Electronic Supplementary Material (ESI) for Green Chemistry

Supporting Information for

Sodium salt effect on the hydrothermal carbonization of biomass: A catalyst to carbon-based nanostructured materials for lithium-ion battery application

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Experimental Part

In-situ investigation of the phase behavior of hydrothermal carbonization (HTC) process: 20 ml aqueous solution of glucose (0.125 g ml^{-1}) was charged into a glass tube and then placed in a sealed viewable autoclave (Fig. S1) at room temperature (Fig.1, 0 min). Subsequently, increase the temperature to 180 °C and *in-situ* record the reaction behavior of HTC by the digital camera. After the reaction of 5 hours, a brown carbon colloidal solution was obtained (Fig. 1a). For comparison, a certain amount of metal salt such as Na_2SO_4 (0.1 M) was added into the aqueous solution of glucose (0.125 g ml^{-1}) and processed the same procedure to investigate the effects of metal salt to the HTC process. The phenomena corresponding to reaction time together their products were presented in Fig. 1b.

In the experiment of synthesis the carbon materials, 30 ml aqueous solution of glucose or glucose-salt was processed in 50 ml autoclave (Fig. S4b), with the aim of getting a larger amount of carbon materials for comparing them more accurately. The obtained carbon micro particles were collected by the filtration and wash with using water to remove the sodium salt completely, while the carbon colloids prepared from HTC of pure glucose aqueous solution were collected by the high speed centrifugation (1,2000 rpm, 30 min). In the experiment, we have found that the sealing of autoclave is quite important for the HTC of biomass. Herein, we strongly suggest the use of autoclave that with a sealing-bottom rather than that with a movable one (Fig. S4a, b). The autoclave with moveable bottom is incompetent for sealing and always gives rise to products with different morphology, rather than dispersive carbon particles. For example, only coral or peanut structured carbon materials were obtained if the movable bottom autoclave were used or the sealing of autoclave is not complete (Fig. S4a1,b1). Therefore, all the experiments include the experiment of coating Fe_3O_4 particle with a layer of porous carbon; we always use the sealing autoclave that without the moveable bottom (Fig. S4b).

Coating Fe_3O_4 particles with a uniform layer of porous carbon: First, Fe_3O_4 particles were prepared according to the previous literature.[S1] 1.0 g Fe_3O_4 particles (m_{Fe3O4} = 1 g) were well dispersed in 2.5 g aqueous solution of glucose-salt (glucose, 0.1875 g g^{-1}; Na_2SO_4, 0.06 g g^{-1}) under ultrasonic treatment for 1 h in a glass bottle (Fig. S2, c1). The theoretical carbon mass (m_C) and mass percent ($m_C\%$) calculated based on the mass of glucose ($C_6H_{12}O_6$, 180 g mol^{-1}, C% = 72/180) is as following:

$m_C = 0.1875 \times 2.5 \times 72/180 \text{ g} = 0.1875 \text{ g}$

$m_C\% = m_C/(m_C + m_{Fe3O4}) = 0.1875/(1+0.1875) = 15.79\%$

After that, the glass bottle was placed in Teflon vessel and sealed in an autoclave to hydrothermal carbonization in an oven at 180 ^{o}C for 4 h. The type of autoclave is the same as we used before which is competent for completely sealing.[S2] Till the autoclave cooled down to the room temperature, take the glass bottle out and dry the slurry at 100 ^{o}C to brown solid cakes of Fe_3O_4@C@salt-Intermeidates (Fig. S4, c2). Crush the solid-cakes into powders and then calcination in the tube-furnace at the temperature of 500 ^{o}C for 4 h under the Ar atmosphere (heating rate, 5 ^{o}C min^{-1}) give rise to the powders of Fe_3O_4@C-salt (Fig. S4, c3). Finally, the core-shell structured Fe_3O_4@porous-C composite were obtained after removing the salt with using H_2O wash. The percentage of salt's recovery (Na_2SO_4) is about 98.5%, demonstrating the Na_2SO_4 could be almost washed completely by water. This is well accordance with the absence of Na1s peaks in XPS spectrum of Fe_3O_4@porous-C (Fig. S6). According to the TGA analysis, the residual carbon mass percent on Fe_3O_4 particles is about 9.6%, and the mass of residual carbon ($m_{C\text{-residual}}$) is about 0.1062 g which was calculated from the equation of $m_{C\text{-residual}}/(m_{C\text{-residual}} + m_{Fe3O4}) = 9.6\%$. Therefore, the effective conversation efficiency of precursors is about 22.7% ($m_{C\text{-residual}}/m_{glucose} = 0.1062/(2.5 \text{ g} \times 0.1875 \text{ g g}^{-1}) = 22.7\%$).

Electrochemical measurement: The electrochemical experiments were carried out using a CR2025 coin-type cell. One typical electrode was prepared by mixing the active materials of Fe_3O_4@porous-C, acetylene black, and polymer binder (polyvinylidene difluoride, PVDF) with a weight ratio of 80:10:10 to slurry, which was casted on a copper foil. After drying, the coated copper foil was roll-pressed and punched into electrode unit with a diameter of 14 mm. The cell was composed of an as-prepared electrode and lithium foil as the counter electrode, which were separated by a Celgard 2400 membrane. The electrolyte was 1 M $LiPF_6$ in a mixed solution of ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 w/w). The cells were assembled in a dry argon-filled glove box with moisture and oxygen concentrations below 1 ppm. Galvanostatic charge-discharge cycles of the cells were performed in the voltage range between 3.0 V and 0.01 V under different current densities.

References:

S1. H. Deng, X. L. Li, Q. Peng, X. Wang, J. P. Chen and Y. D. Li, *Angew. Chem. Int. Ed.*, 2005, **44**, 2782.
S2. J. Ming, Y. Q. Wu, Y. C. Yu and F. Y. Zhao, *Chem. Commun.* 2011, **47**, 5223.

Characterization

The morphology of particles were characterized by field emission scanning electron microscopy (FESEM), which was taken on a XL30 ESEM microscope with a beam energy of 20 kV. The core-shell structure was characterized by transmission electron microscopy (TEM) images using a JEOL-2100F microscope operated at 200 kV. The surface area and porosity of Fe_3O_4 and Fe_3O_4@porous-C composite were determined by using a Quantachrome Autosorb-1-MP automated gas adsorption system using nitrogen as the adsorbate at liquid nitrogen temperature (77 K). The samples were outgassed under vacuum for 48 h at 100 ^{o}C. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method, and the microporous characteristic was determined using the t-plot method. The pore diameters were obtained from the adsorption branch of the isotherm using the Barrett-Joyner-Halenda (BJH) method. The content of carbon layer coated on Fe_3O_4 particles were measured by the thermalgravimetric analysis (TGA, 10 ^{o}C min^{-1}, Air). The sheet resistance of Fe_3O_4@porous-C and primary Fe_3O_4 particles were tested by the semi auto 4-point probe system (Advanced Instrument Technology).

