mail: sunjt@hdu.edu.cn (J. Sun); jguo@hdu.edu.cn (J. Guo)

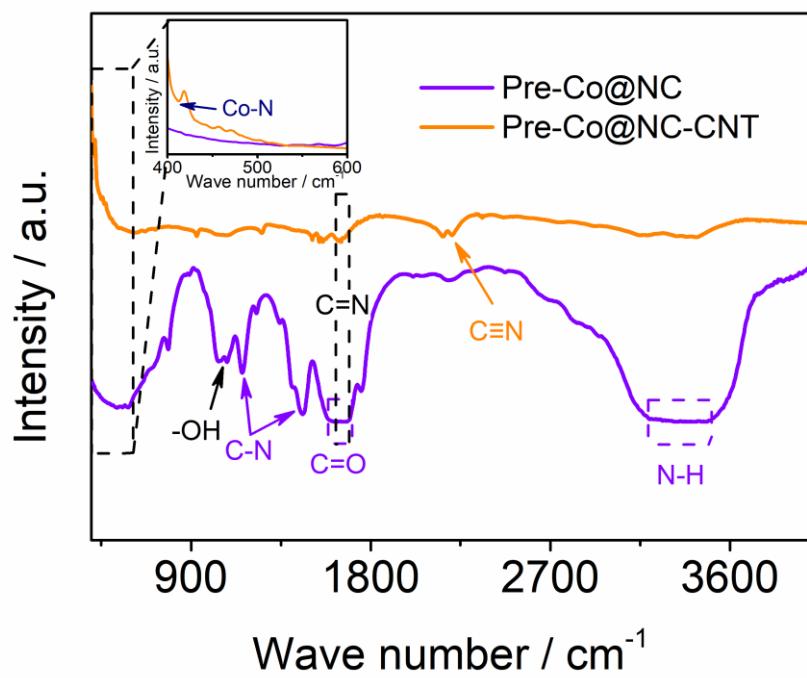
The number of pages: 19

The number of figures: 11

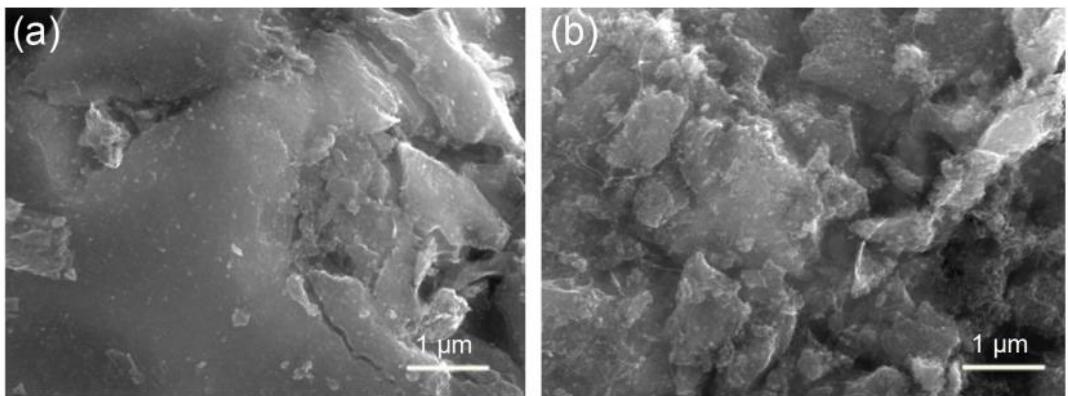
The number of tables: 4



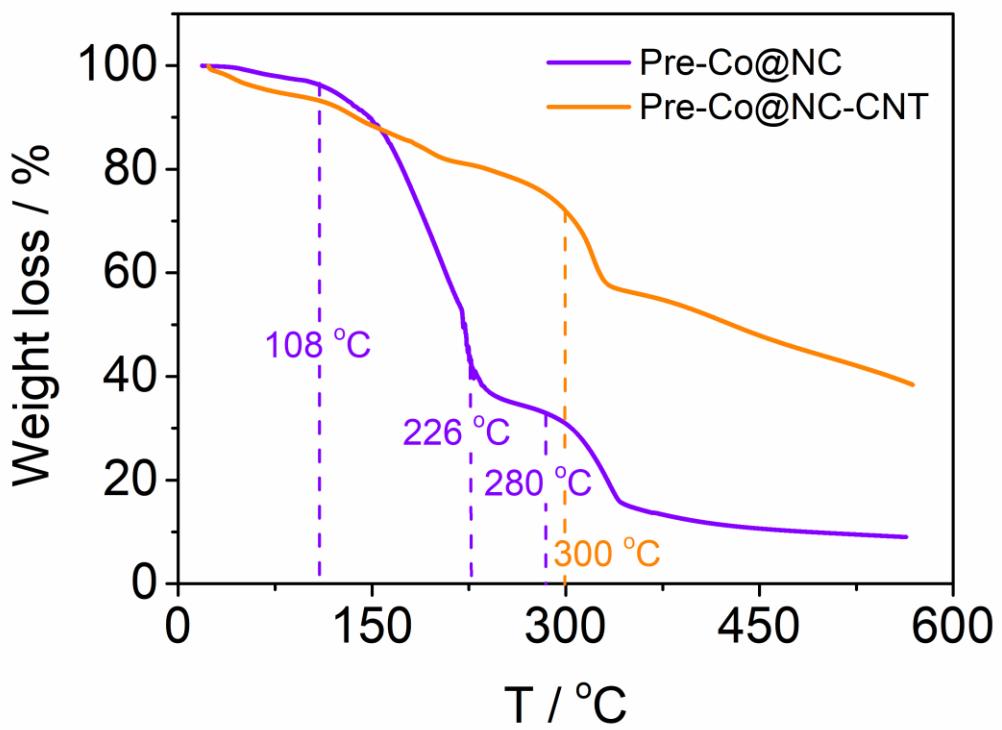
