Supporting Information

Hollow and yolk-shell Co-N-C@SiO$_2$ nanoreactors: Controllable synthesis with high selectivity and activity for nitroarene hydrogenation

Xiaocheng Lan, Babar Ali, Yu Wang, Tiefeng Wang[*]

Beijing Key Laboratory of Green Reaction Engineering and Technology

Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

[*] Corresponding Author: Tel.: 86-10-62797490. Fax: 86-10-62772051.
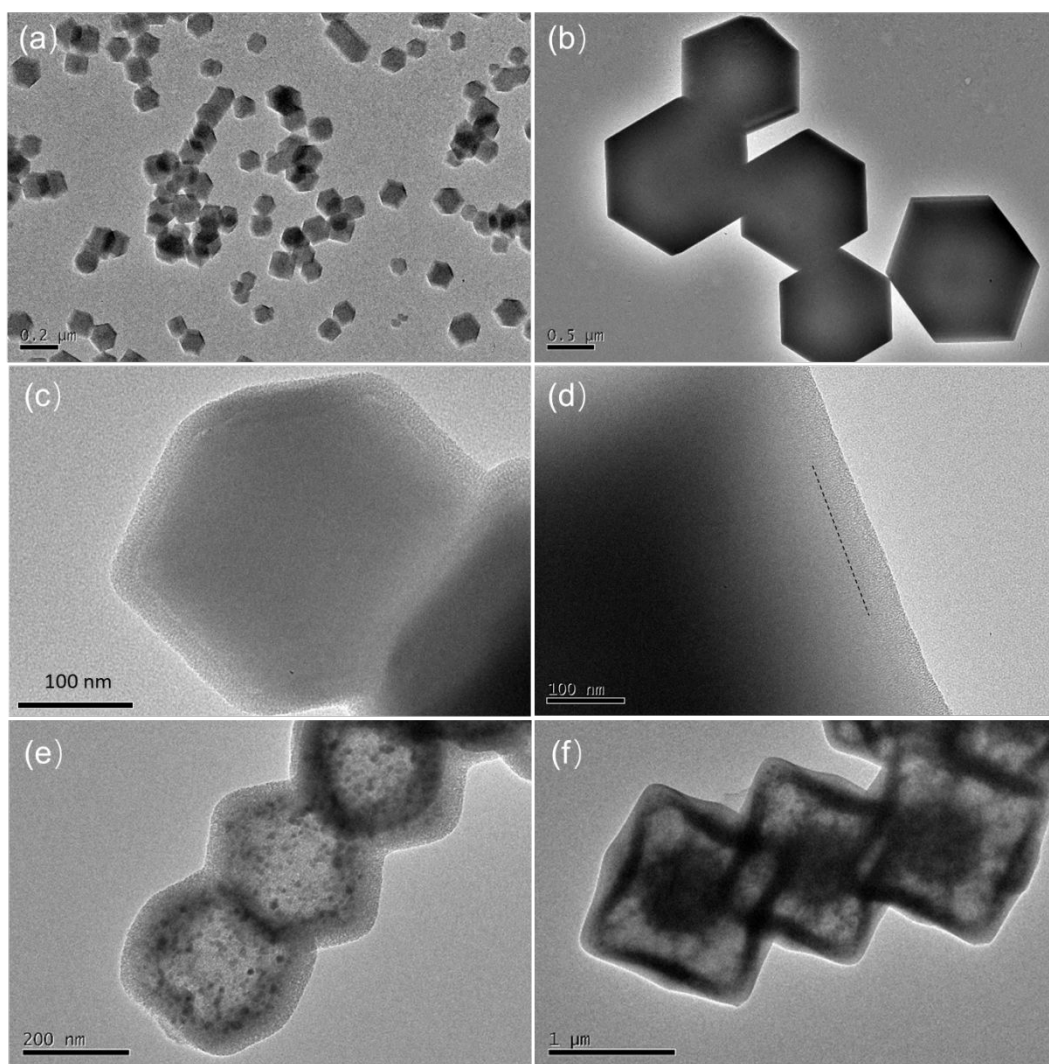
E-mail: wangtf@tsinghua.edu.cn (T. F. Wang)

