

## Supporting information

### **Template-free synthesis of porous carbonaceous solid acids with controllable acid sites and excellent activity for catalyzing synthesis of biofuels and fine chemicals**

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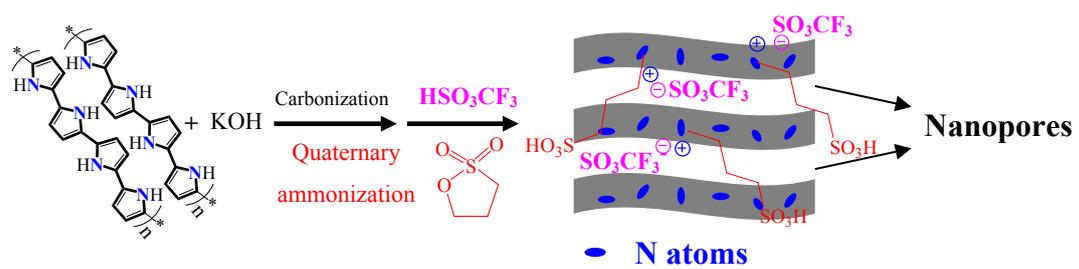
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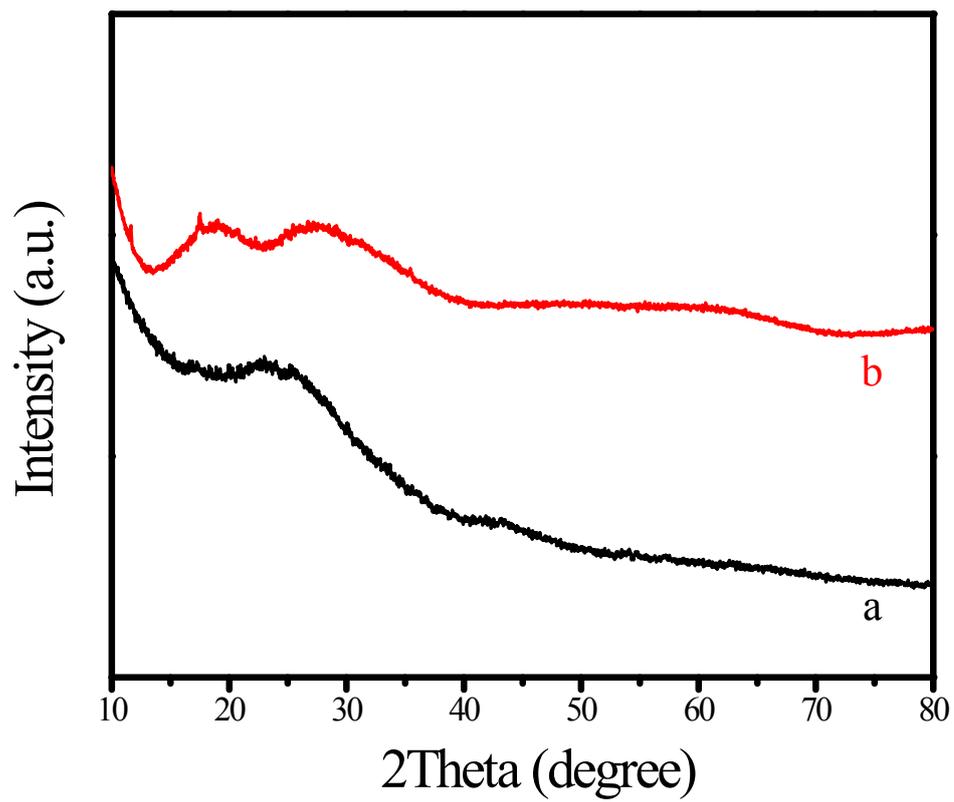
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*Detailed procedures for the synthesis of NPC-[C<sub>3</sub>N][H<sub>2</sub>PW<sub>12</sub>O<sub>40</sub>]*

