

Electronic Supplementary Information

Ultrahigh surface area polypyrrole-based carbons with superior performance for hydrogen storage

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Content:

1. Table S1: Elemental composition of polypyrrole-derived activated carbons.
2. Fig. S1: TGA of polypyrrole under nitrogen flow (Heating rate: 5 °C/min).
3. Fig. S2: Comparison of nitrogen sorption isotherms and pore size distribution curves for carbon samples activated at KOH/PPy weight ratio of 2 or 4 and various temperatures; (a, b) 650 °C, (c, d) 700 °C and (e, f) 800 °C.
4. Fig. S3: a) Infra-red (IR) and b) N 1s core-level spectra of sample CP-4-700.
5. Fig. S4. Raman spectra for the polypyrrole-based carbons.
6. Fig. S4: Correlation between hydrogen storage capacity and micropore volume of the activated carbons.

Table S1. Elemental composition of polypyrrole-derived activated carbons.

Sample	C (%)	H (%)	O (%)	N (%)	S (%)	(O/C)^[a]	(H/C)^[a]	(N/C)^[a]
PPy	65.06	4.54	16.62	13.49	0.29	0.192	0.837	0.178
CP-800*	78.06	1.28	8.87	11.70	0.08	0.085	0.197	0.128
CP-4-600	77.51	1.83	18.04	2.52	0.11	0.175	0.283	0.033
CP-4-650	79.99	1.53	16.95	1.45	-	0.159	0.230	0.016
CP-4-700	91.06	1.05	7.09	0.72	0.08	0.058	0.134	0.007
CP-4-800	95.66	0.35	3.48	0.47	0.04	0.027	0.044	0.004
CP-4-850	93.09	0.49	6.02	0.32	-	0.049	0.063	0.003
CP-2-650	66.25	2.8	26.02	4.05	-	0.295	0.507	0.052
CP-2-700	85.05	1.05	11.71	2.14	0.06	0.103	0.148	0.022
CP-2-800	92.99	0.52	5.60	0.78	0.10	0.045	0.067	0.007

[a] atomic ratio.

* Polypyrrole carbonized at 800 °C under a nitrogen environment.

Elemental analysis (C, H, S and O) was carried out on a LECO CHN-932 microanalyzer.

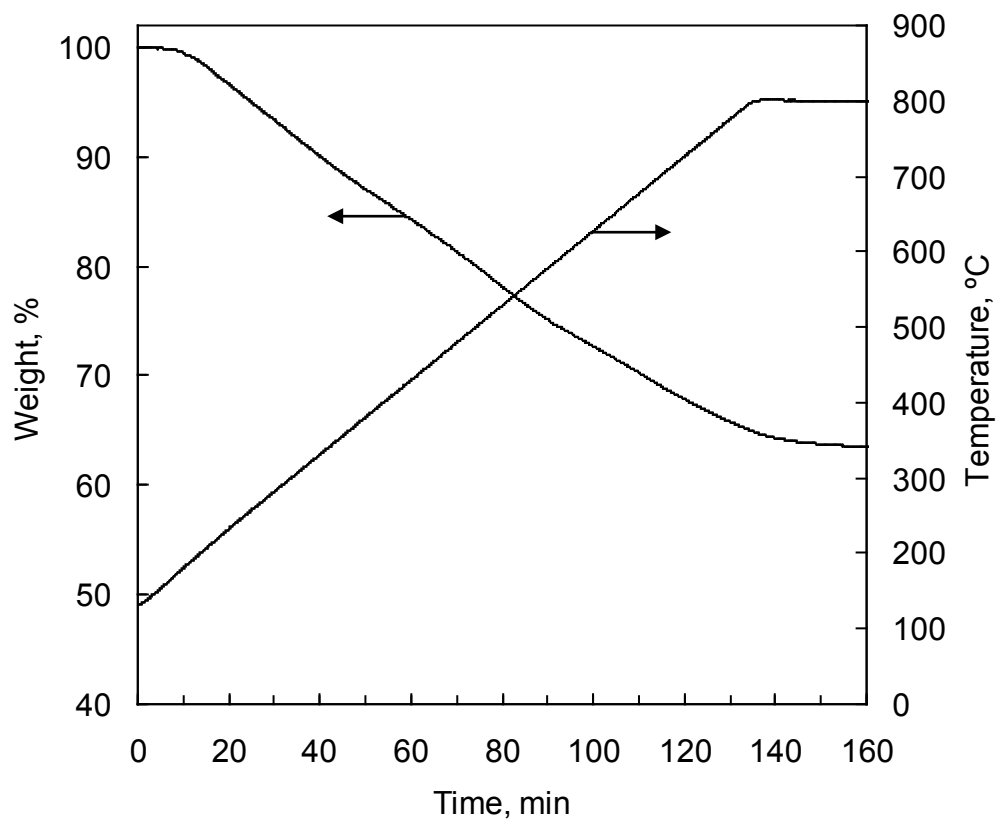


Figure S1. TGA of polypyrrole under nitrogen flow (Heating rate: 5 °C/min).

