Supplementary Information

for

Liquid-assisted grinding/compression: A facile mechanosynthetic route for the production of high-performing Co-N-C electrocatalyst materials

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Table S1. Comparison of the proposed mechanochemical template-assisted methodologies with the solution-based analogues.

Product	**Synthesis conditions**	**Pyrolysis conditions**	**Workup conditions**	**Solvent* (ml/1 g of product)**	**Overall reaction time**	**Reference**
CoNC-LAG	Liquid-assisted grinding/ r.t., 20 min	Ramping 20 °C min^{-1} T=700 °C/2 h	Leaching: 1M HCl, 3 h, 70 °C	EtOH (1.3 ml)	5.5 h	*This work*
3D-CoNC-LAG	Liquid-assisted grinding/ r.t., 20 min	Ramping 20 °C min^{-1} T=700 °C/2 h	Washing: H_2O, 1 h, r.t. Leaching: 1M HCl, 3 h, 70 °C	EtOH (1.3 ml)	6.5 h	*This work*
3D-CoNC-LAC	Liquid-assisted compression/ r.t., 20 min	Ramping 20 °C min^{-1} T=700 °C/2 h	Washing: H_2O, 1h, r.t. Leaching: 1M HCl, 3 h, 70 °C	EtOH (1.3 ml)	6 h	*This work*
3D-CoNC-LAG-LAC	Liquid-assisted grinding and compression/ r.t., 30 min	Ramping 20 °C min^{-1} T=700 °C/2 h	Washing: H_2O, 1 h, r.t. Leaching: 1M HCl, 3 h, 70 °C	EtOH (1.3 ml)	6.5 h	*This work*
3D-Co-N-C	Stirring for 5 h at r.t.	T=900 °C/2h	Washing: no data Leaching: 0.5M HCl, 12 h	No data	19 h	[1]
FeN/C-900@NaCl-A-1	Stirring for 12 h at r.t.	1) Ramping 10 °C min^{-1}, T=900 °C/2 h 2) Ramping 10 °C min^{-1}, T=900 °C/1 h	Washing: no data Leaching: 1M HCl	No data	40 h	[2]

