



木质纤维素生物质转化为高附加 值化学品和材料

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还田（直接、生物炭）



饲料

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WWW.NEWS.CN

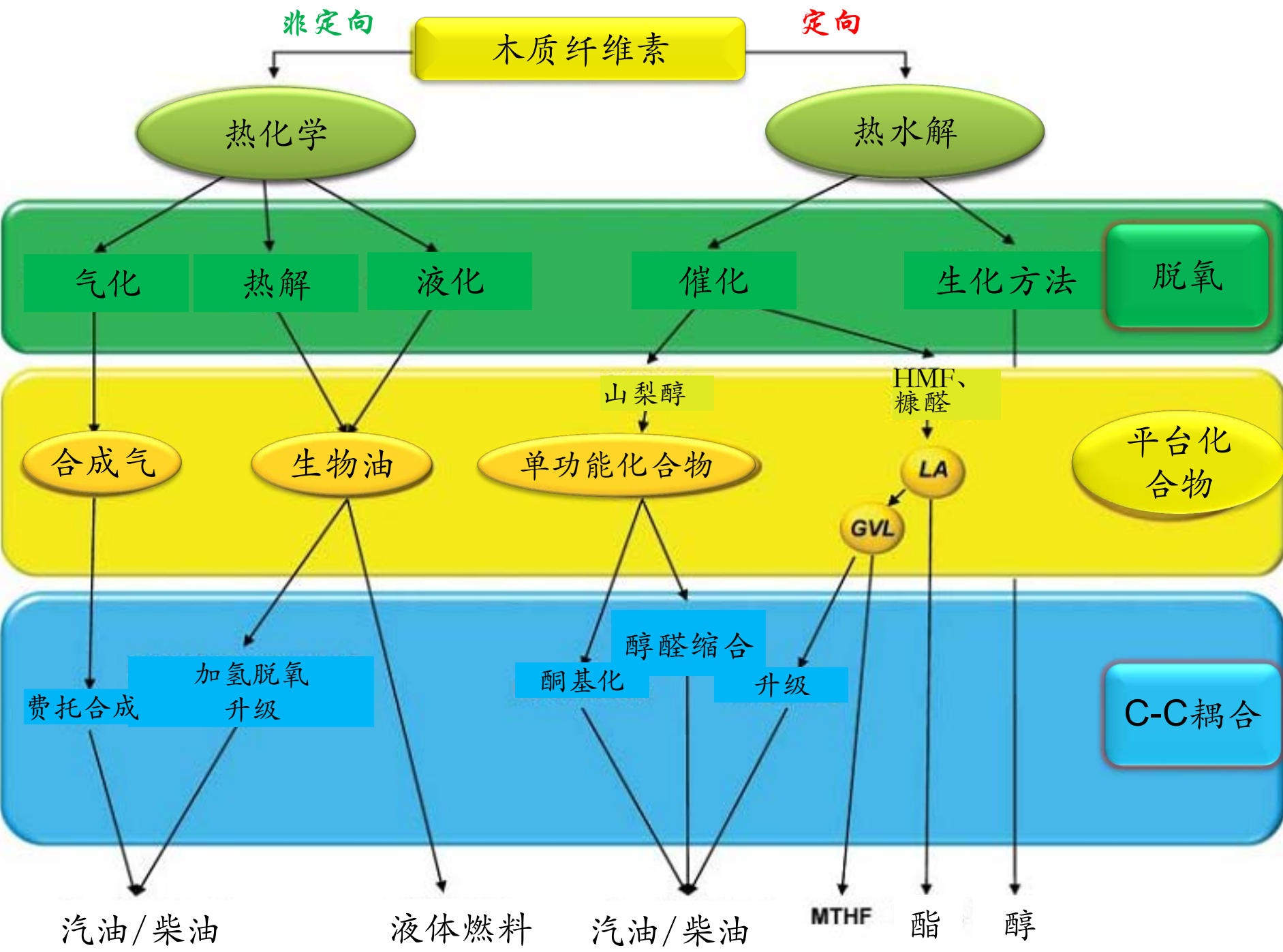
木质纤维素类农业废弃物



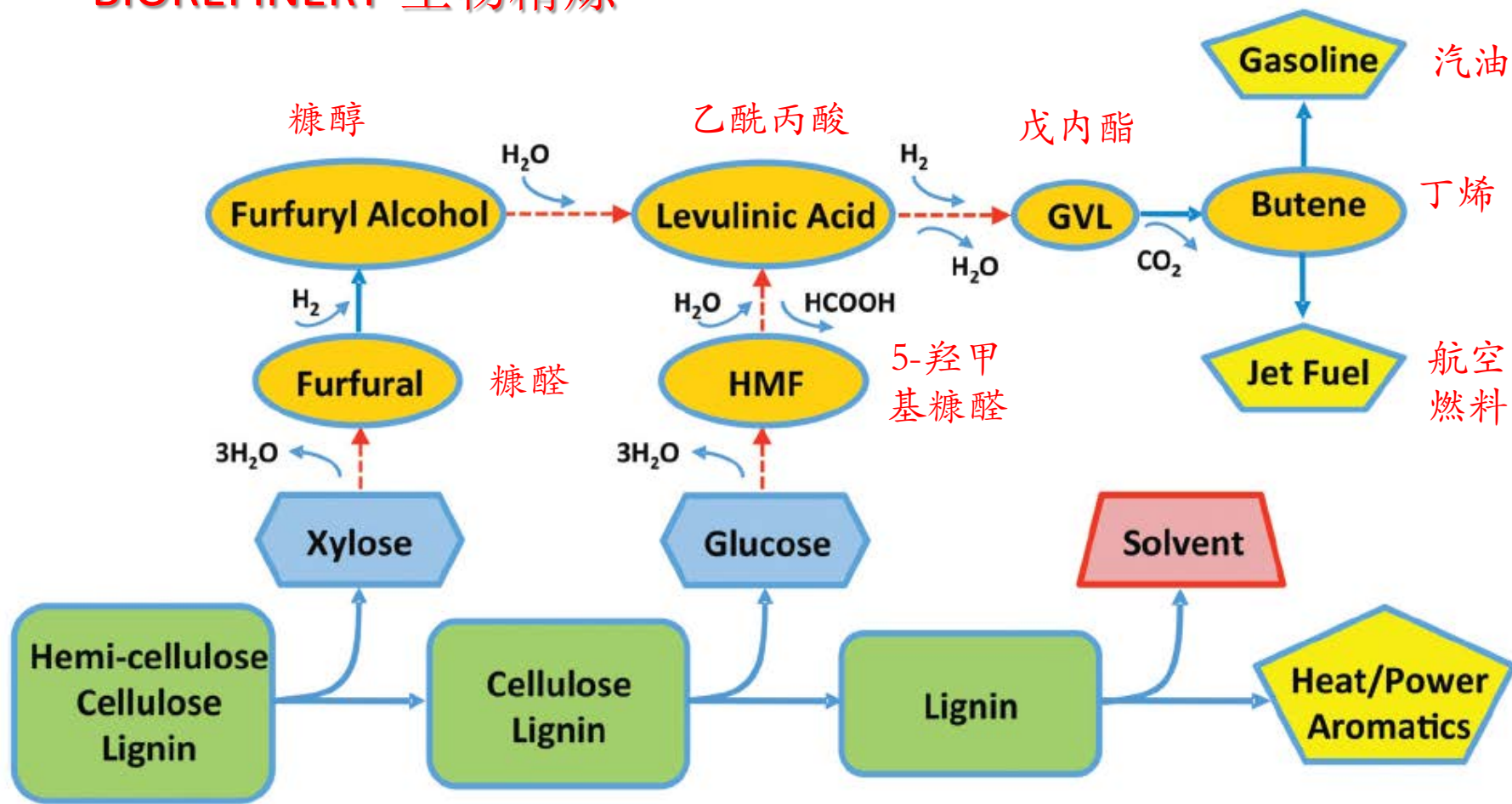
焚烧

燃料
发电





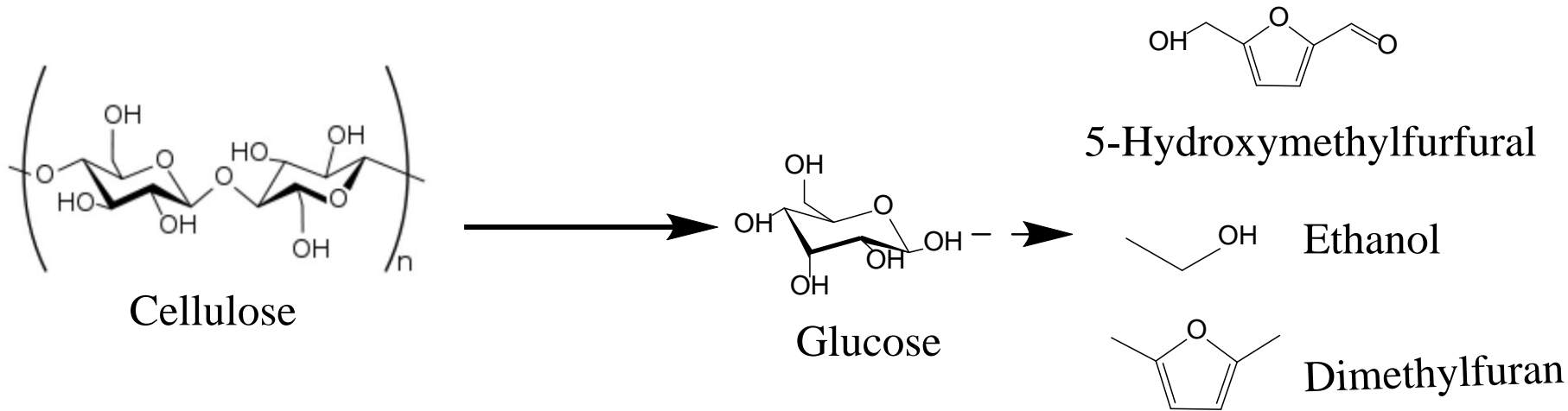
BIOREFINERY-生物精炼



木质纤维素转化为高附加值化学品和能源示意图

纤维素水解

纤维素水解是木质纤维素利用过程中最关键的环节



传统方法

液态酸：腐蚀、废物多、溶剂难于循环

超临界水：高温高压、葡萄糖产率低

酶催化：反应时间长、成本高、不可循环使用

需要开发更绿色
更高效的纤维素
水解工艺过程

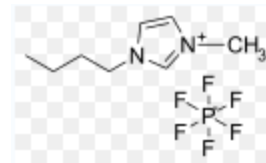
固体酸催化

- 优点：分离简单、可循环利用、无污染
- 缺点：纤维素底物和固体酸之间存在传质阻力，影响催化活性
- 解决途径：离子液体作溶剂

固体酸+离子液体



离子液体

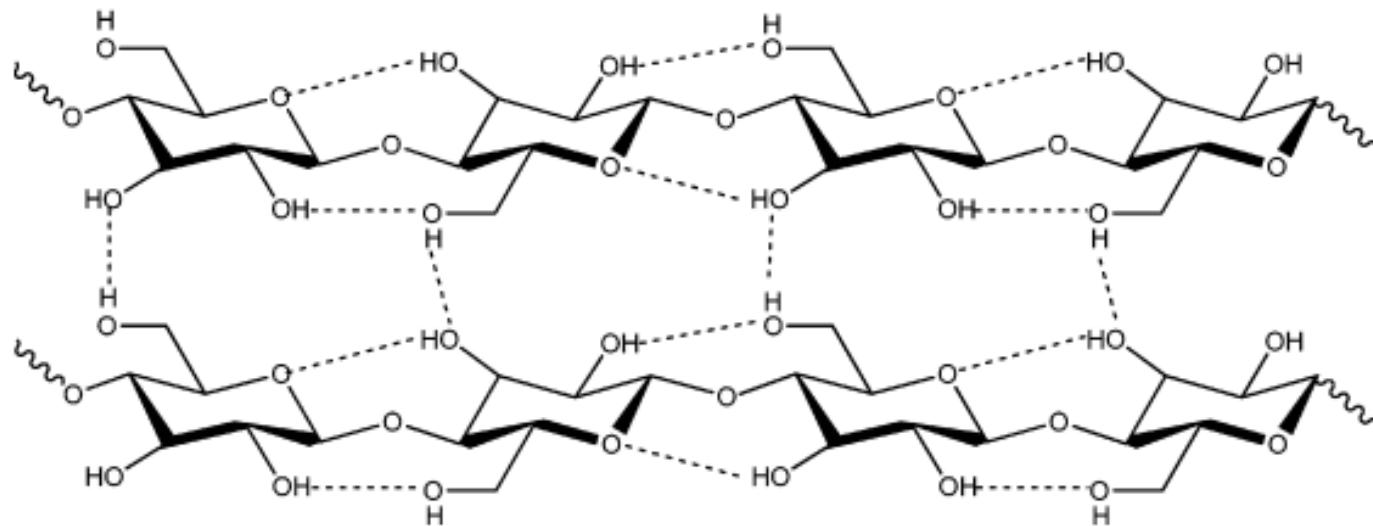


- 离子液体是指全部由离子组成的液体，如高温下的KCl, KOH呈液体状态，此时它们就是离子液体。在室温或室温附近温度下呈液态的由离子构成的物质，称为**室温离子液体**、室温熔融盐、有机离子液体等，目前一般简称为离子液体。

