Electrochemical Performance of a Novel Ionic Liquid Derived Nano Fibrillated Mesoporous Carbon

Babak Karimi*,[a] Hesam Behzadnia,[a] Mohammad Rafiee*,[a] and Hojatollah Vali[b]

[a] Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS),
P.O.Box 45195-1159, Gava Zang, Zanjan, Iran

[b] Anatomy and Cell Biology and Facility for Electron Microscopy Research, McGill
University, 3450 University St., Montreal, Quebec, H3A 2A7 Canada

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Experimental Procedure:

1.1. General experimental details. 1-idooctane, pyridine, catechol derivatives, Sodium hexafluorophosphate, 2-bromoethylbenzene were obtained from Merck and/or Fluka. The ionic liquid 1-octylpyridinum hexafluorophosphate (OPFP) was synthesized as described in the literatures [J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. A. Broker, R. D. Rogers, *Green Chem.* **2001**, *3*, 156]. Pluronic P123 ($EO_{20}PO_{70}EO_{20}$ (EO= ethylene Oxide, PO= Propylene Oxide), M_{av}= 5800) was purchased from Aldrich. 1-Methylimidazole, 2-phenylethyl bromide, Tetraethyl orthosilicate (TEOS), Sulfuric acid (95-98%), Hydrochloric acid (37%) and solvents were obtained from Merck Company and used without purification.

(3-Mercaptopropyl)triethoxysilane and anhydrous Potassium carbonate were purchased from Fluka. The 1,3-Dialkylimidazolium bromide was prepared according to standard methods and their purities were established before utilization by ^{13}C NMR and ^{1}H NMR. Briefly, a solution of absolute toluene (50 mL), freshly distilled 1-methylimidazole (73.1 mmol) and 2-bromo-1-phenylethane (80.3 mmol) was refluxed for 24h under an argon atmosphere. The resulting two phase reaction mixture was then allowed to cool at room temperature. Afterward, the separated ionic liquid (IL) layer was washed with absolute toluene and dry Et_2O and dried under vacuum. The spectral data for the resulted 1-Methyl-3-phenethyl-1*H*-imidazolium bromide is as follows: ^{1}H-NMR (400 MHz, DMSO-d_6): δ_H = 3.16 (t, 2H, J= 7.6 Hz), 3.85 (s, 3H), 4.48 (t, 2H, J= 7.6 Hz), 7.33-7.24 (m, 5H), 7.49-7.40 (1H), 7.84-7.83 (1H), 9.26 (s, 1H); ^{13}C-NMR (100 MHz, DMSO-d_6): δ_C = 137.4, 137.0, 129.2, 129.0, 127.3, 123.9, 122.8, 50.2, 36.2, 35.8.

The anion-exchange reaction was carried out in dry methylene chloride containing 1 mmol of 1,3-Dialkylimidazolium bromide and 1 mmol of H_2SO_4. The solution was refluxed for 48 h until any hydrogen chloride by-product removed. After evaporation of the solvent under vacuum, the 1-Methyl-3-phenethyl-1*H*-imidazolium hydrogen Sulfate (MPIHS) **1** was isolated in good yield. The spectral data for 1-Methyl-3-phenethyl-1*H*-imidazolium hydrogen Sulfate (MPIHS) **1** is as follows: ^{1}H-NMR (400 MHz, DMSO-d_6): δ_H = 3.14 (t, 2H, *J*= 7.6 Hz), 3.82 (s, 3H), 4.44 (t, 2H, *J*= 7.6 Hz), 7.30-7.23 (m, 5H), 7.34 (brs, 3H), 7.70 (s, 1H), 7.79 (s, 1H), 9.20 (s, 1H); ^{13}C-NMR (100 MHz, DMSO-d_6): δ_C = 137.3, 137.1, 129.3, 128.8, 127.3, 123.8, 122.9, 50.1, 36.1, 35.8.

The carbonization process was performed in a Nabertherm furnace (L 3/11/P330) under an inert atmosphere of Ar. The pore structures of the prepared materials were observed by transmission electron microscopy (Philips CM 200FEG microscope, TEM) and were verified further by the nitrogen sorption isotherm (Belsorp, BELMAX, Japan). The Palladium content of the catalysts was determined using atomic absorption spectrometer (Varian). The GC analyses were performed on Varian CP-3800 using a flame ionization detector (FID). NMR spectra were recorded using Bruker (^{1}H frequency: 400 MHz, ^{13}C frequency: 100 MHz).

1.2. Preparation and analysis of SBA-15: The first set of samples was derived from the SBA-15. Briefly, 0.017 mol of pluronic P123 ($EO_{20}PO_{70}EO_{20}$ (EO=ethylene oxide, PO= propylene oxide), M_{Av}=5800, Aldrich) was dissolved in 193 mol of H_2O and 5.9 mol of HCl concentrated at 35 °C. Consequently, 1 mol of tetraethyl orthosilicate (TEOS) was added to the solution. The mixture was stirred vigorously at 35 °C for 20 h followed by an aging step at 80 °C for 24 h. The solid products were filtered off and then washed with ethanol. After drying at room-temperature, SBA-15 was obtained by subsequent removal of the surfactant by extraction with ethanol. [(a) D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka, G. D. Stucky, *Science* **1998**, *279*, 548; (b) D. Zhao, Q. Huo, J. Feng, B. F. Chmelka, G. D. Stucky, *J. Am. Chem. Soc.* **1998**, *120*, 6024). TEM images, adsorption-desorption isotherms and the corresponding curves of the resulting SBA-15 are shown in underneath Figures.

