Electronic Supplementary Material (ESI) for RSC Advances.

Unique Nanotubes from Polynorbornene Derived Graphene Sheets

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Supporting Information

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2. Experimental:

2.1. Materials:

Exo-5-Norbornene carboxylic acid ($C_8H_{10}O_2$), Dimethyl sulfoxide [DMSO-d_6, $(CH_3)_2SO$] were supplied by Aldrich. Dichloro methane (DCM), Ethyl acetate (EtOAc), anhydrous sodium sulphate (Na_2SO_4), Trifluoro acetic acid (F_3CCOOH), Vinyl ethyl ether ($C_2H_5OCH{=}CH2$), diethyl ether ($C_4H_{10}O$), methanol (CH_3OH), Acetone $(CH_3)_2CO$ were supplied by Merk. Boc anhydride $(CH_3COO)_2O$ $(BOC)_2O$, dicyclohexyl carbodiimde (DCC), Dimethyl aminopyridine (DMAP), ethanol amine ($OHCH_2CH_2NH_2$), Triethyl amine (Et_3N) were supplied by spectrochem, Tetrahydro furan (THF) was supplied by Rankem. Graphene carboxylic acid (GCOOH) was supplied by SRL having 0.8- 1.2 nm, APS: 1-5 μm. Iron nanoparticle (Fe_3O_4) was supplied by Aldrich having particle size < 50 nm. Dichloromethane (DCM) was distilled over calcium hydride and used for reactions. Other reagents were analytical grade and were used as received.

2.2. Methods:

Nuclear Magnetic Resonance (NMR) spectroscopy. NMR spectroscopy was carried out on a Bruker 500 MHz and Jeol spectrometer using DMSO-d_6 as a solvent. NMR spectra of solutions in DMSO-d_6 were calibrated to tetramethylsilane as internal standard (δH 0.00).

Gel Permeation Chromatography (GPC). Molecular weights and PDIs were measured by Waters gel permeation chromatography in THF relative to PMMA and PS standards on systems equipped with Waters Model 515 HPLC pump and Waters Model 2414 Refractive Index Detector at 35 °C with a flow rate of 1 mL min^{-1}. HRMS analyses were performed with Q-TOF YA263 high resolution (Waters Corporation) instruments by +ve mode electrospray ionization.

Mass spectral analysis (MS). Maas spectra studies were done on Bruker ultrafleXtreme MALDI-TOF/TOF using LASER (MALDI) in RP_100-1500.par and using Flex contol 3.4 & Flex analysis 3.4 software.

Infrared Spectroscopy (IR). IR spectra were obtained on IR Perkin-Elmer spectrometer at a nominal resolution of 2 cm^{-1}.

Powdered X-ray Diffraction (PXRD). The crystallographic structures of pristine graphite and Graphite oxide were determined by XRD. The XRD study was done with (Rigaku, Cu-Kα target, scan rate 3° /min).

Raman Spectroscopy. Raman spectra were recorded in the range 700-2100 cm^{-1} in a Horiba LabRAM Raman Spectrometer using a He-Ne laser beam having a wavelength of 488 nm, 0.3 cm^{-1} resolution and 1.5 m of optical path length with a CCD detector.

Dynamic Light Scattering (DLS). Particle size was measured by dynamic light scattering (DLS), using a Malvern Zetasizer Nano equipped with a 4.0 mW He-Ne laser operating at λ = 633 nm. All samples were measured in aqueous as well as methanol at room temperature and a scattering angle of 173°.

Field Emission Scanning Electron Microscopy (FESEM). Field Emission SEM was performed on a Zeiss microscope; SUPRA 55VP-Field Emission Scanning Electron Microscope. High performance variable pressure FE-SEM with patented GEMINI column technology. Schottky type field emitter system, single condenser with crossover-free beam path. Resolution: 1.0 nm at 15 kV; 1.6 nm at 1 kV high vacuum mode. 2.0 nm at 30 kV at variable pressure mode.

High Resolution Transmission Electron Microscopy (HRTEM). High resolution transmission electron microscopy (HRTEM) was performed on a JEOL 200 CX microscope.

TEM grids were purchased from Ted Pella, Inc. and consisted of 3-4 nm amorphous carbon film supported on a 400-mesh copper grid.

2.3. Synthetic Procedure:

Synthesis of Boc (Di-tert-butyl-dicarbonate) protected Ethanol amine (EAM-B): 1.97 ml of ethanol amine (32.74 mmole, 1eq) was taken in a round bottom flask and 10 ml of water was added into it with constant stirring for 10-15 minutes keeping it on an ice bath. After that, 2.02 g (36.014 mmole, 1.1 eq) potassium hydroxide (KOH) was added into it. In a dropping funnel, 7.8 ml Boc anhydride [$(Boc)_2O$] {36.014 mmole, 1.1 eq} was taken with 25 ml of tetrahydrofuran (THF) and was added drop wise into the aforesaid mixture kept on an ice bath for 1hr. After removal of ice bath, the total mixture was stirred for another 2 hour (reaction scheme was represented in **Scheme 1**) and was dissolved in DCM. After that the solution was washed with water and organic part was collected. Then the organic part was washed with anhydrous Na_2SO_4 to remove the excess water. The product was collected after evaporation of DCM. NMR (^1H and ^{13}C spectroscopy) was done to confirm the product formation (**Figure S1 and S2** respectively). ^1H NMR (DMSO-d_6, 500MHz): δ 6.6 (t, 1H), 4.6 (t, 1H), 3.3 (q, 2H), 2.9 (q, 2H), 1.4 (s, 9H); ^{13}C NMR (DMSO-d_6, 500MHz): δ 155.6, 77.5, 60.1, 42.7, and 28.3, IR (KBR, cm^{-1}): 3368, 2976, 2936, 2881, 1746, 1691, 1527, 1454, 1395, 1365, 1276, 1250, 1173, 1071, MS (ESI) calculated for $C_7H_{15}NO_3$ [$M + Na^+$], 184.1989; observed, 184.0926.

Synthesis of boc protected ethanolamine monomer1 (BOCM1): 1.5 g (10.86 mmole, 1 eq) 5-exo norbornene carboxylic acid was dissolved in 5 ml of dry DCM in an inert atmosphere and was stirred for 15 minutes. 3.36 g (16.29 mmole, 1.5 eq) of DCC was added to the reaction mixture and stirred for another 15 minutes. 1.99 g DMAP (16.29 mmole, 1.5 eq) was dissolved in 2 ml of DCM in another round bottom flask. To this, 1.57 g of EAM-B (9.78

