Supporting Information

Simultaneous dehydration of biomass derived sugars to 5-hydroxymethyl furfural (HMF) and reduction of graphene oxide in ethyl lactate : One pot dual chemistry

Dibyendu Mondal, [a,b] Jai Prakash Chaudhary, [a,b] Mukesh Sharma, [a,b] Kamalesh Prasad [a,b*]

[a] *Marine Biotechnology and Ecology Discipline, CSIR-Central Salt and Marine Chemicals Research Institute (CSIR-CSMCRI),Council of Scientific & Industrial Research (CSIR),Gijubhai Badheka Marg, Bhavnagar- 364 002, (Gujarat), INDIA , Phone No : +91-278-2567760. Fax No. +91-278-2567562; Email: , kamlesh@csmcri.org / drkamaleshp@gmail.com]*

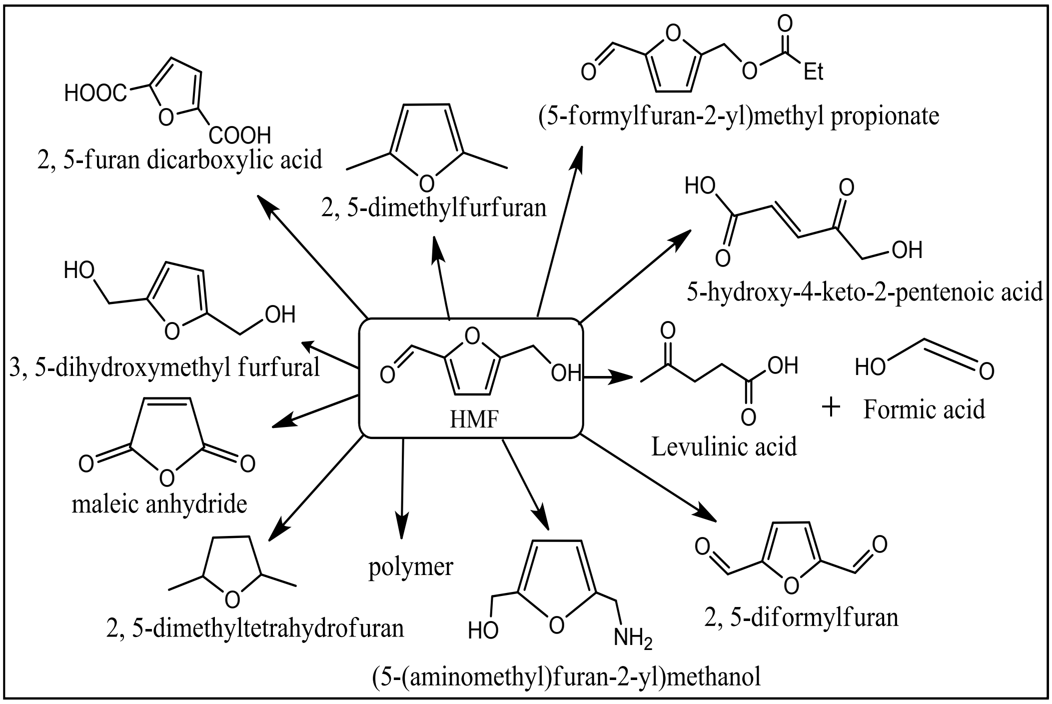
[b] *Academy of Scientific and Innovative Research,CSIR-Central Salt and Marine Chemicals Research Institute (CSIR-CSMCRI), Council of Scientific & Industrial Research (CSIR), Gijubhai Badheka Marg, Bhavnagar- 364 002, (Gujarat), INDIA*

Materials

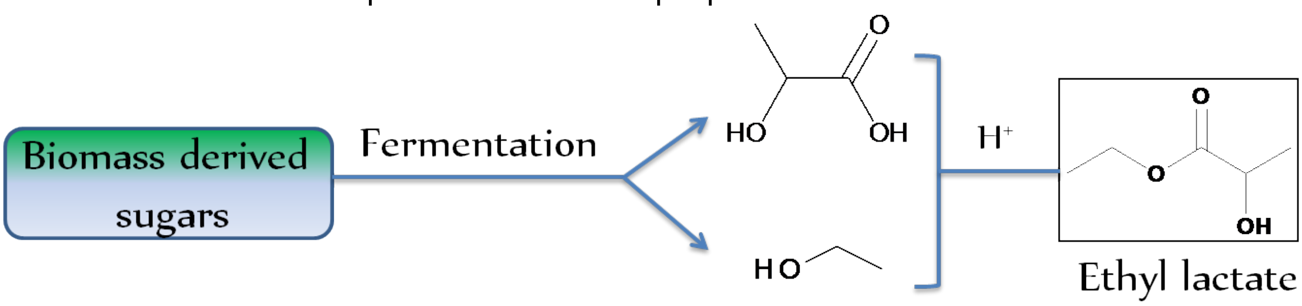
Graphite nano powder (CAS no. 7782-42-5, average particle size: 400 nm), Fructose, glucose, galactose, mannose and sucrose was purchased from SRL Chemicals, Mumbai, India. Sodium nitrate, sulphuric acid (98%), potassium permanganate and hydrogen peroxide (30% v/v) were procured from S.D. Fine Chemicals, Mumbai, India. Standard HMF, ethyl lactate, choline chloride and betaine hydrochloride were procured from TCI (Tokyo Chemical Industry Co., LTD), Tokyo, Japan. All chemicals were analytical grade and were used as received. HPLC grade solvent was used for HPLC and other analysis.