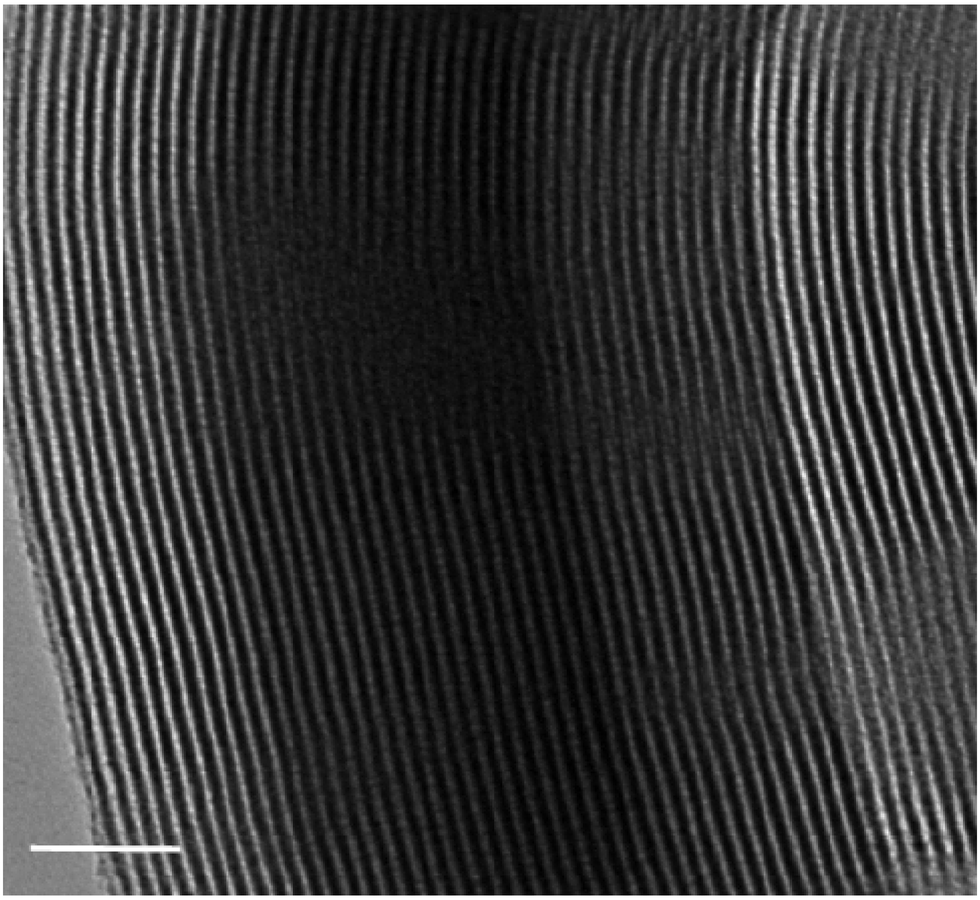


Figure S1. TEM image of SBA-15, sclae bar 60 nm

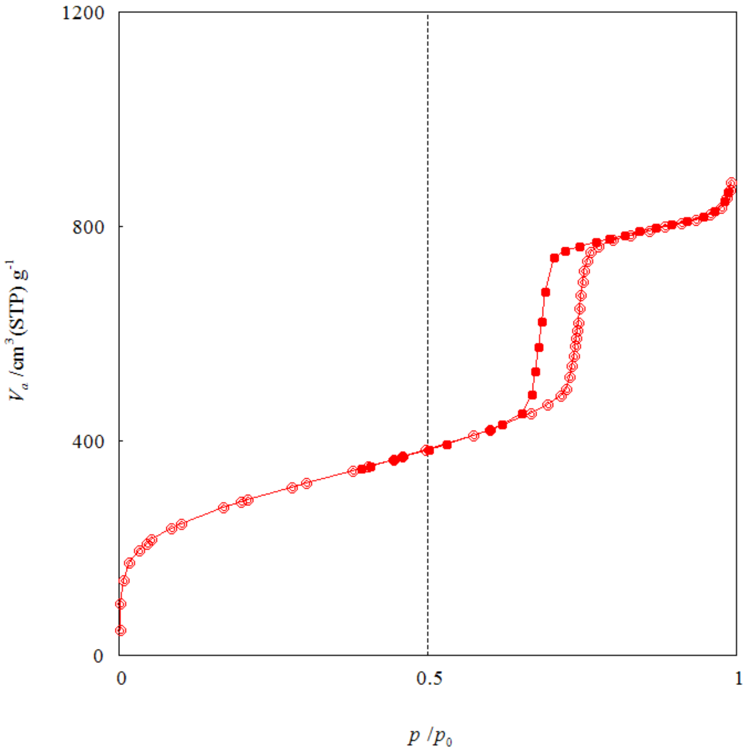


Figure S2. Nitrogen