

## Graphene-based Catalysts in Synergy with Microwave Irradiation for Natural Polysaccharide Depolymerization

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Non-edible biomass, which contains valuable macromolecules and polysaccharides, is of increasing interest as a sustainable, renewable and environment-friendly alternative to fossil fuels as an energy and oxychemicals resource. One of the key pathways towards biomass utilization is to convert major polysaccharides into their constituent monomers, for easy processing. This pathway involves the cleaving of glycosidic bonds through the hydrolysis process and significant attention has focused onto developing economically acceptable and simplified processes. This work, as illustrated in Fig. 1, summarizes the application of graphene-based catalysis in synergy with microwave irradiation (MW) for model biomass (i.e. cellulose in terrestrial and fucoidan in aquatic biomass into glucose and fucose, respectively) depolymerization, using water as the sole solvent and without pretreatments.

In part 1, the synergy of MW and graphene oxide (GO) was used to depolymerize microcrystalline cellulose (MCC). This was made possible by the cooperation amongst the oxygenated functionalities on the surface of GO that disrupted the crystallinity, ushering crystalline-to-amorphous transformation. MW enabled short heating times and conformational changes that led to selective glucose formation in as short as 30 s. The surface attrition mechanism was proposed to best describe the depolymerization process. In part 2, reduced GO with fewer oxygenated functionalities was integrated with MW-subcritical water, whereby the hydronium/hydroxyl ion concentration due to the auto-dissociation of water, is large enough to facilitate acid-base reactions. Random scission mechanism was proposed to best explain the depolymerization process. In part 3, cellulase was immobilized onto GO with an overall aim to operate at lower temperature. Cellulase, bearing hydroxyl binding and carboxylic catalytic sites, can suitably replace the oxygenated functionalities. MW is surmised to activate the enzymes via electron mobility on the GO surface.

In addition, the synergy of GO and MW was applied to fucoidan depolymerization and fatty acids esterification. The highest fucose yield of 54% was achieved at fucoidan: GO: water ratio of 5:5:1, 15 min reaction time, and 600 W. Meanwhile, in the esterification process, 99.2 % fatty acid methyl ester was achieved at 3 min, methanol/oleic acid molar ratio of 12. In the proposed reaction mechanism, it is supposed that aside from being a proton donor, the carbon backbone of GO has potentially adsorbed the oleic acid which enabled the highly reactive methanol to easily access the oleic acid's carboxylate head towards alcoholysis.

Overall, the synergy of graphene-based carbocatalysts in synergy with MW provided an important strategy for polysaccharide depolymerization. The findings reported herein provided significant insights on the properties and usage of graphene-based derivatives as carbon based catalyst under MW. The individual and synergistic roles of graphene based catalysts, microwave and water has also been elicited.

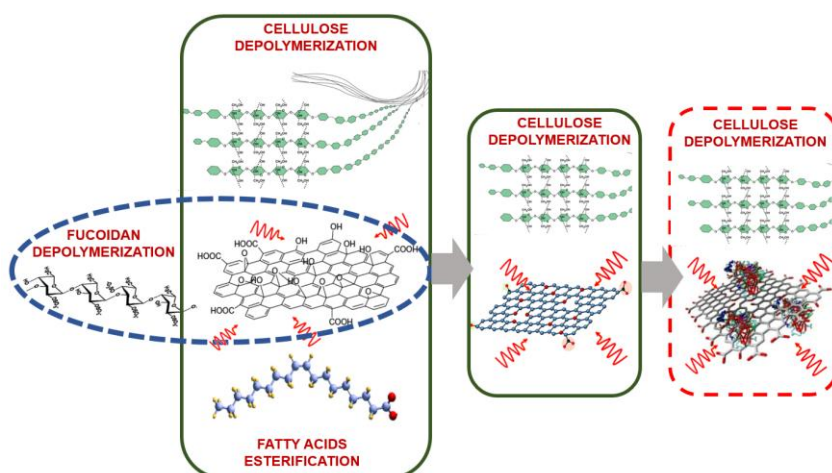


Fig. 1. Schematic representation of the contents of the study

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