

Supplementary Information

High performing and sustainable hard carbons for Na-ion batteries through acid-catalysed hydrothermal carbonisation of vine shoots

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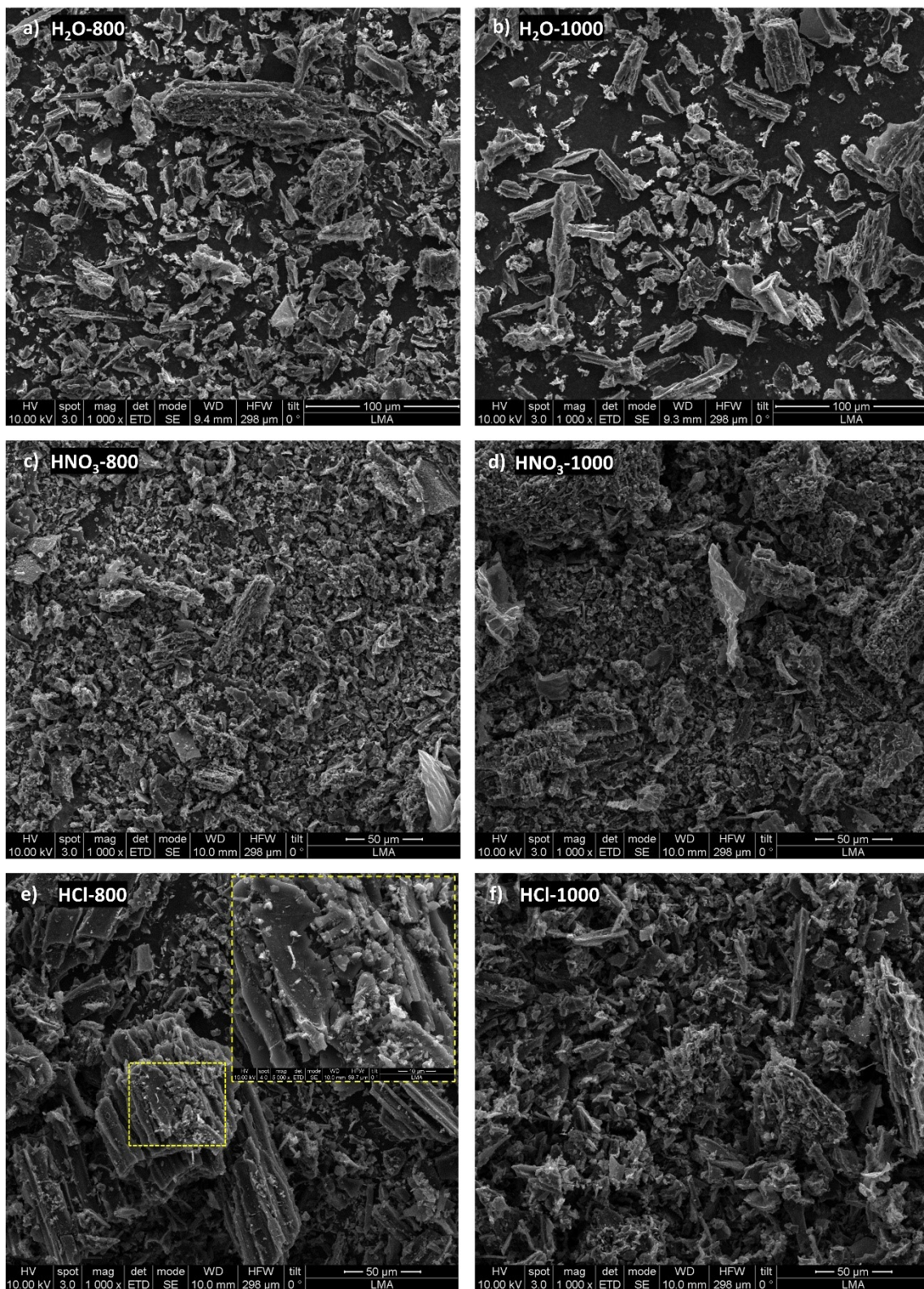


Fig. S1. SEM images of H₂O-800 (a), H₂O-1000 (b), HNO₃-800 (c), HNO₃-1000 (d), HCl-800 (e), and HCl-1000 (f).

Table S1. Mass yields after HTC and annealing steps. Total yield has been calculated with respect to the dry biomass.

	HTC (%)	Annealing (%)	Total yield (%)
H ₂ O-800	59.84	37.12	22.21
H ₂ O-1000	59.12	35.89	21.22
HNO ₃ -800	37.93	37.58	14.26
HNO ₃ -1000	37.93	36.07	13.68
HCl-800	38.37	50.38	19.33
HCl-1000	38.37	52.82	20.27
H ₂ SO ₄ -800	44.01	53.10	23.37
H ₂ SO ₄ -1000	44.01	50.59	22.27
H ₃ PO ₄ -800	48.66	55.11	26.82
H ₃ PO ₄ -800	48.66	53.97	26.26

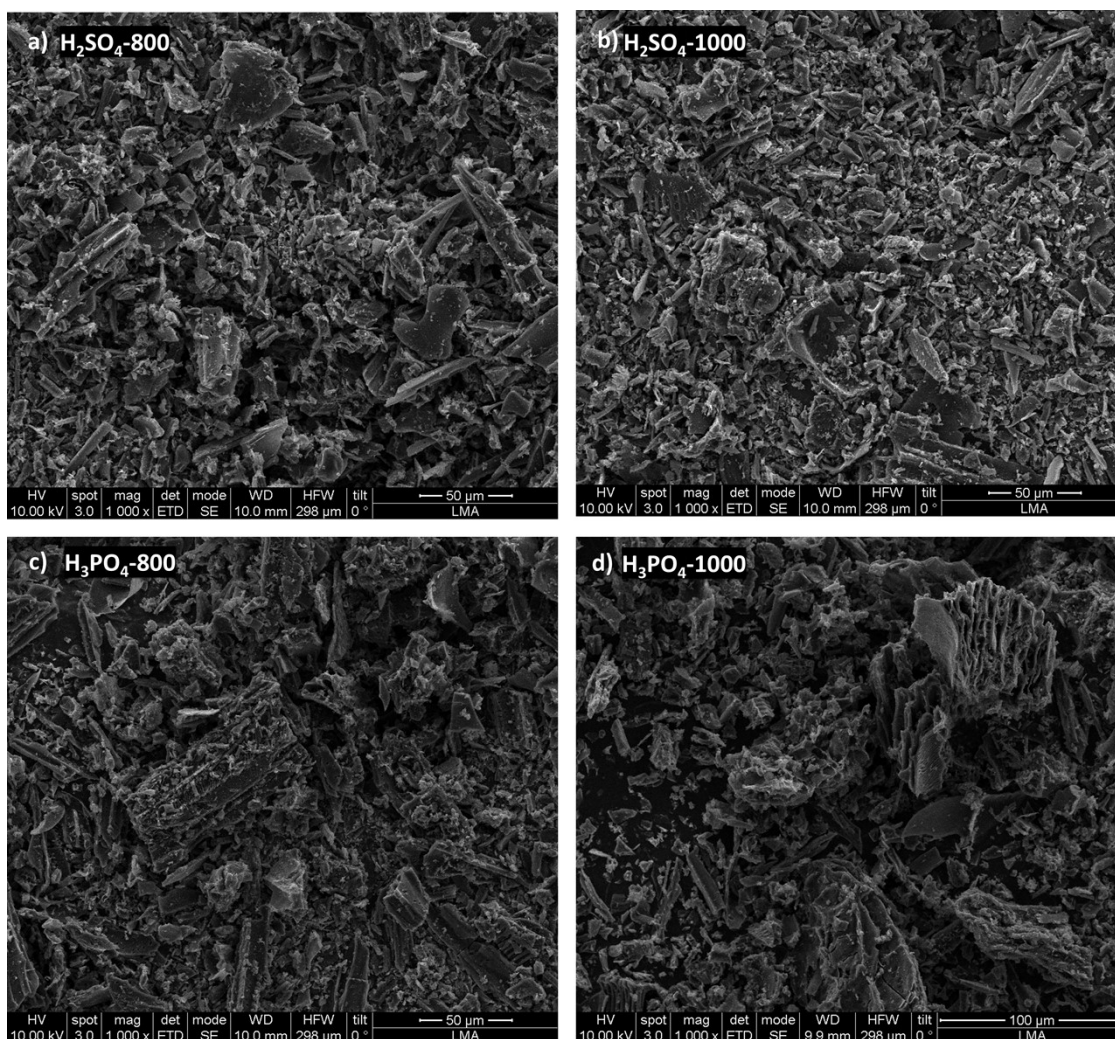


Fig. S2. SEM images of H₂SO₄-800 (a), H₂SO₄-1000 (b), H₃PO₄-800 (c), and H₃PO₄-1000 (d).

Table S2. Surface areas and pore volumes of HCs deduced from CO₂ and N₂ adsorption isotherms

	Surface area BET [m ² g ⁻¹]		Surface area NLDFT [m ² g ⁻¹]		Pore volume NLDFT [cm ³ g ⁻¹]		
	N ₂	CO ₂	N ₂	CO ₂	V_{ultra}	V_{mic}	V_{mes}
H ₂ O-800	82	397	59	602	0.122	0.080	0.025
H ₂ O-1000	17	445	15	634	0.127	0.062	0.030
HNO ₃ -800	5	393	7	613	0.124	0.040	0.018
HNO ₃ -1000	9	284	9	311	0.054	0.048	0.028
HCl-800	659	575	583	799	0.157	0.295	0.240
HCl-1000	127	440	88	637	0.127	0.079	0.212
H ₂ SO ₄ -800	297	428	226	648	0.129	0.139	0.145
H ₂ SO ₄ -1000	31	439	26	643	0.129	0.050	0.123
H ₃ PO ₄ -800	346	452	306	683	0.136	0.175	0.126
H ₃ PO ₄ -1000	42	449	35	664	0.135	0.050	0.124

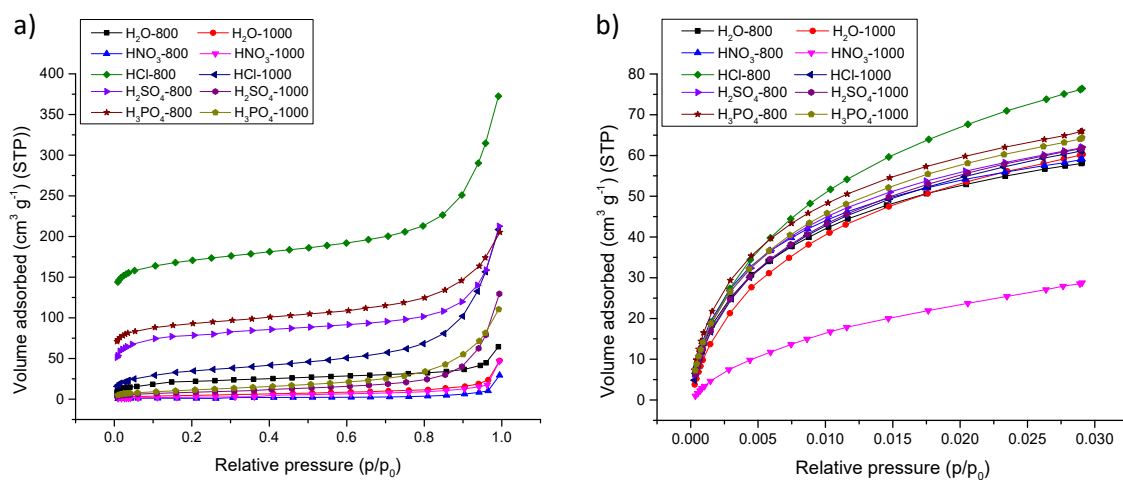


Fig. S3. N₂ adsorption isotherms at -196 °C (a) and CO₂ adsorption isotherms at 0 °C

(b).

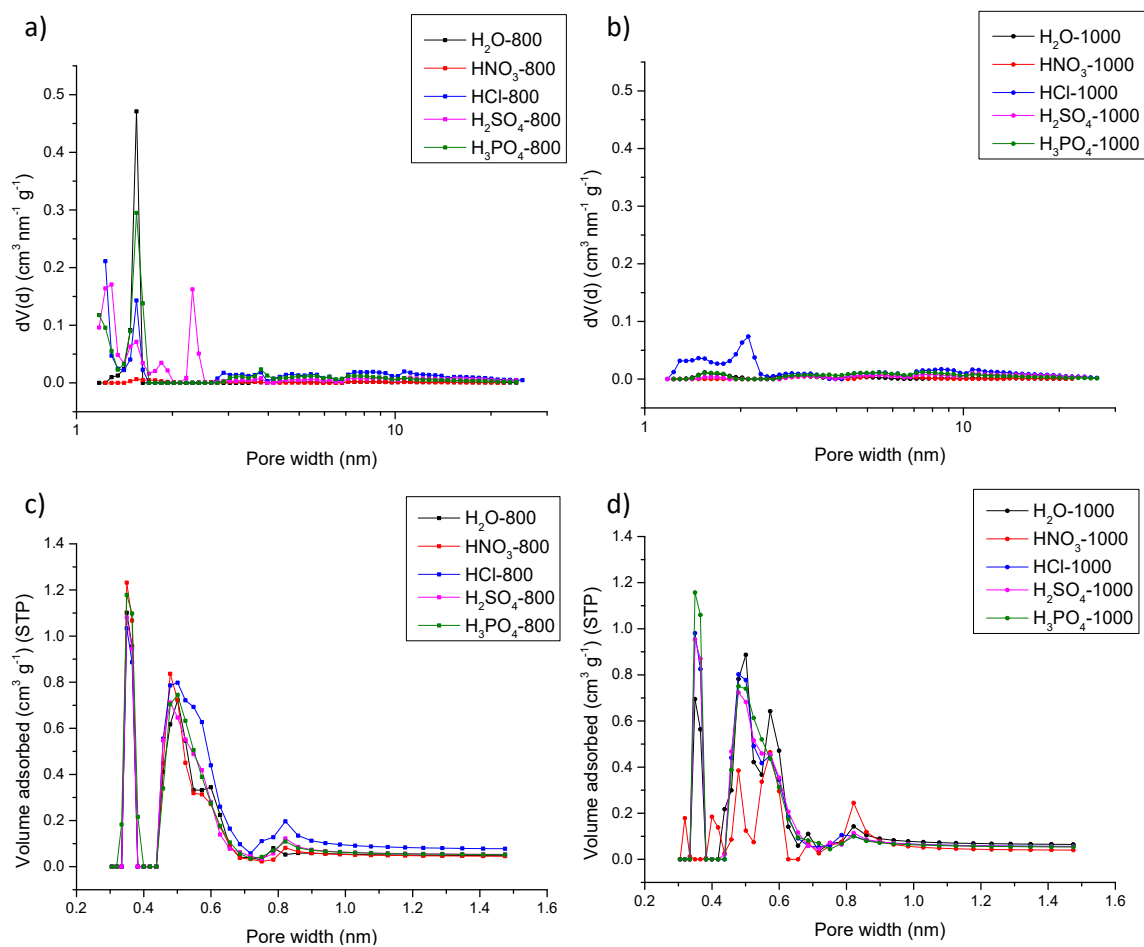


Fig. S4. Pore size distribution diagrams (NLDFT model) for N_2 (a-b) and CO_2 adsorption isotherms (c-d).