Adsorption-Desorption isotherm for SBA-15

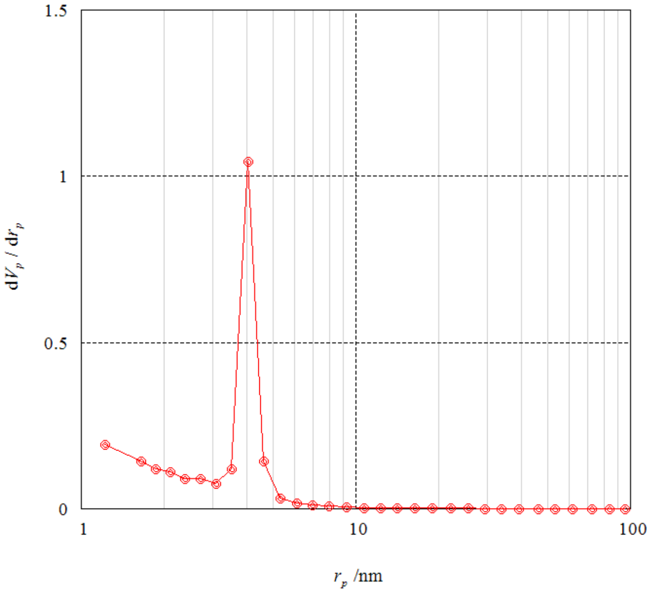
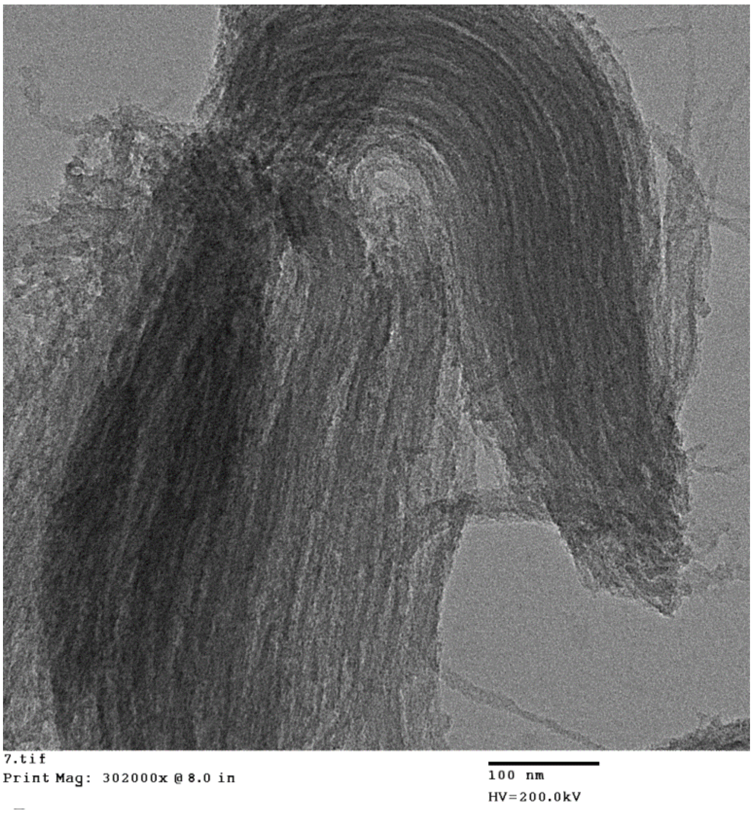
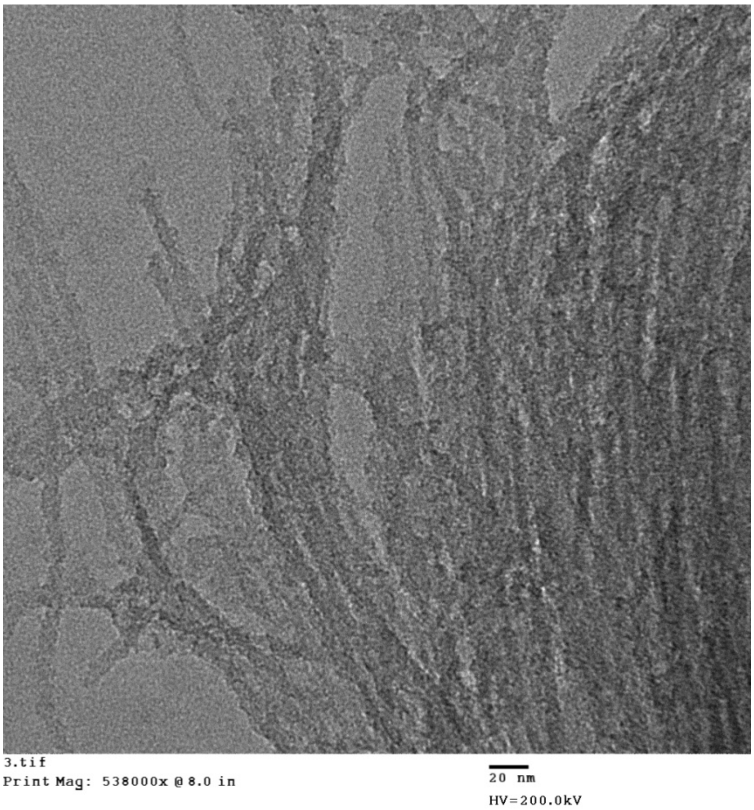