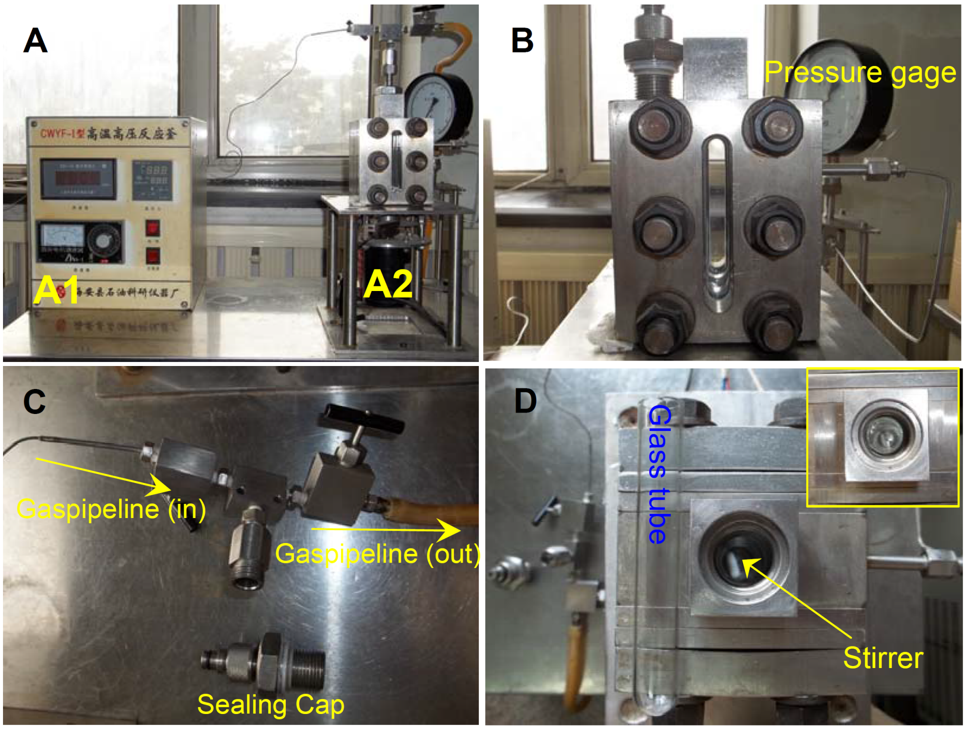


Fig. S1. (A) Total graph of viewable autoclave. (A1) Power control System including the setting of temperature and stirring rate. (A2) This part includes magnetic stirring, heating wire and temperature probe. (B) Viewable autoclave with the transparent quartz window. (C) Gaspipeline and sealing cap of the autoclave. In our experiment to view the behaviors of HTC reaction, we didn't use any special gas and it is just normal air. (D) Top view of the inner of autoclave, in which the stirrer (white one) and glass tube could be used. The main reason of using glass tube here is to avoid the probable effect of steel wall (i.e., the main chemical composition of the autoclave's steel wall is iron) during the HTC, because the solution of HTC is acidic and the PH value is between 2 and 4 (Table S2). But here, we didn't use the stir because most HTC processed under the static conditions. Noteworthy, this viewable instrument is available to view and investigate all the hydrothermal reactions include this HTC process under the situations of static or stirring conditions.

Table S1. The elemental content in the carbon materials prepared from HTC of aqueous glucose solution with using different kind of salt (The standard deviation is less than 1%).

Kind of Salt / mol L^{-1}	C (wt%)	H (wt%)	O (wt%)	N (wt%)
No salt	66.0	4.07	29.93	0
Na_2SO_4 / 0.1	66.16	4.61	29.23	0
NaCl / 0.2	65.95	4.41	29.64	0
$NaNO_3$ / 0.2	65.92	4.43	29.65	0

Table S2 Analysis of the solution before and after HTC reaction at 180 °C for 5 hours under the effect of different sodium salt.

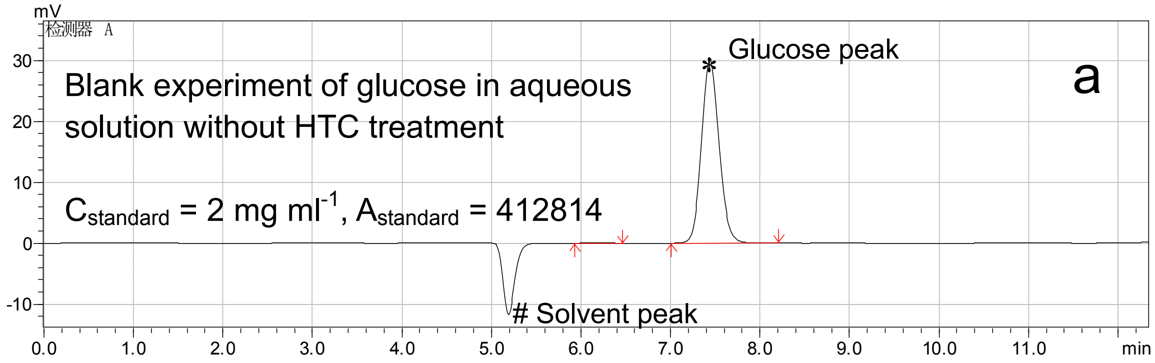
The kind of salt/concentration	pH value of solution before reaction‡	pH value of solution after reaction‡	Concentration of glucose after reaction (mg ml^{-1})[*a]
No salt	7.15	2.57	92.9[b]
Na_2SO_4 / 0.1 M	6.66	2.18	28.9[c]
Na_2CO_3 / 0.1 M	10.54	3.89	4.8[d]
NaCl / 0.1 M	7.12	2.29	88.0[e]
$NaNO_3$ / 0.1 M	6.71	2.3	79.2[f]
NaCl / 0.2 M	6.87	2.02	81.3[g]
$NaNO_3$ / 0.2 M	6.61	2.13	72.6[h]

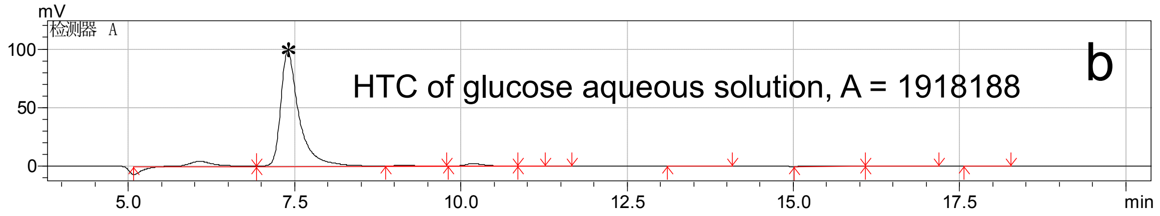
‡The variation of pH value of solution before and after HTC demonstrates the formed solution of intermediates is acidic.

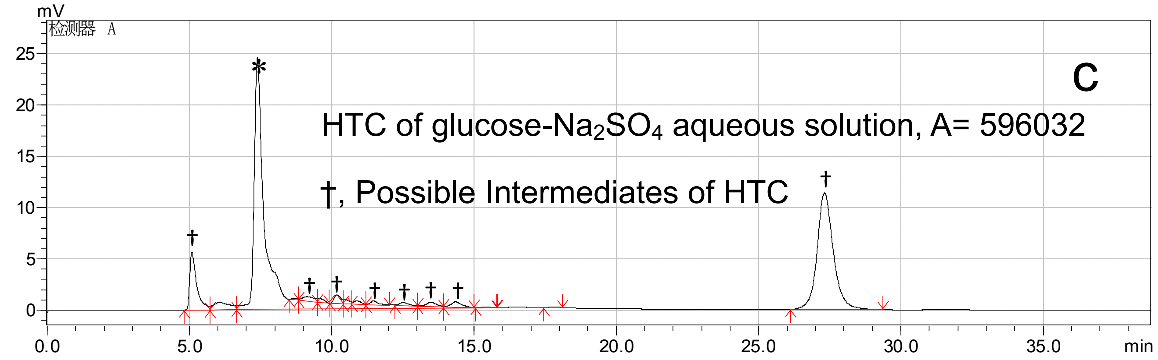
*Reaction conditions: 30 ml aqueous solution of salt-glucose in 50 ml Teflon was completely sealed in the sealing autoclave that without movable autoclave (Fig. S2d), and then hydrothermal carbonization of the solution at 180 °C for 5 hours. Concentration of glucose is 125 mg ml^{-1}. The used mass amount of Na_2SO_4, Na_2CO_3, NaCl, $NaNO_3$ are about 0.4261, 0.3180, 0.1753 / 0.3506, 0.2550 / 0.51 g.

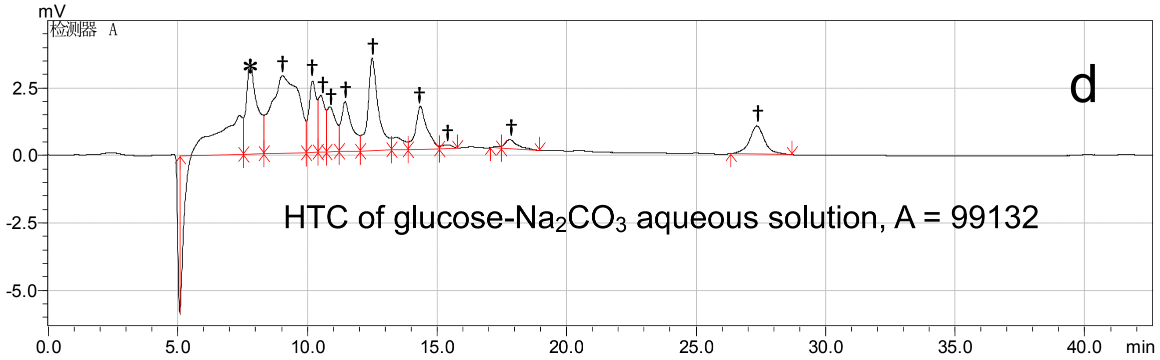
HPLC system (Shimadzu LC-20AB) with RI detector (Shimadzu RID-10A), and an Aminex HPX-87H column (Bio-Rad, 300×7.8 mm), using 0.5 mM H_2SO_4 as eluent at a flow rate of 0.7 ml/min at 328 K, was used to analysis the concentration of glucose in the residual solution (10 times diluted based on primary residual solution before test).

