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

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Low yield of the chemicals is often identified as a major obstacle for the complete utilization of the bioresources as a source of important chemicals and thereby limits their application in industries. The issue of low yield can be partially compensated by integrated processes, i.e., production of two or more chemicals from the same biomass using single or multistep processes. Herewith a simple pathway for simultaneous production of 5-hydroxymethyl furfural (HMF) from biomass derived sugars by dehydration of fructose (molar yield 76.3%) using graphene oxide (GO) as acid catalyst and choline chloride (ChoCl) as additive in ethyl lactate is demonstrated. Further, during the course of reaction GO was reduced to produce six layered graphene nanosheets (96% recovery). Furthermore, the solvent was recycled after the recovery of both the products and successfully reused for subsequent production of the two chemicals with high purity.

Introduction

Biomass is considered as the most appropriate sustainable resources for the production of bio fuels as alternative to the existing fuels derived from fossil resources. The research is geared up recently due to the gradual dwindling of fossil resources. It is proposed that 18% of total manufactured chemicals will be sourced from biomass by 2020.[1] Although there are plenty of reports available in the literature on the conversion of biomass to ethanol or other valuable chemicals,[2] the special attention has been focused on 5-hydroxymethylfurfural (HMF), which is the dehydrated product of simple sugars and is the precursor of the superior biofuel, 2,5-dimethylfuran (DMF).[3-5] Usually, HMF is prepared from fructose, glucose, sucrose, cellulose and inulin.[3] In this line of research, we have recently demonstrated *Kappaphycus alvarezii,* a red seaweed as an effective alternative precursor for the production of HMF along with potassic fertilizer, levulinic acid, formic acid and pure water.[5] HMF is considered as an important platform chemical, required in different biorefinery processes to derive various important chemicals as depicted in Supporting Scheme S1.[2] Although several routes for the synthesis of HMF are reported in the literature including processes using ionic liquids and other solid acid catalysts, [6,7] but there are only few reports available on using bio based catalyst for such syntheses. Recently, it was reported that HMF could be produced with maximum yield of 84% using choline chloride (ChoCl)/betaine hydrochloride (BHC)/water system at 110 ºC under heating for 1 h.[8] Use of ChoCl-H_2O/MIBK (methyl isobutyl ketone) biphasic system in the presence of $AlCl_3$ catalyst at 165 ºC under microwave condition for 15 minute produced HMF with 70% yield.[9,10]

Carbon based materials such as carbon nanotubes and graphene oxide (GO) have been explored as green catalyst for a number of sustainable chemical transformations. [11,12] GO was reported as an efficient catalyst for the dehydration of fructose to HMF (31% yield) at 100 ºC for 24 h. [13] The produced HMF was further reacted with ethanol to yield ethoxymethyl furfural but the fate of GO was not discussed i.e., whether GO was reduced during the reaction was not investigated. [13]

While HMF is no doubt of great importance, it is of immense interest that the economics of renewable bioresources can be made more attractive through integration with the coformation of other essential products having practical commercial applications.[14] Carbon based nano materials, especially graphene is going to play a very vital role in the development of new materials in the future. Graphene is consisted of 2D sheet like structure with “honeycomb” decoration and made up of conjugated Sp^2 carbon. [15] Graphene is used extensively for energy storage, [16] as membranes for separation of gases and for desalination. [17,18] Chemical reduction of GO is one of the potential route to prepare large scale graphene. There are 50 types of different reducing agents used so far for the reduction of GO to graphene.[15] The most commonly used methodology is the reduction using hydrazine or hydrazine derivatives. [19,20] The disadvantage of using such reducing agent is their toxicity and hence requires immense care during reaction to avoid contamination. Poly (diallyldimethylammonium chloride) (PDDA) containing quaternary ammonium salts, ammonia, glucose, fructose and sucrose are reported as effective alternative reducing agent for GO.[21-23]

Thus, keeping all the above literature studies in mind, we proposed for the first time, the use of GO, simple sugars, and choline chloride or betaine hydrochloride in one pot using ethyl lactate (EL) as solvent for the simultaneous synthesis of HMF and reduced graphene oxide nanosheets (rGO) (Scheme 1). Ethyl lactate was chosen as a solvent since it (i) can be derived from biomass as shown in Supporting Scheme S2 [24], which makes entire process bio-based (ii) environment friendly and green alternatives to petrochemical derived solvents (iii) it has been reported as bio based solvent for synthesis of aryl aldimines, [25] disulfide [26] and other reactions. But the potential of this solvent was unexplored so far for the synthesis of HMF and rGO. Moreover the dehydration efficiency of sugars to HMF is dependent on the nature of the solvent employed. Particularly, anhydrous solvent systems which can dissolve sugar in high quantity are useful since it prevent the side reaction of HMF degradation to levulinic acid and formic acid. Accordingly it was worthwhile to select EL as solvent.