Figure S3. BJH average pore size distribution diagram for SBA-15

1.3. Preparation and analysis of IFMC (Ionic Liquid derived Fibrillated Mesoporous Carbon: To synthesize **IFMC**, at first a dry acetonitrile solution of IL (1 ml of 1-Methyl-3-phenethyl-1*H*-imidazolium hydrogen Sulfate (MPIHS) **1** in 25 ml of acetonitrile) was added drop wise to a suspension of SBA-15 in acetonitrile. After 24h of stirring at room temperature, the solvent was removed under reduced pressure. The resulted powdery material was impregnated with aqueous solution of sulfuric acid (4 g H_2O, 0.14 g H_2SO_4) and placed at 100 °C in a vacuum drying oven for 6 h. Consequently the oven temperature was increased to 160 °C and maintained for 6 h at that temperature to afford a dark brown powder. 0.4 ml of MPIHS **1** was incorporated again into mesoporous silica hosts by same procedure. The SBA-15/**1** composite was then kept in an argon flow at 900 °C for 3 h to carbonize the IL. In order to remove the silica template, the generated black powder was stirred in a solution of 2M sodium hydroxide at 50 °C for 24 h. The nanoporous carbon was afforded after filtration, washed several times with copious deionized water and ethanol, and vacuum dried. TEM images, N_2 adsorption-desorption isotherms and the corresponding curves of the resulting **IFMC** are shown in underneath Figures.





