Electronic Supplementary Information

Self-assembly Synthesis of High-content Sulfonic Acid Group Functionalized Ordered Mesoporous Polymer-based solid as a Stable and Highly Active Acid Catalyst

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Synthesis of carbon precursors.

The carbon precursors, low-molecular-weight, soluble phenolic resins, were prepared from phenol and formaldehyde in a base-catalyzed process. In a typical procedure, 8.0 g of phenol was melted at 42-45 °C in a flask and mixed with 0.34 g of 20 wt% sodium hydroxide (NaOH) aqueous solution under stirring. After 10 min, 5.24 g of formalin (37 wt% formaldehyde) was added. Then the mixture was heated to 70 °C. Upon further stirring for 1 h at this temperature, the mixture was cooled to room temperature. The pH value was adjusted with 2 M HCl solution until it reached a value of ~7.0. Subsequently, water was removed by vacuum evaporation below 45 °C. The water- and ethanol-soluble phenolic resins were then dissolved in ethanol (20 wt%) for further use.

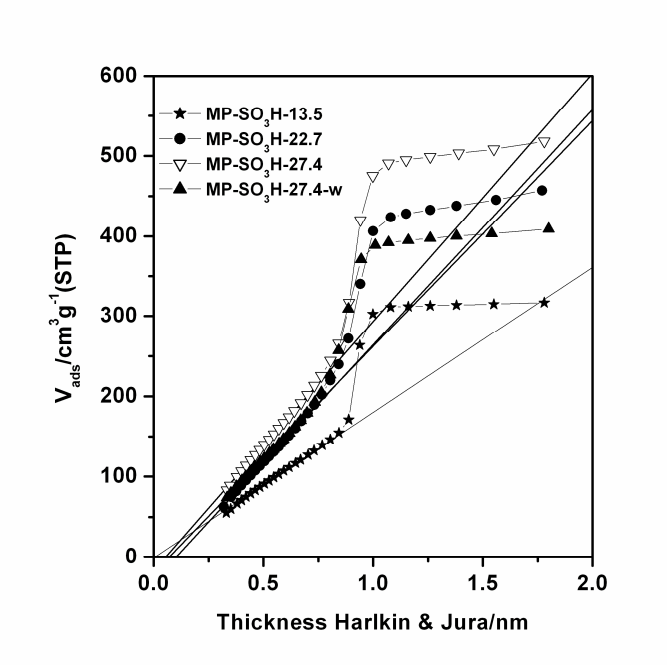
SI Table S1. The preparation conditions for sulfonic acid group functionalized ordered mesoporous polymer-based materials.

Sample	MPTMS (g)	TEOS (g)	Resol (g)	F127 (g)	H_2O_2/sample (g/g)
MP-SO_3H-13.5	0.654	3.458	0.32	2.0	30
MP-SO_3H-22.7	1.308	2.792	0.32	4.0	30
MP-SO_3H-27.4	1.964	2.08	0.32	4.4	30
MP-SO_3H-27.4-w	1.964	2.08	0.32	4.4	2.04
MP-SO_3H-11.4*	0.654	3.458	2.0	3.2	30
MP	0	4.16	0.32	2.0	0

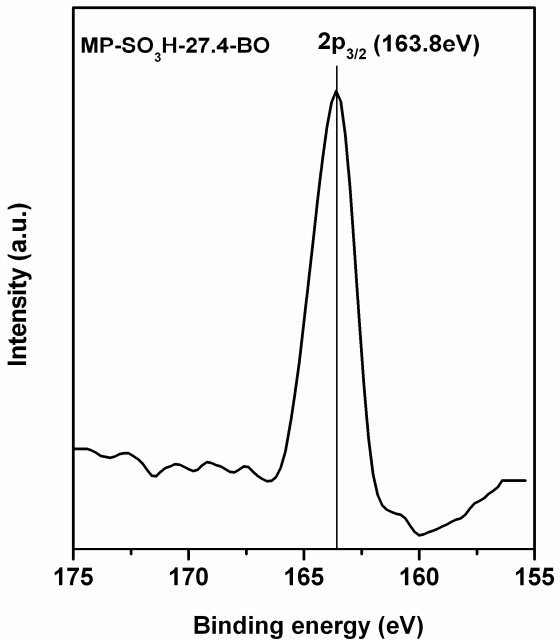
SI Table S2. The conditions for acetalization reactions.