mmole, 0.9 eq) was mixed to the solution and was stirred for another 15 minutes. Then this mixture was added to the mixture of norbornene exo carboxylic acid and DCC and was stirred for 24 hours under nitrogen atmosphere at room temperature (**Scheme 1)**. The side product, Dicyclohexylurea (DCU) was removed by filtration and the filtrate was washed by 2 N HCl and saturated solution of sodium bicarbonate to remove excess DMAP and norbornene exo carboxylic acid respectively. Then, the organic layer was collected in a flask containing Na_2SO_4 to remove the excess water. Then the excess DCM was evaporated and the product was dried under vacuum for overnight. The formation of the monomer was confirmed by ^{1}H NMR and ^{13}C NMR **(Figure S3 and S4** respectively). (^{1}H NMR (DMSO-d_6, 500MHz): δ 6.9 (t, 1H), 6.2 (q, 2H), 6.1 (q, 2H), 4.0 (t, 2H), 3.2 (q, 2H), 3.0 (t, 1H), 2.9 (t, 1H), 2.2 (q, 1H), 1.8 (q, 2H), 1.37 (s. 9H), 1.3 (t, 2H); (^{13}C NMR (DMSO-d_6): δ 175.4, 155.1, 138.3, 135.1, 77.8, 63.0, 46.0, 43.0, 41.0, 39.9 (overlapped with DMSO-d_6 peak), 39.7 (overlapped with DMSO-d_6 peak), 29.9 and 28.2, IR (KBR, cm^{-1}): 3381, 3141, 3068, 2976, 2933, 2874, 2856, 1716, 1692, 1654, 1522, 1449, 1397, 1371, 1333, 1273, 1252, 1166, 1047, MS (ESI) calculated for $C_{15}H_{23}NO_4$[M + Na^+ + $2H^+$], 306.3474; observed 306.2884.

Synthesis of Boc protected polymer1 (BOCP1): 1 g (0.1777 mmole) of monomer (BOCM1) was dissolved in dry DCM and then 29.6 mg (0.001777 mmole) of Grubbs' 2nd generation catalyst (G2) was added into it in a glove box (under Nitrogen atmosphere) and was stirred for 3 hrs (as shown in **Scheme 1)**. The formation of the polymer (**BOCP1**) was confirmed by the disappearance of the vinyl proton at δ 6.12 ppm as well as the appearance of a new peak at 5.5-5.0 ppm from ^{1}HNMR (**Figure S5)**. ^{1}H NMR (DMSO-$d_{6,}$ 500 MHz): δ 6.8 (br, 1H), 5.4 (br, 1H), 5.2 (br, 1H), 4.0-3.9 (br, 2H), 3.1(br, 1H), 3.0-2.9 (br, 2H), 2.6 (br, 1H), 2.8-1.6 (br, 3H), 1.36 (s, 9H), 1.1 (br, 2H), IR (KBr cm^{-1}): 3381, 2976, 2925, 2862, 1716, 1660, 1629, 1527, 1452, 1391, 1366, 1276, 1251, 1167, 1045. The comparison of the

^{1}HNMR spectrum of monomer (**BOCM1**) and that of the corresponding polymer (**BOCP1**) has been given in **Figure 1** and was confirmed by GPC analysis (**Figure 2**).

Synthesis of Polymer (P1) after deprotection of BOCP1: 1g (1 eq) **BOCP1** was taken in a single neck RB flask and 10 ml of dry DCM was added in to it under nitrogen atmosphere. 4.0 ml (10 eq) of TFA was added into it and was allowed to stir for 2 hours (**Scheme 1**). After that the product was washed with diethyl ether (three times) and was allowed to dry under vacuum. Formation of **P1,** after the successful deprotection, was confirmed by the absence of sharp peak at 1.36 ppm, which was the corresponding peak of Boc **(Figure 3)**. IR spectrum of **P1** displayed the significant bands at (KBr, cm^{-1}): 3394, 2926, 2853, 1729, 1522, 1456, 1367, 1289-1256, 1130, 1052.

Synthesis of Graphene Conjugated Polynorbornene (P1) nanocomposites (PNAGR): In 100 ml round bottom flask, 50 mg (1 eq) of **P1** and 5 ml of DMF were added and the solution was stirred for half an hour. To that 0.1 wt % of graphene carboxylic acid (**GCOOH**) in DMF was added to the reaction mixture by drop-wise fashion. Then 1eq of DCC was added and again the reaction mixture was stirred for another half an hour. Then to that solution, **GCOOH** solution was added drop wise and was again stirred for half an hour. Finally, to the whole reaction mixture, catalytic amount of Et_3N was added and was finally stirred for 48 hours. The final solution was washed thoroughly and repeatedly with MeOH to remove unreacted DCU. In this manner, 0.2 wt % and 0.5 wt % of **GCOOH** containing hybrid materials were also synthesized as shown in **Scheme 1**, and the hybrid material was termed as **PNAGR1**.

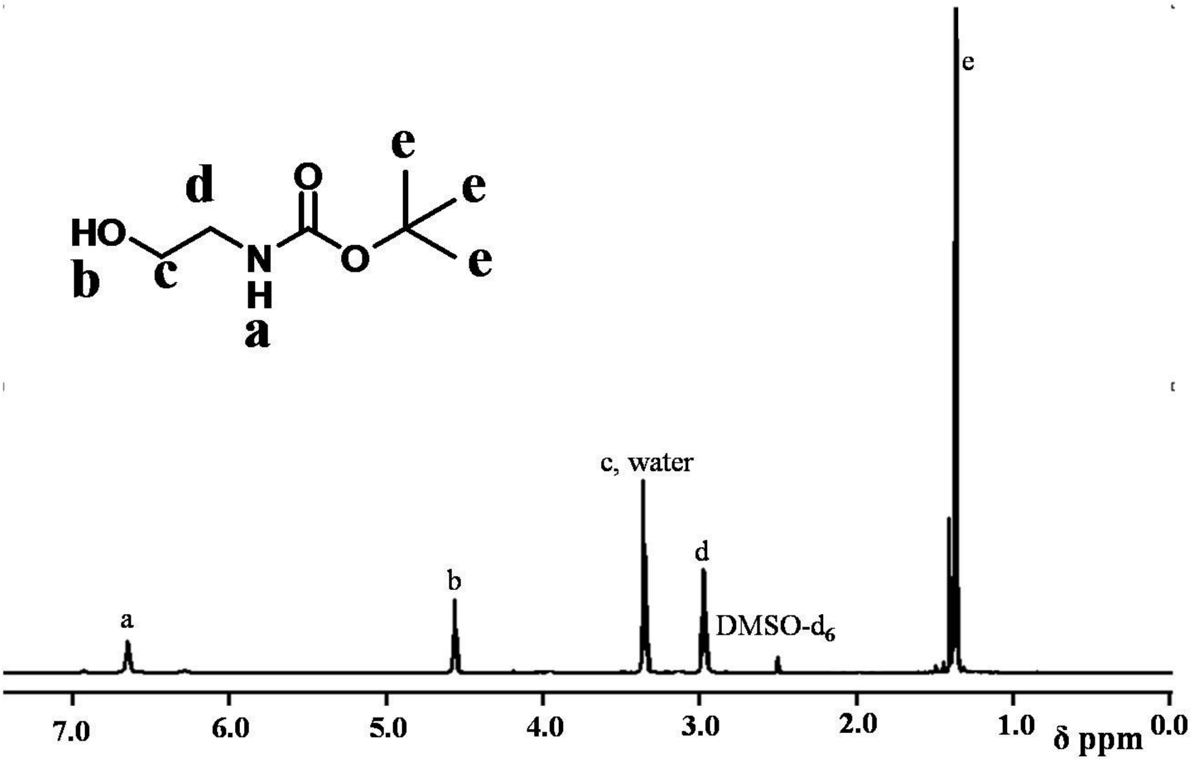


Figure S1: ^1H NMR spectrum of **EAM-B** in DMSO-d_6.

