Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Insitu generation of hydroxyl radical by nanoporous activated carbon derived from rice husk for environmental applications: Kinetic and thermodynamic constants

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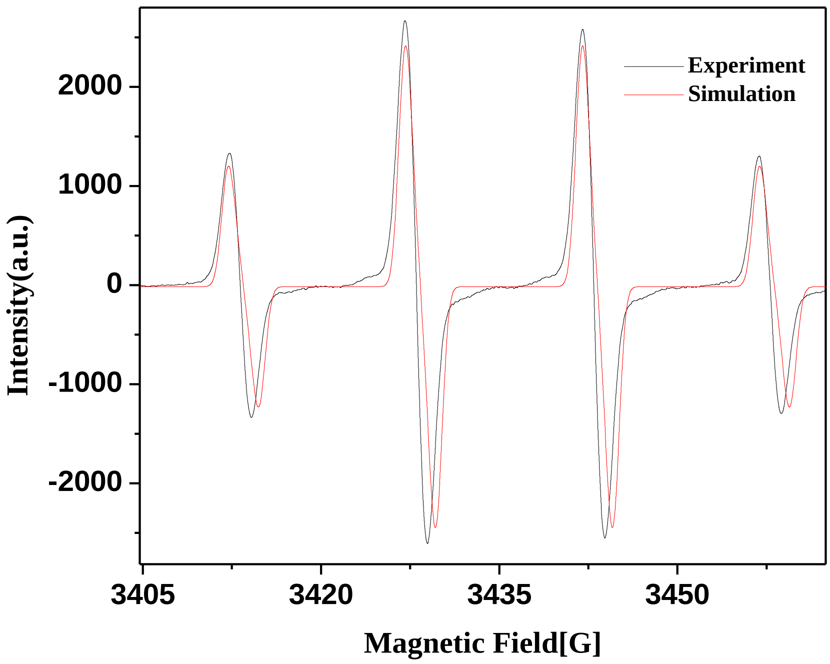

Figure S1. Simulated electron spin resonance spectra of DMPO bound ·OH (red colour) using parameters aN = 14.9 gauss, a_H = 14.9 gauss. Electron spin resonance spectra of DMPO bound ·OH obtained in experiment (black colour) using NPAC and dissolved oxygen

