

Supporting Information

Sulfur Doping versus hierarchical pore structure: the dominating effect on the Fe-N-C site density, activity and selectivity in Oxygen Reduction Reaction electrocatalysis

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S1 Supporting Figures

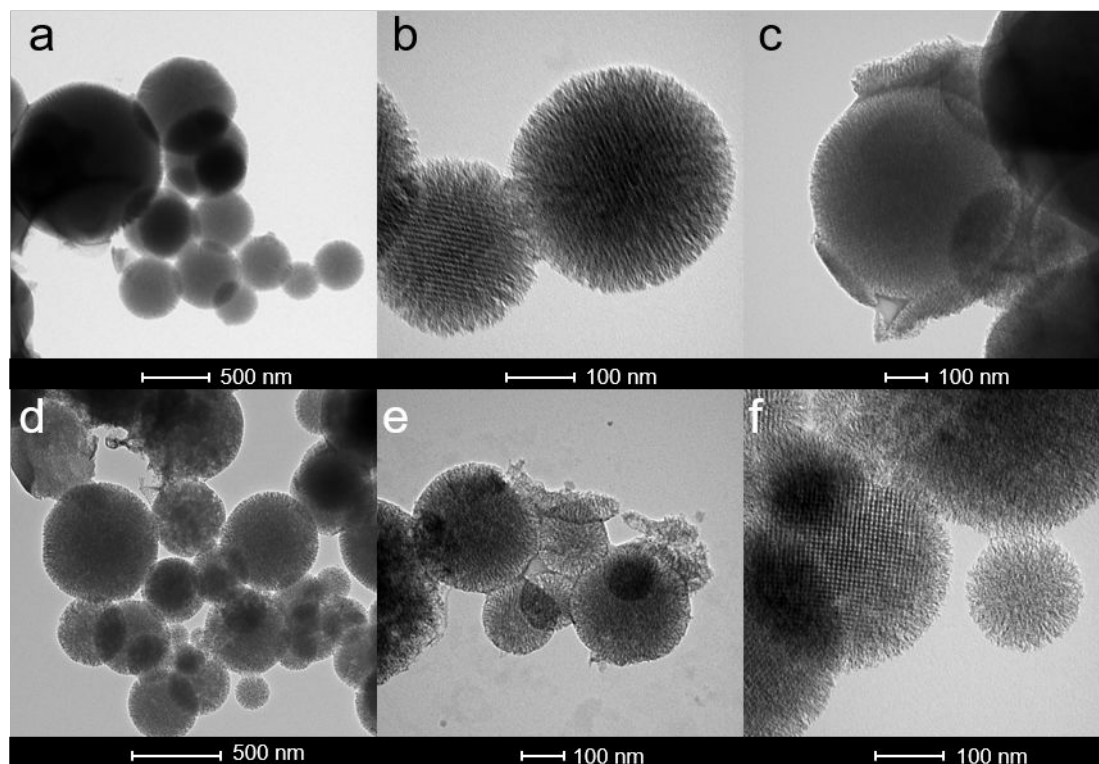


Figure S1: TEM image of (a-c) SMC100, (d-f) SMCS_t60

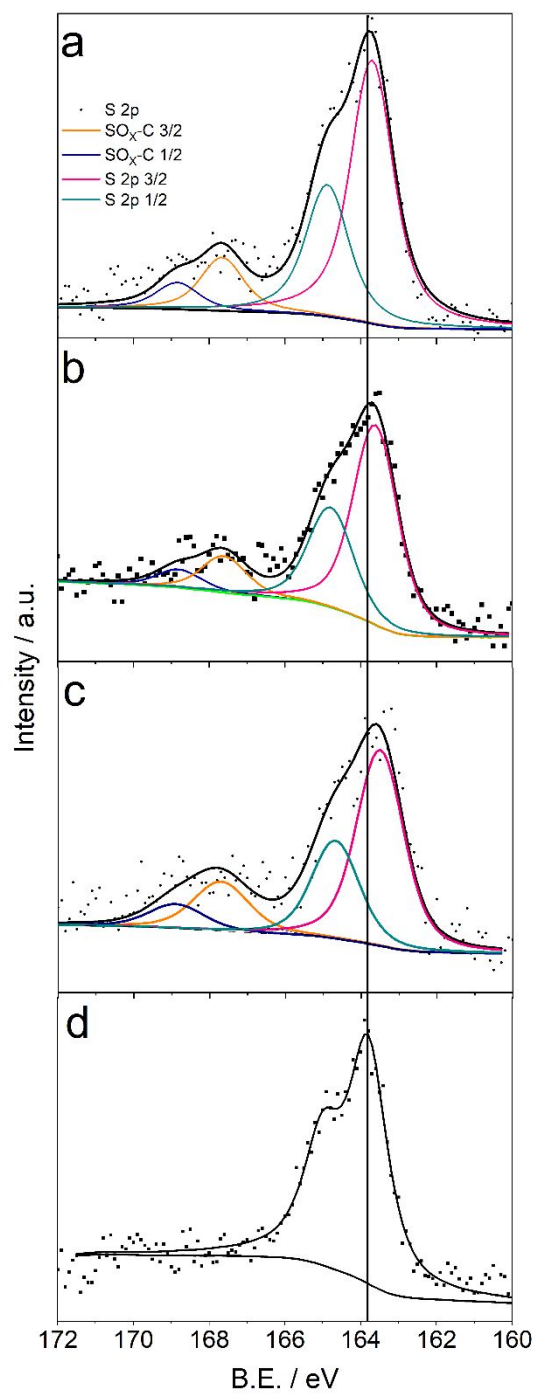


Figure S2: XPS spectra analysis of S 2p components of investigated catalysts (a) FeSMC, (b) FeSMC30, (c) FeSMC50, and (d) SMC.