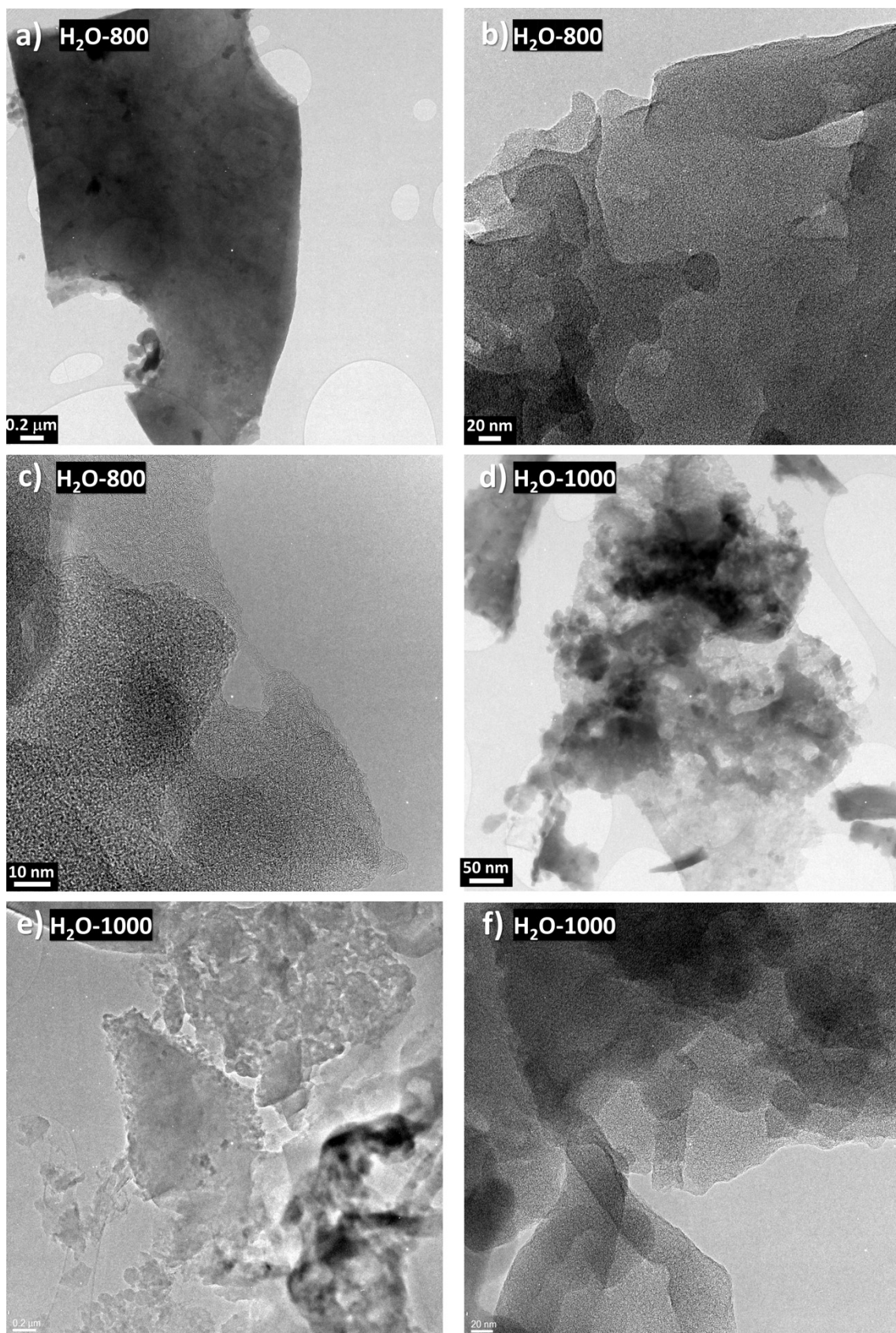


Fig. S5. HR-TEM images of H₂O-800 (a–c) and H₂O-1000 (d–f).

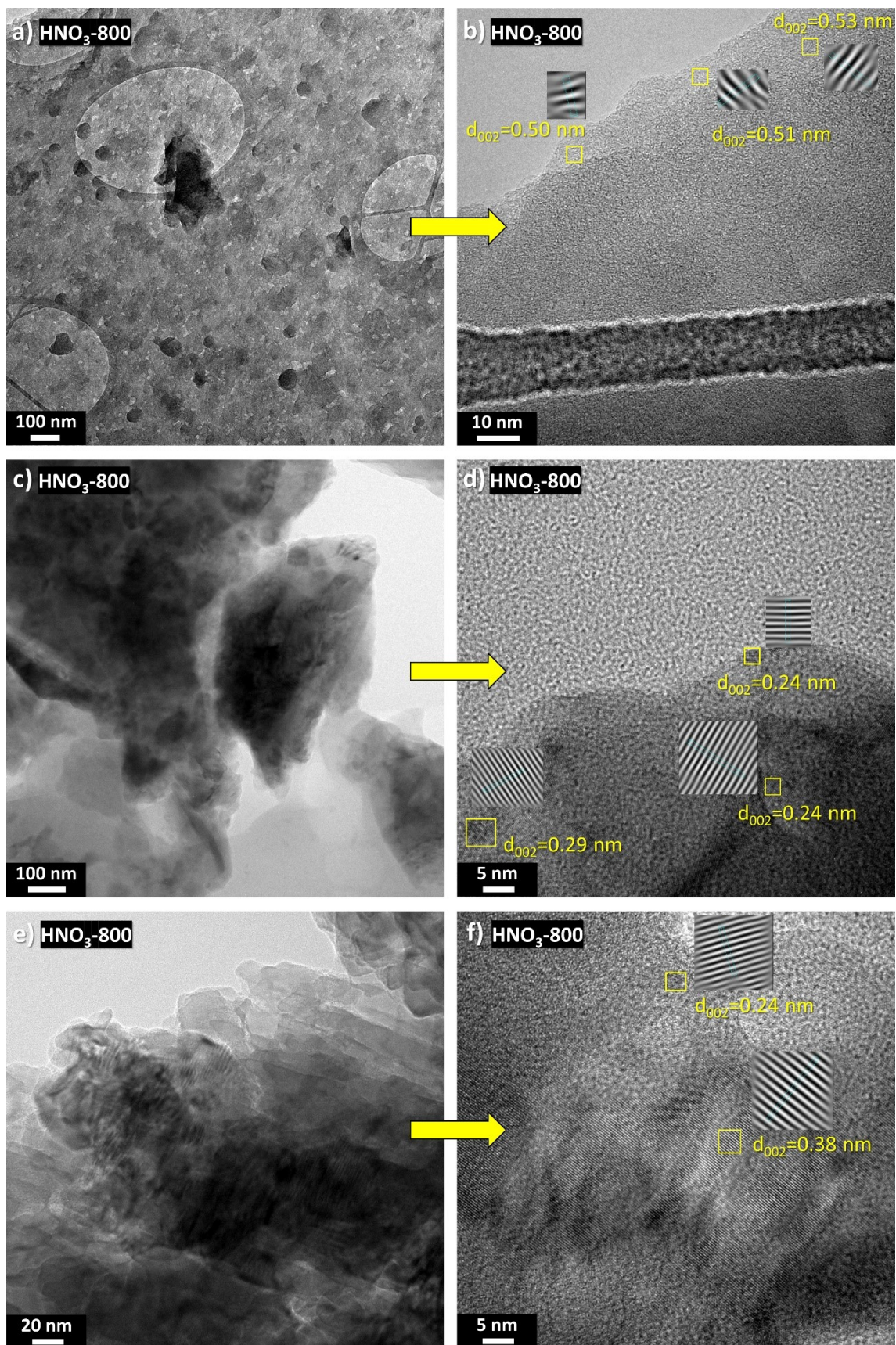


Fig. S6. HR-TEM images of HNO₃-800.

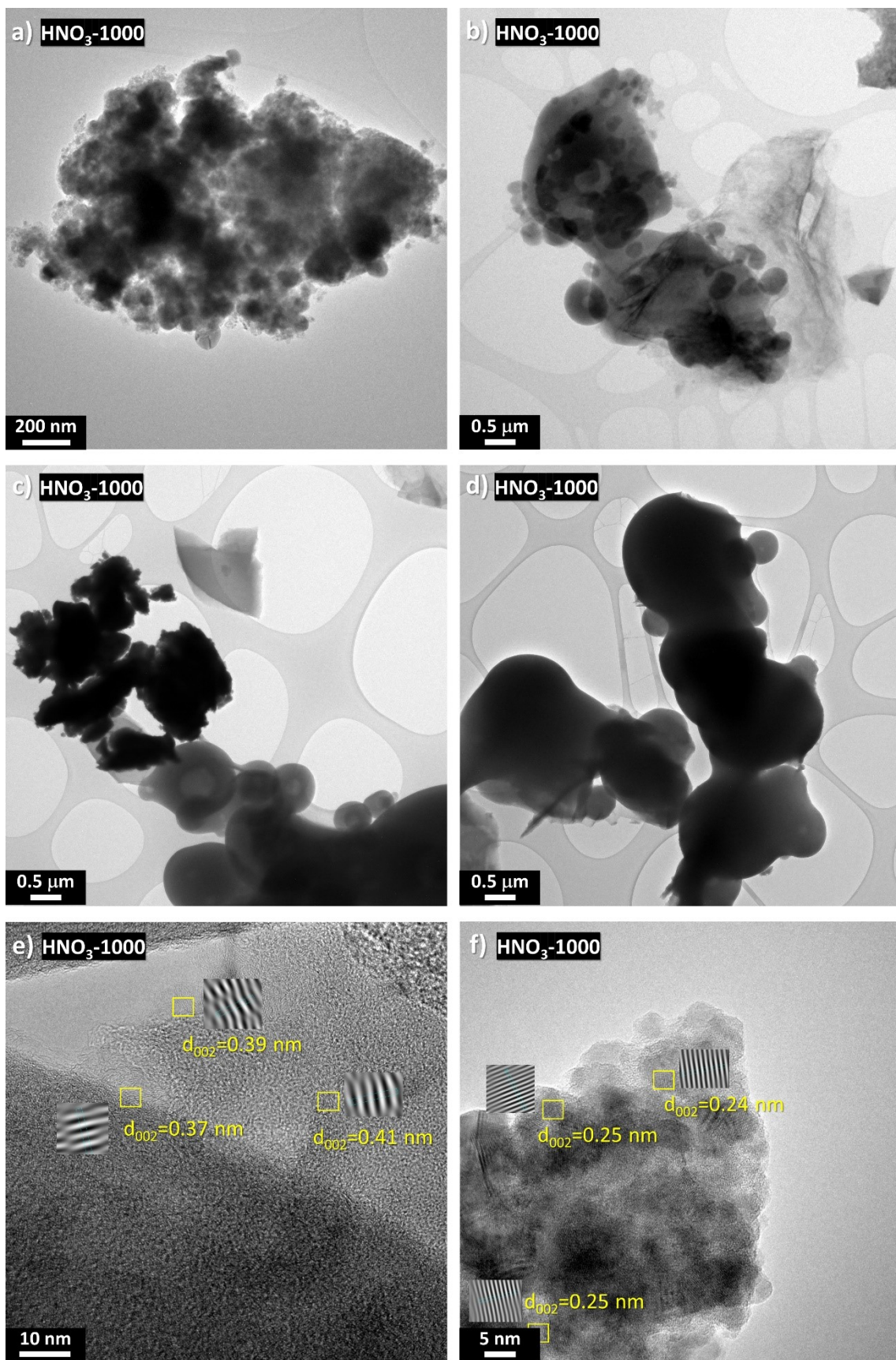


Fig. S7. HR-TEM images of HNO₃-1000.

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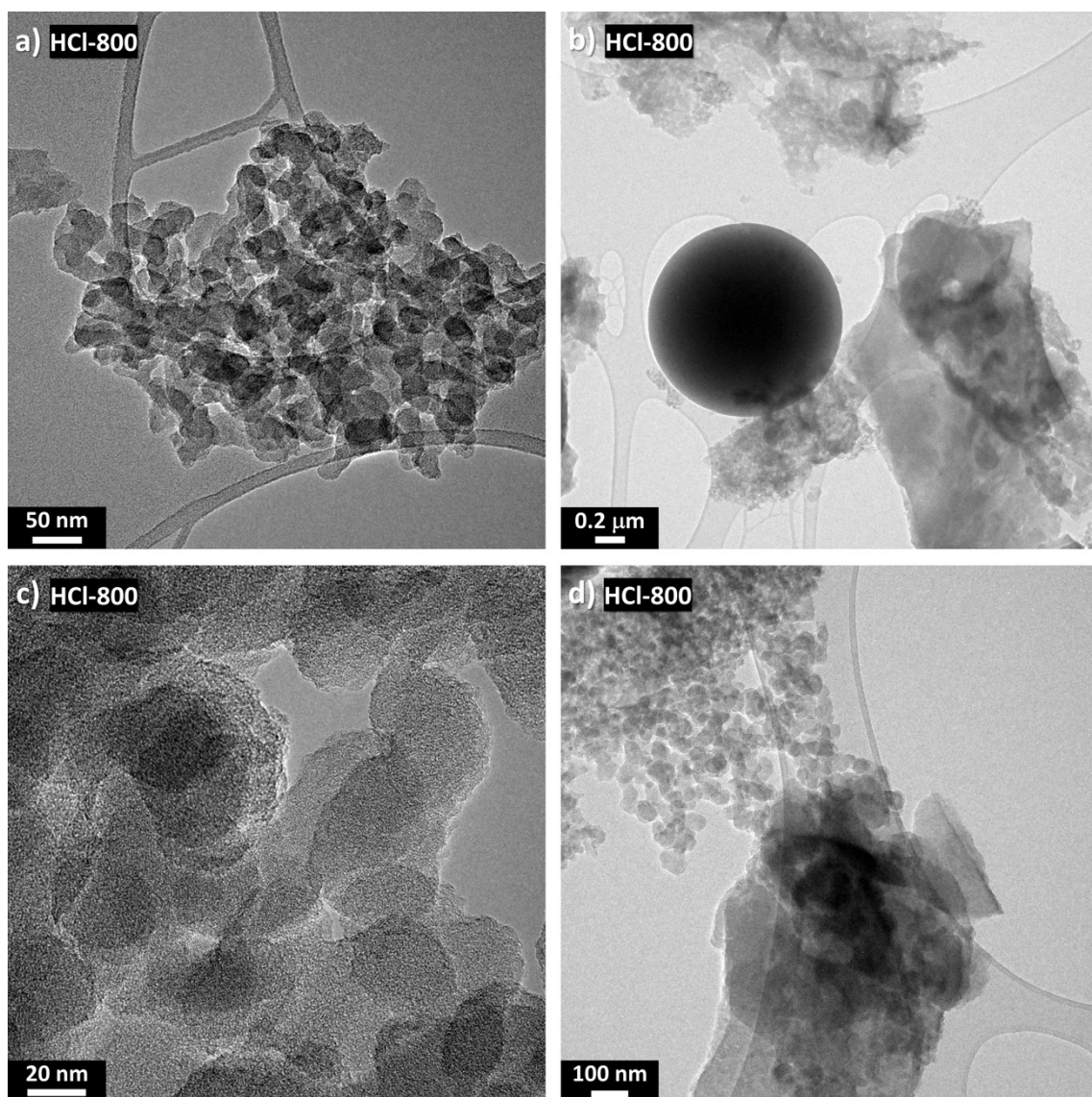


Fig. S8. HR-TEM images of HCl-800.

