Electronic Supplementary Information

One-step antibacterial modification of polypropylene nonwoven fabrics *via* oxidation using photo-activated chlorine dioxide radical

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Contents

1. Supporting figures

Table S1. The result of antibacterial test using nanoparticle aqueous solution.

Bacteria		*Escherichia coli*	
Sample		Control	Ox-60
Log CFU	t=0	4.13	4.13
	t=20	7.56	2.30
A		–	5.26
Percentage reduction (%)		–	99.9994

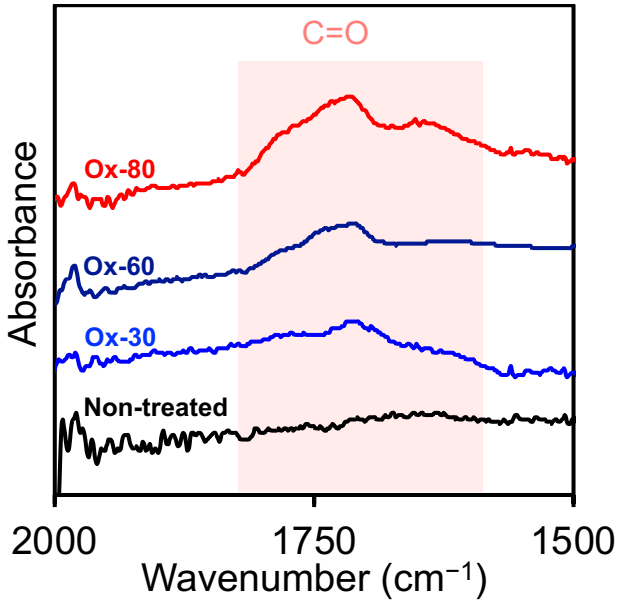

Fig. S1 FT-IR spectra of PP NWFs over wavenumber ranges of 2000−1500 cm^{-1}: non-treated (black), Ox-30 (blue), Ox-60 (navy), and Ox-80 (red).