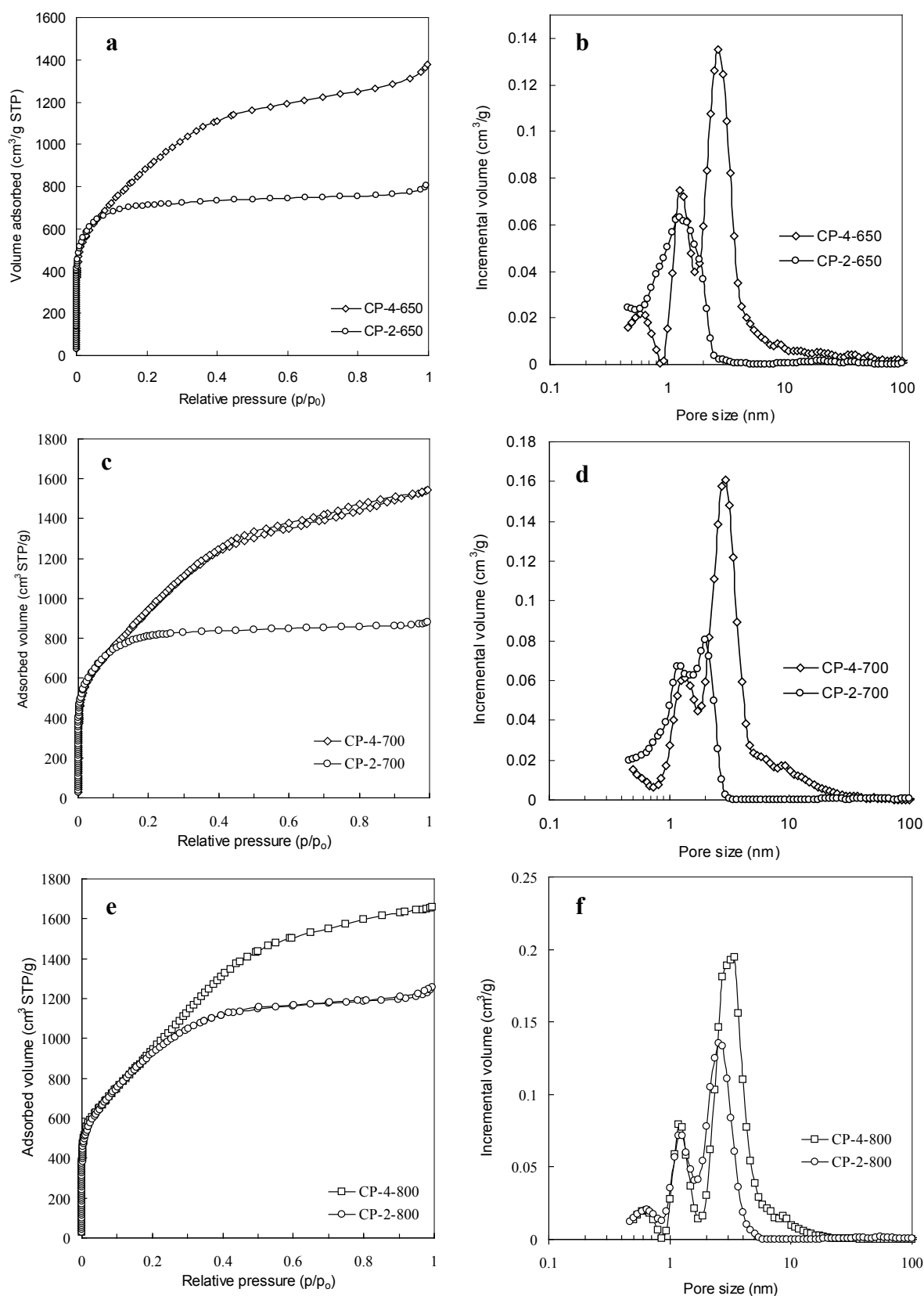


Figure S2. Comparison of nitrogen sorption isotherms and pore size distribution curves for carbon samples activated at KOH/PPy weight ratio of 2 or 4 and various temperatures; (a, b) 650 °C, (c, d) 700 °C and (e, f) 800 °C.