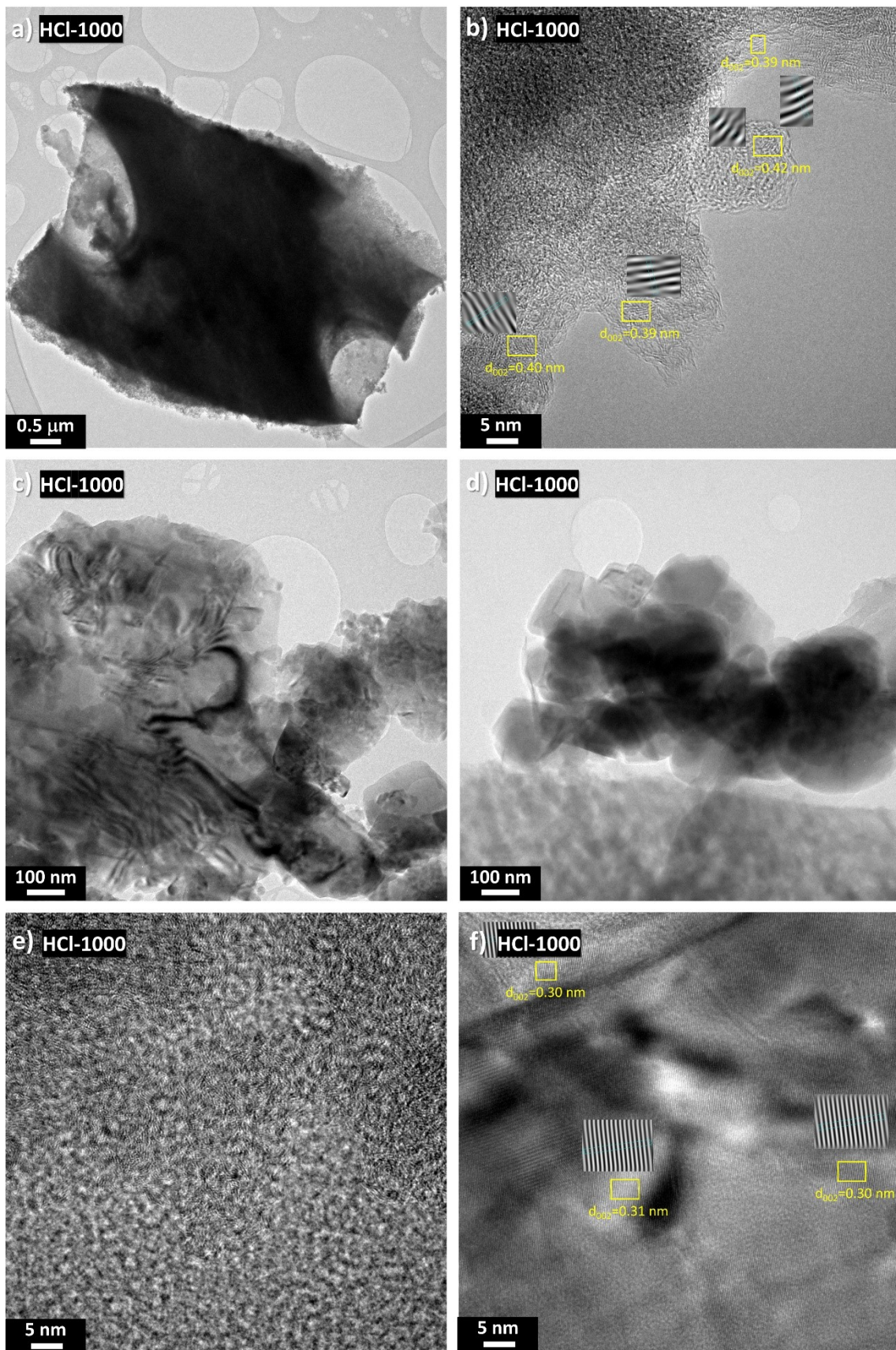


Fig. S9. HR-TEM images of HCl-1000.

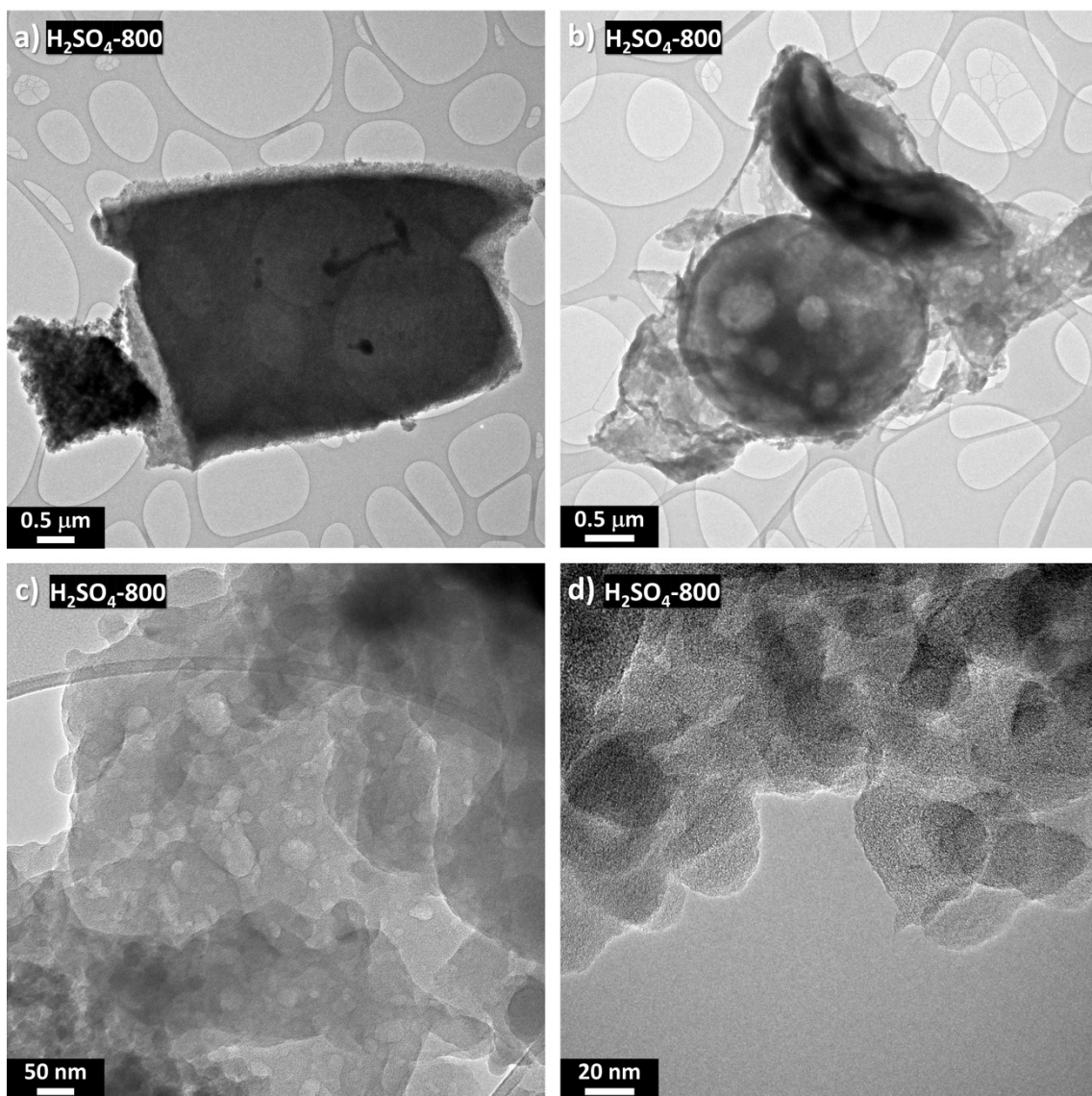


Fig. S10. HR-TEM images of H₂SO₄-800.

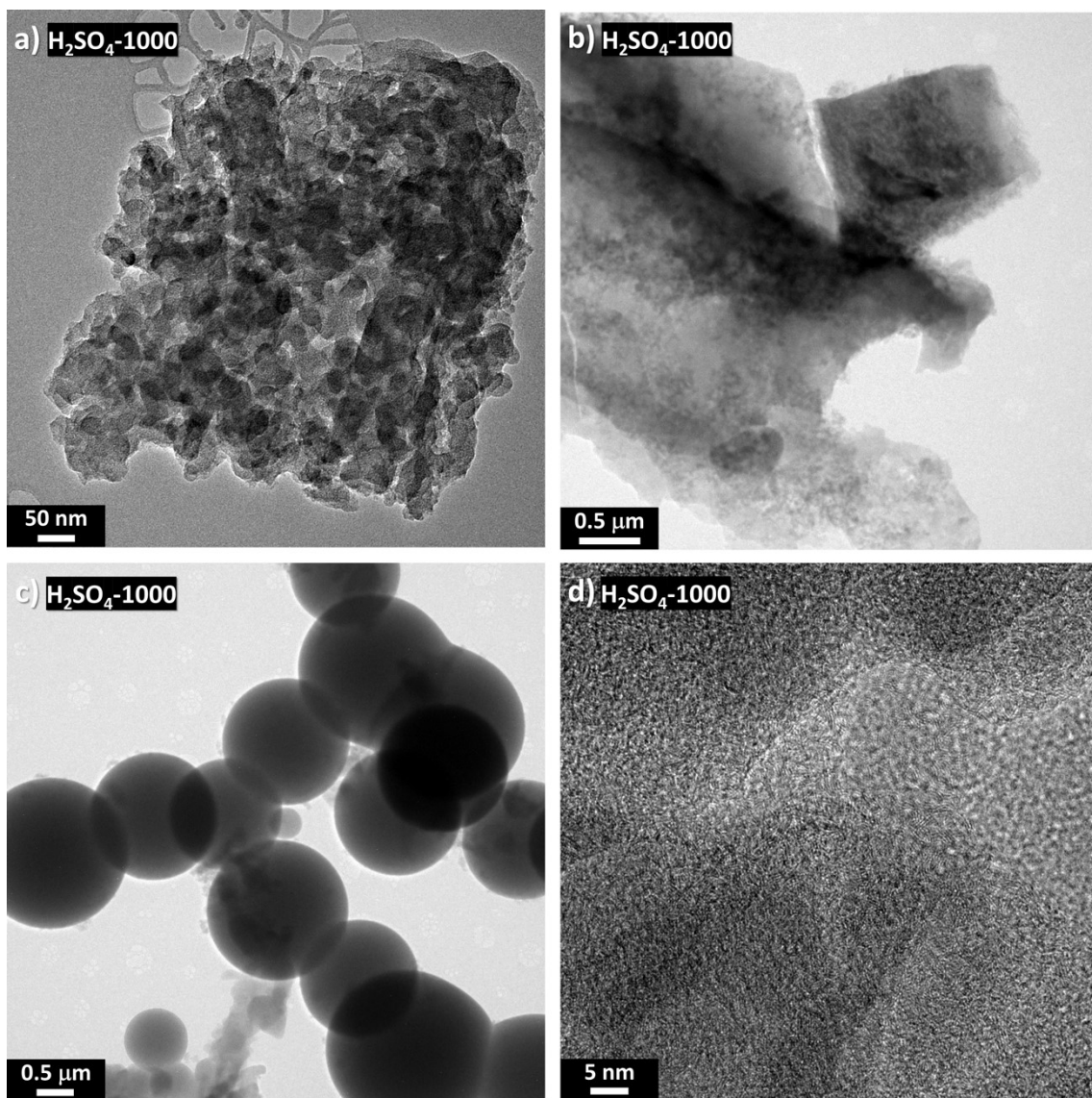


Fig. S11. HR-TEM images of H₂SO₄-1000.

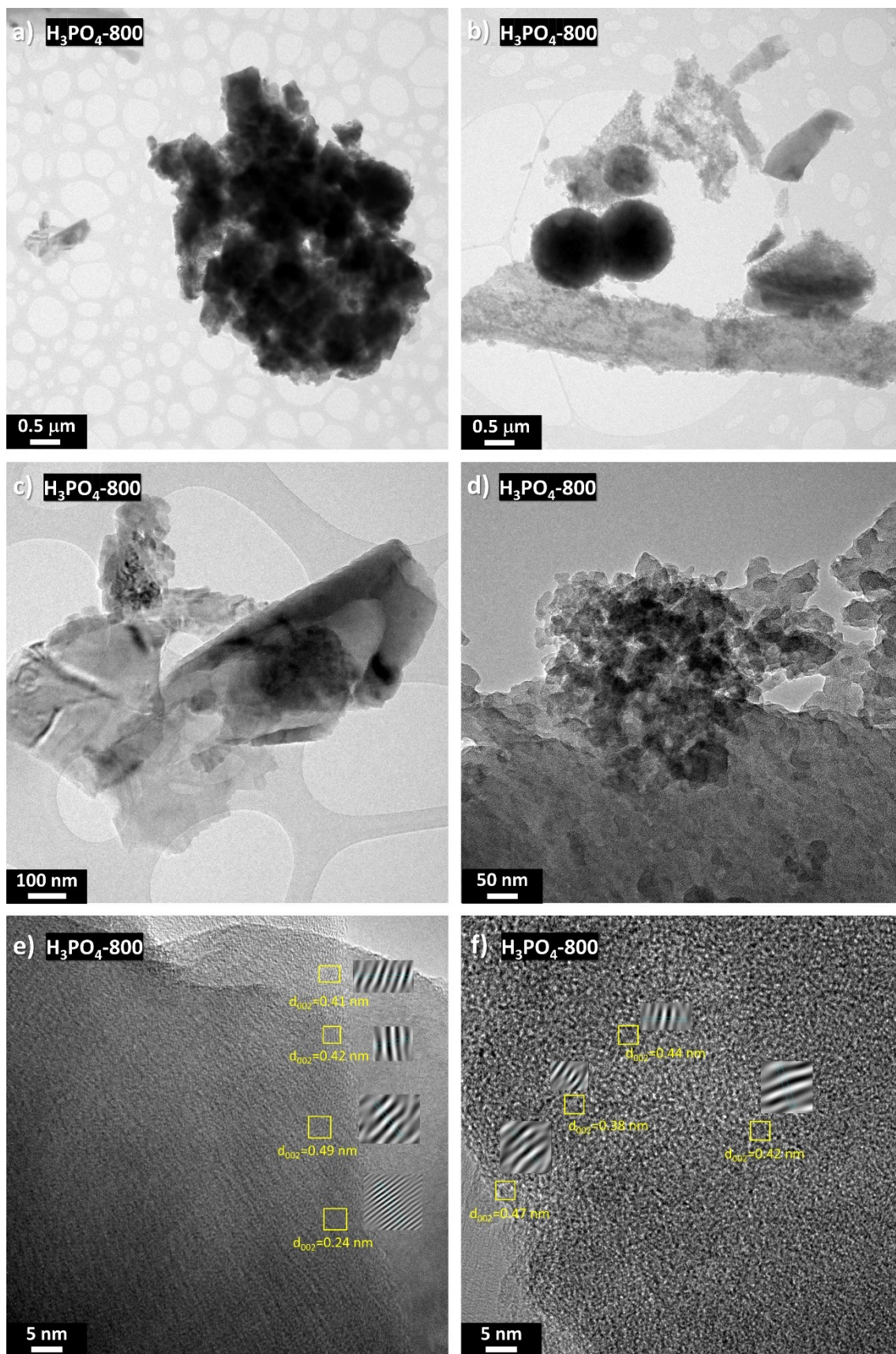


Fig. S12. HR-TEM images of $\text{H}_3\text{PO}_4\text{-800}$.