*Water was not taken into account

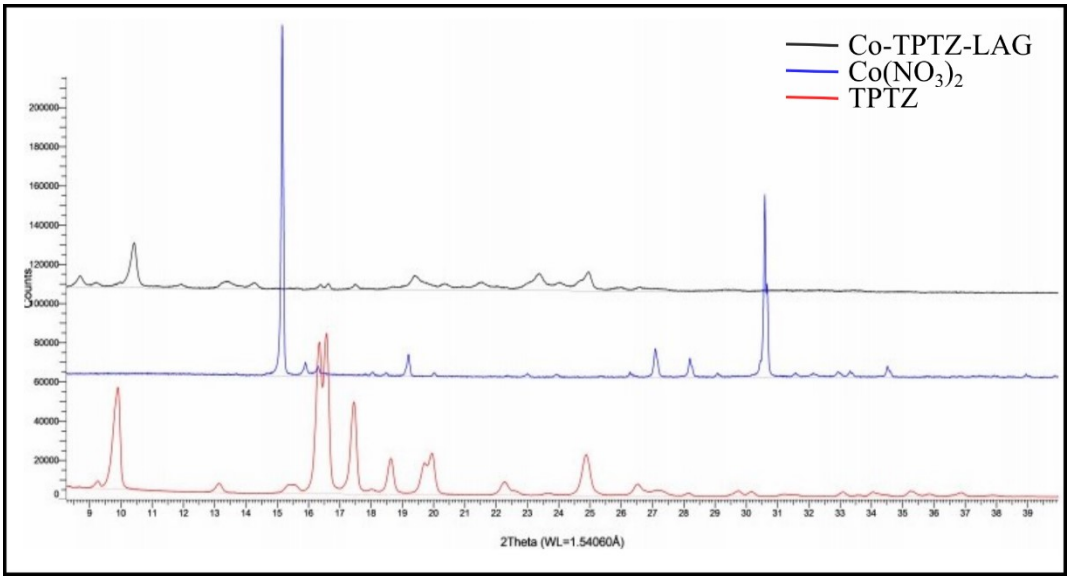

Figure S1. Comparative PXRD patterns of Co-TPTZ-LAG, $Co(NO_3)_2$ and TPTZ

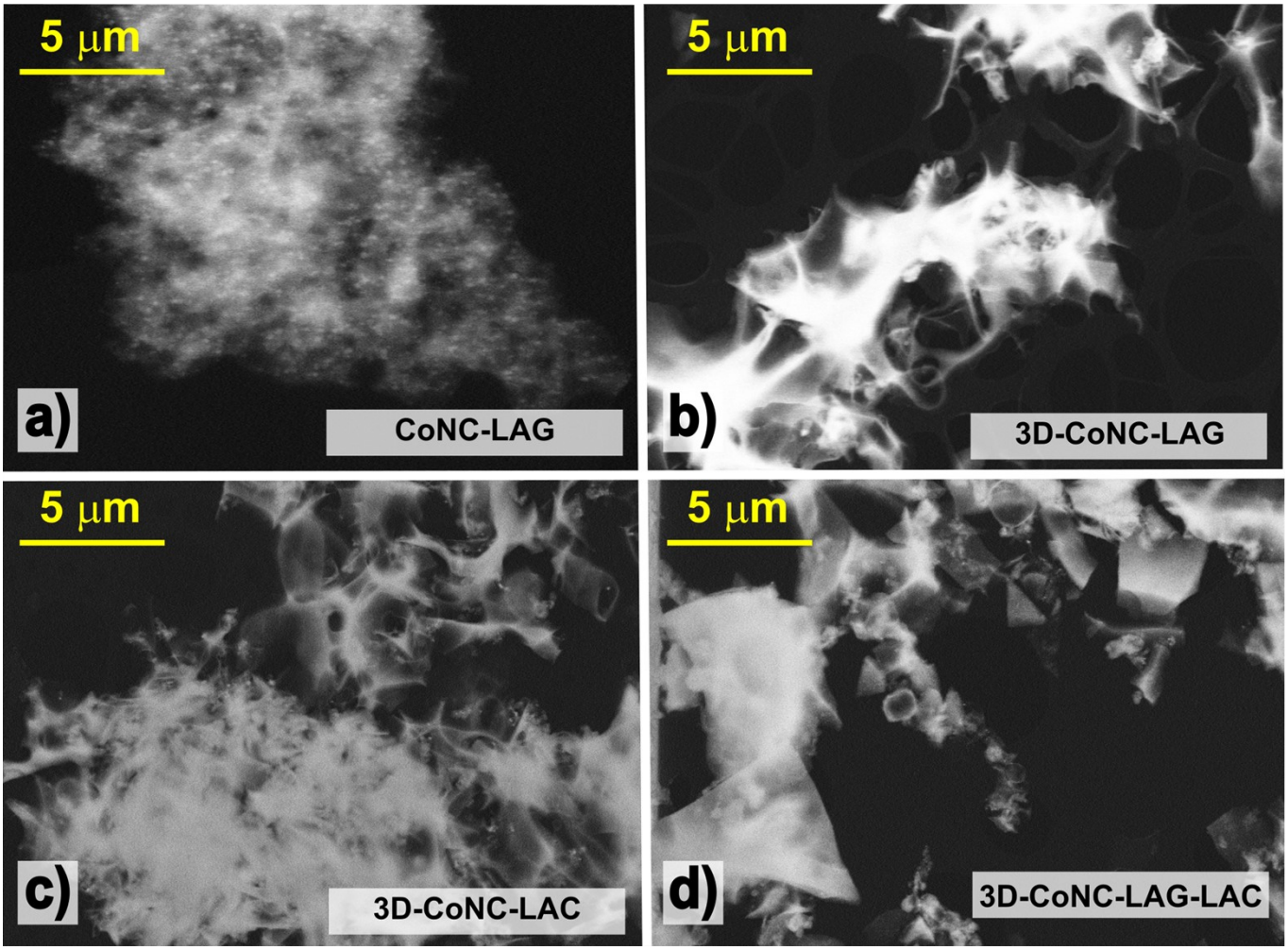

Figure S2. STEM images of (a) **CoNC-LAG**, (b) **3D-CoNC-LAG**, (c) **3D-CoNC-LAC**, and (d) **3D-CoNC-LAG-LAC**.

