

# Supplementary materials

## Supplemental Methods

- 1 SEM observation
- 2 TEM observation
- 3 Determination of sulfate group
- 4 Determination of sulfated polysaccharide

## Supplemental Table

**Supplemental Table S1.** Relative contents of different oligosaccharides produced by photocatalytic degradation

## Supplemental Figures

**Supplemental Figure S1.** SEM images of TiO<sub>2</sub>. 100,000× TiO<sub>2</sub> (a); 50,000 × TiO<sub>2</sub> (b); 30,000 × TiO<sub>2</sub> (c); 10,000 × TiO<sub>2</sub> (d).

**Supplemental Figure S2.** TEM images of TiO<sub>2</sub>. 40,000× TiO<sub>2</sub> (a); 80,000 × TiO<sub>2</sub> (b); 150,000 × TiO<sub>2</sub> (c); 400,000 × TiO<sub>2</sub> (d).

**Supplemental Figure S3.** Molecular weight distribution of fucoidan degraded with 1% TiO<sub>2</sub>, 0.95% H<sub>2</sub>O<sub>2</sub> in the absence of light.

**Supplemental Figure S4.** MS<sup>2</sup> of PMP-labeled oligosaccharides from the DF-3.

**Supplemental Figure S5.** The pseudo-molecular ions of PMP-labelled oligosaccharides from the DF-3.

## Supplemental Methods

### 1. SEM observation

The surface morphologies of Titanium dioxide (TiO<sub>2</sub>) were observed by JSM-7800F scanning electron microscope (Japan Electron Optics Laboratory, Tokyo, Japan). The lyophilized powders of samples were sprayed with a thin gold layer, and fixed onto a copper stub, respectively. Then they were observed under the condition of high vacuum at the voltage of 3.0 kV.

### 2. TEM observation

The micromorphology of TiO<sub>2</sub> was observed using a JEM-2100 electron microscope (JEOL, Tokyo, Japan). The TiO<sub>2</sub> suspension (1 mg/mL) dip-coated on a 300-mesh copper grid coated with a carbon film was air-dried at room temperature before transmission electron microscopy (TEM).

### 3. Determination of sulfate group

The sulfate group content was determined by the BaCl<sub>2</sub>-gelatin turbidity method, using K<sub>2</sub>SO<sub>4</sub> as the standard. The content was calculated according to the following formula: Sulfate group content (%) =  $\left(\frac{f \times C \times d}{W}\right) \times 100$ , where in this formula, f stands for the conversion factor, C is the determined value of the sample, d is dilution ratio and W is the mass of fucoidan sample. And f should be calculated according to the following formula:  $f = w/cd$  (w: the mass of SO<sub>4</sub><sup>2-</sup>, c: the measured mass of SO<sub>4</sub><sup>2-</sup>, d: dilution ratio)

### 4. Determination of sulfated polysaccharide

The content of sulfated polysaccharide was determined by the metachromatic assay with 1,9-dimethylmethylene blue (DMB) at 525 nm by UV-visible spectrophotometer, using fucoidan as the standard. A standard curve was calculated and the corresponding content of standard deduced from the regression equation.

