# Hierarchical Porous Nitrogen-Doped Carbon by Pickering HIPEs Technique: Synthesis and Application in HMF Production

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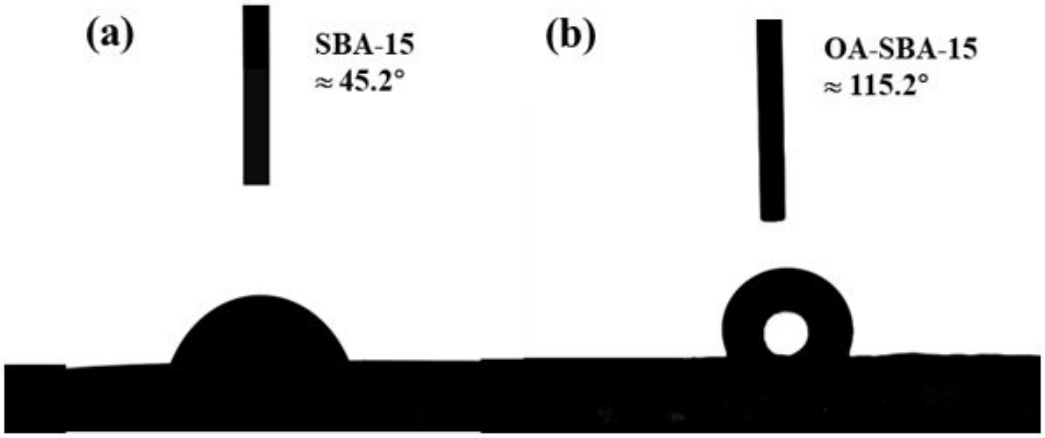
## EXPERIMENTAL SECTION

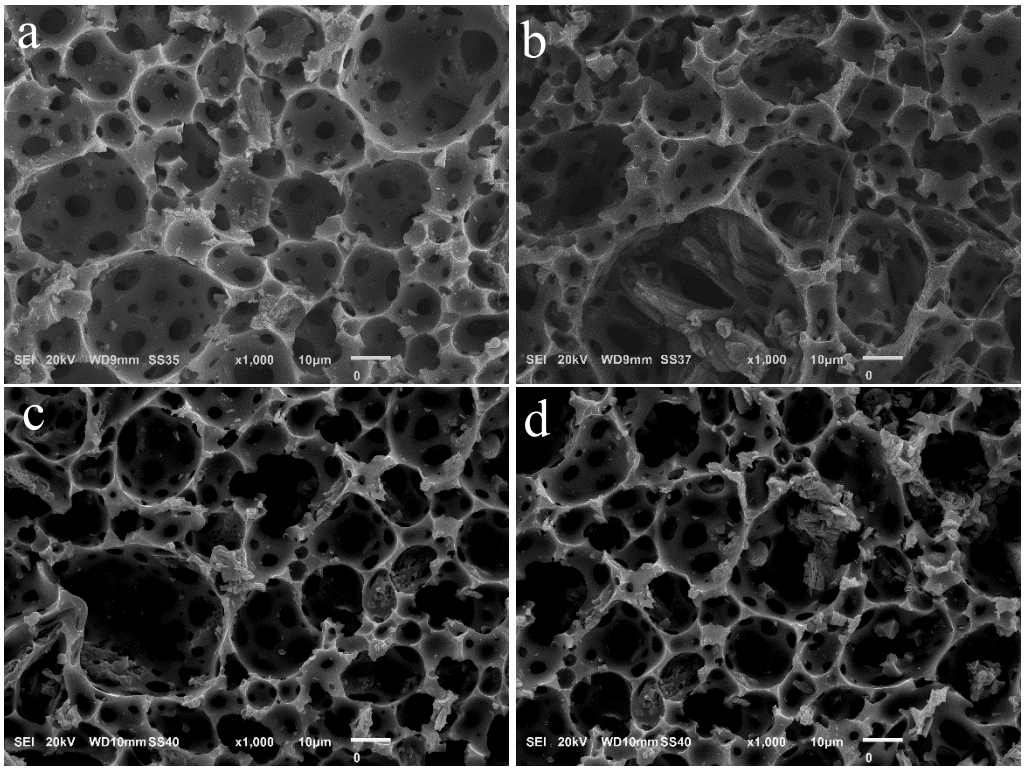
**Synthesis of acid and base catalyst:** Firstly, in order to obtain water-in-oil Pickering HIPEs, we adjusted the hydrophilicity of the obtained SBA-15. The steps of grafting amino on the surface of SBA-15 were as follows: Toluene (285 mL), SBA-15 (1.9 g) and KH-550 (10 mL) were added into a three-mouth flask to disperse evenly. The reaction was placed in an oil bath at 110℃ and refluxed under a nitrogen atmosphere for 12 h. The products were then collected, washed with toluene, centrifuged, and dried in a vacuum at 60 ℃. The amino-grafted SBA-15(1.0 g) was suspended in the mixture of OA and chlorine (1:4 M ratio), stirred for 3.0 h, and oA-SBA-15 was extracted from the solution by methanol precipitation and dried in an oven at 60 °C.