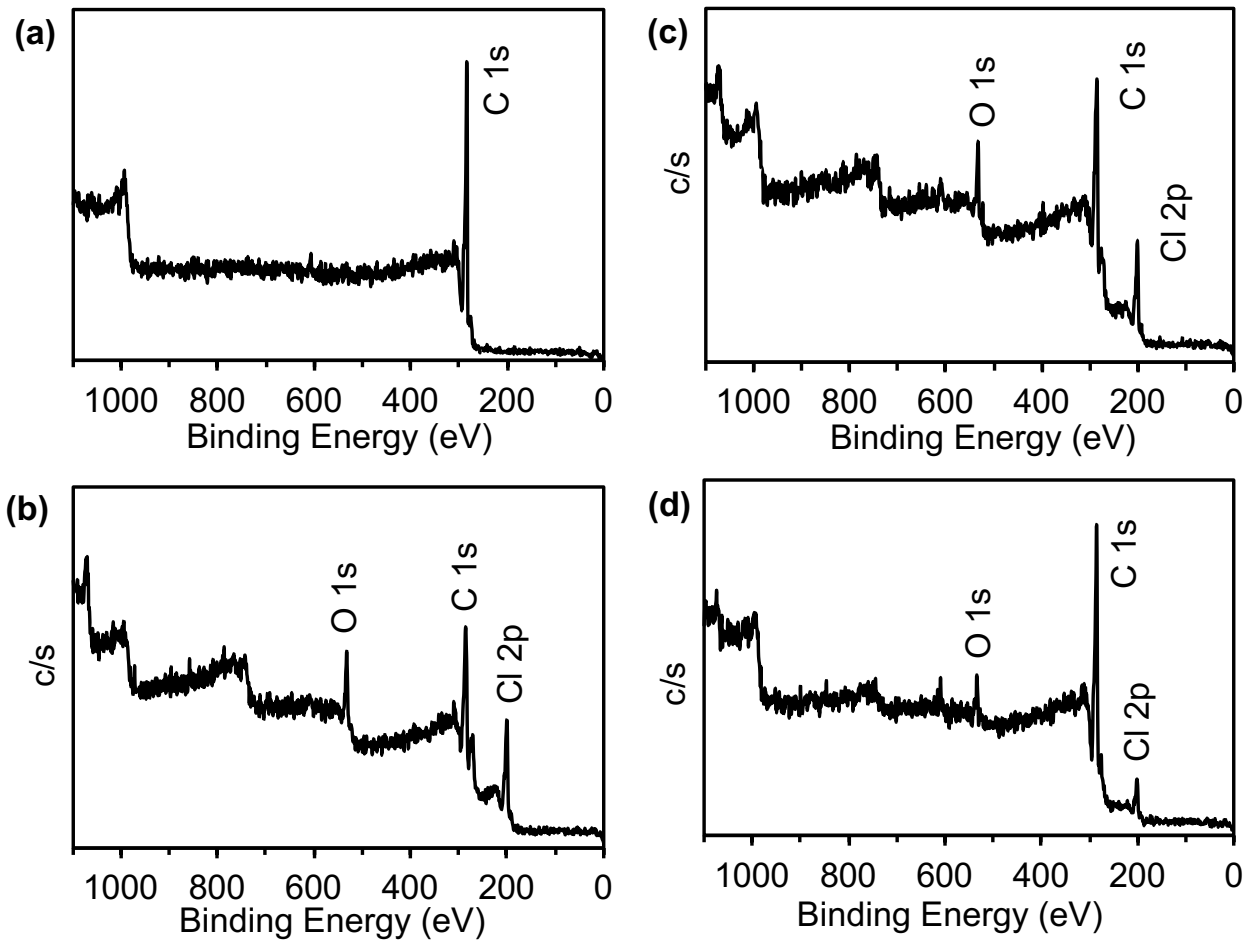

Fig. S2 Wide XPS spectra of (a) non-treated, (b) Ox-30, (c) Ox-80 and (d) Ox-80-EtOH PP NWFs.