Entry	Catalyst	Ketone /aldehyde	Diol	Temperature (°C)	Time (h)
1	MP-SO_3H-22.7	acetophenone	glycol	90	8
2	MP-SO_3H-13.5	cyclohexanone	glycol	100	2
3	MP-SO_3H-22.7	cyclohexanone	glycol	100	2
4	MP-SO_3H-27.4	cyclohexanone	glycol	100	2
5	MP	cyclohexanone	glycol	100	12
6	MP-SO_3H-22.7	butyraldehyde	1,4-butanediol	90	2
7	MP-SO_3H-22.7	propionaldehyde	1,4-butanediol	90	2
8	MP-SO_3H-22.7	cyclohexanone	1,4-butanediol	100	3
9	MCM-SO_3H	butyraldehyde	1,4-butanediol	90	2
10	MCM-SO_3H	cyclohexanone	1,4-butanediol	100	3
11	SBA-SO_3H	butyraldehyde	1,4-butanediol	90	2
12	SBA-SO_3H	cyclohexanone	1,4-butanediol	100	3
13	$MSiO_2$-SO_3H-19.4	butyraldehyde	1,4-butanediol	90	2

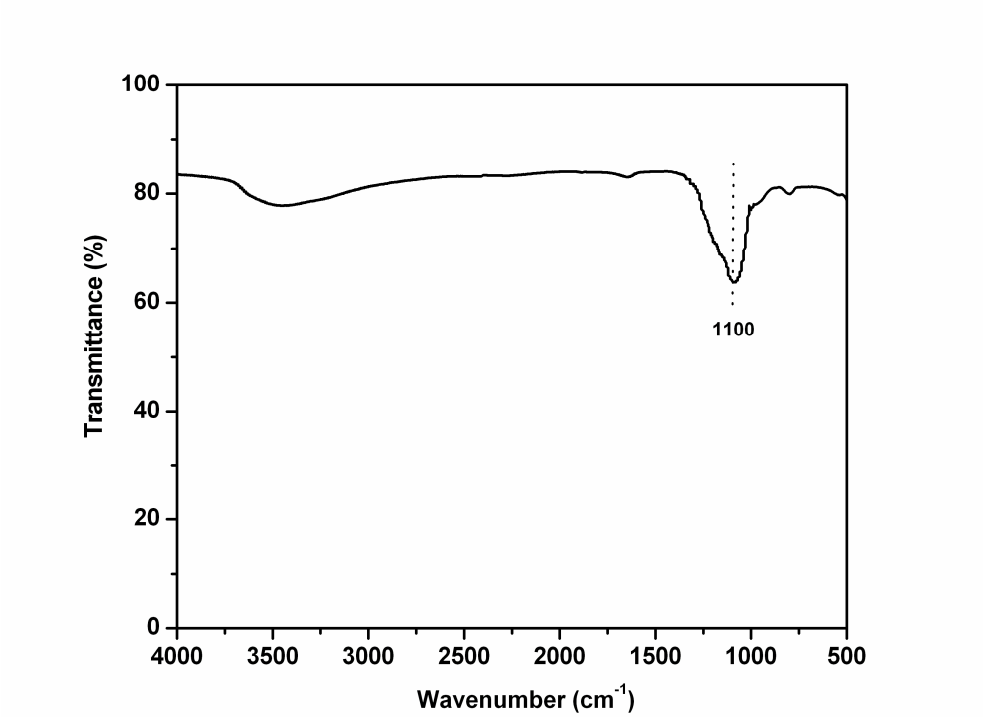
SI Figure S1. *t*-plot analysis for ordered mesoporous polymer-based acidic solids with different sulfonic acid group contents.



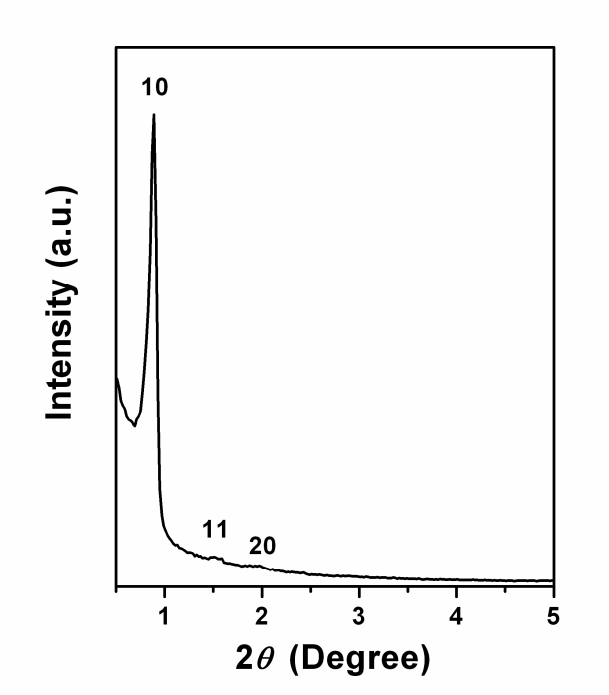
SI Figure S2. XPS spectrum of the mercapto-functionalized mesoporous polymer-based material MP-SO_3H-27.4 before oxidation. Only one strong peak with the binding energy around 163.8 eV in the $2p_{3/2}$ level is observed, demonstrating the presence of thiol group.