Characterization

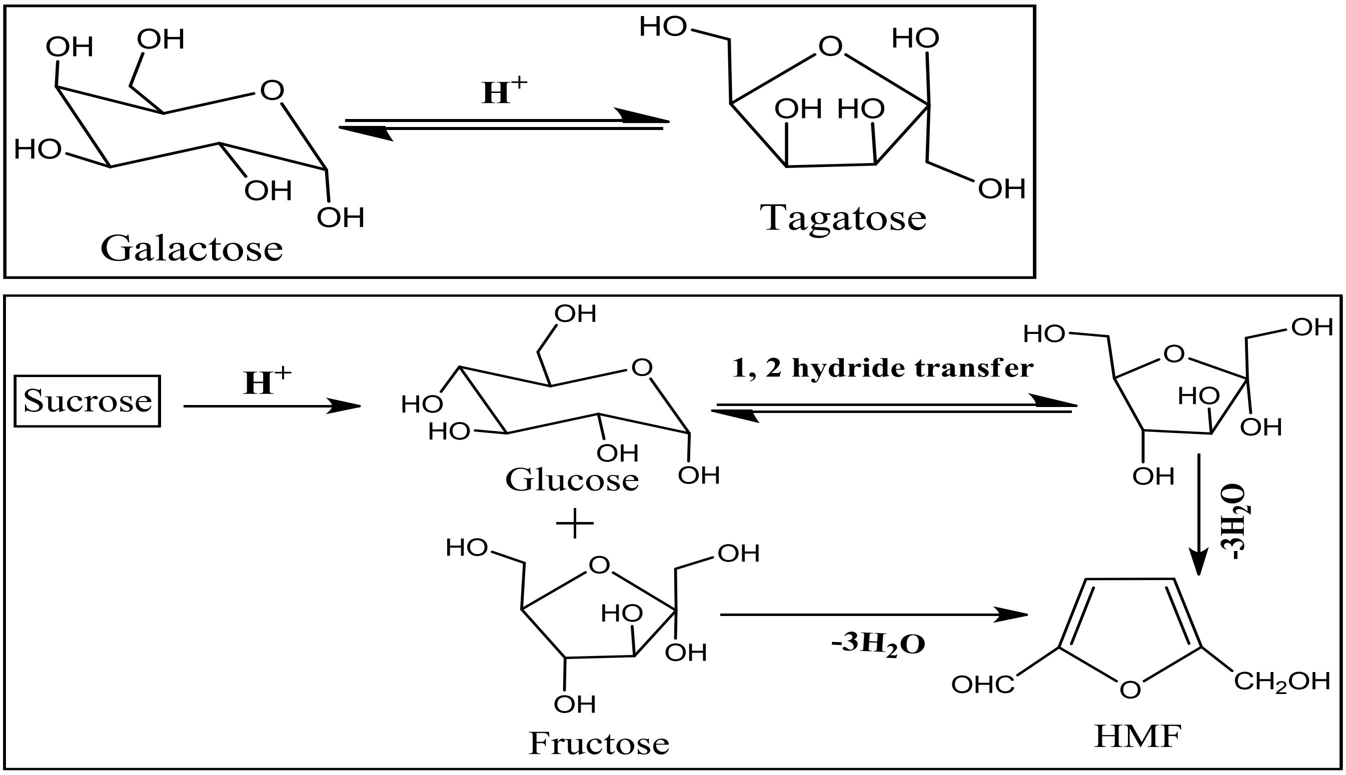
Structural integrity of EL before and after reaction was characterized by ^1H NMR (Brukar Avance III, 500 MHz). HMF was quantified on a HPLC (Waters Separation Module 2695, USA) using a C18 column at 35ºC, 1:4 methanol/water as mobile phase, and 278 nm detection. The injection volume was 20 μl/min. The amount of HMF was assayed through a calibration plot made using known concentrations of standard HMF. The reduction of GO was confirmed mainly by UV-Vis measurement. For the UV-Vis measurement, 0.1 mg/mL GO sample was prepared in milli-Q water and ultrasonicated for 40 min at 50 ^{0}C (Elma, Germany). UV-Vis absorbance spectra were recorded on a CARY 500 Varian 8.01 UV-Vis spectrophotometer. Powder X-ray diffraction patterns of different GO samples were recorded at 298 K on a PAN analytical system using Cu anode, K_α radiation (λ = 0.15405 nm) with 2θ range from 5° to 80° at a scan speed of 0.1° sec^{-1}. Fourier transform infrared (FT-IR) of different GO sample were performed over the wavenumber range of 4000-400 cm^{-1} on a Perkin-Elmer FT-IR machine (Spectrum GX, USA) using KBr pellets (2 mg sample in 600 mg KBr). Thermo gravimetric analysis (TGA) of different GO sample were carried out on a NETZSCH TG 209F1 Libra TGA209F1D-0105-L machine using a temperature programmer 30-800 °C at a heating rate 5 °C min^{-1} under a nitrogen atmosphere. Transmission electron microscope (TEM) images of rGO were recorded on a JEOL HR-TEM (JEOL JEM 2100, Japan) instrument operated accelerating voltage of 200 kV. Raman spectroscopy measurements were taken using a micro-Raman system (Horiba Jobin-Yvon LabRAM HR800 UV-vis μ-Raman) with argon sourced laser excitation at 514.5 nm employing power 10 mW in the scanning range of 100-4000 cm-1.



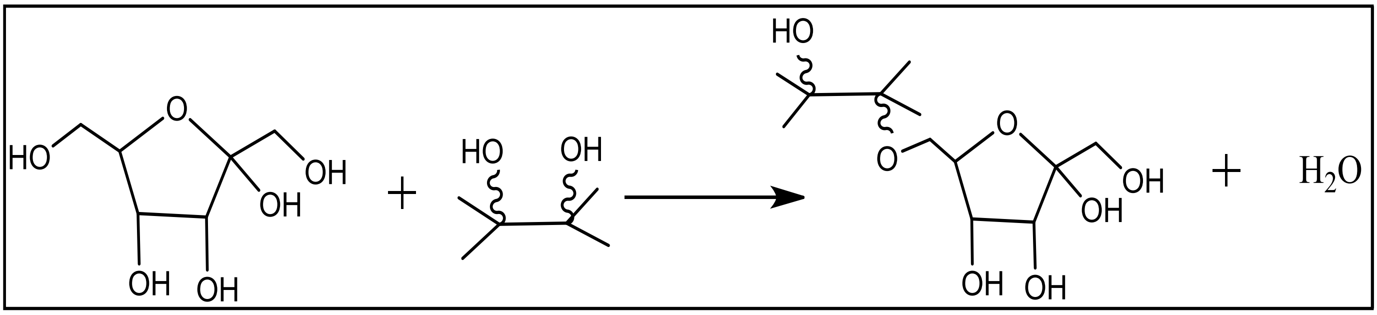
Scheme S1: Schematic representation of multiple products which can be derived from HMF.



Scheme S2: Schematic procedure for synthesis of ethyl lactate from biomass derived sugar.