Figure S1. TEM images of (a) S-ZIF-67, (b) L-ZIF-67, (c) S-ZIF-67@SiO$_2$, (d) L-ZIF-67@SiO$_2$, (e) H-Co-N-C@SiO$_2$-20, and (f) Y-Co-N-C@SiO$_2$-40.
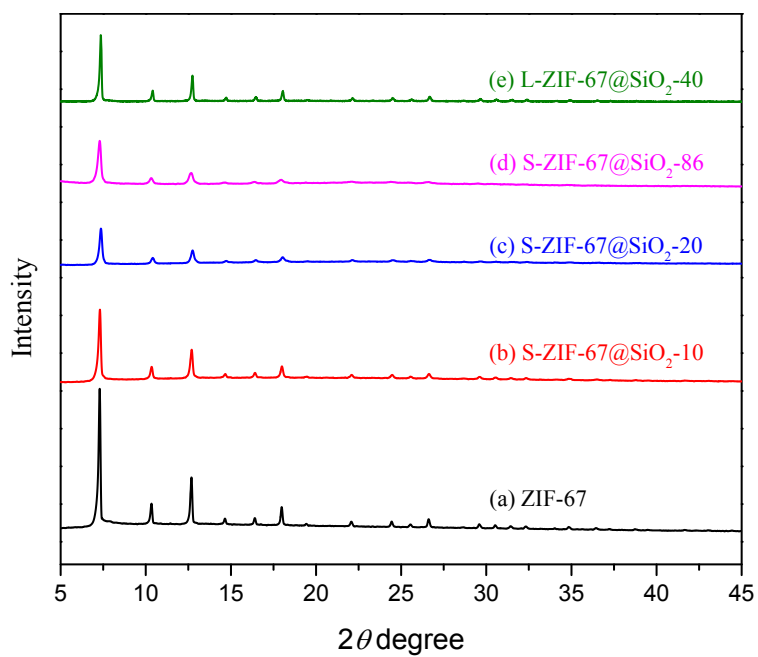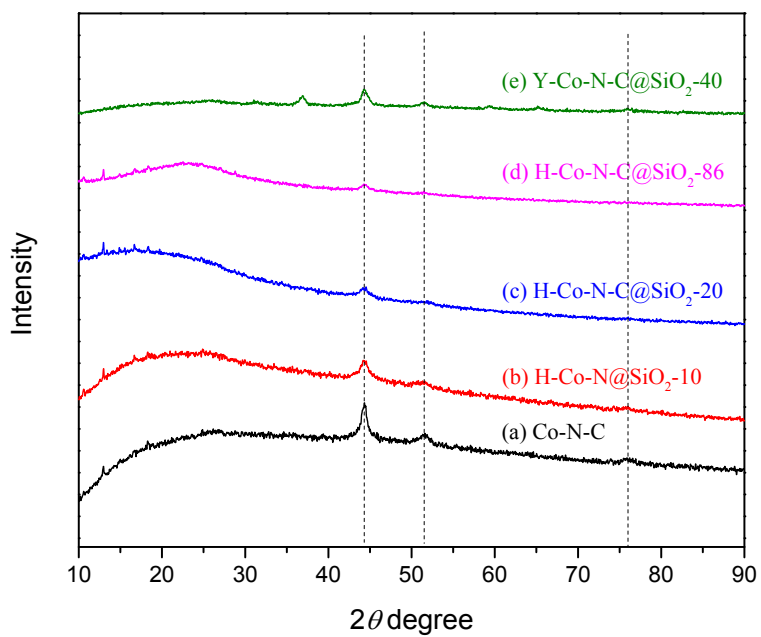
Figure S2. XRD patterns of ZIF-67 and ZIF-67@SiO$_2$.