Secondly, water in oil (W/O) Pickering HIPEs template was formed by using oleic acid modified SBA-15 particles obtained in the previous step as stabilizer. A detailed procedure for acid catalyst is as follows: OA-SBA-15 (1.5 wt% of oil phase mass), AIBN (0.06 g) and polymer 2296 (0.13 g) were dissolved in the mixture of DVB (3.0 mL) and toluene (2.0 mL) to form a continuous external phase under mild stirring. Afterwards, under continuous stirring, the inner water phase (26.7 mL deionized water) was added to the oleic phase dropwise to obtain stable W/O HIPEs. Pickering HIPEs were transferred to a sealed glass mold, polymerized in a 70 ℃ water bath for more than 12 h, and then washed with acetone through Soxhlet extraction for more than 48 h to remove impurities. The resultant polymer foams were dried to a constant weight in a drying oven at 60 ℃. Under the condition of nitrogen atmosphere, the samples were heat-treated for 2.0 h at a heating rate of 5.0 °C $min^{-1}$, The system temperature was 600 ℃. The synthesis procedure of base catalyst was same as acid catalyst except for replacing DVB with a mixture of DVB (3.0 mL) and 1-vinyl imidazole (6.0 mL), the final synthesized base catalyst was named NC-700.

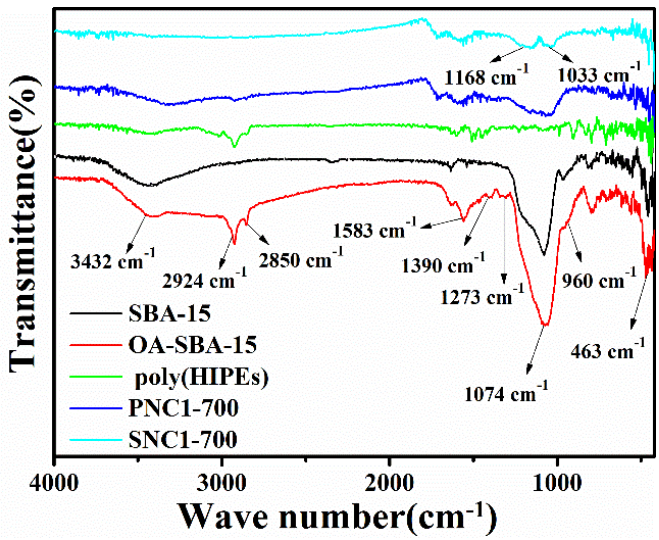
Finally, the acid catalyst prepared in the previous step was sulfonated. In general, acid catalyst (5.0 g) was added into 50 mL concentrated sulfuric acid (98%), protected by nitrogen for 0.5 h, and heated at 180 ℃ for 5.0 h. Then the sulfonated mixture was cooled to room temperature and diluted with deionized water to form a black sediment, filtered and repeatedly washed with a large amount of deionized water until the filtrate was neutral. The obtained samples were dried in a vacuum at 60℃ for 48h, the final synthesized acid catalyst was named SC-700.



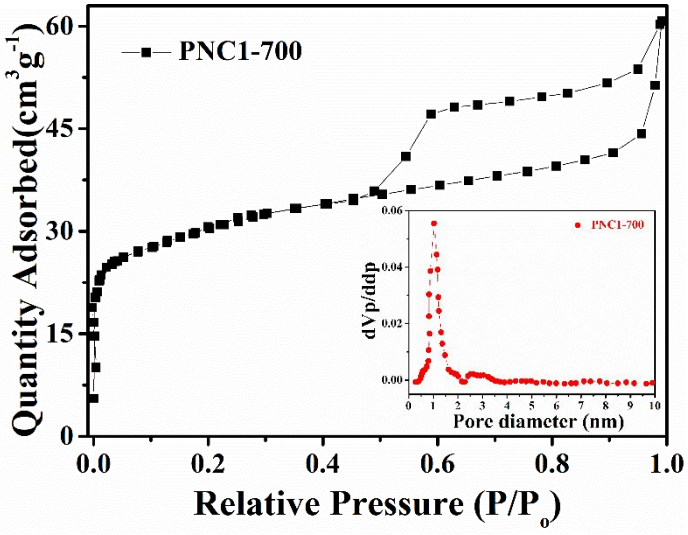

39 **Figure. S1** Water contact angles of SBA-15 and 1:4 OA-SBA-15.