Scheme S3 : Dehydration mechanism of the various sugar substrates used in the study.



Scheme S4 : Formation of C-O bond of glucose with diols.

Table S1 : Abbreviations of the GO containing substrates

Sample name	Description
Pristine GO	GO as synthesized by modified Hummer's method
rGO-Fructose	Recovered and washed GO as obtained after the reaction where HMF synthesis was done using fructose as substrate and only GO as promoter ethyl lactate (EL) as solvent under microwave irradiation 30 min at 100 ^{0}C
rGO-BHC-Fructose	Recovered and washed GO as obtained after the reaction where HMF synthesis was done using fructose as substrate, GO as promoter and BHC as additive using EL as solvent under microwave irradiation for 30 min at 100 ^{0}C
rGO-ChoCl-Fructose	Recovered and washed GO as obtained after the reaction where HMF synthesis was done using fructose as substrate, GO as promoter and ChoCl as additive using EL as solvent under microwave irradiation (optimized reaction condition for HMF synthesis)
rGO-ChoCl-Glucose	Recovered and washed GO as obtained after the reaction where HMF synthesis was done using glucose as substrate, GO as promoter and ChoCl as additive using EL as solvent under microwave irradiation (optimized reaction condition for HMF synthesis)
rGO-ChoCl-Galactose	Recovered and washed GO as obtained after the reaction where HMF synthesis was done using galactose as substrate, GO as promoter and ChoCl as additive using EL as solvent under microwave irradiation (optimized reaction condition for HMF synthesis)
rGO-ChoCl-Mannose	Recovered and washed GO as obtained after the reaction where HMF synthesis was done using mannose as substrate, GO as promoter and ChoCl as additive using EL as solvent under microwave irradiation (optimized reaction condition for HMF synthesis)
rGO-ChoCl-Sucrose	Recovered and washed GO as obtained after the reaction where HMF synthesis was done using sucrose as substrate, GO as promoter and ChoCl as additive using EL as solvent under microwave irradiation (optimized reaction condition for HMF synthesis)

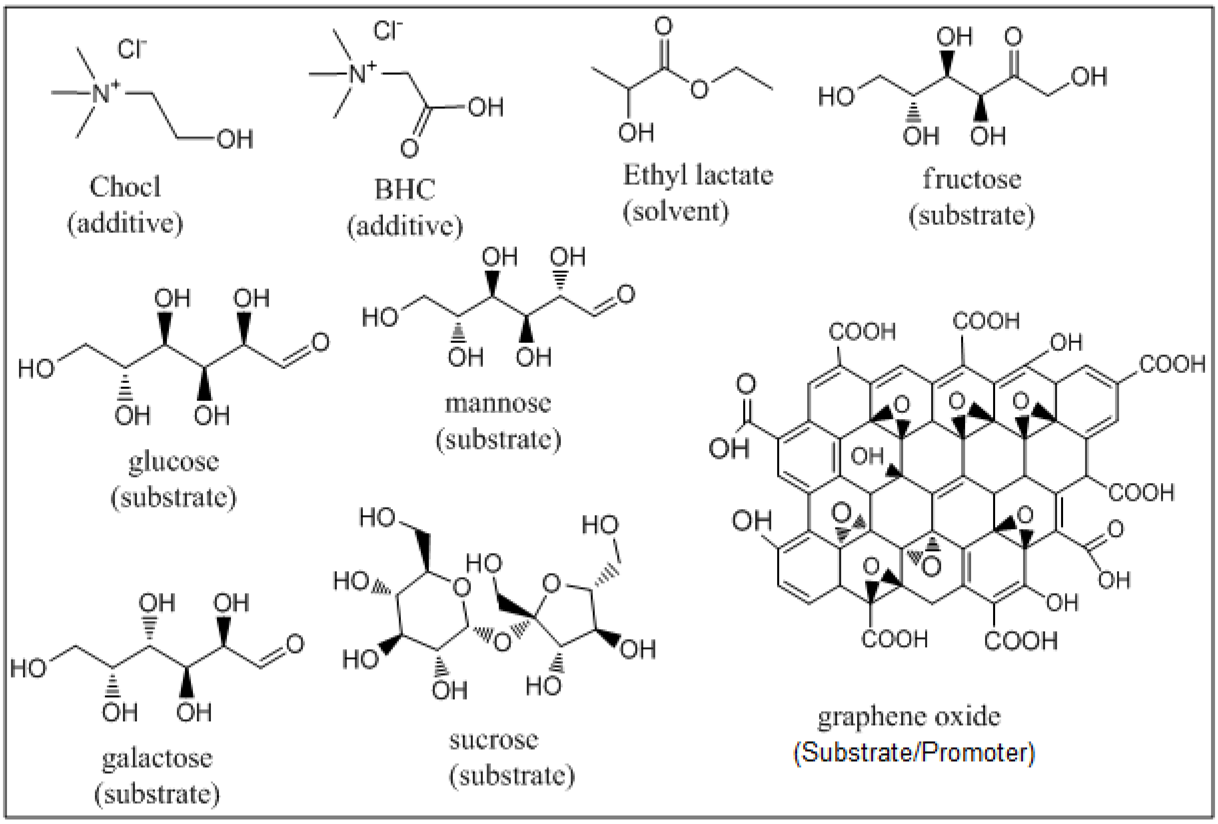


Figure S1 : Chemical structures of various substrates and additives used for the production of HMF in the present study.