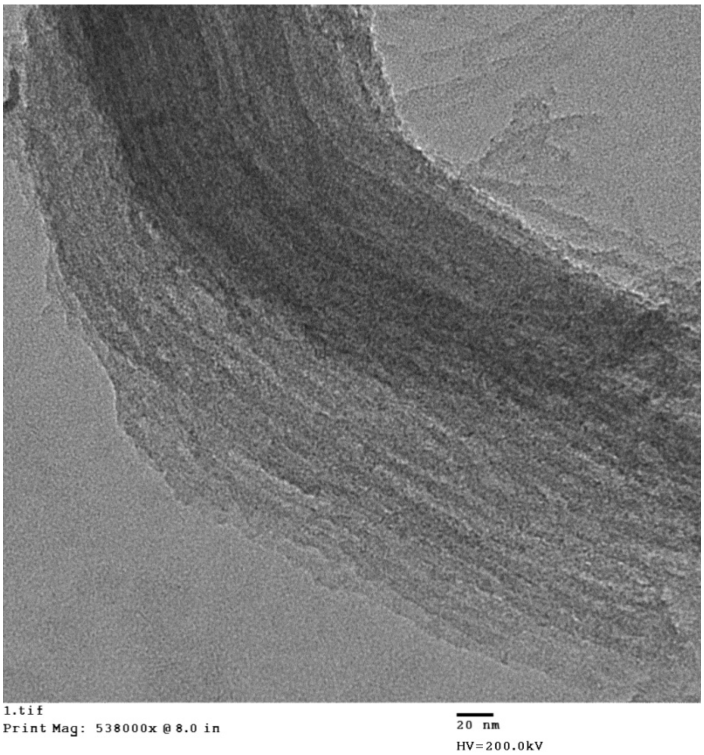


Figure S4. TEM images of IFMC

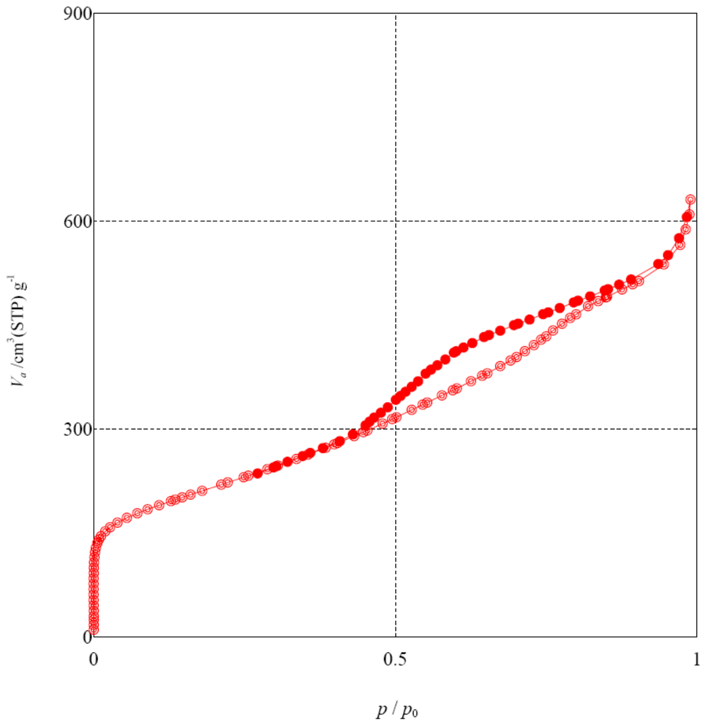


Figure S5. Nitrogen Adsorption-Desorption isotherm for IFMC

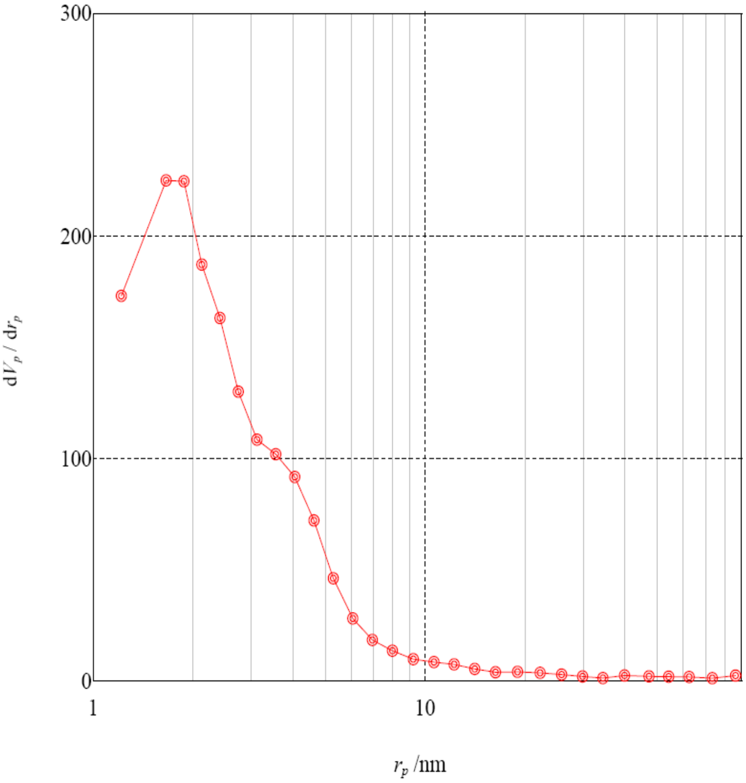


