

Green technique for producing carbon-based catalysts for cellulose hydrolysis

Siqi Deng^{*a}, Kaixun Yao^b, Manabu Kodama^c, Oi Lun Li^d, Nozomi Takeuchi^b

^a Department of Electrical Engineering, Tohoku University

^b Department of Electrical and Electronic Engineering, Institute of Science Tokyo

^c Department of Mechanical Engineering, Institute of Science Tokyo

^d School of Materials Science and Engineering, Pusan National University

*Corresponding author: deng@tohoku.ac.jp

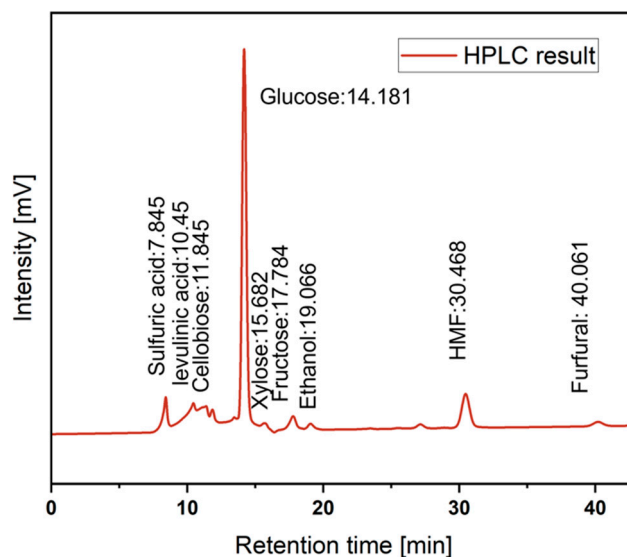


Figure S1: HPLC-RID chromatogram for sugar content analysis of cellulose hydrolysis result.

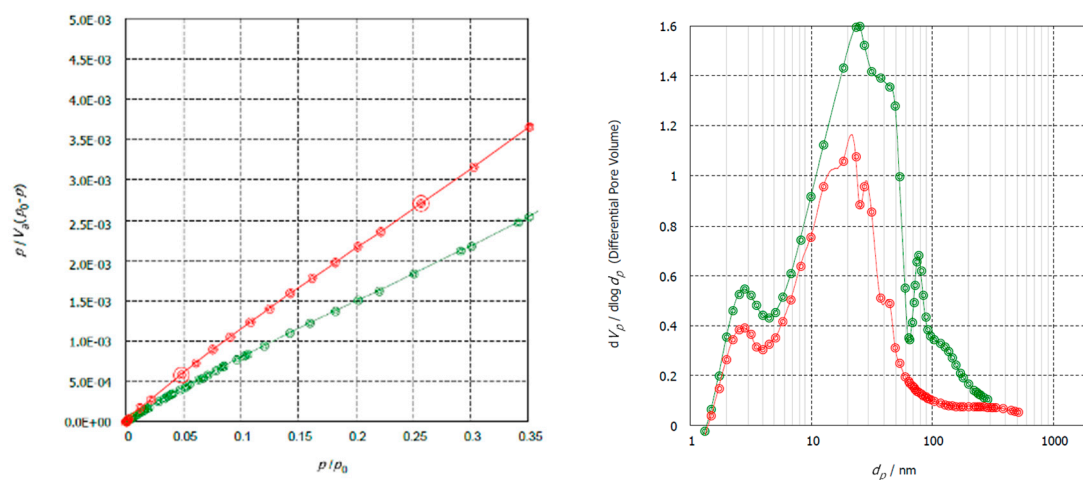


Figure S2: BET plot (left) and BJH plot (right) of original CNT (green line) and treated CNT (red line); Treatment condition: 45 min treatment with 0.5 M $\text{Na}_2\text{S}_2\text{O}_8$ solution.

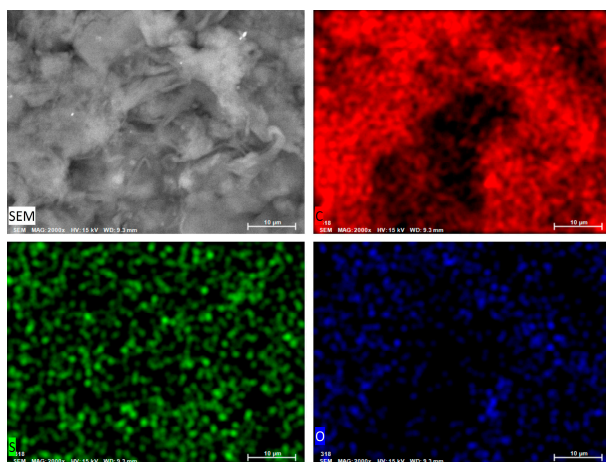


Figure S3: the SEM-EDS image of treated carbon (45 min treatment with 0.5 M $\text{Na}_2\text{S}_2\text{O}_8$ solution). Red: carbon; green: sulfur; blue: oxygen.