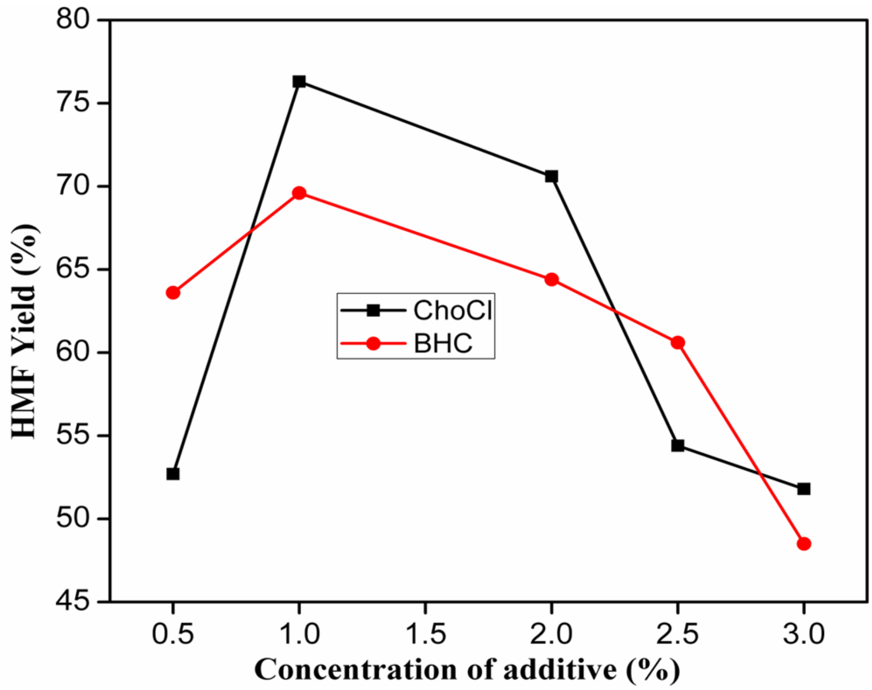


Figure S2 : Effect of concentration of additive (ChoCl and BHC) on the yield of HMF under MW irradiation (600 W) at 100 ^{0}C using GO as promoter, EL as solvent and 2.5 % fructose as substrate

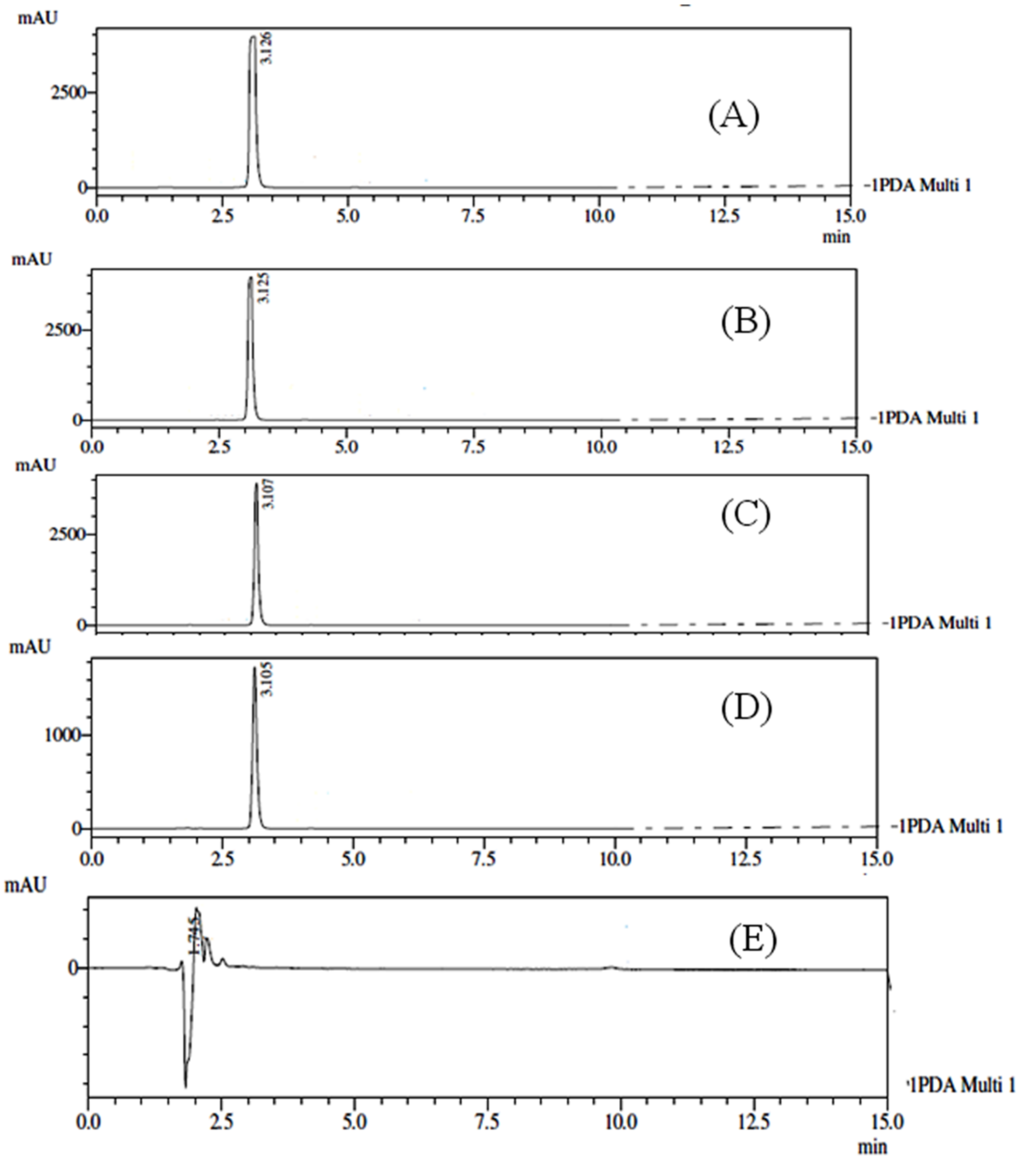


Figure S3. HPLC chromatogram of different HMF samples (A) Standard HMF sample, (B) HMF obtained using GO only as promoter, (C) HMF obtained using GO as promoter and BHC as additive (D) HMF obtained using ChoCl as additive and GO as promoter and (E) sample without any promoter and additive