Figure S3. XRD patterns of Co-N-C, H-Co-N-C@SiO$_2$-x, and Y-Co-N-C@SiO$_2$-x.
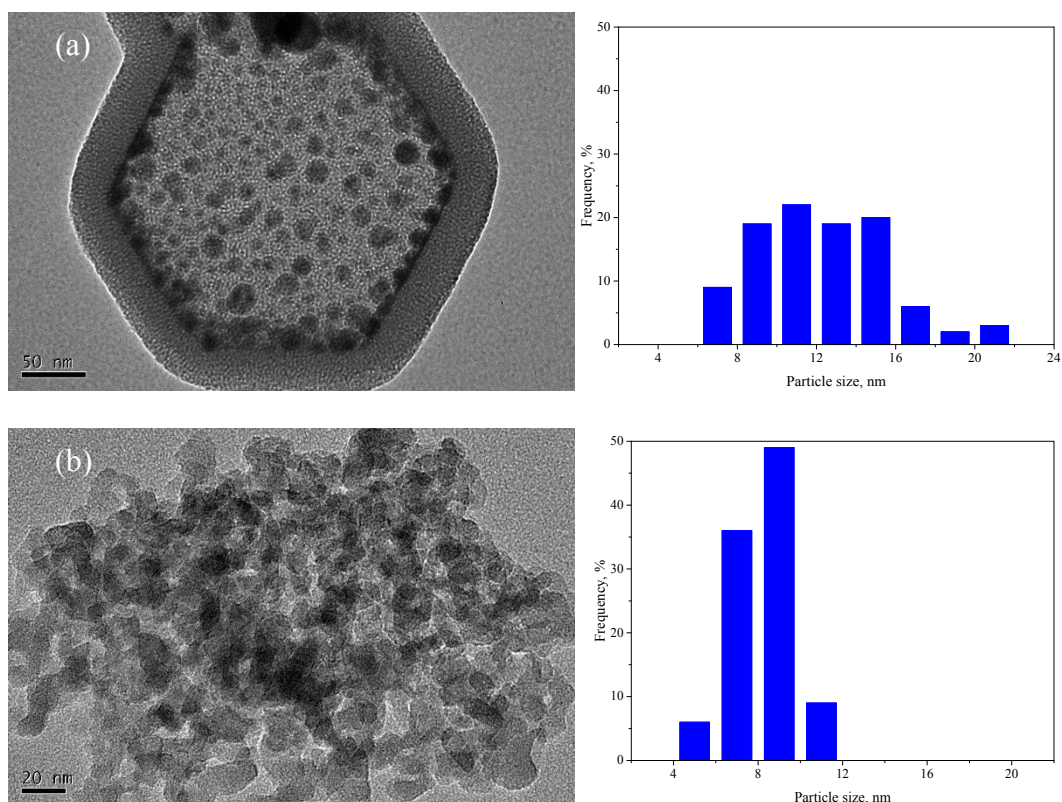
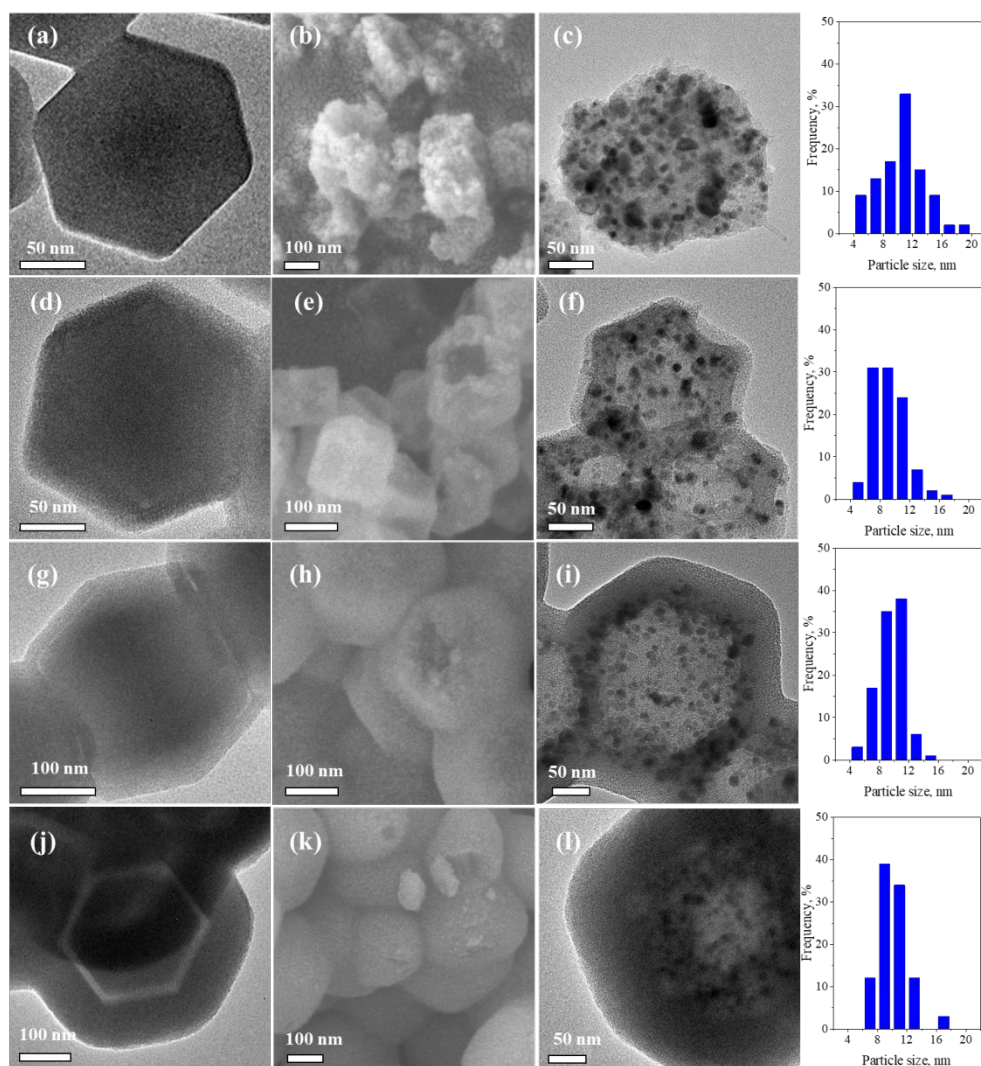Figure S4. TEM and Co particle size distribution of (a) Co@SiO$_2$ and (b) Co/SiO$_2$.