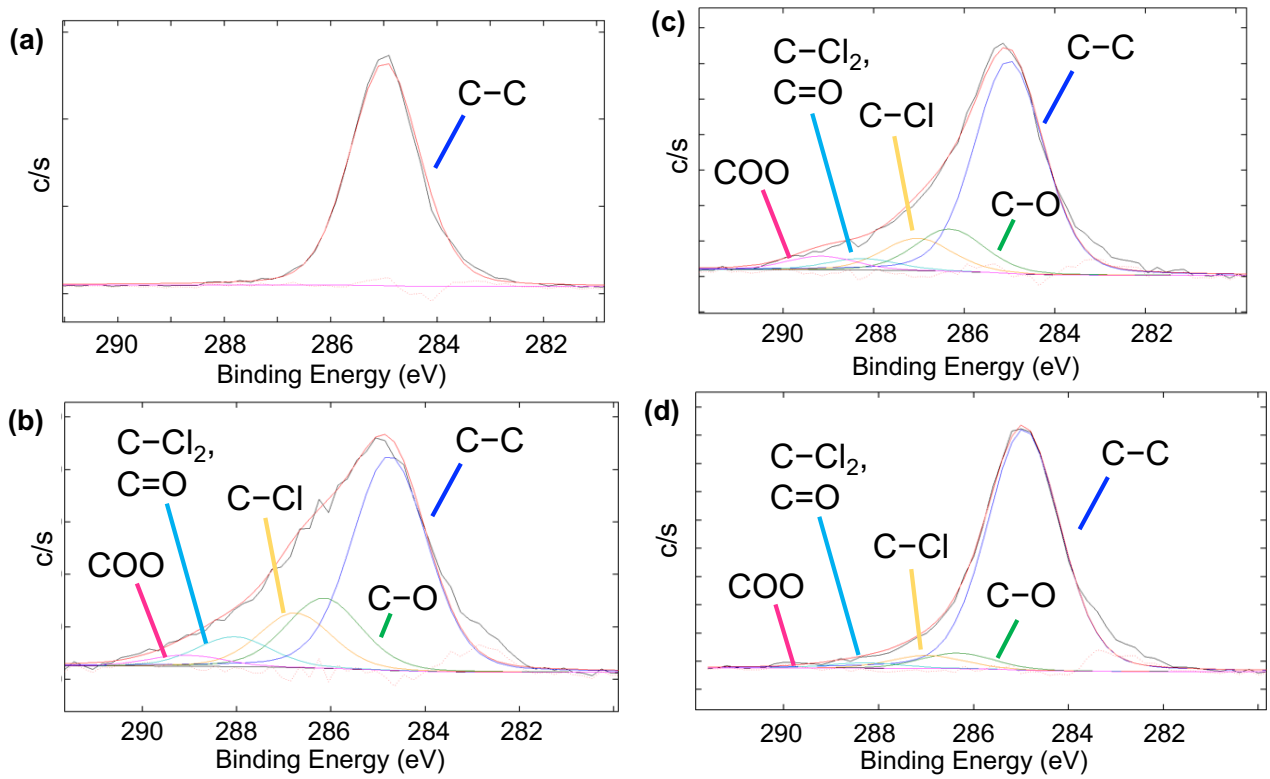

Fig. S3 C1s XPS spectra of (a) non-treated, (b) Ox-30, (c) Ox-80 and (d) Ox-80-EtOH PP NWFs.

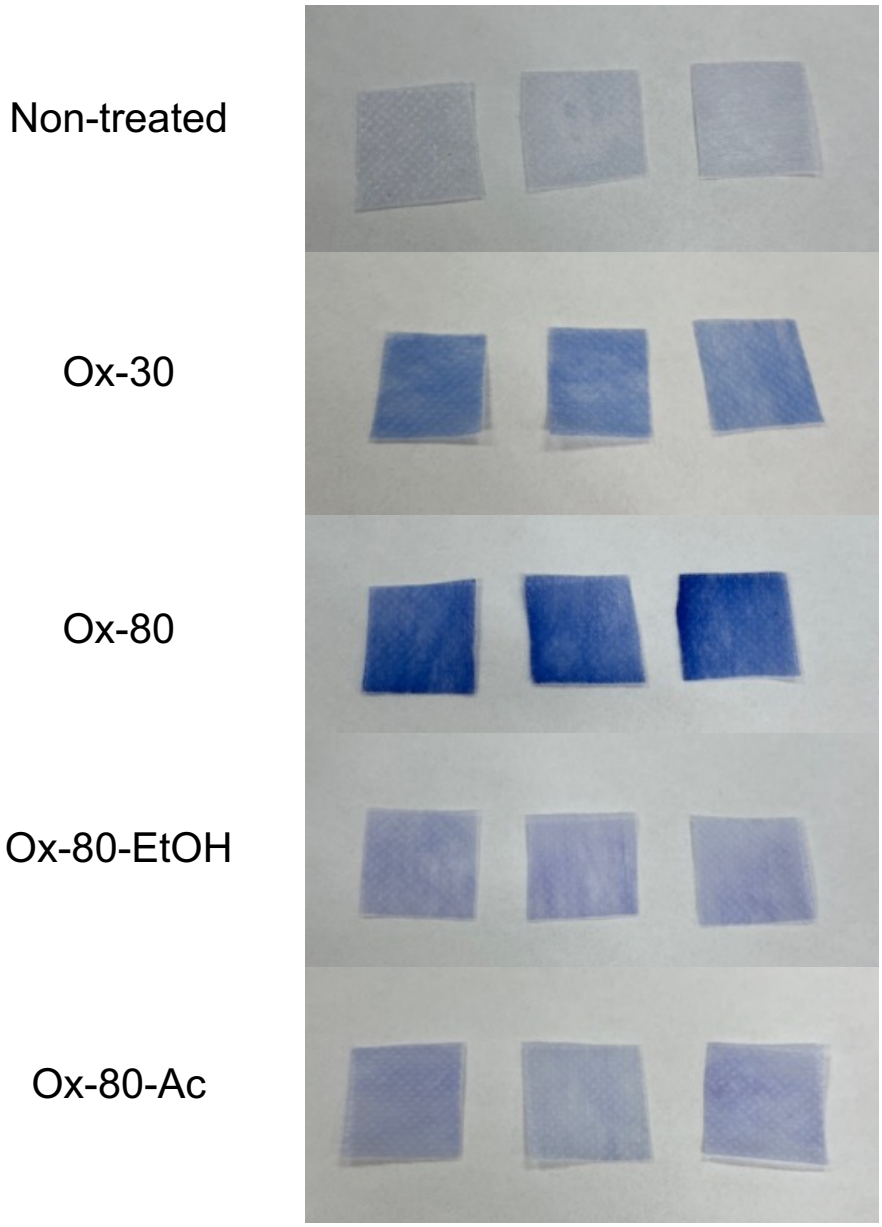

Fig. S4 Images of PP NWFs after TBO assay (n = 3). Size of samples is 20 mm x 20 mm.