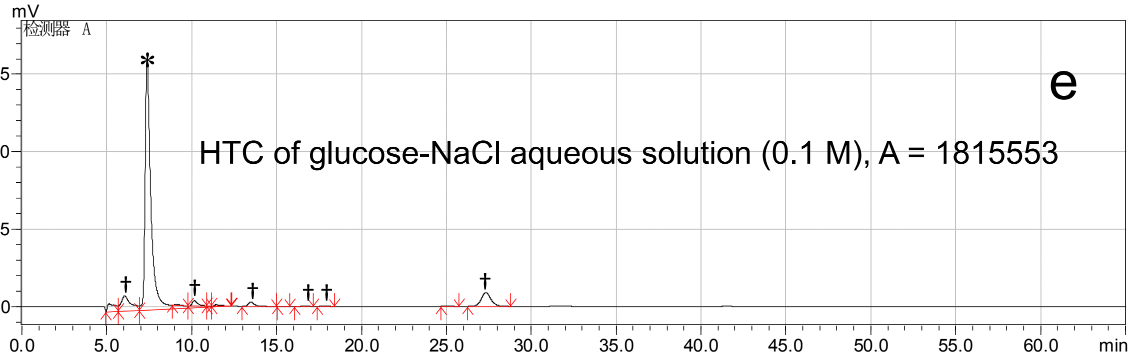
[a] The external standard method was used in the analysis, in which $C_1/A_1 = C_2/A_2$ (C_1, C_2, the concentration of glucose, A_1, A_2, the peak area of glucose). The used standard concentration of glucose is 2 mg ml^{-1} in the blank experiment (a).

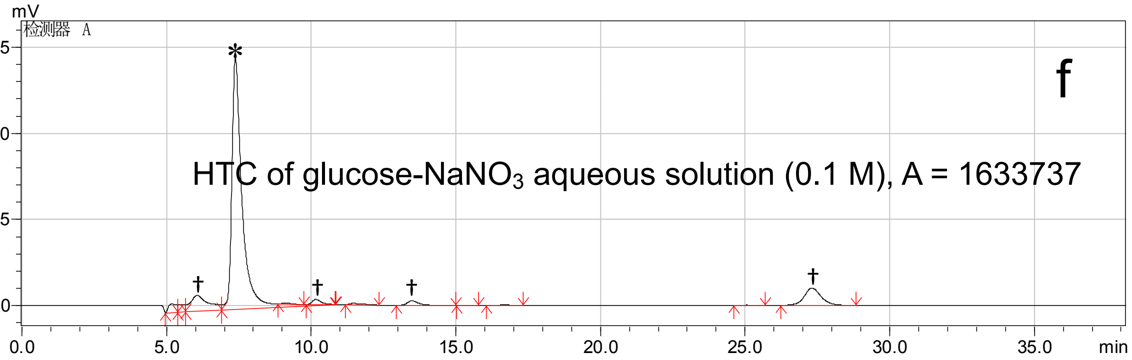

mV
检测器 A
a
Glucose peak
*
Blank experiment of glucose in aqueous solution without HTC treatment
$C_{standard}$ = 2 mg ml^{-1}, $A_{standard}$ = 412814
Solvent peak
30
20
10
0
-10
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
min

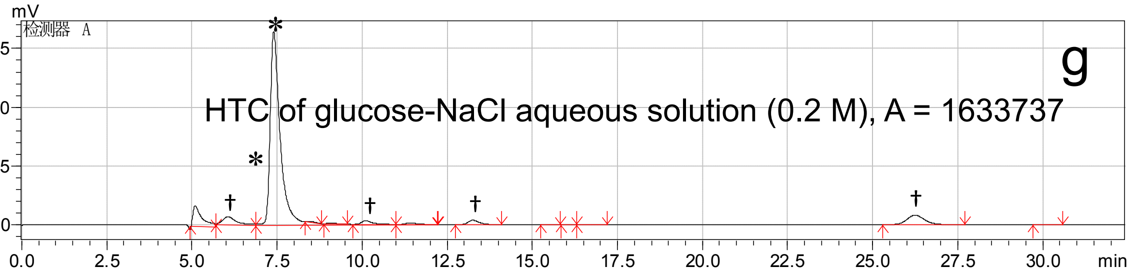

mV
检测器 A
b
*
HTC of glucose aqueous solution, A = 1918188
100
50
0
5.0
7.5
10.0
12.5
15.0
17.5
min

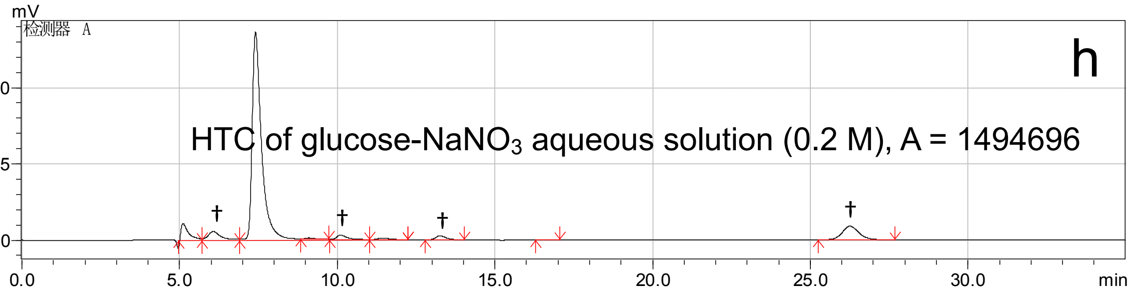

mV
检测器 A
c
*
HTC of glucose-Na_2SO_4 aqueous solution, A= 596032
†, Possible Intermediates of HTC
†
25
20
15
10
5
0
0.0
5.0
10.0
15.0
20.0
25.0
30.0
35.0
min


mV
检测器 A
d
*
†
HTC of glucose-Na_2CO_3 aqueous solution, A = 99132
2.5
0.0
-2.5
-5.0
0.0
5.0
10.0
15.0
20.0
25.0
30.0
35.0
40.0
min


mV
检测器 A
e
HTC of glucose-NaCl aqueous solution (0.1 M), A = 1815553
75
50
25
0
0.0
5.0
10.0
15.0
20.0
25.0
30.0
35.0
40.0
45.0
50.0
55.0
60.0
min
*
†


mV
检测器 A
f
HTC of glucose-NaNO3 aqueous solution (0.1 M), A = 1633737
75
50
25
0
0.0
5.0
10.0
15.0
20.0
25.0
30.0
35.0
min
*
†


mV
检测器 A
g
HTC of glucose-NaCl aqueous solution (0.2 M), A = 1633737
75
50
25
0
0.0
2.5
5.0
7.5
10.0
12.5
15.0
17.5
20.0
22.5
25.0
27.5
30.0
min
*
†


mV
检测器 A
h
HTC of glucose-NaNO3 aqueous solution (0.2 M), A = 1494696
50
25
0
0.0
5.0
10.0
15.0
20.0
25.0
30.0
min
†