S2 Supporting Tables

Table S1: Raman deconvolution parameter

	A_G cm ⁻¹	A_{D3} cm ⁻¹	$D1$ cm ⁻¹	G cm ⁻¹	I_{D1} a.u.	I_G a.u.	I_{D1}/I_G -	A_{D1}/A_G -	R_2 -
FeSMC	59.13	81.64	1333	1597	0.84	0.73	1.14	2.05	0.62
FeSMC70	53.57	104.30	1332	1599	0.76	0.69	1.11	2.08	0.55
FeSMC50	51.58	107.06	1328	1595	0.79	0.70	1.12	2.13	0.65
FeSMC30	61.33	104.78	1334	1600	0.83	0.76	1.10	1.96	0.65
FeMC	44.70	136.69	1328	1594	0.65	0.63	1.04	1.89	0.65
FeSMCSt5	53.25	79.38	1330	1596	0.82	0.74	1.11	2.10	0.57
FeSMCSt20	53.31	78.83	1330	1598	0.86	0.78	1.10	2.12	0.64
FeSMCSt40	54.12	80.84	1331	1597	0.89	0.77	1.15	2.21	0.62
FeSMCSt60	49.92	72.38	1327	1596	0.84	0.76	1.11	2.13	0.64

Table S2: Surface composition and differentiation derived from XPS analysis

	Fe wt. %	N wt. %	S wt. %	N _x %	N _{pyrid} %	N _{graf} %	N _{pyrro} %	C-S-C %	C-SO-C %	SO _x %	SO _x / C-S-C	r ^a -
FeSMC	0.85	1.36	2.45	14.5	23.7	12.7	32.1	79.3	1.8	18.9	0.24	4.0
FeSMC70	0.74	1.34	2.04	14.5	23.6	12.7	32.1	78.1	5.3	16.6	0.21	3.8
FeSMC50	0.53	1.06	0.79	19.9	20.3	11.8	31.3	73.7	4.2	22.1	0.30	1.9
FeSMC30	0.67	1.18	0.82	13.4	25.8	12.5	33.0	76.2	4.4	19.4	0.25	1.6
FeMC	0.72	1.02	0.26	15.7	19.9	13.6	31.6	64.9	0.0	35.1	0.54	0.4
FeSMCSt5	0.23	0.94	0.39	23.4	14.9	14.3	26.8	80.1	-	19.9	0.25	2.4
FeSMCSt20	0.36	0.80	0.54	20.3	20.4	11.8	31.8	82.9	5.8	11.3	0.14	2.2
FeSMCSt40	0.36	0.84	0.34	25.1	21.0	12.2	22.2	82.9	5.8	11.3	0.14	1.3
FeSMCSt60	0.23	0.65	0.39	13.3	26.6	8.7	29.3	65.1	-	34.9	0.54	2.0

^a C-S-C/Fe

Table S3: Electrochemical parameter derived from RRDE analysis at 1600 rpm 1 mV s⁻¹ in 0.5M H₂SO₄

	$E_{1/2}$ V	j_1^{0V} mA cm ⁻²	$j^{0.8V}$ mA cm ⁻²	$j^{0.85V}$ mA cm ⁻²	$j_k^{0.8V}$ A g ⁻¹	$j_k^{0.85V}$ A g ⁻¹	n #	H_2O_2 % ^{0.7V} % ^{0.2V}	
FeSMC	0.725	4.37	0.660	0.162	1.30	0.28	3.97	3.5	1.9
FeSMC70	0.646	4.10	0.348	0.084	0.63	0.14	3.92	8.4	5.9
FeSMC50	0.695	4.94	0.660	0.182	1.27	0.31	3.91	2.7	1.2
FeSMC30	0.646	4.13	0.165	0.044	0.29	0.07	3.98	5.2	5.2
FeMC	0.717	4.35	0.561	0.127	1.07	0.22	3.93	4.8	3.1
FeSMCSt5	0.609	4.53	0.134	0.031	0.23	0.05	3.91	7.4	5.7
FeSMCSt20	0.739	4.76	0.840	0.193	1.70	0.34	3.95	2.6	4.1
FeSMCSt40	0.717	4.77	0.691	0.161	1.35	0.28	3.92	5.6	4.5
FeSMCSt60	0.731	4.97	0.660	0.147	1.27	0.25	3.93	4.4	4.3

Table S4: Stripping data and utilization factor (Φ) calculated from bulk Fe (ICP)

	<i>SD</i>	<i>SD_{BET}</i>	<i>TOF^{0.8V}</i>	<i>TOF^{0.85V}</i>	<i>SD_{MAX,ICP}</i>	Φ
	10 ¹⁸ sites g ⁻¹	10 ¹⁵ sites m ⁻²	s ⁻¹	s ⁻¹	10 ¹⁹ sites g ⁻¹	%
FeSMC	7.51	5.80	1.47	0.50	4.31	17.4
FeSMC70	5.54	5.24	1.19	0.33	7.33	7.6
FeSMC50	9.25	9.33	2.10	0.73	8.63	10.7
FeSMC30	8.75	11.8	0.28	-	11.8	7.4
FeMC	5.71	4.47	1.68	0.44	12.6	4.5
FeSMCSt5	5.54	4.65	1.04	0.34	2.70	20.5
FeSMCSt20	5.22	3.34	3.40	0.97	11.1	4.7
FeSMCSt40	8.56	6.22	1.58	0.38	11.1	7.7
FeSMCSt60	5.87	3.40	3.41	0.87	9.38	6.3