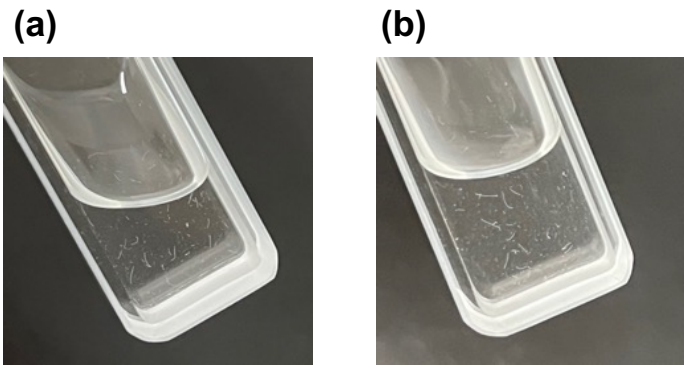

Fig. S5 Images of acetone washing solution of (a) non-treated (b) Ox-80 PP NWF samples in a 10 mm x 10 mm quartz cuvette.

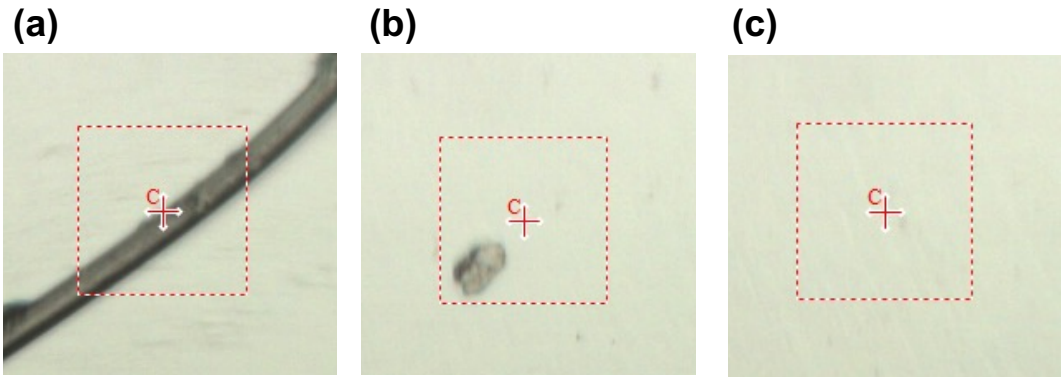

Fig. S6 Optical microscope images of acetone washing solution of non-treated PP NWF samples. (a) Fibers (b) middle particles (around 50 μm) (c) small particles (under 1 μm) were not observed in non-treated sample. The length of a side of a red square was 100 μm.

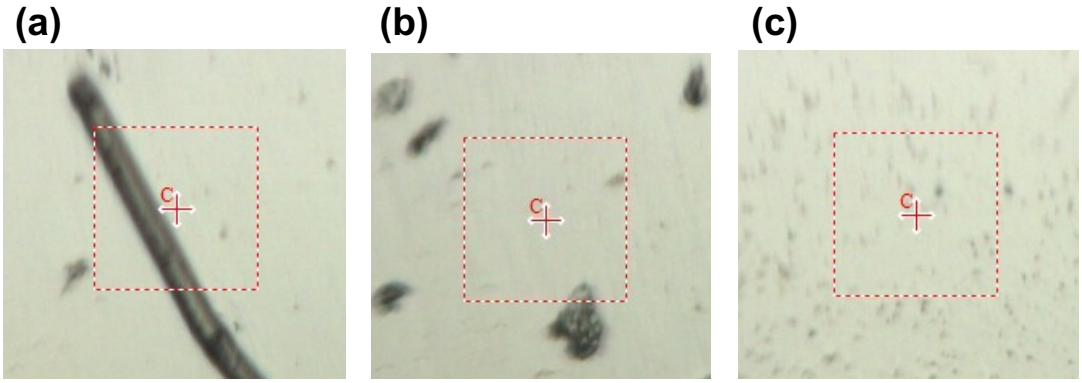

Fig. S7 Optical microscope images of acetone washing solution of Ox-80 PP NWF samples. (a) Fibers (b) middle particles (around 50 μm) (c) small particles (under 1 μm). The length of a side of a red square was 100 μm.