**Fig. S1** (a) photograph of Pre-Co@NC (purple) and Pre-Co@NC-CNT (pink); (b) XRD pattern of Pre-Co@NC; (c) XRD pattern of Pre-Co@NC-CNT.



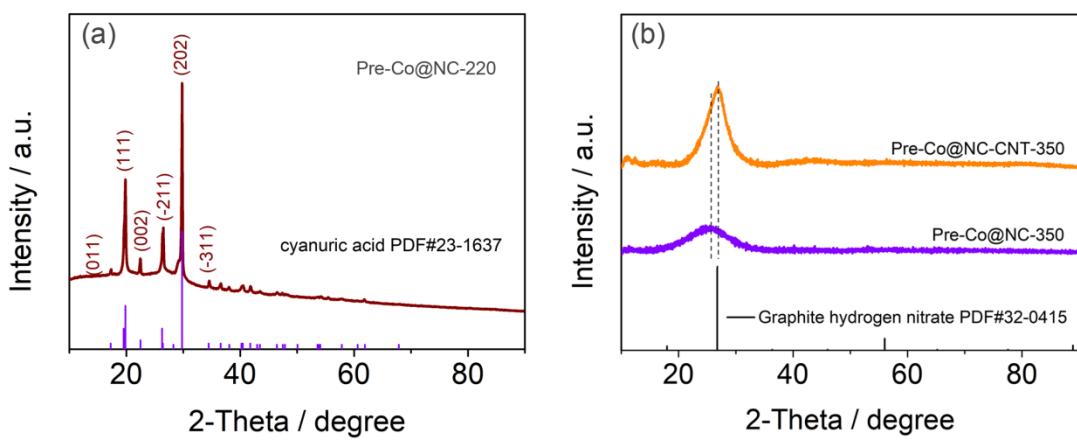
**Fig. S2.** FT-IR spectra of Pre-Co@NC and Pre-Co@NC-CNT.