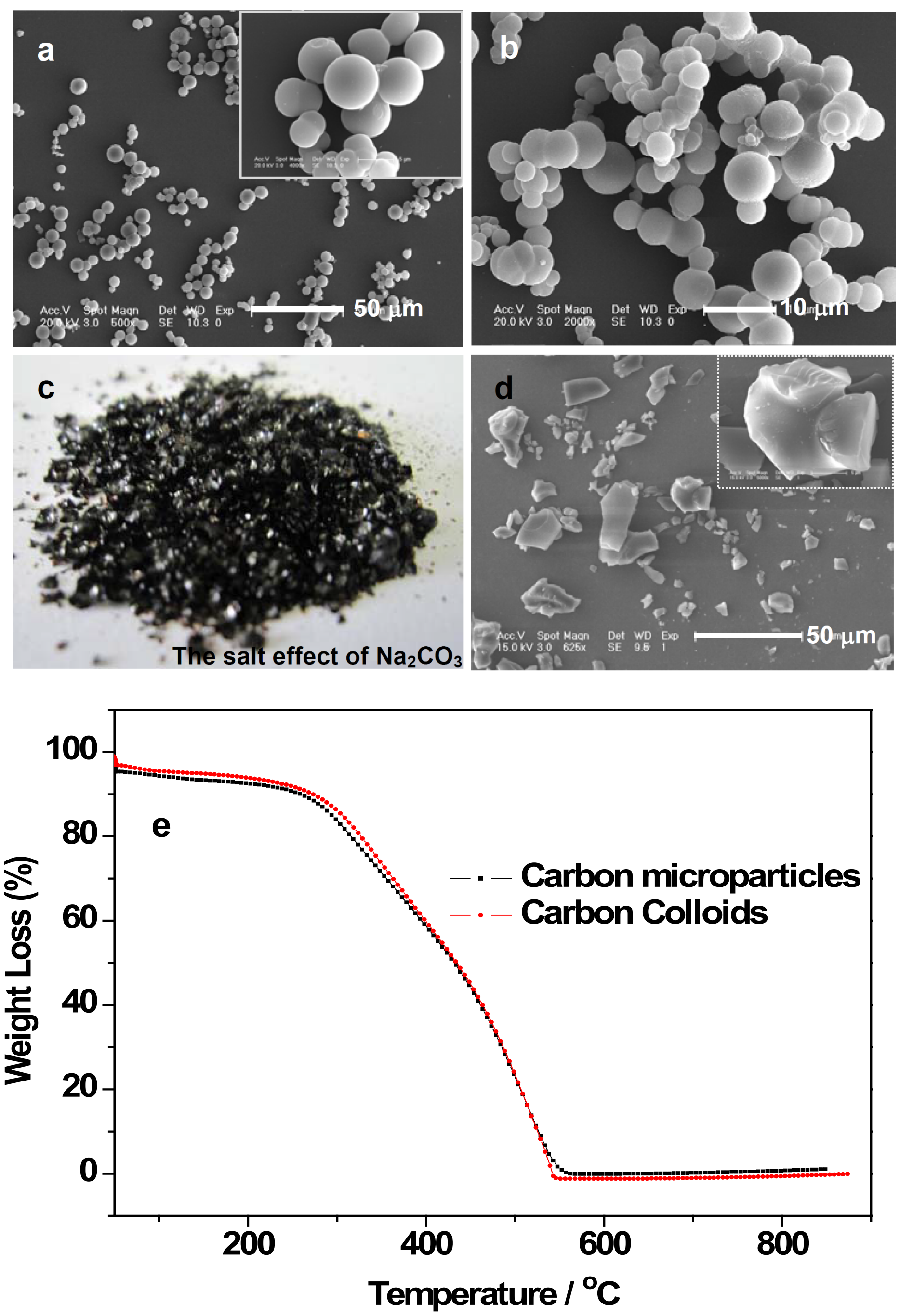
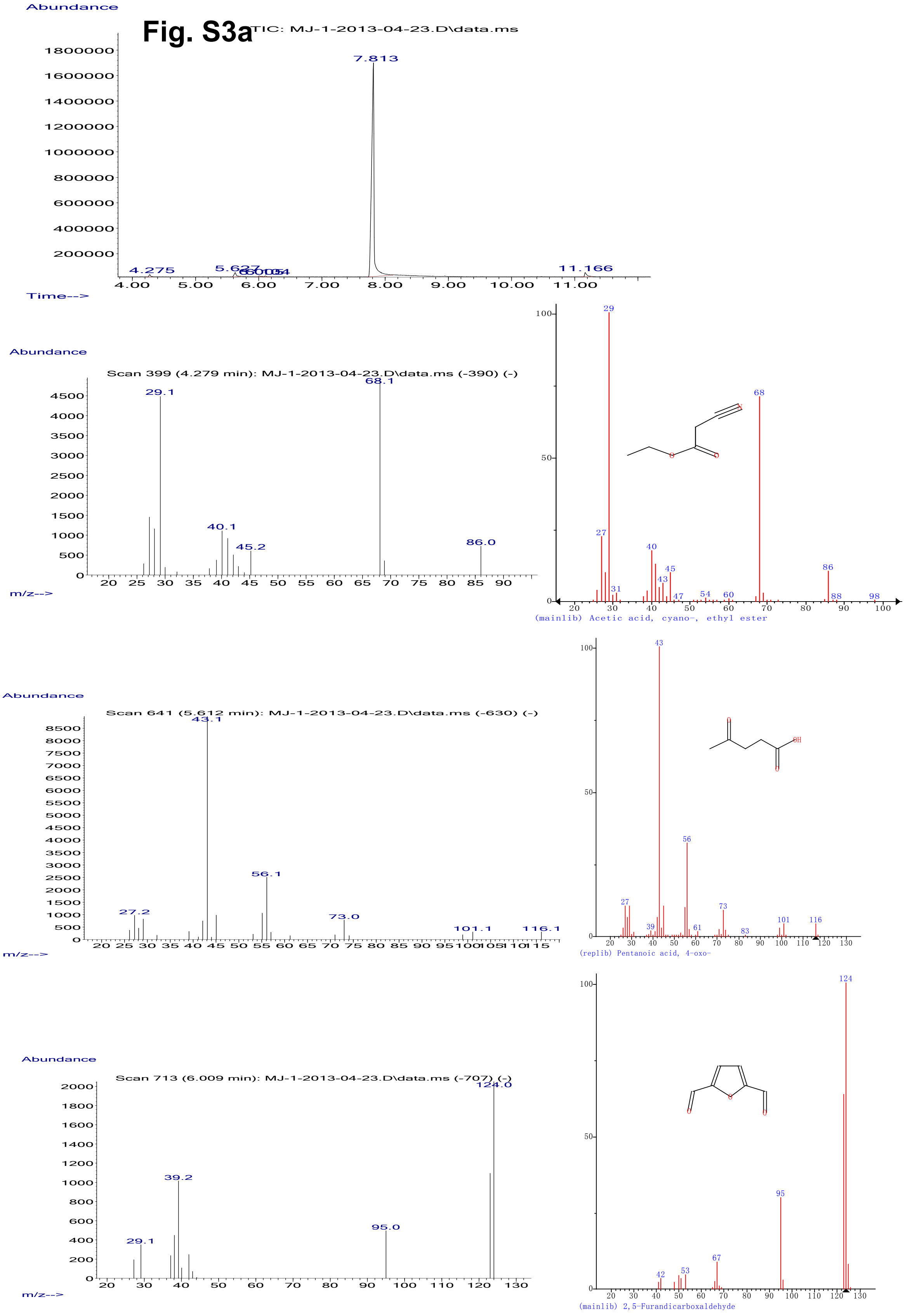


Fig. S2. Digital and SEM images of carbon materials resulted from HTC of (a) NaCl, (b) $NaNO_3$ and (c, d) Na_2CO_3-glucose solution. (e) Comparative TGA analysis of carbon colloids prepared from HTC of glucose and micro particles obtained from HTC of Na_2SO_4-glucose solution.