Experimental section

Synthesis of graphene oxide (GO)

Graphene oxide was synthesized by literature procedure. [27] In a typical experiment, 0.5 g of graphite nano powder was taken in a RBF containing 25 mL of 98% H_2SO_4. The RBF was fitted in an ice bath to maintain the temperature of 0-4 ºC. 0.5 g of sodium nitrate was added into the RBF followed by slow addition of 3 g of potassium permanganate ($KMnO_4$) with constant stirring at 0-4 ºC. After that, the above mixture was transferred to a water bath maintained at 35 ± 5°C and stirred for another 1 h. Then 40 mL of milli-Q water was slowly added, and the temperature was raised to 90 ± 5°C for 30 min with continuous stirring. Finally, 100 mL of milli-Q water was added, followed by slow addition of 3.0 mL of H_2O_2 (30% v/v). When the colour of the solution changed from dark brown to yellowish, it was centrifuged and the residue was washed firstly with 5% HCl then 0.3% H_2O_2 was added followed by addition of pure milli-Q water to remove all the impurities from the oxidized graphite. Finally the residue was collected and freeze dried to obtain GO.

Simultaneous synthesis of HMF and reduced graphene oxide (rGO)

In an optimized reaction procedure, 250 mg of fructose was taken in a 50 mL round bottom flask followed by the addition of 10 mL of EL, 100 mg of ChoCl and 10 mg of GO. The RBF was placed under microwave synthesizer (Star-S, Milestone, Italy) and the reaction mixture was irradiated with 600 W at 100°C for 30 min. After that, the reaction mixture was allowed to cool at room temperature and was processed further as mentioned below.

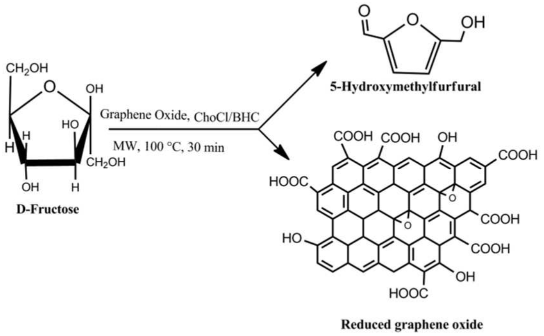
The above reaction mixture was centrifuged to separate GO from the solution. The recovered GO was washed several times with milli-Q water followed by centrifugation and three times with acetone followed by centrifugation. After that, the washed GO was dried at oven for overnight. The total recovery of modified GO was 96% (*w/w*) with respect to GO taken initially and the reduction of GO was confirmed primarily by UV measurement.

A little portion of the solution (20 μL) after recovery of rGO was diluted with HPLC grade water (1.0 mL) for the HPLC measurements to confirm the formation of HMF and to quantify it. The other portion of the solution containing EL, ChoCl and HMF was evaporated under vacuum to separate as much as EL (90% recovery) from the solution and the resulting concentrated solution was diluted with 10 mL milli-Q water and HMF was extracted from this solution by methyl isobutyl ketone (MIBK). After removing MIBK, HMF was obtained with 98% purity as confirmed by HPLC.

For the simultaneous synthesis of HMF and rGO in one pot using BHC as additive, the same procedure was followed as mentioned above except 100 mg BHC was taken instead of 100 mg ChoCl. For the synthesis of HMF and rGO from other sugar substrate (glucose, galactose, mannose, sucrose), the same procedure was followed as described above except 250 mg of respective sugar was taken as a substitute for fructose.