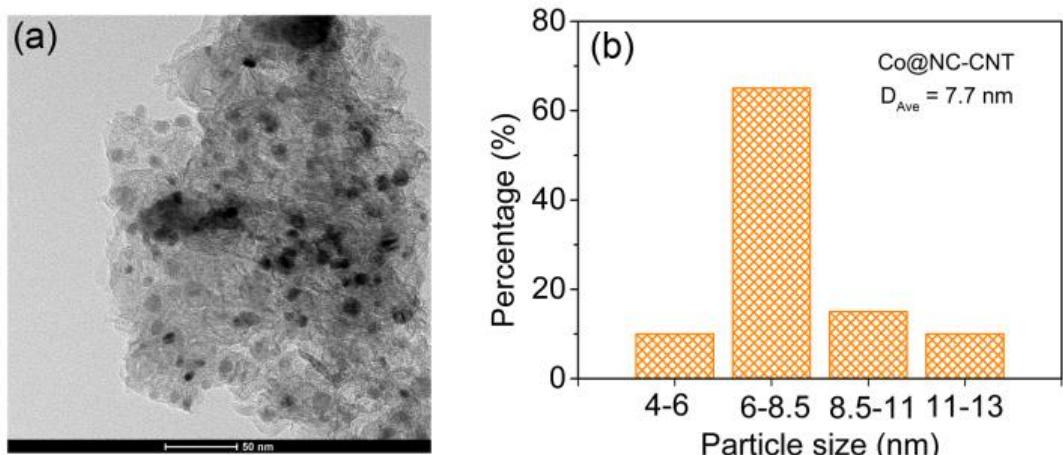
**Fig. S3.** Magnified SEM images of (a) Co@NC and (b) Co@NC-CNT.<sup>1</sup>



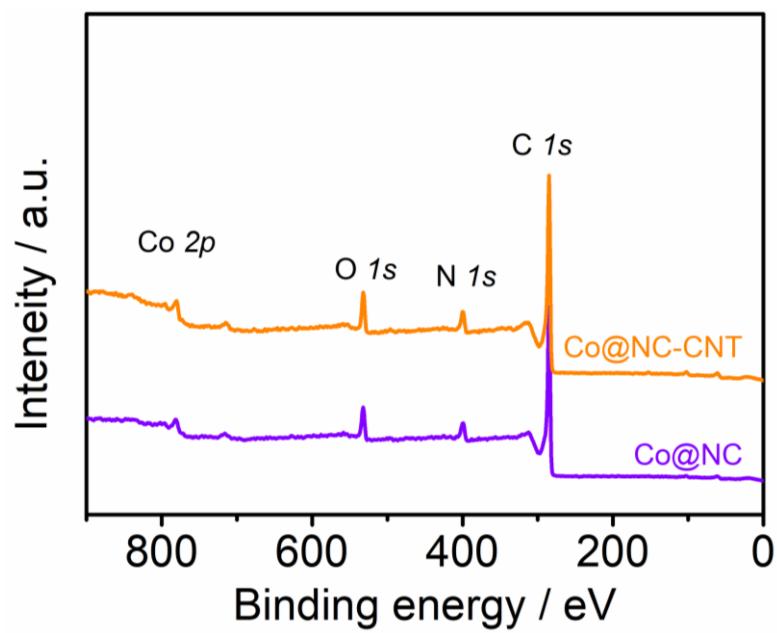
**Fig. S4.** TG curves of Pre-Co@NC and Pre-Co@NC-CNT measured from room temperature to 550 °C with a ramping rate of 10 °C min<sup>-1</sup> under nitrogen atmosphere.