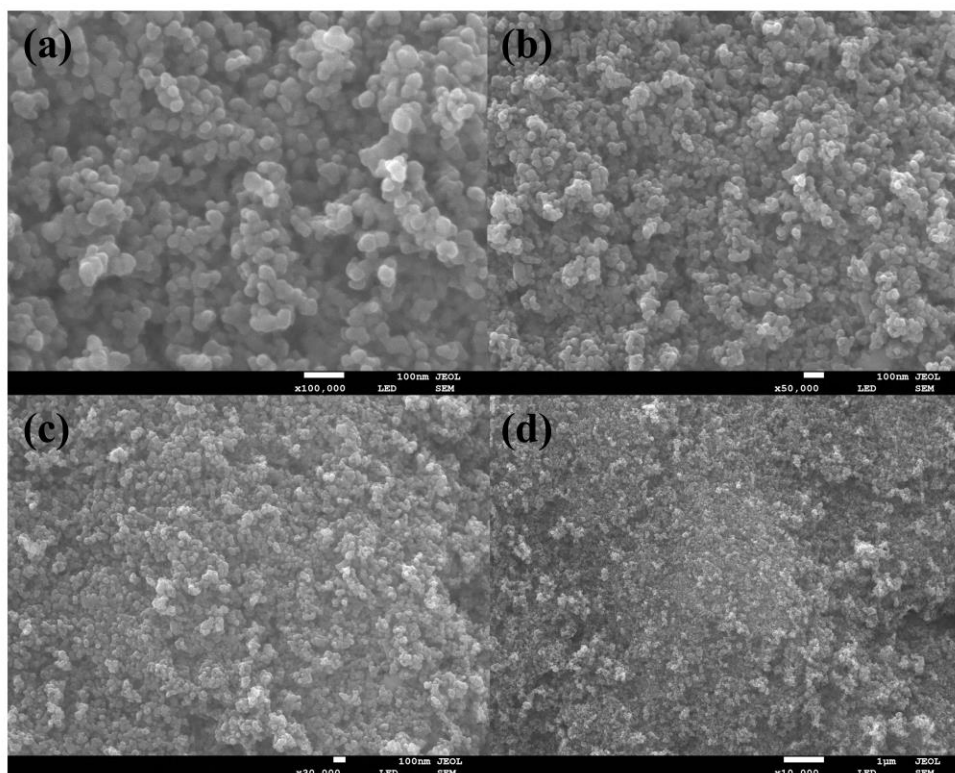
$$\text{Sulfated polysaccharide content (\%)} = \frac{M_{\text{measured}}}{M_{\text{sample}}} \times 100$$

## Supplemental Table

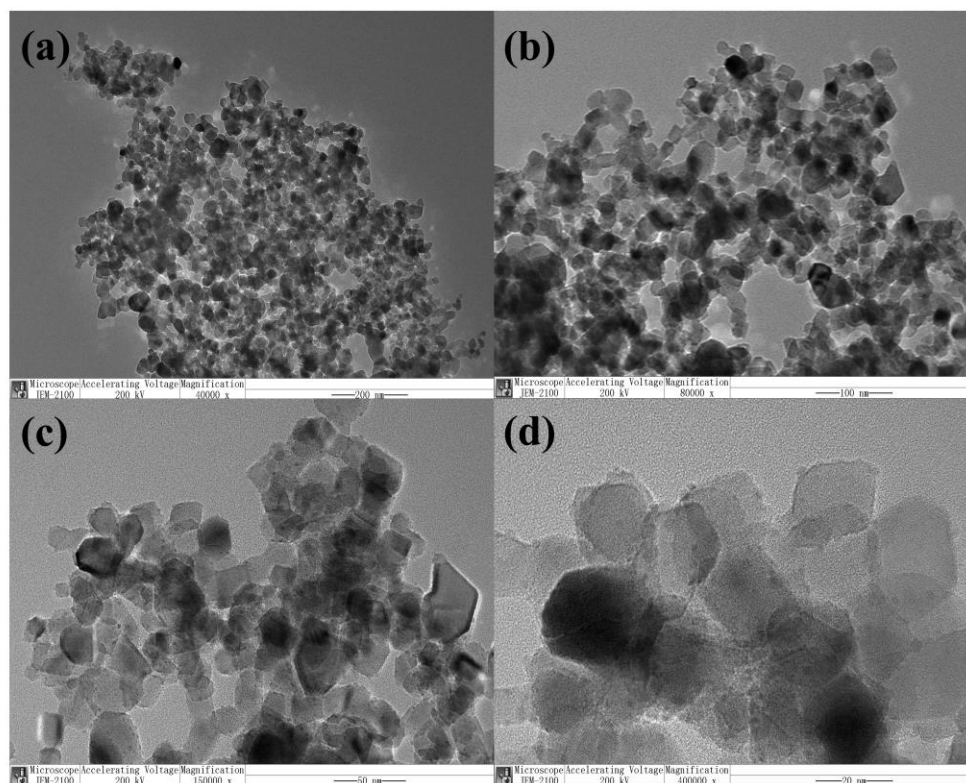
**Table S1.** Relative contents of different oligosac-charides produced by photocatalytic degradation.