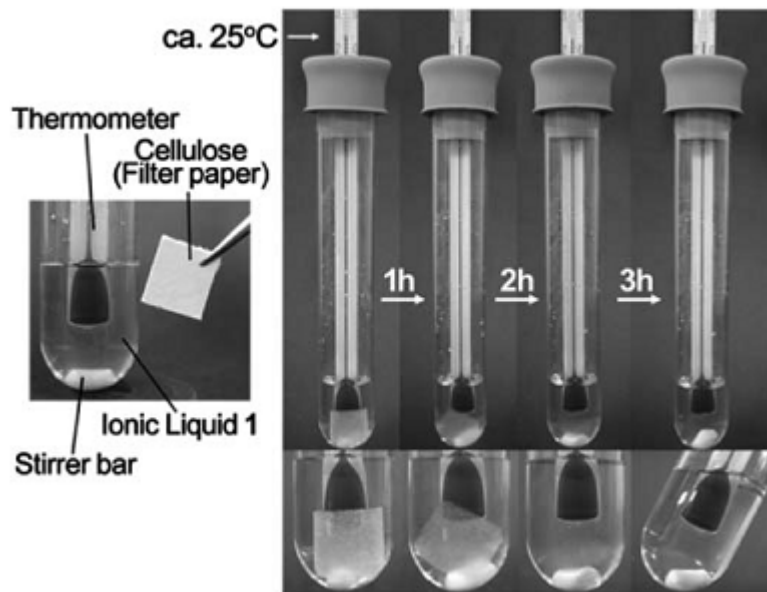
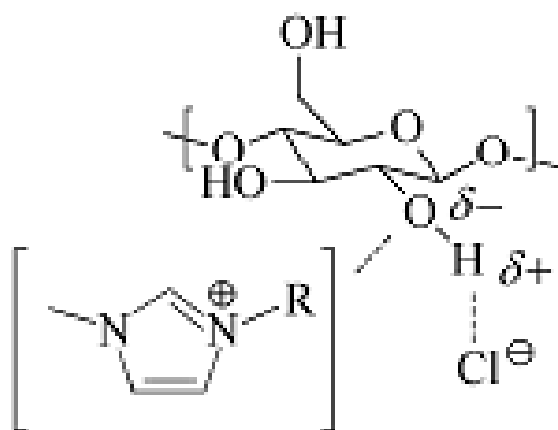
常见离子液体的熔点

Salt	m.p. (°C)
NaCl	803
KCl	772
K ₂ CO ₃	891
AlCl ₃	192
NaCl-KCl (50:50)	658

Ionic liquid	m.p. (°C)
[BMIM][Cl]	65
[BMIM][BF ₄]	-76
[BMIM][PF ₆]	-8
[BMIM][CF ₃ CO ₂]	-14



纤维素分子内和分子间的氢键



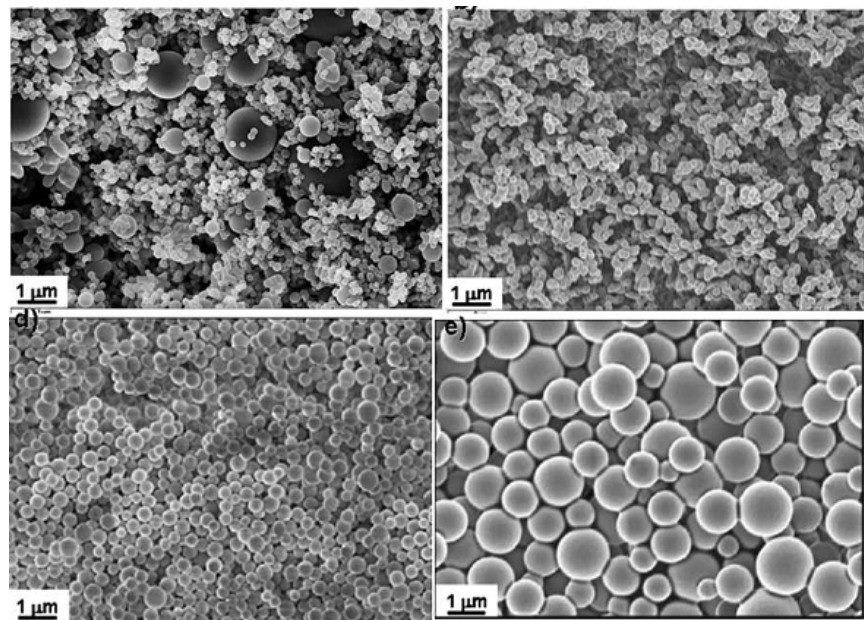
离子液体与纤维素分子的氢键结合

生物质水热碳化制备固体酸

葡萄糖
蔗糖
纤维素
淀粉
农业废弃物

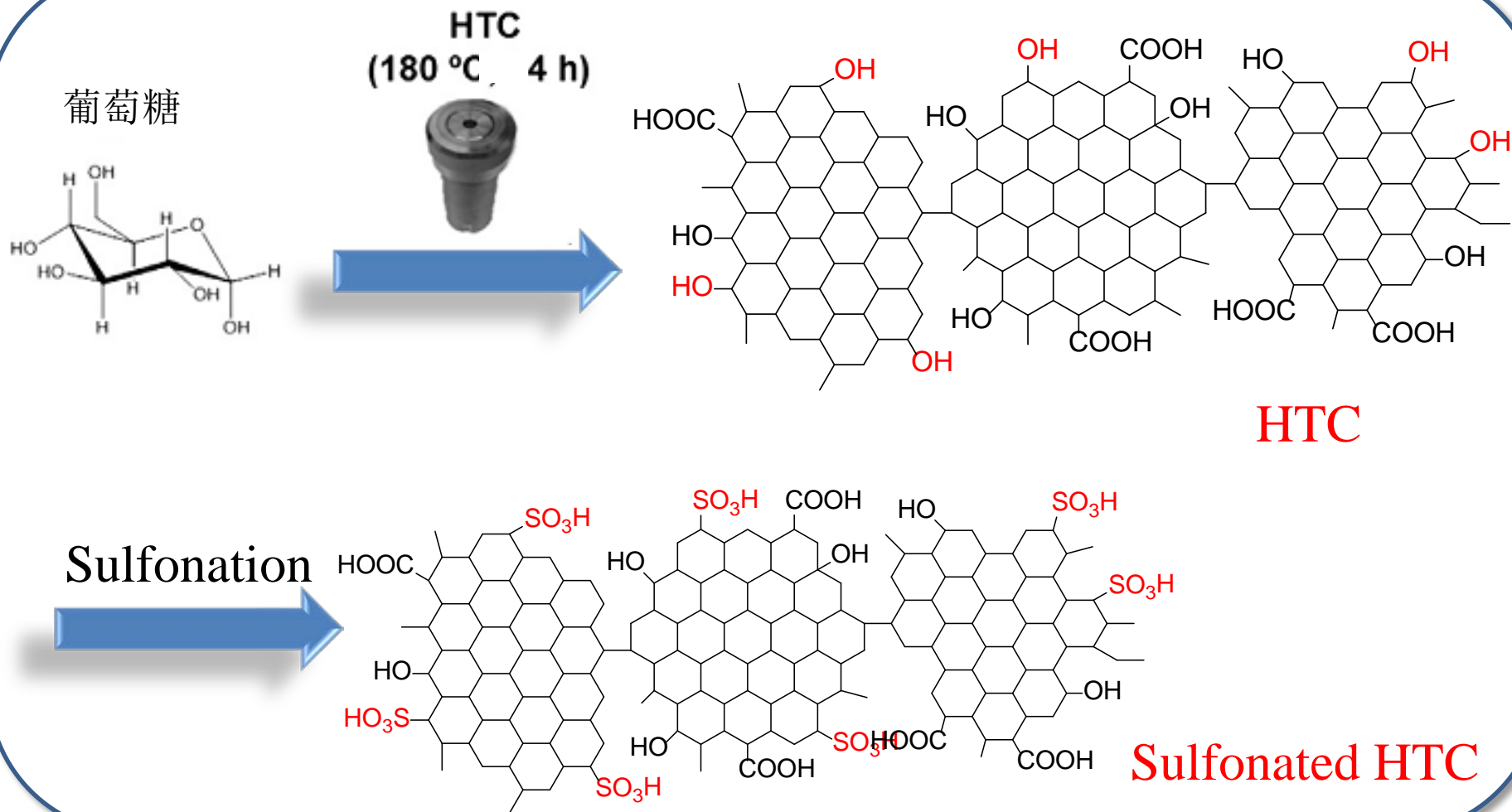


130-250 °C
水热碳化

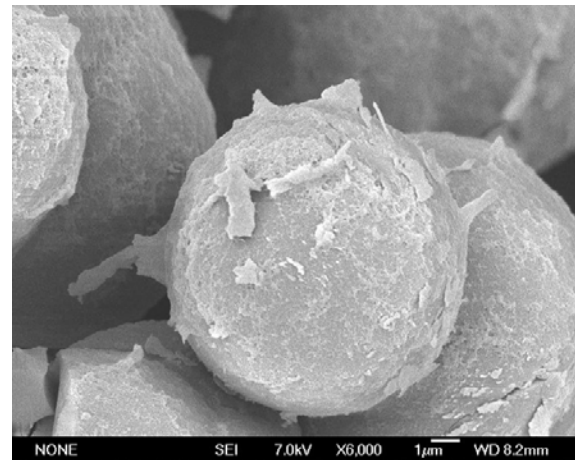
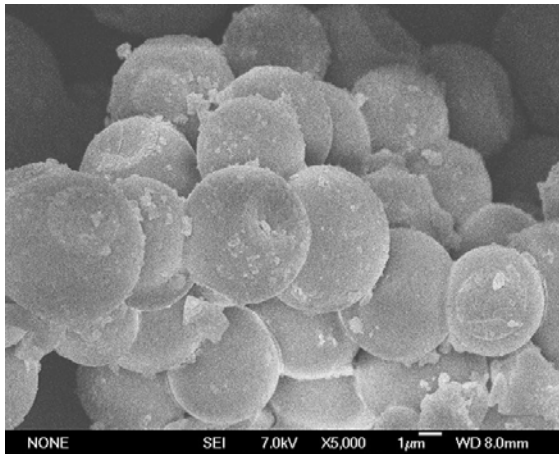


生物质基水热碳

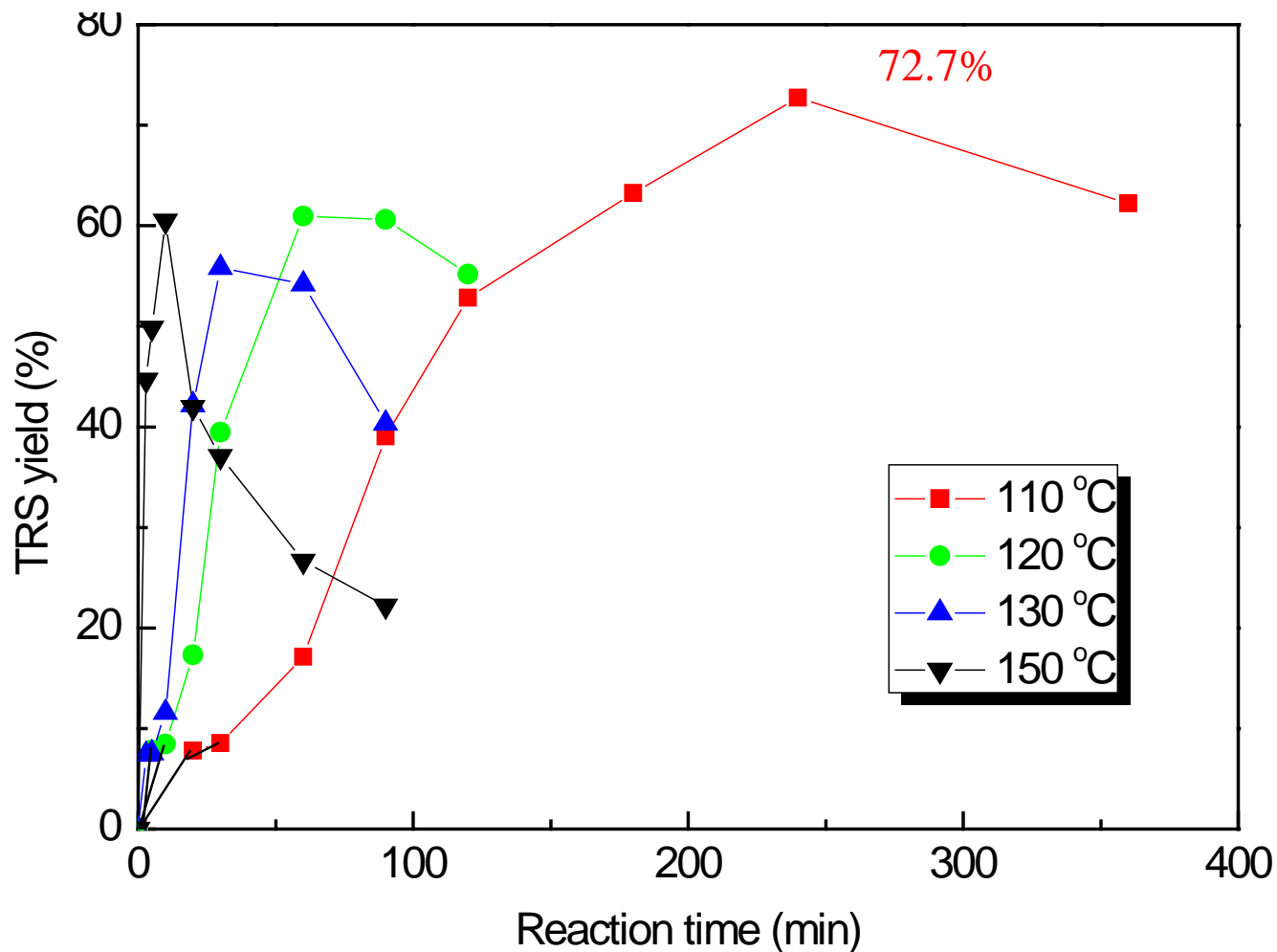
葡萄糖基碳材料固体酸催化纤维素水解



- 葡萄糖的水热碳化



SEM images of carbon material prepared from hydrothermal carbonization of glucose aqueous solution at 180 °C for 4 h followed by sulfonation with H₂SO₄ at 200 °C for 12 h.



