Electronic Supplementary Material (ESI) for Materials Advances.

SUPPLEMENTARY INFORMATION

Extent of carbon surface oxygen affinity and its effects on the activity of metal-free carbon catalysts in oxygen reduction reaction: Interplay of porosity and N-, O- and S- enriched surface chemistry

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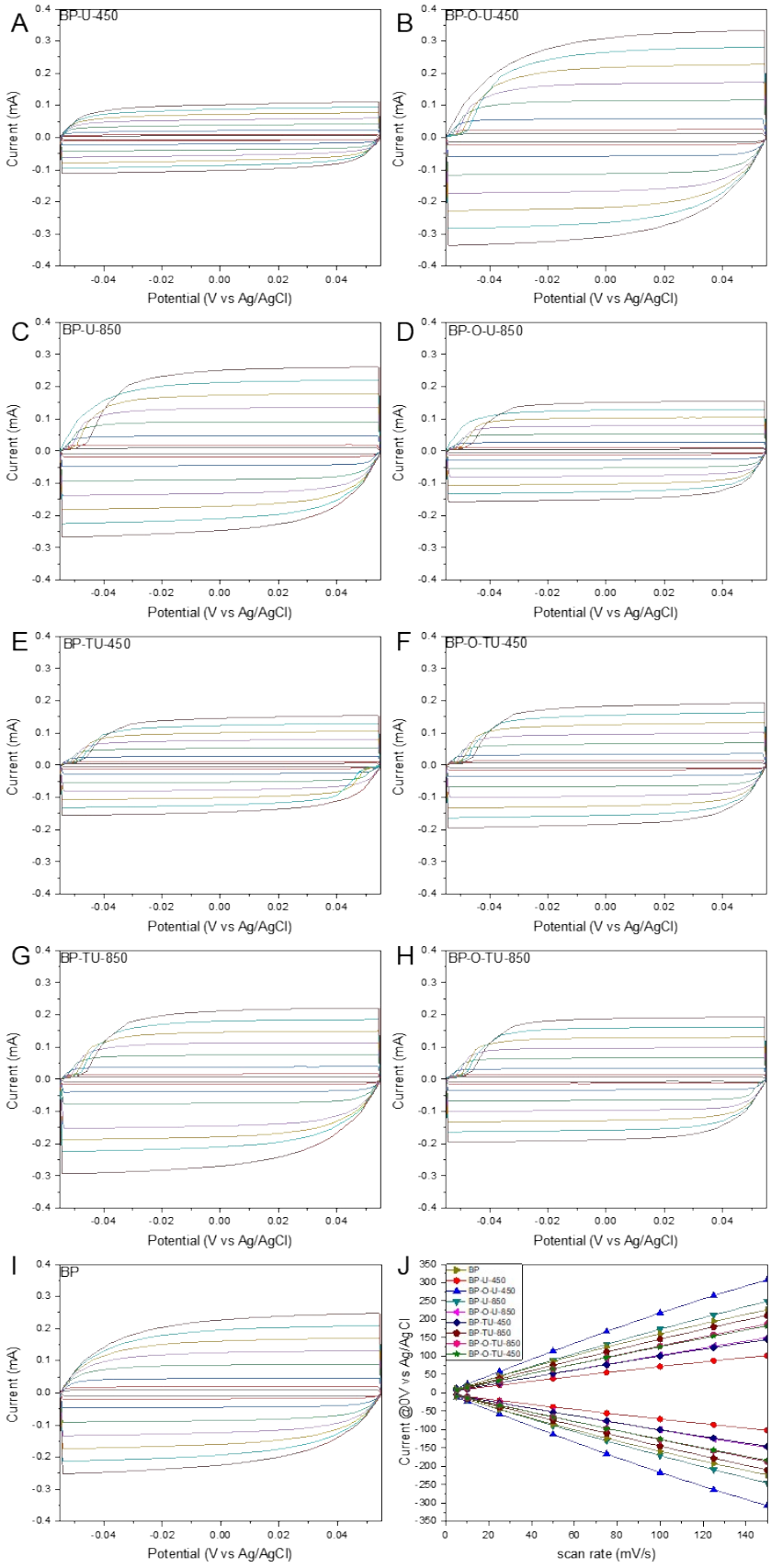

Figure S1. CV curves of measures with 5, 10, 25, 50, 75, 100, 125 and 150 mV/s scan rates; (J) Anodic (I_a) and cathodic (I_c) currents, at 0V as a function of the sacn rate (ν)