Table S1: Surface area, XPS peak assignment and atomic percentage (at. %) for original CNT and treated CNT (45 min treatment with 0.5 M $\text{Na}_2\text{S}_2\text{O}_8$ solution)

Sample	Surface area ($\text{m}^2 \text{g}^{-1}$)	Total C 1s at. %	Total O 1s at. %	Total S2p at. %	Contributions from O to C 1s spectra at. %			
					C-OH	C-O-C	COOH	C=O
Original CNT	519	98.50	1.50	0.00	2.33	0.01	2.72	1.51

Treated CNT	424	91.11	7.63	1.26	3.54	0.06	2.79	2.11
----------------	-----	-------	------	------	------	------	------	------

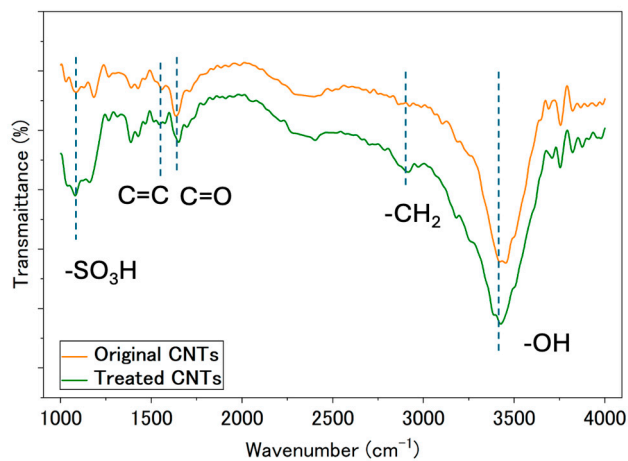


Figure S4: FTIR spectra of original and treated carbon materials (45 min treatment with 0.5 M $\text{Na}_2\text{S}_2\text{O}_8$ solution)

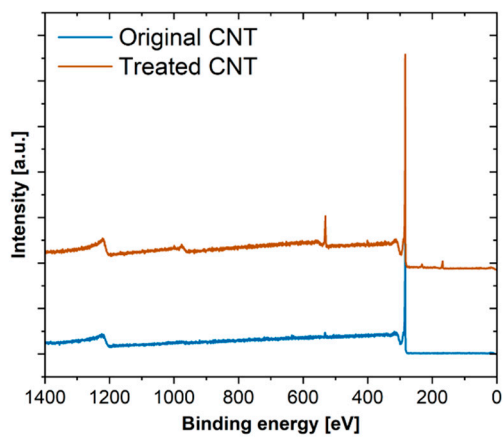


Figure S5: Survey XPS spectra of original and treated carbon materials (45 min treatment with 0.5 M $\text{Na}_2\text{S}_2\text{O}_8$ solution)

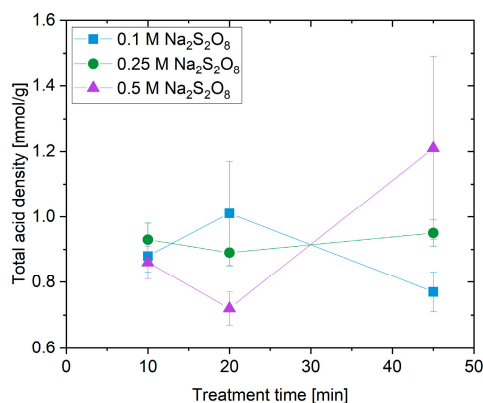


Figure S6: the variation of the total acid density of treated carbon with treatment time. (The total acid density of original CNT is 0.22 mmol g⁻¹)

Table S2: The glucose yield and cellulose conversion after the 2nd run hydrolysis; the SO_4^{2-} in the solution after each hydrolysis. (CNT was treated with 0.25 M $\text{Na}_2\text{S}_2\text{O}_8$ solution for 10 min)

	Glucose yield [%]	Cellulose conversion [%]	SO_4^{2-} ion in the solution after hydrolysis [ppm]
1 st run	15.9	25.5	113.5
2 nd run	12.6	18.5	110.5

Table S3: Sulfonation results of CNTs treated by hydrothermal method.

