Supplementary information

Efficient biomass transformations catalyzed by graphene-like nanoporous carbons functionalized with strong acid ionic liquids and sulfonic group

Fujian Liu a,c, Weiping Kong a, Liang Wang c, Xianfeng Yi b, Iman Noshadi d, Anmin Zheng* b and Chenze Qi* a

a Key Laboratory of Alternative Technologies for Fine Chemicals Process of Zhejiang Province, Department of Chemistry, Shaoxing University, Shaoxing, 312000, China. E-mail: qichenze@usx.edu.cn

b Wuhan Center for Magnetic Resonance, State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences, Wuhan 430071, China. E-mail: zhenganm@wipm.ac.cn

c Department of Chemistry, Zhejiang University (XiXi Campus), Hangzhou, 310028, China.

d Polymer Program, Institute of Materials Science and Department of Chemistry, University of Connecticut, Storrs, CT, 06269, United States.
Experimental section

Chemicals and reagents

All reagents were of analytical grade and used as purchased without further purification. 1,3-propanesultone, HSO$_3$CF$_3$, H$_2$SO$_4$, DMSO, toluene, sunflower oil, dicyandiamide, glucose, tetraethylorthosilicate (TEOS), NaOH, potassium sodium tartrate, sodium sulfite, 3,5-dinitrosalicylic acid, H$_3$PW$_{12}$O$_{40}$, melamine, phenol and CH$_2$Cl$_2$ were obtained from Beijing Chemical Agents Company. Crystalline cellulose of Avicel (extra pure, average particle size 50 m, crystalline degree: 80~90 %), 3-mercaptopropyltrimethoxysilane (3-MPTS), Amberlyst 15, nonionic block copolymer surfactant poly(ethyleneoxide)-poly(propyleneoxide)-poly(ethyleneoxide) block copolymer (P123), tripalmitin, 1-n-butyl-3-methylimidazolium chloride ([C$_4$ mim]Cl ionic liquid), 1-vinylimidazole and 5-hydroxymethylfurfural (HMF) were purchased from Sigma-Aldrich Co.

The recovery of biodiesel (methyl palmitate) from the reaction mixture

After the reaction of tripalmitin with methanol, the biodiesel of methyl palmitate could be isolated as follows: First, the reaction mixture was cooled down to room temperature. Then, 2.5 mL of ethanol, which acts as a solvent was introduced into the mixture and the unreacted tripalmitin and solid catalyst were separated from centrifugation. After vacuum distillation to remove of alcohols at 70 °C, a mixture contains methyl palmitate and the byproduct of glycerol was obtained. The glycerol could be removed by introducing a certain content of water, resulting in phase separation of methyl palmitate and glycerol aqueous solution. After removing of the lower water layer, the biodiesel was collected and dried under vacuum conditions for 5 h (110 °C, 0.01 Torr).

Preparation of DNS Reagent

As a typical run for preparation of DNS solution, 91 g of potassium sodium tartrate was added into 250 mL of hot deionized water at 50 °C. Then, 3.15 g of 3,5-dinitrosalicylic acid and 131 mL of 2 M
NaOH were added. Once dissolved, 2.5 g of phenol and 2.5 g of sodium sulfite were also introduced into the solution upon vigorous stirring until a homogeneous solution was obtained. The hot solution was cooled to room temperature and diluted with deionized water to 500 mL to give the DNS reagent.

**Characterization methods**

Nitrogen isotherms were measured using a Micromeritics ASAP 2020M system. The samples were outgassed for 10 h at 150 °C before the measurements were taken. The pore-size distribution was calculated using the Barrett-Joyner-Halenda (BJH) model. FTIR spectra were collected by using a Bruker 66V FTIR spectrometer. A X-ray powder diffraction (XRD) of samples was recorded on a Rigaku D/max2550 PC powder diffractometer, using nickel-filtered CuKα radiation at approximately 10°≤2θ≤60°. Transmission electron microscopy (TEM) images were taken on a JEM-3010 electron microscope (JEOL, Japan) with an acceleration voltage of 300 kV. CHNS elemental analysis was performed on a Perkin-Elmer series II CHNS analyzer 2400. XPS spectra were performed on a Thermo ESCALAB 250 with Al Kα radation at y=901 for the X-ray sources. The binding energies were calibrated using the C1s peak at 284.9 eV.