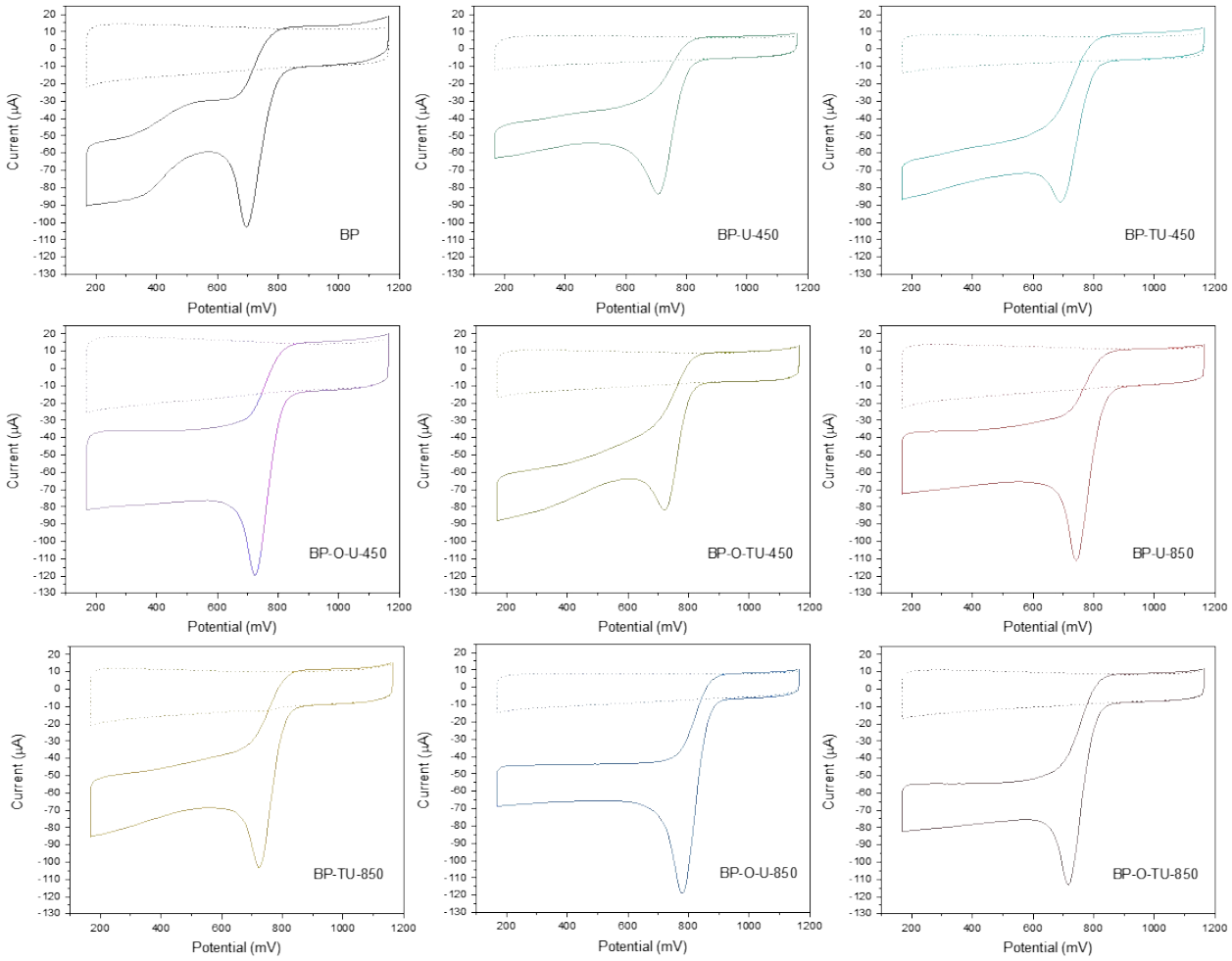

Figure S2. CV curves in N_2 (thin lines) and in O_2 (thick lines) saturated electrolytes