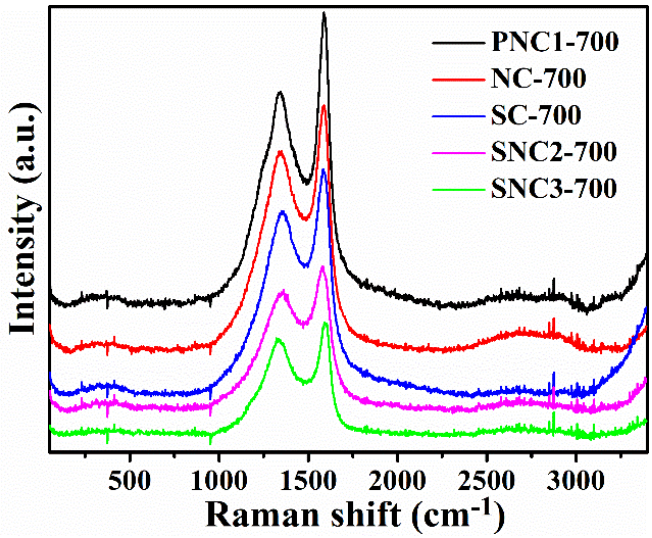

40 **Figure. S2** (a-d) SEM images of SNC2-700, SNC3-700, NC-700, SC-700.




41 **Figure. S3** FT-IR spectra of SBA-15, OA-SBA-15, poly (HIPEs), PNC1-700 and SNC1-700.

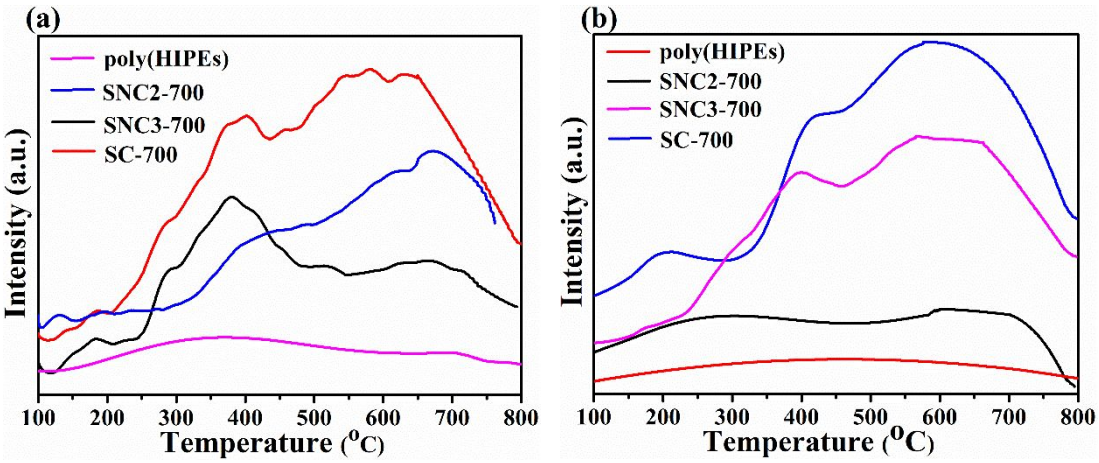



42 **Figure. S4** Nitrogen adsorption–desorption isotherms and pore size distributions of PNC1-700.

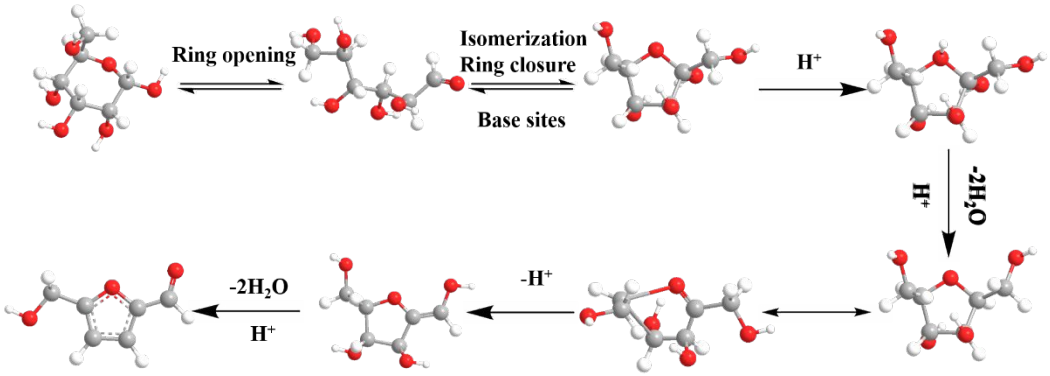



43 **Figure. S5** Raman spectra of PNC1-700, SNC2-700, SNC3-700, SC-700, NC-700 materials at

44 different pyrolysis temperatures.




45 **Figure. S6** $CO_2$-TPD (a) and $NH_3$-TPD (b) curves of catalysts.




46 **Figure. S7** The plausible catalytic scheme for the conversion of glucose into HMF over our

47 developed acid-base bi-functional catalyst.