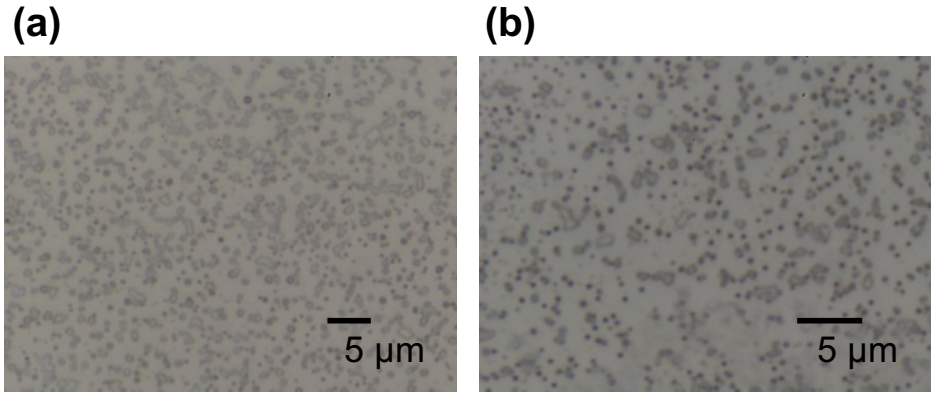

Fig. S8 Optical microscope images of acetone washing solution of Ox-80 PP NWF samples. (a) ×10000 (b) ×15000.

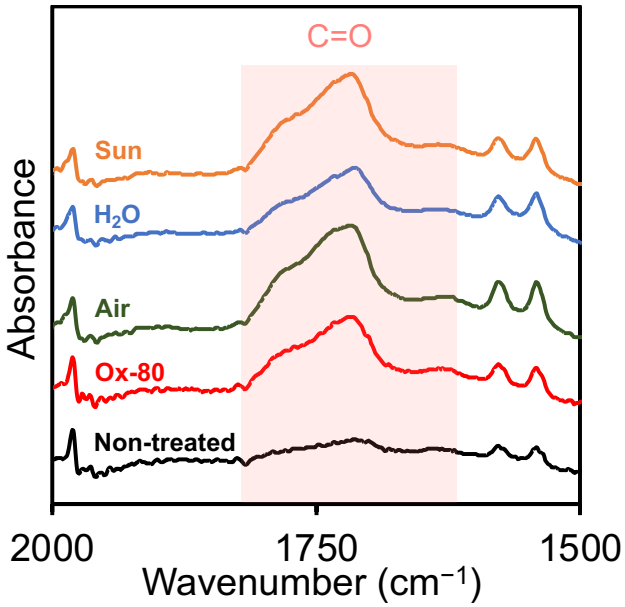

Fig. S9 We examined 3 storage conditions of Ox-80 to evaluate the stability of modified effects. Ox-80 PP NWF samples were stored for 7 days in 3 different conditions including in air, in distilled water (H_2O), and under sun light (Sun). The figure shows FT-IR spectra of PP NWFs over wavenumber ranges of 2000−1500 cm^{-1}: non-treated (black), Ox-80 (red), Air (green), H_2O (blue), and Sun (orange).

2. Analysis of soluble components in the acetone washing solution of Ox-80

Method

First, the soluble compounds in acetone as a washing solution were analysed by thin-layer chromatography (TLC). Analytical TLC was performed using glass plates pre-coated with silica gel impregnated with a fluorescent indicator (254 nm). TLC plates were visualized by exposure to ultraviolet light (UV) and by immersion in phosphomoribdic acid ethanol solution solution followed by heating. The compounds were separated by column chromatography with silica gels. Then, the eluents were utilized in order hexane, chloroform, chloroform:methanol (5:1 v/v). The chemicals of the separated compounds were determined by nuclear magnetic resonance (NMR) spectroscopy. ^1H NMR spectra in $CDCl_3$ were recorded on a 400 MHz spectrometer JNM-ECS400 FT-NMR (JEOL, Japan). TMS was used as an internal reference for chemical shift.

