Supplementary Information for:

Integrating Reduced Graphene Oxide with Microwave-Subcritical Water for Cellulose Depolymerization

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1. **C1s and O1s XPS spectra of graphene oxide (GO), rGO1 (microwave-hydrothermal reduced GO) and rGO2 (thermally annealed GO)**

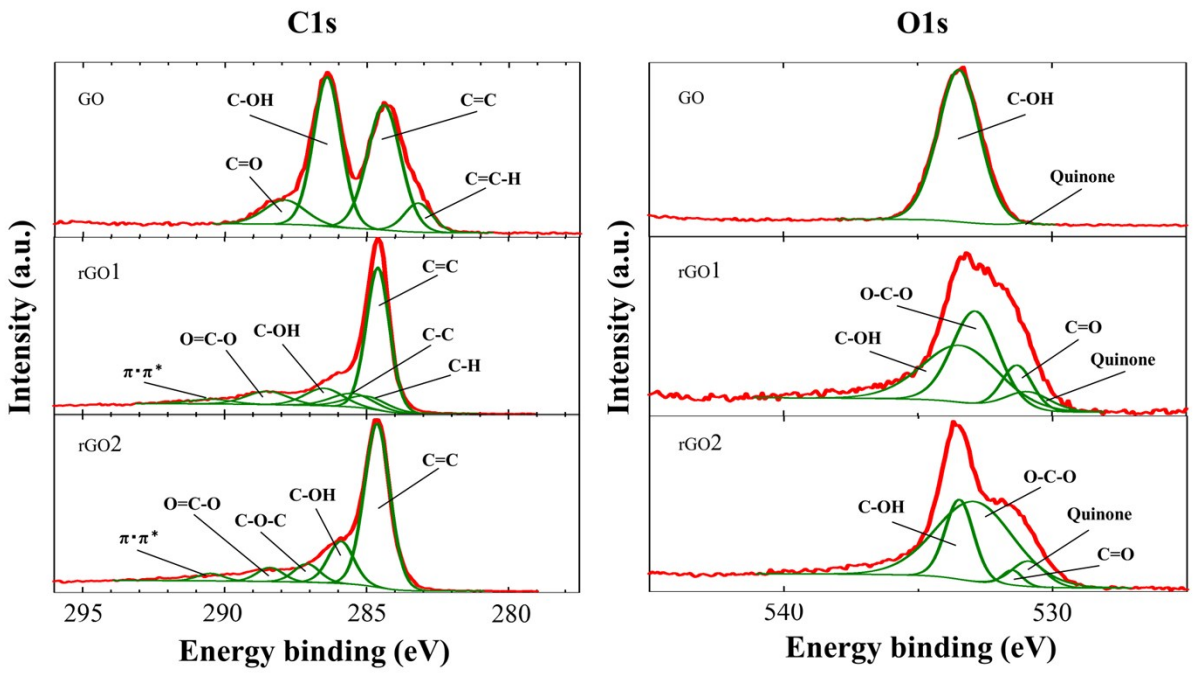

Fig. S1. X-ray photoelectron spectroscopy for graphene oxide (GO), microwave reduced graphene oxide (rGO1) and thermally annealed graphene oxide (rGO2).

