

# Bottom-up Synthesis Strategies Enabling the Investigation of Metal Catalyst-Carbon Support Interactions

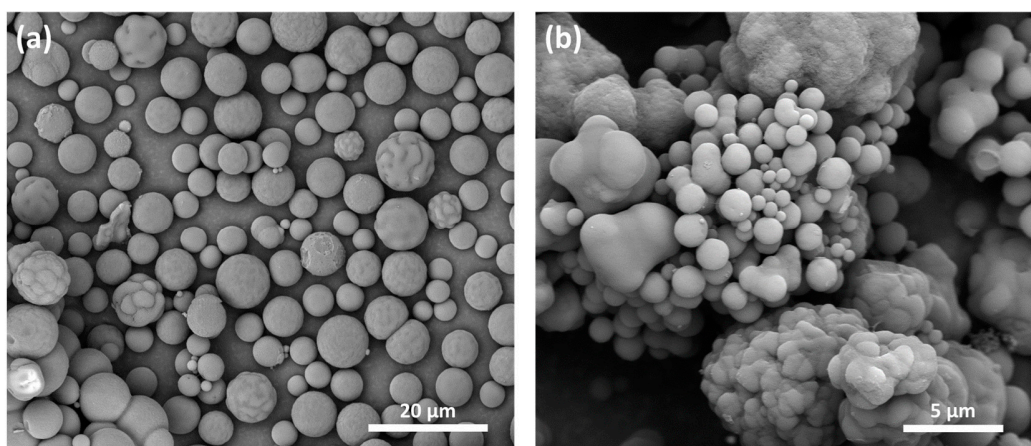
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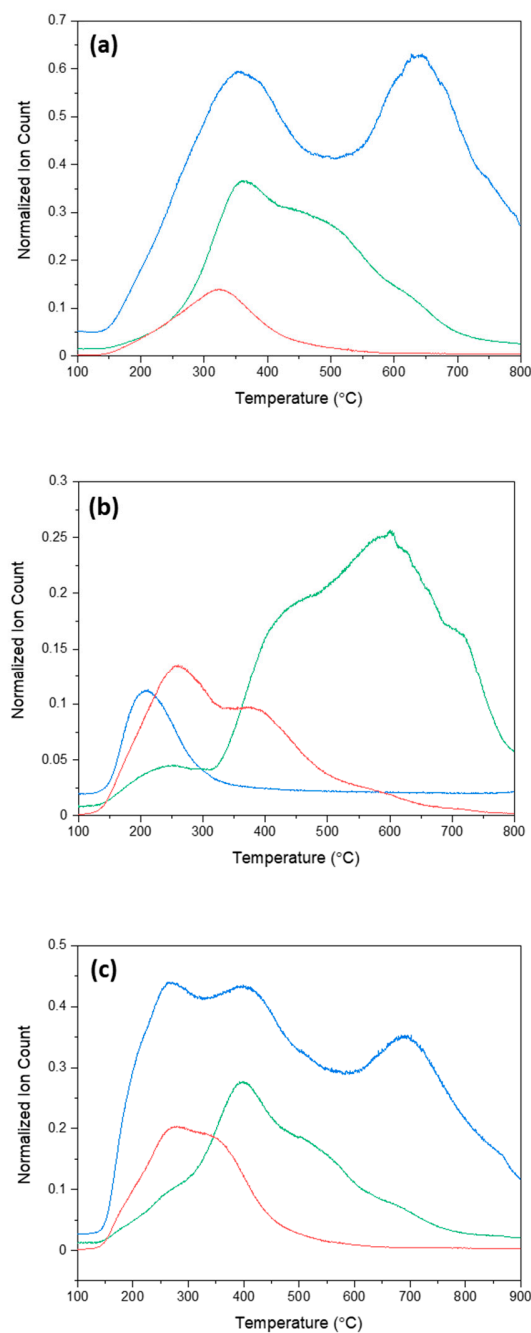
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## Supplementary Materials