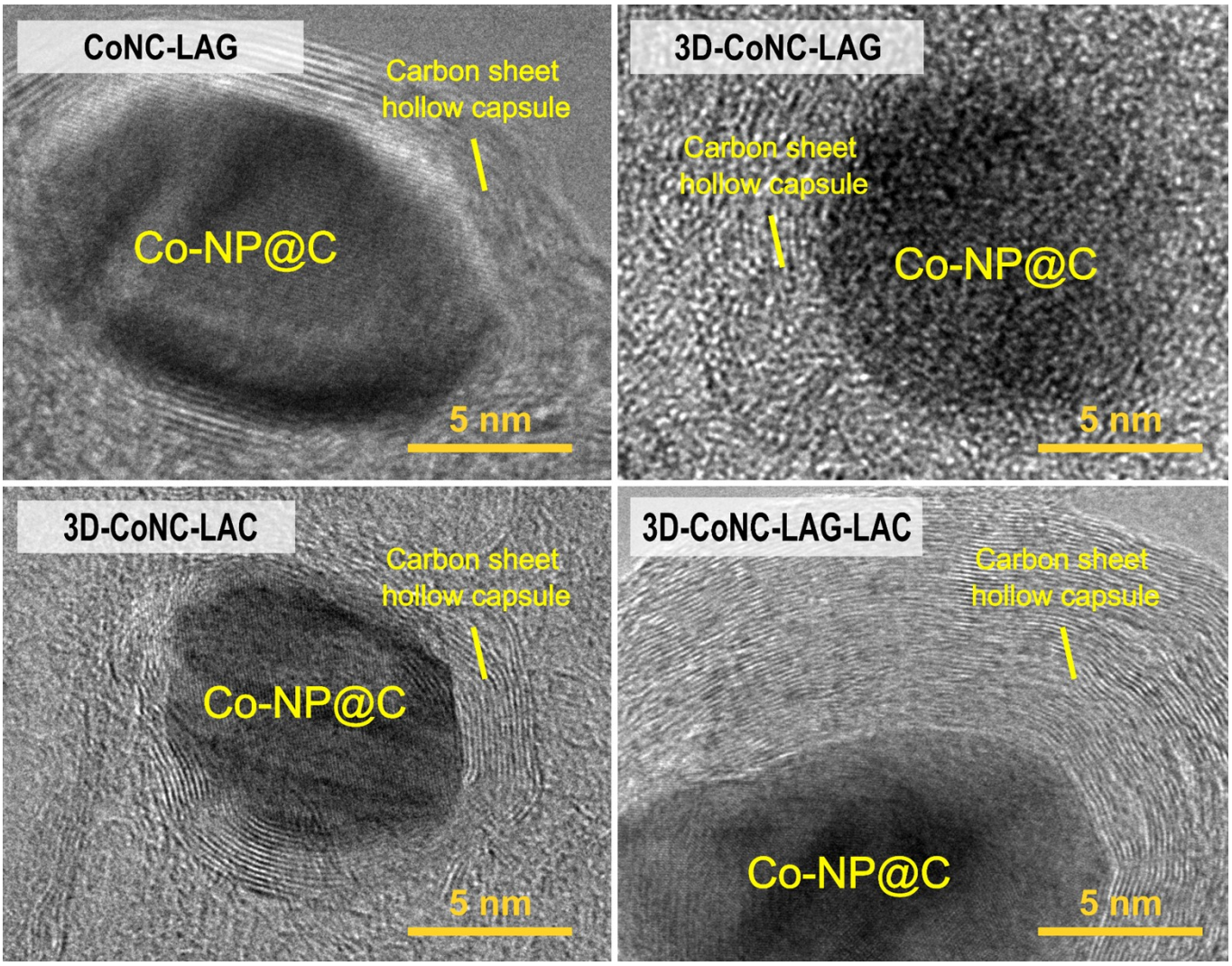

Figure S3. HR-TEM images of Co-nanoparticles coated by carbon sheets forming hollow nanocapsules within the catalyst materials.

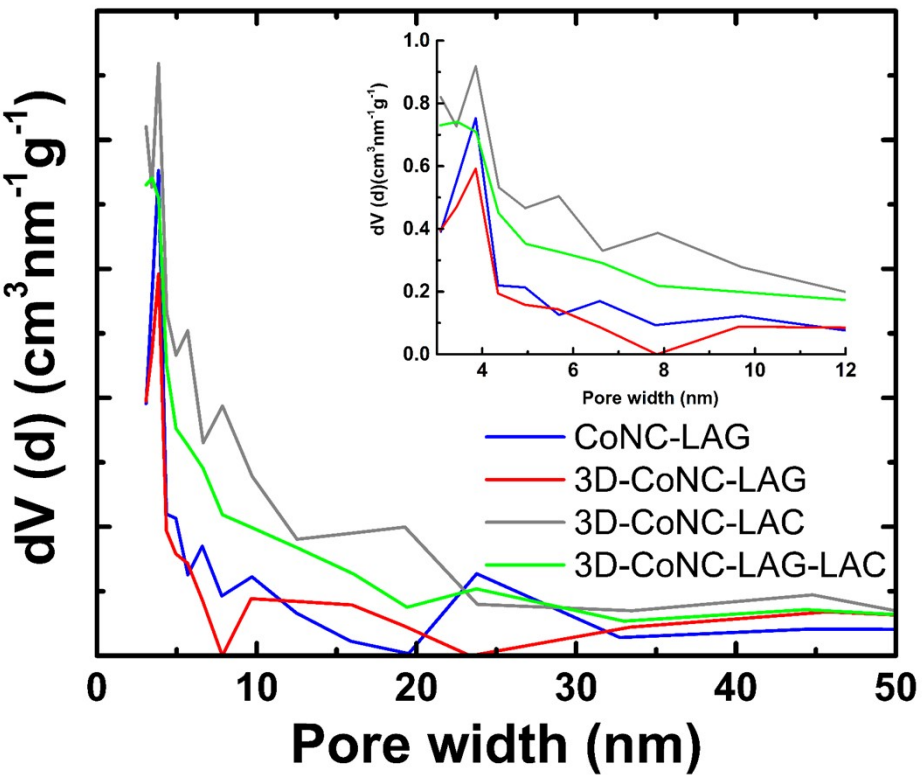

Figure S4. Pore size distribution among the Co-N-C catalysts.