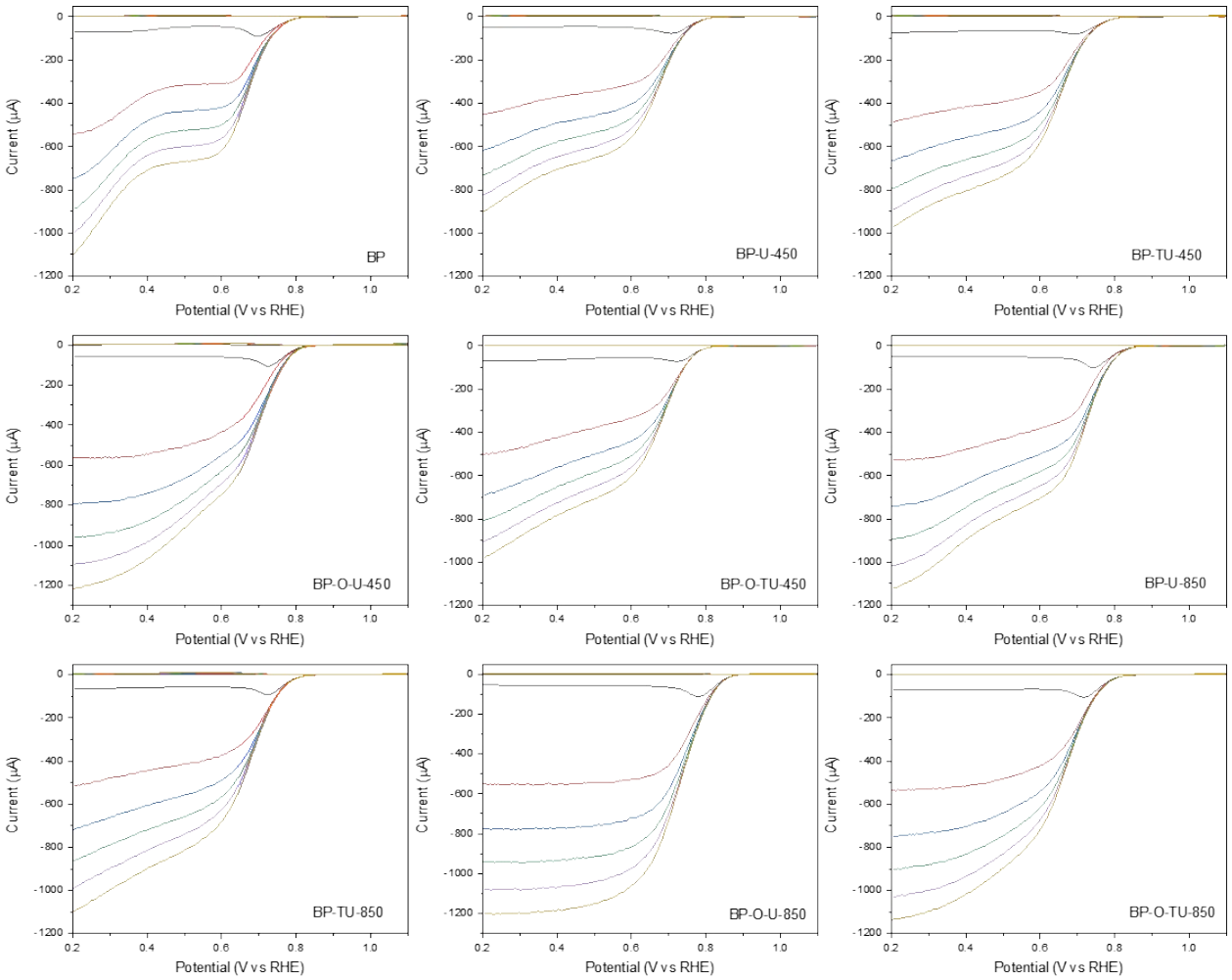

Figure S3. LSV curves at various rotation speeds (between 0 and 2000 rpm) of the differents samples

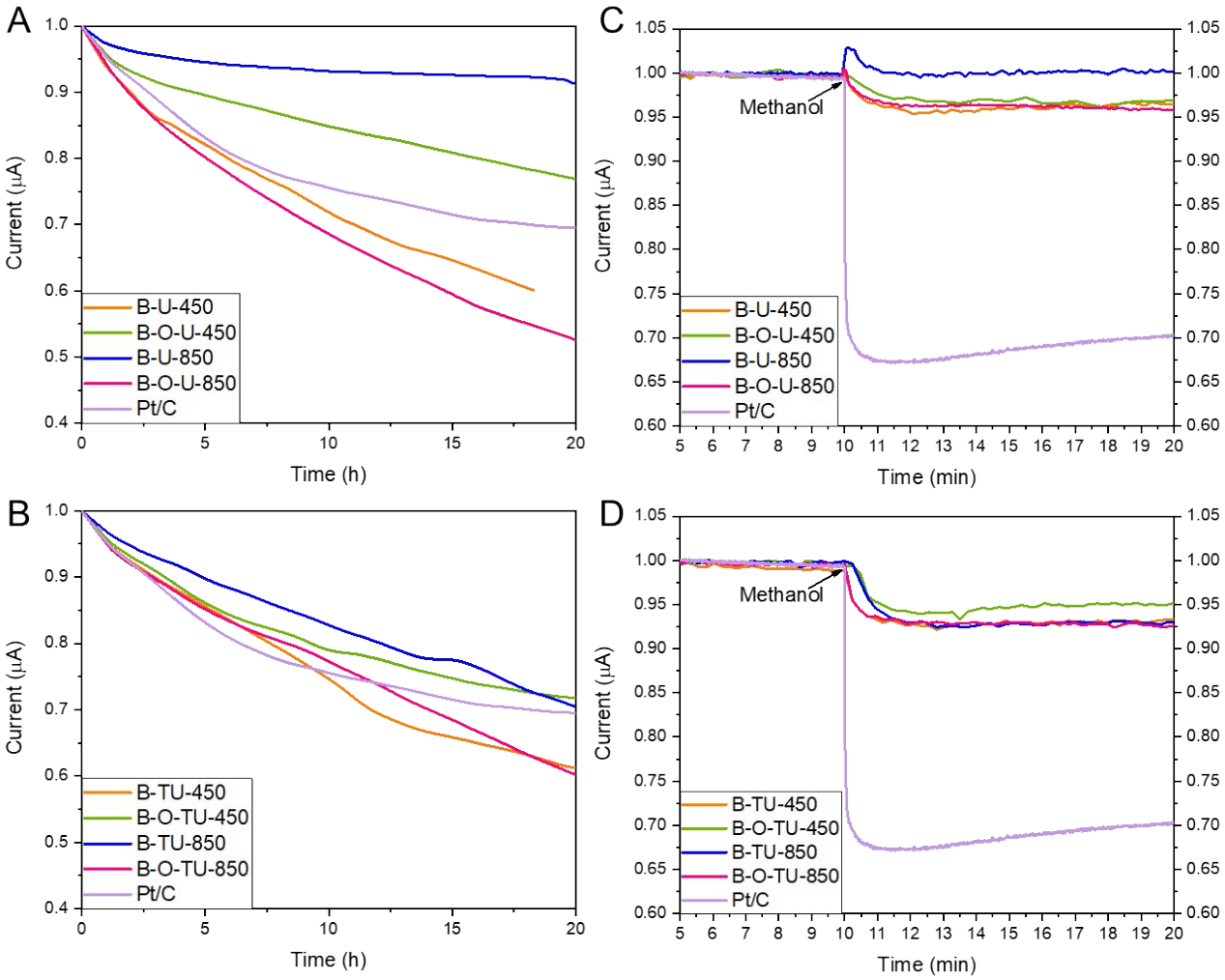

Figure S4. Stability of the catalytic performance for the urea-modified samples (A) and the thiourea-modified samples (B); resistance to methanol cross-over for the urea-modified samples (C) and the thiourea-modified samples (D).