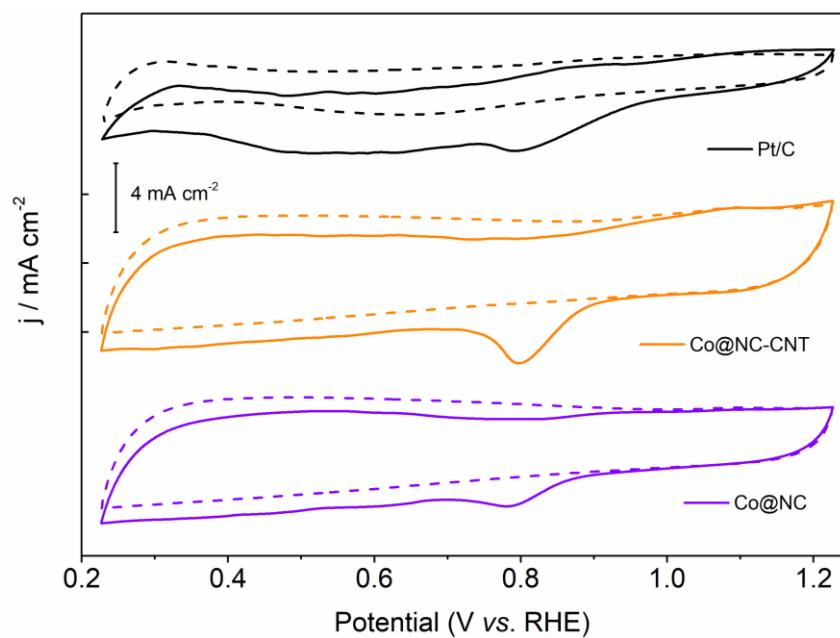
**Fig. S5.** XRD patterns of (a) pyrolyzed Pre-Co@NC at 220 °C; (b) Pre-Co@NC and Pre-Co@NC-CNT pyrolyzed at 350 °C.



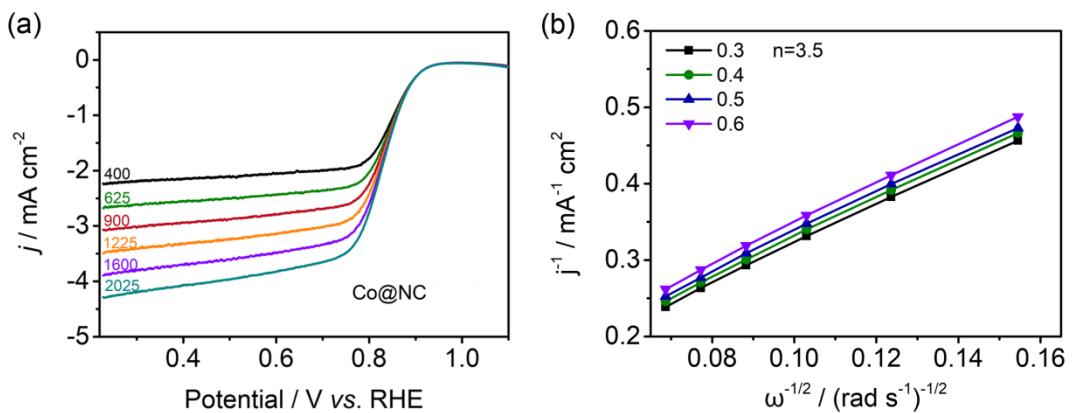
**Fig. S6.** (a) TEM images of Co@NC-CNT; (b) pore size distribution of Co@NC-CNT calculated according to the left TEM images.