Fig. S3a


Abundance
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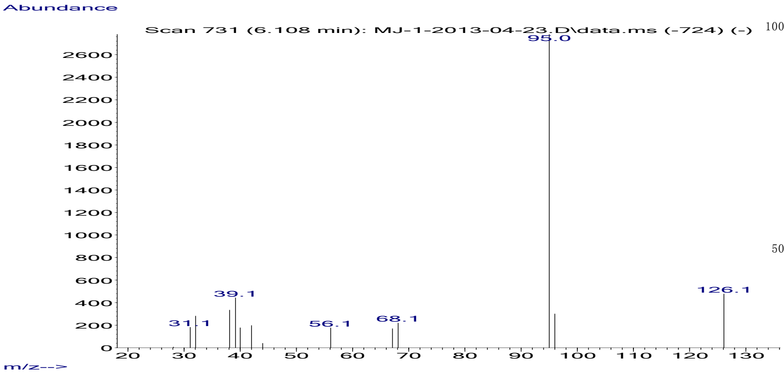
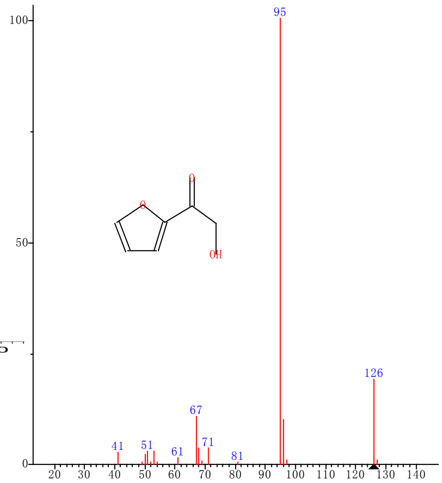
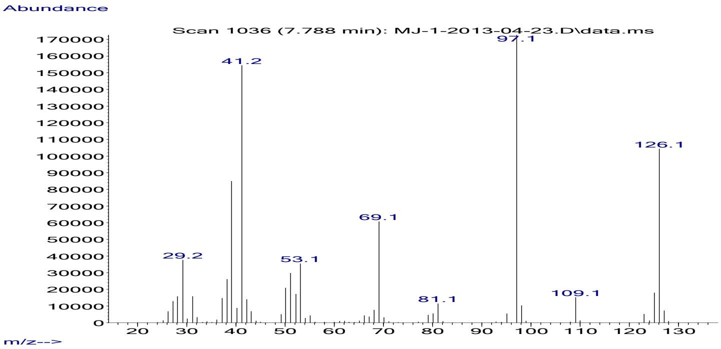
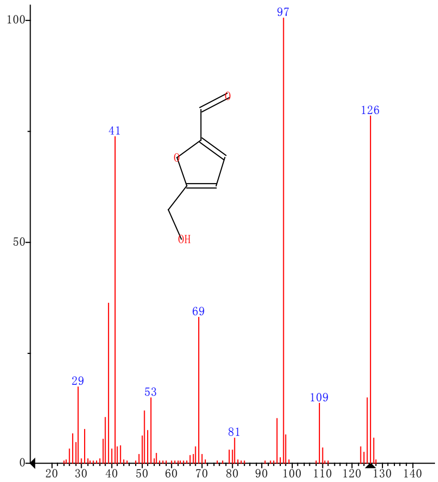
1600000
1400000
1200000
1000000
800000
600000
400000
200000
7.813
4.275
5.627
6.005
11.166
4.00 5.00 6.00 7.00 8.00 9.00 10.00 11.00
Time-->
Abundance
Scan 399 (4.279 min): MJ-1-2013-04-23.D\data.ms (-390) (-)
29.1
68.1
40.1
45.2
86.0
m/z-->
29
68
27
40
45
43
31
47
54
60
86
88
98
(mainlib) Acetic acid, cyano-, ethyl ester
Abundance
Scan 641 (5.612 min): MJ-1-2013-04-23.D\data.ms (-630) (-)
43.1
56.1
27.2
73.0
101.1
116.1
m/z-->
43
56
27
73
39
61
83
101
116
(replib) Pentanoic acid, 4-oxo-
Abundance
Scan 713 (6.009 min): MJ-1-2013-04-23.D\data.ms (-707) (-)
124.0
39.2
29.1
95.0
m/z-->
124
95
67
53
42
(mainlib) 2,5-Furandicarboxaldehyde



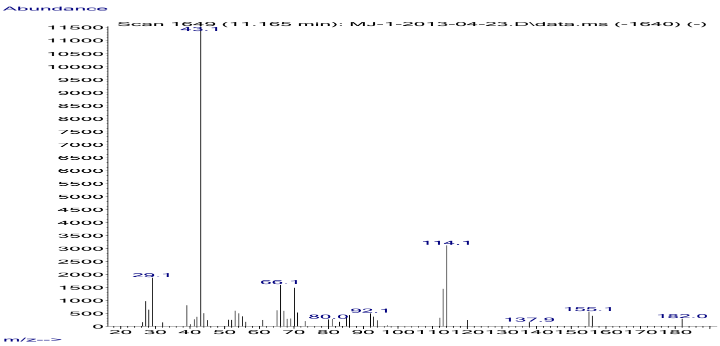


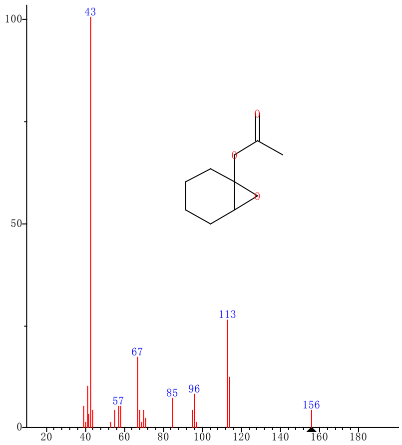
(mainlib) Furyl hydroxymethyl ketone





(mainlib) 2-Furancarboxaldehyde, 5-(hydroxymethyl)-





(mainlib) 7-Oxabicyclo[4.1.0]heptan-1-ol, acetate

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 peak   R.T.  first  max  last  PK   peak       corr.    corr.    % of
  #     min    scan scan  scan  TY  height      area     % max.   total
 ---   -----  ----- ---- ---- ---  -------    -------   ------   -------