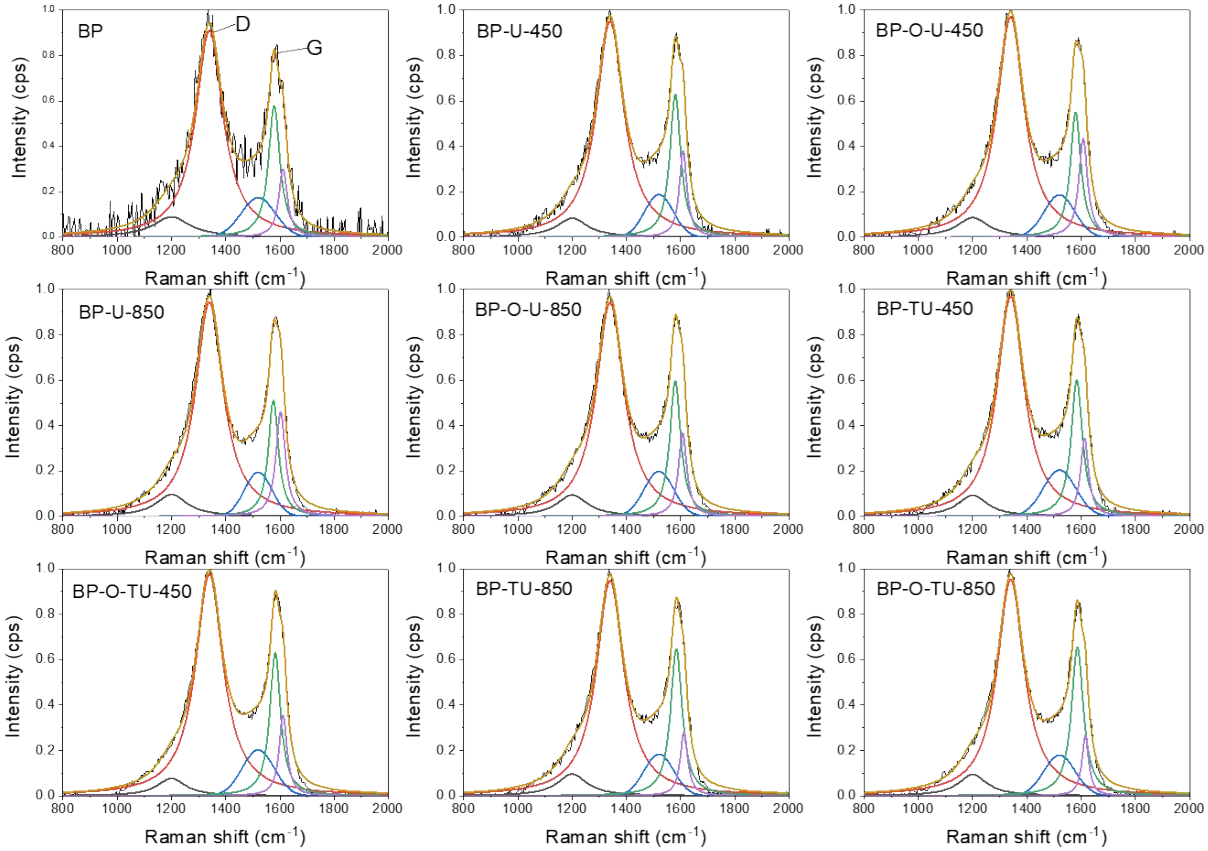

Figure S5. Raman spectra of the tested samples

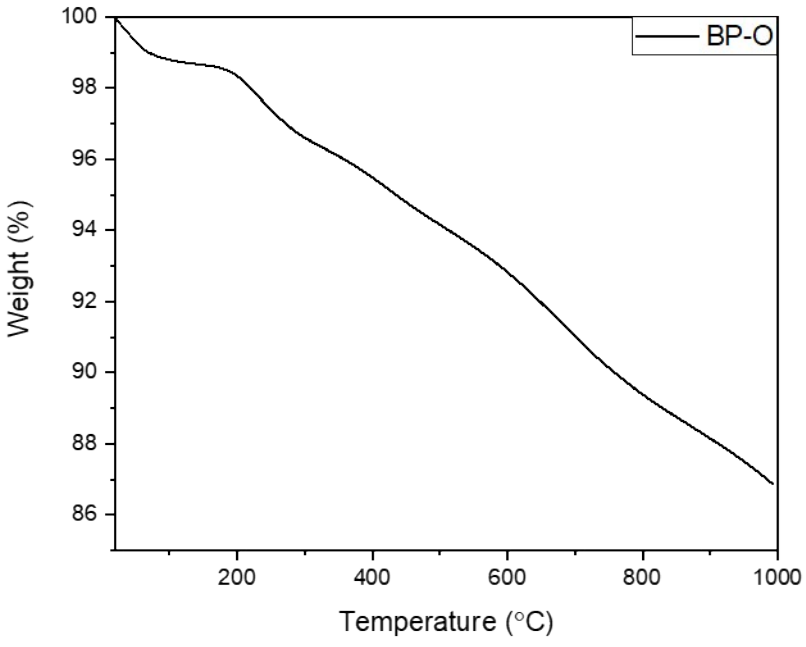

Figure S6. TG curve of the oxidized BP sample.