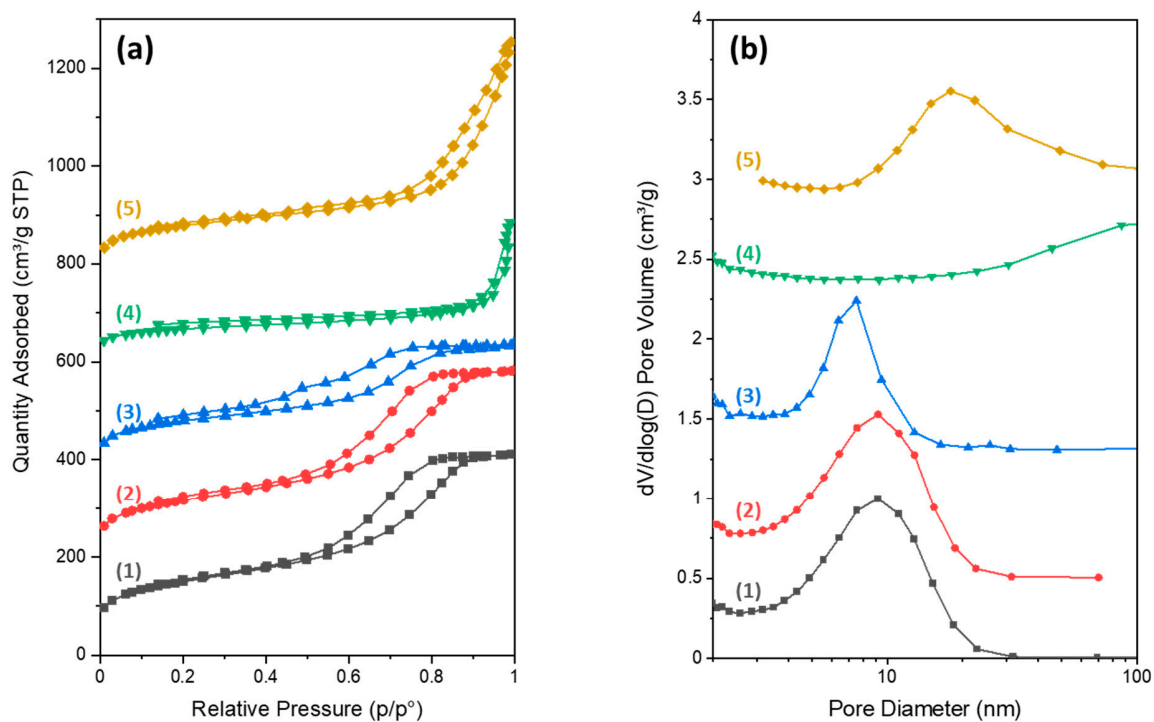


**Figure S1.** SEM images of HTC material synthesized in the presence of PAA: (a) hydrochloric acid-catalyzed HTC; (b) formic acid-catalyzed HTC