Catalyst	Sulfonation Temperature (°C)/ Time (h)	SO_3H / COOH & OH density (mmol g ⁻¹)	Total acid densities (mmol g ⁻¹)
CNTs	150/10	0.36/1.10	1.46

Table S4: The glucose yield and cellulose conversion after the 2nd run hydrolysis; the SO_4^{2-} in the solution after each hydrolysis. (CNTs treated by hydrothermal method)

	Glucose yield [%]	Cellulose conversion [%]	SO_4^{2-} ion in the solution after hydrolysis [ppm]
1 st run	24.8	30.8	141.9
2 nd run	12.5	16.9	109.2

We evaluated thermal durability by isothermal oven heating followed by gravimetry. 30 mg of sample was heated in air at 150, 200, and 250 °C for 1 h at each step, cooled to room temperature, and weighed on a balance. The mass loss (%) at each temperature was calculated relative to the mass before that step. Pristine CNTs were measured as a control under identical conditions.

The treated CNTs exhibited 6.7 %, 3.3 %, and 13.0 % mass loss after 1 h at 150, 200, and 250 °C, respectively, compared with 6.7 %, 6.7 %, and 10.0 % for pristine CNTs. The larger loss of the treated sample at 250 °C (extra ~3 % absolute) indicates partial decomposition of grafted –SO₃H/–OSO₃H groups, while the similar behavior at 150 °C is consistent with removal of physisorbed water/volatiles in both materials. The small difference at 200 °C likely reflects experimental scatter and competing adsorption/desorption processes. Overall, these observations support the expected onset of sulfonic-group degradation around 200–250 °C, aligning with literature reports for sulfonated carbons[1,2].

Table S5: Comparison of the catalytic performance of treated carbon catalyst.

Catalyst & method	Preparation conditions	Total acid-site density (mmol g ⁻¹)	Cellulose hydrolysis condition (temperature, time; substrate; mass ratio of cellulose:catalyst)	Cellulose conversion (%)	Glucose yield (%)
This work	0.5 M Na ₂ S ₂ O ₈ , 45 min	1.52	150 °C, 24 h, H ₂ O, 1:1	31.60%	23.18%
Plasma-assisted sulfonated CNTs [3,4]	Plasma discharge with 1 M H ₂ SO ₄ solution	3.47	150 °C, 15 h, H ₂ O, 9:10	37.4%	27.2%
Amberlyst-15 [5]	Commercial sulfonated	4.40	100 °C, 5 h, H ₂ O, 1:1	12%	-

	polymer resin				
Hydrothermal sulfonated active carbon[6]11/5/2025 11:28:00 AM	Concentrated H ₂ SO ₄ (18 M), 150 °C, 10 h	0.72	150 °C, 24 h, H ₂ O, 1:1	-	21%

Reference:

1. Corrêa, A.P. da L.; Cardoso Bastos, R.R.; Filho, G.N. da R.; Roberto Zamian, J.; da Conceição, L.R.V. Preparation of Sulfonated Carbon-Based Catalysts from Murumuru Kernel Shell and Their Performance in the Esterification Reaction. **2020**, doi:10.1039/D0RA03217D.
2. Knauth, P.; Hou, H.; Bloch, E.; Sgreccia, E.; Di Vona, M.L. Thermogravimetric Analysis of SPEEK Membranes: Thermal Stability, Degree of Sulfonation and Cross-Linking Reaction. *Journal of Analytical and Applied Pyrolysis* **2011**, 92, 361–365, doi:10.1016/j.jaap.2011.07.012.
3. Qin, L.; Ishizaki, T.; Takeuchi, N.; Takahashi, K.; Kim, K.H.; Li, O.L. Green Sulfonation of Carbon Catalysts via Gas–Liquid Interfacial Plasma for Cellulose Hydrolysis. *ACS Sustainable Chem. Eng.* **2020**, 8, 5837–5846, doi:10.1021/acssuschemeng.9b07156.
4. Li, O.L.; Ikura, R.; Ishizaki, T. Hydrolysis of Cellulose to Glucose over Carbon Catalysts Sulfonated via a Plasma Process in Dilute Acids. *Green Chem.* **2017**, 19, 4774–4777, doi:10.1039/C7GC02143G.
5. Rinaldi, R.; Palkovits, R.; Schüth, F. Depolymerization of Cellulose Using Solid Catalysts in Ionic Liquids. *Angewandte Chemie International Edition* **2008**, 47, 8047–8050, doi:10.1002/anie.200802879.
6. Lai, D.; Deng, L.; Li, J.; Liao, B.; Guo, Q.; Fu, Y. Hydrolysis of Cellulose into Glucose by Magnetic Solid Acid. *ChemSusChem* **2011**, 4, 55–58, doi:10.1002/cssc.201000300.