2. **Table S1. Combustion Elemental Analysis data**

	C%	H%	N%	S%	C/O
GO	44.1	2.06	0.43	1.96	0.86
rGO1	75.34	0.51	0.33	0	3.16
rGO2	71.78	0.50	0.48	0	2.64

3. Representative HPLC spectra

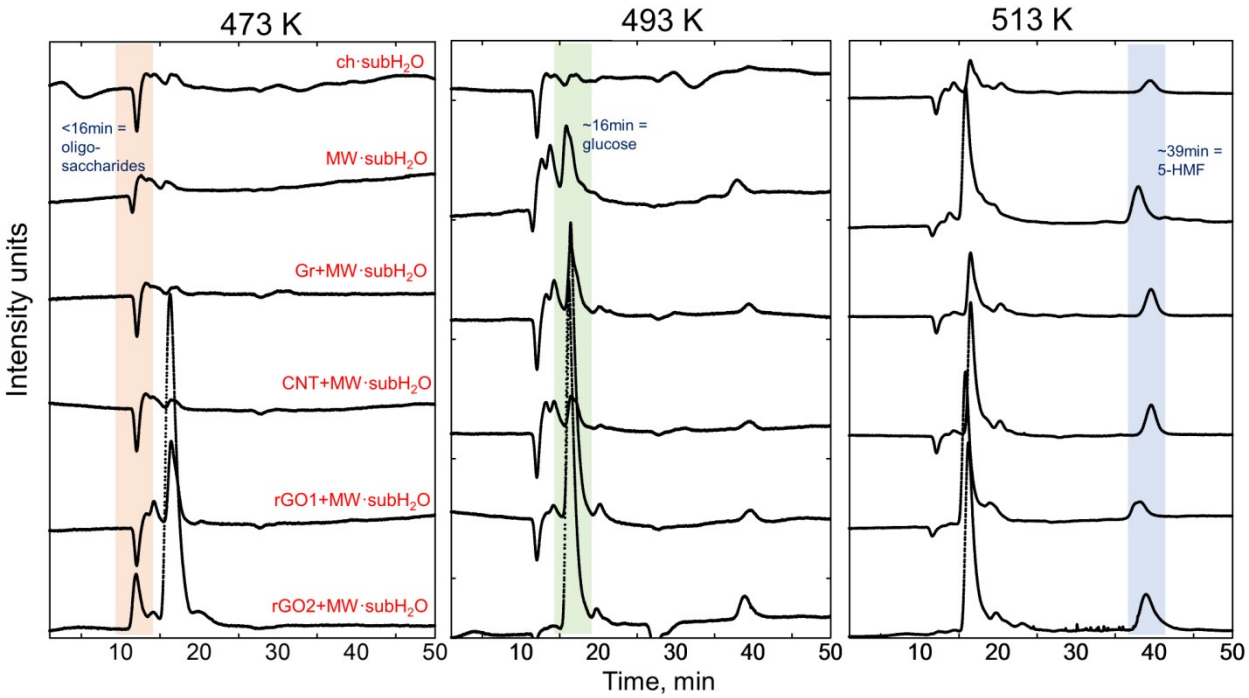

Fig. S2. Representative high performance liquid chromatography (HPLC) spectra for the combinations used in this study.

4. **Table S2: Product distribution table in wt% yields**

				Yield (wt%)		
Entry	Carbon catalyst	Heating type	Temperature (K)	Oligo saccharides	Glucose	5-HMF
1	--	Ch	473	-	0	-
2	--	Ch	493	0.8	0.3± 0.1	-
3	--	Ch	513	3	6.75 ± 0.6	4.5
4	--	MW	473	-	0	-
5	--	MW	493	0.2	2.8 ± 0.2	-
6	--	MW	513	0.15	11.5 ± 0.1	8.3
7	rGO1	ch	513		38.6 ± 4.3	
8	rGO1	MW	473	-	6.1	-
9	rGO1	MW	493	-	15 ± 4.2	-
10	rGO1	MW	513	-	36 ± 4	12.9
11	rGO2	ch	513		16	
12	rGO2	MW	473	-	6.5	-
13	GO2	MW	493	-	38 ± 7	4.4
14	GO2	MW	513	-	65.5 ± 3.7	12.8
15	CNT	MW	473	-	0.3 ± 0.1	-
16	CNT	MW	493	3.7	3.4 ± 1.4	-
17	CNT	MW	513	1.1	27.4 ± 1.6	12.2
18	Gr	MW	473	-	0.2 ± 0.1	-
19	Gr	MW	493	3.6	3.9 ± 1	-
20	Gr	MW	513	0.9	12.9 ± 0.2	10.1

Ch : conventional heating; MW : microwave irradiation; rGO1 : microwave - reduced graphene oxide; rGO2 : thermally annealed reduced graphene oxide; CNT : carbon nanotubes; Gr: graphite
Conditions: cellulose 200 mg, rGO 1 and 2 200 mg, 10 ml distilled water, 200 W, holding time 5 min

5. Glucose production from cellulose by various carbon materials

In this summary, only carbon materials which served as main catalyst has been considered. Those carbon materials that acted as support or scaffold has been excluded.