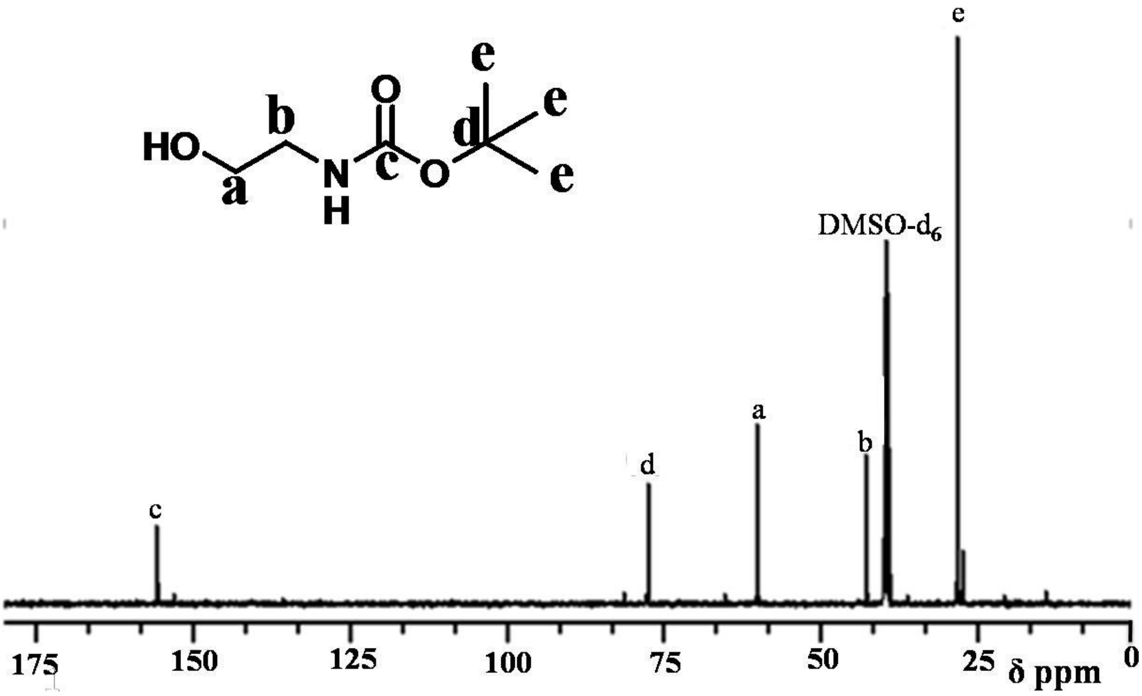


Figure S2: ^{13}C NMR spectrum of **EAM-B** in DMSO-d_6.

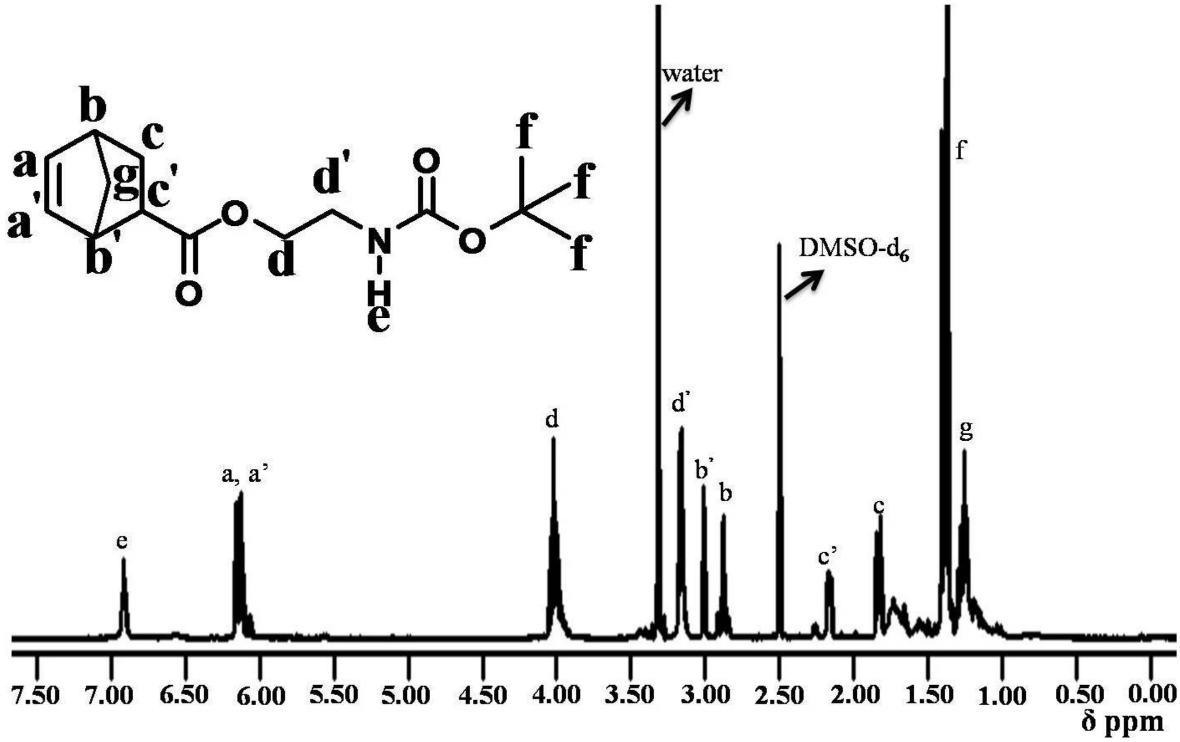


Figure S3: ^{1}H NMR spectrum of **BOCM1** in DMSO-d$_6$.