Figure S5. Characterization of HSN with different SiO_2 shell thickness. TEM images of (a) ZIF-67, (c) Co-N-C, (d) ZIF-67@SiO_2-10, (f) H-Co-N-C@SiO_2-10, (g) ZIF-67@SiO_2-20, (i) H-Co-N-C@SiO_2-20, (j) ZIF-67@SiO_2-86, and (l) H-Co-N-C@SiO_2-86. SEM images of (b) Co-N-C, (e) H-Co-N-C@SiO_2-10, (h) H-Co-N-C@SiO_2-20, and (k) H-Co-N-C@SiO_2-86.
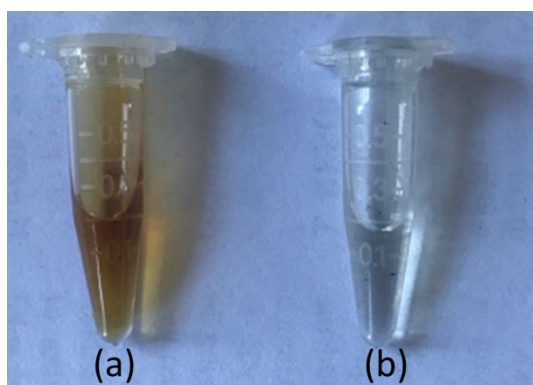