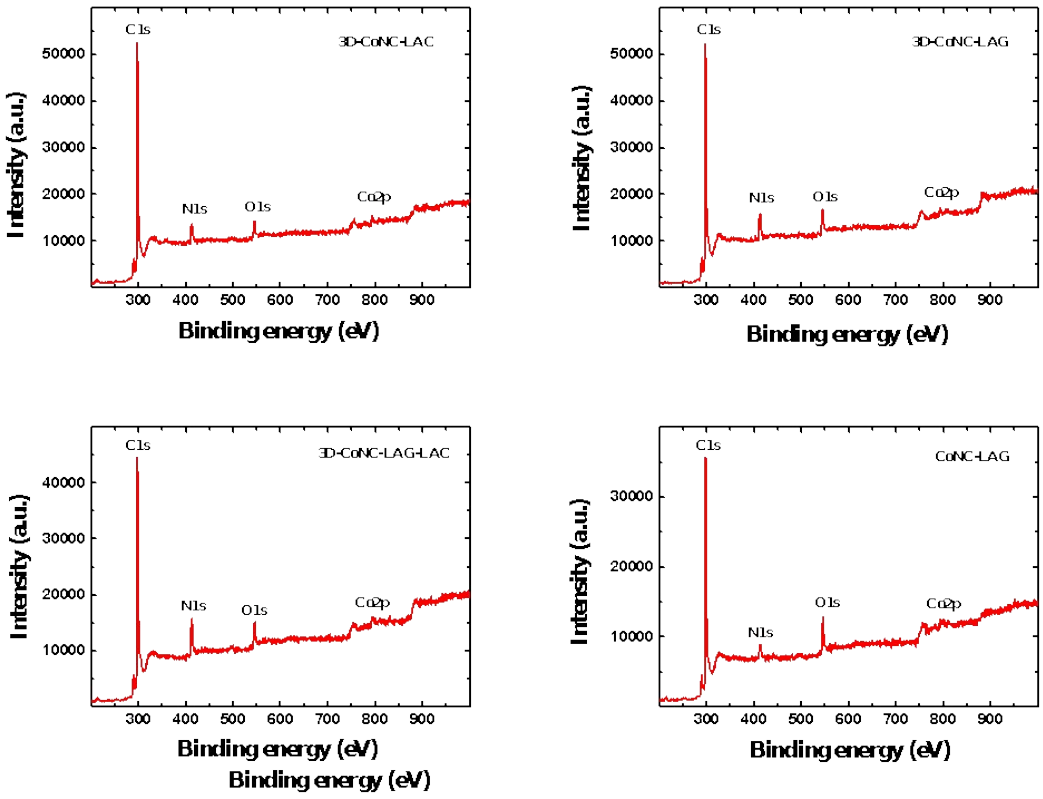

Figure S5. Survey XPS spectra recorded for all investigated samples.