Results and discussion

Various sugars namely D-fructose, D-glucose, D-mannose, D-galactose and D-sucrose were used as substrates for the production of HMF using ethyl lactate as solvent under microwave irradiation (MW). GO played a role as acid catalyst [13] and choCl and BHC was used as additives in the process (Supporting Figure. S1). As shown in Table 1, various reaction parameters were optimized to achieve maximum quantity of HMF from fructose. It can be seen that, dehydration of only fructose in EL did not give formation of HMF, whereas highest molar yield of HMF (76.3%) was achieved from the dehydration of 2.5% *w/v* fructose, 0.1% *w/v* of GO, 1% *w/v* of choCl at 100 ºC in 30 min under MW irradiation. Further, HMF up to 69.6% molar yield was achieved using BHC alone. However, only 21.7% molar yield of HMF was achieved in the absence of GO indicating that it worked as catalyst in the process. Furthermore, at 0.5% concentration of additive, choCl & BHC the yield of HMF was 53% and 64% respectively. Upon increasing the additive concentration up to 1% the yield of HMF increased significantly and further increment of additive concentration resulted decrease in the HMF yield as can seen from the Table 1. At higher concentration of additive, HMF may degrade to levulinic acid which is responsible for the observed reduction in the HMF yield. Taking inference from these observations, the reaction parameters of entry 9 in Table 1 was chosen as an optimized reaction conditions for the production of HMF from fructose (Scheme 1).



Scheme 1: Simultaneous production of HMF and reduced graphene oxide from fructose promoted by graphene oxide using choline chloride and betaine hydrochloride as additives.

It can be observed from Figure 1, that the yield of HMF was highest when fructose was used as substrate followed by glucose, sucrose, mannose and galactose. The least conversion in the case of galactose is due to the dehydration of the sugar to tagatose, [4] unlike the rest of the sugars which dehydrated to HMF (Supporting Scheme S3). Further, it was observed that the additives (ChoCl and BHC) affected the yield of the produced HMF (supporting Figure S2). When 1% of ChoCl was used the highest HMF produced was 76.3%, while the production was 69% with similar amount of BHC. The HMF formed was quantified using HPLC and the chromatograms obtained with various reaction parameters are shown in Supporting

Figure S3. EL used in the process was recycled and in the ^{1}H NMR studies, the peaks of impurities were absent indicating purity of the recycled solvent (Supporting Figure S4), which was successfully re used for HMF production.

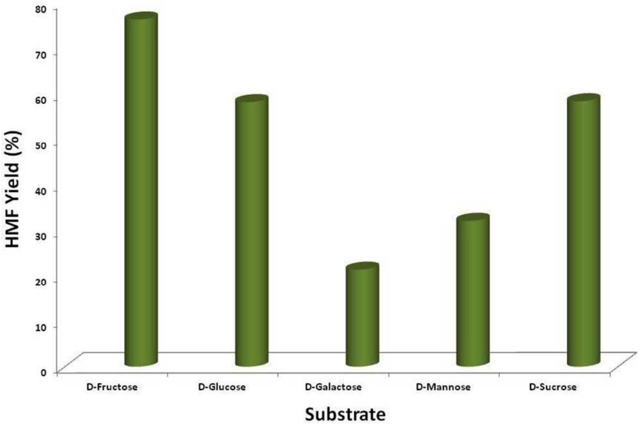


Figure 1: Effect of substrate concentration on HMF yield under MW irradiation (600 W) at 100 °C using GO as acid catalyst, EL as solvent.

Table 1 : Optimization of reaction conditions to achieve maximum HMF yield from fructose

Entry[a]	Fructose concentration (% w/v)	GO (% w/v)	ChoCl (% w/v)	BHC (% w/v)	Ethyl lactate (mL)	Reaction temperature (°C)	Reaction time (min)	Molar yield of HMF (%)[b]
1	2.5	---	---	---	10.0	100	30	0.0
2	2.5	0.1	---	---	10.0	100	30	12.0
3	2.5	---	1.0	---	10.0	100	30	18.4
4	2.5	---	---	1.0	10.0	100	30	21.7
5	2.5	0.1	1.0	---	10.0	100	10	61.5
6	2.5	0.1	1.0	---	10.0	100	20	65.8
7	2.5	0.1	1.0	---	10.0	80	30	51.5
8	2.5	0.1	1.0	---	10.0	90	30	58.9
9	2.5	0.1	1.0	---	10.0	100	30	76.3
10	2.5	0.1	1.0	---	10.0	110	30	60.0
11	2.5	0.1	---	1.0	10.0	80	30	55.6
12	2.5	0.1	---	1.0	10.0	90	30	64.9
13	2.5	0.1	---	1.0	10.0	100	30	69.6
14	2.5	0.1	---	1.0	10.0	110	30	54.8