离子液体[BMIM][Cl] 中碳固体酸催化纤维素水解 (0.05g cellulose, 0.01 g water, 1g of [BMIM][Cl], 0.03g carbon catalyst)

不同催化体系中纤维素的水解

Solvent	Catalyst	Reaction temperature (°C)	Reaction time (h)	TRS yield (%)	References
[BMIM][Cl] ^a	Carbon catalyst	120	1	63.0	This work
[BMIM][Cl] ^b	H ₂ SO ₄	120	1	44.9	This work
[BMIM][Cl]	HY zeolite	Unknown ^c	0.13	47.5	(Zhang and Zhao, 2009)
[BMIM][Cl]	Amberlyst [®] 15 resin	100	5	28	(Rinaldi et al., 2008)
[BMIM][Cl]-H ₂ O	Nafion [®] NR50 resin	160	4	35	(Kim et al., 2010)
H ₂ O	H ₃ PW ₁₂ O ₄₀	180	3	58.8	(Tian et al., 2010)
H ₂ O	Carbon material	100	3	4 ^d	(Suganuma et al., 2008)
H ₂ O	Sn _{0.75} PW ₁₂ O ₄₀	150	2	23	(Shimizu et al., 2009)
H ₂ O	AC-SO ₃ H	150	3	21	(Lai et al., 2011)

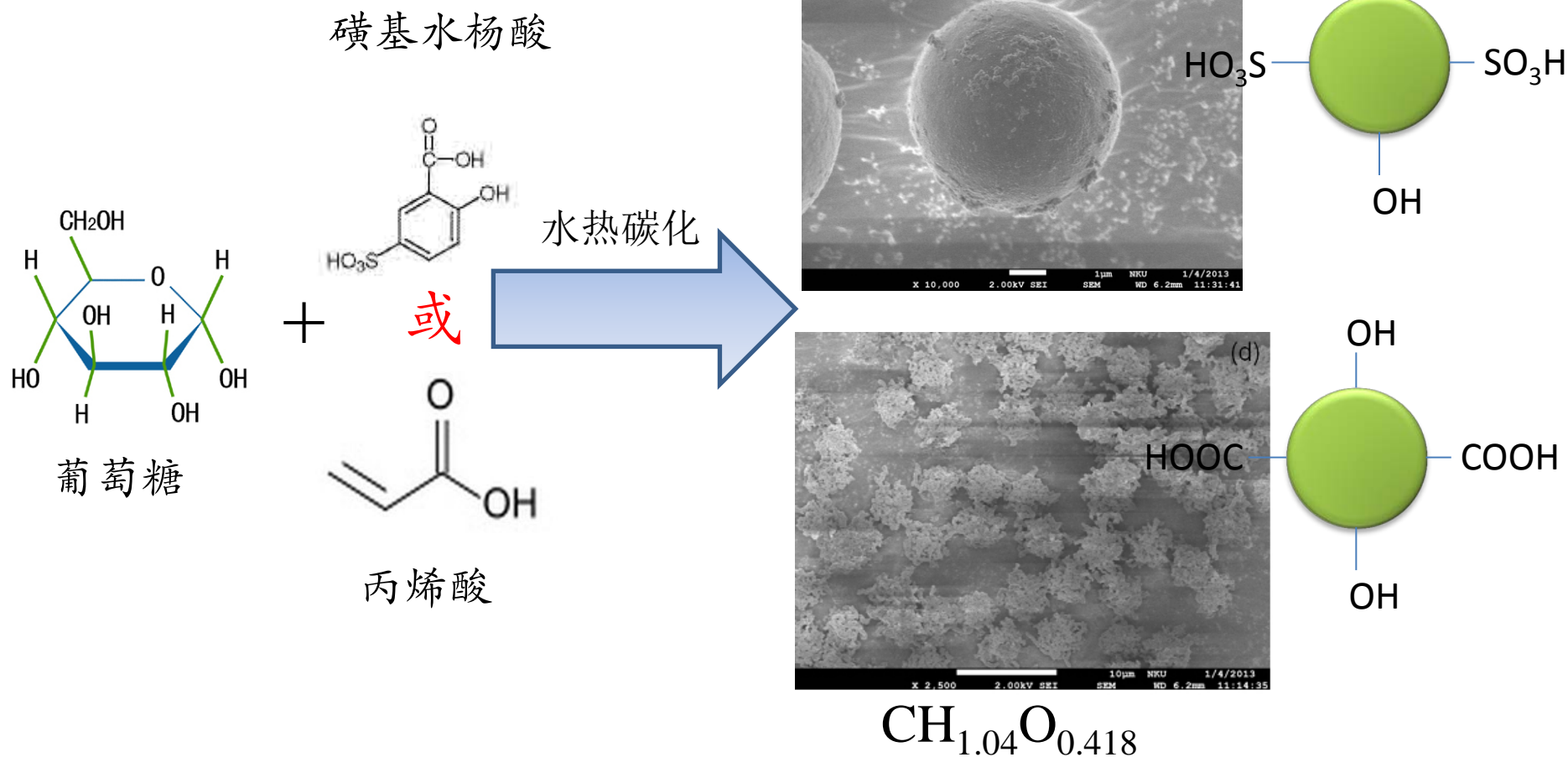
^a Reaction conditions: 0.03 g catalyst, 1 g [BMIM][Cl], 0.05 g cellulose, 0.01 g H₂O.

^b Reaction conditions: 0.2 mmol H₂SO₄, 1 g [BMIM][Cl], 0.05 g cellulose, 0.01 g H₂O.

^c Microwave heating at 240 W.

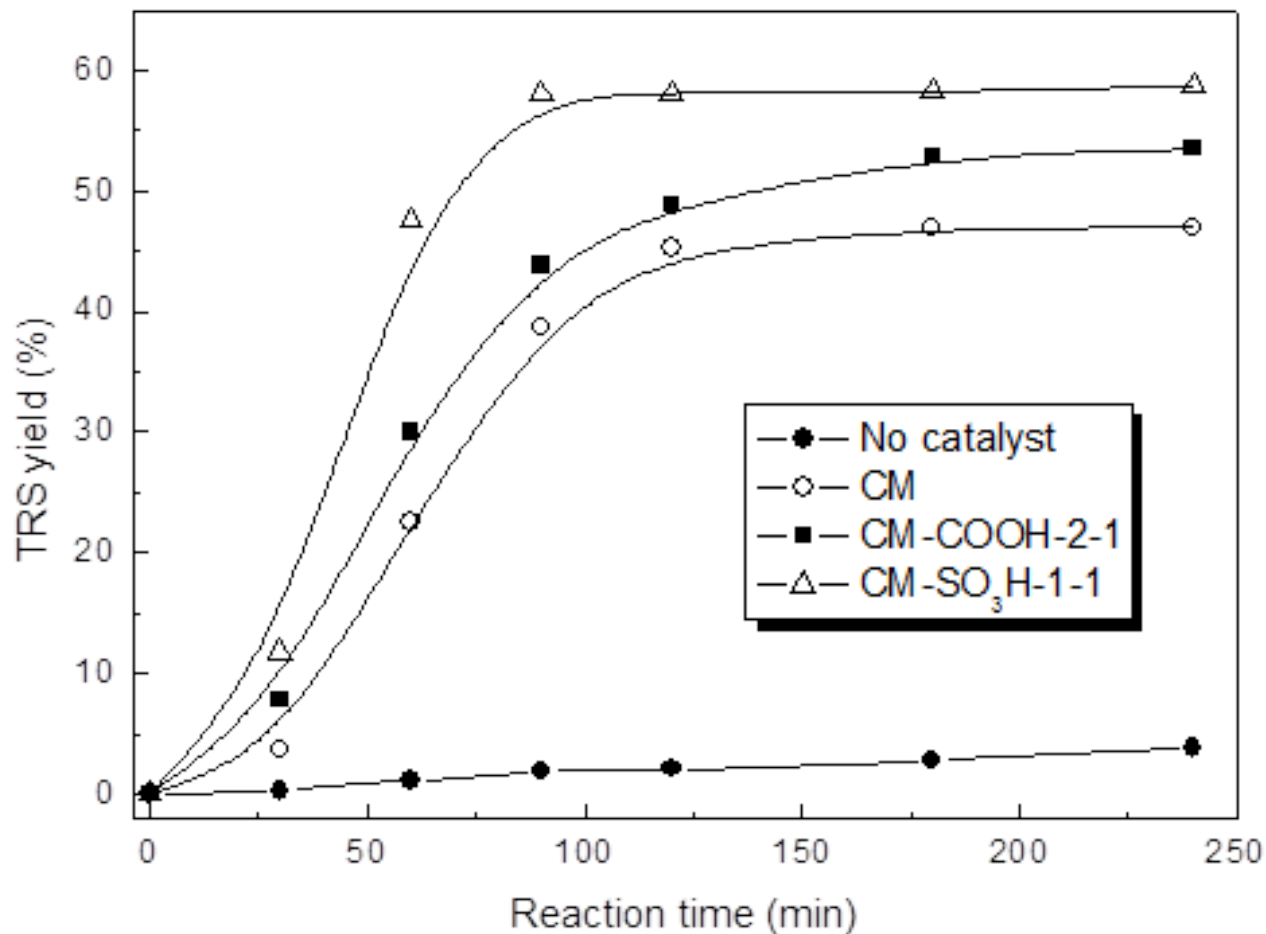
^d Glucose yield.

葡萄糖水热碳化一步法制备碳固体酸用于纤维素水解



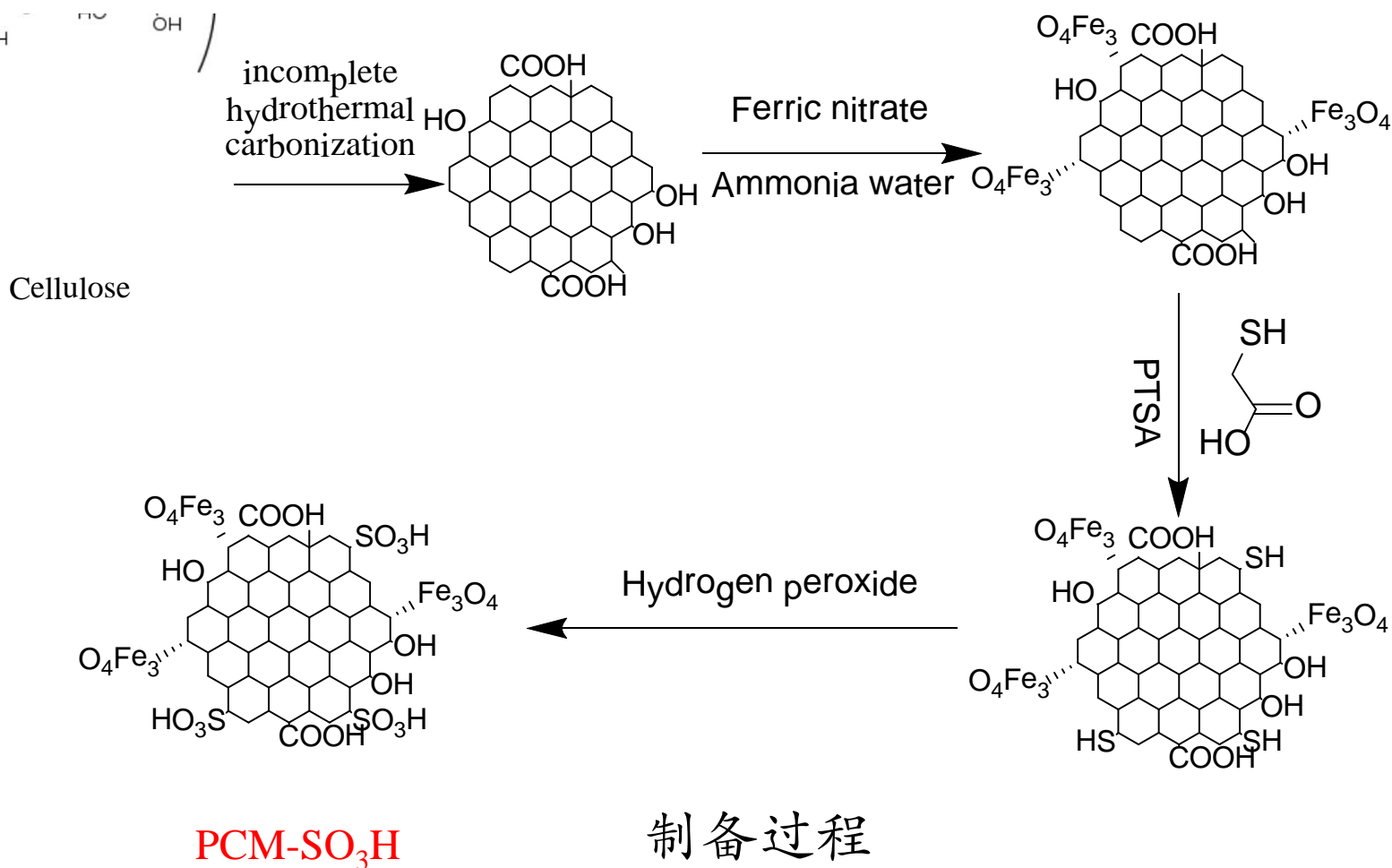
不同碳材料固体酸的酸度分布

Samples ^a	Total acid sites (mmol/g) ^b	Sulfonic groups (mmol/g) ^c	Carboxylic groups (mmol/g) ^d	Phenolic groups (mmol/g) ^e	Lactonic groups (mmol/g) ^f
CM	3.59	0	1.37	1.56	0.66
CM-SO ₃ H	4.22	0.12	1.82	1.60	0.68
CM-COOH	4.37	0	2.22	1.50	0.65