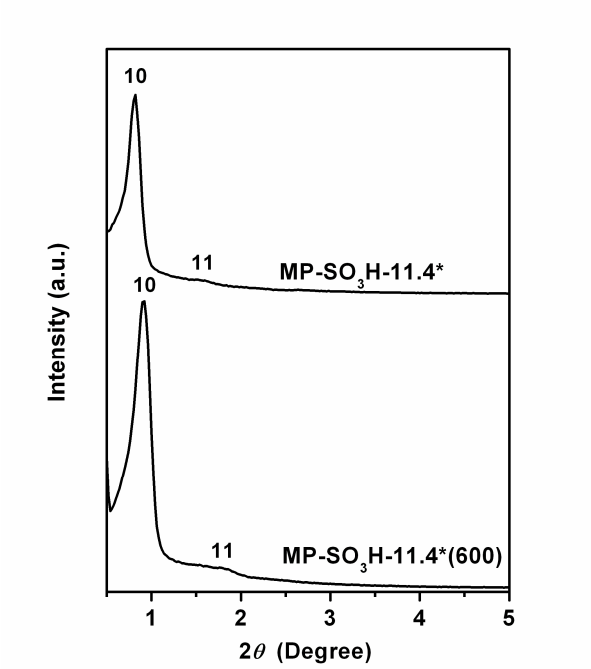
SI Figure S3. FT-IR spectrum for the mesoporous carbon-based product MP-SO_3H-22.7(600) obtained by heating MP-SO_3H-22.7 at 600 °C under protection of nitrogen.



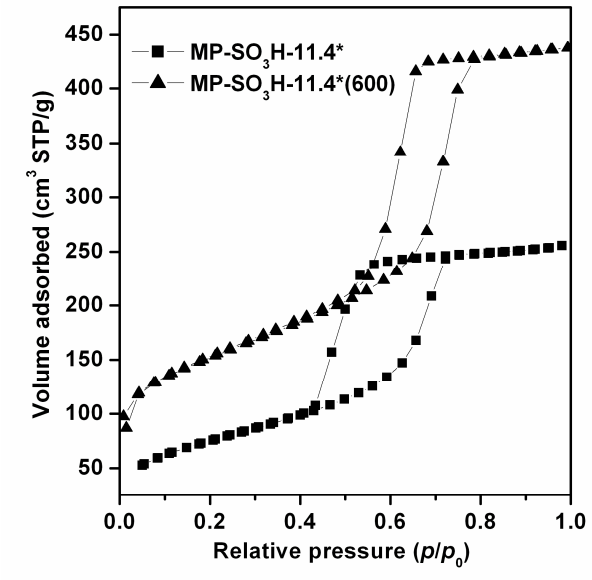
SI Figure S4. Small-angle XRD pattern for the mesoporous carbon-based product MP-SO_3H-22.7(600) obtained by heating MP-SO_3H-22.7 at 600 °C under protection of nitrogen.



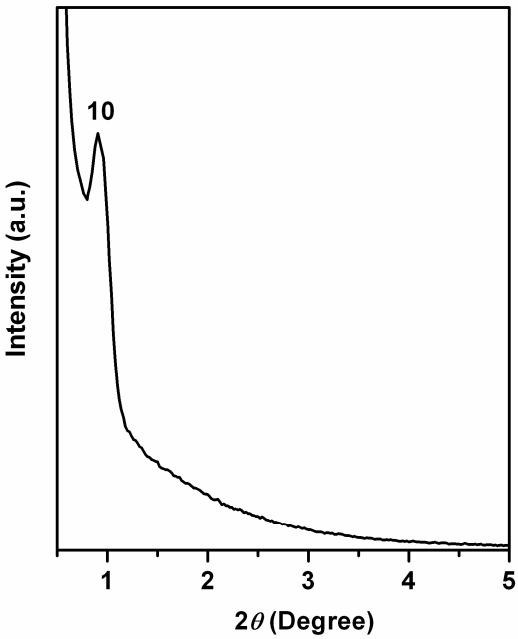
SI Figure S5. Small-angle XRD pattern for the mesoporous polymer-based acidic solid MP-SO_3H-11.4* synthesized *via* the evaporation induced self-assembly of triblock copolymer F127, low-polymerized phenolic resins, TEOS and MPTMS (initial 8.11 mmol TEOS and 1.89 mmol MPTMS): 1.0 g phenolic resins), and the sample heated at 600 °C under protection of nitrogen MP-SO_3H-11.4*(600).



SI Figure S6. N_2 sorption isotherms for the mesoporous polymer-based acidic solid MP-SO_3H-11.4*, and the sample heated at 600 °C under protection of nitrogen MP-SO_3H-11.4*(600).



SI Figure S7. Small-angle XRD pattern for the mesoporous carbon product after dissolution of silica component from MP-SO_3H-11.4*(600).



SI Figure S8. (a) N_2 sorption isotherms and (b) pore-size distribution curve for the mesoporous carbon product after dissolution of silica component from MP-SO_3H-11.4*(600).