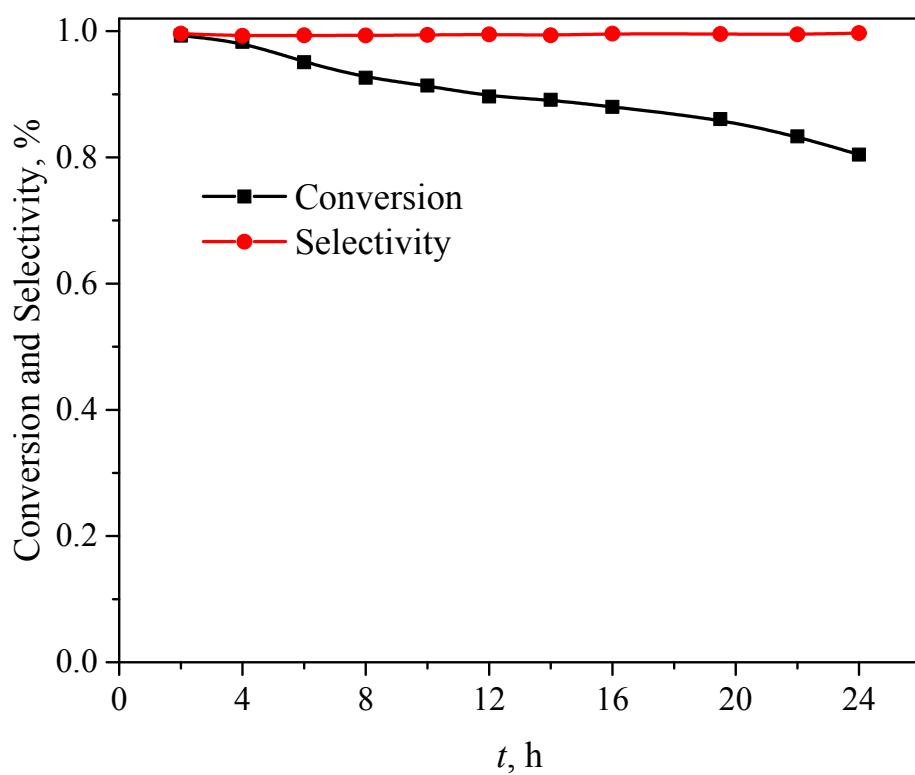Figure S6. Typical reaction samples after reaction. (a) Co@SiO_2, (b) H-Co-N-C@SiO_2-20.

Figure S7. Long-term stability of H-Co-N-C@SiO$_2$-20. Reaction conditions: 35 mg catalyst, 0.5 mL

reactant dissolved in 30 mL solvent (24 mL ethanol + 6 mL H$_2$O), 110 °C, 2.7 MPa hydrogen pressure

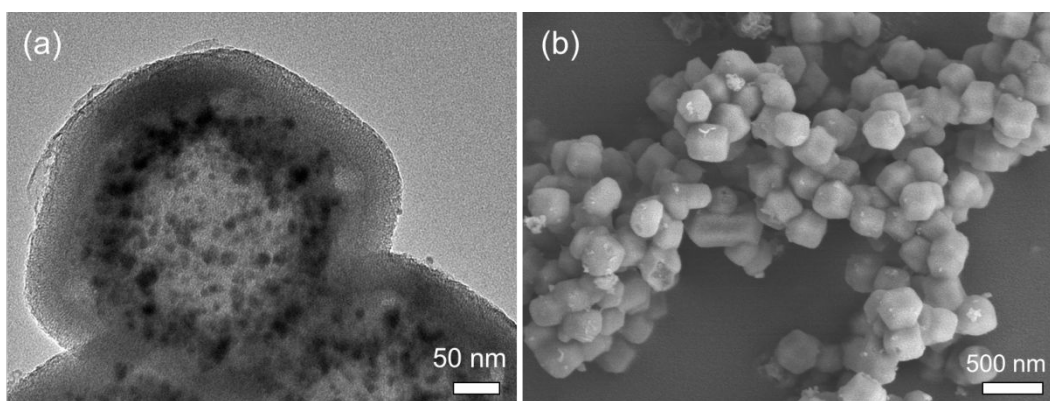with a gas flow of 50 mL/min, and 0.1 mL/min feeding rate.