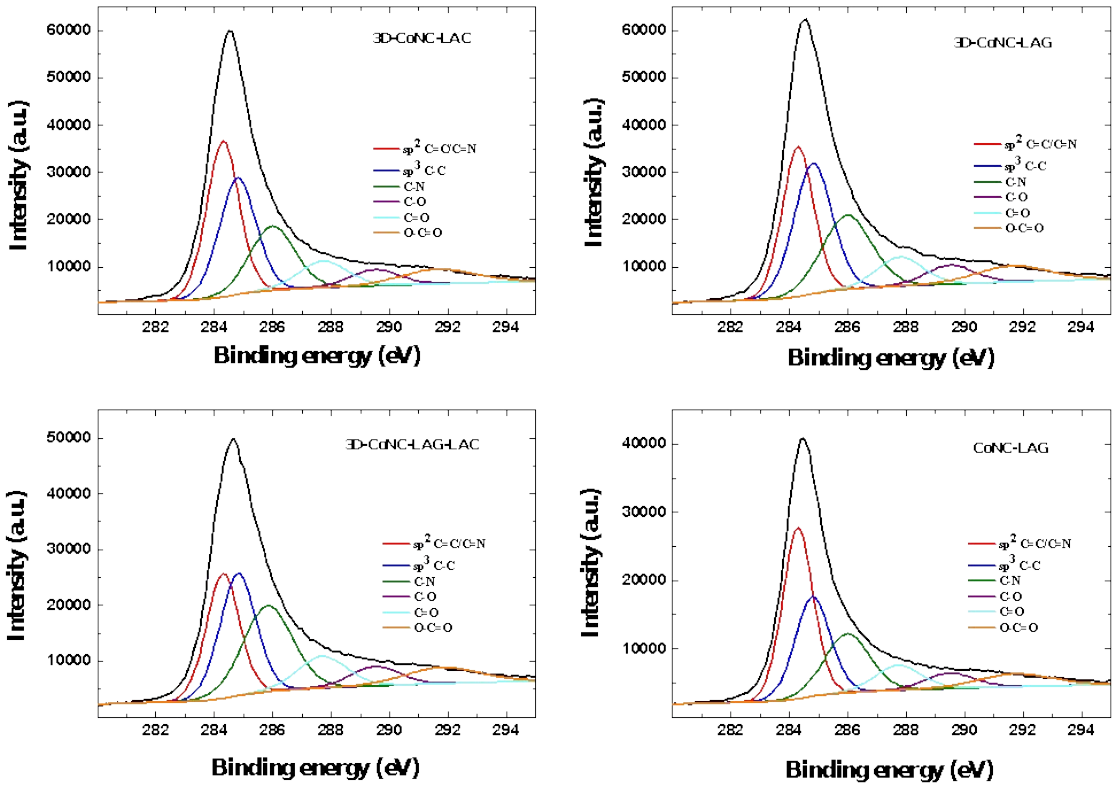

Figure S6. Deconvoluted high-resolution C1s photoelectron spectra of the obtained catalysts.

Table S2. Comparison of ORR/OER bifunctional activity ($\Delta E = E_{10}^{OER} – E_{1/2}^{ORR}$) for recently reported Co-N-C based composites.

Catalyst	$E_{1/2}$ (V) ORR	E_{onset} (V) ORR	$E_{j=10}$ OER (V)	ΔE (V)	Ref.
3D-CoNC-LAG-LAC	*0.83*	*0.98*	*1.70*	*0.87*	*This work*
Co-N-3DOM/mC	0.85	0.95	1.67	0.82	[3]
Co/MMCs	0.84	1.00	1.41	0.57	[4]
3DOM Co@N C-1-090	0.88	1.04	1.50	0.62	[5]
CoSAs@CNTs	0.86	0.99	1.64	0.78	[6]
$Co_2N_{0.67}$-BHPC	0.86	0.93	1.57	0.71	[7]
TAL-2-900	0.85	1.00	1.60	0.75	[8]
Co-N/PDC	0.80	0.86	1.59	0.79	[9]
Co-N/CDC	0.80	0.88	1.59	0.79	[9]
Co@N-HCCs@NG	0.86	0.98	1.53	0.67	[10]
$CoO_x/CoN_y@CN_{z,700}$	0.83	0.90	1.51	0.70	[11]
UNT Co SAs/N-C	0.89	0.97	1.61	0.72	[12]

Table S3. Comparison of the proposed mechanochemical template-assisted methodology with recently reported procedures for production of Co-N-C based electrocatalysts.

Product	Synthesis conditions	Pyrolysis conditions	Workup conditions	Solvent* (ml/1 g of product)*	Overall reaction time	Reference