Peak	Ratio	Peak	Ratio	Peak	Ratio	Peak	Ratio	Peak	Ratio
1	3.4	6	4.2	11	7.8	16	3.9	21	6.5
2	4.3	7	3.0	12	2.8	17	3.8	22	12.7
3	2.4	8	1.0	13	3.1	18	8.8	23	8.4
4	1.7	9	7.0	14	1.8	19	6.0	24	6.5
5	3.8	10	4.1	15	2.5	20	10.4	25	5.9

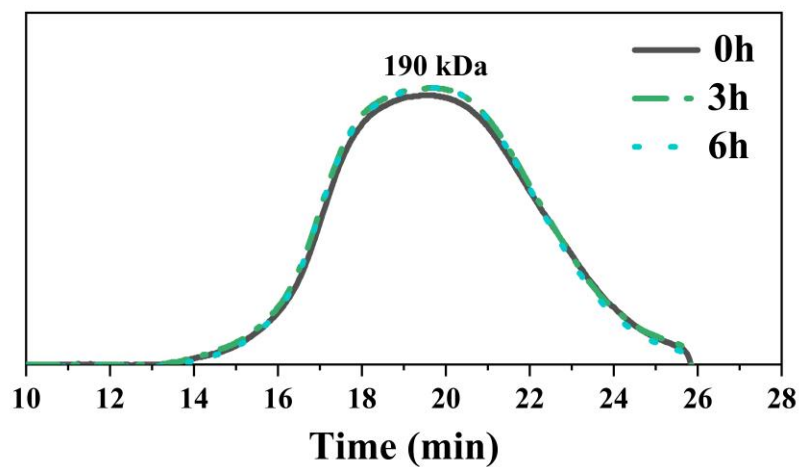
## Supplemental Figures



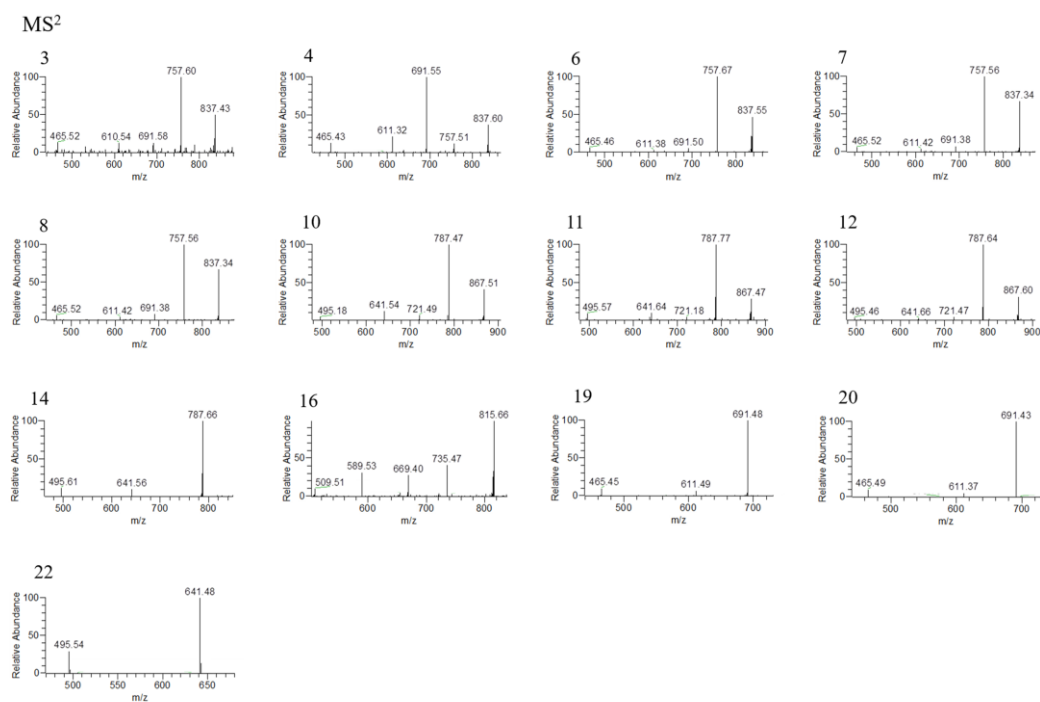
**Figure S1.** SEM images of TiO<sub>2</sub>. 100,000× TiO<sub>2</sub> (a); 50,000 × TiO<sub>2</sub> (b); 30,000 × TiO<sub>2</sub> (c); 10,000 × TiO<sub>2</sub> (d).