Results and discussion

We analysed soluble components in the acetone as a washing solution of Ox-80. We performed thin-layer chromatography (TLC) to determine the number of components. From the examinations in TLC, we found 3 main compounds (Fig. S10). The 3 compounds were isolated by the column chromatography, analysed by ^1H NMR spectra in $CDCl_3$. The UV absorption spectra of 2 main

compounds (No. 2 and 3 in Fig. S11) were observed at λ_{max} = 254 nm due to the aromatic ring moiety. The 2 spots were also observed in non-treated sample in TLC analyses (Fig. S10). In addition, the peaks in ^{1}H NMR spectra were observed in the ranges of 4.1–4.3 ppm and 7.5–7.8 ppm, which were assigned to ester and aromatic protons, respectively. The peaks at 4.1–4.3 and 7.5–7.8 ppm in ^{1}H NMR spectra were also detected in acetone as a washing solution of non-treated PP NWFs (Fig. S11). Thus, the 2 compounds were considered as fumarate esters containing in PP fibers as plasticizers.[S1] The examination in TLC indicated that the last 1 compound (No.1 in Fig. S10) had low polarity. In addition, the peaks in ^{1}H NMR spectra were observed in the range of 0.7−1.3 ppm (Fig. S11). Thus, the compound was considered as a hydrocarbon. We reasoned that the hydrocarbon was formed by the main chain scission of PP due to the UV-light irradiation.

