

# The roles of formic acid and levulinic acid on the formation and growth of carbonaceous spheres by hydrothermal carbonization

Yujie Qi<sup>a</sup>, Biying Song<sup>a</sup> and Yang Qi<sup>ab\*</sup>

<sup>a</sup> Department of Materials Physics and Chemistry, Northeastern University, Shenyang 110819, China.

<sup>b</sup> Key Laboratory for Anisotropy and Texture of Materials (MOE), Northeastern University, Shenyang 110819, China.

## Supporting Information

**Table S1.** Synthesis conditions and statistic results for carbonaceous spheres obtained from 0.100 M sucrose solutions.

Sample	Time (h)	100% Range		90% Range		50% Range		Standard deviation (nm)
		Mean diameter (nm)	Range (nm)	Mean diameter (nm)	Range (nm)	Mean diameter (nm)	Range (nm)	
A-1	3	162.72	47.49~817.35	159.09	96.42~244.06	156.08	125.35~190.25	54.07
A-2	3.25	139.93	73.81~324.11	138.78	98.69~186.01	138.17	121.18~154.95	27.40
A-3	3.5	189.70	93.3~475.86	188.18	140.42~249.86	185.63	166.88~209.85	35.38
A-4	3.75	138.19	75.11~251.97	137.55	104.82~182.05	136.75	123.59~149.71	22.82
A-5	4	192.72	74.61~400.05	190.55	145.48~259.40	186.11	169.86~208.21	38.70

A-6	4.5	192.31	89.07~329.50	191.47	142.56~250.70	191.26	173.05~209.27	31.58
A-7	5	208.22	81.34~378.08	206.98	154.13~277.26	203.46	183.09~228.32	37.99
A-8	5.5	287.99	139.47~499.13	287.36	211.60~366.45	287.95	260.08~314.43	46.09
A-9	6	287.85	107.66~459.59	288.61	213.79~348.87	290.83	262.29~316.75	42.51

**Table S2.** Synthesis conditions and statistic results for carbonaceous spheres obtained from 0.100 M sucrose and 0.159 M formic acid mixed solutions.

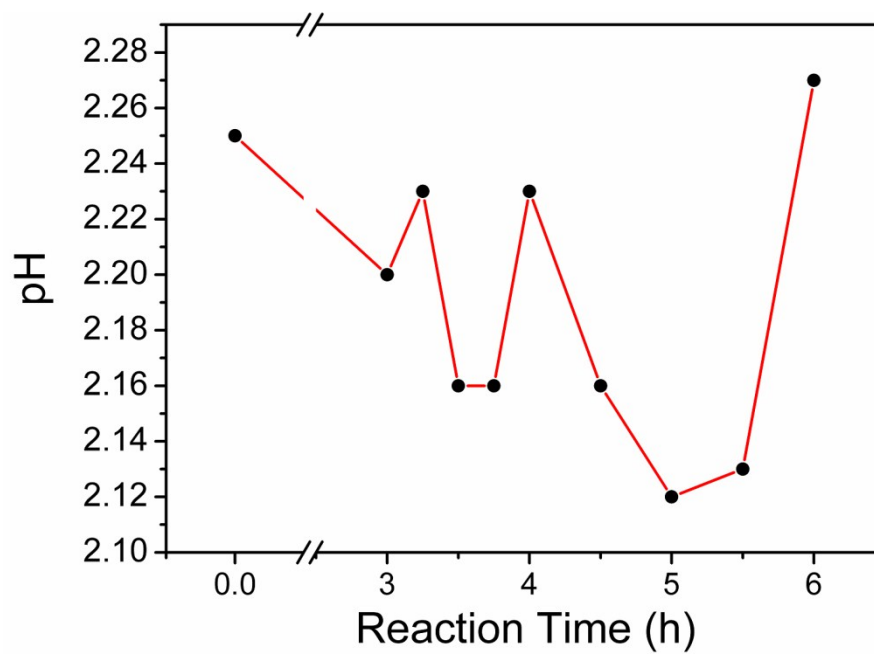
Sample	Time (h)	100% Range		90% Range		50% Range		Standard deviation (nm)
		Mean diameter (nm)	Range (nm)	Mean diameter (nm)	Range (nm)	Mean diameter (nm)	Range (nm)	
B-1	3	535.14	190.92~691.77	536.37	481.21~580.35	537.773	518.55~554.49	31.05
B-2	3.25	619.18	202.87~741.06	620.89	550.99~673.63	622.56	600.04~645.07	37.70
B-3	3.5	724.31	557.47~936.85	724.50	653.95~797.46	723.30	695.74~751.79	46.47
B-4	3.75	516.21	332.19~681.73	518.05	449.95~570.30	519.69	496.21~541.56	39.10
B-5	4	602.43	52.27~900.89	607.60	522.44~672.01	610.06	582.28~632.23	58.96
B-6	4.5	775.90	543.17~2207.31	775.20	680.68~853.36	777.37	745.94~806.78	72.22
B-7	5	906.14	651.50~1089.79	907.85	823.68~978.08	909.04	879.38~936.50	49.91
B-8	5.5	1037.65	620.03~2677.35	1027.42	900.32~1168.57	1023.22	975.77~1079.85	146.17
B-9	6	1120.63	757.84~1646.71	1117.73	992.38~1269.51	1115.74	1067.66~1162.24	88.56