[a]Reaction condition= Microwave irradiation, 600 W power; [b] yields are based on HPLC quantification. GO=Graphene oxide; ChoCl= Choline chloride; BHC= Betaine hydrochloride

GO present in the above reaction mixture after the completion of the reaction was isolated by ultra centrifugation and purified by repeated washing with water and acetone (total recovery of modified GO was 96% *w/w* with respect to GO taken initially). The brownish colour solution containing GO turned black upon above reaction as shown in Figure 2 showing visual evidence for the conversion of GO to rGO. Due to the π – π transitions of aromatic C-C bonds which present in GO, an absorbance at λ_{max}= 230 nm was observed in pristine GO. The different GO samples which were recovered during the course of HMF synthesis showed λ_{max}= ~265 nm. This red shifted absorbance maxima indicated the reduction of pristine GO (Figure 2). [27] Although for all the samples the λ_{max}= 230 nm was shifted to λ_{max}= 265 nm, but superior reduction was observed for the systems where choCl was used as additive and sucrose, fructose and glucose were used as substrates (rGO-ChoCl-Sucrose, rGO-ChoCl-Fructose and rGO-ChoCl-Glucose) (Please refer to supporting Table S1 for the abbreviations).

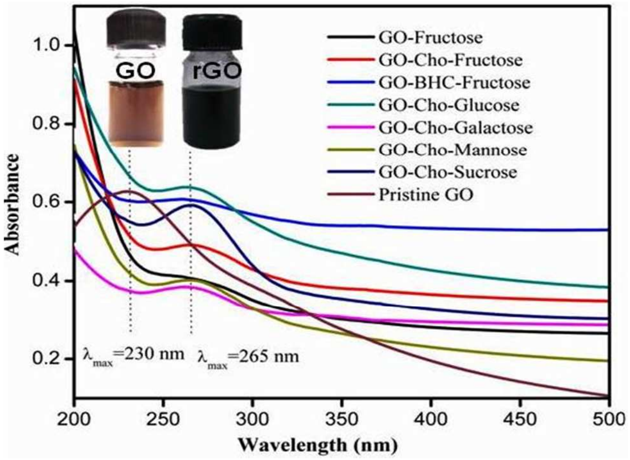


Figure 2: UV-Vis spectra of reduced GO in presence of various additives and substrates.

The reduction of GO during the course of HMF synthesis was also confirmed by FT-IR spectra (Figure 3). Various oxygen functionalities in the GO structure were observed in the FT-IR spectra. The bands at 3437 cm^{-1} and 1040 cm^{-1} can be ascribed due to C-OH vibration whereas the bands at 1729 cm^{-1} is due to C=O stretching vibration of carbonyl of COOH functionality. The peak position at 1627 cm^{-1} and 1580 cm^{-1} are due to Sp^2 hybridized in plane stretching vibration and the absorption bands at 1360 cm^{-1} and 1220 cm^{-1} are responsible for C-O-C stretching vibration of epoxide functionalities present in the GO moiety. [28] As can be seen from the figure that the peak positions for C=O and C-O-C reduced significantly in the case of GO obtained from GO-ChoCl-Fructose sample as compared to the GO obtained from GO-Fructose sample. The FT-IR spectra for reduced GO in presence of sucrose and pristine GO is shown in supporting Figure S5 and S6 respectively.

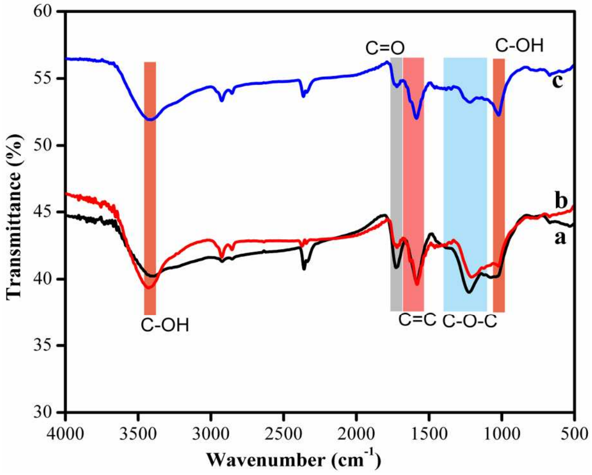


Figure 3: FT-IR spectra of (a) GO-Fructose, (b) GO-BHC-Fructose and (c) GO-ChoCl-Fructose