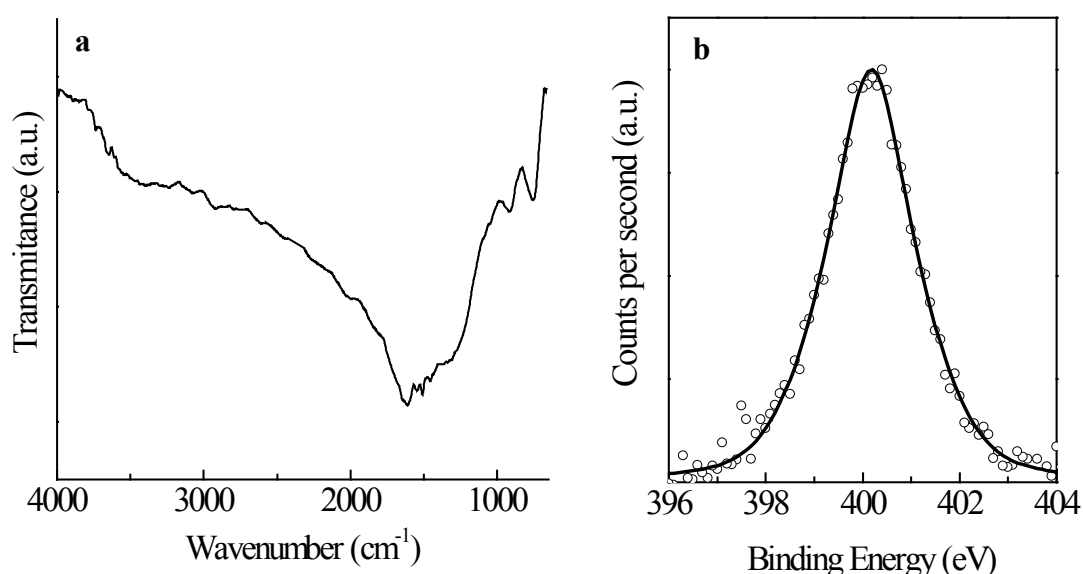


Figure S3. a) Infra-red (IR) and b) N 1s core-level spectra of sample CP-4-700.

The IR spectrum was recorded on a Nicolet Magna-IR 560 spectrometer fitted with a diffuse reflection attachment. The activated carbon prepared at 700°C and KOH/PPy weight ratio of 4 exhibits broad and overlapped bands (due to strong carbon absorption of) which correspond to N-H and/or O-H stretching vibrations (3000 – 3700 cm⁻¹), C=C stretching vibrations (1620 and 1520 cm⁻¹), C-N stretching vibrations (1350 cm⁻¹), in-plane C-H and N-H deformations (1230 cm⁻¹) and out-of-plane C-H and N-H deformations (760-920 cm⁻¹).¹

The nitrogen species on the surface of the activated carbons was further examined by X-ray photoelectron spectroscopy (XPS) carried out on a Specs spectrometer, using Mg K α (1253.6 eV) radiation from a double anode at 50 w. Binding energies for the high-resolution spectra were calibrated by setting C 1s to 284.6 eV. The N 1s core level spectrum of sample CP-4-700 exhibits only one peak at ~ 400 eV, which corresponds to pyrrolic nitrogen or pyridone nitrogen.² For some activated carbons, an additional peak at 398 eV was observed, which corresponds to pyridinic nitrogen.

[1] a) X. Zhang, J. Zhang, W. Song, Z. Liu, *J. Phys. Chem. B* **2006**, *110*, 1158-1165. b) M. R. Nabid, A. A. Entezami *J. Appl. Polym. Sci.* **2004**, *94*, 254-258. c) C. Della Pina, E. Falletta, M. Lo Faro, M. Pasta, M. Rossi *Gold Bull.* **2009**, *42*, 27-33. d) Z-G. Li, F. Wei, M-R. Huang, Y-B. Xie *J. Phys. Chem. B* **2007**, *111*, 5829-5836.

[2] J. R. Pels, F. Kapteijn, J. A. Moulijn, Q. Zhu, K. M. Thomas *Carbon* **1995**, *33*, 1641-1653.