**Table S3.** Synthesis conditions and statistic results for carbonaceous spheres obtained from 0.100 M sucrose and 0.100 M levulinic acid mixed solutions.

Sample	Time (h)	100% Range		90% Range		50% Range		Standard deviation (nm)
		Mean diameter (nm)	Range (nm)	Mean diameter (nm)	Range (nm)	Mean diameter (nm)	Range (nm)	
C-1	3	182.19	118.72~332.41	181.18	148.17~216.37	180.98	167.92~194.72	23.43
C-2	3.25	178.96	64.98~335.23	178.77	135.16~221.72	178.63	161.74~197.13	28.27
C-3	3.5	222.15	74.22~337.65	222.90	167.43~270.13	223.54	202.40~244.55	32.35
C-4	3.75	249.50	121.33~368.88	249.88	194.61~299.87	251.28	228.72~271.49	32.69
C-5	4	234.51	91.98~418.92	234.82	164.45~290.12	237.23	211.73~260.13	40.39
C-6	4.5	223.57	135.64~420.39	222.85	165.95~282.95	222.27	200.96~244.60	35.42
C-7	5	252.04	102.01~439.12	251.67	188.32~317.27	251.15	225.05~278.59	39.62
C-8	5.5	354.71	209.00~650.83	355.41	284.15~415.67	357.57	327.77~382.85	41.85
C-9	6	464.52	176.89~581.95	468.47	348.59~546.46	473.34	434.01~506.76	60.81

**Table S4.** Synthesis conditions and statistic results for carbonaceous spheres obtained from 0.100 M sucrose, 0.050 M formic acid and 0.100 M levulinic acid mixed solutions.

Sample	Time (h)	100% Range		90% Range		50% Range		Standard deviation (nm)
		Mean diameter (nm)	Range (nm)	Mean diameter (nm)	Range (nm)	Mean diameter (nm)	Range (nm)	
		D-1	3	252.82	132.42~429.59	253.85	191.23~298.41	
D-2	3.25	461.31	201.38~683.24	463.19	382.79~516.53	465.44	439.50~489.10	41.98
D-3	3.5	383.47	198.55~512.51	384.87	317.37~438.66	386.82	360.65~408.63	37.75
D-4	3.75	460.09	263.50~582.14	461.65	388.24~511.39	463.89	438.83~488.54	38.71
D-5	4	441.75	190.61~605.86	442.86	376.90~498.10	444.15	420.39~466.15	37.40
D-6	4.5	524.37	257.71~665.96	526.71	434.85~589.09	530.19	499.83~557.60	48.49
D-7	5	794.98	527.34~995.57	797.13	680.82~887.27	800.67	758.40~833.71	62.30
D-8	5.5	965.25	554.59~1480.96	967.29	857.71~1045.46	969.99	934.86~1002.22	59.88
D-9	6	885.35	575.57~1917.08	884.97	749.87~1013.60	885.83	828.46~938.24	89.35



**Figure S1.** The variation of pH values of solutions from the adding formic acid system under different reaction time.