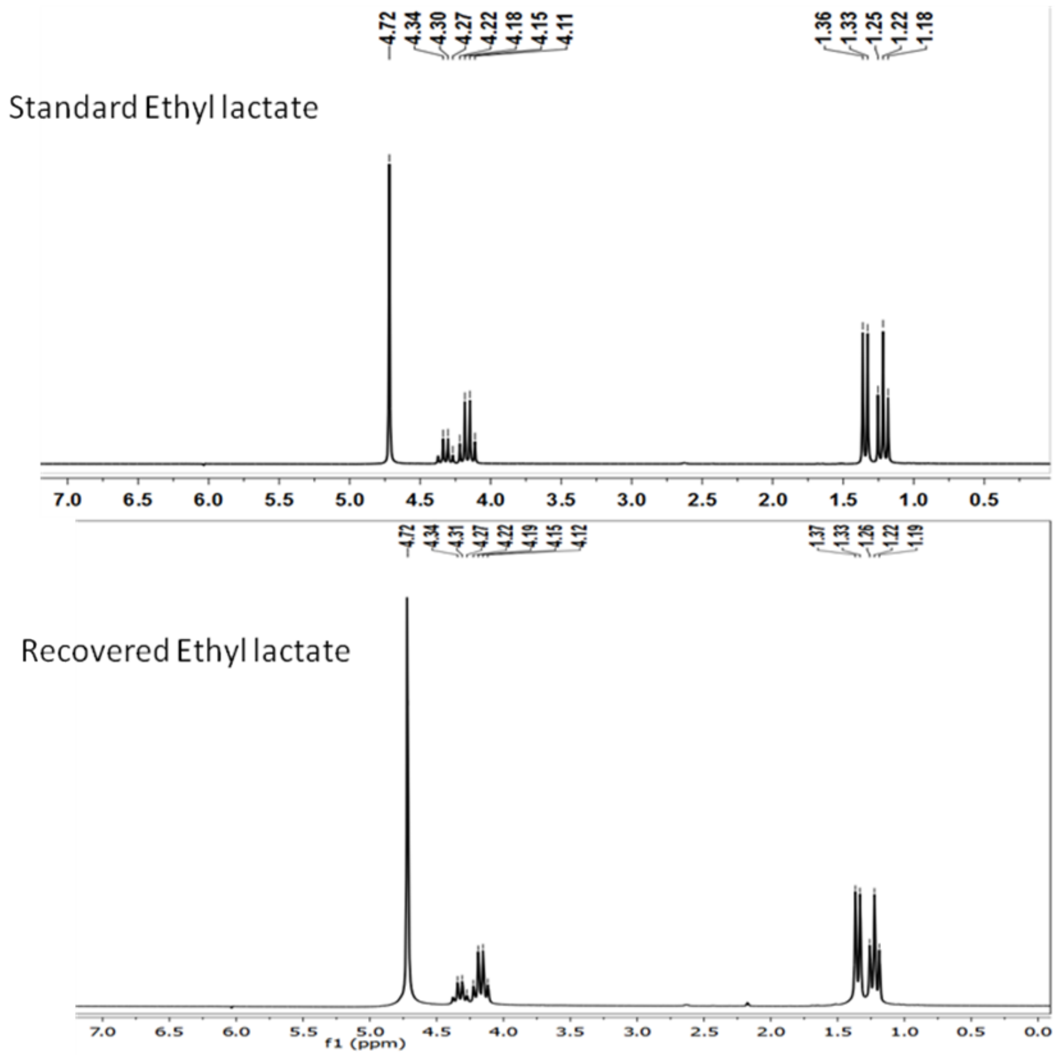


Figure S4. ^1H NMR of pristine and recycled ethyl lactate

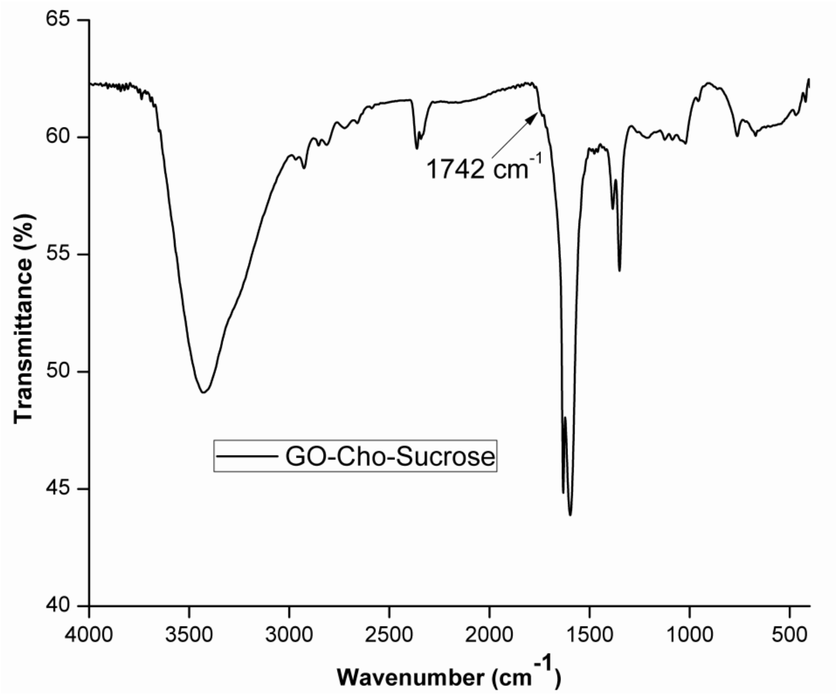


Figure S5 : FT-IR spectra of rGO obtained using Sucrose as substrate and choline chloride as additive.