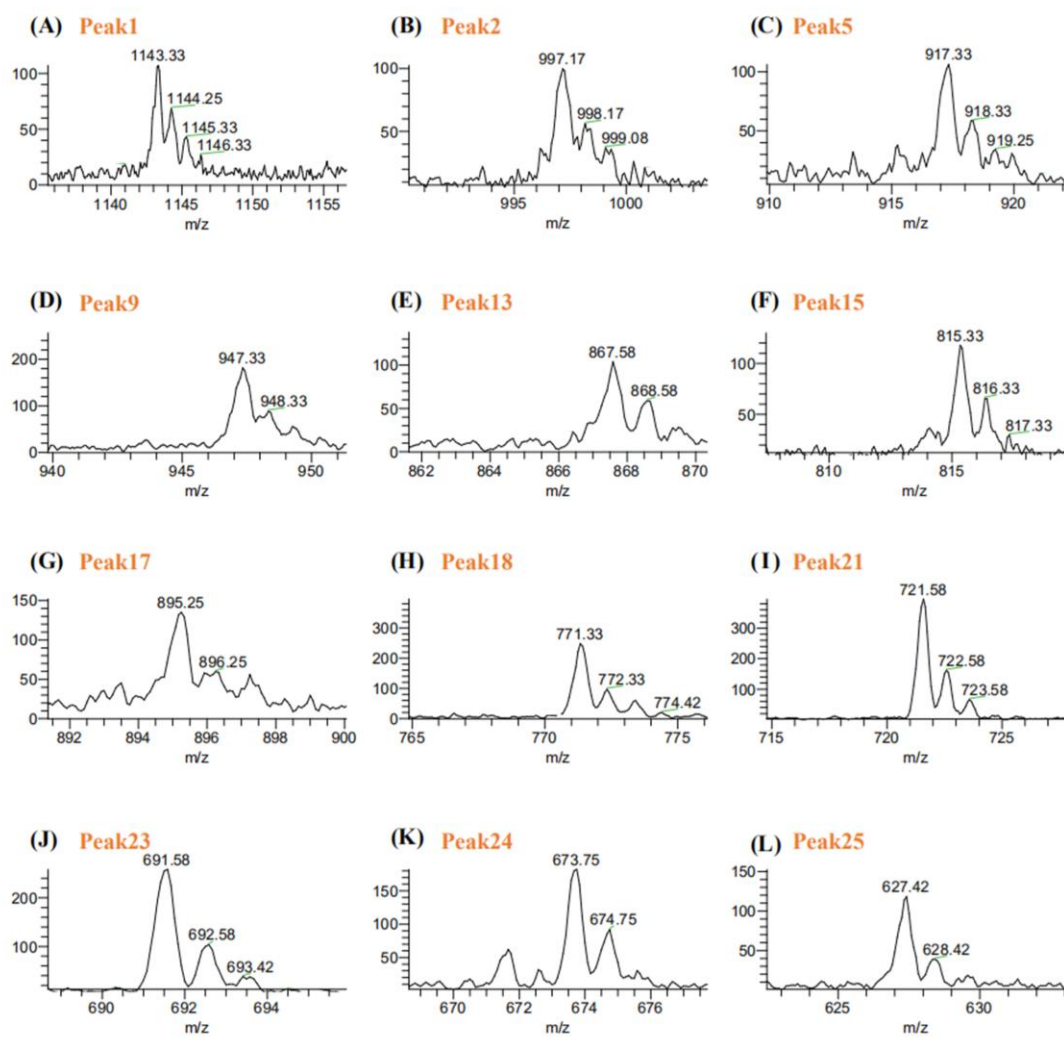
**Figure S2.** TEM images of  $\text{TiO}_2$ . 40,000 $\times$   $\text{TiO}_2$  (a); 80,000 $\times$   $\text{TiO}_2$  (b); 150,000 $\times$   $\text{TiO}_2$  (c); 400,000 $\times$   $\text{TiO}_2$  (d).



**Figure S3.** Molecular weight distribution of fucoidan degraded with 1% TiO<sub>2</sub>, 0.95% H<sub>2</sub>O<sub>2</sub> in the absence of light.



**Figure S4.** MS<sup>2</sup> of PMP-labeled oligosaccharides from the DF-3.



**Figure S5.** The pseudo-molecular ions of PMP-labelled oligosaccharides from the DF-3.