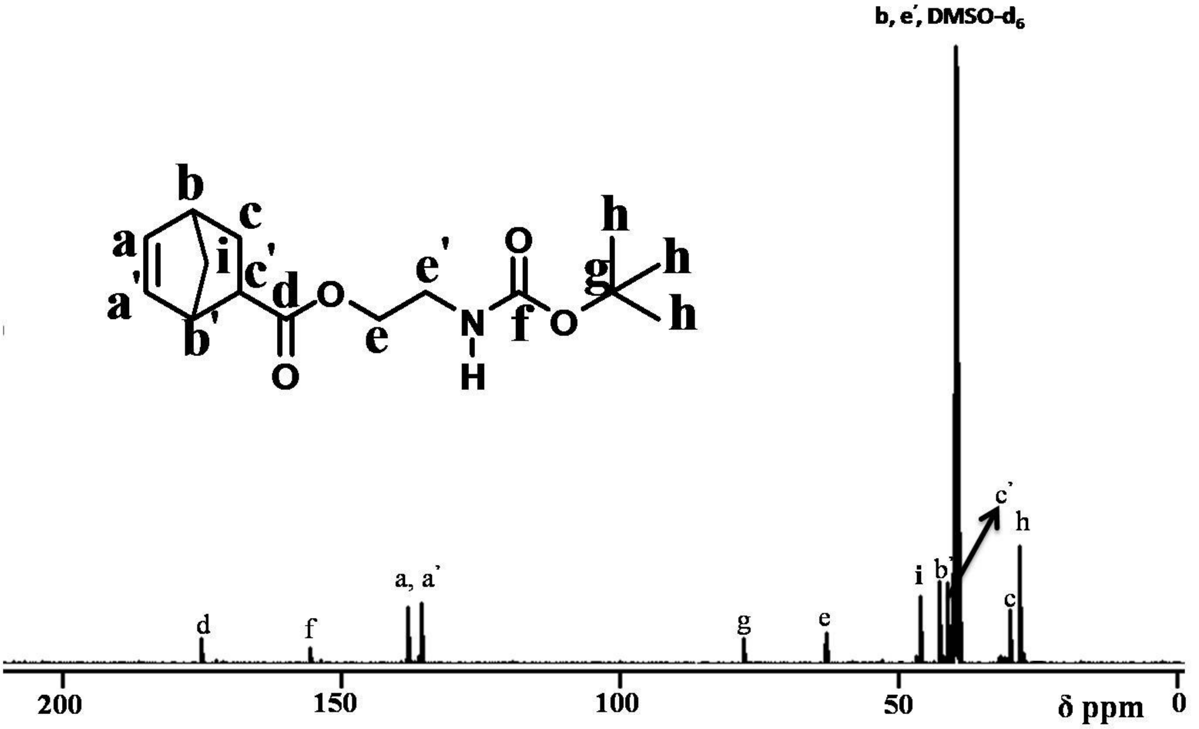


Figure S4: ^{13}C NMR spectrum of **BOCM1** in DMSO-d_6.

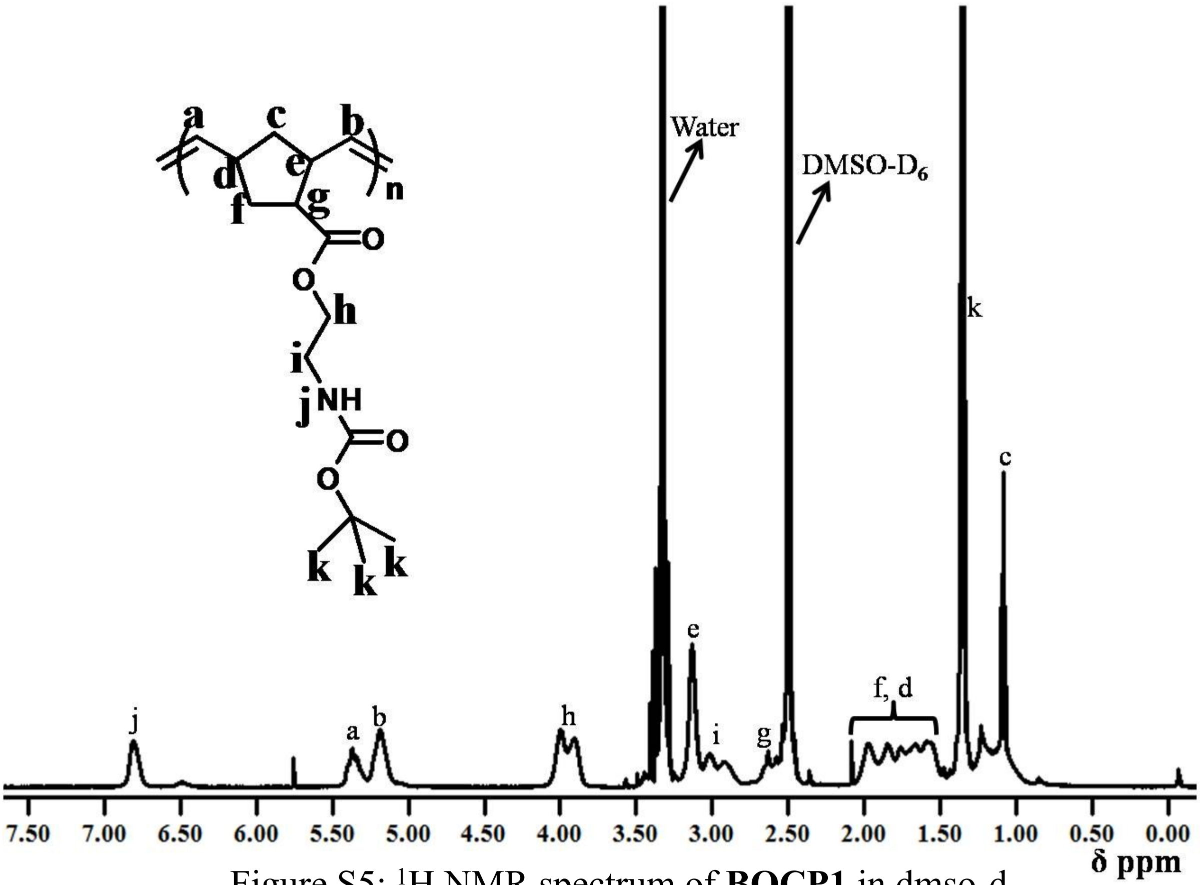


Figure S5: ^{1}H NMR spectrum of **BOCP1** in dmso-d$_6$.