  1    4.275   389  398  405   M2    18550     324652    0.72%    0.685%
  2    5.627   635  644  662   M     33523     878795    1.95%    1.855%
  3    6.005   704  712  723   M3     7927     202394    0.45%    0.427%
  4    6.104   725  730  748   M3     7304     206819    0.46%    0.436%
  5    7.813  1025 1041 1097   M   1730211   44976633  100.00%   94.923%
  6   11.166  1639 1649 1668   M     33209     792758    1.76%    1.673%
```

The intermediates in residual solution of HTC of glucose include:

(2) Pentanoic acid; 4-oxo-;

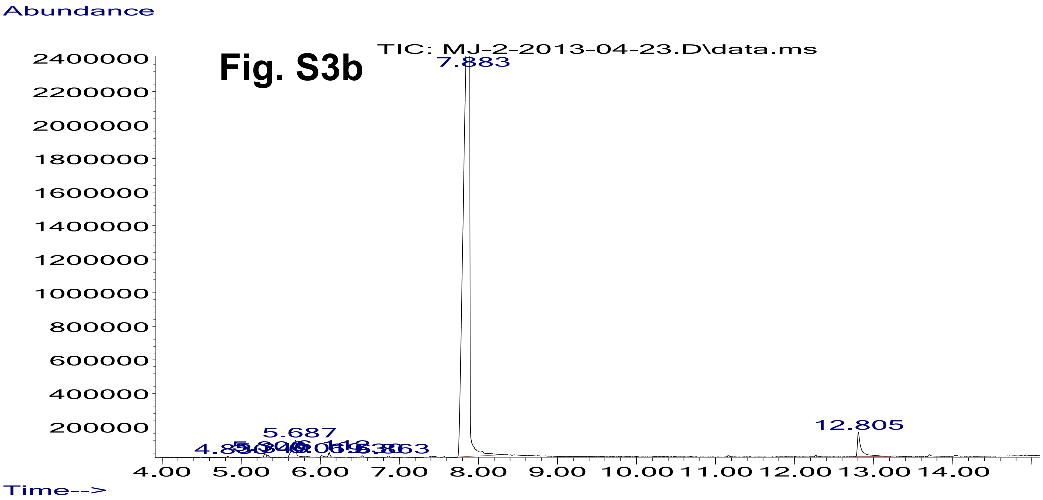
(3) 2,5-Furan dicarboxaldehyde;

(4) Furyl hydroxymethyl ketone;

(5) 2-Furancarboxal dehyde,5-(hydroxymethyl)-;

(6) 7-Oxabicyclo [4.1.0] heptan-1-ol,acetate.

Fig. S3b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12.805
Time-->
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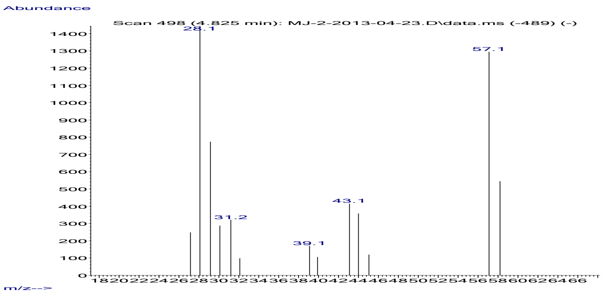
11.00
12.00
13.00
14.00


Abundance
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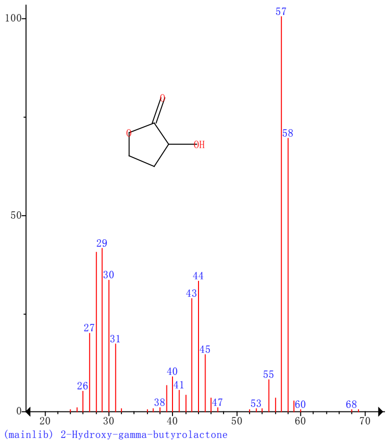
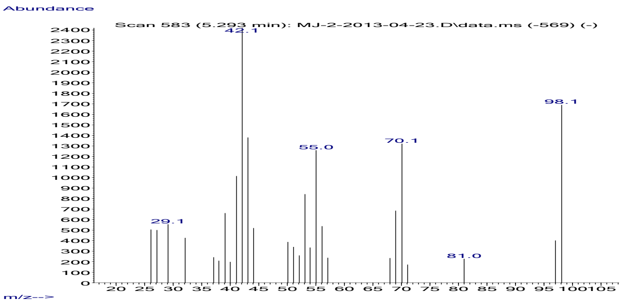
57.1
31.2
39.1
43.1
m/z-->


57
58
29
30
27
31
44
43
45
40
41
26
38
47
53
55
60
68
(mainlib) 2-Hydroxy-gamma-butyrolactone


Abundance
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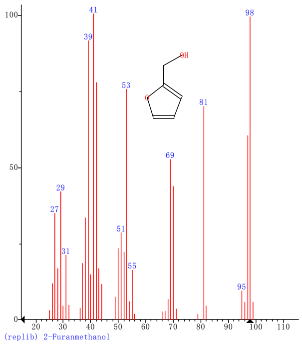
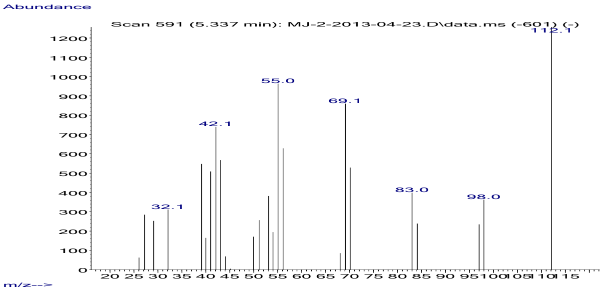
98.1
70.1
55.0
29.1
81.0
m/z-->


41
98
39
53
81
69
29
27
31
51
55
95
(replib) 2-Furanmethanol


Abundance
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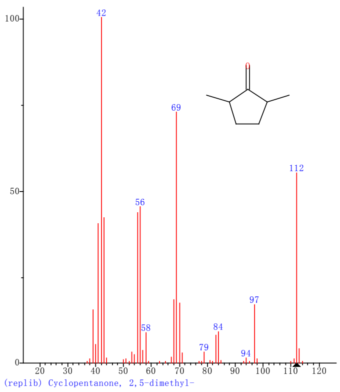
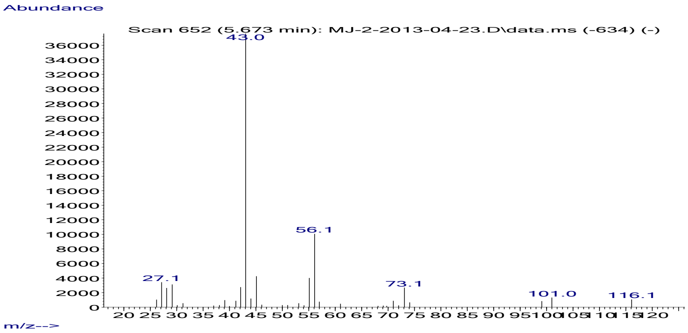
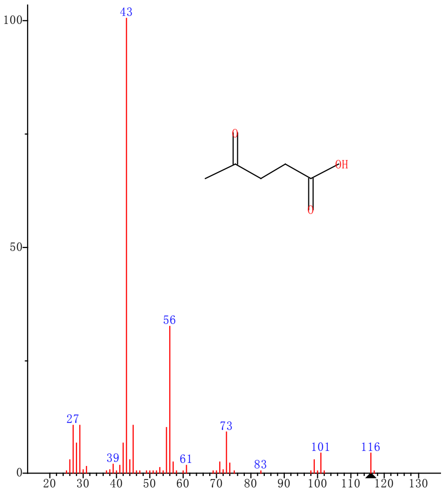
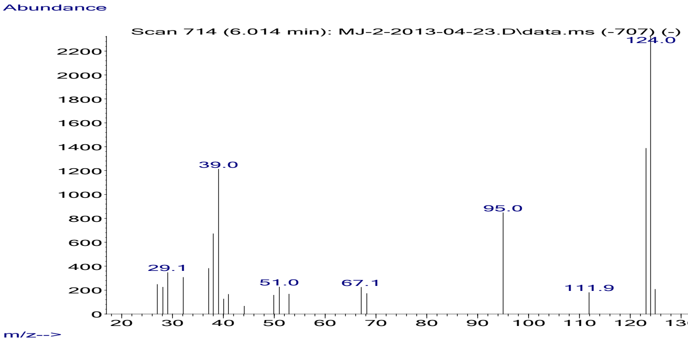
55.0
69.1
42.1
32.1
83.0
98.0
m/z-->

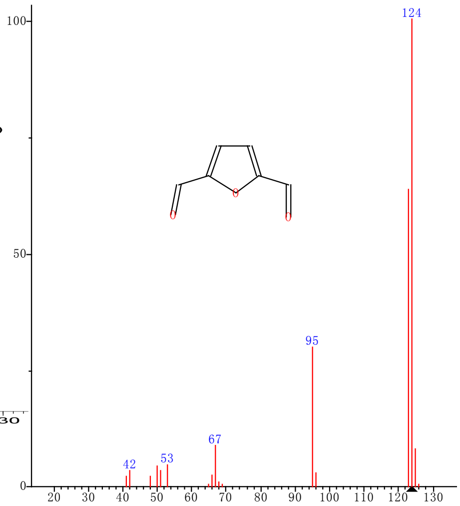

42