The X-ray diffraction (XRD) patterns of pristine GO exhibited a characteristic peak of (001) at 2θ = 11.29 ° having interlayer spacing of 7.68 Å, ensured the presence of oxygen functionality after oxidation of graphite. The peaks of (002) at 2θ = 26.46 ° and (010) at 2θ = 42.18 ° are due to original graphite peaks. [29] The XRD pattern of GO (GO-Fructose) obtained after HMF synthesis using GO as catalyst showed a new peak broadening to (002) at $2\theta = 22.96\ ^{0}$, having much lower interlayer spacing of ~ 4.40 Å, but the peak of (001) at $2\theta = 11.29\ ^{0}$ with interlayer spacing ~ 7.78 Å also remained which indicated only partial reduction of GO (Table 2). The similar trend was observed for GO obtained during HMF synthesis from fructose using BHC as additive (GO-BHC-Fructose) (supporting Figure S7). Whereas the GO obtained during HMF synthesis using ChoCl as additive, showed mainly the peak broadening of (002) at $2\theta = 25.41^{0}$ having d-spacing = 3.9 Å (0.39 nm) indicates complete reduction of GO (supporting Figure S8).

Table 2: d-Spacing of pristine GO and reduced GO obtained during the course of HMF synthesis using different sugars in presence of choline chloride/betaine hydrochloride under optimized microwave condition (100 ^{0}C, 600 W and 30 minutes).

Sample ID	d-spacing (Å)	Reference
Pristine GO	7.68	Present Study
Hydrazine reduced GO	3.86	Park et al., 2009 [30]
GO-Fructose	4.40	Present Study
GO-BHC-Fructose	4.00	Present Study
GO-ChoCl-Fructose	3.91	Present Study
GO-ChoCl-Glucose	4.17	Present Study
GO-ChoCl-Galactose	3.94	Present Study
GO-ChoCl-Mannose	4.02	Present Study
GO-ChoCl-Sucrose	4.14	Present Study

To further confirm the reduction of GO, the micro-Raman spectra of the samples were recorded. The peak for HGO at G band (1594 cm^{-1}) was down shifted to 1583 cm^{-1} indicating reduction of GO (Figure 4). [31] Further, HGO exhibited D/G intensity ratio of 0.87 and after the reaction the ratio was changed to 0.94 indicating formation of more crystalline domains after the reduction and supported the reduction of GO described above.

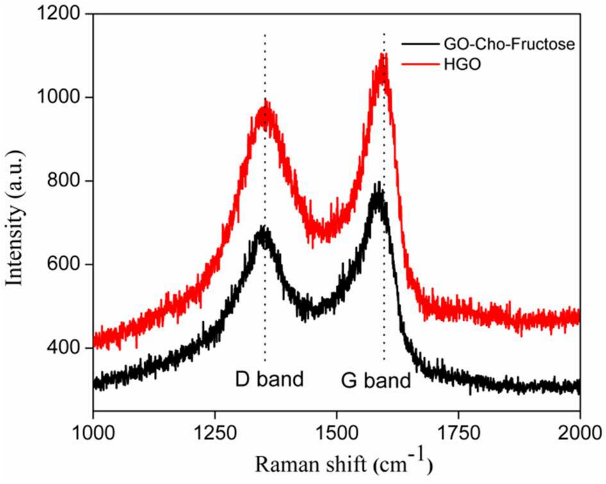
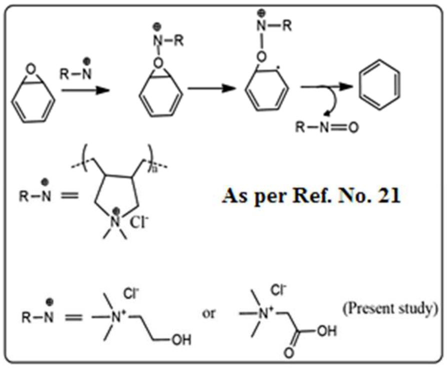


Figure 4 : Raman spectra of Hummers GO (red) and GO reduced in presence of fructose and choline chloride (black).