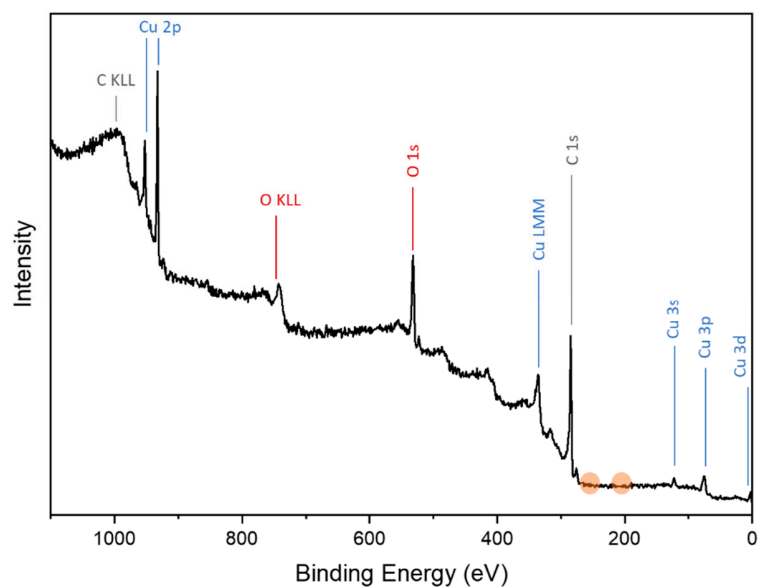


**Figure S2.** The results of TPD-MS analysis: (a) as-synthesized HTC material, (b) nitric acid-treated-HTC material, and (c) hydrogen peroxide-treated HTC material. The blue, green, and red lines represent  $m/z$  profiles of 18, 28, and 44, respectively, normalized to the ion count of Ar and the amount of initial samples to enable comparisons across the experiments. The samples were annealed at 1000 °C prior to oxidation. Nitric acid treatment was performed using 70% acid at 100 °C for 4h. The hydrogen peroxide oxidation was conducted using a 30% solution at 80 °C for 3h. The TPD-MS results in **Figure S2 (a)** suggest that HTC undergoes a dehydration reaction during thermal treatment. This phenomenon can be attributed to the decomposition of the thermolabile furanic backbone, reconfiguration of adjacent oxygen functionalities,

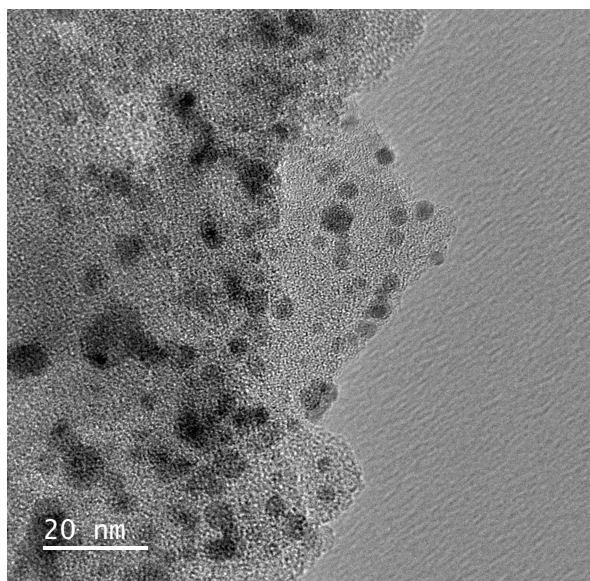
and a remarkable reconfiguration in the carbon structure [1,2]. The formation of a broad CO peak ( $m/z=28$ ) during the TPD-MS suggests the presence of a diverse set of oxygen moieties such as aldehyde (500-700 K), carboxylic anhydride (800-950 K), phenol (950-1000 K), ether (~973 K), carbonyl (1100-1150 K), and quinone (1100-1150K). The CO<sub>2</sub> formation can be partly attributed to the embedded levulinic acid. However, the potential presence of carboxylic acids in the structure should not be overlooked given the large amount of CO<sub>2</sub> formation within 500-700K. The CO<sub>2</sub> formation at higher temperatures could be attributed to the presence of a small number of carboxylic anhydrides in the structure as well. **Figure S2 (b)** results suggest the presence of a large number of carboxylic acids and phenols along with anhydrides and carbonyls group in the nitric acid oxidized HTC. The annealing at a high temperature can increase the degree of aromatization and stabilize the carbon structure by removing/transforming the furan-based fragments. However, the lack of oxygen functionalities could inversely influence the metal particle distribution on a highly defunctionalized support. Thus, an oxidation process using nitric acid or hydrogen peroxide can be used to reintroduce the oxygen functionalities, as shown in **Figure S2 (b,c)**. Such an approach provides great flexibility in adjusting the surface chemistry of the sample by changing the operating conditions. For instance, hydrogen peroxide could introduce a large number of hydroxyl groups into the structure while the nitric acid treatment is expected to introduce carboxylic acids and phenols along with anhydrides and carbonyls group [3]. In contrast to what was reported previously [4], the oxidation level for the H<sub>2</sub>O<sub>2</sub>-treated carbon sample exceeded the oxidation level obtained by the nitric acid treatment. The TPD-MS results showed that the amount of water, CO, and CO<sub>2</sub> evolved from the samples were 20.04:1, 0.86:1, and 1.32:1 for the H<sub>2</sub>O<sub>2</sub>-treated sample compared to the HNO<sub>3</sub>-treated counterpart. The evolution of water at high temperatures could be due to the rearrangement of adjacent oxygen moieties due to the thermal decomposition [5] or the formation of oligomeric carbon species due to the harsh oxidation conditions.



