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Supplementary Information for:

Carbocatalysed hydrolytic cleaving of the glycosidic bond in fucoidan under microwave irradiation

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I. Experimental methods

a. Materials

Graphene nanoplatelets, and fucoidan from *Undaria pinnatifida* (F-UP) and from *Fucus vesiculosus* (F-FV) were purchased from Sigma Aldrich (USA). Graphite powder, sulfuric acid (98%), sodium nitrate, potassium permanganate and hydrogen peroxide (30%) were all supplied by Wako Pure Chemicals Industries (Osaka, Japan). Multiwalled carbon nanotubes were obtained from Sigma Aldrich (USA). All chemicals were used as received.

b. Graphene oxide synthesis and characterization

The GO used in this study was synthesized in-house following the modified Hummer's method that was described in full detail in previous publications.^{1,2} The resulting GO dispersion from the oxidation-exfoliation of graphite was dried and milled to obtain the GO powder. GO dispersion for F-FV experiments were obtained through partial evaporation until the desired concentration was reached. The resulting GO powder was subjected to various characterization techniques such as FTIR and XRD. Reduced graphene oxide (rGO) was prepared via thermal annealing under nitrogen atmosphere in accordance to the procedure reported in previous studies.^{3,4}

c. Catalytic depolymerization method

The depolymerisation of F-UP in water was performed using the Microwave Assisted Reactor System apparatus (MARS 6, CEM Matthews NC Company, USA) and XP1500 teflon closed vessel. Meanwhile, the depolymerization of F-FV was carried out in a microwave-microreactor (Shikoku Instrumentation Co., Ltd., Kagawa, Japan) under atmospheric conditions and condenser for reflux to avoid the loss of reactant due to vaporization. Both reactors were equipped with a fiber optic thermocouple and a pressure sensor. Stirring was introduced into the system using a magnetic bar. Samples were cooled down after each reaction and subjected to filtration to separate the solid components and the hydrolysate.

d. Hydrolysate Characterization

The hydrolysates were subjected to high performance liquid chromatography (HPLC) for fucose quantification and gel permeation chromatography (GPC) for polymer chain characterization. HPLC analyses were performed with a Shodex Sugar SH1011 column at 333 K with 3 mM HClO4 aqueous solution as the eluent supplied at 0.5 ml/min and with a refractive index (RI) detector. Samples were filtered through a 0.45 μ m syringe, 10 μ l of which is injected into the system. Fucose yield was calculated using the following equation:

Fucose yield, wt% = $\frac{Fucose in hydrolysate \times 0.89}{Initial fucoidan loading} \times 100\%$

The GPC analysis was performed using Shodex OHpak SB 803HQ operated at 333 K with 0.1 M CaCl₂ as the eluent supplied at of 0.5 ml/min and with an RI detector. The elution time of Shodex P-82 pullulan standards (6.1, 9.6, 21.1, 47.1 and 107 kDa) with known molecular weights were compared to that of the initial substrate fucoidan and hydrolysates.

II. Molecular weights from gel permeation chromatography



Fig. S1 Gel permeation chromatogram for Shodex P-82 Pullulan standards (MW of 6.1 to 107 kDa) in comparison with fucoidan from *U. pinnatifida* (61 kDa) and from *F. vesiculosus* (1.1 kDa)

III. Mechanisms of the hydrolysis of fucoidan and cellulose

Quantum calculations were performed using the semi-empirical PM3^{5,6} method in the gas phase, as implemented in GAMESS (US)^{7,8}, to determine the mechanisms of the hydrolysis of fucoidan and cellulose. The representative structures were constructed from three repeating units of sulphated fucose and glucose for fucoidan from *Fucus vesiculosus* (F-FV) and cellulose, respectively. The stability of each resulting intermediate along the reaction pathway was confirmed by the absence of an imaginary frequency. On the other hand, the structure of a transition state was verified by the presence of a single imaginary frequency and by the generation of the intrinsic reaction coordinate (IRC)⁹ between the corresponding reactant and product states. The starting structures were generated using Avogadro¹⁰ and the output of GAMESS (US) was analysed using MacMolPlt¹¹. The mechanisms for the hydrolysis of F-FV and cellulose are shown in **Error! Reference source not found.** and **Error! Reference source not found.**



Fig. S2 Mechanism of the hydrolysis of fucoidan from *F. vesiculosus*. The lengths in ångströms of the bond interchanges in the transition states are shown in blue.



Fig. S3 Mechanism of the hydrolysis of cellulose. The lengths in ångströms of the bond interchanges in the transition states are shown in blue.



IV. Gel permeation results for blank experiments: without GO and with MW

Fig. S4 Gel permeation chromatograms of the hydrolysates resulting from the depolymerization of fucoidan from *U. pinnatifida* without graphene oxide and without microwave. [Without catalyst conditions: 50 mg fucoidan, 10 ml water, 200 W, 120° C, 15 min; Without microwave conditions: 50 mg fucoidan, 10 ml water, 200 W, 120° C, 15 min; Without microwave conditions: 50 mg fucoidan, 10 ml water, 120°C, 6 minutes to heat up + 15 min reaction time]

V. Depolymerisation of fucoidan from *U. pinnatifida* using graphene and multiwalled carbon nanotubes coupled with trace amounts of different acids

To investigate the contribution of acids in the depolymerization of fucoidan, control experiments employing graphene and multiwalled carbon nanotubes with trace amounts of sulfuric, formic, and acetic acid were performed. The concentration of the acids were deduced from the amount of functional groups quantified on the surface of GO. The GPC chromatograms (**Error! Reference source not found.**) show that the combination of either graphene or MWCNT with the trace acids showed peaks that were slightly different from those exhibited by graphene-, MWCNT-, GO-, or rGO-catalysed depolymerisation. The peaks were rather broad with tailings indicating that the oligomers were of non-uniform chain length with molecular weights ranging between 2.9 and 3.7 kDa. As shown in **Error! Reference source not found.**, the highest fucose yield of 72.5wt % was achieved only when about 188 μ L of H₂SO₄ in combination with graphene was used. While this value is about 200 times bigger than the amount of sulfo group present in GO, it still has not proceeded to complete depolymerization. This suggests that a single type of acid is not enough to completely depolymerize fucoidan.



Fig. S5 Gel permeation chromatograms of the hydrolysates from the depolymerisation of fucoidan from *U. pinnatifida* using different catalysts: a) graphene + 1 μ L H₂SO₄, b) graphene + trace amounts of sulfuric acid, formic acid, and acetic acid, c) multiwalled carbon nanotubes + trace amounts of sulfuric acid, formic acid, and acetic acid, d) graphene + 188 μ L H₂SO₄, and e) 30 μ L H₂SO₄



Fig. S6 Yields of fucose from the depolymerisation of fucoidan from *U. pinnatifida* using different catalysts: a) graphene + 1 μ L H₂SO₄, b) graphene + trace amounts of sulfuric acid, formic acid, and acetic acid, c) multiwalled carbon nanotubes + trace amounts of sulfuric acid, formic acid, and acetic acid, d) graphene + 188 μ L H₂SO₄, and e) 30 μ L H₂SO₄

VI. Effect of temperature and reaction time in the depolymerisation of fucoidan from *U. pinnatifida*



Fig. S7 High performance liquid chromatograms of the hydrolysates resulting from the depolymerization of fucoidan from U. pinnatifida under different temperatures and reaction time [Reaction conditions: 50 mg fucoidan, 50 mg catalyst, 10 ml water, 200 W]

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