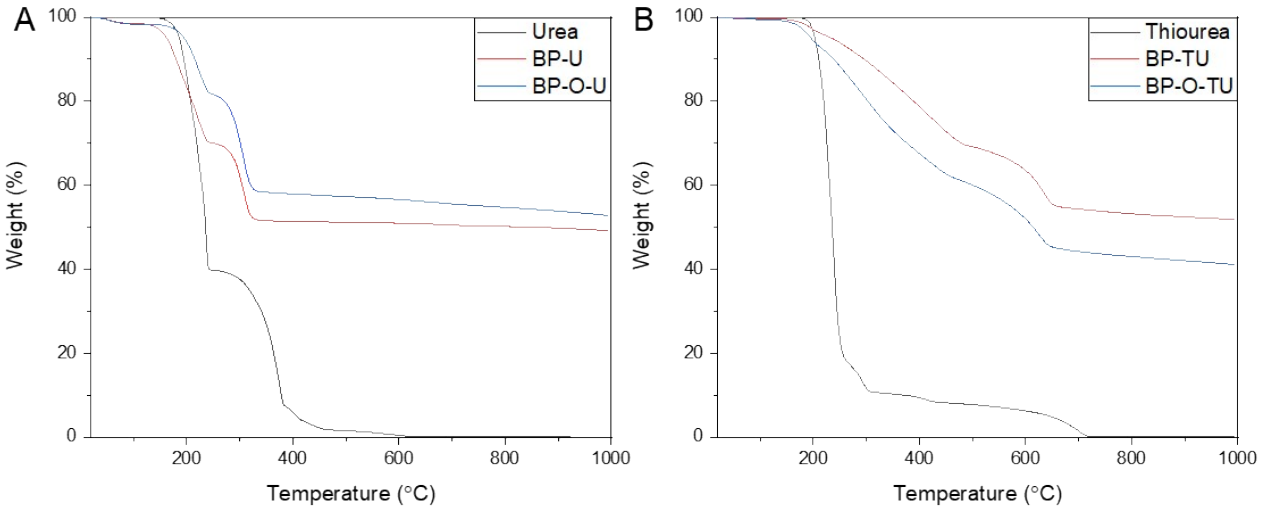

Figure S7. TG curves for urea and BP and its oxidized counterpart BP-O impregnated with urea (A) and thiourea and BP, and BP-O impregnated with thiourea (B).

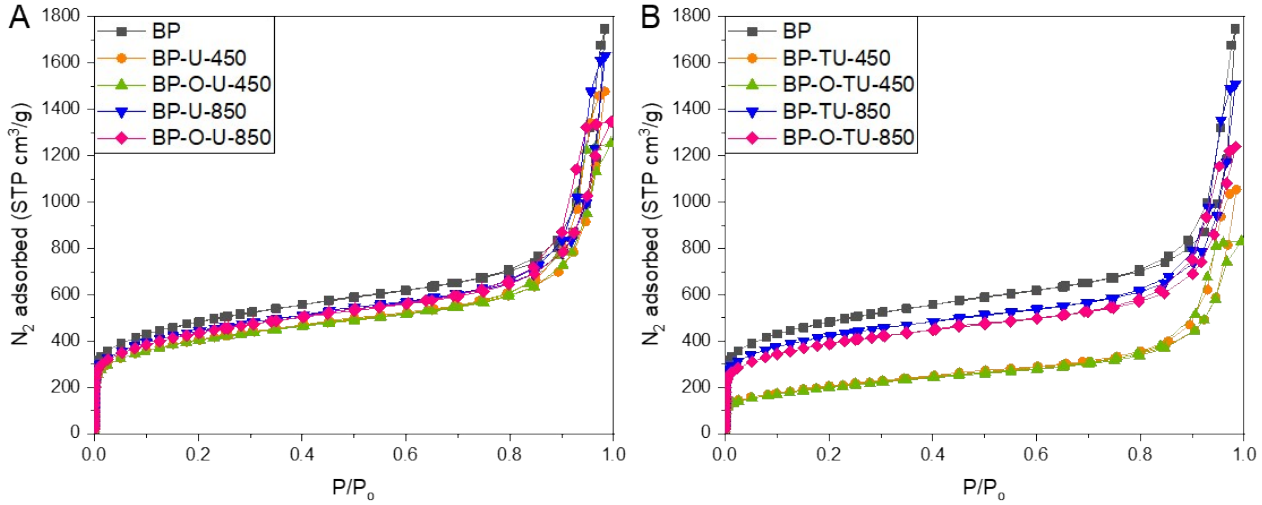

Figure S8. Nitrogen adsorption isotherms for the urea-modified samples (A) and thiourea-modified ones (B).