Figure S8. (a) TEM and (b) SEM images of the spent H-Co-N-C@SiO$_2$-20 catalyst.

Table S1. N/Co molar ratio and proportion of deconvoluted peaks

		H-Co-N-C@SiO$_2$-20	Co@SiO$_2$
N/Co, molar ratio	XPS	1.75	0.34
	EDS	1.54	0.27
Co 2p$_{3/2}$	Co, %	9.7	2.5
	Co-O$_x$, %	22.9	63.3
	Co-N$_x$, %	67.4	34.2
N 1s	Pyridinic-N, %	9.4	11.8
	Cobalt-N$_x$, %	32.9	8.3
	Pyrrolic-N, %	15.9	22.1
	Graphitic-N, %	35.7	35.7
	Oxidized-N, %	6.0	22.0

Table S2. TOFs of Co^0 and Co-N$_x$ active sites

	r, h^{-1}	d_{TEM} [a], nm	D [b], %	TOF [c], h^{-1}	$P_{Co\text{-}Nx}$ [d], %	TOF$_{Co}$, h^{-1}	TOF$_{Co\text{-}Nx}$, h^{-1}
Co/SiO$_2$	11.8	8.2	12.2	46	0.0	46	--
H-Co-N-C@SiO$_2$-20	32.8	9.3	10.8	146	67.5	46	194

[a] Particle size was calculated based on TEM results, [b] Metal dispersion was calculated by D = 1.00 / d_{TEM}[1],

[c] TOF was the turnover frequency based on surface Co atoms, [d] $P_{Co\text{-}Nx}$ was the proportion of Co-N$_x$ identified from XPS results.

The TOF of the H-Co-N-C@SiO$_2$-20 catalyst was defined as the total activity of Co^0 and Co-N$_x$ active sites. In order to quantitatively compare the activity of different active sites, we assumed that the TOF$_{Co}$ of Co^0 was equal for Co/SiO$_2$ and H-Co-N-C@SiO$_2$-20. Thus, the TOF of Co-N$_x$ species (TOF$_{Co\text{-}Nx}$) was calculated as:
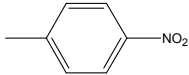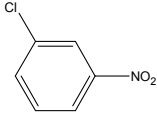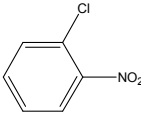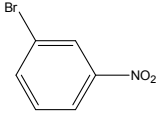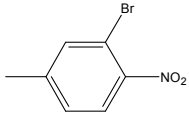
$$TOF_{Co\text{-}Nx} = (TOF - TOF_{Co} \times (1 - P_{Co\text{-}Nx})) / P_{Co\text{-}Nx} \qquad (S\text{-}1)$$

Table S3. Effect of SiO$_2$ shell on hydrogenation of nitrobenzene [a]

Entry	Catalysts	Co, mg	t, h	X, %	S, %	r, h^{-1}
1	Co-N-C	4.8	2.5	82.4	>99	28.2
2	H-Co-N-C@SiO$_2$-10	5.5	2.5	100.0	>99	35.3
3	H-Co-N-C@SiO$_2$-20	5.3	2.5	98.6	98.6	32.8
4	H-Co-N-C@SiO$_2$-86	4.6	2.5	68.2	92.0	23.2

[a] Reaction conditions: reactant 3 mmol, internal standard (isopropyl benzene) 0.15 mL, solvent (ethanol) 30 mL.