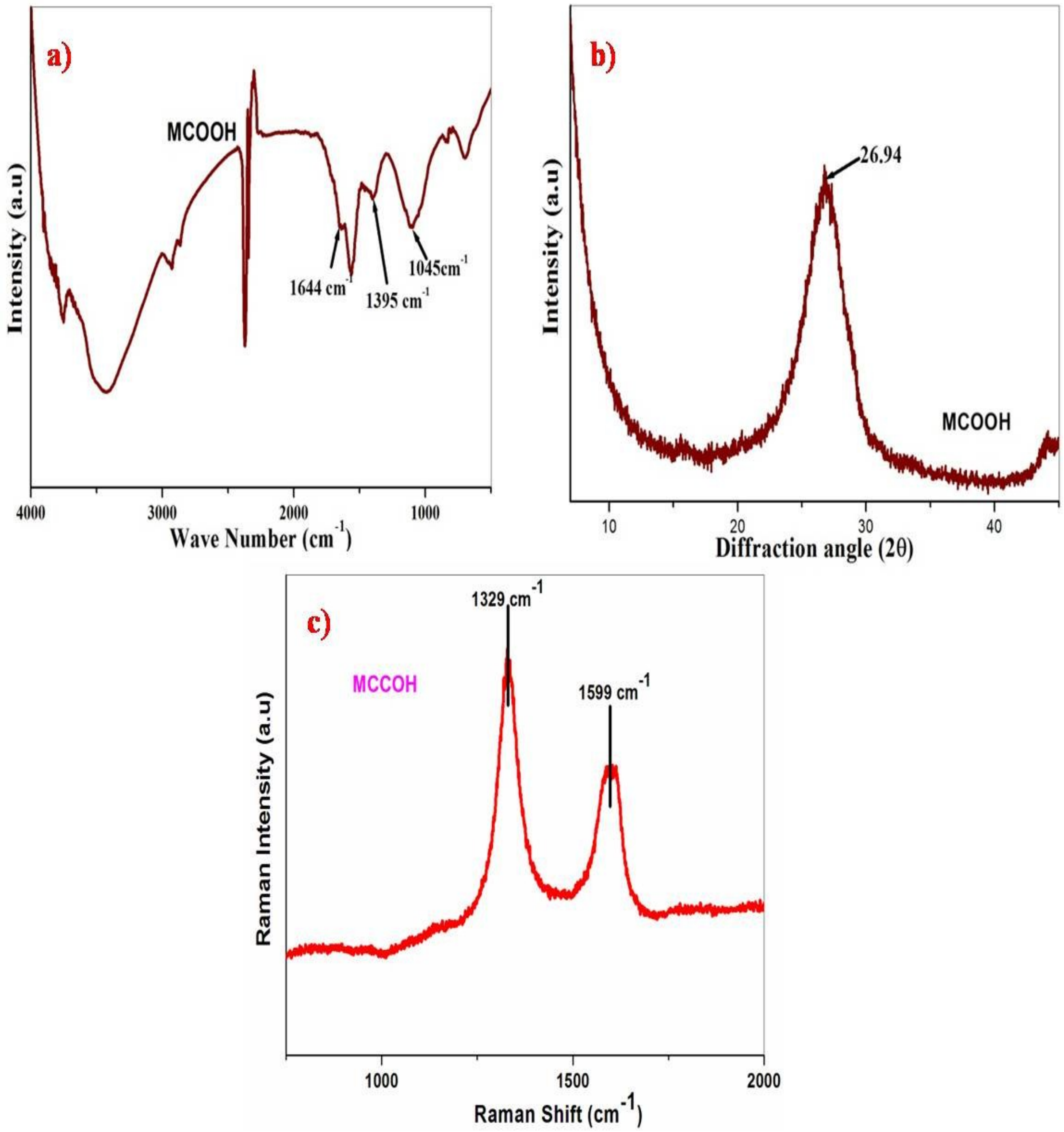
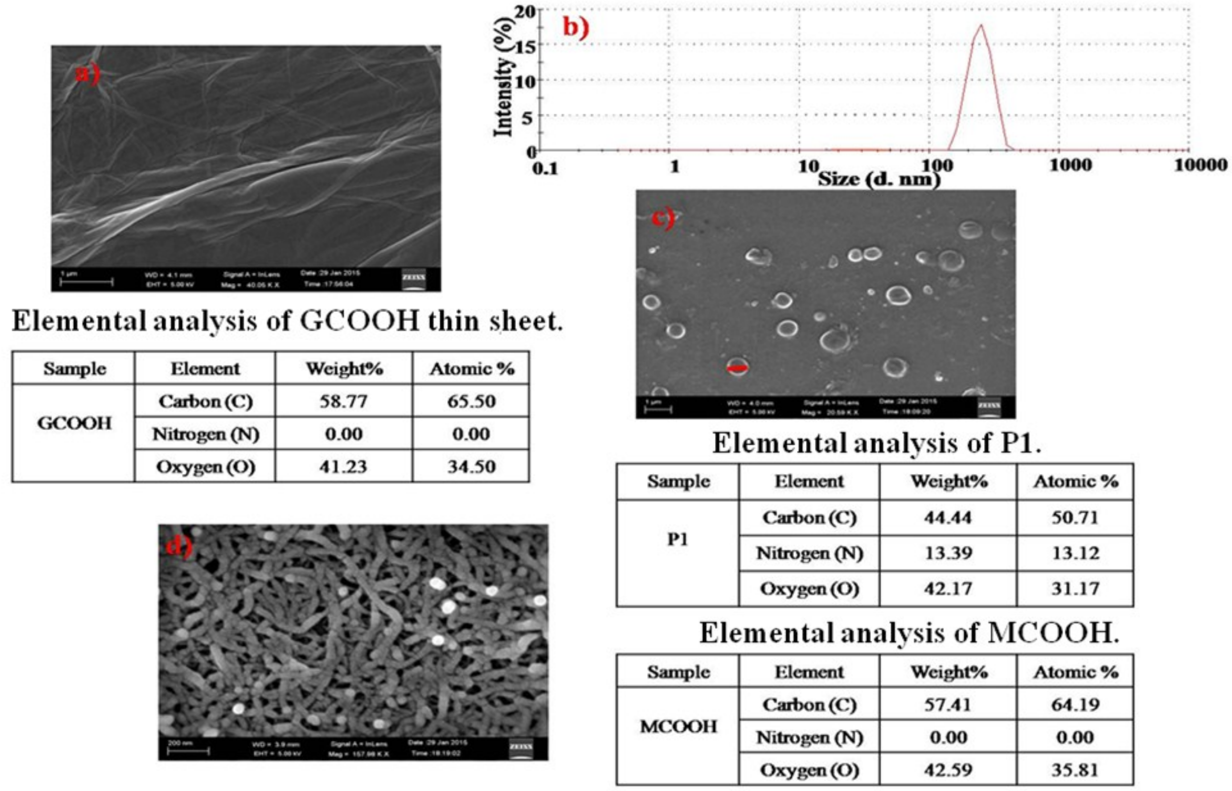


Figure S6: a) IR spectrum of **MCOOH**, b) PXRD pattern of **MCOOH** and c) Raman spectrum of **MCOOH**.



Elemental analysis of GCOOH thin sheet.

Sample	Element	Weight%	Atomic %
GCOOH	Carbon (C)	58.77	65.50
	Nitrogen (N)	0.00	0.00
	Oxygen (O)	41.23	34.50

Elemental analysis of P1.

Sample	Element	Weight%	Atomic %
P1	Carbon (C)	44.44	50.71
	Nitrogen (N)	13.39	13.12
	Oxygen (O)	42.17	31.17

Elemental analysis of MCOOH.

Sample	Element	Weight%	Atomic %
MCOOH	Carbon (C)	57.41	64.19
	Nitrogen (N)	0.00	0.00
	Oxygen (O)	42.59	35.81

Figure S7: a) FESEM micrograph of **GCOOH**, b) DLS profile of **P1**, c) FESEM micrograph of **P1** and d) FESEM micrograph of **MCOOH**.