3D-CoNC-LAG-LAC	Liquid-assisted grinding and compression/r.t., 30 min	Ramping 20 °C min^{-1} T=700 °C/2 h	Washing: H_2O, 1 h, r.t. Leaching: 1M HCl, 3 h, 70 °C	EtOH (1.3 ml)	6.5 h	This work
Co-N-3DOM/mC	1) Mixing of SMs*/30 min 2) Polymerization/ T=100 °C, 24 h	1) T=350 °C/2 h 2) T=900 °C/3 h	-	*i*-proparnol (7 ml) Ethanol (20 ml)	29 h	3
Co/MMCs	1) Electrodeposition/10 min 2) Co-incorporation T=60 °C/ 8.5 h	T=800 °C/2 h	-	DMF (6 ml)	11 h	4
3DOM Co@N C-1-090	1) SiO_2 templating/T=60 °C 2) MOF templating/T=90 °C	T=800 °C/3 h	SiO_2 etching: HF (5%)	DMF (80 ml)	no data	5
CoSAs@CNTs	1) ZIF-67 synthesis/r.t., 4.5 h 2) ZIF-67 drying/60 °C, 10 h	T=750 °C/2 h	Washing: HCl, MeOH	MeOH (25 ml)	16.5 h	6
$Co_2N_{0.67}$-BHPC	1) Mushrooms drying/ T=120 °C, 24 h 2) MR: H2TPP1/CoTPP synthesis: stirring/r.t., 5 h	Ramping 5 °C min^{-1} T=700 °C/2 h	-	DCM (no data)	31 h	7
Co-N/PDC	Co-N/PDC synthesis/ r.t., ball mill, 2 h	1) T=800 °C/3 h 2) T=800 °C/1.5 h	-	-	6.5 h	8
$CoO_x/CoN_y@CN_{z,700}$	1) CoPc@MCA synthesis/r.t. 2) CoPc@MCA drying/60 °C	Ramping 2 °C min^{-1} T=700 °C/2 h	-	DMSO (55 mL)	no data	11
UNT Co SAs/N-C	1) UNT CCH synthesis/150 °C, 12 h 2) UNT-ZIF-67 synthesis/150 °C, 2 h 3) UNT-ZIF-67 drying/70 °C, 12 h	Ramping 5 °C min^{-1} T=500 °C/2 h	-	-	26 h	12