Table S3: Summary of glucose production from cellulose by various carbon materials

Entry	Catalyst	Substrate	Intensification technique	Reaction temperature	Reaction time	Yield	Reference
1	Reduced graphene oxide	Microcrystalline cellulose	Microwave irradiation (200 W)	240^{O}C	5 min	66%	This method
2	Graphene oxide	Microcrystalline cellulose	Microwave irradiation (200 W)	180^{O}C	60 min	61%	Mission et al., 2017
3	Air oxidized cellulose + HCl	Woody biomass (Eucalyptus)	Mix-milling (2h)	Heating 488 K then lowered to 298 K	1 h	78-82%	Kobayashi et al., 2016
4	Sulfonated Magnetic Carbonaceous acid (Pyrolyzed glucose and magnetic Fe3O4 nanoparticles)	Ball-milled cellulose	Microwave irradiation	190 ^{O}C	3.5 h	25.3%	Su et al., 2015
5	Sucralose-derived solid acid catalyst with –Cl and –SO3H functionalities	Microcrystalline cellulose	Ionic liquids	120 ^{O}C	24 h	55%	Hu et al., 2014
6	Sulfonated activated carbon	Ball-milled cellulose	-	423 K	24 h	41.4	Onda et al., 2009
7	Sulfonated Magnetic reduced graphene oxide (Fe3O4-RGO-SO3H)	Microcrystalline cellulose	-	150^{O}C	5 h	28%	Yang et al., 2015
8	Biomass char sulfonic acid (BC-SO3H)	Microcrystalline cellulose	Microwave irradiation (350 W)	90^{O}C	1 h	16.7	Wu et al., 2009
9	Amorphous carbon + SO3H+ COOH + OH	Microcrystalline cellulose	-	373 K	3h	4% + 64% β 1,4 glucan	Suganuma et al
10	Activated carbon + HCl	Microcrystalline cellulose	Mix milled	453 K	1 h	88%	Kobayashi et al.`