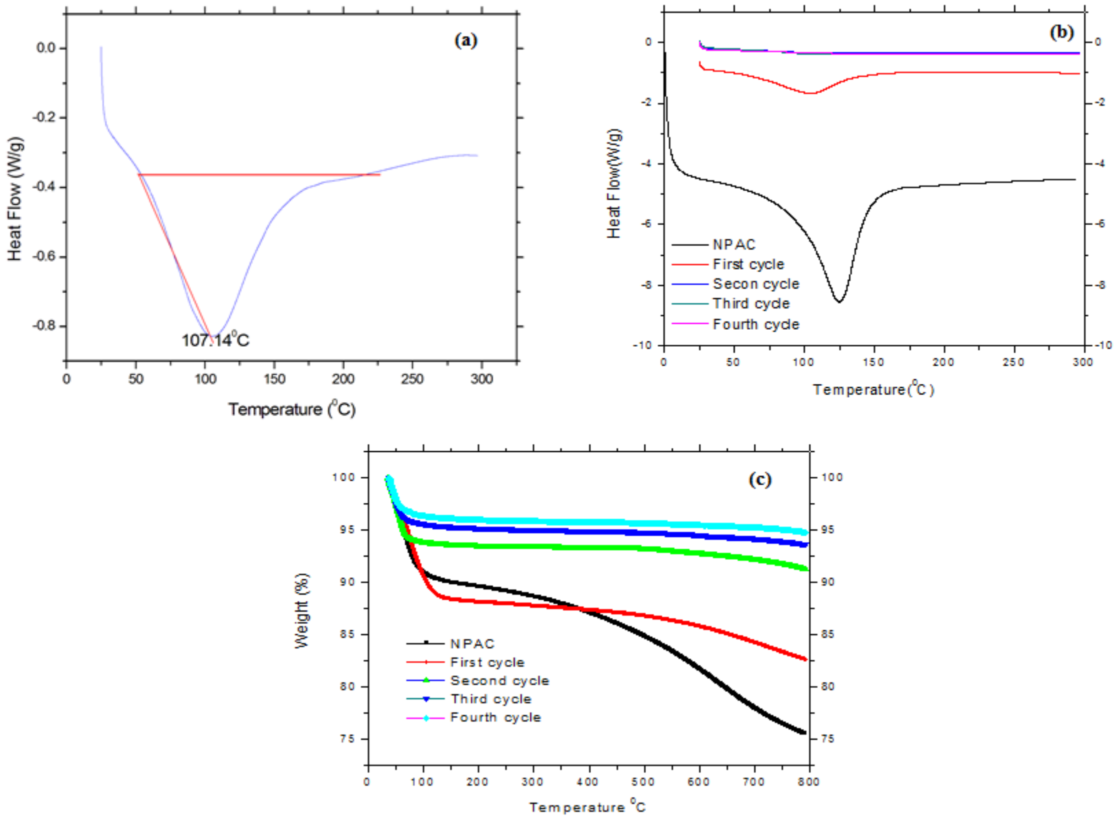

Figure S2. DSC spectrum of NPAC (a), the thermal stability of NAPC for four cycles as shown in Fig.S2b and Fig.S2c

Fig.S2a shows that maximum heat absorption at 107.14^{0}C, owing to the presence of moisture content in NPAC. The characteristic peaks in DSC spectra recorded for the recycled NPAC samples. The heat absorption was decreased and almost nil in fourth cycle. Fig.S2c shows that the loss of mass in NPAC was 24.48 % owing to elimination of moisture. The same catalyst was recycled in the subsequent experiments. TGA analyses showed that the loss of mass were 17.33%, 9.03%, 6.31% and 5.16% in first, second, third and fourth cycles respectively. It is, thus, concluded that NPAC was more stable even after 4 cycles. Fig.S2 (c) Thermo gravimetric analysis (TGA) demonstrates that with increasing temperature of preparation, the thermal stability increases and the resultant materials become similar to activated carbons[1-3].

TableS1

Thermodynamic constants for generation of hydroxyl radical by NPAC and dissolved O_2

S.No	ΔG(kJ/mol)	ΔH(kJ/mol)	ΔS(J/molK)
1	-1.36		
2	-2.58	17.73	61.01
3	-3.80		
4	-5.02		

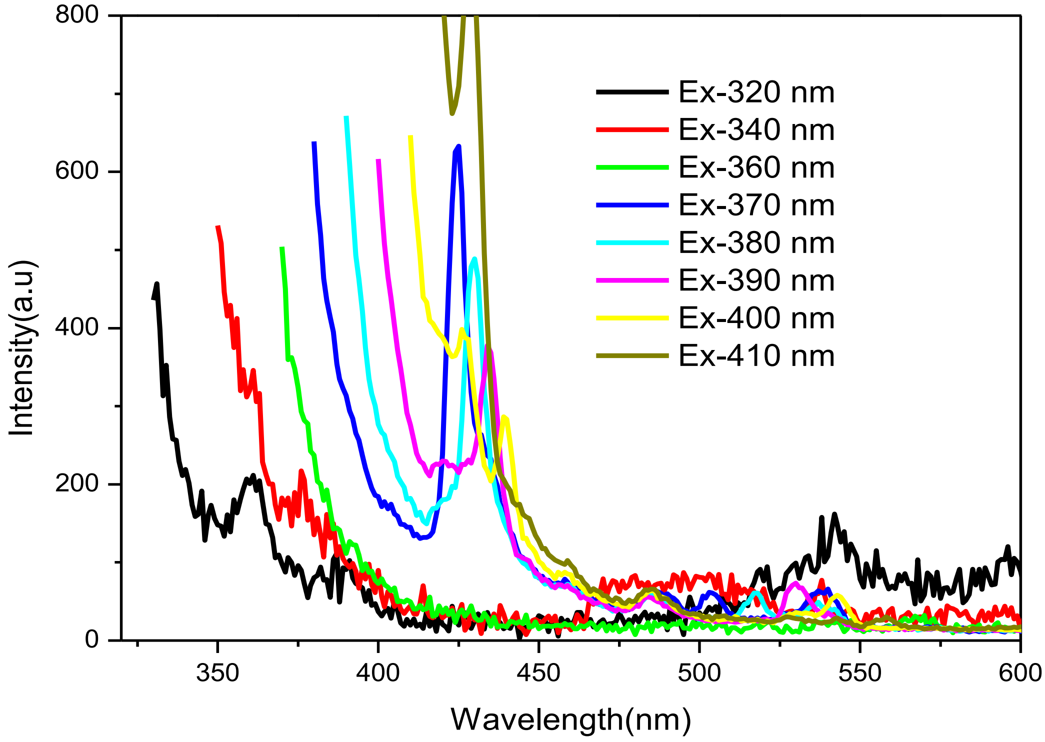

Figure S3. PL solid state emission spectra (recorded for progressively longer wavelengths from 320 to 410 nm) of NPAC