Figure S6-1. BJH average pore diameter diagram of IFMC from adsorption branch

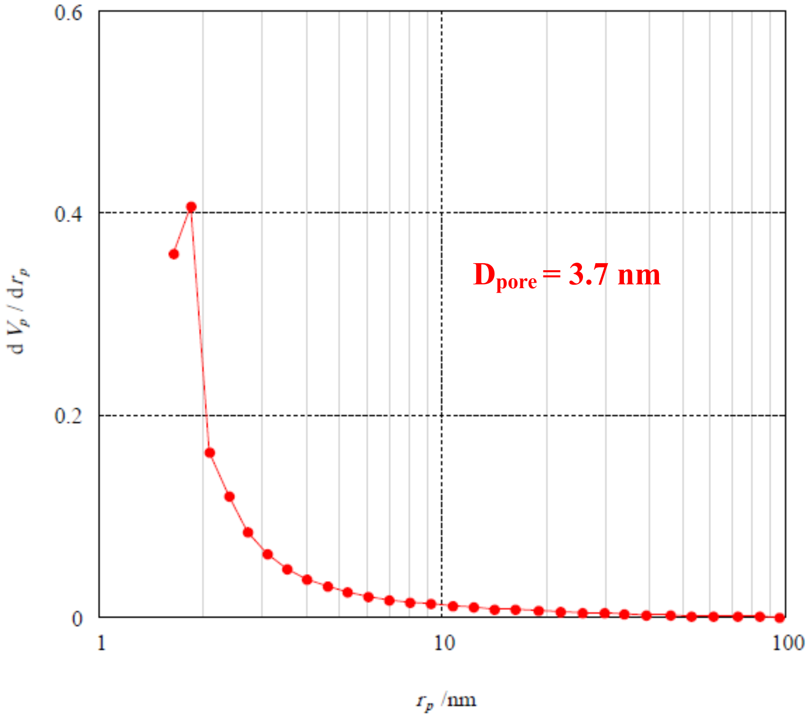
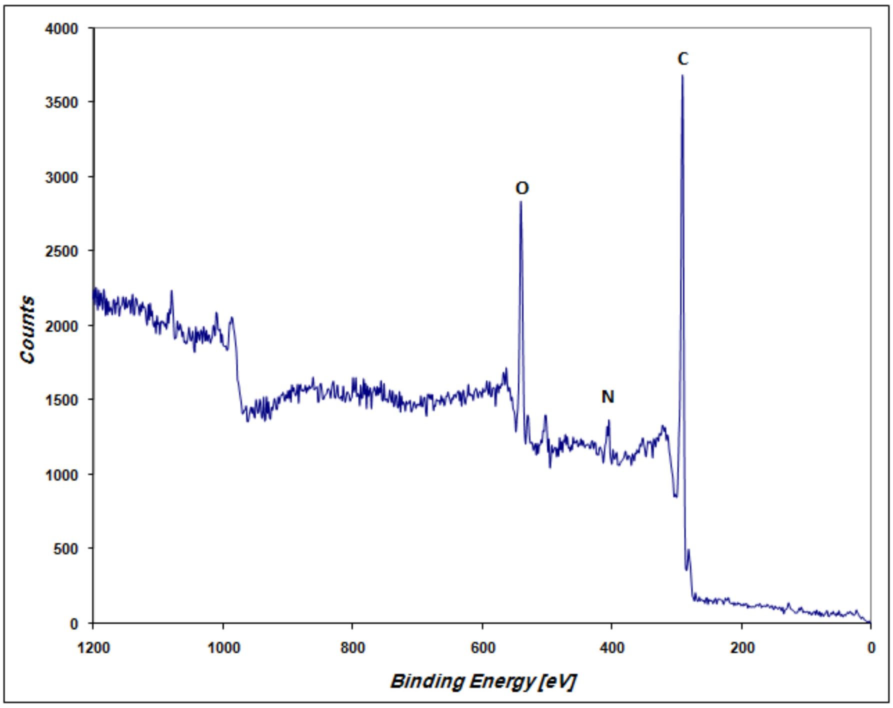
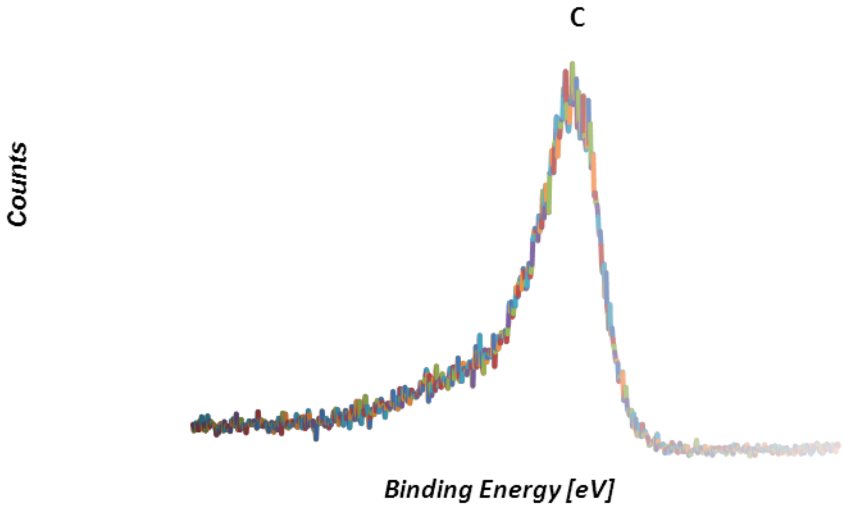