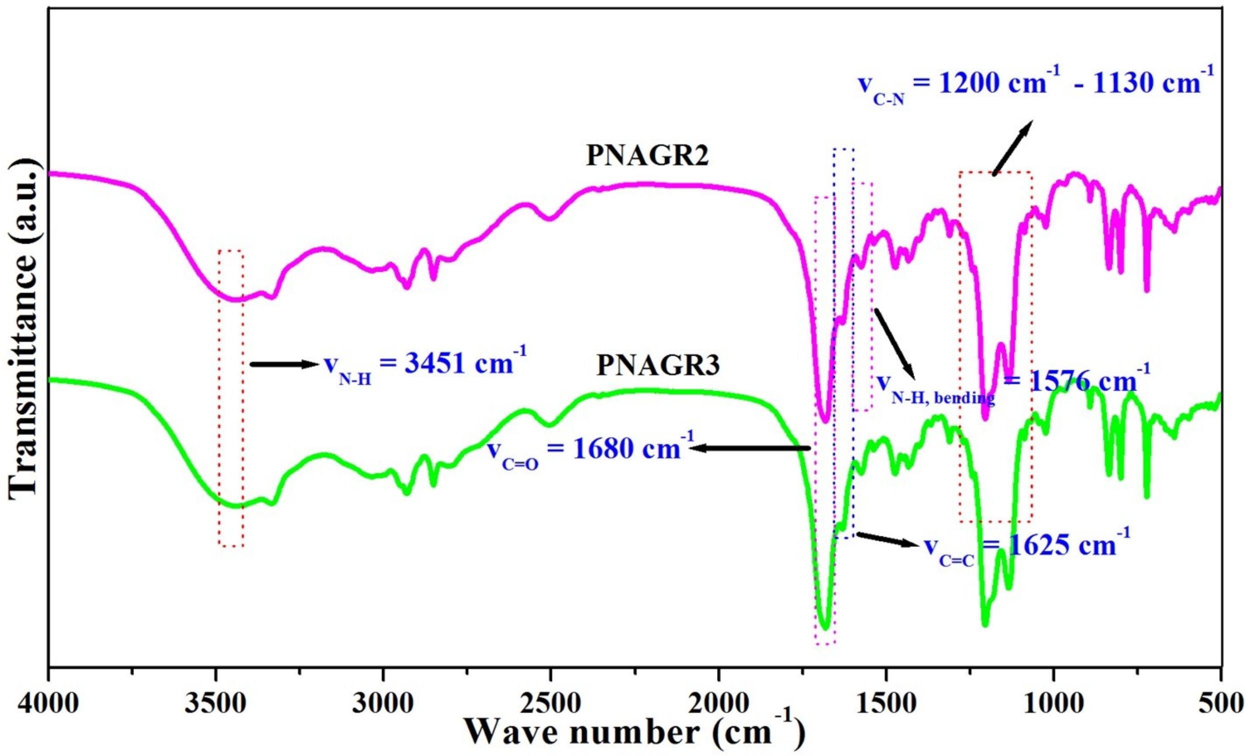


Figure S8: IR spectra of **PNAGR2** and **PNAGR3**.

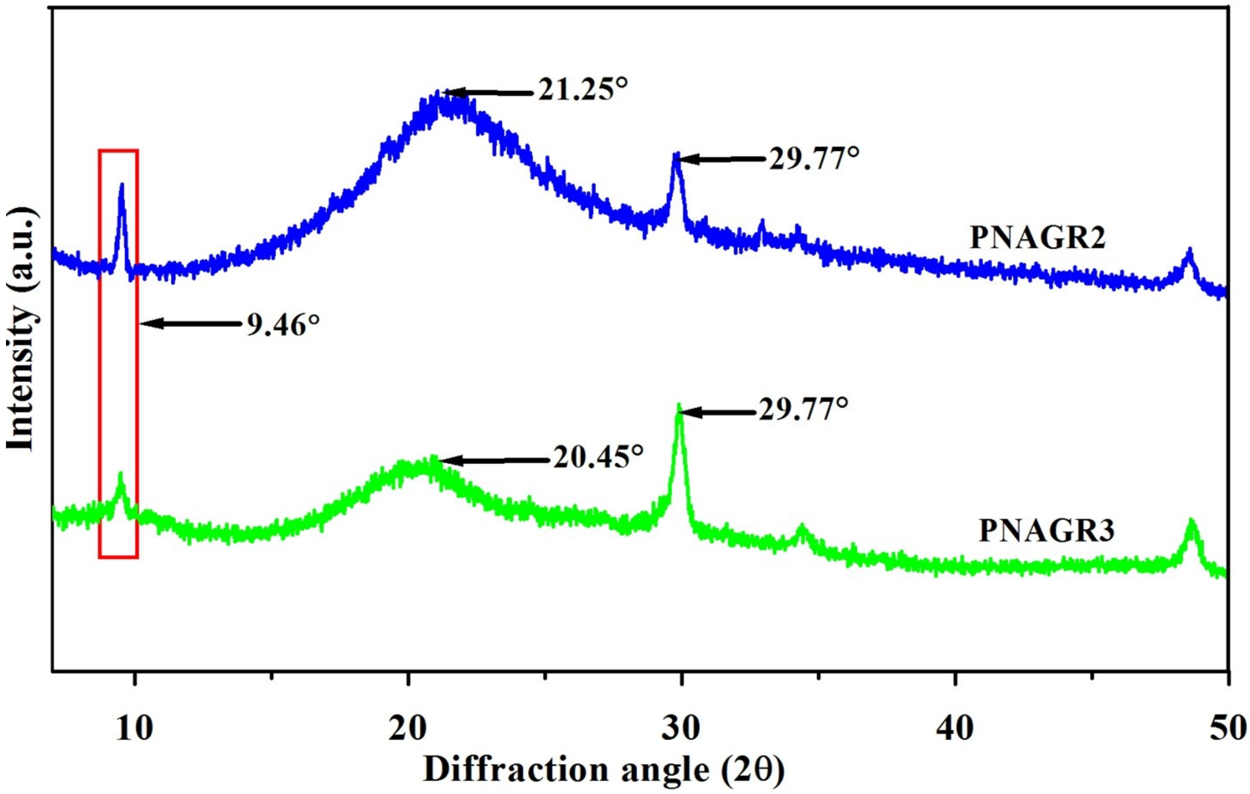


Figure S9: PXRD pattern of **PNAGR2** and **PNAGR3**.