6. Spent rGO2 characterization

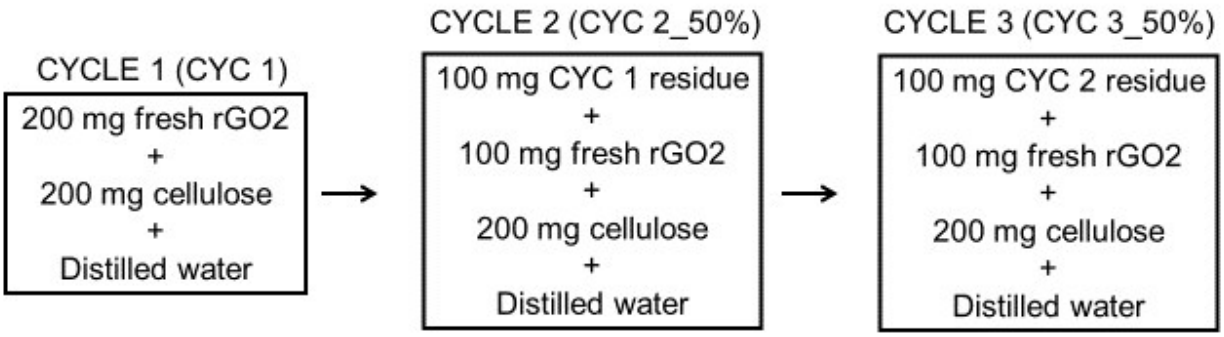

Figure S3. Catalyst reuse scheme

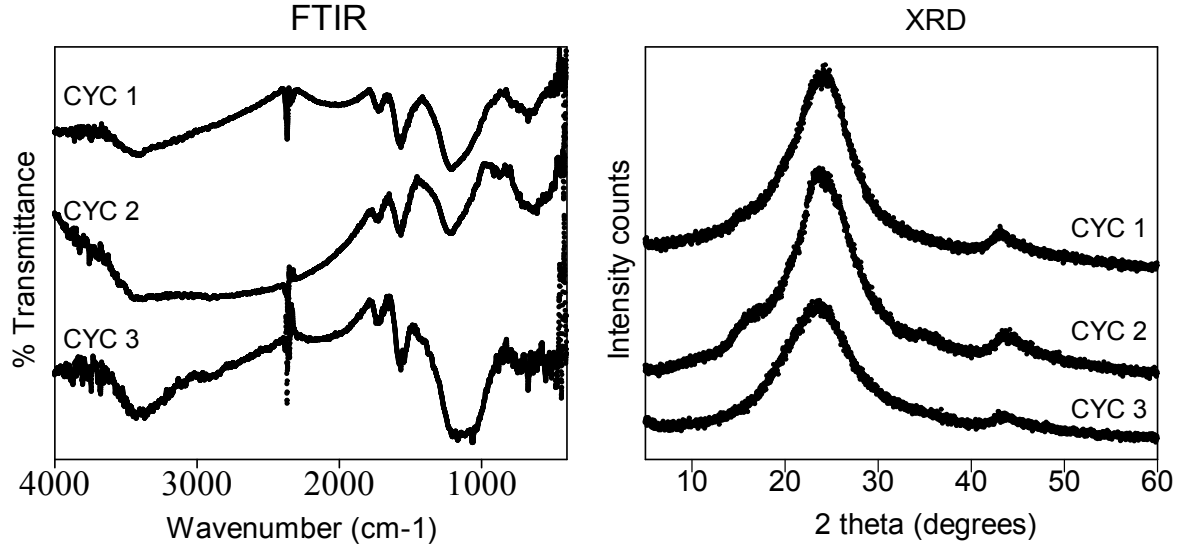

Figure S4. Fourier transform infrared spectra (FTIR, left) and X-ray diffractograms (XRD, right) spectra of rGO2 utilized in several cycles: CYC1 – first cycle, pure fresh rGO2; CYC2 – 50% residue from CYC1 and 50% fresh rGO2; CYC 3 – 50% residue from CYC2 and 50% fresh rGO2

Table S4: C1s and O1s positions and intensities obtained by deconvolution

Sample	Elemental Composition (%)		C1s Deconvolution							O1s Deconvolution					
Code	C	O	C=C-H	C=C sp^2	C-H	C-C sp^3	C-OH	C-O-C	C=O	O=C-O	π · π*	Quinone	C=O	O-C-O	C-OH
CYC1	65.9	34.1	-	66.6	-	-	17.1	7.5	-	5.7	3.1	8.8	3.1	64.4	23.7
CYC2	79.1	20.9	-	56.51	-	-	23.41	-	15.68	-	4.40	4.34	1.64	5.11	88.92