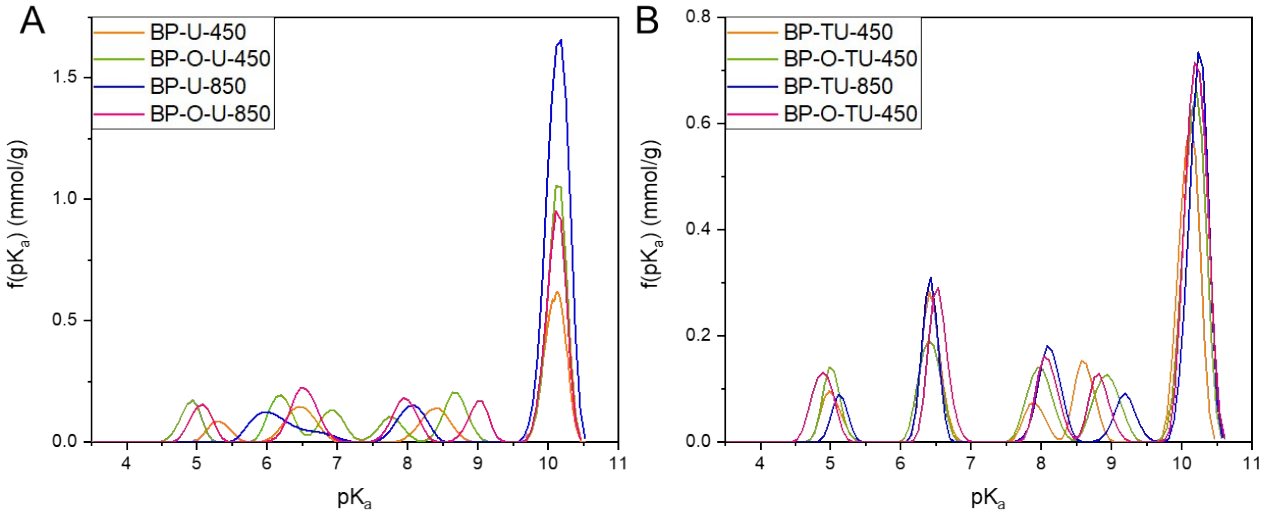

Figure S9. pK_a distribution of the dissociating groups on the surface of the urea-modified samples (A) and thiourea-modified ones (B).