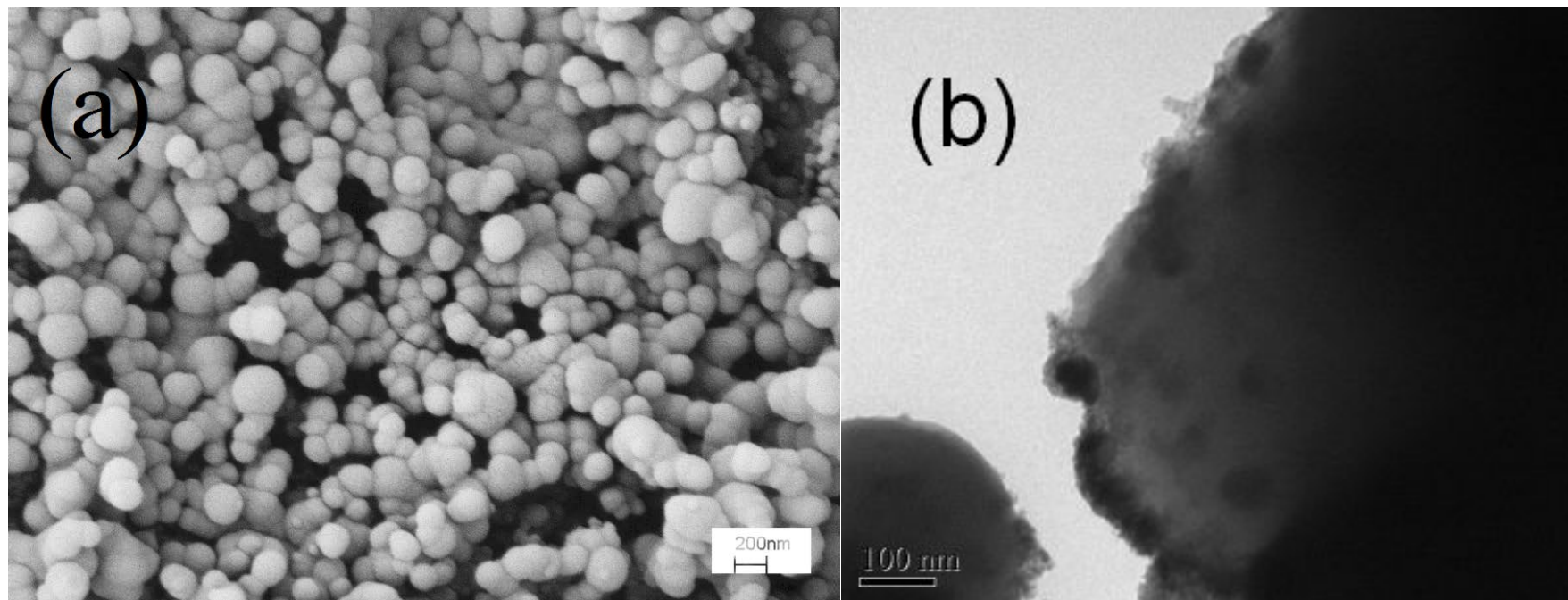


不同固体酸催化纤维素水解 (Reaction conditions: cellulose (0.05 g), [BMIM][Cl] (1 g), catalyst (0.05 g), 130 °C) .

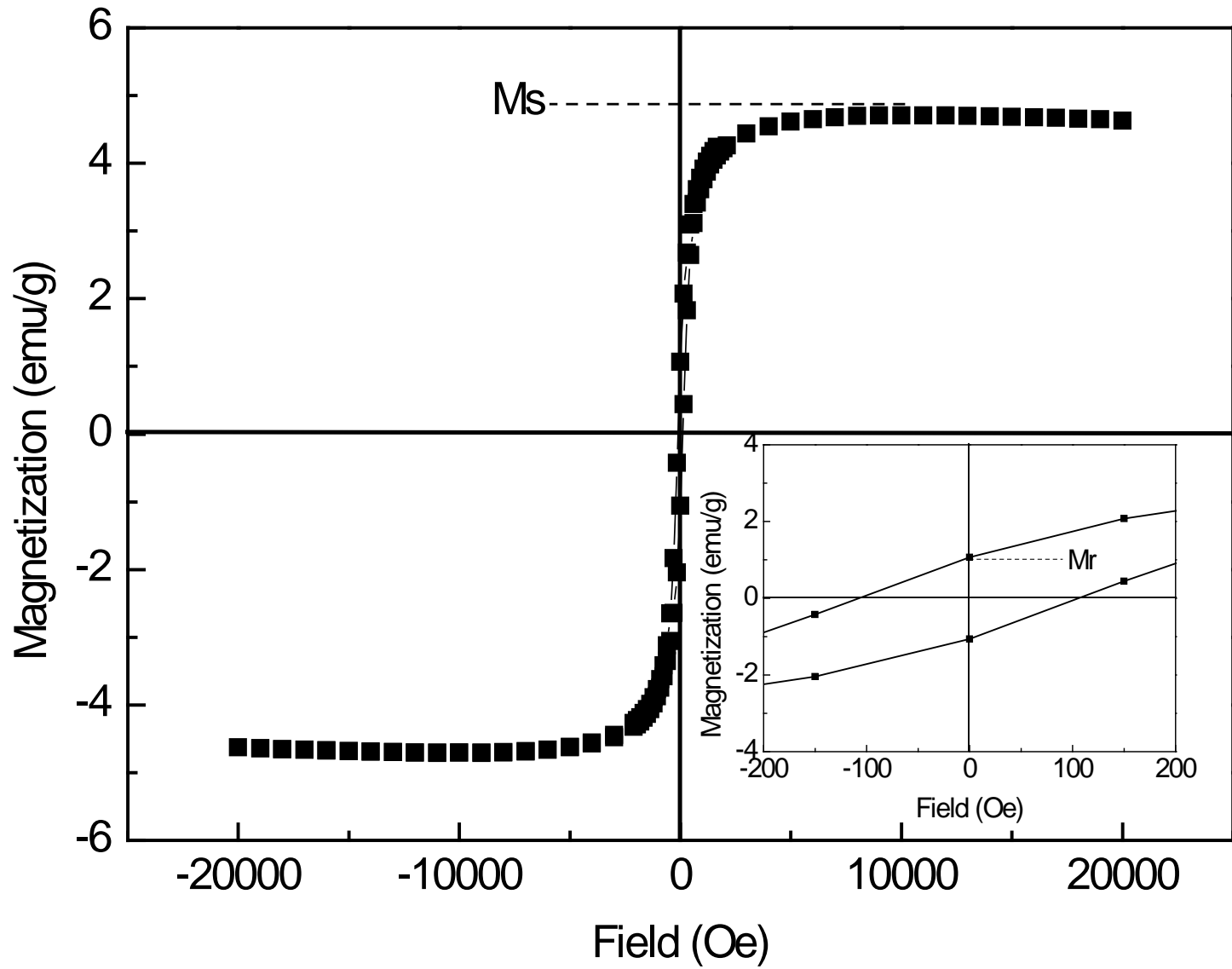
纤维素基磁性碳材料用于纤维素水解



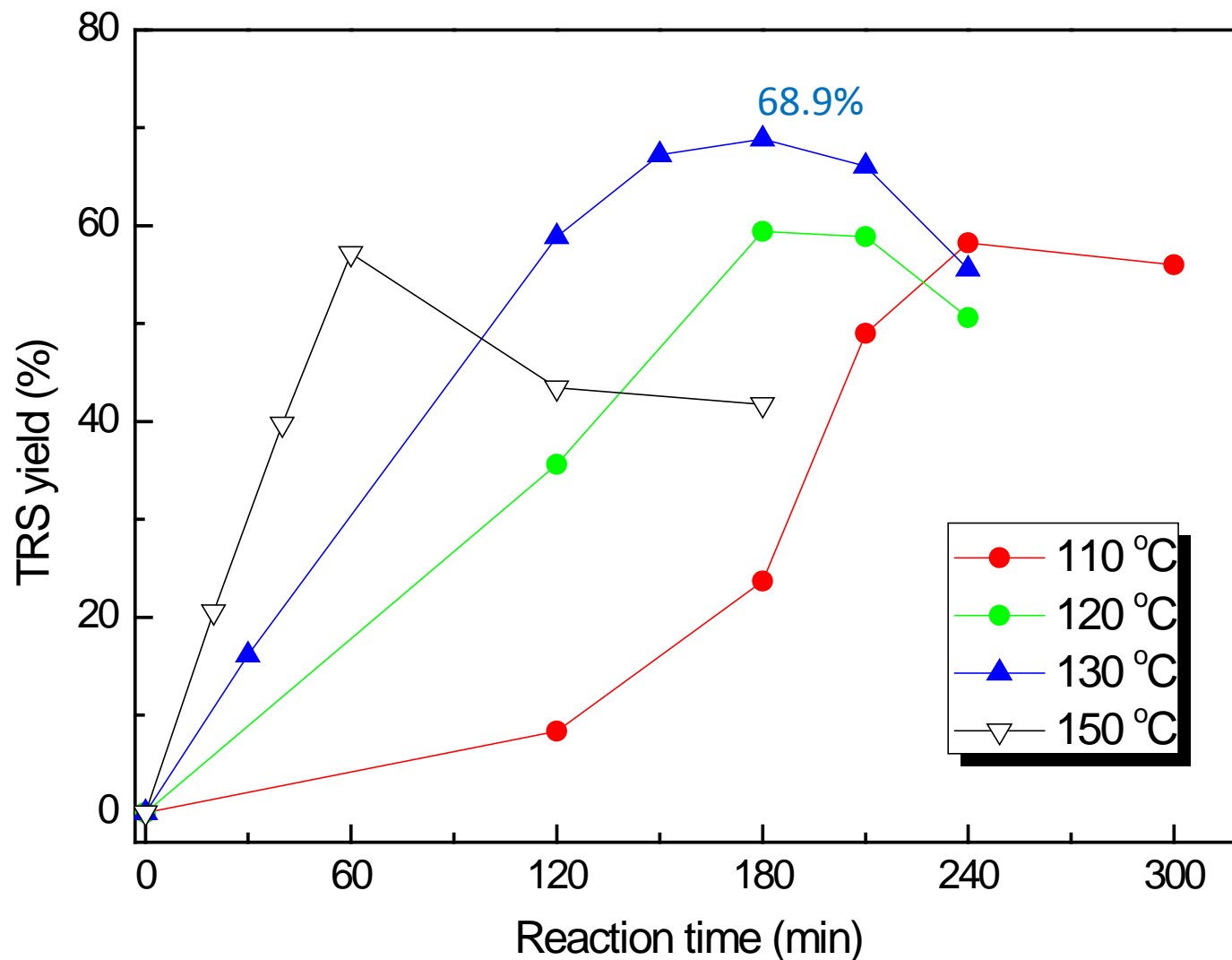
-SO₃H: 0.64 mmol/g



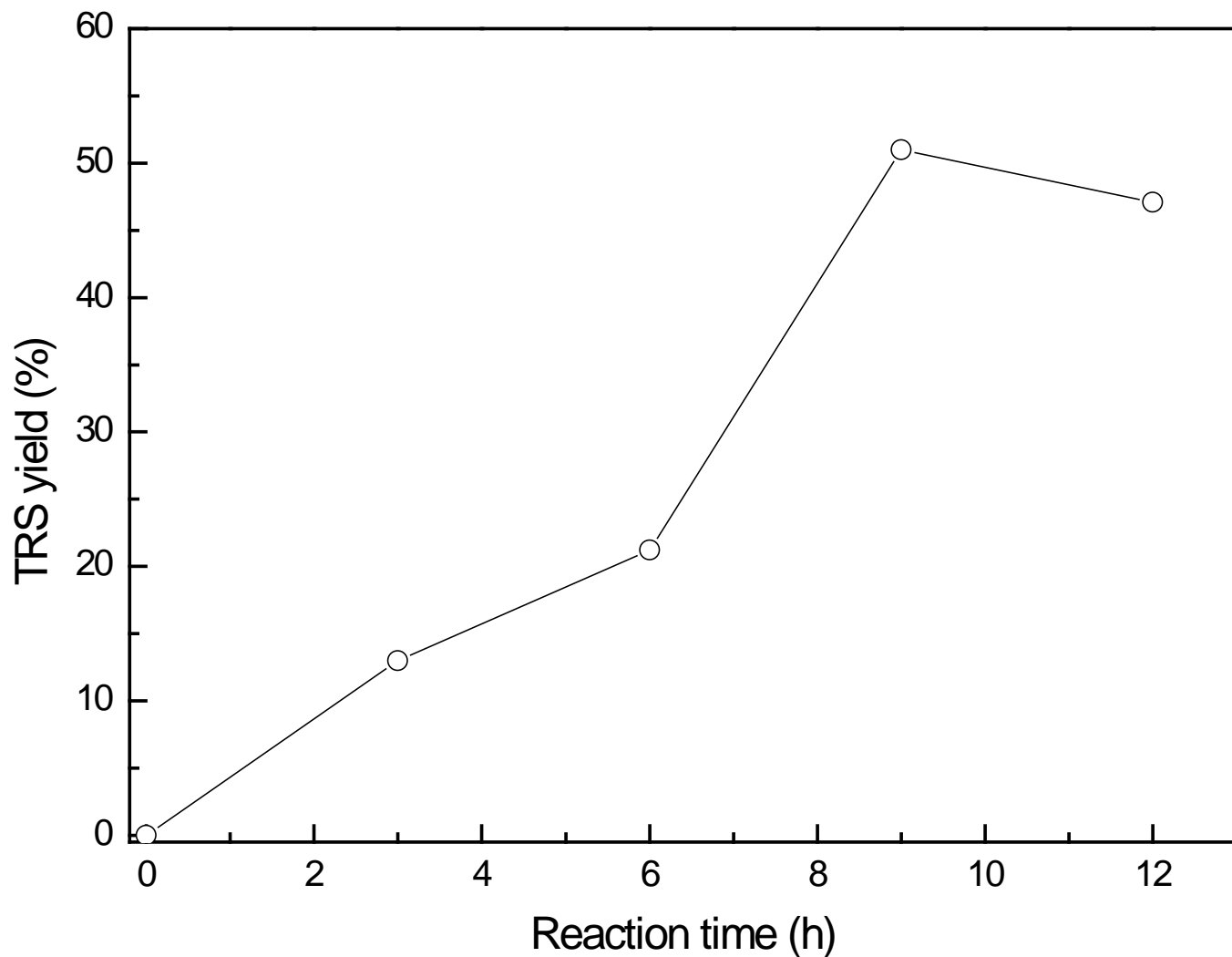
(a) 纤维素水热碳化得到的碳材料(CM)的扫描电镜图 (250 °C for 4 h) ; (b) 磺酸基功能化的超顺磁性碳材料(PCM-SO₃H)的透射电镜图。