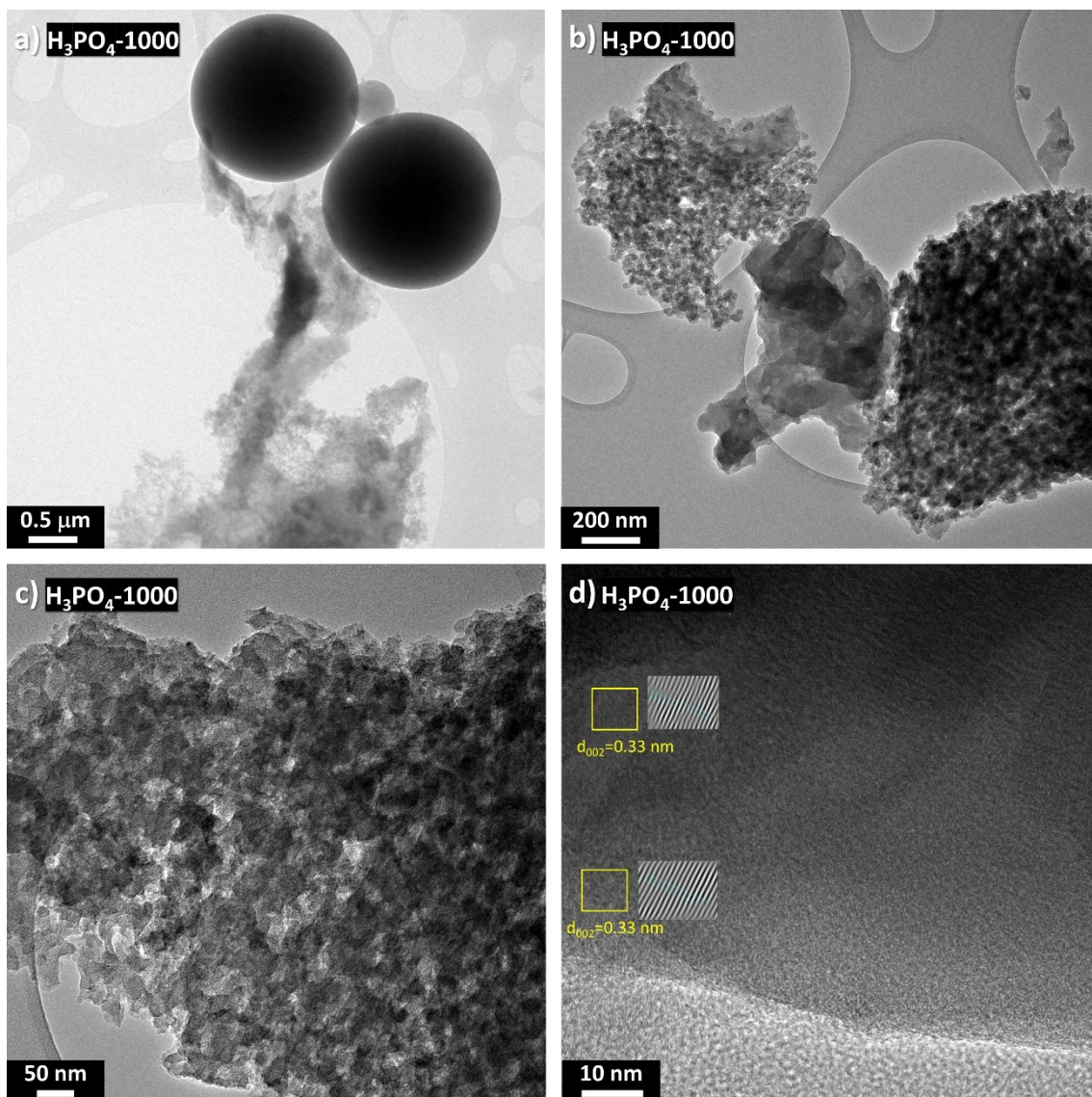


Fig. S13. HR-TEM images of $\text{H}_3\text{PO}_4\text{-1000}$.

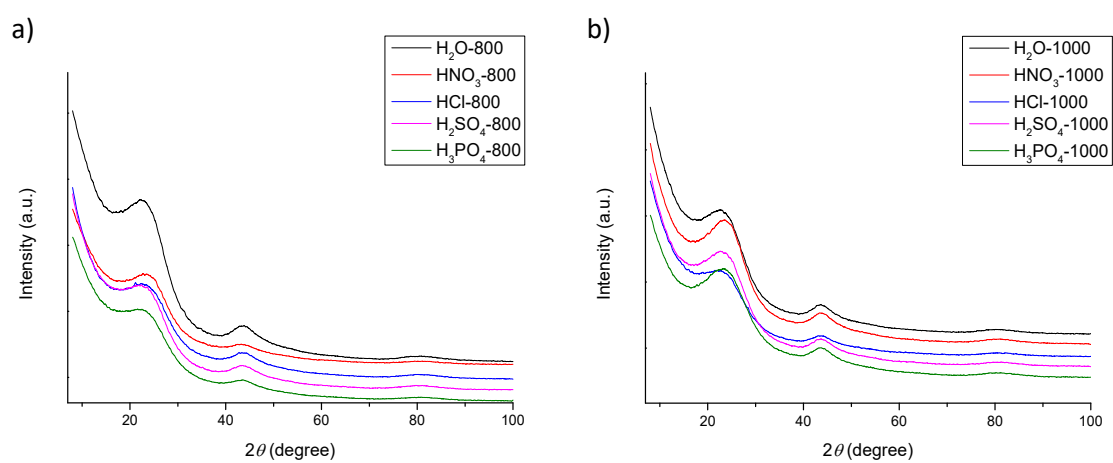


Fig. S14. XRD patterns.

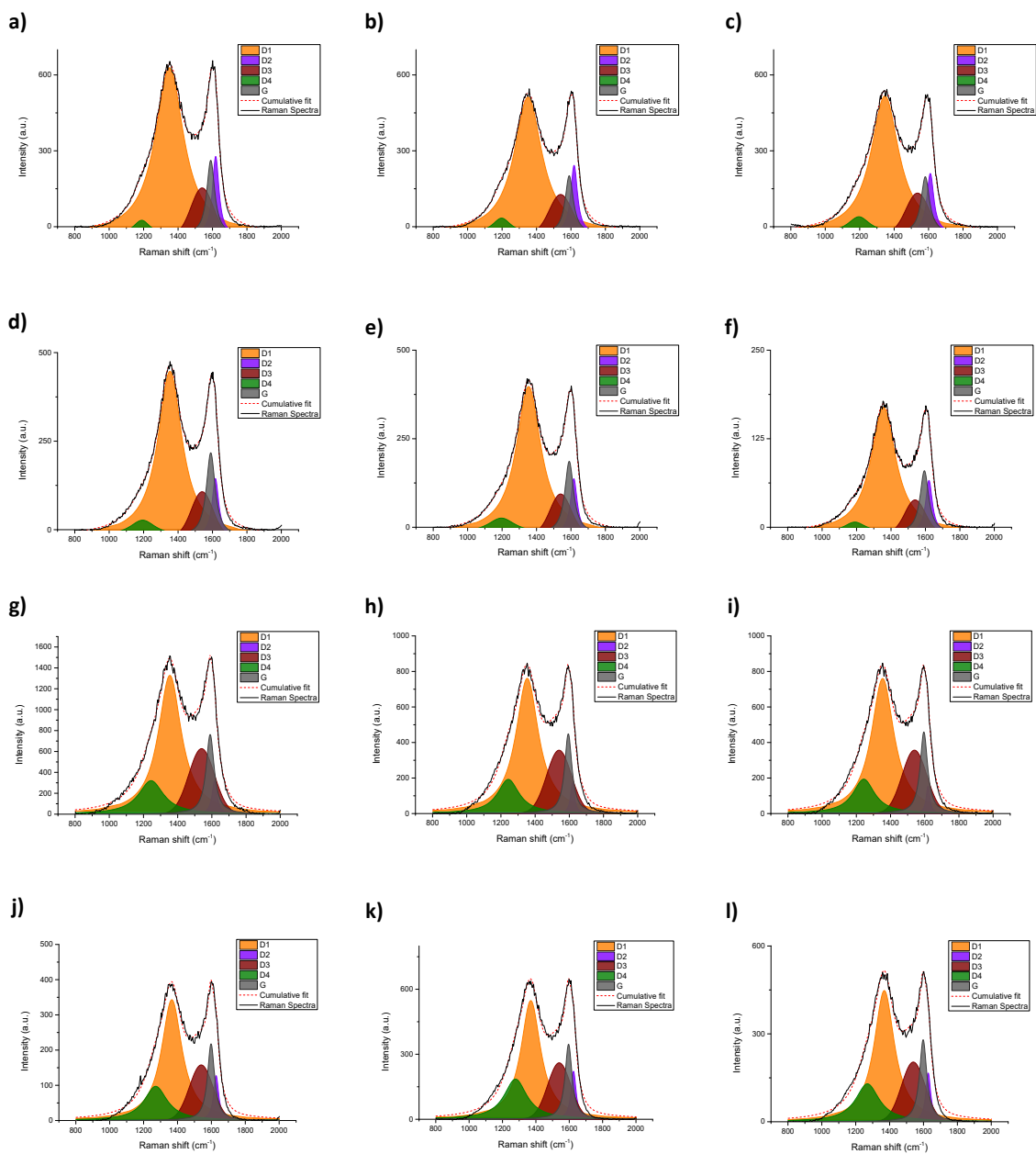


Fig. S15. Raman peaks deconvolution for H₂O-800 (a–c), H₂O-1000 (d–f), HNO₃-800 (g–i), and HNO₃-1000 (j–l) samples.

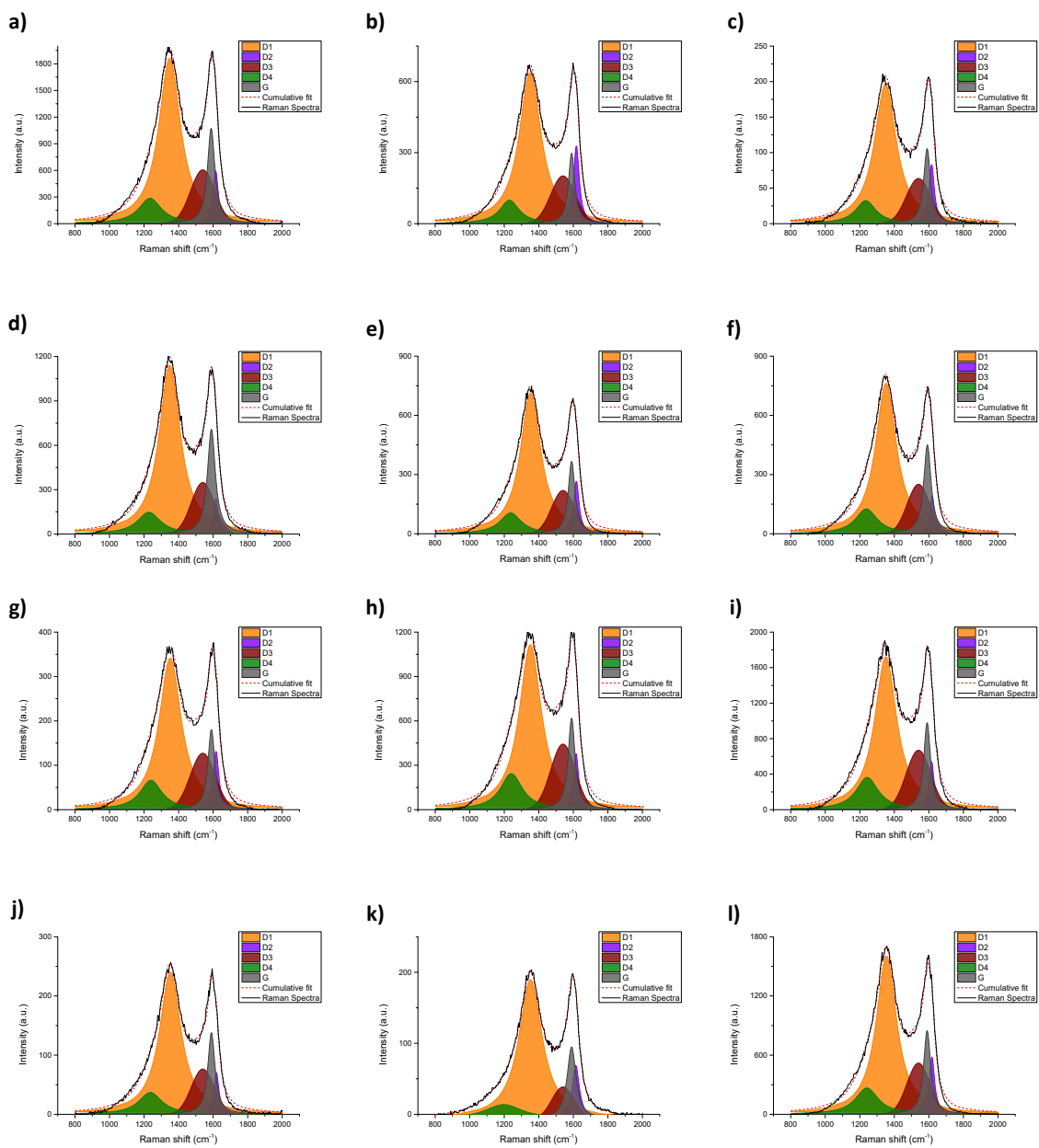


Fig. S16. Raman peaks deconvolution for HCl-800 (a–c), HCl-1000 (d–f), H₂SO₄-800 (g–i), and H₂SO₄-1000 (j–l) samples.

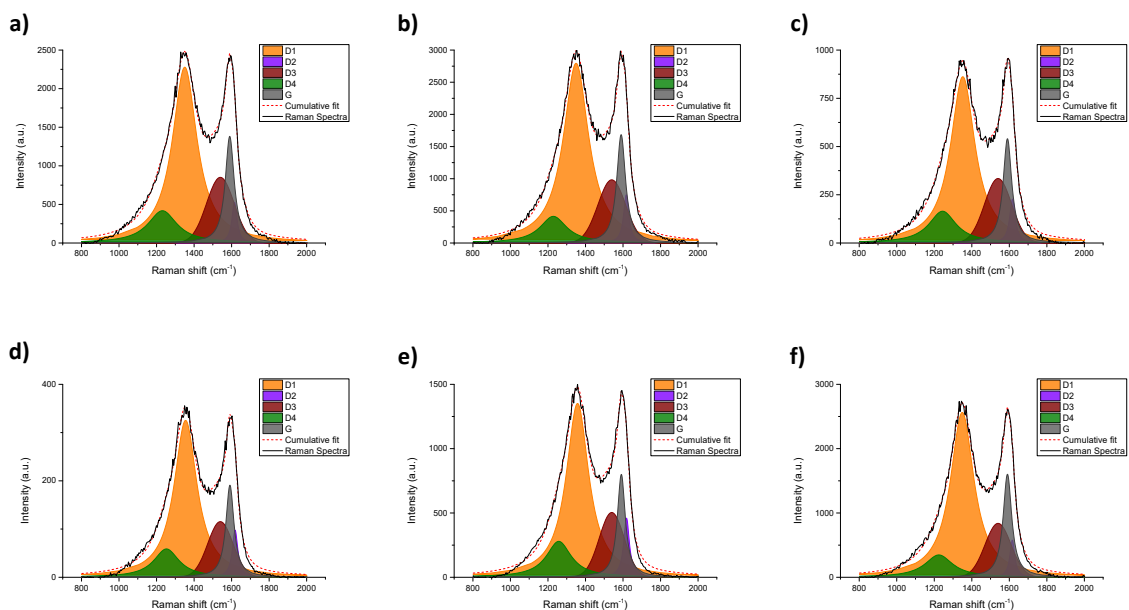


Fig. S17. Raman peaks deconvolution for H_3PO_4-800 (a-c) and H_3PO_4-1000 (d-f).