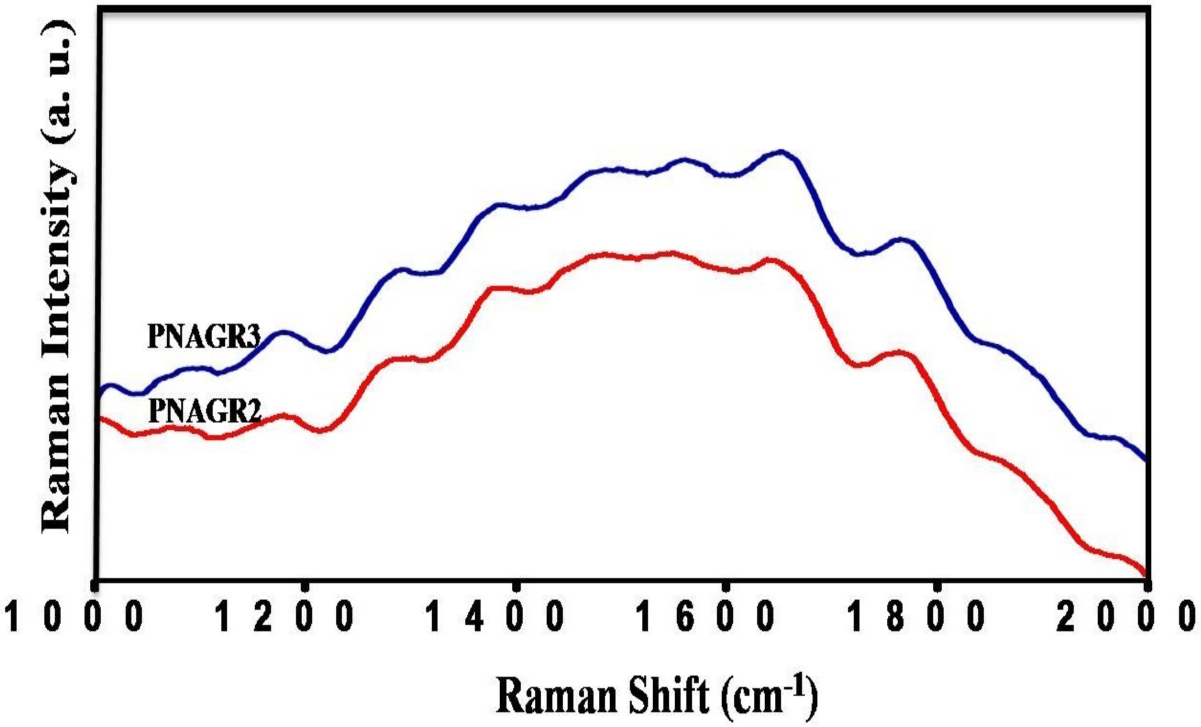
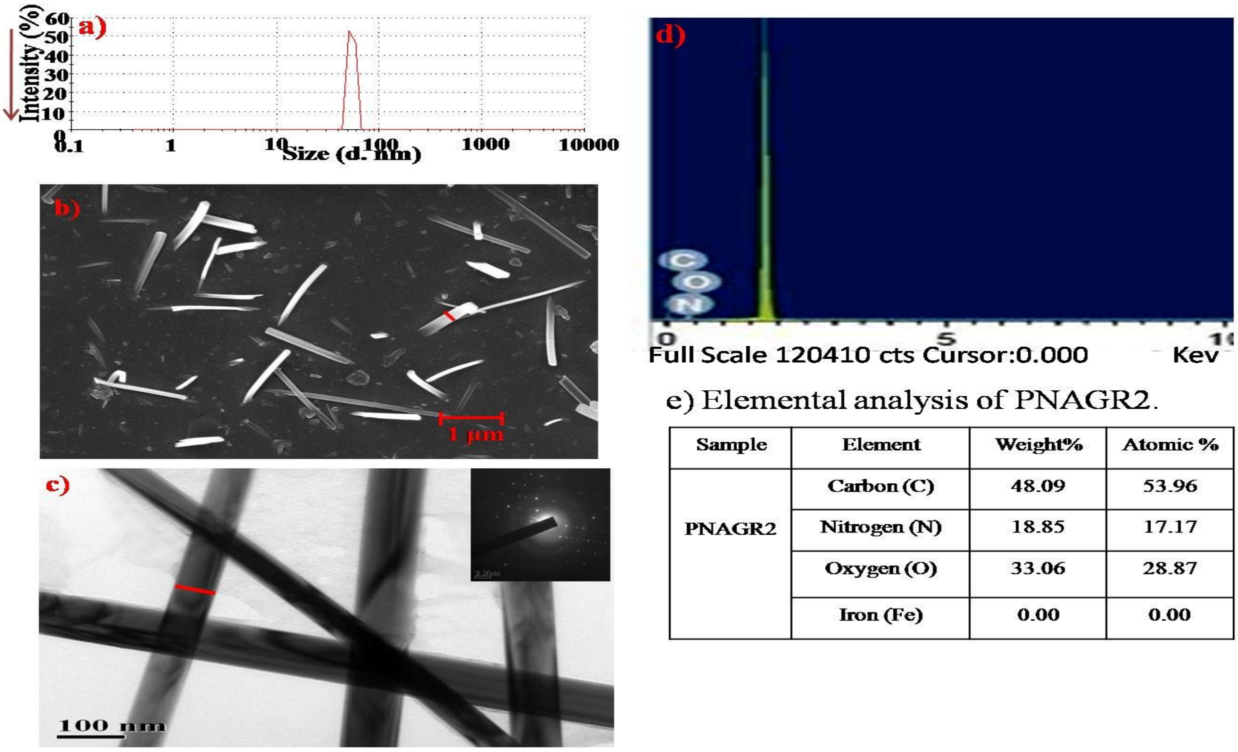


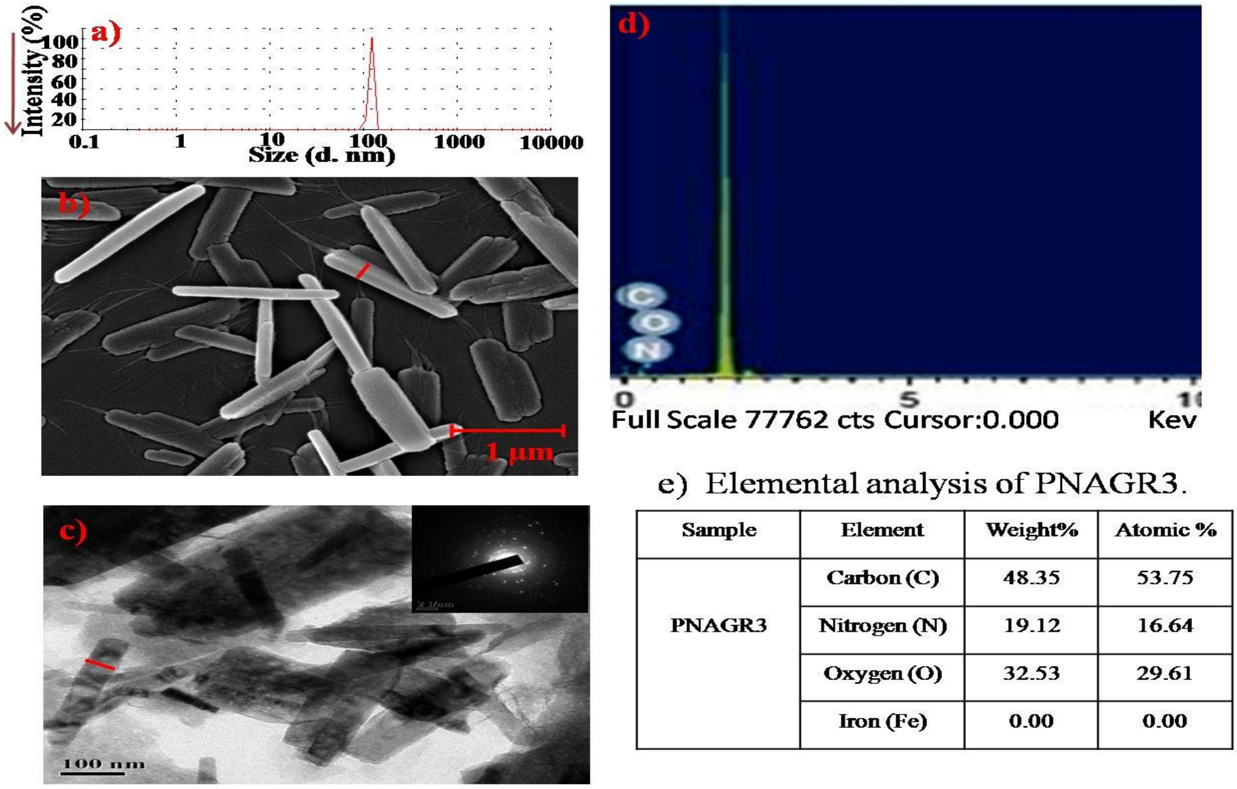
Figure S10: Raman spectra of **PNAGR2** and **PNAGR3**.



e) Elemental analysis of PNAGR2.