Figure S6-2. BJH average pore diameter diagram of IFMC from desorption branch





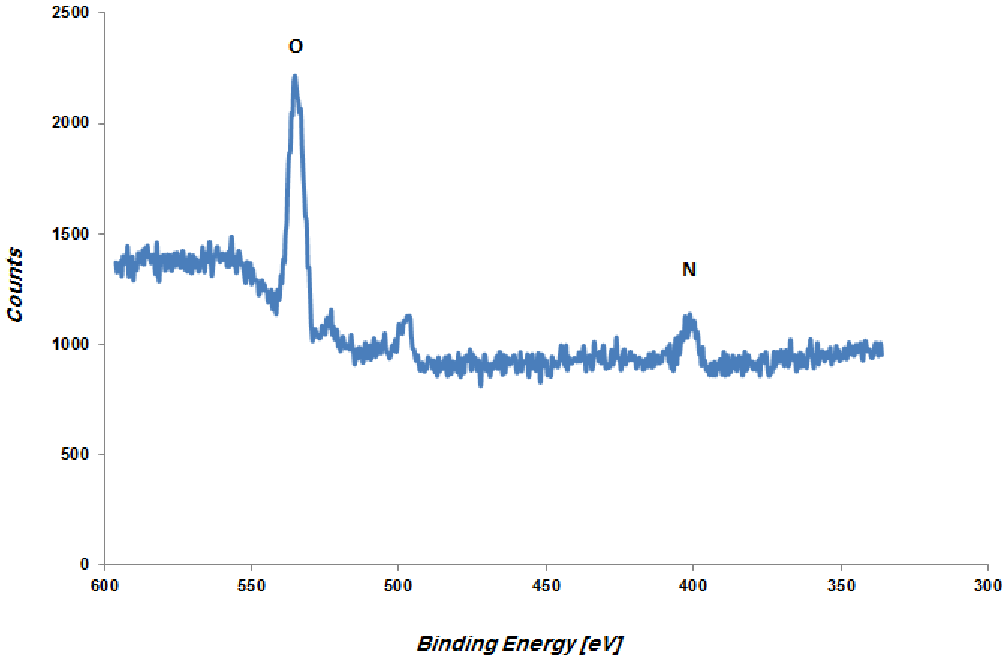


Figure S7. The XPS spectrums of the IFMC

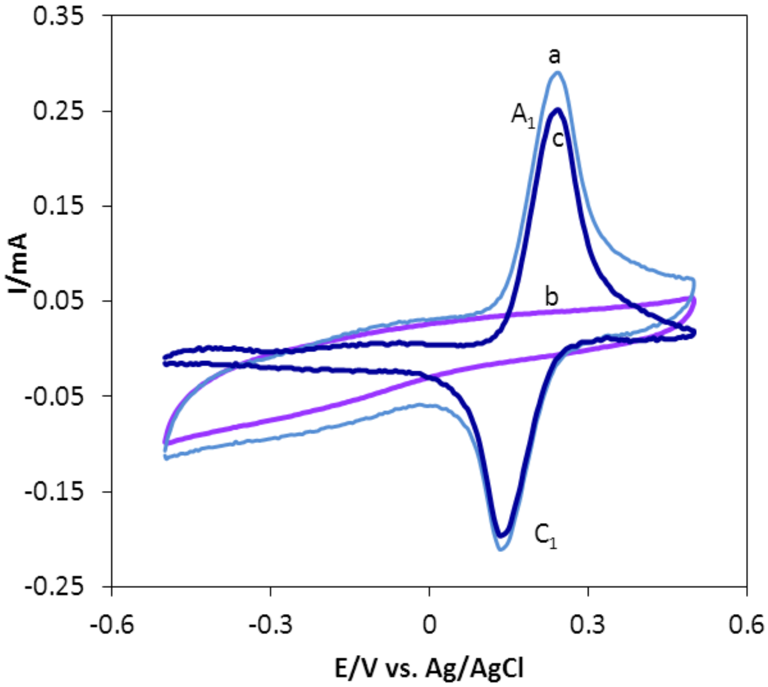


Figure S8. a) Regular and c) background corrected cyclic voltammograms of 4-*tert*-butylcatechol (1.0 mM) and b) background current at IFMC/OPFP modified electrode, scan rate 80 mVs^{-1}.

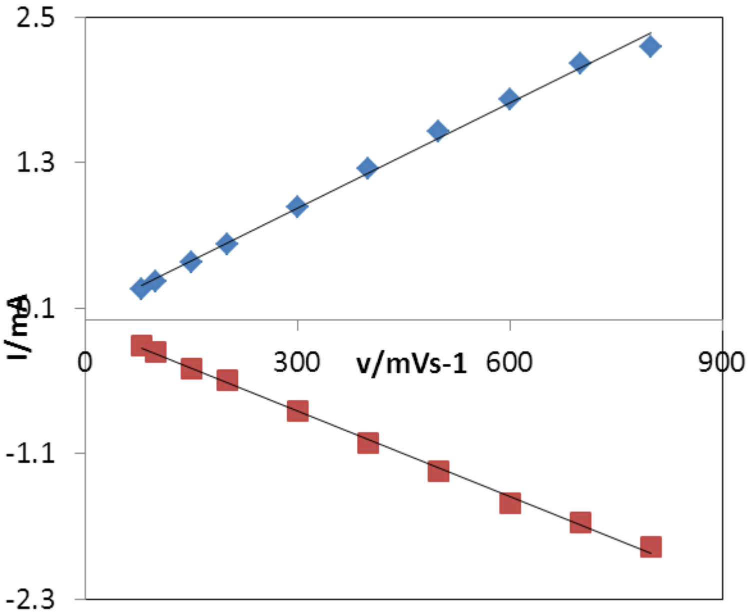


Figure S9. Inset variation of anodic and cathodic peak currents versus scan rate.

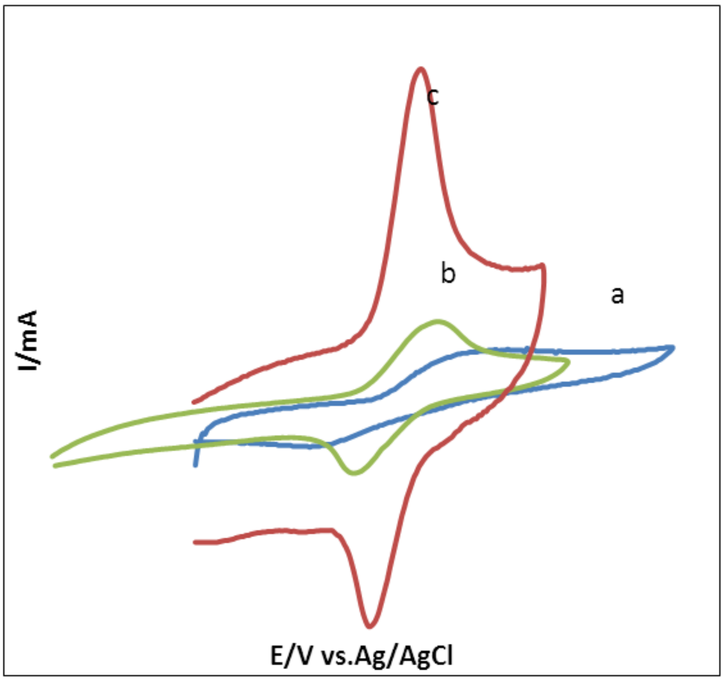


Figure S10. Cyclic voltammograms of catechol a) on graphite electrode and b) graphite powder/OPFP (used as commercially available materials of paste electrodes) modified electrode and c) IFMC/OPFP modified electrode; after electrode heating, pH=7 .

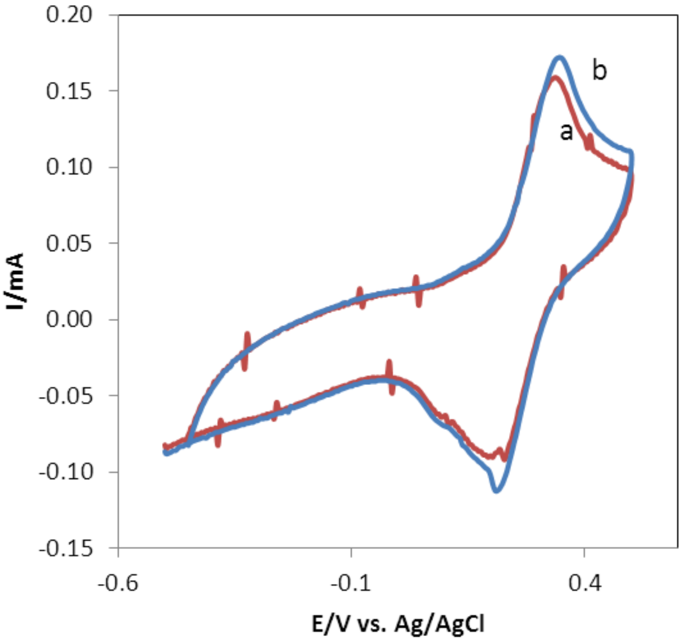


Figure S11. Cyclic voltammograms of IFMC modified electrode in aqueous solution containing 1.0 mM 3,4-dihydroxybenzoic acid at recording times a) 0.5 and b) 20 minutes, pH 7.0.