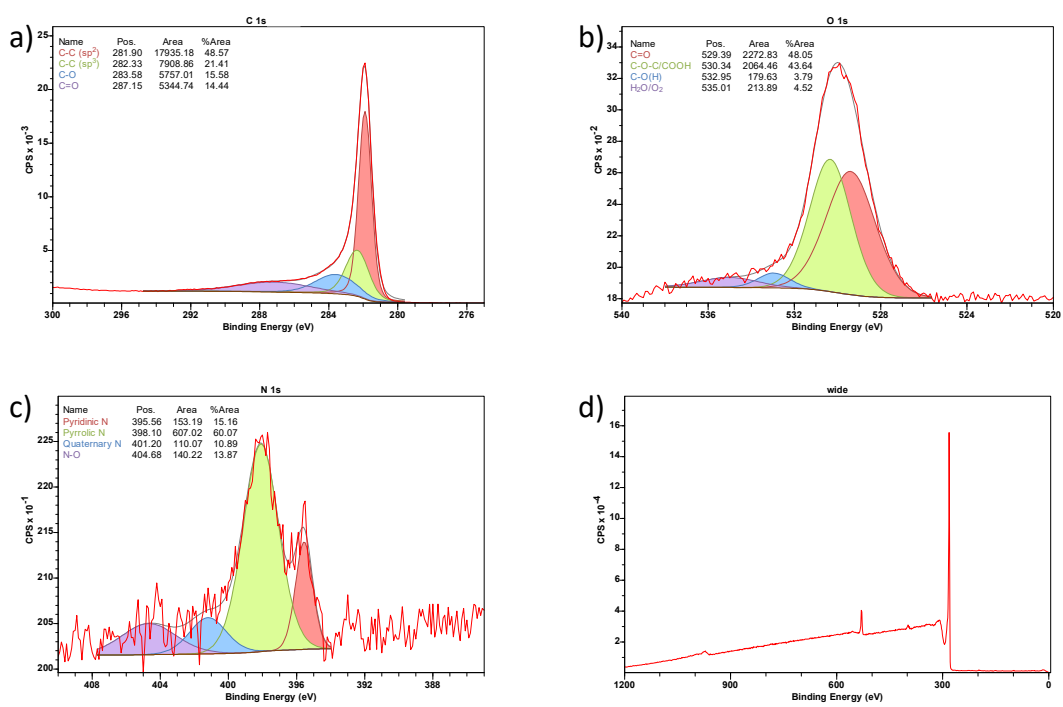


Fig. S18. XPS spectra of H_2O-800 .

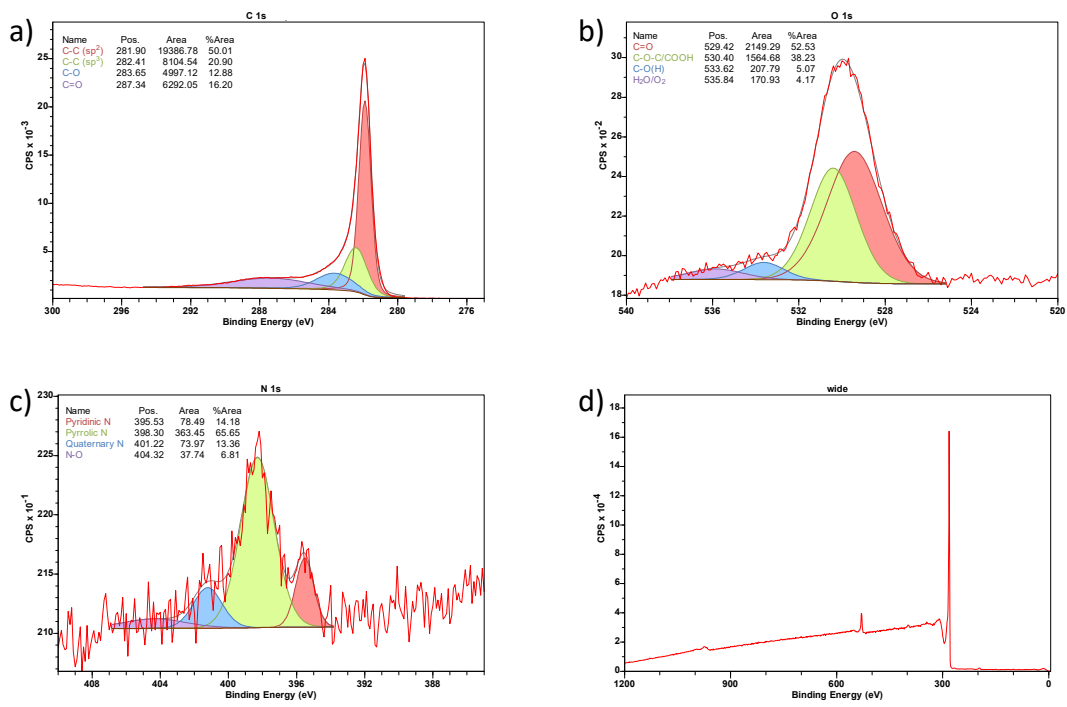


Fig. S19. XPS spectra of H₂O-1000.

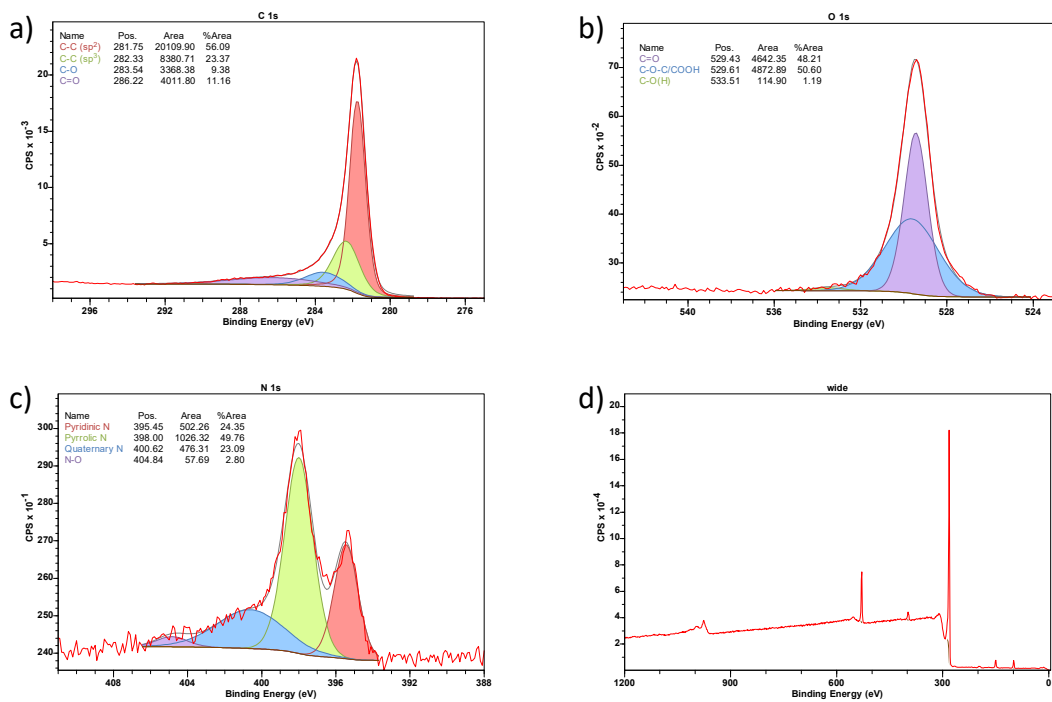


Fig. S20. XPS spectra of HNO₃-800.

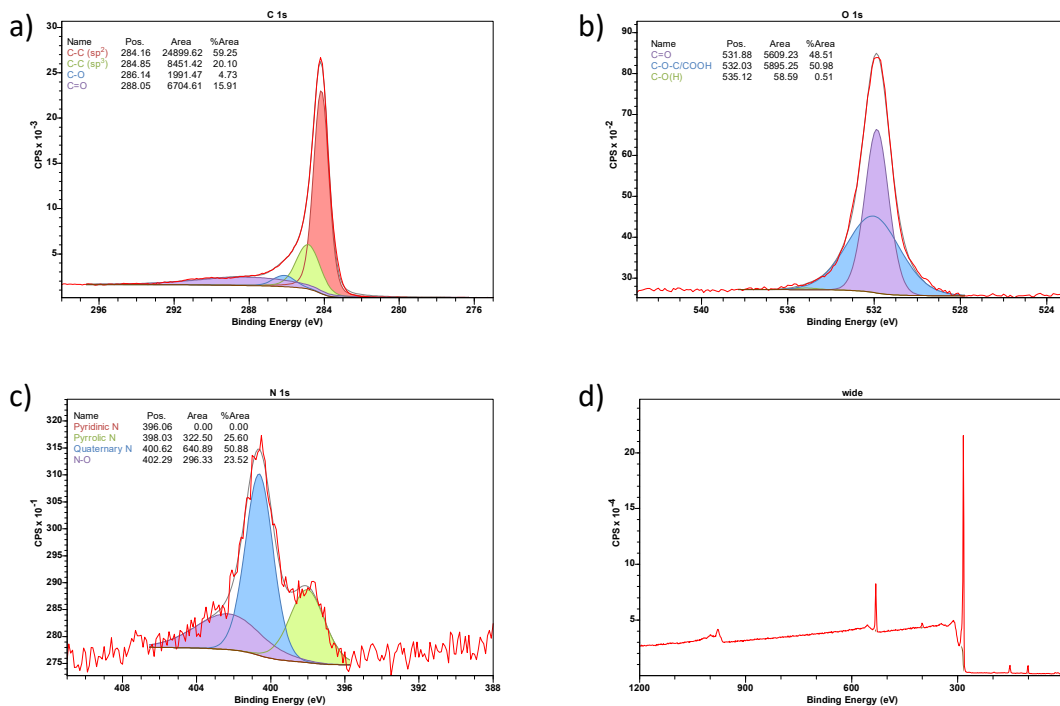


Fig. S21. XPS spectra of HNO₃-1000.

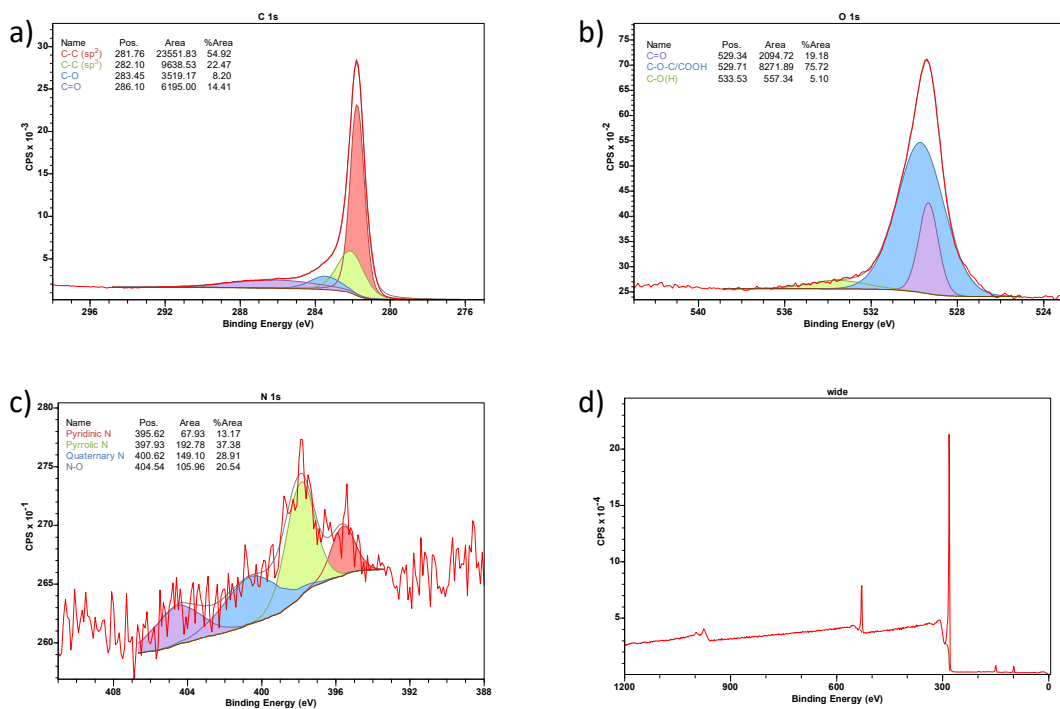


Fig. S22. XPS spectra of HCl-800.

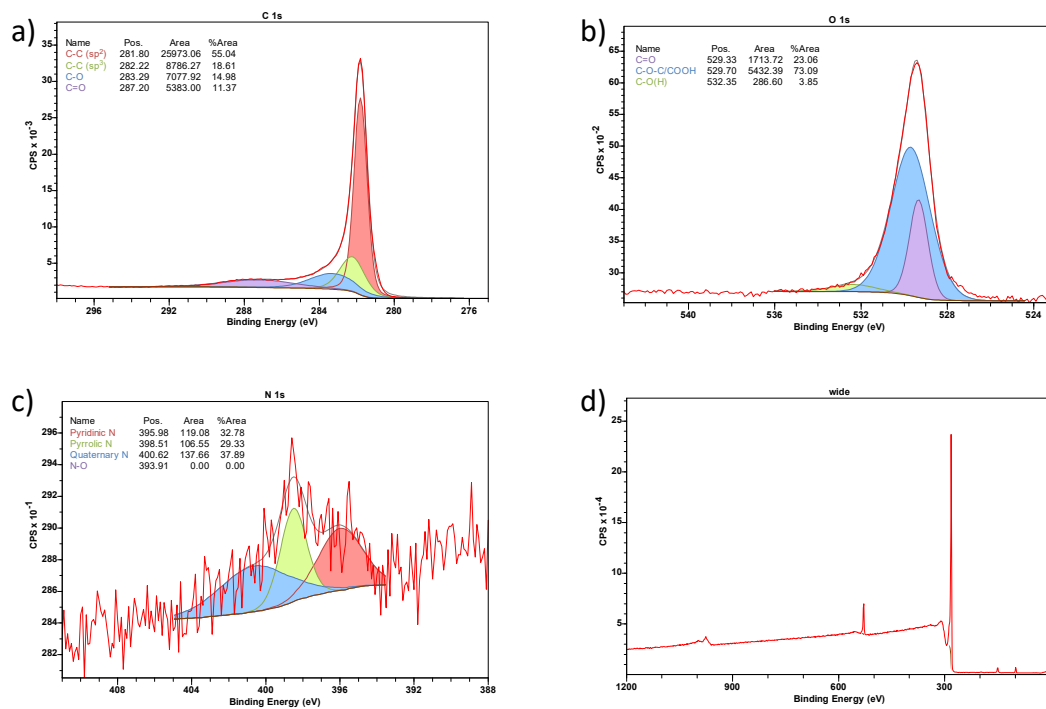


Fig. S23. XPS spectra of HCl-1000.