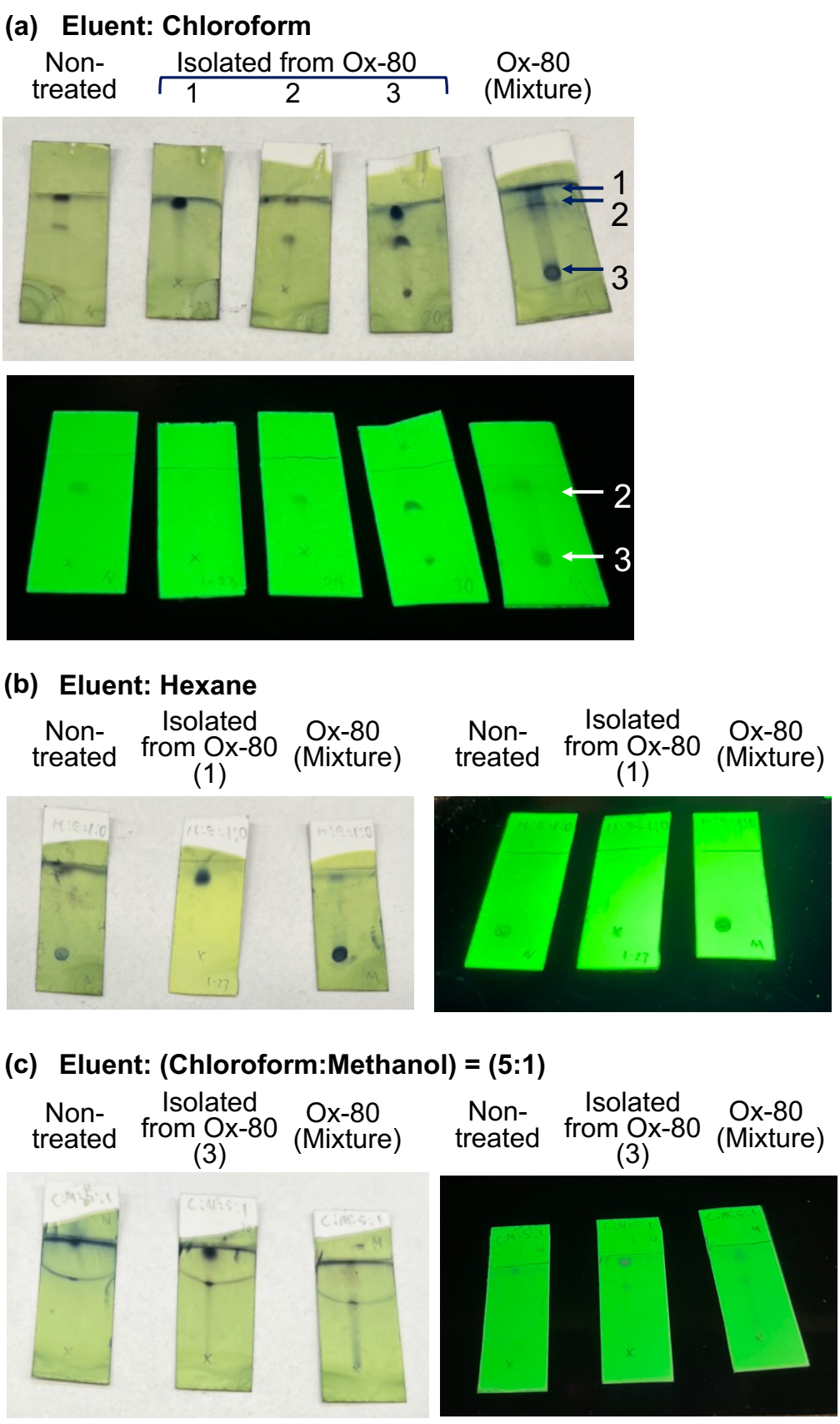

Fig. S10 Images of TLC.