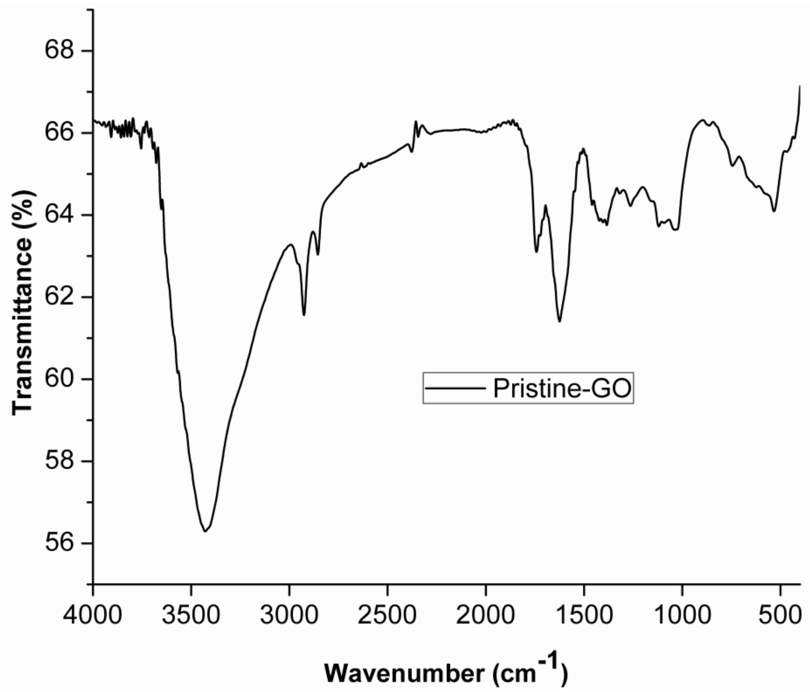


Figure S6: FT-IR spectra of pristine GO

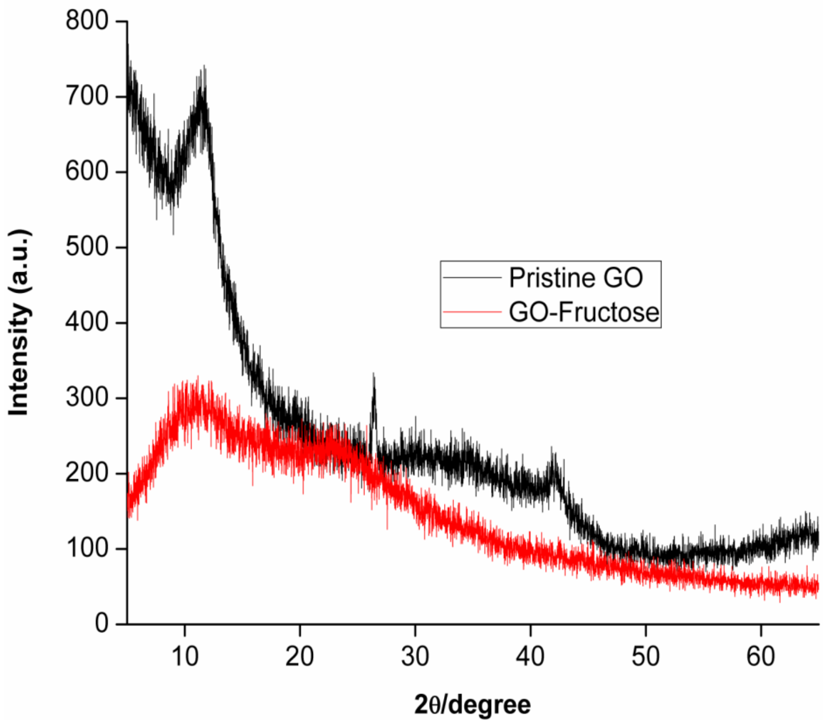


Figure S7 : Powder XRD graphs of Pristine Graphene Oxide and GO reduced in presence of fructose (GO-Fructose)

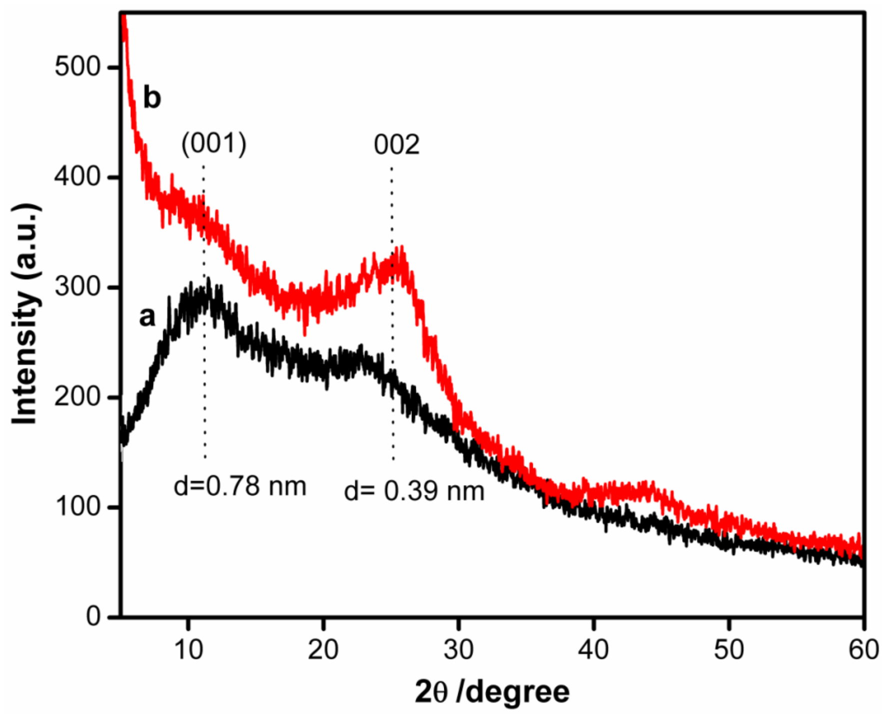


Figure S8 : Powder XRD of GO reduced (a) in presence of fructose using BHC as additive and (b) in presence of fructose using ChoCl as additive