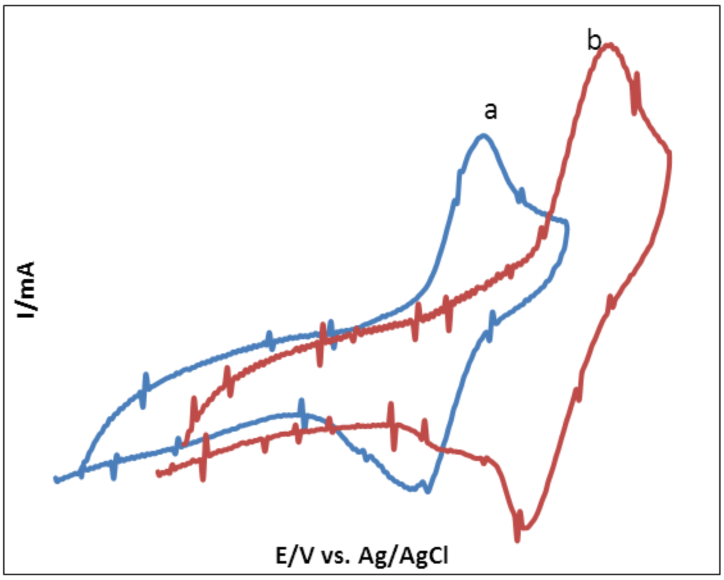


Figure S12. Cyclic voltammograms of IFMC modified electrode in aqueous solution containing 1.0 mM 3,4-dihydroxybenzoic acid at a) pH 7.0 and b) pH 3.0.

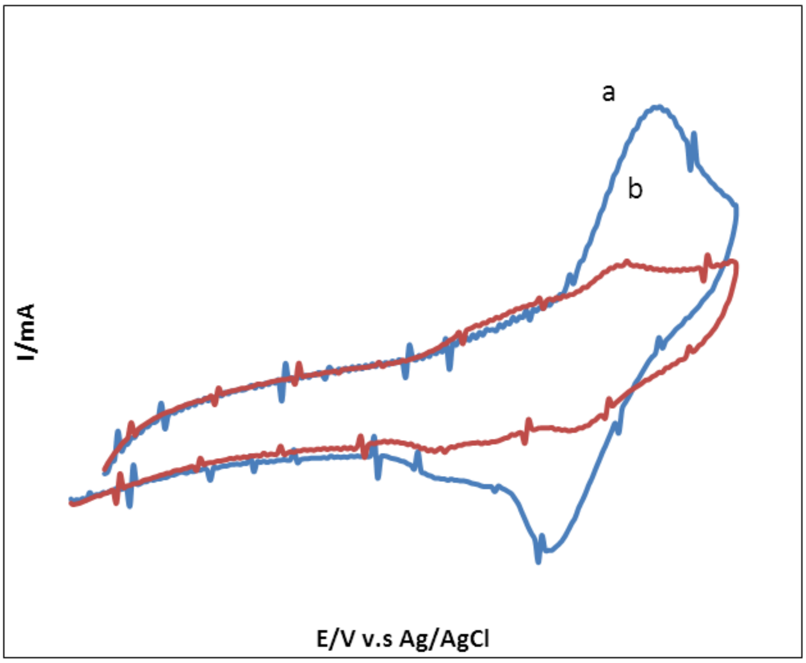


Figure S13. Cyclic voltammograms of IFMC modified electrode in aqueous solution containing 1.0 mM 3,4-dihydroxybenzoic acid at pH 3, b) Cyclic voltammograms of 3,4-dihydroxybenzoic acid adsorbed electrode in aqueous buffer solution

Table 1S. Some examples of anodic to cathodic peak separation for catechol and 4-methylcatechol on various carbon based electrode.

Electrode	ΔE_p for catechol	Peak current density ($\mu A/cm^2$)
Pyridine treated glassy carbon electrode	53 mV[a]	---
Glassy carbon electrode	85-110	380
carbon nanotube modified electrodes	100-140[b,c]	400
Carbon paste electrode	287[d]	223
Graphite /Ionic liquid composite electrode	135[d]	373
IFMC modified electrode	90	2830

a) S.H. DuVall, R.L. McCreery *Anal. Chem.***1999**, *71,* 4594.

b) Z. Xu, X. Chen, X. Qu, S. Dong *Electroanalysis,***2004**,*16*, 684.

c) Y. Umasankar, A. P. Periasamy, S. M. Chen, *Anal. Biochem.***2011**,*411*, 71.

d) N. Maleki, A. Safavi, F. Tajabadi *Anal. Chem.***2006**, *78*, 3820.