69
56
112
58
97
84
79
94
(replib) Cyclopentanone, 2,5-dimethyl-



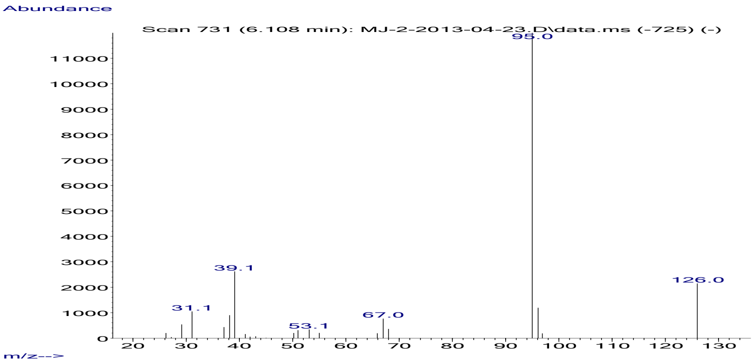


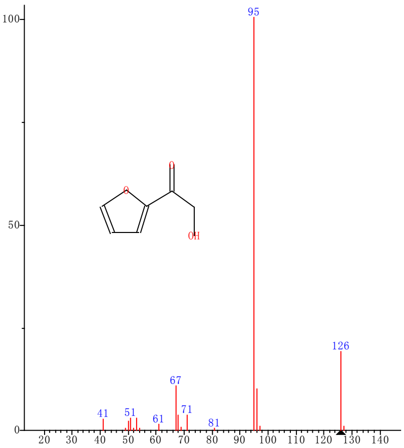
(replib) Pentanoic acid, 4-oxo-



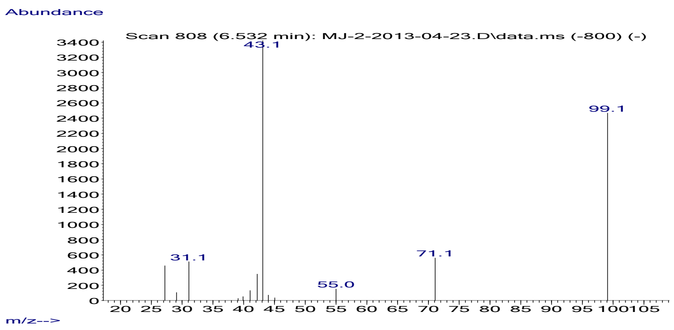


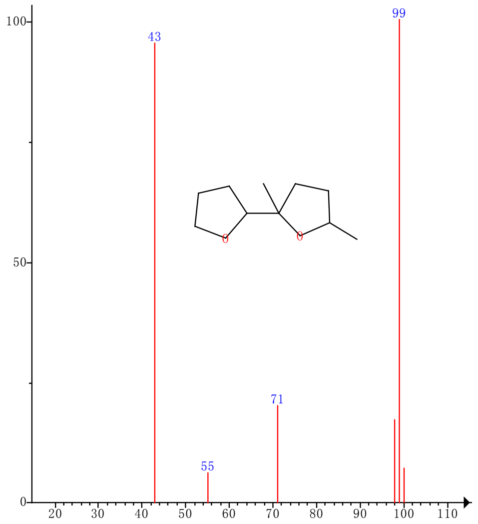
(mainlib) 2,5-Furandicarboxaldehyde



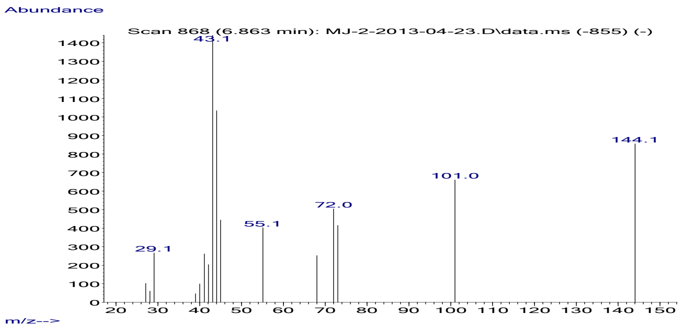


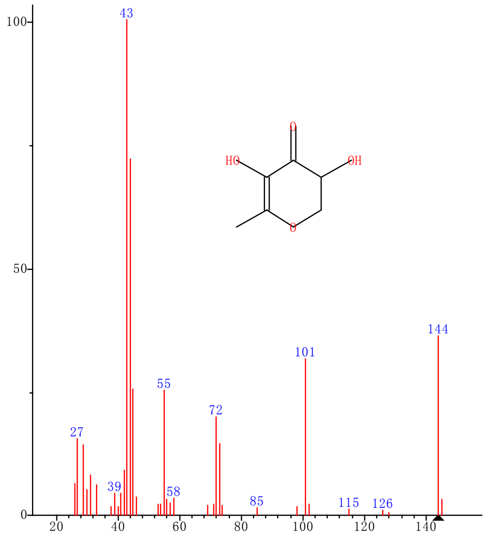
(mainlib) Furyl hydroxymethyl ketone



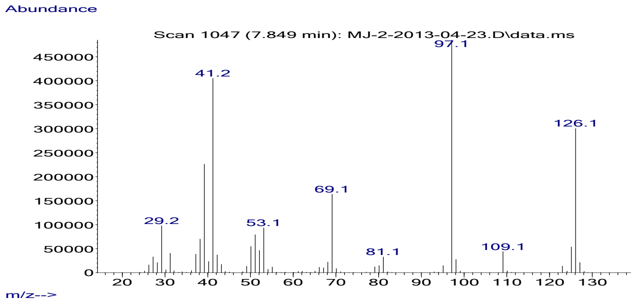


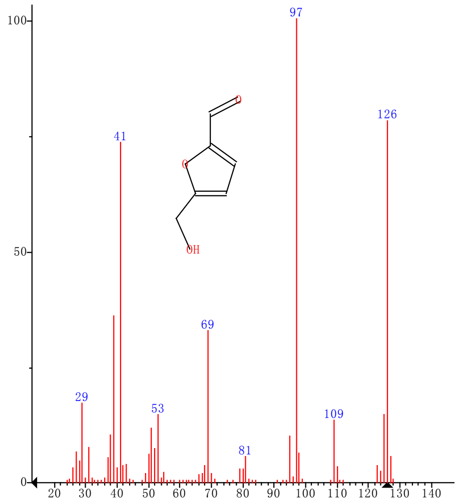
(mainlib) 2,5-Dimethyl-2-(2-tetrahydrofuryl)tetrahydrofuran



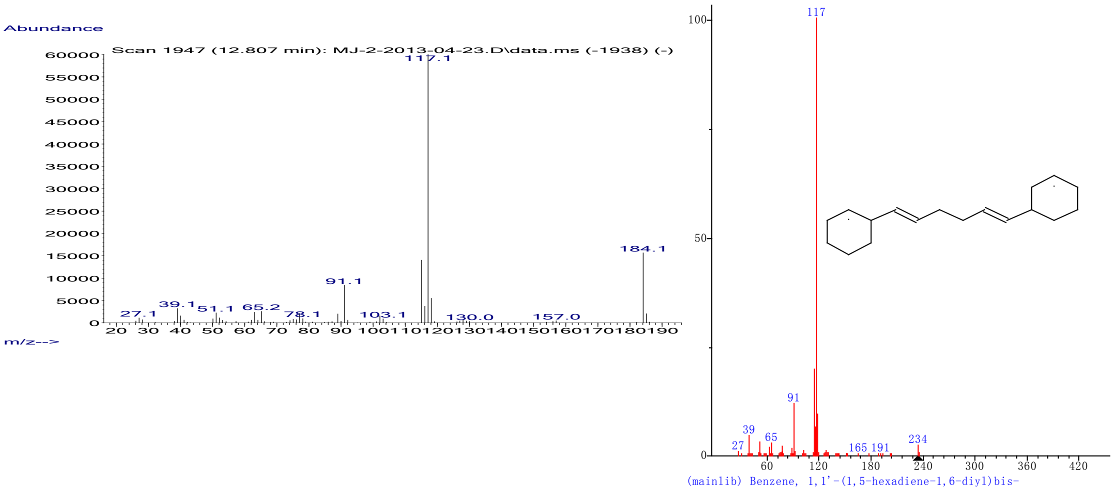


(mainlib) 4H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl-





(mainlib) 2-Furancarboxaldehyde, 5-(hydroxymethyl)-



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 peak   R.T.  first  max  last  PK    peak       corr.     corr.    % of
  #     min   scan  scan  scan  TY   height      area     % max.   total
 ---  -----  -----  ----  ----  ---  -------   -------   ------  -------

  1   4.830   492   499   506   M5     6824     178458    0.11%   0.103%
  2   5.300   573   584   587   M4    22768     423968    0.26%   0.244%
  3   5.340   588   592   599   M3    11237     211426    0.13%   0.122%
  4   5.687   634   655   674   M    105192    3937380    2.42%   2.269%
  5   6.019   702   715   722   M3    10354     251308    0.15%   0.145%
  6   6.112   727   732   745   M     28191     489010    0.30%   0.282%
  7   6.530   799   808   826   M3     9222     197254    0.12%   0.114%
  8   6.863   858   868   877   M4     7403     150489    0.09%   0.087%
  9   7.883  1020  1053  1129   M   3460139  162483448  100.00%  93.627%
 10  12.805  1935  1947  2018   M    146487    5220294    3.21%   3.008%
```