The emission spectrum of NPAC is attributed to carboxylate groups that exist on the particle surface was the origin for PL spectrum (Fig. S3). Hydrothermal and phosphoric acid activation method produced some carbon & oxygen containing radicals, and oxygen-containing groups on the surface of the starting material ($NPAC_{800}$). One factor leading to tuneable performance was due to the presence of different particle size, as observed in semiconductor nanocrystals. Another factor was due to the different oxygen-containing groups. The presence of surface energy centres, which become emissive upon surface passivation in PL , assumes importance from fundamental and an application viewpoints. PL is considered to be one of the most fascinating features of C-dots and thus, the PL spectrum recorded at longer wavelength, 320-410 nm, suggest the presence of C-dots in NPAC.

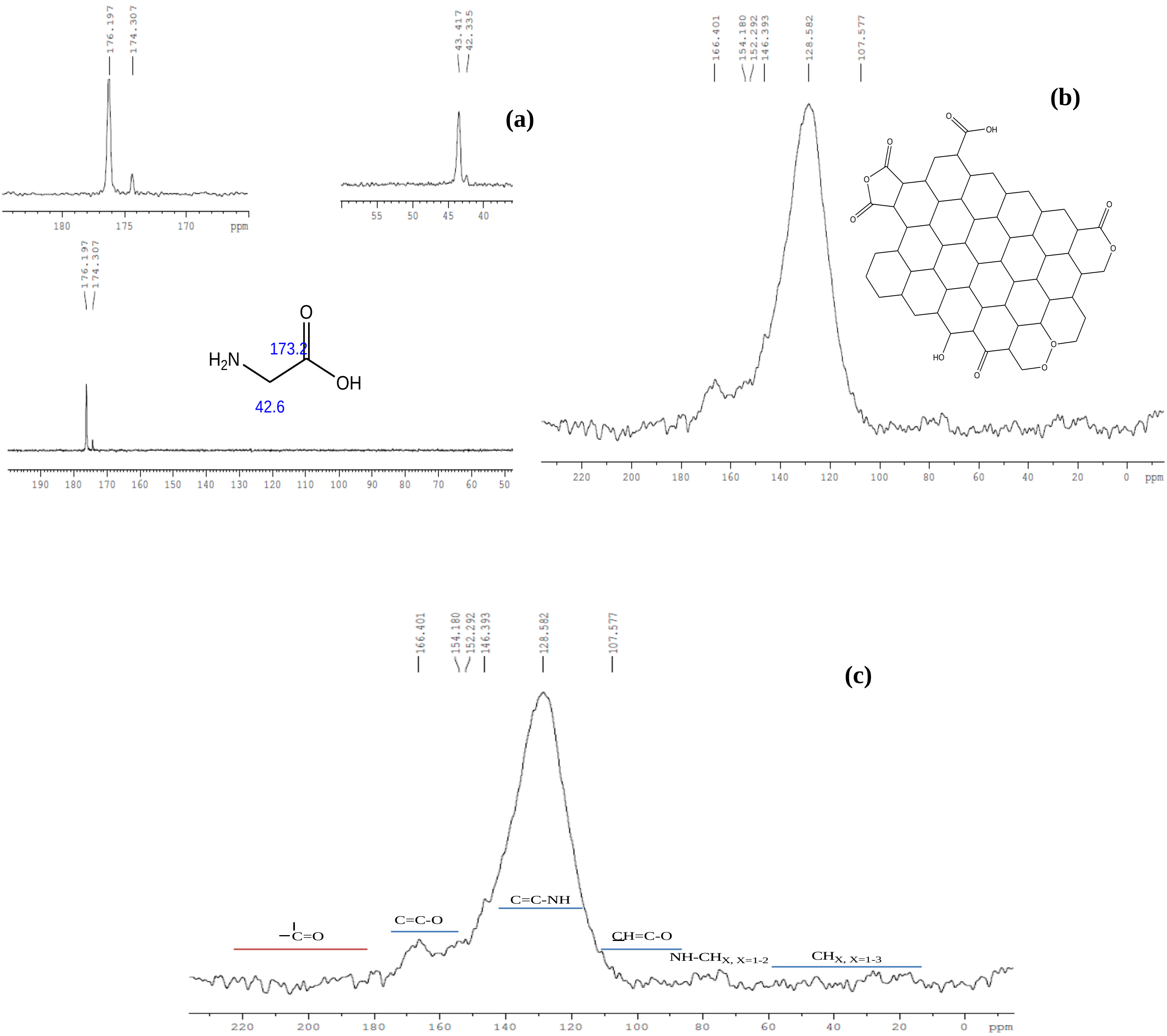

Figure S4. Solid state ^{13}C-NMR spectra of standard Glycine (a) and NPAC (b,c)