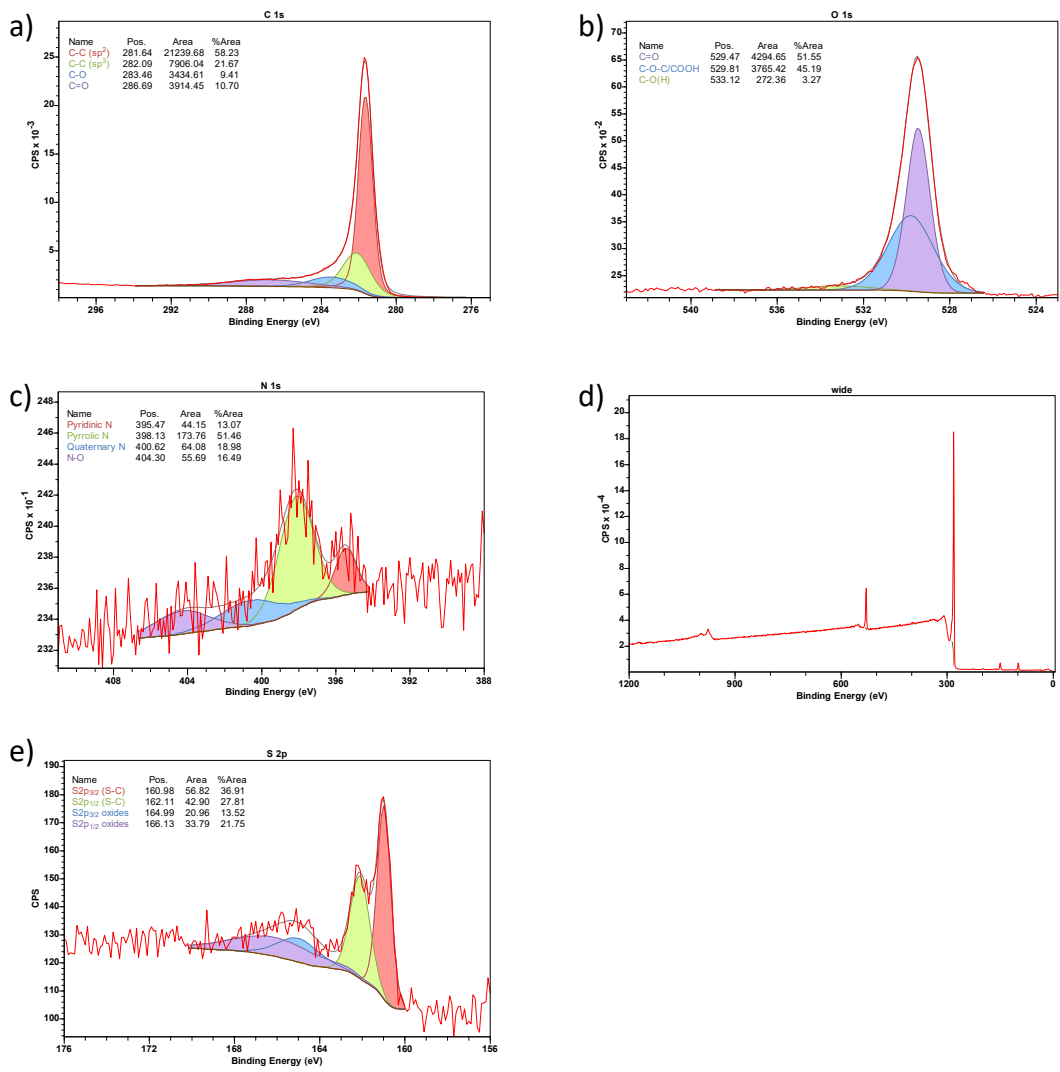


Fig. S24. XPS spectra of H₂SO₄-800.

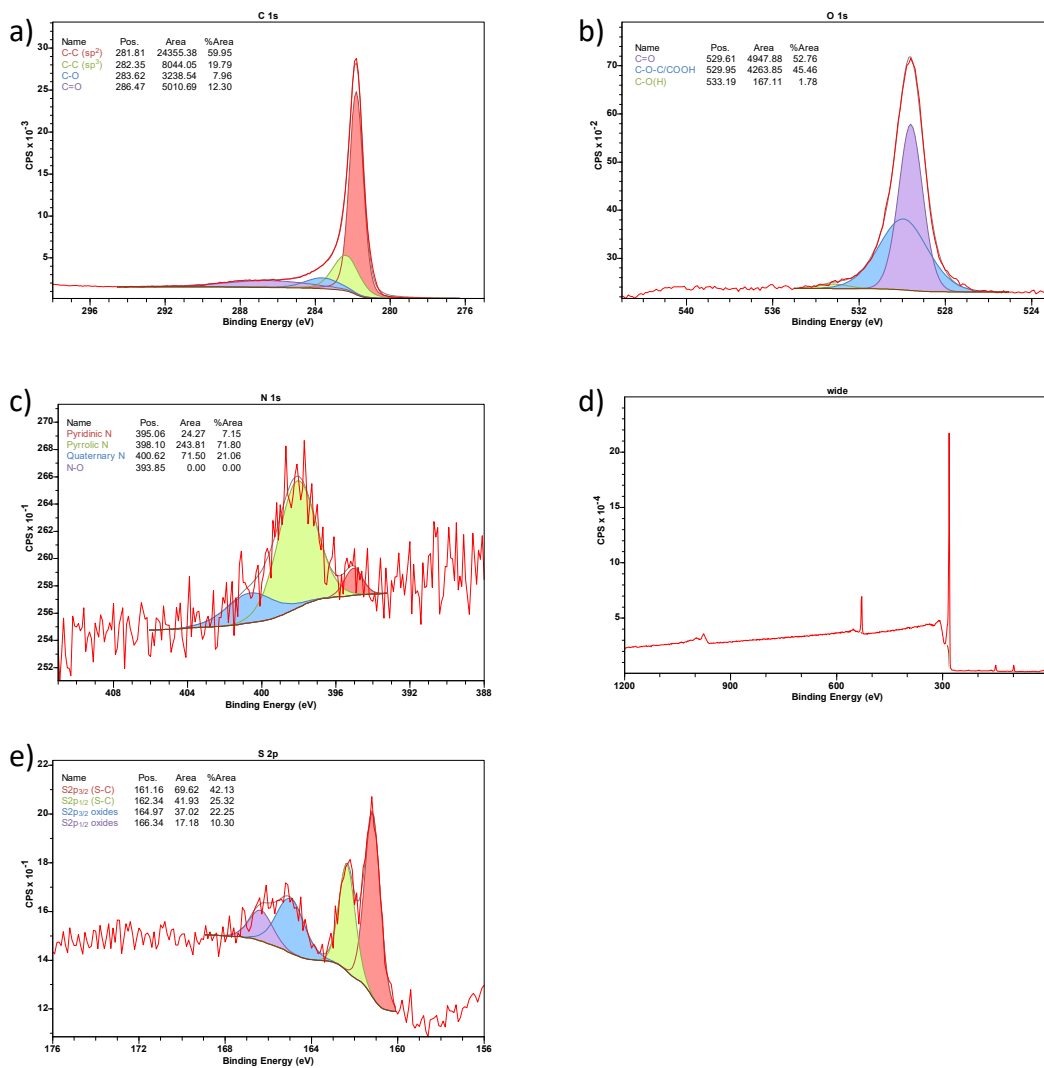


Fig. S25. XPS spectra of H₂SO₄-1000.

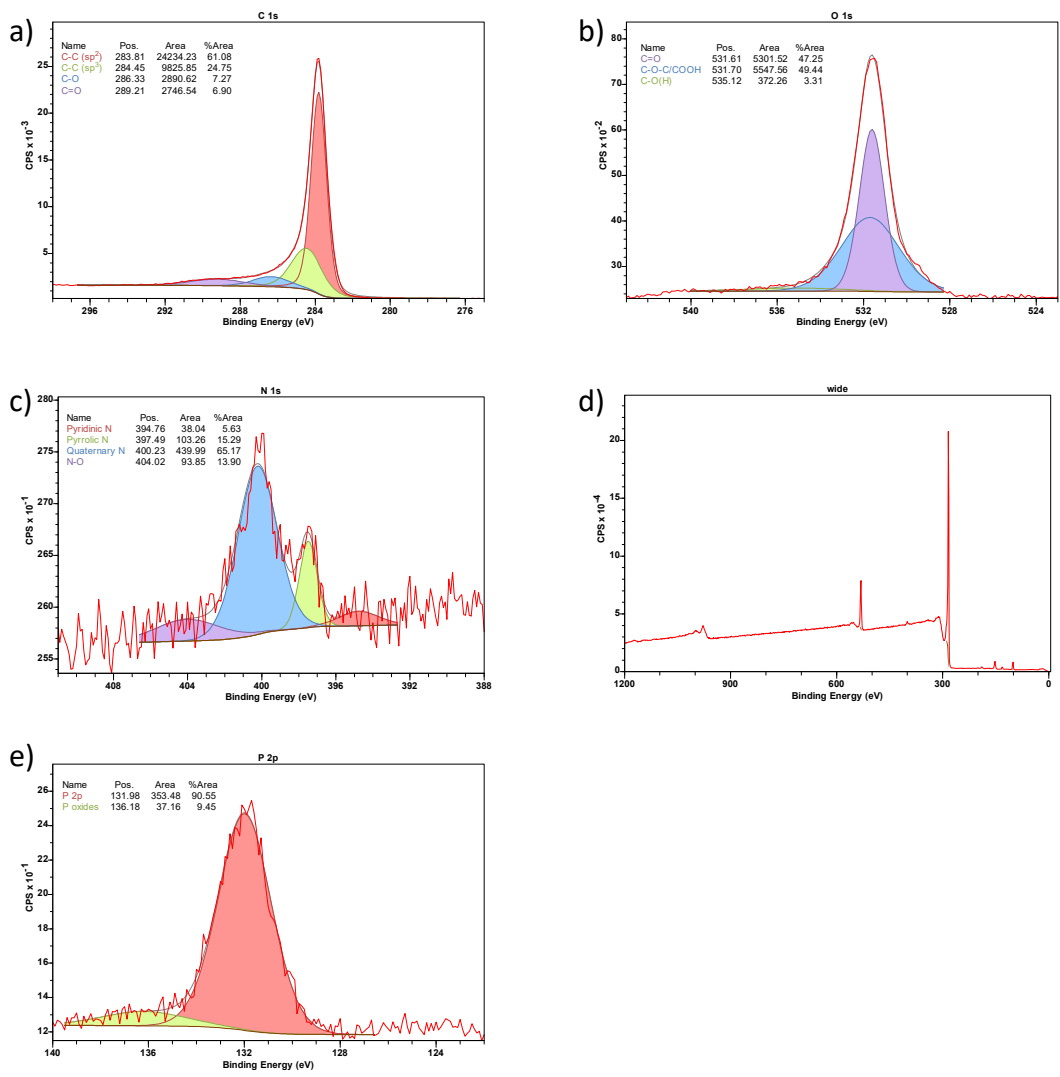


Fig. S26. XPS spectra of H₃PO₄-800.

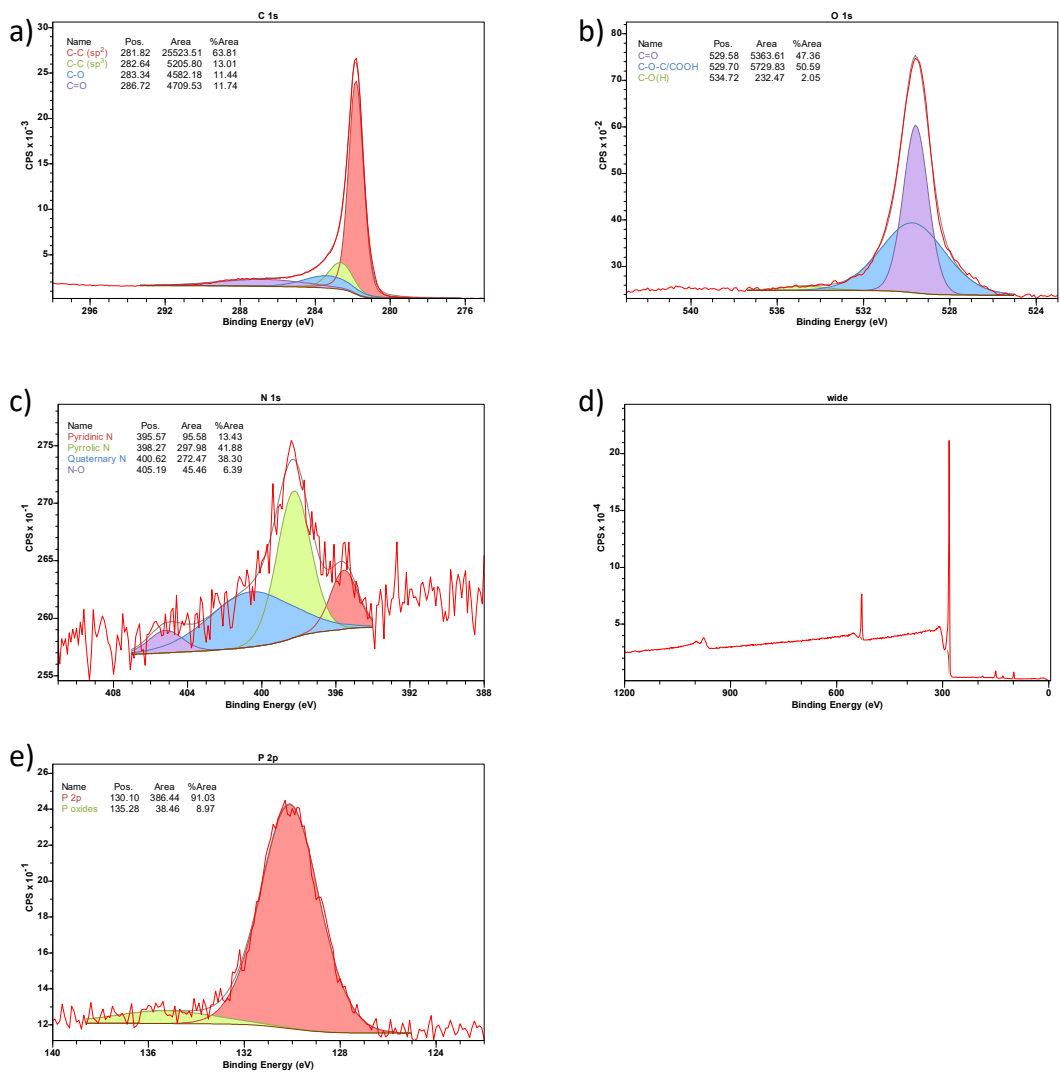


Fig. S27. XPS spectra of H₃PO₄-1000.

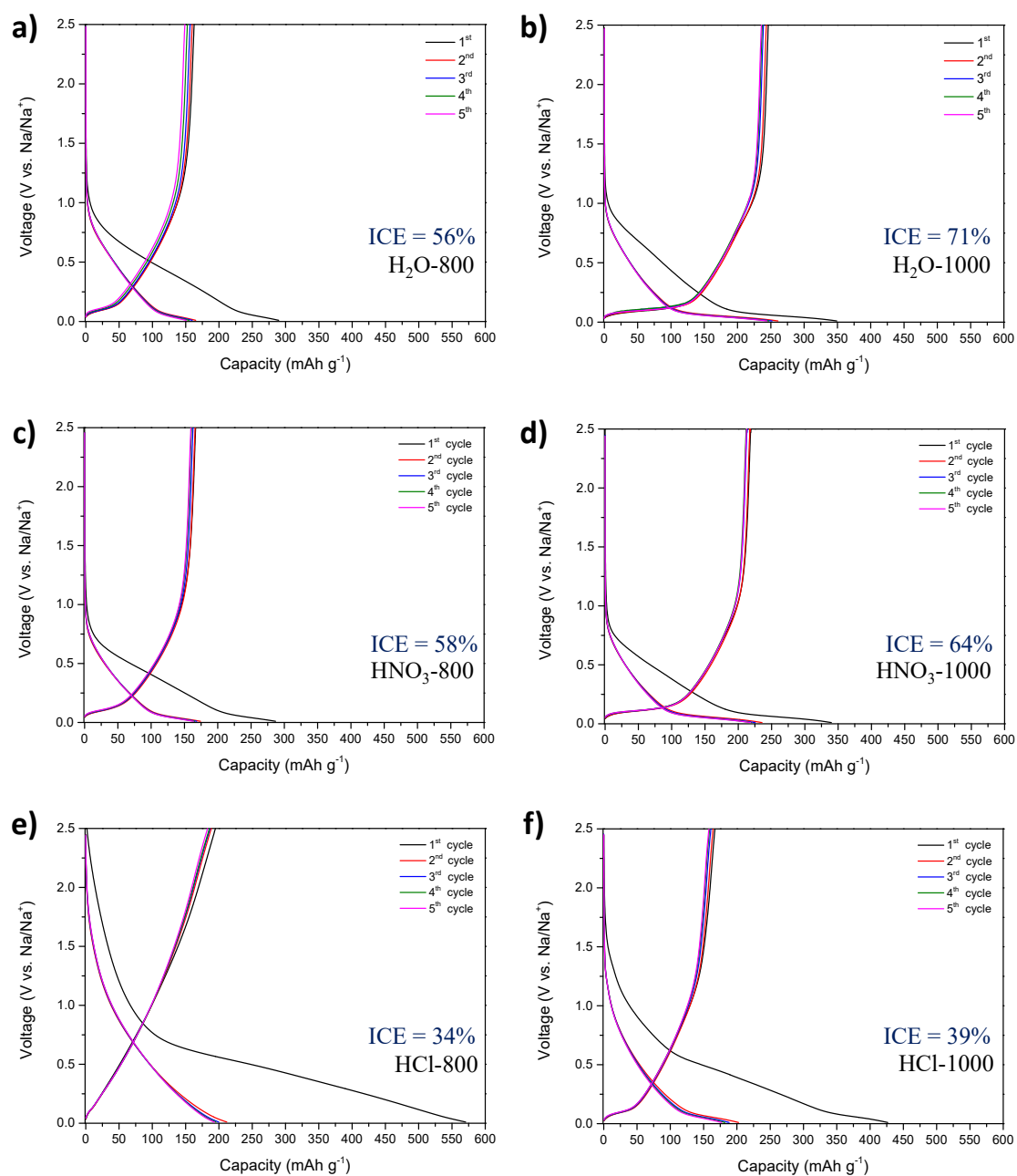


Fig. S28. Galvanostatic dis/charge profiles at a current rate of 0.1 Ag^{-1} in NaTFSI/EC:DMC for (a) H₂O-800, (b) H₂O-1000, (c) HNO₃-800, (d) HNO₃-1000, (e) HCl-800, and (f) HCl-1000.