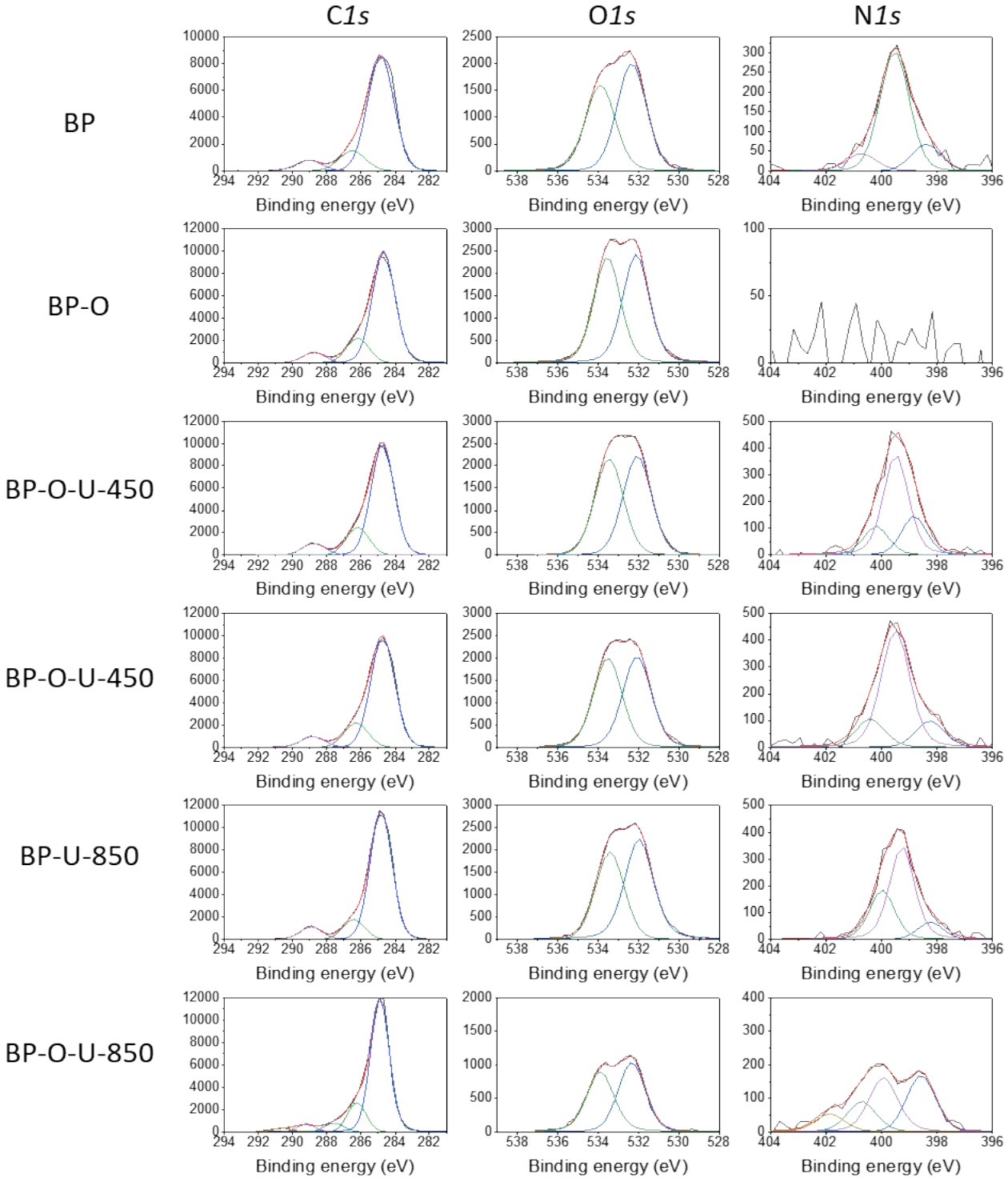

Figure S10. Deconvolution of C 1s, O 1s and N 1s for the series of urea samples.

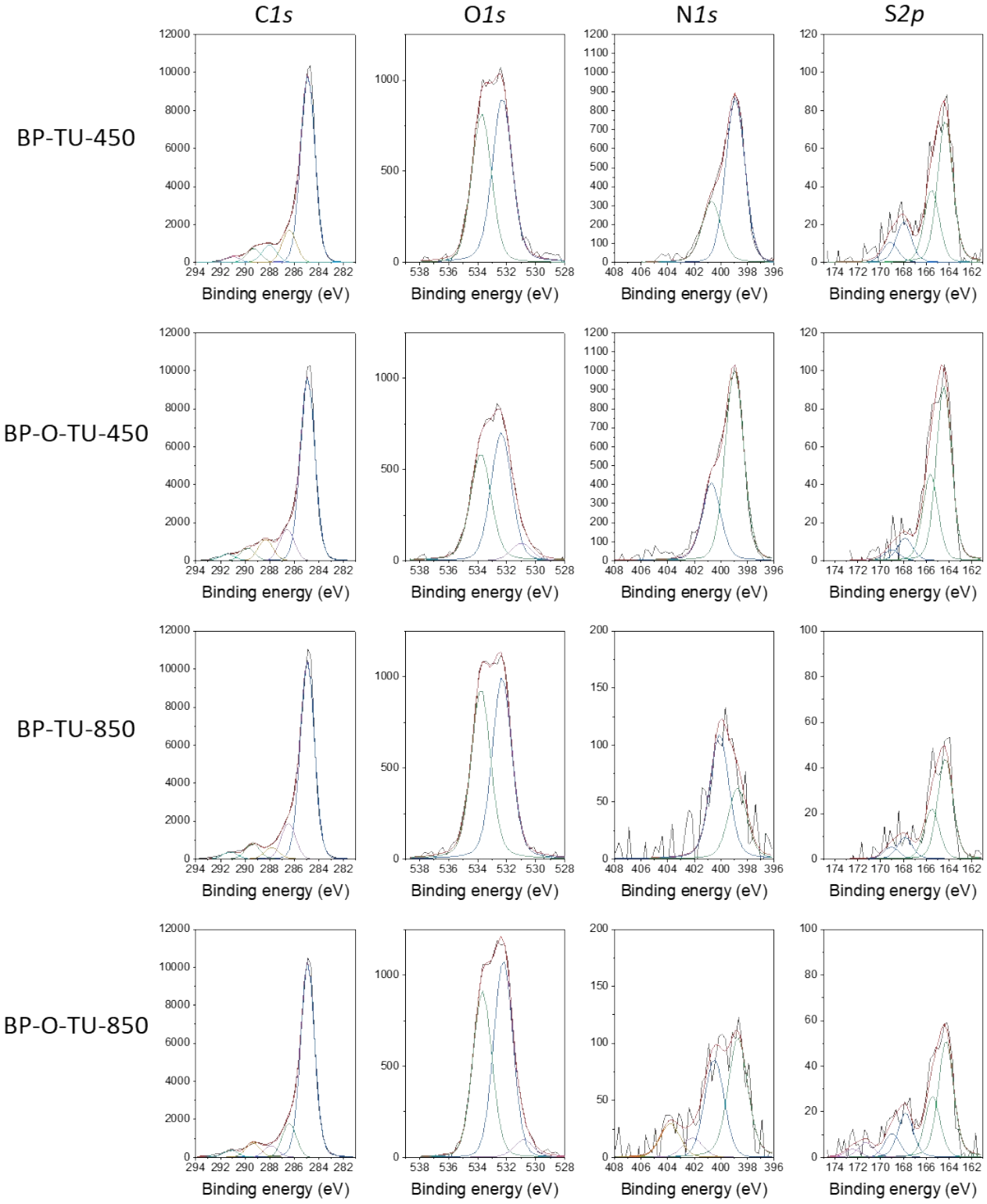

Figure S11. Deconvolution of C 1s, O 1s, N 1s and S 2 p for the series of thiourea-modified samples