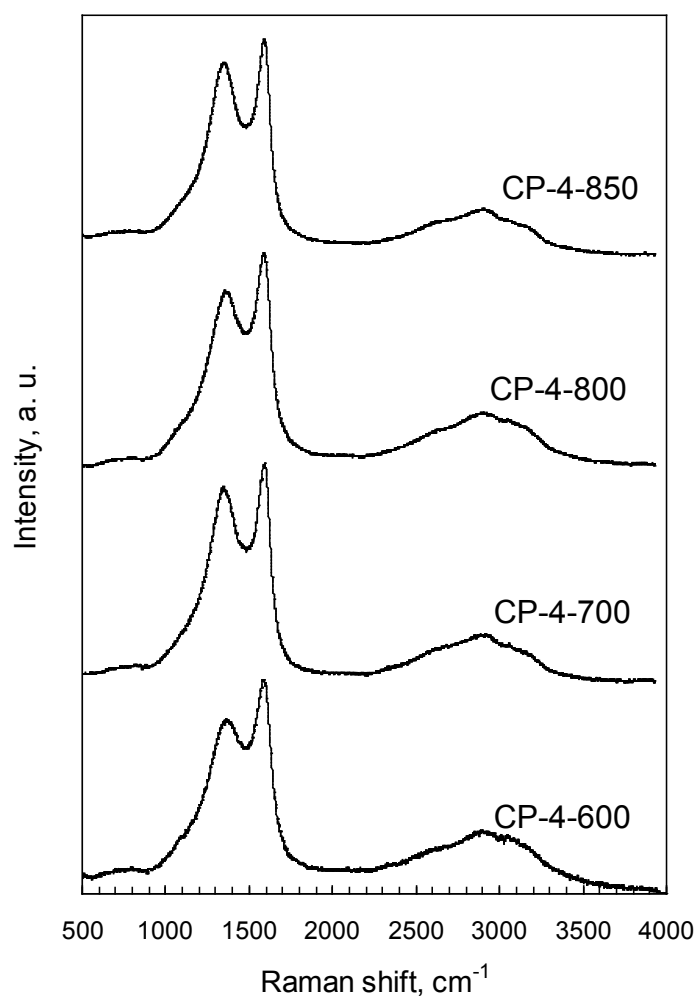


Figure S4. Raman spectra for the polypyrrole-based carbons.

The structural order of the synthesized carbons was examined by means of Raman spectroscopy. Figure S4 shows the spectra recorded for several activated carbons. The two broad peaks centered at around 1370 cm⁻¹ and 1595 cm⁻¹ are ascribed to the D-peak for disordered carbon and the G-peak for graphitic carbons, respectively. The intensity of the D-peak to G-peak ratio (I_D/I_G) is in the 0.80-0.90 range. The I_D/I_G ratio is somewhat higher for carbons activated at ≥ 700 °C, which is consistent with decrease in ‘graphitisation’ at higher levels of activation. Overall, however, the position of the G band and the value of the I_D/I_G ratio are characteristic of carbon materials with a certain graphitic order. Furthermore, additional broad bands appear in the 2300-3300 cm⁻¹ range (not shown), which can be attributed to overtones and to combinations of the vibration modes of the graphitic layers. Their appearance confirms the existence of relatively well-organized carbon structures.

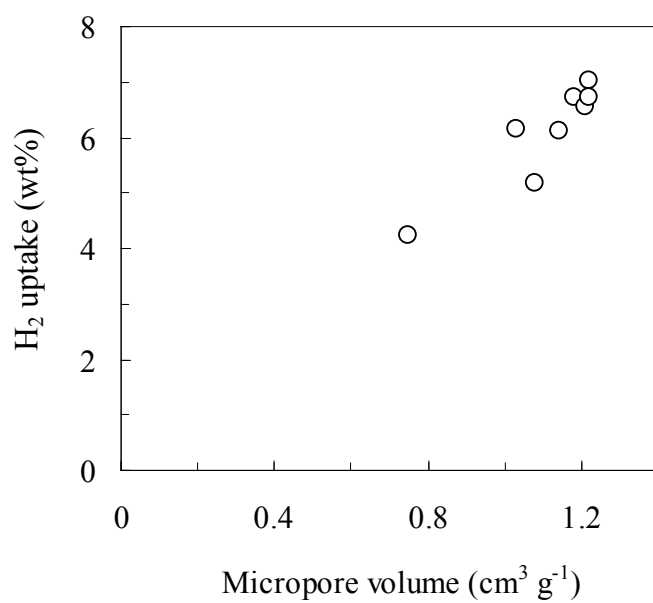


Figure S5. Correlation between hydrogen storage capacity and micropore volume of the activated carbons.