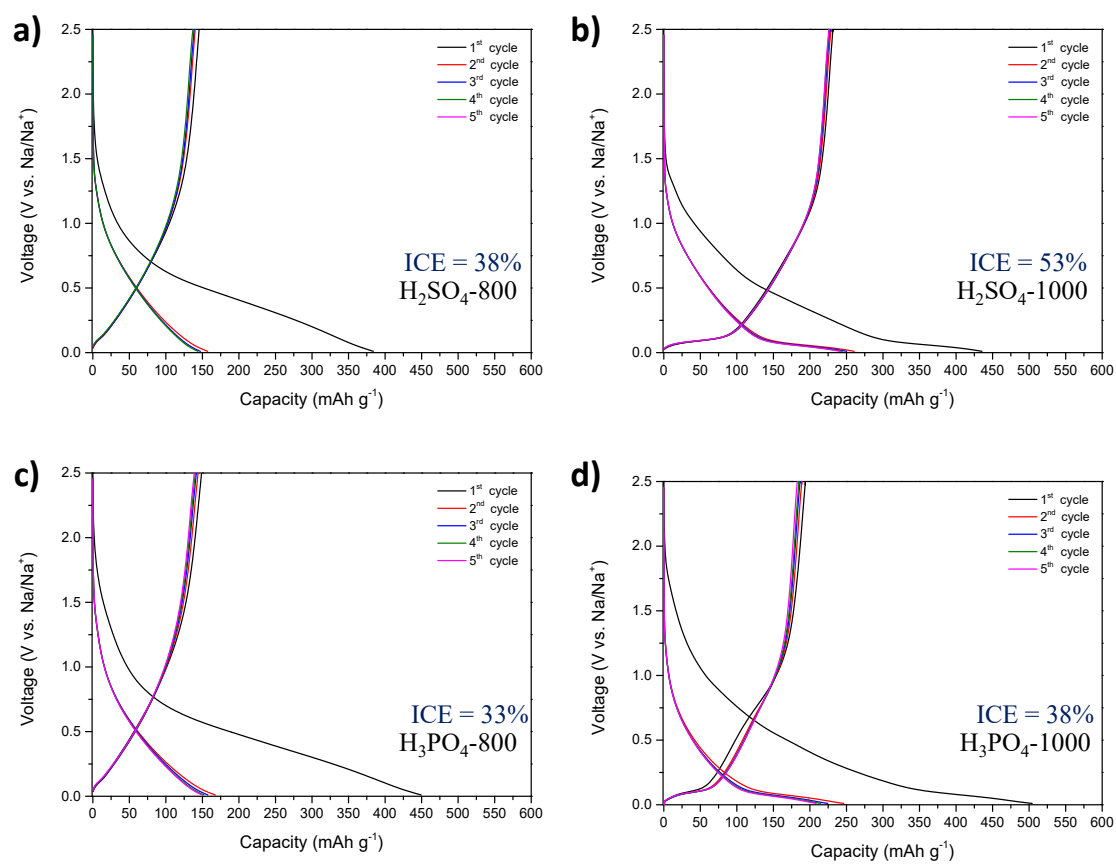


Fig. S29. Galvanostatic dis/charge profiles at a current rate of 0.1 Ag^{-1} in NaTFSI/EC:DMC for (a) $\text{H}_2\text{SO}_4\text{-800}$, (b) $\text{H}_2\text{SO}_4\text{-1000}$, (c) $\text{H}_3\text{PO}_4\text{-800}$, and (d) $\text{H}_3\text{PO}_4\text{-1000}$.

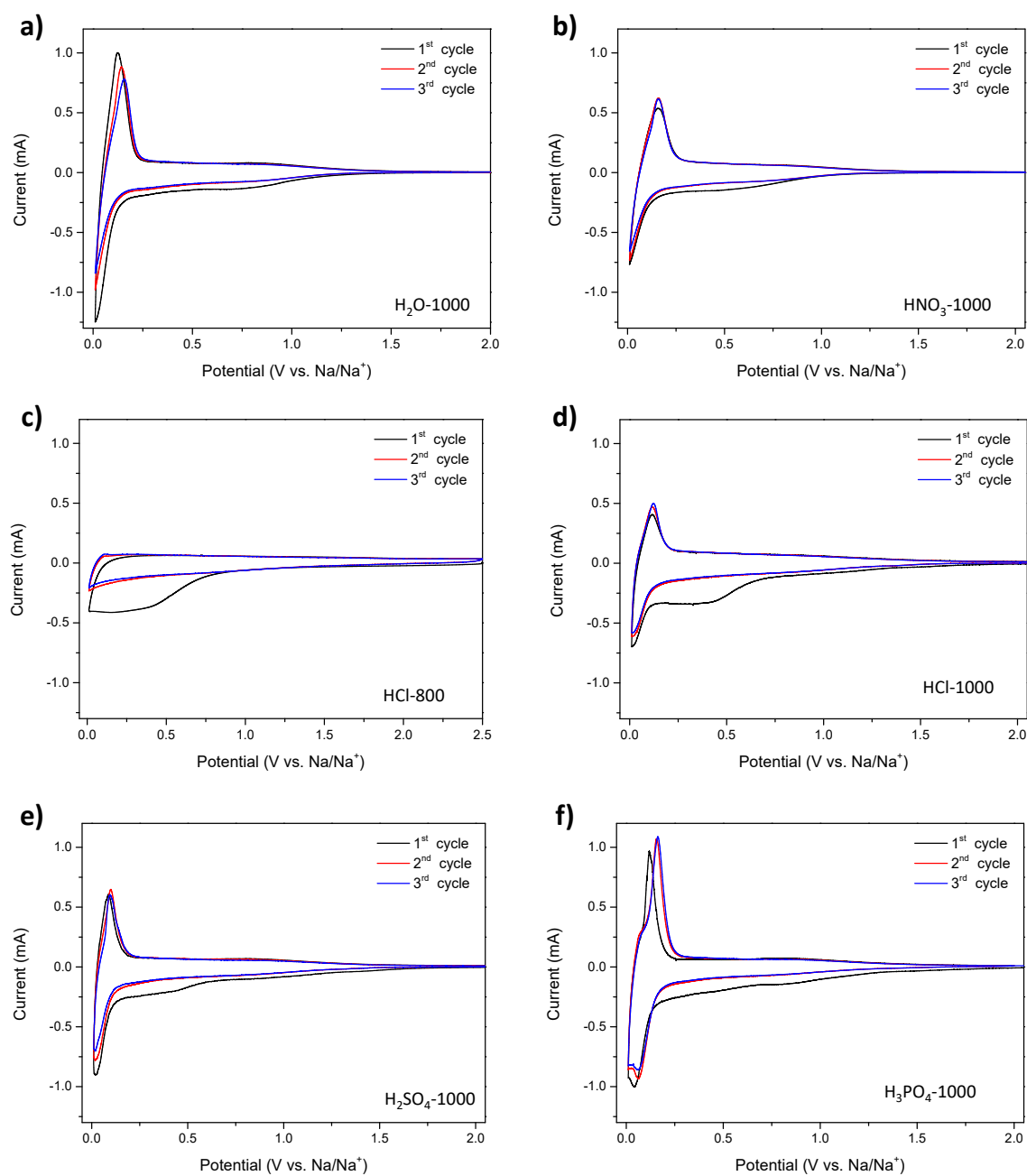


Fig. S30. CV curves of the first five cycles of (a) H₂O-1000, (b) HNO₃-1000, (c) HCl-800, (d) HCl-1000, (e) H₂SO₄-1000, and (f) H₃PO₄-1000 cycled in NaTFSI/DC:DMC electrolyte.

Table S3. Capacity of HCs annealed at 800 °C along cycles at different applied current intensities in NaTFSI_EC:DMC (results referred to the mass of active material in the electrode)

Cycle (A g ⁻¹)	H ₂ O-1000		HNO ₃ -1000		HCl-1000		H ₂ SO ₄ -1000		H ₃ PO ₄ -1000	
	Discharge (mAh g ⁻¹)	Charge (mAh g ⁻¹)	Discharge (mAh g ⁻¹)	Charge (mAh g ⁻¹)	Discharge (mAh g ⁻¹)	Charge (mAh g ⁻¹)	Discharge (mAh g ⁻¹)	Charge (mAh g ⁻¹)	Discharge (mAh g ⁻¹)	Charge (mAh g ⁻¹)
1 (0.1)	289	162	287	167	571	195	384	146	449	149
2 (0.1)	165	160	174	166	212	188	157	140	168	144
3 (0.1)	160	157	168	163	200	187	147	139	158	142
4 (0.1)	155	153	165	160	196	186	144	137	152	140
5 (0.1)	151	149	163	160	193	183	142	136	149	139
6 (0.5)	104	92	105	92	171	146	121	106	123	104
7 (0.5)	91	90	94	93	149	145	105	104	105	102
8 (0.5)	90	90	95	94	149	146	104	103	103	101
9 (0.5)	91	90	95	94	149	146	103	102	102	101
10 (0.5)	91	91	96	96	148	146	103	101	102	100
11 (1)	77	72	74	69	137	126	90	84	87	79
12 (1)	73	72	70	70	128	125	84	84	80	79
13 (1)	73	73	70	70	127	125	84	84	80	80
14 (1)	73	73	71	70	127	125	84	84	80	79
15 (1)	74	74	71	70	126	125	84	84	81	80
16 (2)	57	52	50	45	111	102	69	63	64	57
17 (2)	53	53	46	45	103	102	65	65	59	59
18 (2)	53	53	46	45	103	102	65	65	60	59
19 (2)	53	53	46	45	103	102	65	65	59	59
20 (2)	53	53	45	45	102	102	65	65	60	59
21 (0.1)	130	153	147	167	141	177	110	133	111	136
22 (0.1)	152	151	170	166	183	177	136	132	142	136
23 (0.1)	151	149	169	166	183	177	134	131	141	135
24 (0.1)	150	149	169	165	182	176	134	130	140	134
25 (0.1)	150	149	168	165	181	176	133	130	139	134

Table S4. Capacity of HCs annealed at 1000 °C along cycles at different applied current intensities in NaTFSI_EC:DMC (results referred to the mass of active material in the electrode)

Cycle ($A\ g^{-1}$)	H ₂ O-1000		HNO ₃ -1000		HCl-1000		H ₂ SO ₄ -1000		H ₃ PO ₄ -1000	
	Discharge (mAh g ⁻¹)	Charge (mAh g ⁻¹)	Discharge (mAh g ⁻¹)	Charge (mAh g ⁻¹)	Discharge (mAh g ⁻¹)	Charge (mAh g ⁻¹)	Discharge (mAh g ⁻¹)	Charge (mAh g ⁻¹)	Discharge (mAh g ⁻¹)	Charge (mAh g ⁻¹)
1 (0.1)	349	246	341	219	427	167	438	232	506	194
2 (0.1)	261	243	237	218	202	164	261	230	247	190
3 (0.1)	252	239	226	214	188	161	251	228	225	187
4 (0.1)	247	237	220	213	182	159	245	228	216	186
5 (0.1)	244	236	219	213	177	158	243	227	209	183
6 (0.5)	122	110	105	93	137	122	189	173	166	147
7 (0.5)	104	102	89	88	123	118	167	163	144	139
8 (0.5)	101	101	86	85	122	118	166	164	137	133
9 (0.5)	101	101	85	85	122	118	170	167	132	129
10 (0.5)	102	101	84	84	123	119	171	169	129	126
11 (1)	75	71	60	55	103	96	133	126	101	94
12 (1)	73	72	56	56	99	97	128	126	89	88
13 (1)	73	72	56	56	100	98	129	127	85	84
14 (1)	72	72	56	56	101	99	130	129	81	80
15 (1)	72	72	56	56	101	100	128	127	78	77
16 (2)	52	48	34	30	83	77	98	92	57	52
17 (2)	50	50	32	32	79	79	93	92	51	50
18 (2)	50	50	32	32	81	80	93	92	49	49
19 (2)	50	50	32	32	80	79	92	92	48	48
20 (2)	50	50	32	32	79	78	92	92	47	47
21 (0.1)	219	233	194	209	148	158	211	225	158	170
22 (0.1)	233	228	210	207	169	157	233	224	178	167
23 (0.1)	232	228	209	206	168	157	232	224	175	165
24 (0.1)	233	228	207	204	167	156	231	225	173	164
25 (0.1)	233	229	206	204	166	156	232	224	171	163

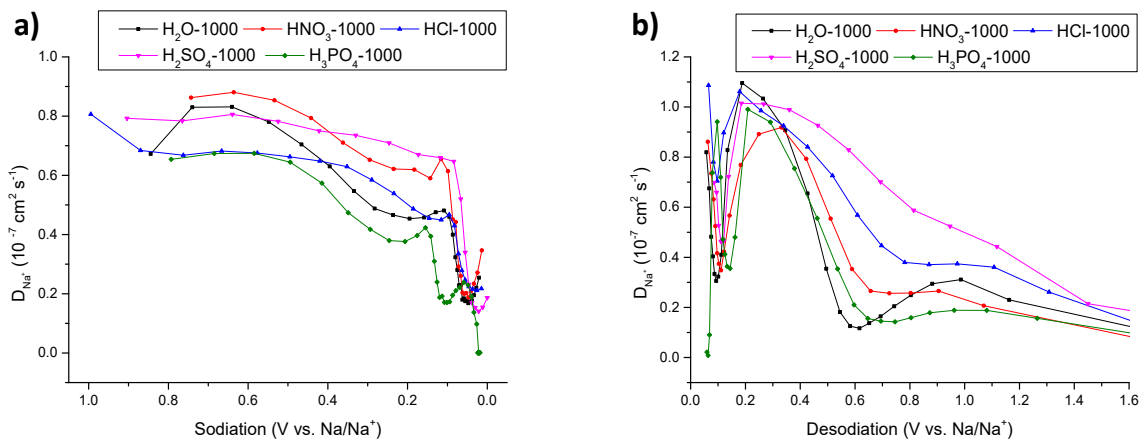


Fig. S31. D_{Na^+} values calculated from GITT measurements along c) sodiation and d) desodiation in NaTFSI/EC:DMC electrolyte.