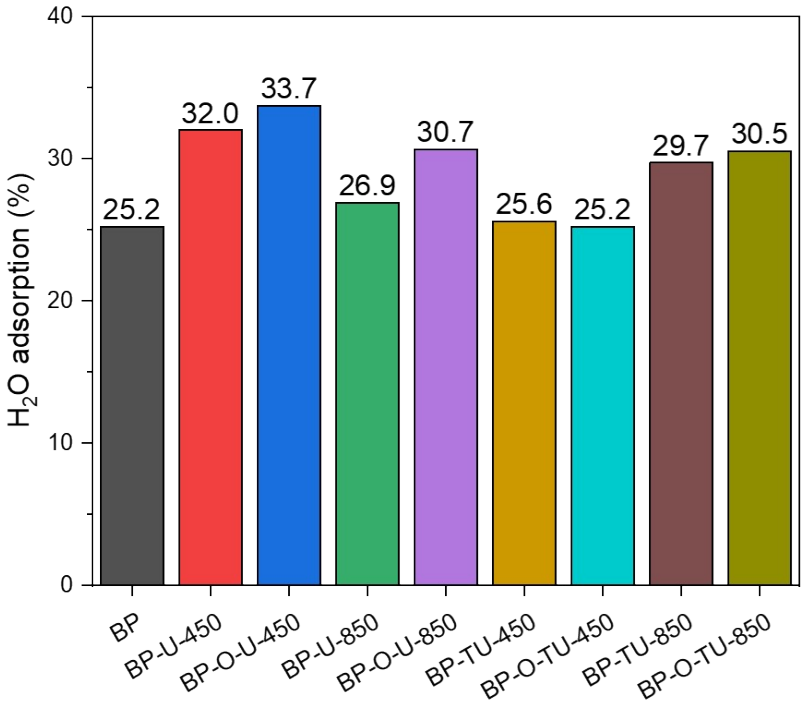

Figure S12. Comparison of the amount of water adsorbed after 4 hours of exposure to saturated vapors.

Table S1. Surface pH, pK_a values of the groups on the surface and their corresponding amounts (in mmol/g)

Sample	pH	pK_a							Total groups (mmol/g)
		4-5	5-6	6-7	7-8	8-9	9-10	10-11	
BP	8.0		0.04	0.07	0.01	0.07		0.22	0.41
BP-U-450	6.9		0.03	0.08		0.07		0.24	0.42
BP-O-U-450	7.5	0.06		0.13	0.04	0.08		0.35	0.67
BP-U-850	7.6			0.10		0.07		0.67	0.85
BP-O-U-850	7.9		0.06	0.11	0.08		0.07	0.33	0.65
BP-TU-450	6.8		0.03	0.09	0.03	0.05		0.22	0.42
BP-O-TU-450	6.8		0.04	0.08	0.06	0.06		0.26	0.50
BP-TU-850	7.5		0.03	0.09		0.07	0.03	0.25	0.47
BP-O-TU-850	7.7	0.05		0.09		0.11		0.29	0.54

Table S2. Atomic % of the element on the surface (in bold) and the results of the deconvolution of C 1s, O 1s, N 1s and S 2p core energy level spectra (in % contribution).

		BP	BP-O	BP-U-450	BP-O-U-450	BP-U-850	BP-O-U-850	BP-TU-450	BP-O-TU-450	BP-TU-850	BP-O-TU-850
C 1s		**86.3**	**87.4**	**86.0**	**86.8**	**85.8**	**93.4**	**87.6**	**88.9**	**92.7**	**91.2**
284.7- 284.9	C-C	77.0	79.7	74.7	75.8	76.9	74.0	72.5	72.1	73.7	74.1
286.2 - 286.6	C-O, C-N	16.0	12.0	18.0	16.4	16.4	15.3	12.3	12.0	13.0	12.4
287.8 - 288.3	C=O, N-C=O						4.7	7.3	8.3	4.7	4.5
289.3 - 289.8	O-C=O	7.0	8.3	7.3	7.8	6.8	3.8	5..5	4.9	5.9	5.9
290.6 - 291.4	π						2.2	2.5	2.7	2.7	3.0
O 1s		**12.3**	**12.6**	**12.3**	**11.2**	**12.4**	**5.2**	**5.7**	**4.2**	**5.9**	**7.1**
530.8 - 531.0									6.8		5.2
532.0 - 532.4	O=C	57.3	51.0	50.7	50.7	55.6	52.1	53.7	49.3	51.4	50.9
533.4 - 533.9	O-C	42.7	49.0	49.3	49.3	44.4	47.9	46.3	43.8	48.6	43.8
N 1s		**1.4**	**-**	**1.7**	**2.0**	**1.8**	**1.5**	**6.2**	**6.5**	**1.2**	**1.4**
398.7 - 399.0	Imine	15.6		22.5	15.1	10.5	33.5	71.0	69.5	36.4	45.9
399.1-399.5	Amine, Pyridine	73.3		60.3	68.1	58.6					
400.1 - 400.7	Pyridone, amide	11.1		17.2	16.7	30.9	35.1	29.0	30.5	63.6	34.4
401.5 - 402.1	Imide						19.4				7.2
403.8 - 404.1	Quaternary (N^+)						12.1				12.5
S $2p^{3/2}$								**0.5**	**0.5**	**0.3**	**0.2**
164.3 - 164.5	Thiol, thiophenes							77.4	88.4	81.6	66.2
167.8 - 168.0	Sulfones Sulfoxides							22.6	11.7	18.4	25.0
171.3	Sulfonate										8.8