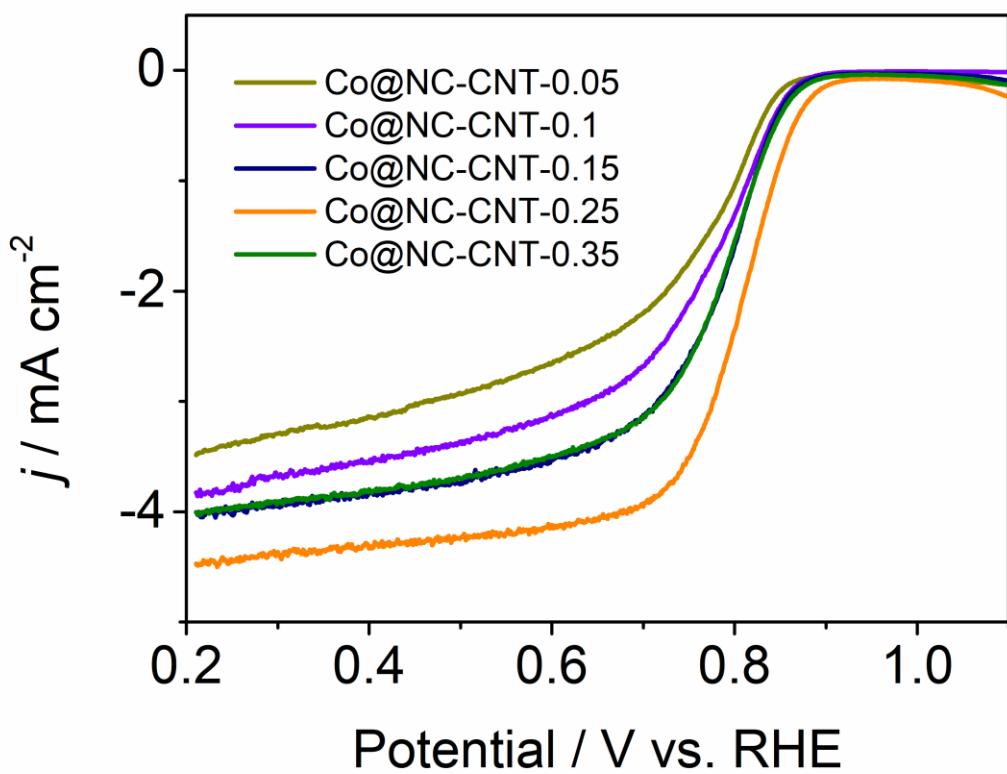
**Fig. S7.** XPS survey spectra of Co@NC and Co@NC-CNT.



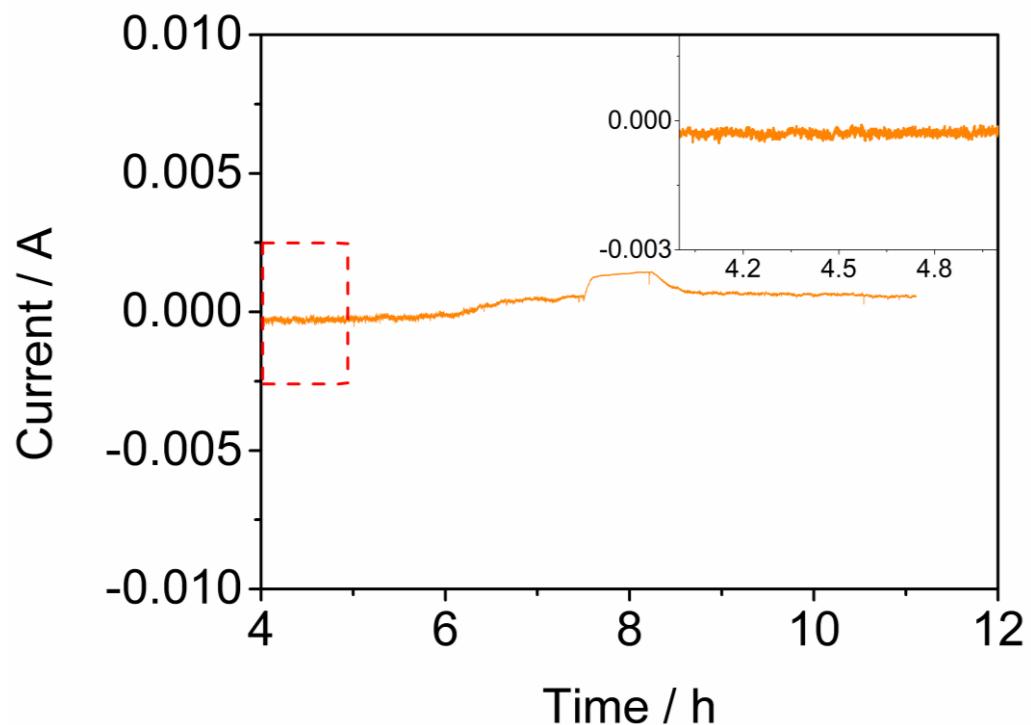
**Fig. S8.** CV curves of Co@NC, Co@NC-CNT and Pt/C measured in  $\text{N}_2$ - and  $\text{O}_2$ -saturated electrolyte at a scanning rate of  $50 \text{ mV s}^{-1}$ .