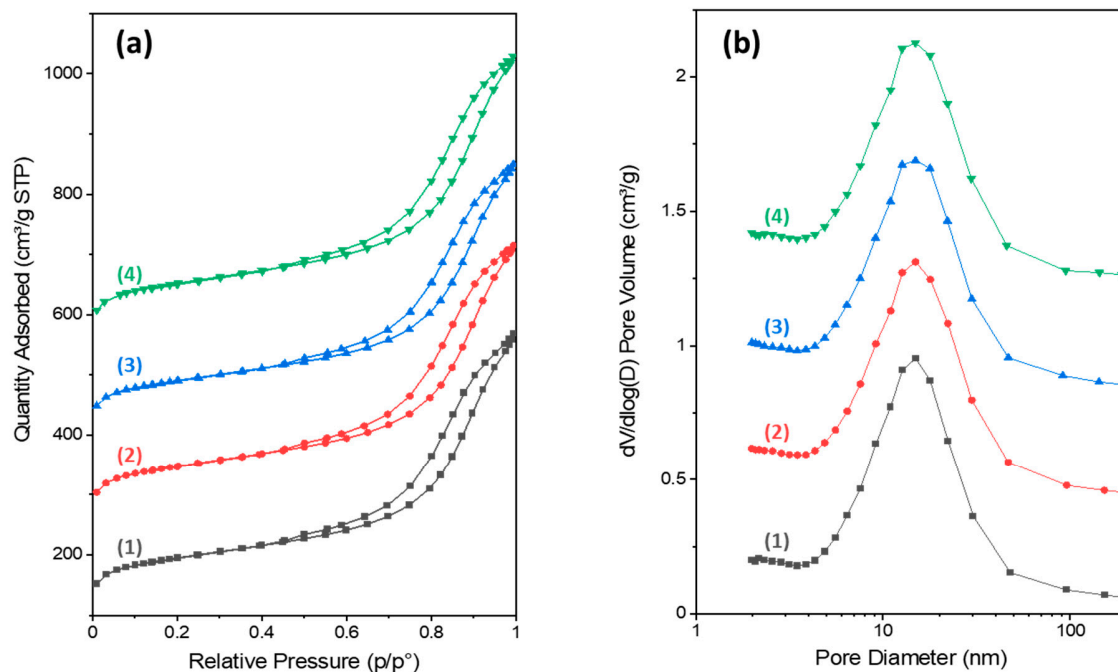
**Figure S3.** Nitrogen physisorption analysis of MC samples: (a) adsorption-desorption isotherms; offsets of 175, 350, 600, and 700 cm<sup>3</sup>/g were applied for clarity to the isotherms (2)-(5), respectively; (b) pore size distributions calculated using the BJH model. The catalysts used for the preparation of each sample were (1) formic acid, (2) citric acid, (3) nitric acid, (4) acetic acid, and (5) hydrochloric acid. Offsets of 0.5, 1.3, 2.3, and 2.8 cm<sup>3</sup>/g were applied to the pore size distributions (2)-(5), respectively.



**Figure S4.** XPS Survey spectrum of purified functionalized MC showing no Cl peak was identified on the spectrum (highlighted spots in orange circles) confirming the removal of this impurity from the structure after washing carbon with ethanol, acetone, and water.



**Figure S5.** TEM image of the carbon-supported Pd catalyst obtained by incipient wetness impregnation of as-carbonized MC (at 400 °C) with tetraammoniumpalladium (II) nitrate solution showing large Pd aggregates.



**Figure S6.** Nitrogen physisorption analysis: (1) Pd/MC-ox200, (2) Pd/MC-ox400, (3) Pd/MC-ox600, (4) Pd/MC-ox800. (a) adsorption-desorption isotherms (a constant 150 cm<sup>3</sup>/g offset was applied between the isotherms); (b) pore size distributions (PSD) calculated using the BJH model (a constant 0.4 cm<sup>3</sup>/g offset was applied between the PSDs).