纤维素基磁性碳固体酸的磁力曲线图



离子液体([BMIM][Cl])中磁性纤维素基碳固体酸催化纤维素水解 (0.05g cellulose, 0.01 g water, 1g of [BMIM][Cl], 0.03g catalyst)



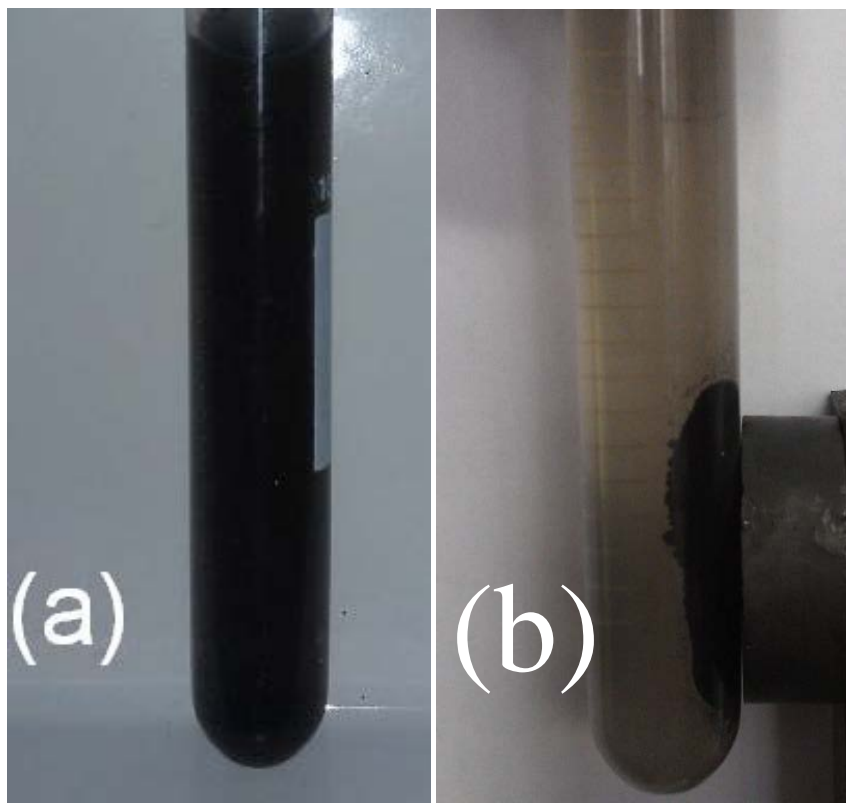
水溶液中磁性纤维素基碳固体酸催化纤维素水解
((0.5g cellulose, 0.1 g catalyst, 50 mL water, 180 °C))

离子液体[BMIM][Cl]中PCM-SO₃H催化水稻秸秆水解

Run	Reaction Temperature (°C)	Reaction time (h)	TRS yield (%) ^b
1	130	1	8.6
2	130	2	16.0
3	130	3	19.1
4	130	4	34.4
5	150	2	35.5
6	150	3	30.3

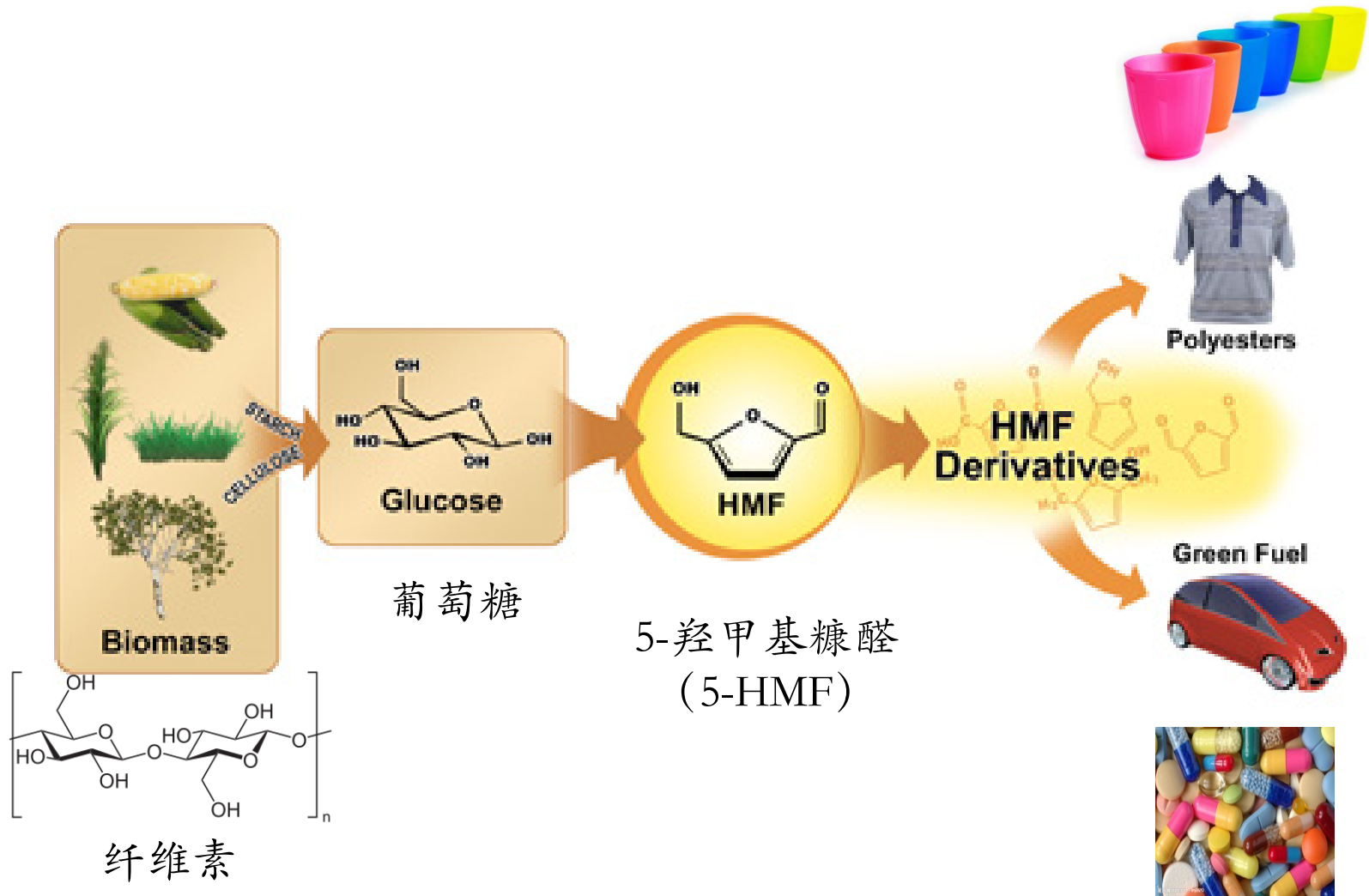
^a Reaction conditions: (0.05 g rice straw, 0.01 g water, 1g [BMIM][Cl], 0.03 g catalyst).

^b TRS yield based on the total weight of loaded rice straw substrate.