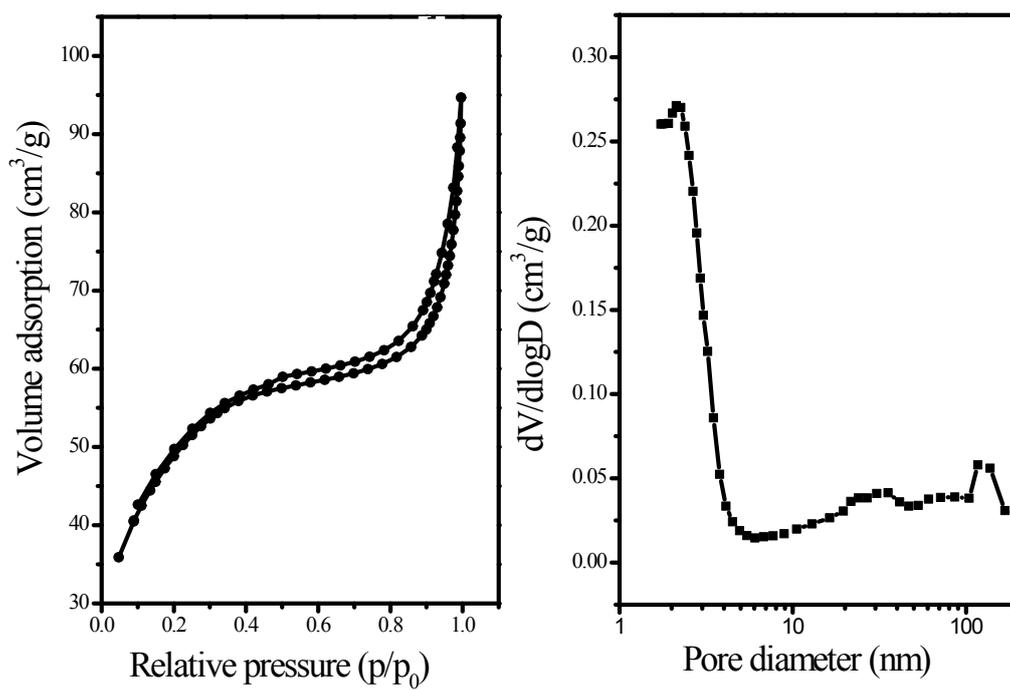
As a typical run for the synthesis of NPC-[C<sub>3</sub>N][H<sub>2</sub>PW<sub>12</sub>O<sub>40</sub>], 1.0 g of NPC was dispersed into a mixture contains 20 mL of toluene and 0.5 g of 1,3-propanesultone, after stirring of the reaction mixture at 110 °C for 24 h under refluxing, the reaction was finished and the mixture was cooled down to room temperature (25 °C). The resultant sample of NPC-[C<sub>3</sub>N]<sup>+</sup> could be obtained from centrifugation, washing with abundant CH<sub>2</sub>Cl<sub>2</sub> and drying at 60 °C under vacuum conditions. To get NPC-[C<sub>3</sub>N][H<sub>2</sub>PW<sub>12</sub>O<sub>40</sub>], 0.5 g of NPC-[C<sub>3</sub>N]<sup>+</sup> was added into a mixture containing 13 mL of ethanol/water (3:1) and 0.42 g of H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, after stirring of the mixture at 100 °C for 12 h, NPC-[C<sub>3</sub>N][H<sub>2</sub>PW<sub>12</sub>O<sub>40</sub>] could be obtained from centrifugation, washing with abundant ethanol and water, and drying at 100 °C under vacuum conditions.



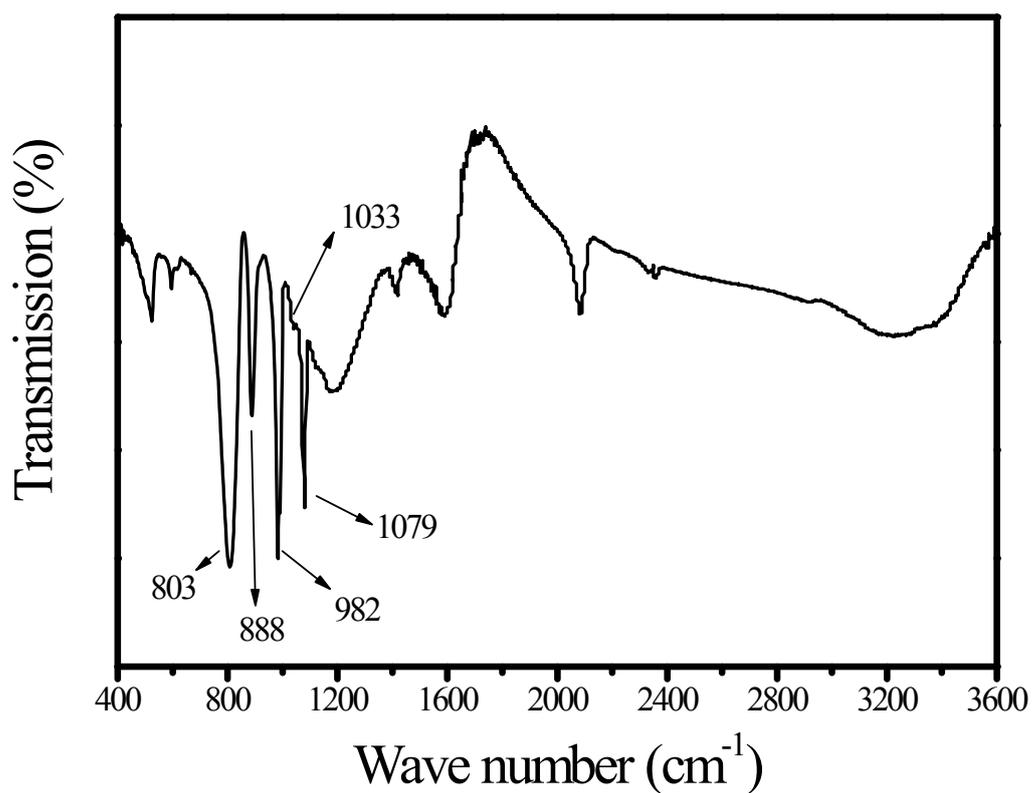
**Figure S1** The scheme for the synthesis of NPC-[C<sub>3</sub>N][SO<sub>3</sub>CF<sub>3</sub>].



