Supplementary Information (SI) for Chemical Communications.

Supplementary Information

Photo- and thermal catalysis of nitrate to nitrite by manganese ions under light up to 600 nm

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Experimental Section

All reagents were commercially available reagent-grade chemicals and used without further purification.

Characterization

The light absorbance property of a 0.1 M $Mn(NO_3)_2$ aqueous solution was characterized using ultraviolet–visible (UV–vis) spectroscopy (V-770 spectrophotometer, JASCO, Ltd.). The concentrations of manganese ions and total organic carbon (TOC) in the reaction solution before and after the reaction were measured using an inductively coupled plasma atomic emission spectrometer (ICPE-9820, Shimadzu Corp.) and a TOC analyzer (TOC-L CSH, Shimadzu Corp.), respectively.

Reduction of NO_3^- to NO_2^-

Typically, 3 mL of a 1.0 M $Mn(NO_3)_2$ aqueous solution and 27 mL of pure water were added into a test tube (ϕ30 × 200 mm); then, 20 μmol of phenol was added. After being sealed with a silicone stopper, the test tube was cooled or heated while stirring in an ice bath (~5 °C) or a water bath set to 20, 30, 40, and 60°C (ambient air conditions), respectively. Then, the test tube was photoirradiated at $\lambda > 420$ nm using a 300 W Xe illuminator (Eagle engineering Co. Ltd.) equipped with a cutoff filter (HOYA Corp., L42). For comparison, reactions were performed either without light irradiation or, in the absence of Mn^{2+}, using $NaNO_3$, $Al(NO_3)_3$, $Ca(NO_3)_2$, $Cu(NO_3)_2$, $Ni(NO_3)_2$, and $Co(NO_3)_2$ as both catalysts and NO_3^- sources.

The effects of the light irradiation wavelength on the reduction of NO_3^- were investigated by photoirradiating the test tube in the water bath (30°C) at $\lambda > 300$, 420, 520, or 600 nm using a 300 W Xe illuminator equipped with or without cutoff filters (HOYA Corp., L42, Y52 and R60).

The effects of the reaction atmosphere on the reduction of NO_3^- were investigated by the same procedure in a water bath (30°C), except that the aqueous solution of $Mn(NO_3)_2$ and phenol was bubbled with Ar or O_2 for 45 min at 500 mL min^{-1}.

The effects of organic compound conditions on the reduction of NO_3^- were investigated by the same procedure in a water bath (30°C), except that methanol (120 μmol) or formic acid (120 μmol) were used instead of phenol. In addition, the reaction without organic compounds was also performed.

The concentration of the generated NO_2^- was measured using Saltzmann colorimetry based on the color change caused by 4,4'-diaminodiphenylsulfone (DDS) and N-1-naphthylethylenediamine dihydrochloride (NEDA・2HCl) using a UV–vis spectrophotometer (PD-3500UV, APEL Co., Ltd.). Briefly, 160 μL of 0.1% DDS in a 50 vol% ethanol aqueous solution and 80 μL of 0.5% NEDA・2HCl aqueous solution were added to an aqueous solution containing 2.0 mL of the sample and 80 μL of a 1.0 M HCl aqueous solution. The NO_2^- concentration was calculated from the absorbance at 542 nm of the mixed solution.

The amount of phenol in the liquid phase was determined using a Shimadzu GC-2014 gas chromatographer equipped with a DB-1 capillary column (30 m × 0.53 mm). Biphenyl was used as an internal standard sample; then, the amount of phenol was determined from the ratio of the phenol peak areas to the biphenyl peak areas. The amount of CO_2 generated in the gas phase was measured using a Shimadzu GC-8A gas chromatographer equipped with a Porapak Q column. The conversion to CO_2 as a measure of the mineralization (detoxification) efficiency can be calculated according to Equation S1.

$$\text{Conversion to } CO_2\ (\%) = (\text{amount of generated } CO_2\ [\text{mol}] \times 100) / (\text{amount of phenol before reaction } [\text{mol}] \times 6) \qquad \text{(S1)}$$

NO_2^- degradation test

Typically, 3 mL of a-1.0 M $Mn(NO_3)_2$ or $MnCl_2$ aqueous solution and 26 mL of pure water were added into a test tube (ϕ30 × 200 mm); then, 20 μmol of phenol and 1 mL of a 0.05 M $NaNO_2$ aqueous solution were added. After being sealed with a silicone stopper, the test tube was cooled or heated while stirring in an ice bath (~5 °C) or a water bath (set to 30, and 60°C), respectively, for 30 min. Then, the test tube was photoirradiated at $\lambda > 420$ nm using a 300 W Xe illuminator (Eagle engineering Co. Ltd.) equipped with a cutoff filter (HOYA Corp., L42). The concentration of NO_2^- was measured using Saltzmann colorimetry (measurement wavelength: 542 nm).