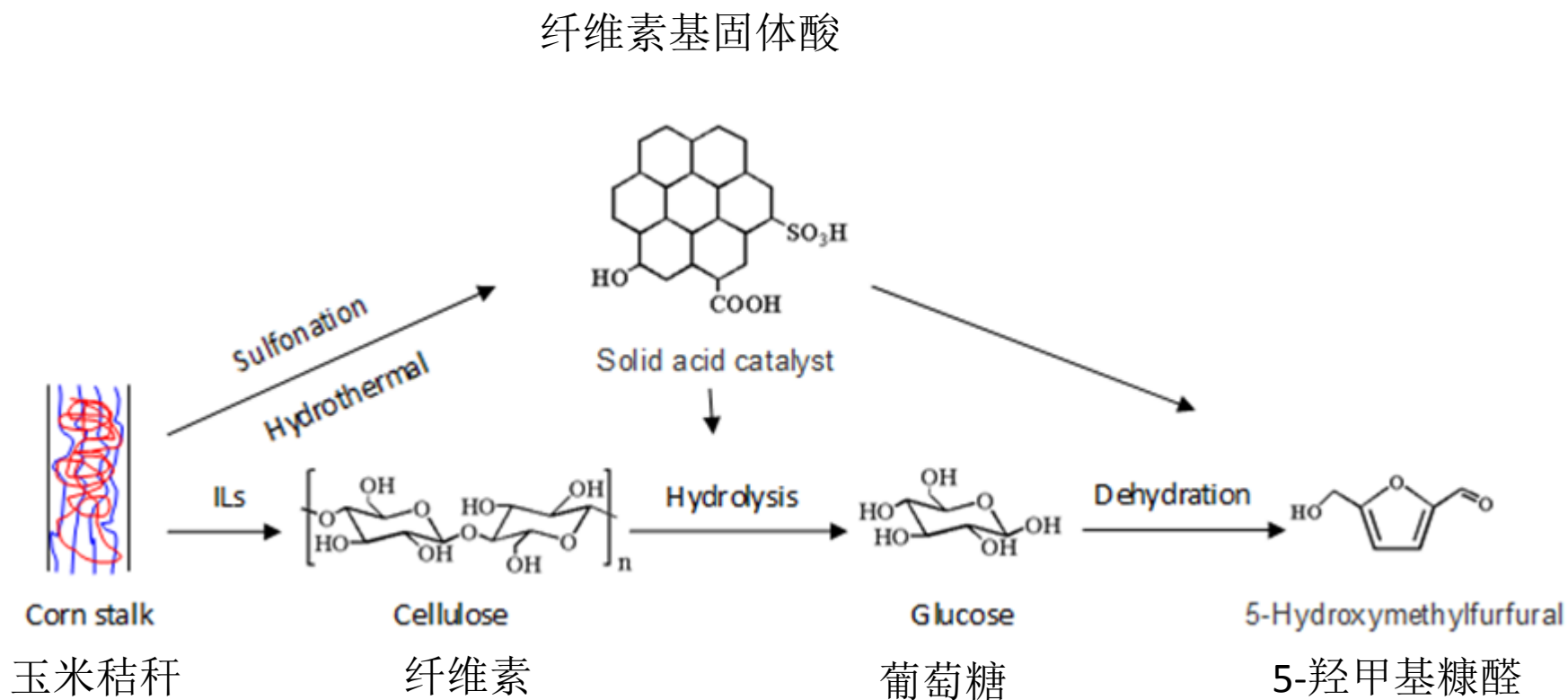


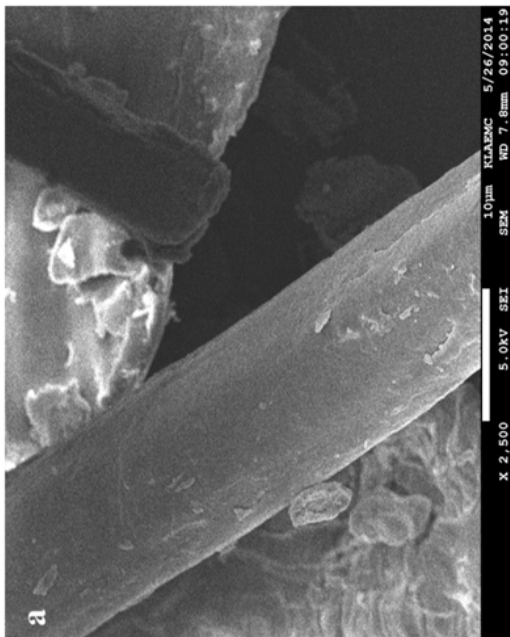
催化剂PCM-SO₃H的分离

纤维素及其衍生物转化为高附加值化学品5-羟甲基糠醛

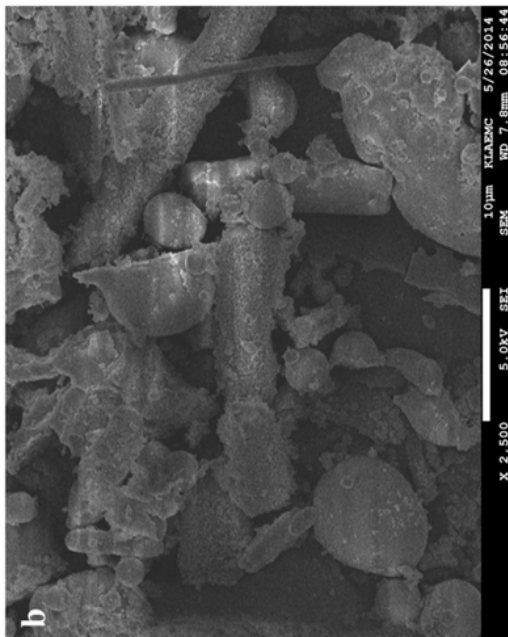


玉米秸秆基碳固体酸催化玉米秸秆为5-羟甲基糠醛

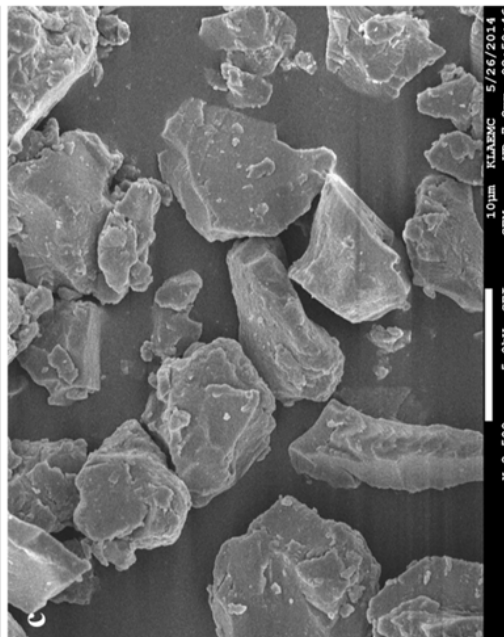




秸秆



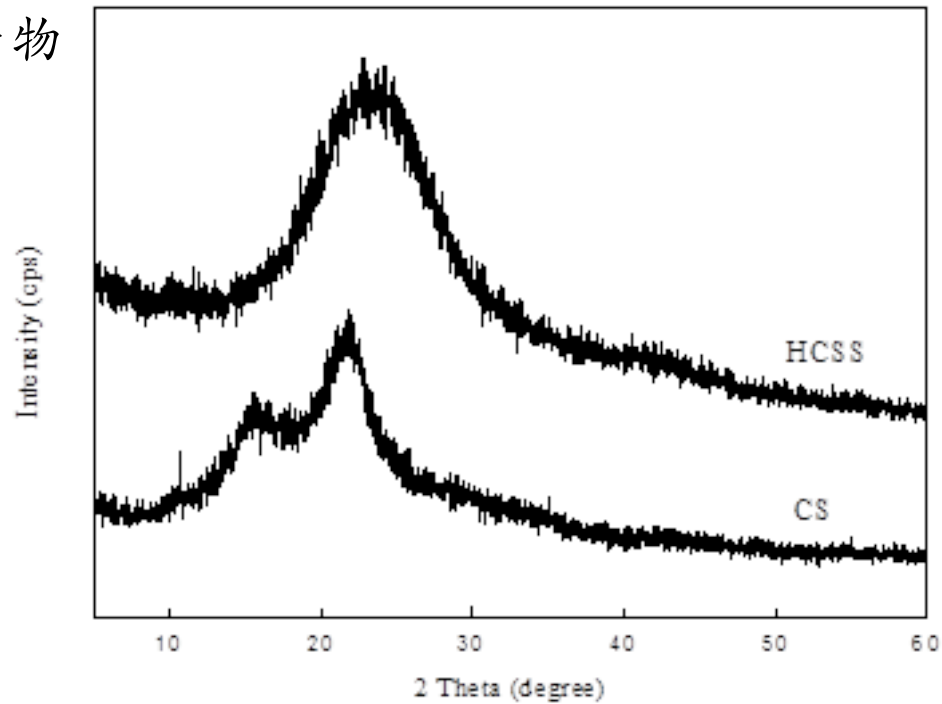
秸秆水热碳化产物

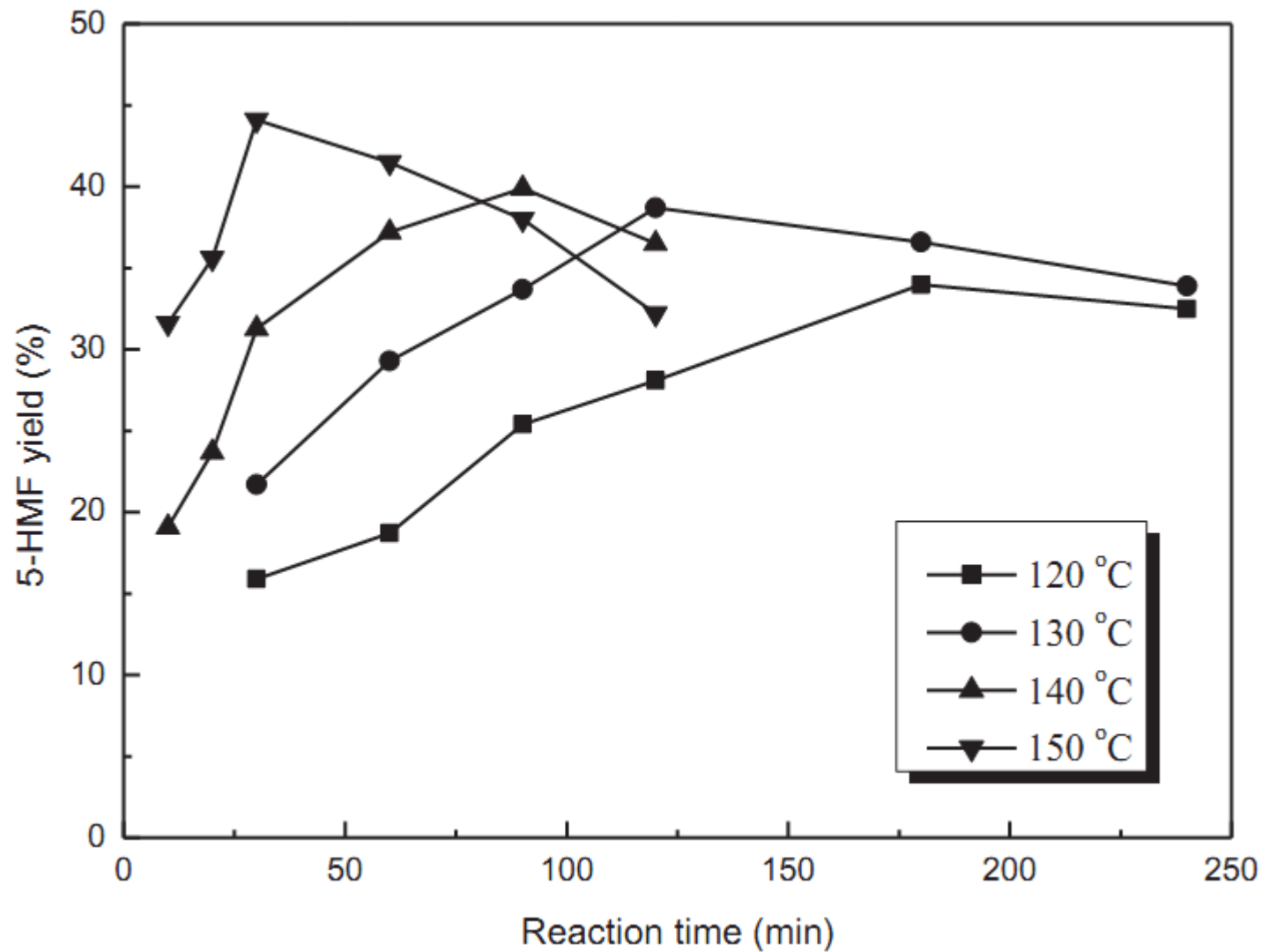


秸秆水热碳化
+ 磺酸化产物

SEM

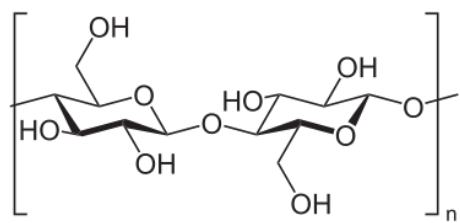
XRD





玉米秸秆基碳固体酸催化转化玉米秸秆为5-羟甲基糠醛 (5-HMF)
(Reaction conditions: corn stalk 0.05 g, [BMIM][Cl] 1 g, HCSS 0.05 g.)

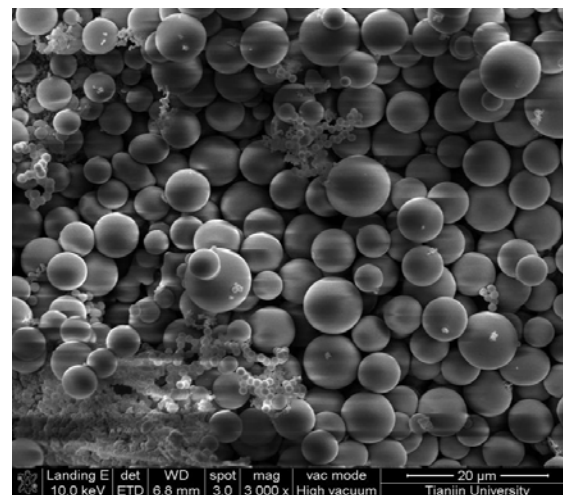
纤维素基功能化纳米碳微球的制备及其应用



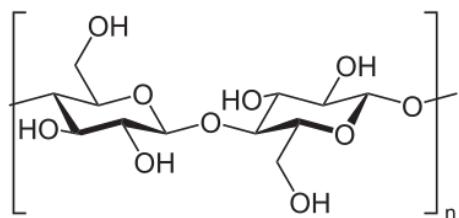
纤维素



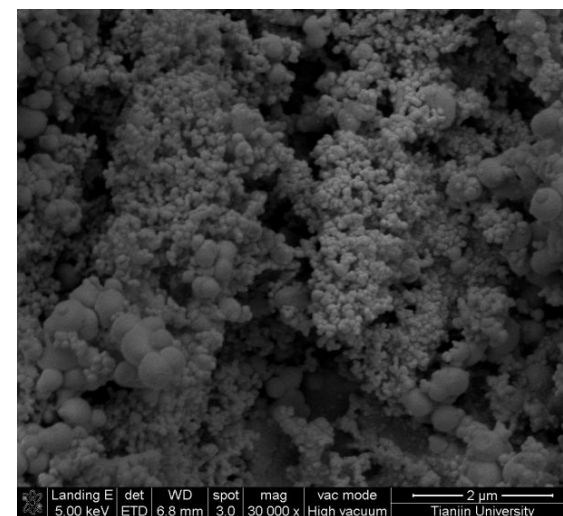
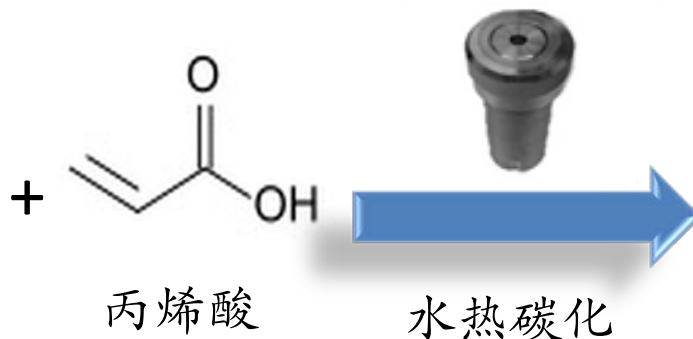
水热碳化