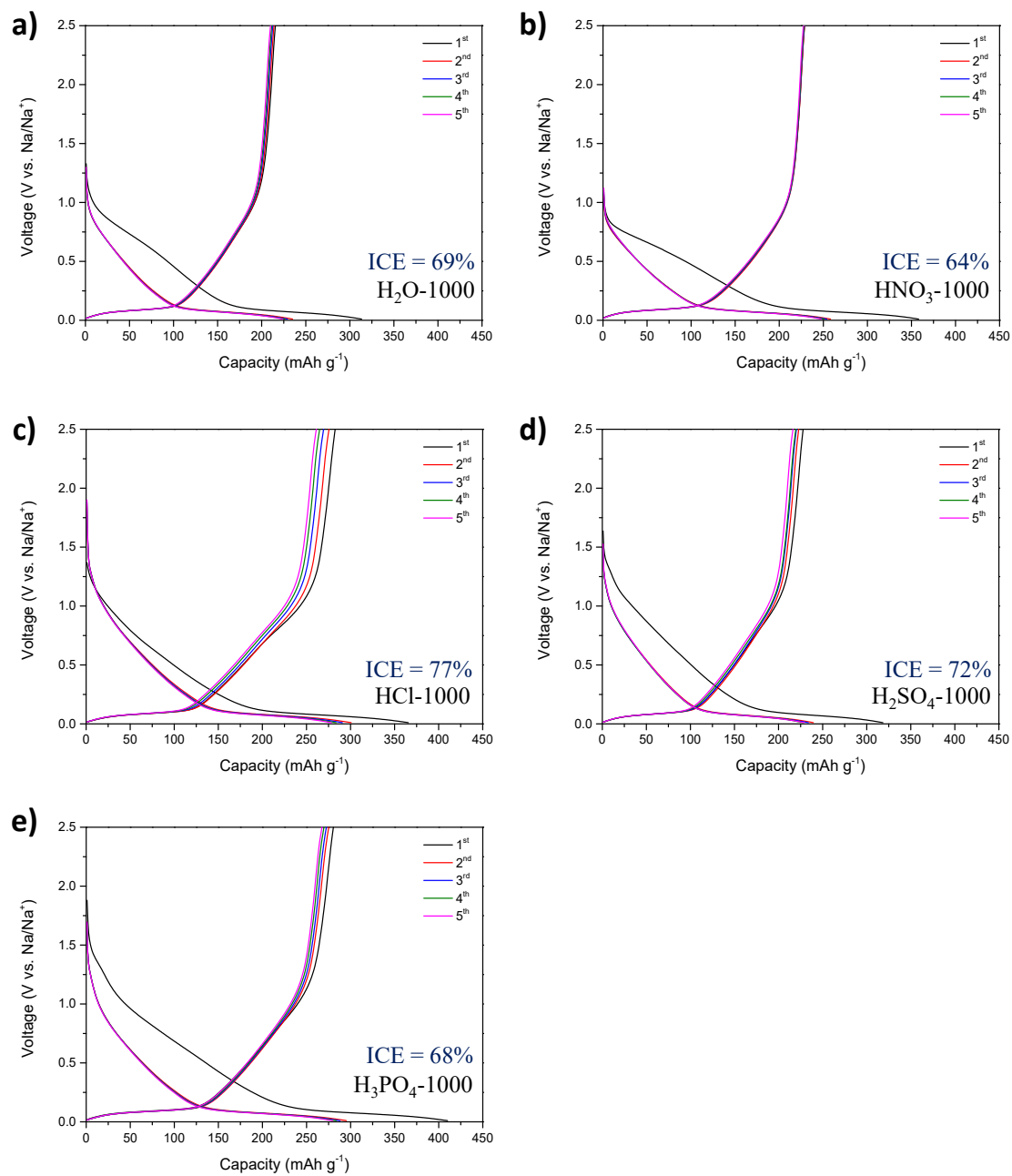


Fig. S32. Galvanostatic dis/charge profiles at a current rate of 0.1 Ag^{-1} in NaPF_6/DGM for a) H_2O -1000, b) HNO_3 -1000, c) HCl -1000, d) H_2SO_4 -1000, and e) H_3PO_4 -1000.

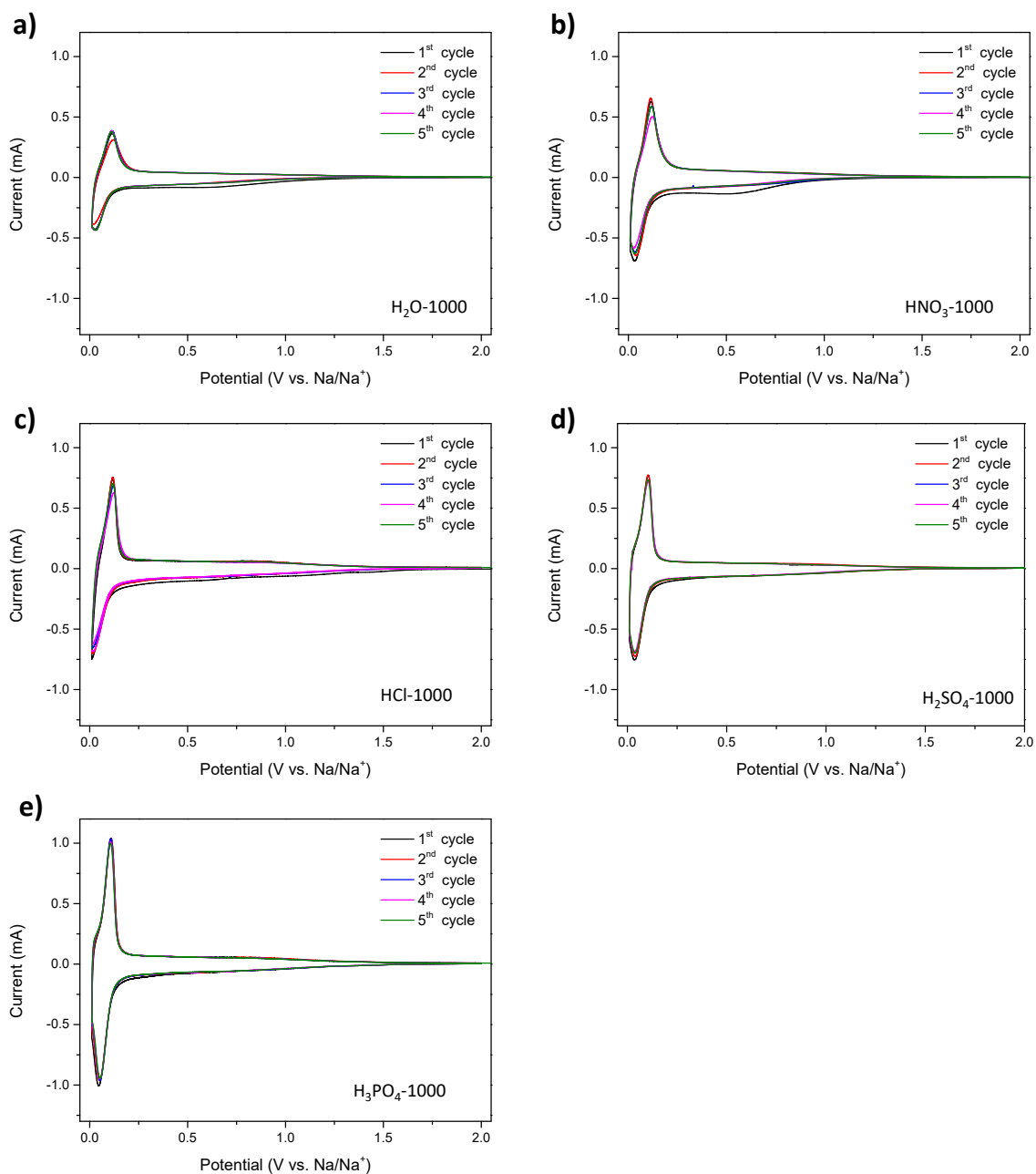


Fig. S33. CV curves of the first five cycles of a) H₂O-1000, b) HNO₃-1000, c) HCl-1000, d) H₂SO₄-1000, and e) H₃PO₄-1000 cycled in NaPF₆/DGM electrolyte.

Table S5. Capacity of HCs along cycles at different applied current intensities in NaPF₆/DGM (results referred to the mass of active material in the electrode)

Cycle (A g ⁻¹)	H ₂ O-1000		HNO ₃ -1000		HCl-1000		H ₂ SO ₄ -1000		H ₃ PO ₄ -1000	
	Discharge (mAh g ⁻¹)	Charge (mAh g ⁻¹)	Discharge (mAh g ⁻¹)	Charge (mAh g ⁻¹)	Discharge (mAh g ⁻¹)	Charge (mAh g ⁻¹)	Discharge (mAh g ⁻¹)	Charge (mAh g ⁻¹)	Discharge (mAh g ⁻¹)	Charge (mAh g ⁻¹)
1 (0.1)	313	215	358	229	366	283	318	228	413	281
2 (0.1)	235	214	258	229	301	276	240	223	295	275
3 (0.1)	229	213	254	228	291	269	234	220	288	273
4 (0.1)	226	211	251	228	284	265	228	220	284	270
5 (0.1)	224	210	248	227	278	261	229	216	280	268
6 (0.5)	204	188	214	194	255	241	213	200	260	245
7 (0.5)	191	188	200	195	244	240	202	198	247	244
8 (0.5)	190	187	199	195	242	239	200	197	245	242
9 (0.5)	189	186	198	195	241	237	199	196	244	241
10 (0.5)	189	186	198	195	239	236	198	195	243	240
11 (1)	179	172	180	171	231	223	192	187	232	226
12 (1)	173	172	173	171	226	223	186	186	226	225
13 (1)	173	171	173	171	225	222	186	185	225	224
14 (1)	172	171	173	171	224	221	185	185	224	224
15 (1)	172	171	173	171	223	221	184	184	224	223
16 (2)	156	149	137	130	208	202	176	171	206	200
17 (2)	150	149	131	130	203	202	171	171	200	199
18 (2)	149	149	131	130	202	201	170	170	199	199
19 (2)	149	148	131	130	202	201	170	170	199	198
20 (2)	148	148	131	130	201	200	169	169	198	198
21 (0.1)	188	206	208	227	241	249	195	209	241	259
22 (0.1)	216	205	239	227	259	248	216	208	264	256
23 (0.1)	216	205	239	226	255	244	216	206	263	254
24 (0.1)	212	203	238	226	254	242	213	204	262	253
25 (0.1)	212	202	237	225	252	242	210	202	260	251
26 (5)	85	62	78	53	114	94	146	122	104	80
27 (5)	67	65	57	55	99	97	127	125	85	83
28 (5)	69	67	57	56	100	99	125	124	85	84
29 (5)	71	69	58	57	100	100	124	124	86	85
30 (5)	73	71	59	58	101	100	124	124	86	85
31 (8)	49	53	41	44	86	84	95	99	63	68
32 (8)	47	53	38	45	82	84	91	98	60	68
33 (8)	47	53	38	45	82	84	91	98	60	68
34 (8)	47	53	39	45	83	84	91	97	61	67
35 (8)	48	53	39	45	83	83	90	97	61	67
36 (10)	42	44	33	36	76	76	78	81	55	58
37 (10)	40	44	32	36	75	75	76	80	54	58
38 (10)	41	44	32	36	75	76	75	80	54	58
39 (10)	41	44	32	36	75	76	76	79	54	58
40 (10)	41	44	33	37	75	76	75	79	54	58

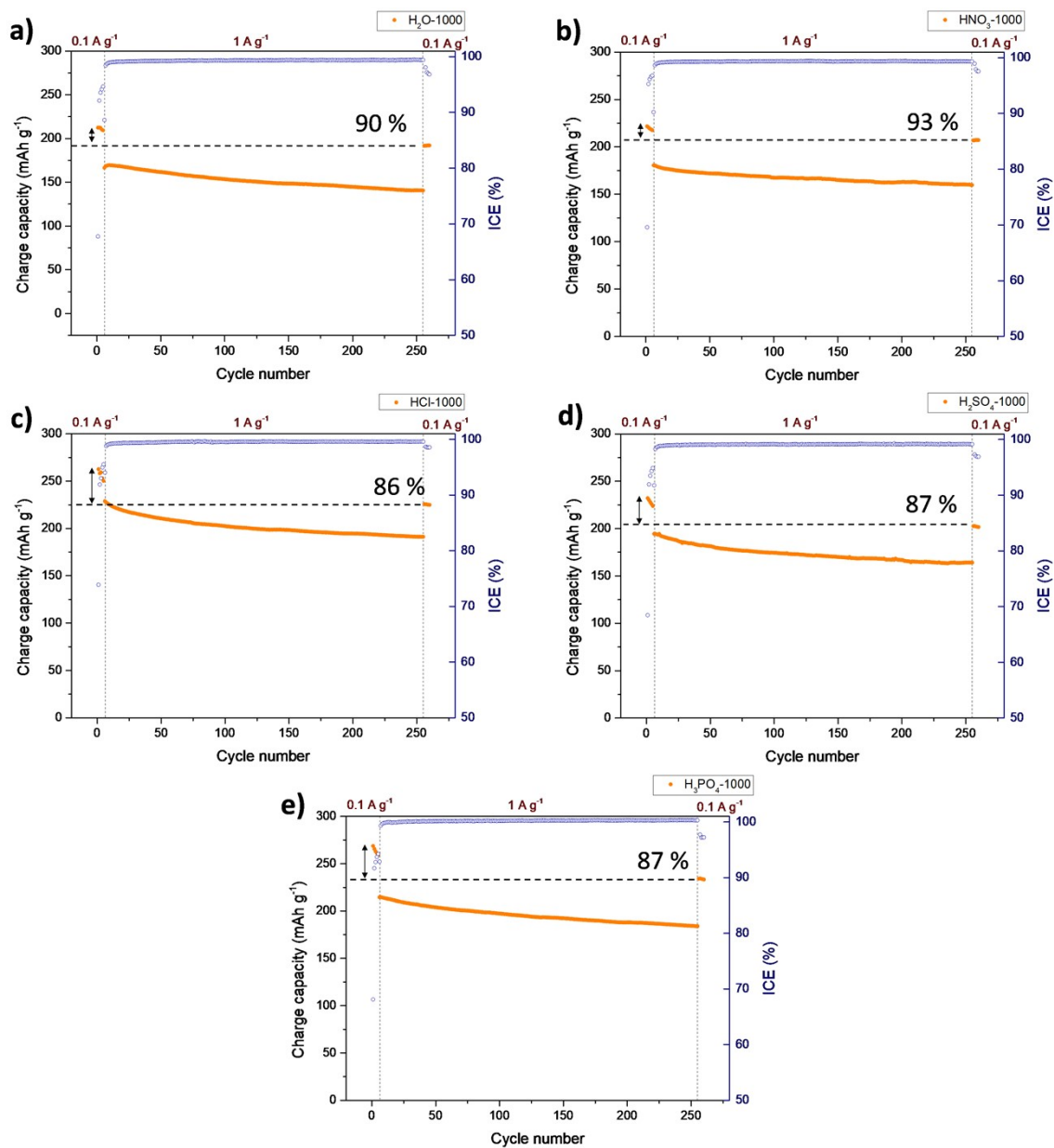


Fig. S34. Cycling performance in terms of charge capacity vs. number of cycles of a) H₂O-1000, b) HNO₃-1000, c) HCl-1000, d) H₂SO₄-1000, and e) H₃PO₄-1000 for 250 cycles at 1 A g⁻¹ in NaPF₆/DGM electrolyte.