The solid $^{31}$P NMR spectrum over GNC-[C$_3$N][SO$_2$CF$_3$] catalyst was performed as follows: prior to trimethylphosphine (TMP) sorption of probe molecules, the sample was placed in a glass tube and then connected to a vacuum line for dehydration. The sample was kept at the final temperature, 393 K, with the pressure below 10$^{-3}$ Pa, over a period of 24 h. Then, it was cooled. After TMP sorption, the sealed sample tube was opened and the sample was transferred into a NMR rotor with a Kel-F end cap under a dry nitrogen atmosphere in a glove box.

All $^{31}$P NMR experiments were performed on a Bruker Ascend-500 spectrometer at a resonance frequency of 202.34 MHz with a 4 mm triple-resonance MAS probe at a sample spinning rate of 12.5 kHz. Pulse width ($\pi/2$) for $^{31}$P was measured to be 4.5 μs. $^{31}$P MAS NMR spectra were recorded with a recycle delay of 30 s. The chemical shifts for the $^{31}$P resonance were referred to 1M aqueous H$_3$PO$_4$. 
Figure S1 (A) N$_2$ isotherms and (B) pore size distribution of (a) NPG and (b) NPG-[C$_3$N][SO$_3$CF$_3$].

Figure S1 showed N$_2$ isotherms and pore size distribution of GNCs and GNC-[C$_3$N][SO$_3$CF$_3$]. Notably, GNC exhibits type-IV curve with a sharp capillary condensation step at p/p$_0$=0.8-0.95 and a H$_2$-type hysteresis loops, giving high BET surface area (945 m$^2$/g) and large pore volume (3.1 cm$^3$/g), which indicate presence of abundant nanopores in GNC S1. Correspondingly, the pore diameter of GNC was centered at 3.8 & 33.7 nm, respectively, indicating the formation of hierarchically nanoporous structure in GNC. After functionalization of GNC with strong acid ionic liquids and sulfonic group, giving the sample of GNC-[C$_3$N][SO$_3$CF$_3$], the pore diameters were centered at 3.6 & 31.2 nm, respectively. However, its BET surface area and pore volume were considerably decreased to 184 m$^2$/g and 0.59 cm$^3$/g. Compared with GNC, the decreased BET surface area and pore diameters in GNC-[C$_3$N][SO$_3$CF$_3$] were mainly attributed to the introduction of acidic ionic liquids, sulfonic group inside the GNC, which dramatically increases the weight of network and partially blocks the nanopores of GNC, similar results have also been reported previously S2.
Figure S2 TEM images of (a&b) N containing nanoporous graphene-like nanoporous carbon synthesized from carbonization of the mixture of melamine and glucose, and (c&d) graphene-like nanoporous carbons functionalized with strong acid ionic liquids and sulfonic group.
Figure S3 FT-IR spectra of (a) GNC-[C$_3$N][SO$_3$CF$_3$] and (b) GNC-[C$_3$N][SO$_3$H].
Figure S4 The GC-MS chromatograms of transesterification of (a) tripalmitin and (b) sunflower with methanol catalyzed by GNC-[C$_3$N][SO$_3$CF$_3$] catalyst.
Figure S5 (a) $^1$H and (b) $^{13}$C NMR spectra of isolated biodiesel of methyl palmitate.
Figure S6 HPLC analysis of the reaction mixture of depolymerization of crystalline cellulose into sugars over GNC-[C$_3$N][SO$_3$CF$_3$] catalyst.
**Figure S7** GNC-\([\text{C}_3\text{N}]\text{[SO}_3\text{CF}_3]\) dispersed into the reaction mixture of (a) transesterification of sunflower oil with methanol, and (b) depolymerization of crystalline cellulose into sugars.
Figure S8 Wide angle XRD pattern of crystalline cellulose of Avicel.
Supplementary references