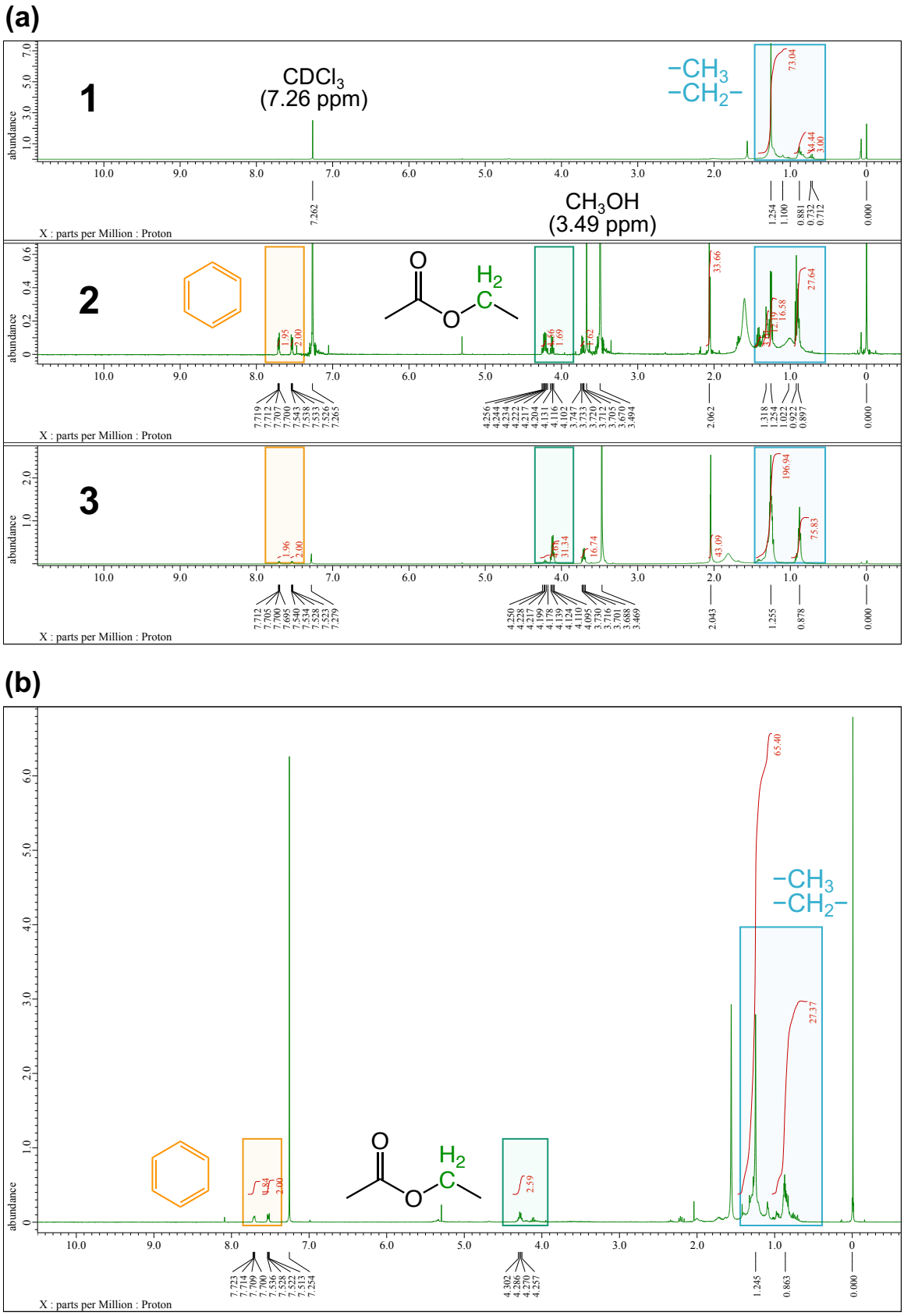

Fig. S11 (a) NMR spectra in $CDCl_3$. Compounds extracted from acetone washing solution of Ox-80 PP NWFs (No.1−3 in Fig. S7). (b) NMR spectrum in $CDCl_3$. Compounds extracted from acetone washing solution of non-treated PP NWFs.

Reference

S1 S. Genay, F. Feutry, M. Masse, C. Barthélémy, V. Sautou, P. Odou, B. Décaudin and N. Azaroual, *Anal. Bioanal. Chem.* 2017, **409**, 1271–1280.

3. Antibacterial test of nanoparticle aqueous solution

Method

To examine the antibacterial nanoparticles formed by the photo-oxidation, we performed the antibacterial test in the following procedure. Bacteria in LB medium ($1-3 \times 10^5$ CFU/mL; 1 mL) and nanoparticle aqueous solution (1 mL) were co-incubated at 37 °C for 20 h with 90 rpm shaking, and the growth rate of bacteria was examined. The pour plate method was utilized to measure the number of living bacteria. 10-fold dilution series of incubated solution (1 mL) was plated with standard agar medium, and plates with 30─300 colonies were used for calculating the number of living bacteria. *E. coli* (NBRC 3001) was selected as a test bacteria. Nanoparticle solutions were prepared by acetone washing of PP NWF samples (4 × 4 cm; 55±1 mg). PP NWF samples including non-treated, Ox-30, and Ox-80 were placed in acetone and shaking for 1 min. The acetone washing solution was heated at 70 °C to remove acetone. The reside was re-dispersed in 100 μL of acetone followed by adding 900 μL of distilled water. As a control, 1 mL of 10% acetone was co-incubated with bacteria solution. The growth inhibition rate of bacteria (%) was calculated using the following formula:

$$\text{(Growth inhibition rate:\%)} = (C-T)/C \times 100$$

where C is the number of living bacteria on control sample after 20 h incubation. T is the number of living bacteria on test samples after 20 h incubation.

Results and discussion

We investigated the antibacterial property of nanoparticles formed by the oxidation. Bacteria solution and nanoparticle aqueous solution were co-incubated at 37 °C for 20 h with 90 rpm shaking, and the growth rate of bacteria was examined by plating 10-fold dilution series of incubated solution. Nanoparticle aqueous solutions were prepared by acetone washing of PP NWF samples (non-treated and Ox-80). Table S2 shows the growth inhibition rate of each sample, respectively. The growth inhibition rate of non-treated sample was only 55.3%, which means non-treated sample did not affect the bacteria growth. In contrast, the growth inhibition rate of Ox-80 sample was over 99.9%, which indicates that the components in acetone washing solution of oxidised PP NWFs at 80 °C show the antibacterial against *E. coli*. Considering the above results, we suggested that the excellent antibacterial of Ox-80 PP NWFs were attributed to the nanoparticles around 80 nm formed by the photo-oxidation.

Table S2. The result of antibacterial test using nanoparticle aqueous solution.

Bacteria		*Escherichia coli*		
Sample		Control	Non-treated	Ox-80
Log CFU	t=20	10.13	9.87	3.59
Growth inhibition rate (%)		−	55.3	99.99997