**Fig. S9** (a) LSV curves of Co@NC at different rotating speed in O<sub>2</sub>-saturated electrolyte with a scanning rate of 5 mV s<sup>-1</sup>; (b) Koutecky-Levich (K-L) plots of Co@NC.



**Fig. S10** LSV curves of Co@NC-CNT obtained using various Co content in precursor.



**Fig. S11** Chronoamperometry curves of Co@NC-CNT exhibited from 15000 s to 40000 s.

**Table S1** Relative percentage of micropores, mesopores and macropores.

	<b>Pore volume (cm<sup>3</sup> g<sup>-1</sup>)</b>	<b>Micropores (%)</b>	<b>Mesopores (%)</b>
Co@NC	0.17	45.9	40.6
Co@NC-CNT	0.29	21.1	76.2

**Table S2** Summary of C, N, O, Co atomic contents of Co@NC and Co@NC-CNT from XPS analysis.

	C at.%	N at.%	O at. %	Co at. %
Co@NC	84.4	7.2	7.2	1.2
Co@NC-CNT	84.5	6.9	7.2	1.4

**Table S3** Atomic percentage of different types of nitrogen of Co@NC-CNT-x (x refers to U, D, and M) from divided N 1s XPS spectra.

	N-6 % (398.7eV)	Co-N % (399.5eV)	N-5 % (400.1eV)	N-G % (400.9eV)	N-O % (402.7eV)
Co@NC	33.8	11.6	14.3	27.4	12.7
Co@NC-CNT	35.2	14.0	5.6	29.7	15.5

**Table S4** Comparison of ORR electrocatalytic activity of Co@NC prepared from different nitrogen source. .

	<b>N source</b>	<b>E<sub>onset</sub></b> <b>(V)</b>	<b>E<sub>1/2</sub></b> <b>(V)</b>	<b>n</b>	<b>Co</b> <b>loading</b>	<b>Ref.</b>
Co-DCDA-C	dicyandiamide	0.94*	0.847	3.9*	1.01	2 at.%
Co@NCNT	melamine	0.98	0.86	3.85	3.78	3 at.%
H-Co@FeCo/N/C	dopamine	1.03	0.91	3.9*	0.94	4 at.%
Co-N-CDC-CNT	dicyandiamide	0.91	0.82	3.6	0.11	5 at.%
CoNC-AT	dicyandiamide	0.924	0.82	3.6	1.60	6 at.%
Co/NC	Polypyrrole	0.94	0.86	3.95	0.75	7 at.%
Co-Cat-T500	melamine	0.96	0.86	3.7	--	8
Co/N-CNTs	ZIF-67	0.975	0.85	3.9	0.63	9 at.%
Co-NC-900	melamine	0.93*	0.84	3.75	0.25	10 at.%
Co@NC	urea	0.94	0.80	3.5	1.2 at.%	This work
Co@NC-CNT	dicyandiamide	0.97	0.85	3.9	1.4 at.%	This work