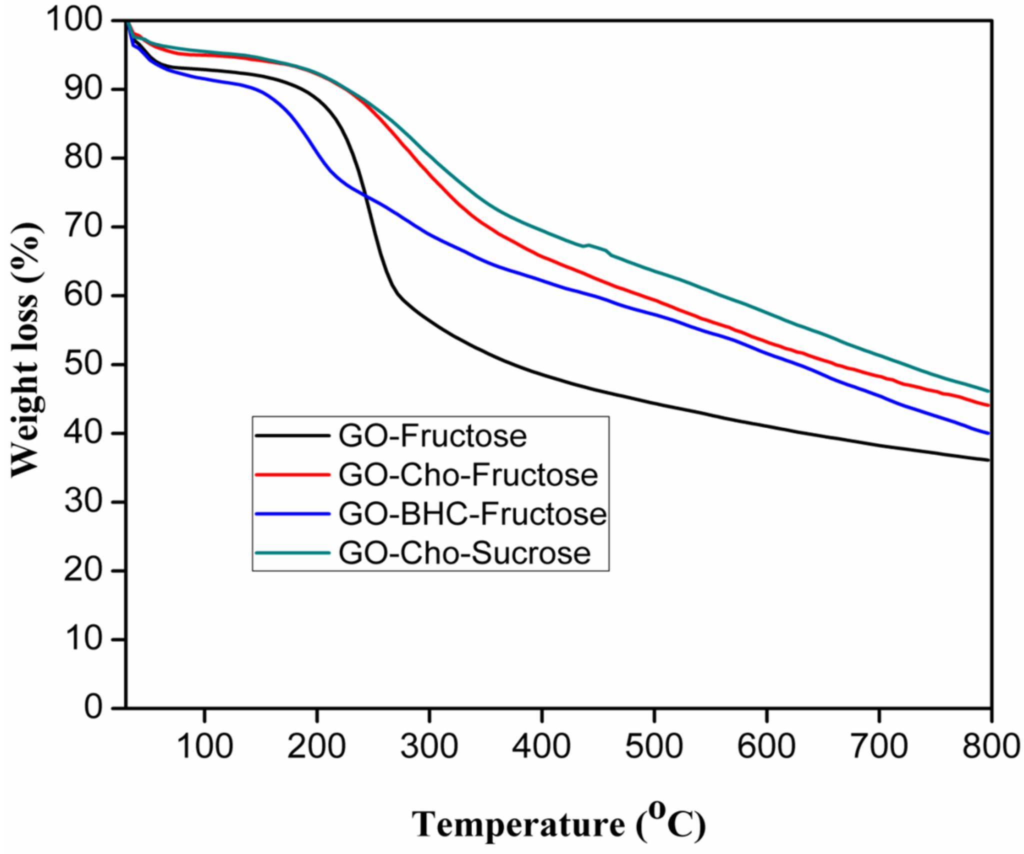


Figure S9 : TGA of (a) GO-Fructose, (b) GO-BHC-Fructose, (c) GO-ChoCl-Fructose

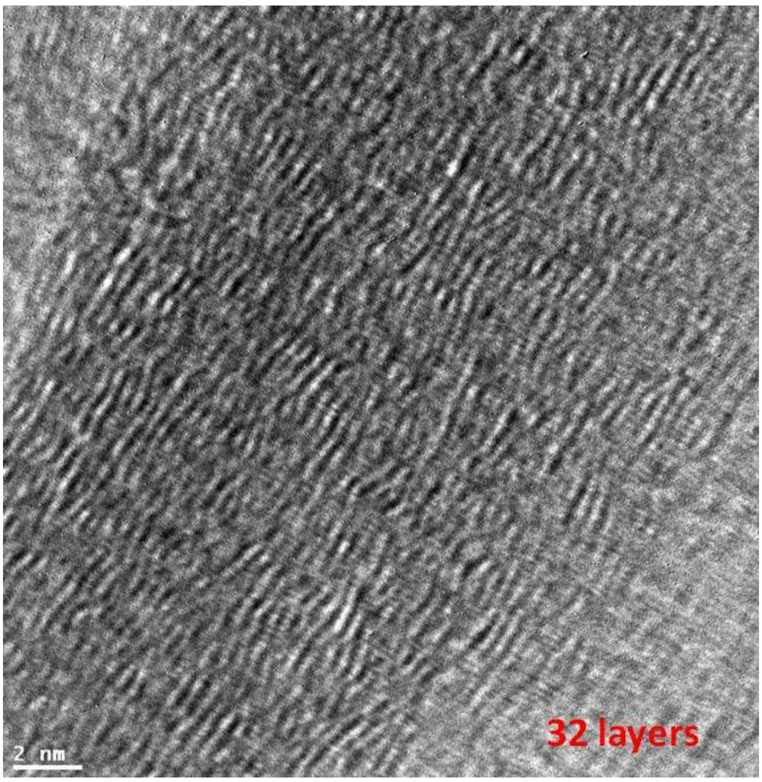
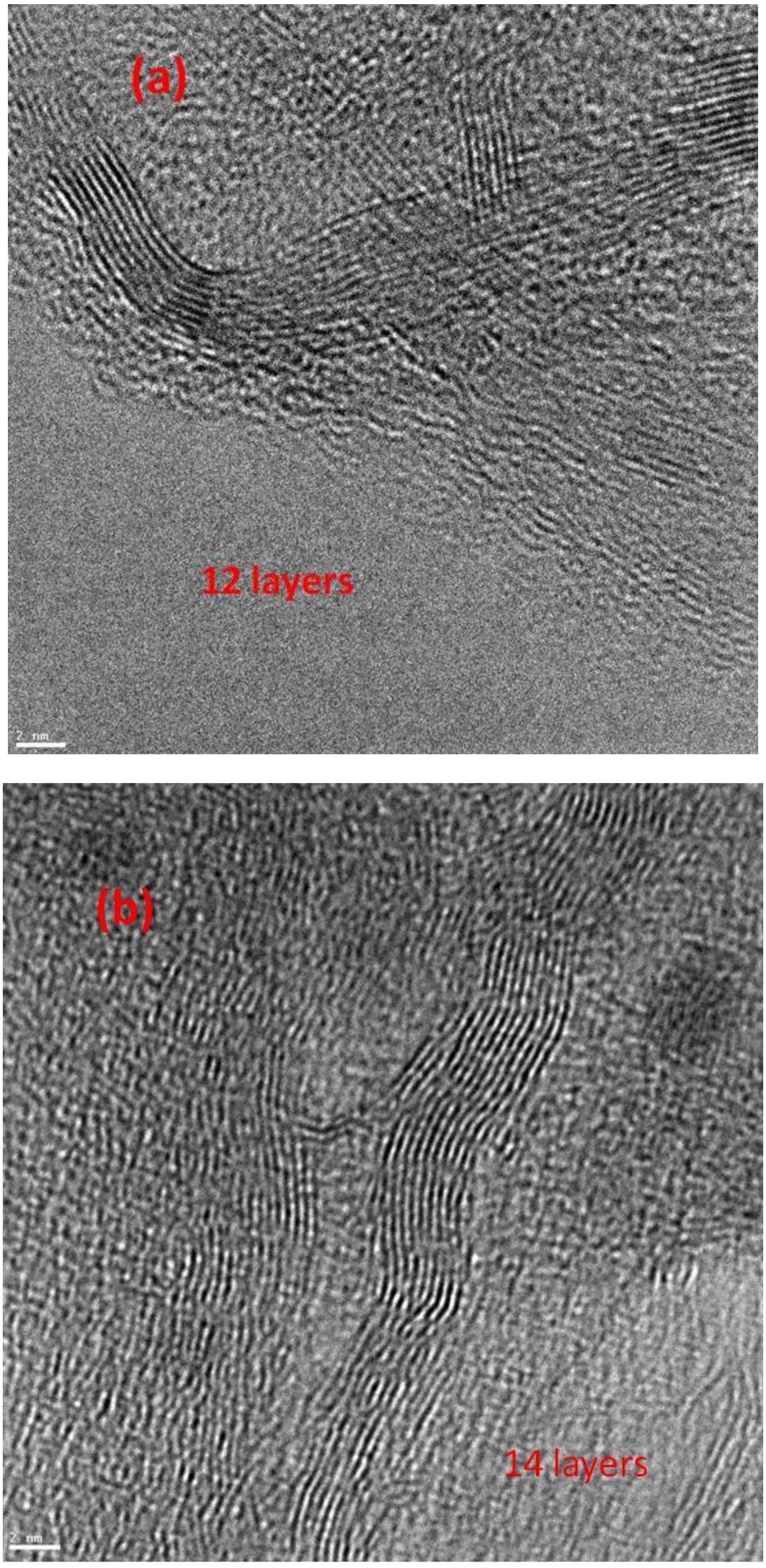