The loss of CO, CO_2 and water molecule from carboxylic and hydroxyl functionality present in the GO sheets, took place in the temperature range ~120 ^{o}C to ~265 ^{o}C (supporting Figure S9). In this temperature range 30.8% and 18.5% weight loss were observed for GO-Fructose and GO-BHC-Fructose respectively which indicated the partial reduction of GO as observed in XRD analysis. Whereas the weight loss of 11.0% and 9.6% were observed in the above mentioned temperature range for GO-ChoCl-Fructose and GO-ChoCl-Sucrose respectively, which confirmed almost complete reduction of GO for these samples.



Scheme 2 : A plausible mechanism for the opening up of epoxides ring of graphene oxide.

TEM images of GO prepared by Hummers method and reduced by hydrazine showed presence of 32 layers with interlayer distance of 0.39 nm (Supporting Figure S10). The GO reduced using fructose as substrate and without any additive showed presence of 19 layers with interlayer distance of 0.36 nm (Figures 5a and 5b). However, GO reduced using choCl as additive and fructose as substrate showed presence of 6 layers with interlayer distance of 0.34 nm (Figures 5c and 5d). The lesser number of sheets is due to exfoliation of rGO in presence of the additive. The presence of choCl facilitated the formation of rGO with few layers. Due to the importance of few layered graphene in applications such as selective gas separation, [32] it is considered of immense interest to prepare graphene having single or few layers. However, the rGO obtained for other sugars such as galactose, sucrose and mannose had 12, 14 and 17 layers respectively (Supporting Figure S11a-c). Moreover, when BHC was used as additive and fructose was used as substrate then 10 layered rGO was formed (Supporting Figure S12).

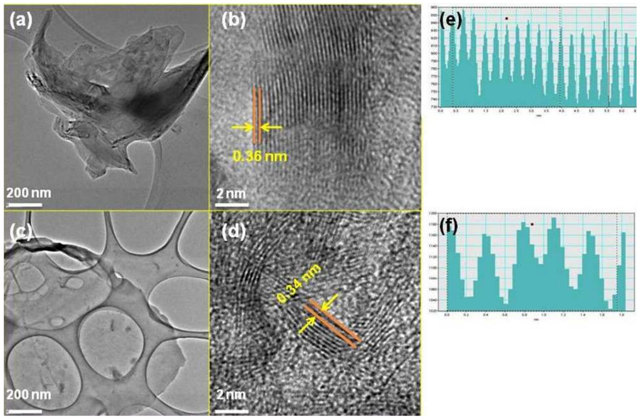


Figure 5: TEM images (a,b) graphene oxide reduced in presence of fructose and (c,d) graphene oxide reduced in the in presence of fructose and choline chloride.

A tertiary ammoniaum salt, diallyldimethylammonium chloride (PDDA) has been reported to adsorb through π-π and electrostatic interactions which induces electrostatic repulsion between the graphene nanosheets and prohibited aggregation in aqueous suspensions.[21] It was hypothesized that the inherent positive charge of PDDA containing N$^+$ groups, may hit the oxygen atom of epoxide in graphene oxide which stimulates a ring opening reaction facilitating a lone electron on the α-carbon and following elimination of the nitroso group to afford formation of an olefin (Scheme 2). In a similar manner, the choCl and BHC used in the present study interacted with the nano sheets of GO resulted electrostatic repulsion among them and perhaps reason behind the lowering of the number of sheets of rGO (Scheme S2). However, BHC exists in zwitterionic form in solution (Supporting Figure S13). The presence of anion in the structure resulted dual competitive interaction with GO and hence reduction efficiency of graphene oxide was less when BHC was used as additive instead of choCl and resulted formation of more layers (10 layers).

Furthermore, it is reported that simple sugars like glucose has the ability to form chemical bond with the carbon of GO as shown in supporting Figure S6. [23] This type of chemical bonding is similar to phosphate group binding with glucose. [33] This type of chemical bonding between sugar and GO carbon resulted steric interaction which prevent π-π stacking interaction among the graphene sheets and promoted the conversion of stacking GO structure to few layered GO nanosheets.

Conclusions

In summary, we have demonstrated a facile integrated path way for the simultaneous dehydration of simple sugars to 5-hydroxymethyl furfural and reduction of graphene oxide, which was used as acid catalyst in the process in a bio-based green solvent, ethyl lactate. The solvent was recycled and successfully reused in the process. The molar yield of HMF was as high as 76.3% when fructose was used as substrate and choline chloride as additive. The reduced graphene oxide obtained herewith had lower number of sheets in comparison to GO reduced by conventional method.

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Notes and references

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