The intermediates in residual solution of HTC of glucose-Na_2SO_4 include:

(1) 2-Hydroxy-gama-butyrolactone; (2) 2-Furanmethanol ;

(3) Cyclopentanone, 2,5-dimethyl-; (4) Pentanoic acid; 4-oxo-;

(5) 2,5-Furan dicarboxaldehyde; (6) Furyl hydroxymethyl ketone ;

(7) 2,5-Dimethyl-2-(2-tetrahydrofuryl) tetrahydrofuran;

(8) 4-H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl-;

(9) 2-Furancarboxal dehyde, 5-(hydroxymethyl)-;

(10) Benzene, 1,1’-(1,5-hexadiene-1,6-diyl) bis- (3.088%).

Fig. S3. GC-MS analysis of intermediates in the residual solution of (a) glucose and (b) glucose-Na_2SO_4 solution after HTC at 180 ^{o}C for 5 hours (Aglient GC-MS (6890N-5975)).

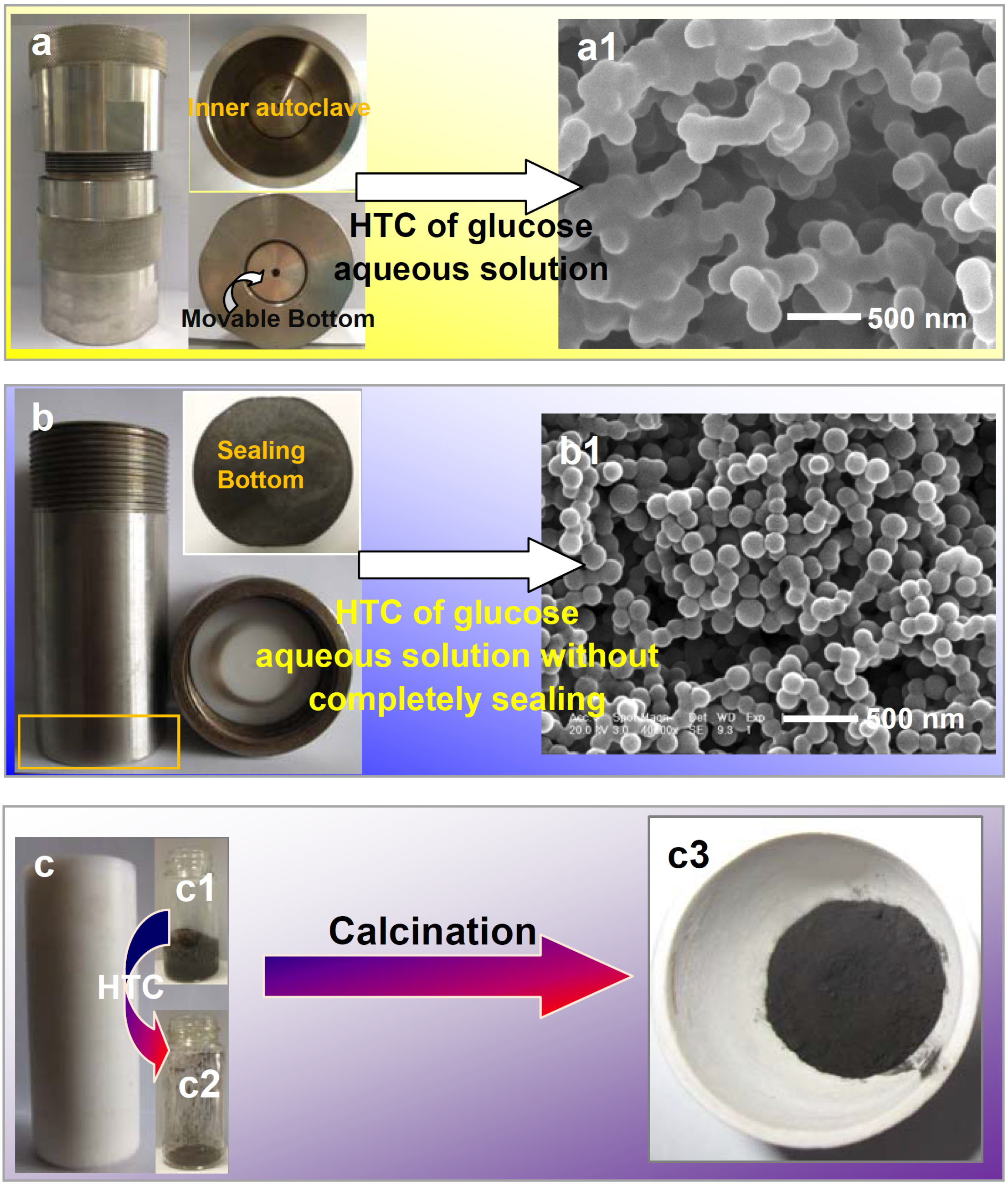

Fig. S4. Two types of hydrothermal autoclaves.

(a) with a movable bottom to facilitate the out of Teflon lining from the autoclave after reaction and **(b)** with a sealing bottom. **(a1)** and **(b1)** are the SEM images of carbon particles obtained from the autoclaves of (a), and (b) without completely sealing, with using the same glucose aqueous solution (0.125 g ml^{-1}) and reaction conditions (180 °C, 5h).

(c) Teflon lining in the autoclave of (b) and HTC of **(c1)** mixture of Fe_3O_4 particles and aqueous solution of glucose-Na_2SO_4 to **(c2)** Fe_3O_4@C@salt-Intermeidates, and then calcination to **(c3)** Fe_3O_4@C-salt.

Herein, a glass bottle was used as inside lining in Teflon to load the mixture for the reasons of (i) the easy collection of the product, (ii) avoiding the contamination of the Teflon lining and (iii) finely controlling the reaction conditions especially under a limited solution used. **(d)** Coral and **(e)** peanut structured carbon obtained from autoclave (a) and autoclave (b) that without completely sealing.

Detail reasons of using a glass bottle and the optimization of this coating process in Fig. S4 as following:

(i) The first, the glass bottle could be easily put into and take out from the Teflon, which is more easily to collect the samples from a bottle. Moreover, the product could be scraped from the wall of glass bottle very easily due to the smooth of bottle surface, but it is difficult to scrape the product from the Teflon wall because the deep position of Teflon and the easily-be-scraped plastic Teflon-wall.

(ii) Teflon and glass bottle are all inert resisting material in HTC of biomass, but the Teflon could be easily become black in the repeated utilization due to the contamination of carbon and then it is hard to clean. Generally, the impurities probably could affect the results of new experiment. The reason of using Teflon is for completely sealing, and the reason of using glass bottle is for the convenience of collecting samples and the repeated utilization.

(iii) With using the glass bottle, we can minimize the space for the reactants (1 g Fe_3O_4, 2.5 g aqueous solution of Na_2SO_4-glucose), and then the attachment of reactants on the walls could be is quite minimized. But it is hard to image that putting such small amount of reactants into a 50 ml Teflon. Moreover, the attachment of reactant on the Teflon wall and the operation (*e.g.*, ultrasonic treatment) should be become quite complex if processed directly in the Teflon. So, it is very easy to control with using a glass bottle as an inner reactor.

(iv) The reactant consisting of 1 g Fe_3O_4 and 2.5 g aqueous solution of

Na_2SO_4-glucose is like a uniform gel, so it is unnecessary to stirring. More importantly, the normal magnetic stir is not suitable for Fe_3O_4, because all the Fe_3O_4 particles could be strongly adsorbed on the magnetic stir, which will seriously affects the uniform carbon coating during the carbonization. Therefore, ultrasonic treatment for 1 hour is enough for dispersing of Fe_3O_4 particles in the solution of Na_2SO_4-glucose.

(v) 1 g Fe_3O_4 particles were dispersed in 2.5 g solution. Less solvent was used, less waste and energy consumption could be achieved. After the reaction, it is unnecessary to separate by centrifugation, because the gel-like reactants could be easily dried in oven for collecting the materials. In this way, the waste of carbon precursor of glucose and its intermediates could be maximally avoided in the process of drying, and then the carbon coating on Fe_3O_4 particles could be well controlled as shown in Fig. S5.

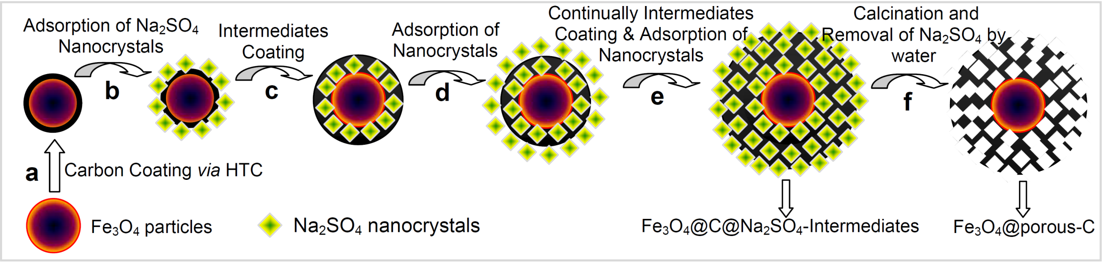

Fig. S5. Detail process of coating individual Fe_3O_4 particle with porous carbon. (a) An initial carbon coating formed on the Fe_3O_4 particle *via* HTC. (b-e) Continually adsorption of re-crystallized Na_2SO_4 nanocrystals and intermediates on the Fe_3O_4 surface during the process of drying. (f) Calcination and removal the Na_2SO_4 to form porous carbon. The Na_2SO_4 nanocrystals could be homogeneously dispersed in the intermediates/carbon matrix without aggregation due to their protection, and then it will form pores after removing with the water.

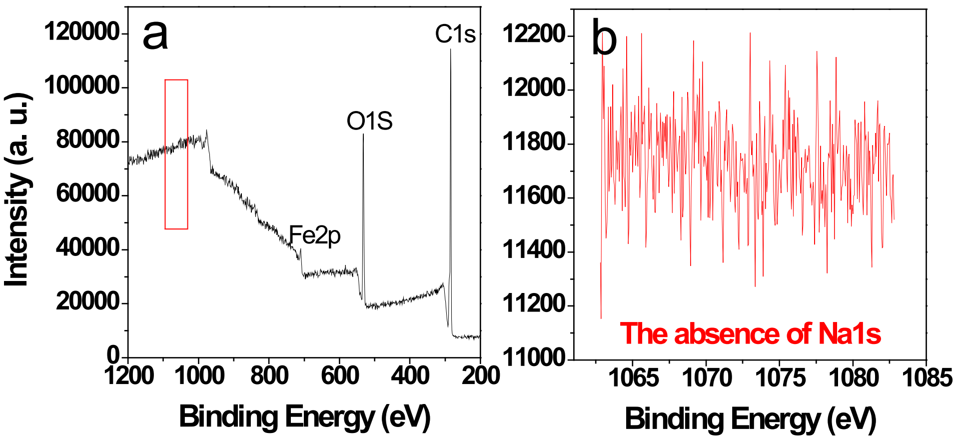

Fig. S6. (a) XPS spectrum of the Fe_3O_4@porous-C and (b) a high-resolution spectra of the Na1s. The absence of Na1S peak (~1071 ± 5 eV) in XPS analysis confirms that the Na_2SO_4 was almost removed completely, which is well accordance with the salt's recovery of 98.5%