Figure S10 : TEM image GO prepared by Hummers method and reduced using hydrazine.


(a)
12 layers
2 nm
(b)
14 layers
2 nm

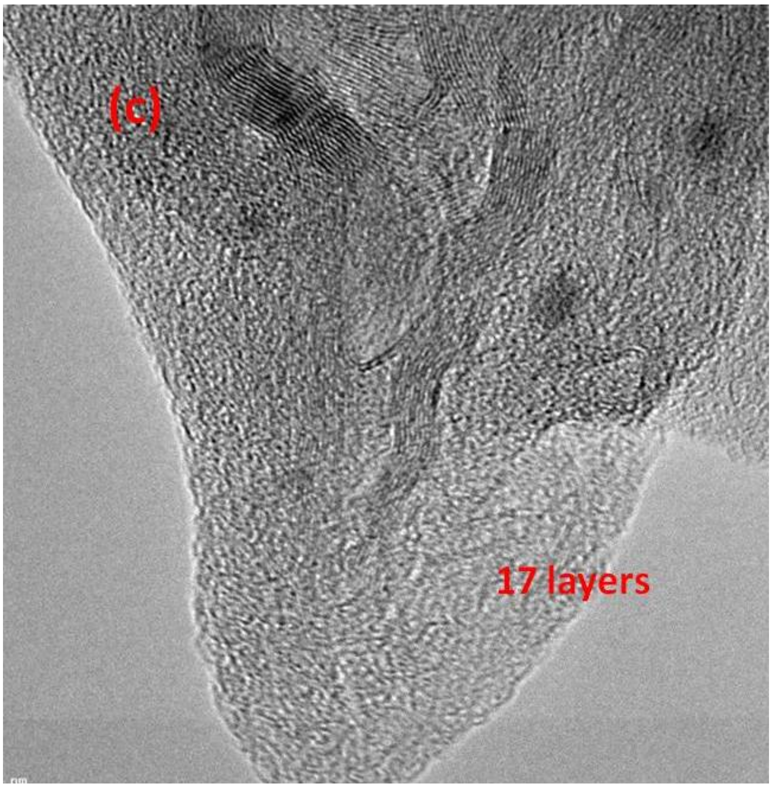


Figure S11 : TEM images of rGO obtained using (a) galactose (b) sucrose and (c) mannose as substrates.

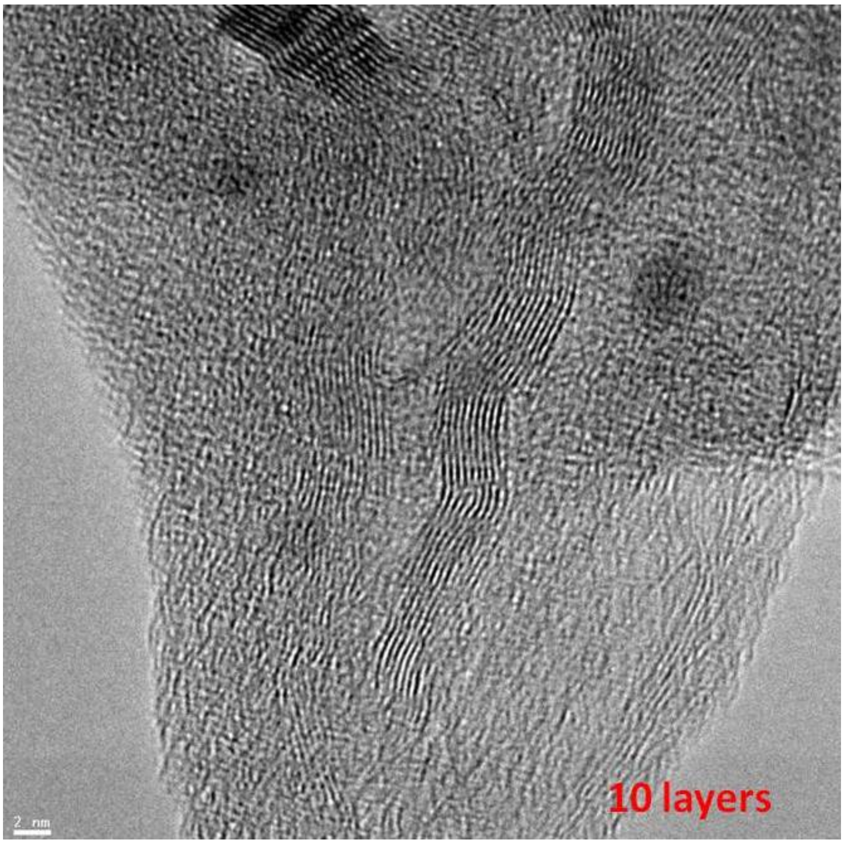


Figure S12 : TEM images of rGO obtained using fructose as substrates and betaine hydrochloride as additive.

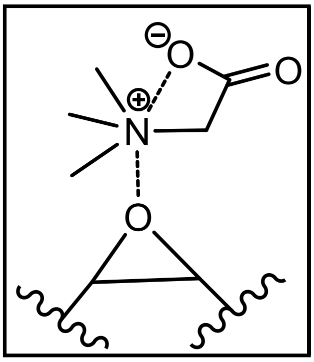


Figure S13 : Zwetterionic structure of betaine hydrochloride in solution.