

**A novel clean catalytic method for waste-free modification of
polysaccharides by oxidation**

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Supplementary Information

Experimental

Materials. Potato native starch (gift from Raisio Chemicals, Finland) contained 80% amylose and 20% amylopectine on a dry basis and the moisture content was 16 wt%. Figure S1A gives a SEM image of native potato starch showing the presence of 5 – 50 μm granules. Starches from rice, wheat, corn and corn starch enriched with amylopectin were obtained from Sigma. Hydrogen peroxide (35 %) was purchased from Aldrich. Metal complexes of tetrasulfonatophthalocyanine (MPcS) were prepared by a modified Weber-Busch procedure (S1,S2).) Tetracarboxyphthalocyanine of iron was prepared by following the procedure reported in (S3).

Methods. The carbonyl and carboxyl degrees of substitution were determined by Smith's method (S4) using Titrino SM 702 apparatus. The Fe contents in modified starch were measured using inductively coupled plasma-mass spectrometry method. Water contents of materials were determined by TGA.

References and Notes

- S1. J.H. Weber, D.H. Busch, *Inorg. Chem.* **4**, 469 (1965).
- S2. A. Hadasch, A.B. Sorokin, A. Rabion, B. Meunier, *New J. Chem.*, **22**, 45 (1998).
- S3. H. Shirai, A. Maruyama, K. Kobayashi, N. Hojo, *Macromol. Chem.* **181**, 575 (1980).
- S4. P. Parovuori, A. Hamunen, P. Forssell, K. Autio, K. Poutanen, *Starch/Stärke* **47**, 19 (1995).

Table S1. Oxidation of starches from different sources by the dry method at 58°C.

Origin of the starch	Amylose %	Amylopectin %	Granule size μm	T_{gelatin} °C	COOH per 100 GU	CO
Potato	20	80	5 – 100	50-68	4.0	8.0
Corn	27	73	5 – 30	62-80	3.6	6.0
Corn	0	100	5 – 30	63-72	3.65*	6.2*
Rice	19	81	1 – 3	66-78	3.1	6.1
Wheat	25	75	1 – 45	52-85	4.3*	5.85*
					1.5	3.6
					2.9*	6.3*
					3.5	6.1

* - 70°C, molar ratio catalyst : H_2O_2 : AGU = 1 : 1450 : 6500.

Fig. S1. Structure of iron tetrasulfonatophthalocyanine (one of four possible positional isomer is shown).

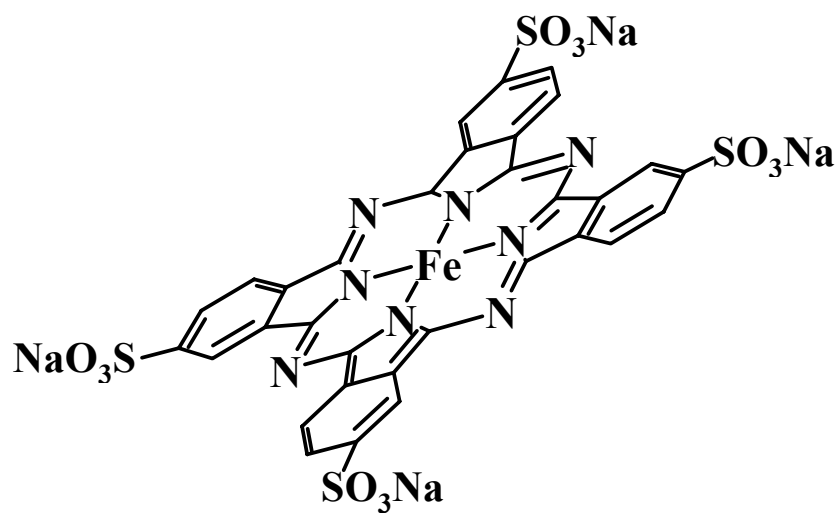


Figure S2. SEM pictures of native potato starch (A) ; oxidised potato starch having $DS_{CO} = 2.84$, $DS_{COOH} = 0.27$ (B) and oxidised potato starch having $DS_{CO} = 8.50$, $DS_{COOH} = 4.60$ (C).