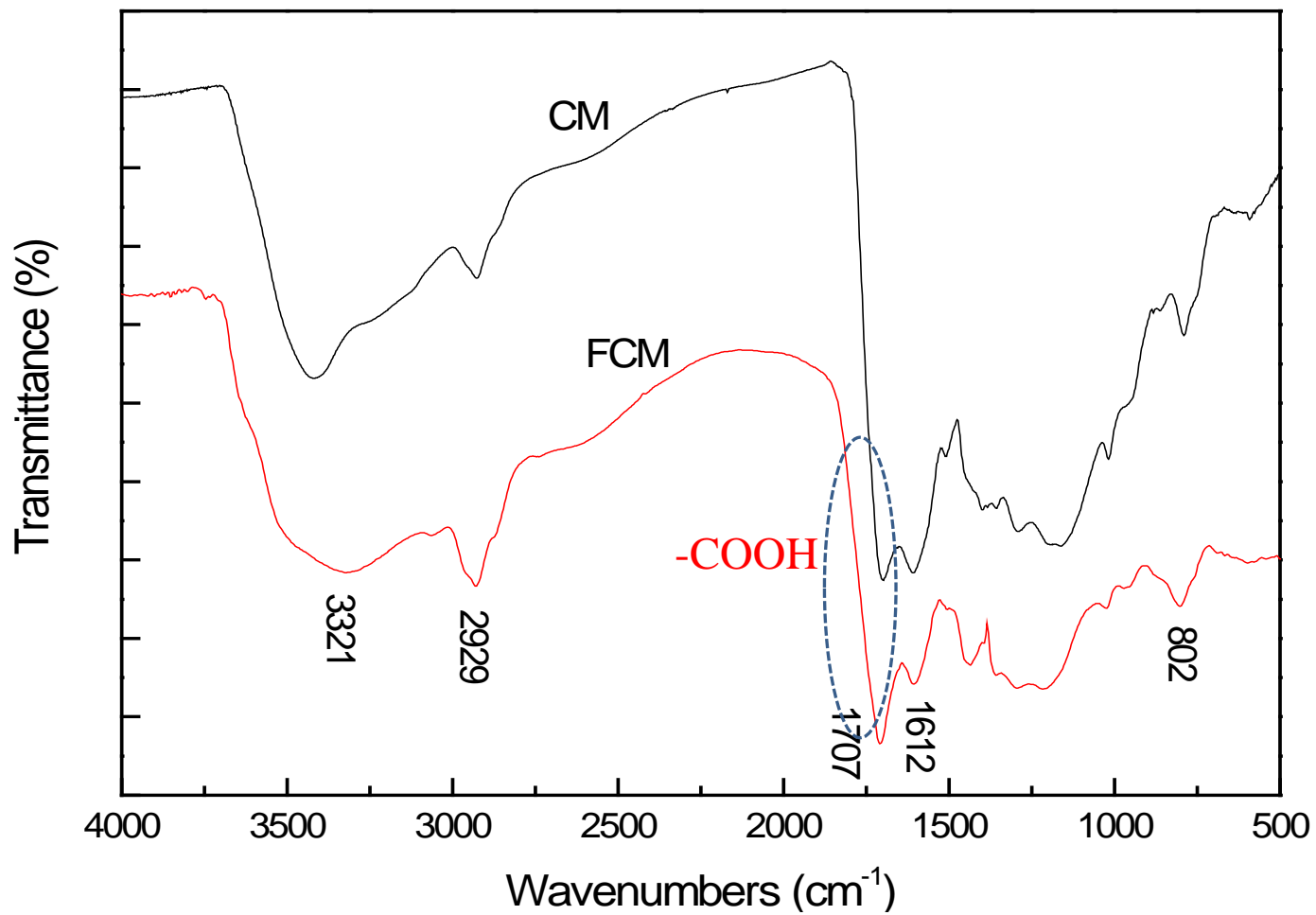
CM



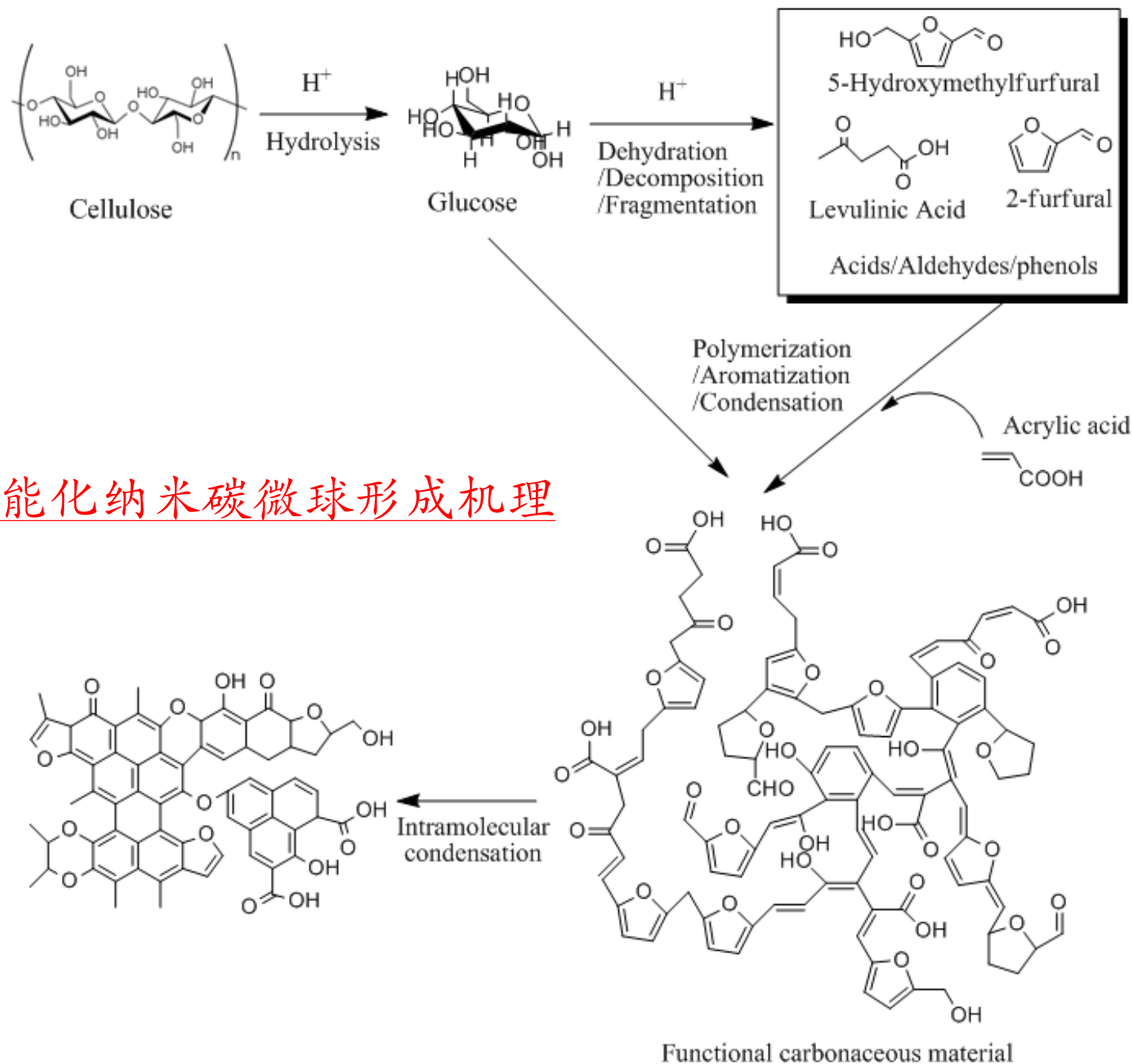
纤维素



FCM



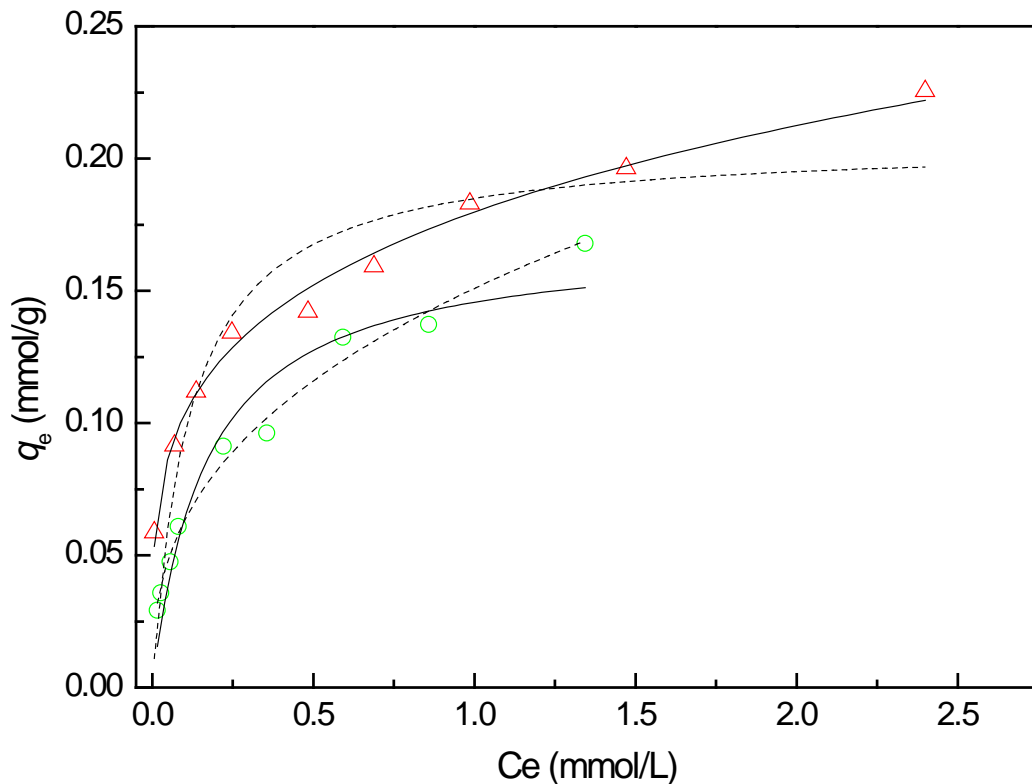
CM和FCM的红外图谱



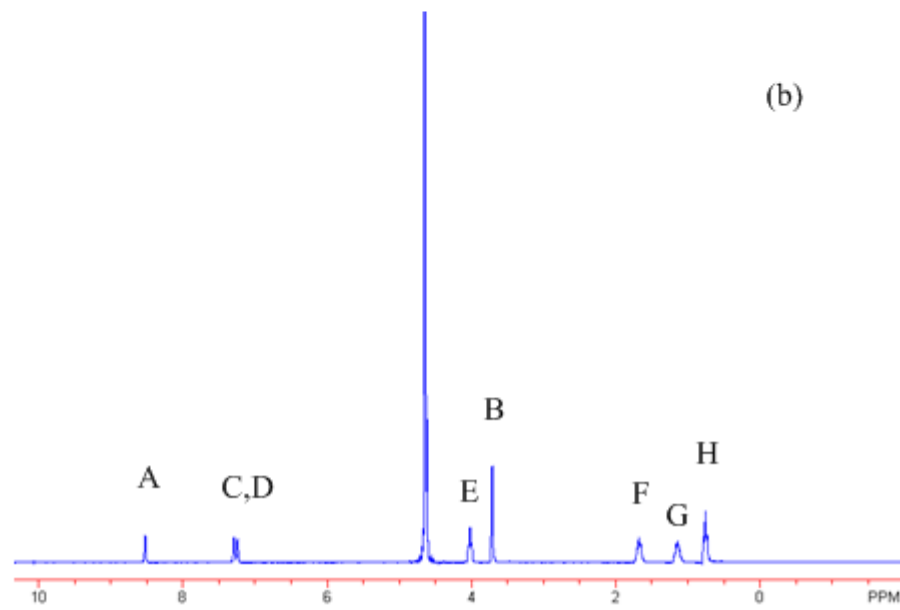
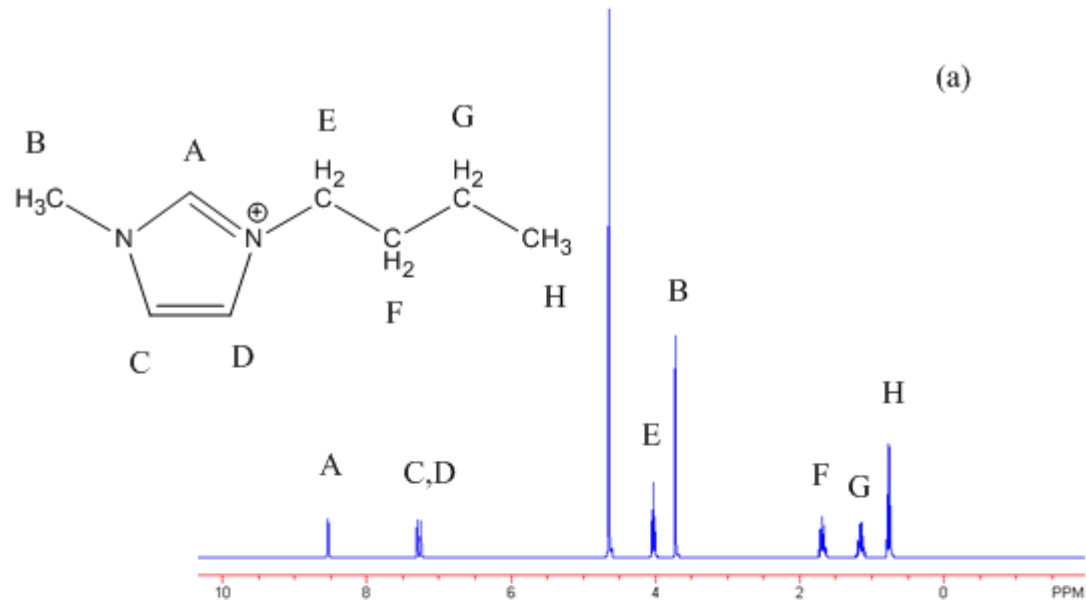
丙烯酸促功能化纳米碳微球形形成机理

Physical and chemical characterization of the hydrothermal prepared carbonaceous material (CM), the prepared functional carbonaceous material (FCM) and commercial activated carbon (AC)

Adsorbent	A_{BET} (m^2/g)	V_{microp} (cm^3/g)	$V_{dp<8\text{ nm}}$ (cm^3/g)	V_{mesop} (cm^3/g)	V_{total} (cm^3/g)	C %	H %	O %
FCM	20	0.051	0.067	0.035	0.086	68.5	4.9	26.6
AC	980	0.099	0.410	0.590	0.736	90.1	1.4	8.5
CM	0.5	0.006	0.006	0	0.006	71.7	4.2	24.1

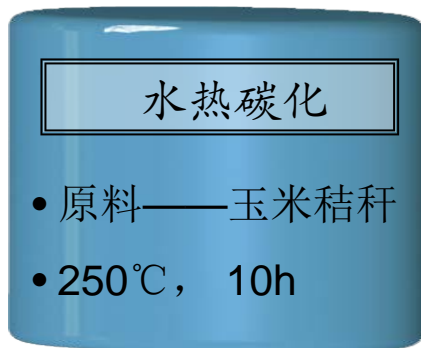


Adsorption isotherms of the prepared functional carbonaceous material adsorbent (FCM) and commercial activated carbon (AC) for [BMIM][Cl] (Conditions: 25 °C, dosage of AC or FCM adsorbent: 2.5 g/L, 24 h, pH: 6.94). ○-FCM, △-AC, Simulation by Langmuir model (- - -) and Freundlich model (—).



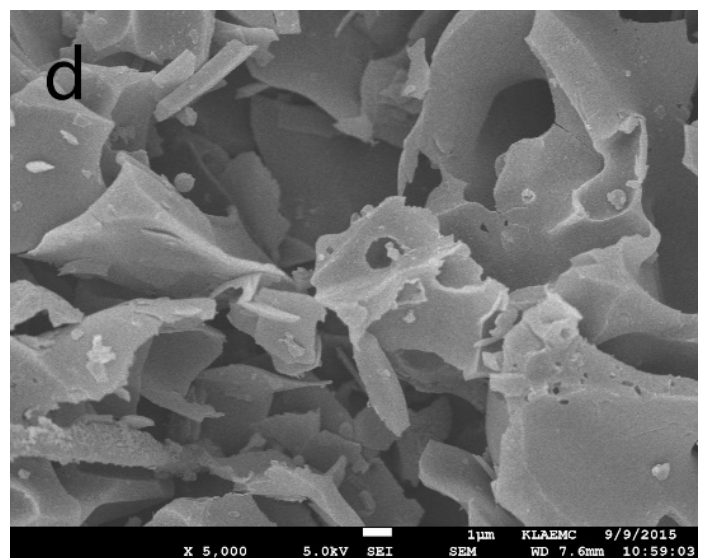
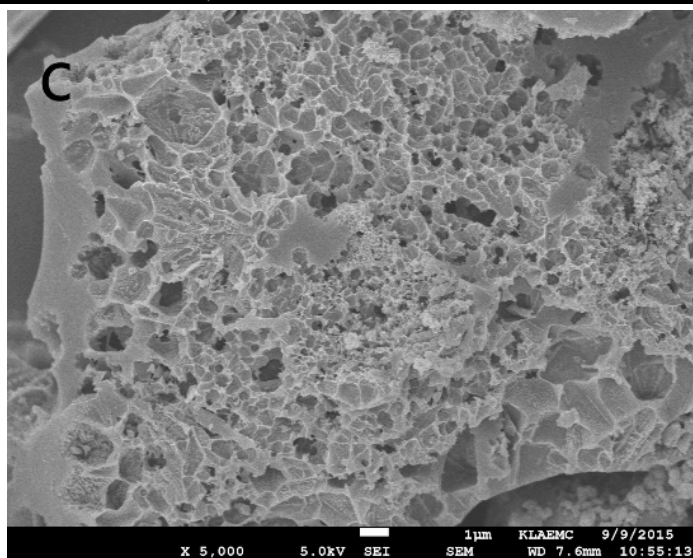
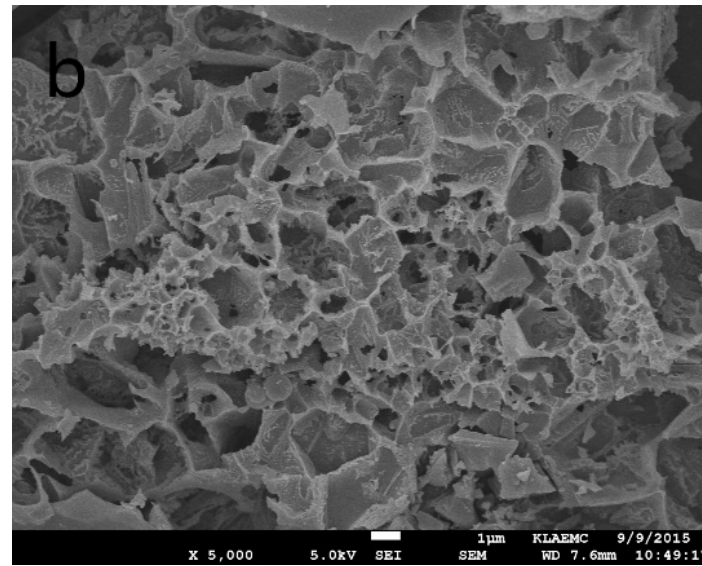
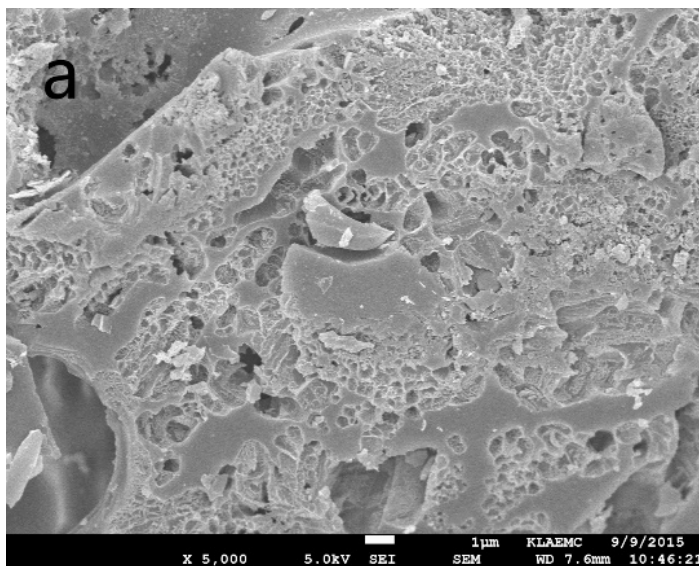
^1H -NMR spectra of (a) fresh [BMIM][Cl] and (b) regenerated [BMIM][Cl] from the adsorbent.