**Table S1.** Textural properties of samples prepared using post treatment of HTC samples.

No	Sample Name	Treatment conditions	Surface Area (m <sup>2</sup> /g)			Average Pore Diameter (nm)	BJH Area/BET Area (%)
			BET	t-Plot Micropore	BJH – Ads.		
1	HTC	5g Glucose in 20 ml HCl 0.2M	<5	-	-	-	-
2	HTC-400air	Sample 1 treated at 400 °C in air	293	201	54	3.96	18.3%
3	HTC-400air-800N <sub>2</sub>	Sample 2 treated at 800 °C in N <sub>2</sub>	540	457	69	5.71	12.9%
4	HTC-Formic	5g Glucose in 20 ml Formic Acid 0.2M	<5	-	-	-	-
5	HTC-Formic-400air	Sample 4 heat treatment at 400 °C in air	415	312	81	3.10	19.4%
6	HTC-Formic-400air-800N <sub>2</sub> (20C/min)	Sample 5 treated at 800 °C in N <sub>2</sub> – fast heating	512	475	33	2.73	6.4%
7	HTC-Formic-400air-800N <sub>2</sub> (1C/min)	Sample 5 treated at 800 °C in N <sub>2</sub> – slow heating	531	484	42	2.73	7.9%
8	HTC-80ox1-400air-800N <sub>2</sub>	Sample 1 oxidized using 30% H <sub>2</sub> O <sub>2</sub> at 80°C for 1h	696	621	49	2.26	7.1%
9	HTC-80ox2-400air-800N <sub>2</sub>	Sample 1 oxidized using 30% H <sub>2</sub> O <sub>2</sub> at 80°C for 2h	139	106	25	4.54	17.9%
10	HTC-80ox3-400air-800N <sub>2</sub>	Sample 1 oxidized using 30% H <sub>2</sub> O <sub>2</sub> at 80°C for 3h	529	480	43	2.13	8.1%
11	HTC-90ox1-400air-800N <sub>2</sub>	Sample 1 oxidized using 30% H <sub>2</sub> O <sub>2</sub> at 90°C for 1h	475	427	32	2.49	6.7%
12	HTC(2.4Glu)-400air-800N <sub>2</sub>	Glucose 0.5g F127, 4.38 mg mesitylene - 48h	414	342	52	3.86	12.5%
13	HTC(2.4Fru)-400air-800N <sub>2</sub>	Fructose, 0.5g F127, 4.38 mg mesitylene in - 48h	516	421	73	3.63	14.2%



## References

1. Nikolov, P.Y.; Yaylayan, V.A. Thermal decomposition of 5-(hydroxymethyl)-2-furaldehyde (HMF) and its further transformations in the presence of glycine. *J. Agric. Food Chem.* **2011**, *59*, 10104–10113. <https://doi.org/10.1021/jf202470u>.
2. Zhao, M.; Li, B.; Cai, J.-X.; Liu, C.; McAdam, K.G.; Zhang, K. Thermal & chemical analyses of hydrothermally derived carbon materials from corn starch. *Fuel Process. Technol.* **2016**, *153*, 43–49. <https://doi.org/10.1016/j.fuproc.2016.08.002>.
3. Gerber, I.; Oubenali, M.; Bacsá, R.; Durand, J.; Gonçalves, A.; Pereira, M.F.R.; Jolibois, F.; Perrin, L.; Poteau, R.; Serp, P. Theoretical and Experimental Studies on the Carbon-Nanotube Surface Oxidation by Nitric Acid: Interplay between Functionalization and Vacancy Enlargement. *Chem.–Eur. J.* **2011**, *17*, 11467–11477, doi:doi.org/10.1002/chem.201101438.
4. Gomezserrano, V.; Acedoramos, M.; Lopezpeinado, A.; Valenzuelacalahorro, C. Oxidation of activated carbon by hydrogen peroxide. Study of surface functional groups by FT-i.r. *Fuel* **1994**, *73*, 387–395. [https://doi.org/10.1016/0016-2361\(94\)90092-2](https://doi.org/10.1016/0016-2361(94)90092-2).
5. Eigler, S.; Dotzer, C.; Hirsch, A.; Enzelberger, M.; Müller, P. Formation and Decomposition of CO<sub>2</sub> Intercalated Graphene Oxide. *Chem. Mater.* **2012**, *24*, 1276–1282. <https://doi.org/10.1021/cm203223z>.