Table S4. Substrate scope of H-Co-N-C@SiO$_2$-20 in hydrogenation of nitroarenes.[a]

Entry	Nitroarenes	t, h	X, %	S, %
1		2	99.5	>99
2		3	100	>99
3		2	80.5	>99
4		3	99.4	>99
5		2	95.2	>99
6		2	62.8	>99

[a] Reaction conditions: reactant 3 mmol, internal standard (isopropyl benzene) 0.15 mL, solvent: 24 mL ethanol + 6 mL H$_2$O.

Experimental details

1. Catalyst characterization

The morphology and element distribution line scan of the samples were obtained by a scanning electron microscope (SEM, JSM7401) and transmission electron microscope (TEM, JEM2010) equipped with an energy dispersive spectrometer (EDS, OXFORD). HRTEM and elemental mapping images were obtained by high angle annular dark field scanning transmission electron microscopy (HAADF-STEM, FEI Titan Cubed G2 300) at 300 kV. All of the samples were ultrasonically dispersed in ethanol for 30 min and then dropped onto a carbon film supported on copper grid. The particle size distribution was analyzed by collecting 100 particles. The elemental chemical states of $Co@SiO_2$ and $H\text{-}Co\text{-}N\text{-}C@SiO_2\text{-}x$ were determined by XPS (Thermal Scientific ESCALAB 250Xi) with a CAE pass energy 100.0 eV analyser mode and an Al Kα X-ray source. The deconvolution of N 1s and Co 2p were based on previous works[2-5]. The X-ray diffraction (XRD) powder patterns of $ZIF\text{-}67@SiO_2$, Co-N-C, $H\text{-}Co\text{-}N\text{-}C@SiO_2\text{-}x$ and $Y\text{-}Co\text{-}N\text{-}C@SiO_2\text{-}x$ were obtained by a Bruker Advance D8 X-ray diffractometer with Cu Kα (λ = 1.5406 Å) monochromatic radiation. The samples were prepared by tableting the powder on a single crystal Si substrate. The metal loading of Co on the catalysts was confirmed by inductively coupled plasma (ICP) analysis, where the metal was dissolved by boiling the catalyst powder in aqua regia. The porosity of the samples was determined by N_2 adsorption at -196 °C on an Autosorb-IQ$_2$-MP-C system (Quantachrome, USA). The samples were evacuated at 300 °C for 10 h before analysis.

References

[1] G. Bergeret, P. Gallezot, Particle size and dispersion measurements, Handbook of Heterogeneous Catalysis: Online, (2008) 738-765.

[2] T.S. Olson, S. Pylypenko, P. Atanassov, K. Asazawa, K. Yamada, H. Tanaka, Anion-exchange membrane fuel cells: Dual-site mechanism of oxygen reduction reaction in alkaline media on cobalt− polypyrrole electrocatalysts, *J. Phys. Chem. C*, 114 (2010) 5049-5059.

[3] A. Morozan, P. Jegou, B. Jousselme, S. Palacin, Electrochemical performance of annealed cobalt-benzotriazole/CNTs catalysts towards the oxygen reduction reaction, *Phys. Chem. Chem. Phys.*, 13 (2011) 21600-21607.

[4] Y.Z. Chen, C. Wang, Z.Y. Wu, Y. Xiong, Q. Xu, S.H. Yu, H.L. Jiang, From Bimetallic Metal-Organic Framework to Porous Carbon: High Surface Area and Multicomponent Active Dopants for Excellent Electrocatalysis, *Adv. Mater.*, 27 (2015) 5010-5016.

[5] X. Li, X. Huang, S. Xi, S. Miao, J. Ding, W. Cai, S. Liu, X. Yang, H. Yang, J. Gao, J. Wang, Y. Huang, T. Zhang, B. Liu, Single Cobalt Atoms Anchored on Porous N-Doped Graphene with Dual Reaction Sites for Efficient Fenton-like Catalysis, *J. Am. Chem. Soc.*, 140 (2018) 12469-12475.