## REFERENCES

1. Li, W.; Wang, D.; Zhang, Y.; Tao, L.; Wang, T.; Zou, Y.; Wang, Y.; Chen, R.; Wang, S., Defect Engineering for Fuel-Cell Electrocatalysts. *Adv. Mater.* **2020**, 32, (19), e1907879.
2. Wang, D.; Yang, P.; Xu, H.; Ma, J.; Du, L.; Zhang, G.; Li, R.; Jiang, Z.; Li, Y.; Zhang, J.; An, M., The dual-nitrogen-source strategy to modulate a bifunctional hybrid Co/Co-N-C catalyst in the reversible air cathode for Zn-air batteries. *J. Power Sources*. **2021**, 485, 229339.
3. Li, Y.; Gao, J.; Zhang, F.; Qian, Q.; Liu, Y.; Zhang, G., Hierarchical 3D macrosheets composed of interconnected in situ cobalt catalyzed nitrogen doped carbon nanotubes as superior bifunctional oxygen electrocatalysts for rechargeable Zn-air batteries. *J. Mater. Chem. A*. **2018**, 6, (32), 15523-15529.
4. Wu, Y.-j.; Wu, X.-h.; Tu, T.-x.; Zhang, P.-f.; Li, J.-t.; Zhou, Y.; Huang, L.; Sun, S.-g., Controlled synthesis of FeNx-CoNx dual active sites interfaced with metallic Co nanoparticles as bifunctional oxygen electrocatalysts for rechargeable Zn-air batteries. *Appl. Catal. B: Environ.* **2020**, 278, 119259.
5. Lilloja, J.; Kibena-Põldsepp, E.; Sarapuu, A.; Kodali, M.; Chen, Y.; Asset, T.; Käärik, M.; Merisalu, M.; Paiste, P.; Aruväli, J.; Treshchalov, A.; Rähn, M.; Leis, J.; Sammelselg, V.; Holdcroft, S.; Atanassov, P.; Tammeveski, K., Cathode Catalysts Based on Cobalt- and Nitrogen-Doped Nanocarbon Composites for Anion Exchange Membrane Fuel Cells. *ACS Appl. Energ. Mater.* **2020**, 3, (6), 5375-5384.

6. Kisand, K.; Sarapuu, A.; Danilian, D.; Kikas, A.; Kisand, V.; Rahn, M.; Treshchalov, A.; Kaarik, M.; Merisalu, M.; Paiste, P.; Aruvali, J.; Leis, J.; Sammelselg, V.; Holdcroft, S.; Tammeveski, K., Transition metal-containing nitrogen-doped nanocarbon catalysts derived from 5-methylresorcinol for anion exchange membrane fuel cell application. *J. Colloid Interf. Sci.* **2021**, 584, 263-274.
7. Zhang, D.; Sun, P.; Zhou, Q.; Li, B.; Wei, Y.; Gong, T.; Huang, N.; Lv, X.; Fang, L.; Sun, X., Enhanced oxygen reduction and evolution in N-doped carbon anchored with Co nanoparticles for rechargeable Zn-air batteries. *Appl. Surf. Sci.* **2021**, 542, 148700.
8. Zhong, H.; Estudillo-Wong, L. A.; Gao, Y.; Feng, Y.; Alonso-Vante, N., Cobalt-Based Multicomponent Oxygen Reduction Reaction Electrocatalysts Generated by Melamine Thermal Pyrolysis with High Performance in an Alkaline Hydrogen/Oxygen Microfuel Cell. *ACS appl. Mater. Interf.* **2020**, 12, (19), 21605-21615.
9. Liu, B.; Zhou, H.; Jin, H.; Zhu, J.; Wang, Z.; Hu, C.; Liang, L.; Mu, S.; He, D., A new strategy to access Co/N co-doped carbon nanotubes as oxygen reduction reaction catalysts. *Chinese Chem. Lett.* **2021**, 32, (1), 535-538.
10. Zhang, S.; Shang, N.; Gao, S.; Meng, T.; Wang, Z.; Gao, Y.; Wang, C., Ultra dispersed Co supported on nitrogen-doped carbon: An efficient electrocatalyst for oxygen reduction reaction and Zn-air battery. *Chem. Eng. Sci.* **2021**, 234,

116442.