**Figure S2** XRD patterns of NPC (black) and NPC-[C<sub>3</sub>N][H<sub>2</sub>PW<sub>12</sub>O<sub>40</sub>] (Red).

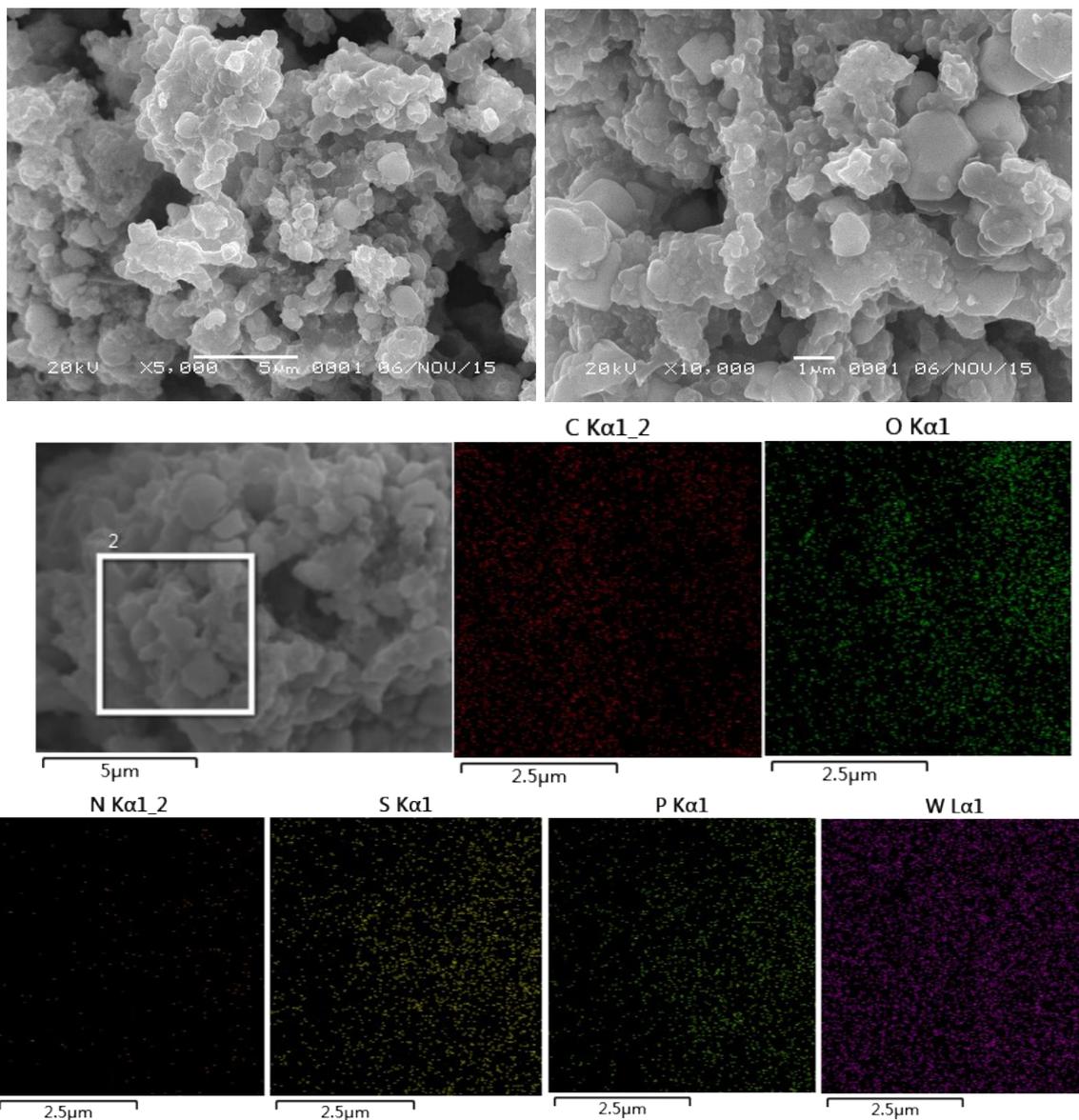


**Figure S3** N<sub>2</sub> isotherms of NPC-[C<sub>3</sub>N][H<sub>2</sub>PW<sub>12</sub>O<sub>40</sub>].

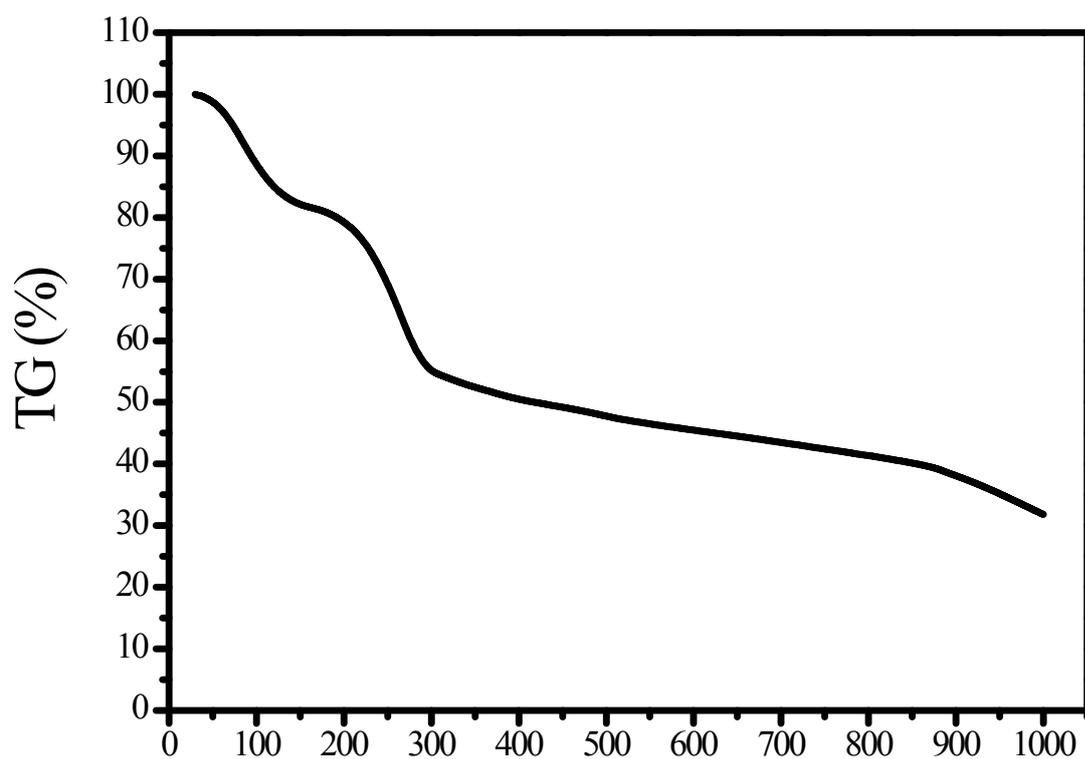


**Figure S4** FT-IR spectrum of NPC-[C<sub>3</sub>N][H<sub>2</sub>PW<sub>12</sub>O<sub>40</sub>].

The peaks at around 803, 888, 982 and 1079 cm<sup>-1</sup> were assigned to ???. On the other hand, the peak at around 1033 cm<sup>-1</sup> was assigned to C-S bond, which indicate both heteropolyacid and sulfonic group have been successfully grafted onto the network of NPC.



**Figure S5** SEM images and elemental maps of NPC-[C<sub>3</sub>N][H<sub>2</sub>PW<sub>12</sub>O<sub>40</sub>].



**Figure S6** TG curve of NPC-[C<sub>3</sub>N][SO<sub>3</sub>CF<sub>3</sub>] tested under N<sub>2</sub> condition.