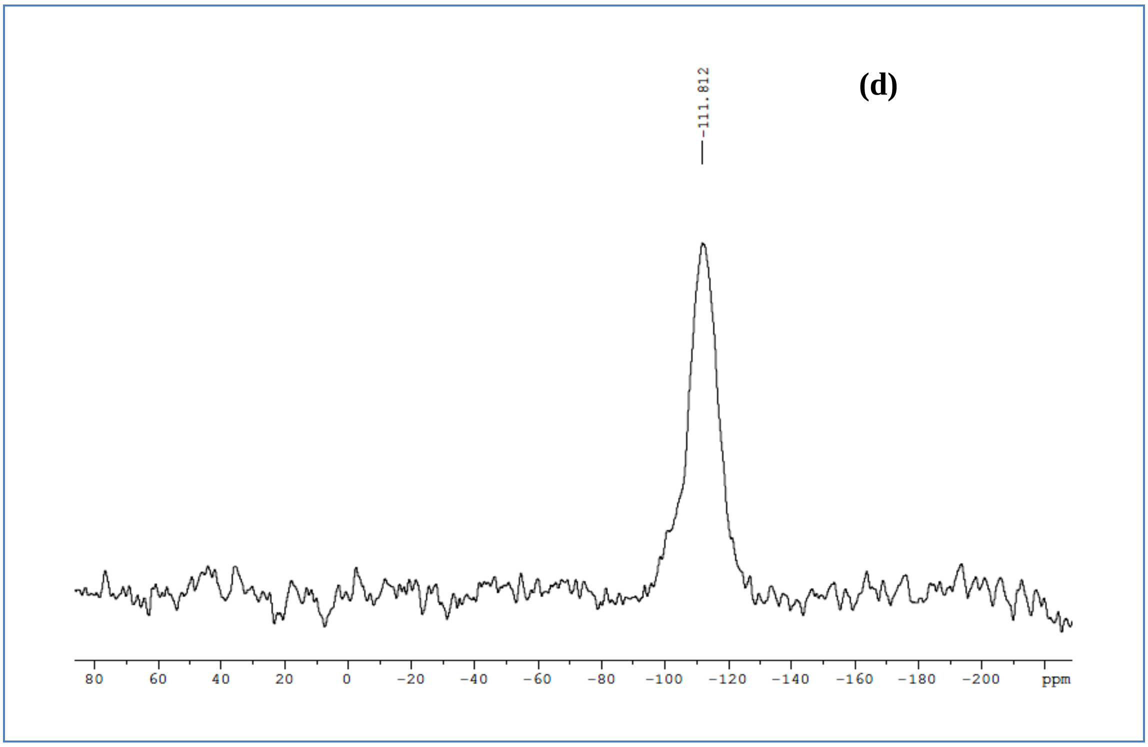

Figure S4-d. **^{29}Si-solid state NMR spectrum of NPAC**

Figure S4-d. Shows the ^{29}Si-NMR spectrum of NPAC, consisting of a broad line with maximum intensity at δ -111 ppm. The magnitude of chemical shift corresponds to silicon component. Furthermore, the asymmetric shoulder of this NMR line, spacing values from δ-200 to -80ppm, NMR signals indicate the highly distorted status of the silica particles in the NPAC.

References

(1)V. Budarin, J. H. Clark, Jeffrey J. E. Hardy, R. Luque, K. Milkowski, Stewart J. Tavener, Ashley J. Wilson, Starbons: New starch-derived mesoporous carbonaceous materials with tunable Properties, *Angew. Chem.*, 2006, 118, 3866 –3870

(2) W. Chaikittisilp, K. Ariga, Y. Yamauchi, A new family of carbon materials: synthesis of MOF derived nanoporous carbons and their promising applications, *J. Mater. Chem. A*, 2013, 1, 14–19

(3) W. Chaikittisilp,M. Hu, H. Wang,ab Hou-Sheng Huang, T. Fujita, Kevin C.-W. Wu, Lin-Chi Chen, Y.Yamauchi, K. Ariga, Nanoporous carbons through direct carbonization of a zeolitic imidazolate framework for supercapacitor electrodes, *Chem. Commun.*, 2012,48, 7259–7261.