CYC3	76.8	23.2	-	48.64	-	-	18.14	-	16.60	11.58	5.04	3.43	-	-	96.57

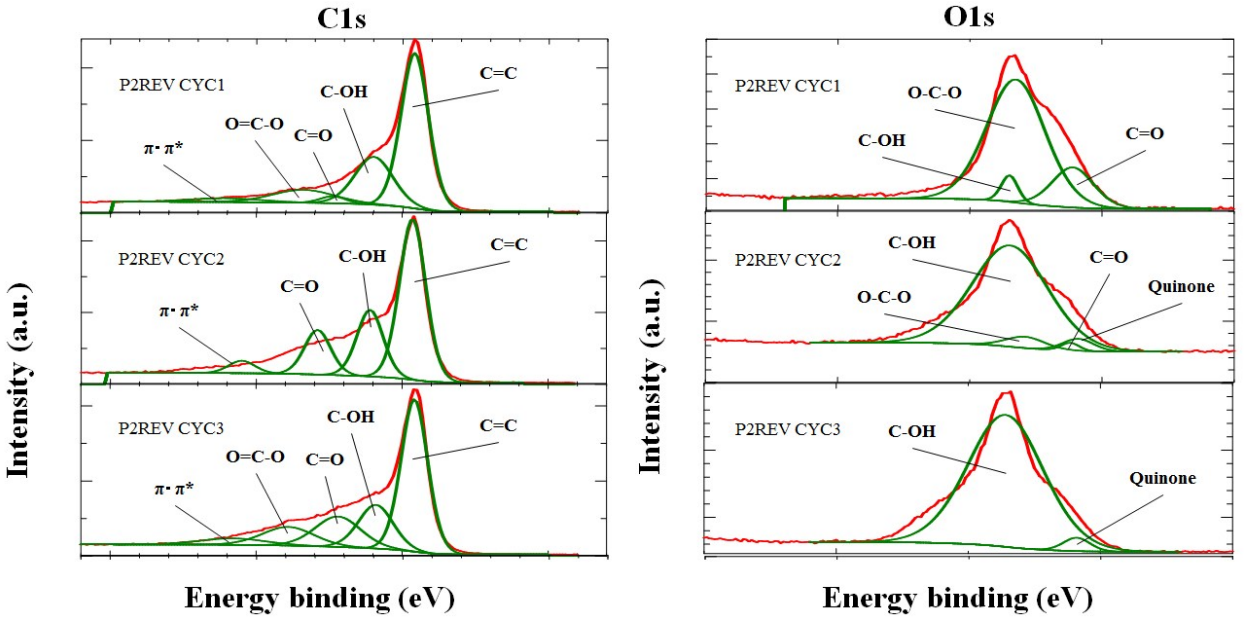

Fig. S5. X-ray photoelectron spectroscopy of rGO2 utilized in several cycles: CYC1 – first cycle, pure fresh rGO2; CYC2 – 50% residue from CYC1 and 50% fresh rGO2; CYC 3 – 50% residue from CYC2 and 50% fresh rGO2

7. Particle size analysis of oligosaccharides

In the proposed reaction mechanism, it was suggested that β-glucans or oligosaccharides could be trapped in between the nanopores and nanovoids of the rGO2 which could have facilitated faster hydrolysis reaction. In order to support this suggestion, we have measured the particle size of cellobiose, which is the most detected oligosaccharides or β-glucans, as per HPLC analysis.

We have prepared a solution of cellobiose and measured the particle size using dynamic light scattering technique (DLS; Zetasizer Nano ZS Malvern Instruments, Ltd. UK). A representative histogram distribution of the particle size measurement is shown below (Fig. S5), and we found out that the range of cellobiose particle size is 0.6 to 5560 nm with an average of 56 nm. With nanopore average of about 28 nm, it is possible that cellobiose having particle size at the lower segment of the distribution could be trapped into the nanovoids as suggested.

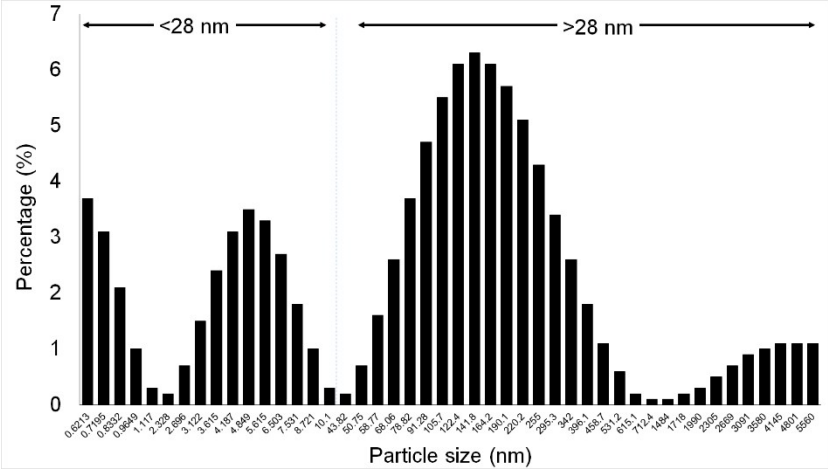

Figure S6. Representative histogram distribution of particle size for cellobiose as measured using Zeta-sizer Nano

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