Sample	Element	Weight%	Atomic %
PNAGR2	Carbon (C)	48.09	53.96
	Nitrogen (N)	18.85	17.17
	Oxygen (O)	33.06	28.87
	Iron (Fe)	0.00	0.00

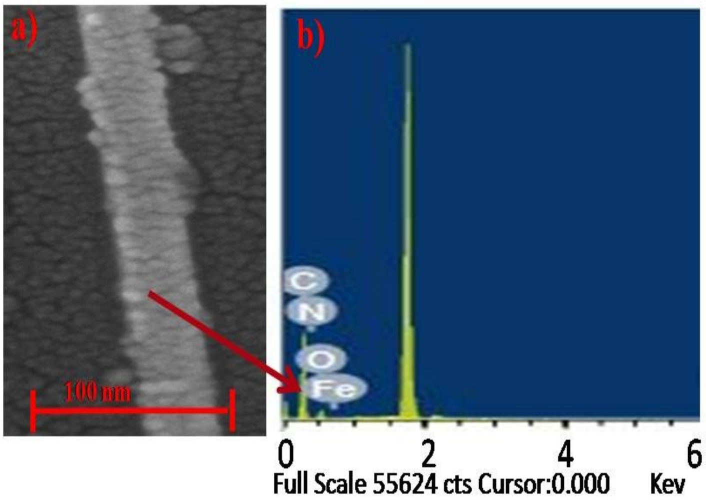
Figure S11: a) DLS profile of **PNAGR2**, b) FESEM micrograph of **PNAGR2**, c) HRTEM micrograph of **PNAGR2** (inset SAED of **PNAGR2**) and d) EDX of **PNAGR2** and e) Elemental analysis of **PNAGR2**.



e) Elemental analysis of PNAGR3.

Sample	Element	Weight%	Atomic %
PNAGR3	Carbon (C)	48.35	53.75
	Nitrogen (N)	19.12	16.64
	Oxygen (O)	32.53	29.61
	Iron (Fe)	0.00	0.00

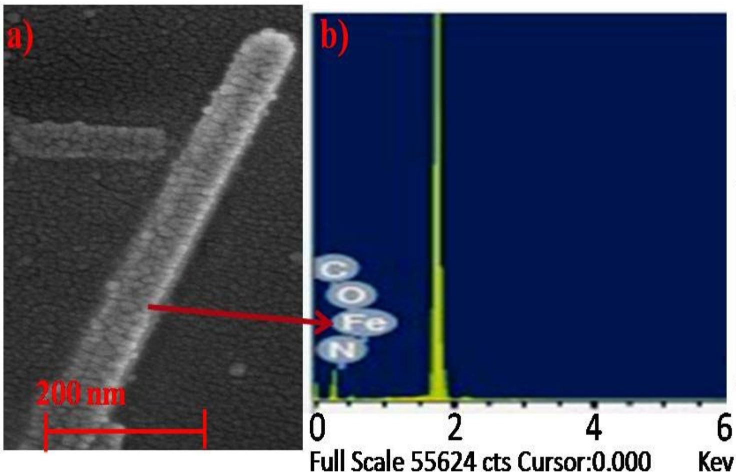
Figure S12: a) DLS profile of **PNAGR3**, b) FESEM micrograph of **PNAGR3**, c) HRTEM micrograph of **PNAGR3** (inset SAED of **PNAGR3**) and d) EDX of **PNAGR3** and e) Elemental analysis of **PNAGR3**.



c) Elemental analysis of PNF2.

Sample	Element	Weight%	Atomic %
PNF2	Carbon (C)	64.90	71.15
	Nitrogen (N)	9.27	8.72
	Oxygen (O)	23.91	19.68
	Iron (Fe)	1.92	0.45

Figure S13: a) FESEM micrograph of **PNF2**, b) EDX of **PNF2** and c) Elemental analysis of **PNF2**.



c) Elemental analysis of PNF3.

Sample	Element	Weight%	Atomic %
PNF3	Carbon (C)	57.78	65.30
	Nitrogen (N)	11.30	10.95
	Oxygen (O)	26.81	22.75
	Iron (Fe)	4.11	1.00

Figure S14: a) FESEM micrograph of **PNF3**, b) EDX of **PNF3** and c) Elemental analysis of **PNF3**.

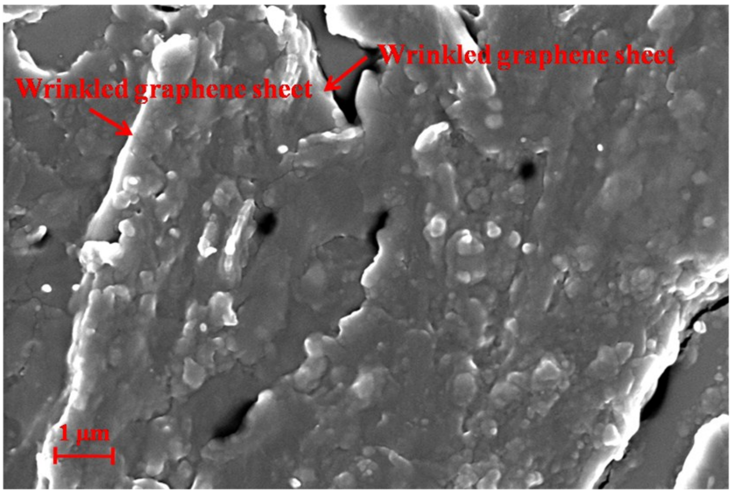
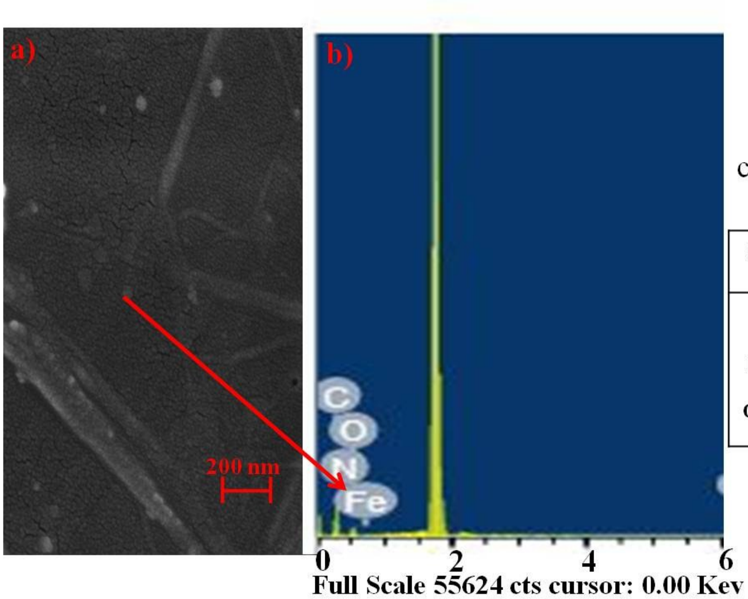


Figure S15: FESEM micrograph of **PNAGR1** in MeOH.



c) Elemental ananlysis of iron nano - particle loaded GCOOH.

Sample	Element	Weight%	Atomic %
Iron nano particle loaded GCOOH	Carbon (C)	60.26	66.62
	Nitrogen (N)	0.80	0.57
	Oxygen (O)	38.24	32.65
	Iron (Fe)	0.70	0.16

Figure S16: a) FESEM micrograph, b) EDX analysis, and c) Elemental analysis of iron nano-particle loaded **GCOOH**.