玉米秸秆制备高性能微孔碳材料吸附CO₂

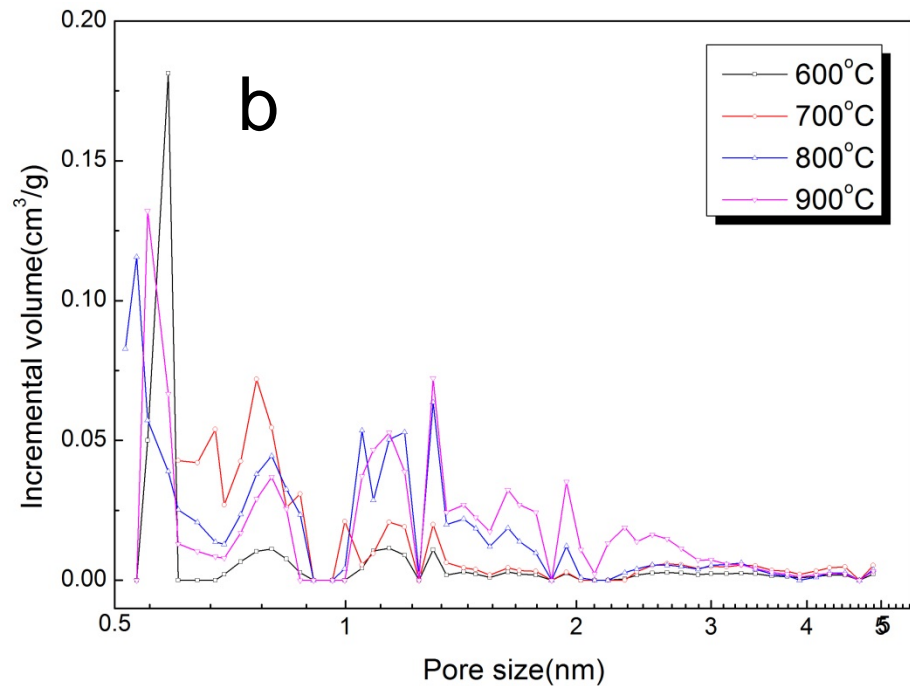
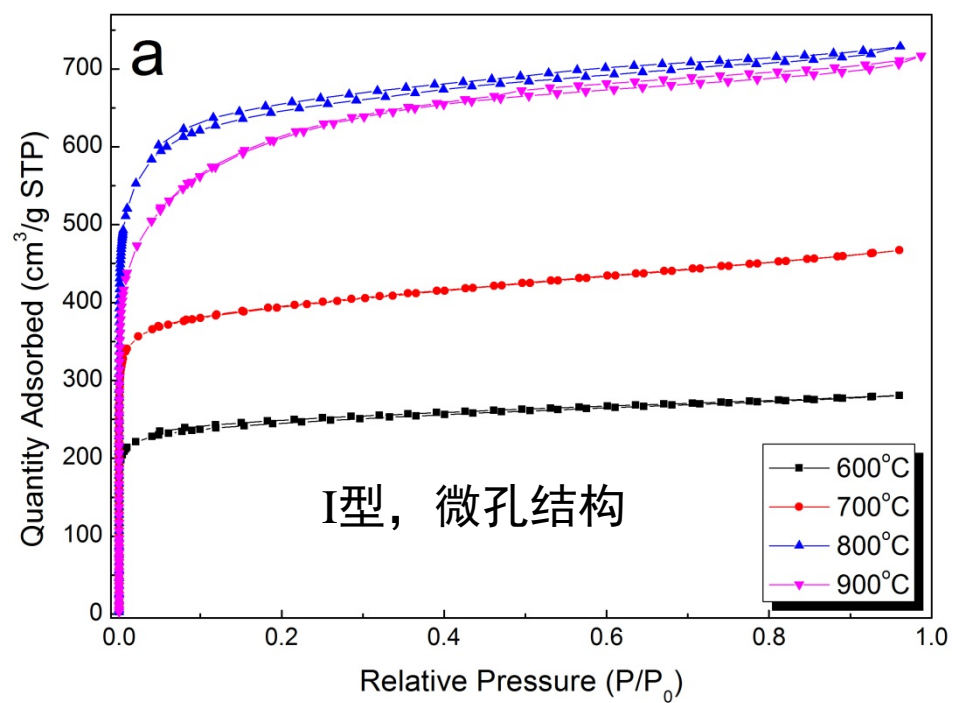


比表面积2442 m²/g,
孔容1.56 cm³/g





不同活化温度下碳材料的扫描电镜图（(a) 600 °C, (b) 700 °C, (c) 800 °C, (d) 900 °C）（活化时间2h, KOH与HC的质量比=2）



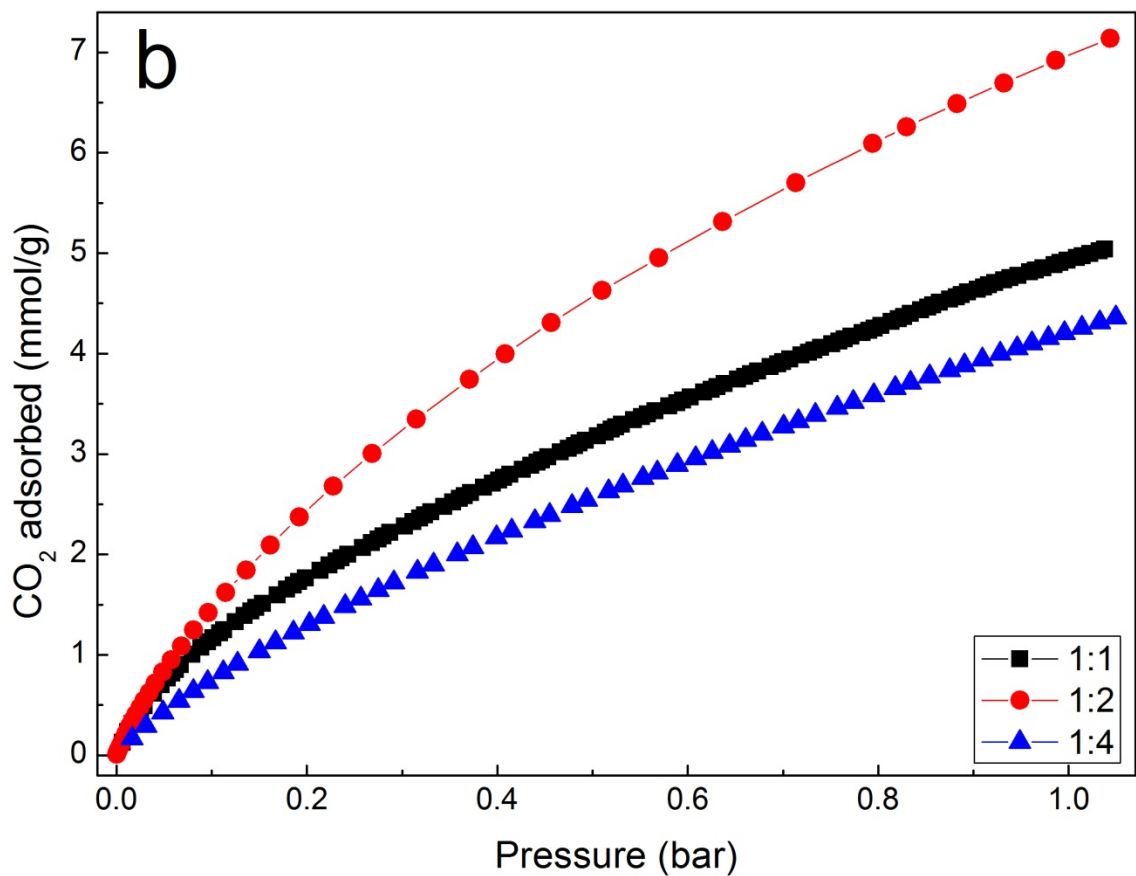
不同活化温度得到的碳材料的 N_2 吸附等温线 (a) 和孔径分布图 (b)。

不同制备条件下得到的碳材料的表面性质和元素组成

Sample	S_{BET} (m^2/g)	S_{micro} (m^2/g)	V_t (cm^3/g)	V_0 (cm^3/g)	C (%)	N (%)	H (%)
HC	11.35	-	0.04	-	43.40	0.48	6.22
AC600-2-2	955	788	0.43	0.31	57.46	0.66	3.37
AC700-2-2	1539	1232	0.72	0.48	59.20	0.34	3.70
AC800-2-2	2442	2149	1.56	0.86	60.41	0.24	3.91
AC900-2-2	2225	1199	1.11	0.49	64.91	0.24	3.12
AC800-1-2	1543	1439	0.71	0.61	66.56	0.86	2.99
AC800-4-2	2170	1983	1.27	0.66	54.94	0.24	2.19
AC800-2-1	1630	1553	0.69	0.60	76.91	0.22	2.73
AC800-2-4	1862	1753	0.81	0.69	58.22	0.20	3.79

ACx-y-z: x-温度, y-KOH/HC质量比, z-活化时间

玉米秸秆基多孔碳（不同活化剂使用量）对CO₂的吸附性能



Sample	S _{BET} (m ² /g)	S _{micro} (m ² /g)	V _t (cm ³ /g)	V ₀ (cm ³ /g)	C (%)	N (%)	H (%)	CO ₂ uptake (mmol/g)
AC800-1-2	1543	1439	0.71	0.61	66.56	0.86	2.99	5.06
AC800-2-2	2442	2149	1.56	0.86	60.41	0.24	3.91	7.14
AC800-4-2	2170	1983	1.27	0.66	54.94	0.24	2.19	4.86

本工作与文献中报道的碳材料对CO₂ 吸附性能的比较 (0 °C and 1 bar)

Adsorbent	Activating agents	CO ₂ uptake (mmol/g)
Nanoporous nitrogen-doped sorbent	KOH	6.8 [1]
Polypyrrole	KOH	6.2 [2]
Activated graphite fibres	KOH	1.3 [3]
Fungi derived activated carbon	KOH	5.5 [4]
Sawdust derived activated carbon	KOH	6.1 [5]
Coconut shell derived porous carbon	CO ₂	5.6 [6]
Corn stalk derived porous carbon	KOH	7.1 (our work)

- Reference [1] Bai, R., *Carbon* 2015, 81, 465-473
[2] M. Sevilla, *Adv. Funct. Mater.*, 2011, 21, 2781-2787
[3] L.-Y. Meng, *Colloid Interface Sci.*, 2010, 352, 498
[4] J.C. Wang, *J. Mater. Chem.* 22 (2012) 13911–13913.
[5] M. Sevilla, *Energy Environ. Sci.*, 2011, 4, 1765-1771
[6] Ello, A. S., *Micropor. Mesopor. Mater.*, 2013, 180, 280-283.

结论与展望

通过葡萄糖的水热碳化可以获得富含 $-\text{SO}_3\text{H}$, $-\text{COOH}$ 和酚羟基官能团的碳材料，其对离子液体中纤维素的水解体现了良好的催化活性。

纤维素的水热碳化制得了具有超顺磁性的碳材料固体酸催化剂，其对纤维素和水稻秸秆的水解均体现出了良好的活性，且可简单地利用外部磁场从反应体系中分离。

开发了将葡萄糖、纤维素和玉米秸秆转化为高附加值化学品5-羟甲基糠醛的高效过程。

纤维素的水热体系中加入一定量的丙烯酸可以获得大量羧基功能化的纳米级碳微球，可以广泛应用于吸附、催化、分析、化工等领域。

玉米秸秆水热碳化结合化学活化获得了具有巨大比表面积和孔容的碳材料，其对 CO_2 的吸附容量可以达到 7.1 mmol/g ，显著优于文献报道的吸附效果。

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**Thank
You For
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