Evaluation of the conversion efficiency from NO_3^- to NO_2^-

Typically, 3 mL of a 1.0 M $MnCl_2$ aqueous solution, 27 mL of pure water and 200 μL of a 0.1 M $NaNO_3$ aqueous solution were added into a test tube (ϕ30 × 200 mm); then, 20 μmol of phenol was added. After being sealed with a silicone stopper, the test tube was heated while stirring in an oil bath set to 50°C (ambient air conditions). Then, the test tube was photoirradiated at $\lambda > 420$ nm using a 300 W Xe illuminator (Eagle engineering Co. Ltd.) equipped with a cutoff filter (HOYA Corp., L42).

Electrochemical characterization of Mn^{2+}

A two-compartment cell separated by an anion-exchange membrane was used. In one of the cells, a platinum (Pt) coil and a silver/silver chloride (Ag/AgCl) electrode were employed as the working and reference electrodes, respectively; in the other cell, a Pt coil was employed as the counter electrode. 45 mL of a 0.1 M $Mn(NO_3)_2$ aqueous solution was added to both cells and stirred for 30 min. A fixed voltage of +0.5 V *vs.* Ag/AgCl was applied using a potentiostat/galvanostat analyzer (EC FRONTIER Co., Ltd., ECstat-301). The solution was irradiated with UV and visible light (at $\lambda > 300$, 420, 520, or 600 nm) using a 300 W Xe illuminator equipped with or without cutoff filters (HOYA Corp., L42, Y52, and R60); the irradiation light was switched ON and OFF every 5 s.

The effects of adding organic compounds to the photoresponsivity were investigated by adding 30 μmol of phenol, 180 μmol of methanol, and 180 μmol of formic acid to the cell side of the working electrode.

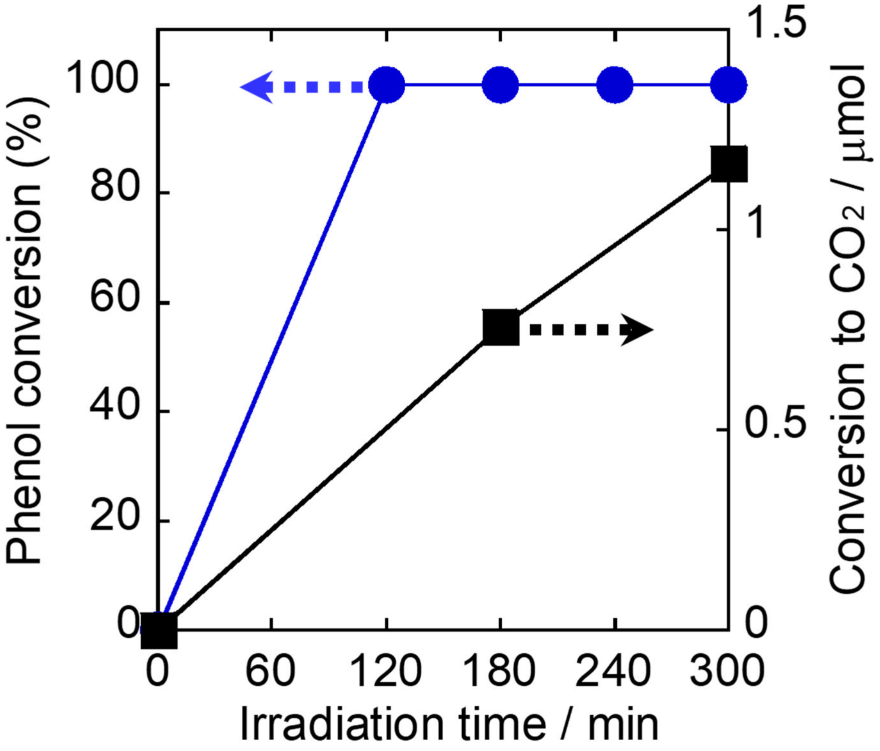

Fig. S1 Phenol conversion and conversion to CO_2 under visible light (λ > 420 nm) irradiation at 30 °C (ambient air conditions) in an aqueous solution of $Mn(NO_3)_2$ and phenol.