*Water was not taken into account

References

1. C. Guo, Y. Li, W. Liao, Y. Liu, Z. Li, L. Sun, C. Chen, J. Zhang, Y. Si and L. Li, *J. Mater. Chem. A*, 2018, **6**, 13050–13061.
2. C. Guo, R. Zhou, Z. Li, Y. Si, W. Liao, W. Sun, S. Xiang, X. Luo, M. Luo and Z. Luo, *Microporous Mesoporous Mater.*, 2020, **303**, 110281.
3. Z. Meng, N. Chen, S. Cai, R. Wang, W. Guo and H. Tang, *Int. J. Energy Res.*, 2021, **45**, 6250–6261.
4. N. Huang, L. Yang, M. Zhang, S. Yan, Y. Ding, P. Sun and X. Sun, *ChemElectroChem*, 2019, **6**, 4522–4532.
5. Z. Cai, S. Lin, J. Xiao, T. Muhmood and X. Hu, *Adv. Mater. Interfaces*, 2021, **8**, 2001922.
6. S. Dilpazir, H. He, Z. Li, M. Wang, P. Lu, R. Liu, Z. Xie, D. Gao and G. Zhang, *ACS Appl. Energy Mater.*, 2018, **1**, 3283–3291.
7. X. Lv, Z. Xiao, H. Wang, X. Wang, L. Shan, F. Wang, C. Wei, X. Tang and Y. Chen, *J. Energy Chem.*, 2021, **54**, 626–638..
8. K. Ping, M. Alam, S. R. Kahnert, R. Bhadoria, A. Mere, V. Mikli, M. Käärik, J. Aruväli, P. Paiste, A. Kikas, V. Kisand, I. Järving, J. Leis, N. Kongi and P. Starkov, *Mater. Adv.*, 2021, **2**, 4009–4015.
9. P. Teppor, R. Jäger, M. Paalo, R. Palm, O. Volobujeva, E. Härk, Z. Kochovski, T. Romann, R. Härmas, J. Aruväli, A. Kikas and E. Lust, *Electrochem. Commun.*, 2020, **113**, 106700.
10. Y. Zhang, P. Wang, J. Yang, S. Lu, K. Li, G. Liu, Y. Duan and J. Qiu, *Carbon*, 2021, **177**, 344–356.
11. J. Liu, C. Wang, H. Sun, H. Wang, F. Rong, L. He, Y. Lou, S. Zhang, Z. Zhang and M. Du, *Appl. Catal. B Environ.*, 2020, **279**, 119407.
12. X. Sun, S. Sun, S. Gu, Z. Liang, J. Zhang, Y. Yang, Z. Deng, P. Wei, J. Peng, Y. Xu, C. Fang, Q. Li, J. Han, Z. Jiang and Y. Huang, *Nano Energy*, 2019, **61**, 245–250.