ICP-AES analysis confirmed that the concentration of manganese ions remained unchanged before and after the reaction (3.1 mmol) at 30°C for 3 h under visible light (λ > 420 nm) irradiation in the presence of Mn^{2+} and ambient air, indicating negligible precipitation to MnO_x species under the reaction conditions. Although slight turbidity was observed after the reaction, TOC (total organic carbon) analysis showed a decrease from 122.6 to 65.3 μmol-C. While CO_2 was detected (as shown in Fig. S1), its amount did not fully account for the TOC decrease, suggesting the formation of partially oxidized, water-insoluble organic intermediates. These intermediates, which are presumed to remain at this reaction stage, are likely responsible for the observed turbidity rather than Mn-derived solids.

To evaluate the practical significance of the catalytic activity, the conversion efficiency of NO_3^- to NO_2^- was examined using $MnCl_2$ (3 mmol) as the Mn^{2+} source and $NaNO_3$ (20 μmol) as the NO_3^- source. The reaction was carried out at 50 °C in an oil bath under visible light irradiation ($\lambda > 420$ nm) in ambient air. Under these conditions, the NO_3^- to NO_2^- conversion reached 30% after 24 h and 52% after 48 h.

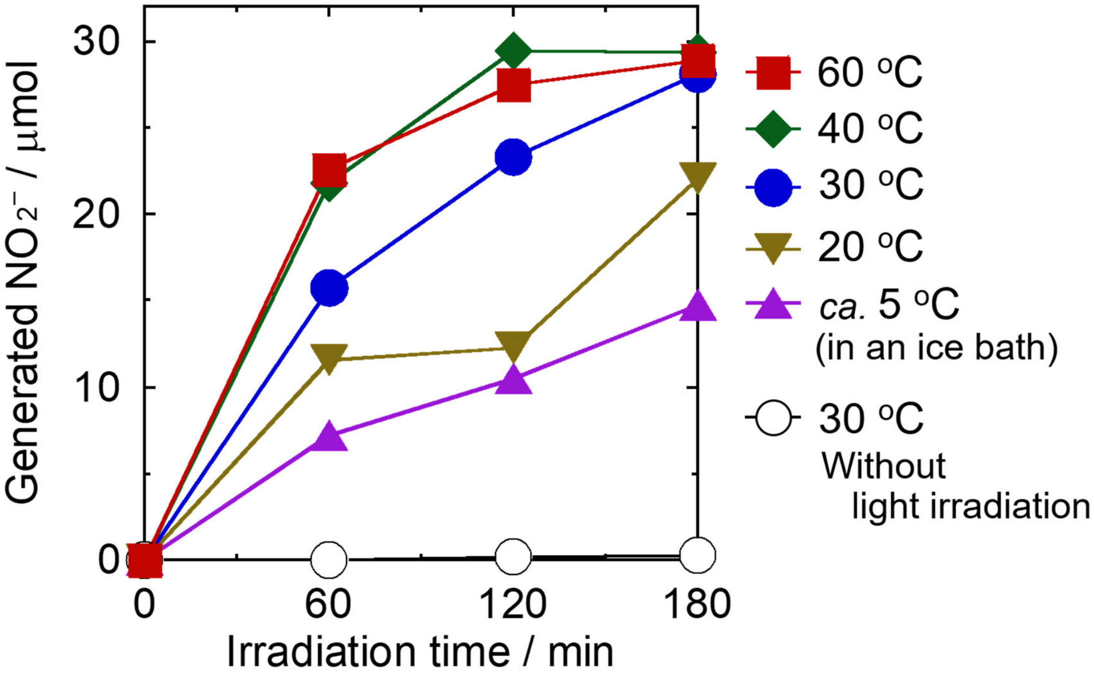

Fig. S2 Variation with time of NO_2^- generated by the reduction of NO_3^- under visible light (λ > 420 nm) irradiation and ambient air conditions at 5, 20, 30, 40 or 60 °C in an aqueous solution of $Mn(NO_3)_2$ and phenol.

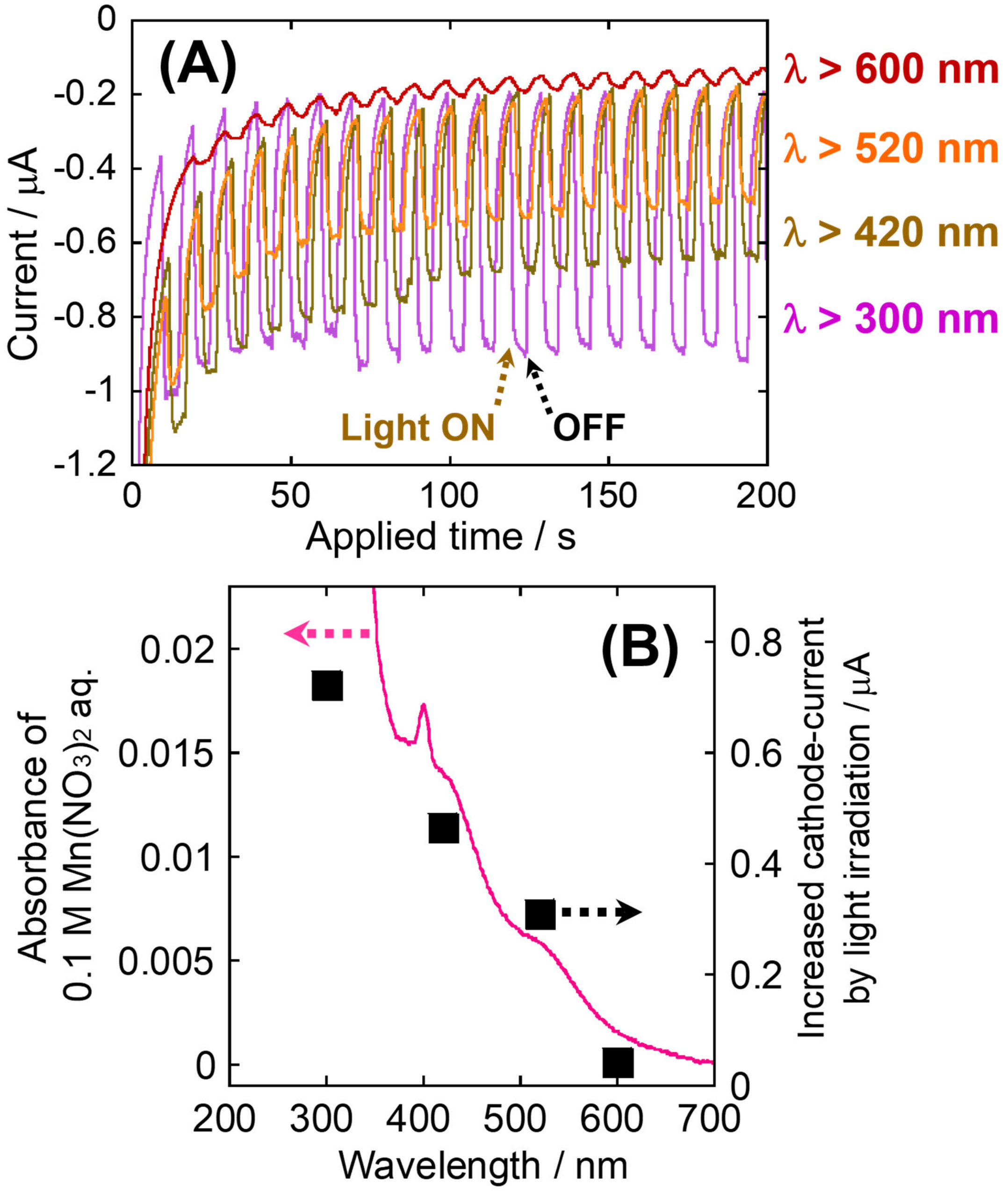

Fig. S3 (A) Current vs. time: effects of the irradiation wavelength in the absence of organic compounds on the photoelectrochemical properties of a 0.1 M aqueous solution of $Mn(NO_3)_2$ on a Pt electrode at an applied voltage of +0.5 V *vs.* Ag/AgCl (light irradiation was performed every 5 s) and (B) photoreduction current, *i.e.*, increase in the reduction current under UV or visible light irradiation relative to the generated current without light irradiation (shown in Fig. S3(A)) and the UV-vis spectrum of a 0.1 M $Mn(NO_3)_2$ aqueous solution.

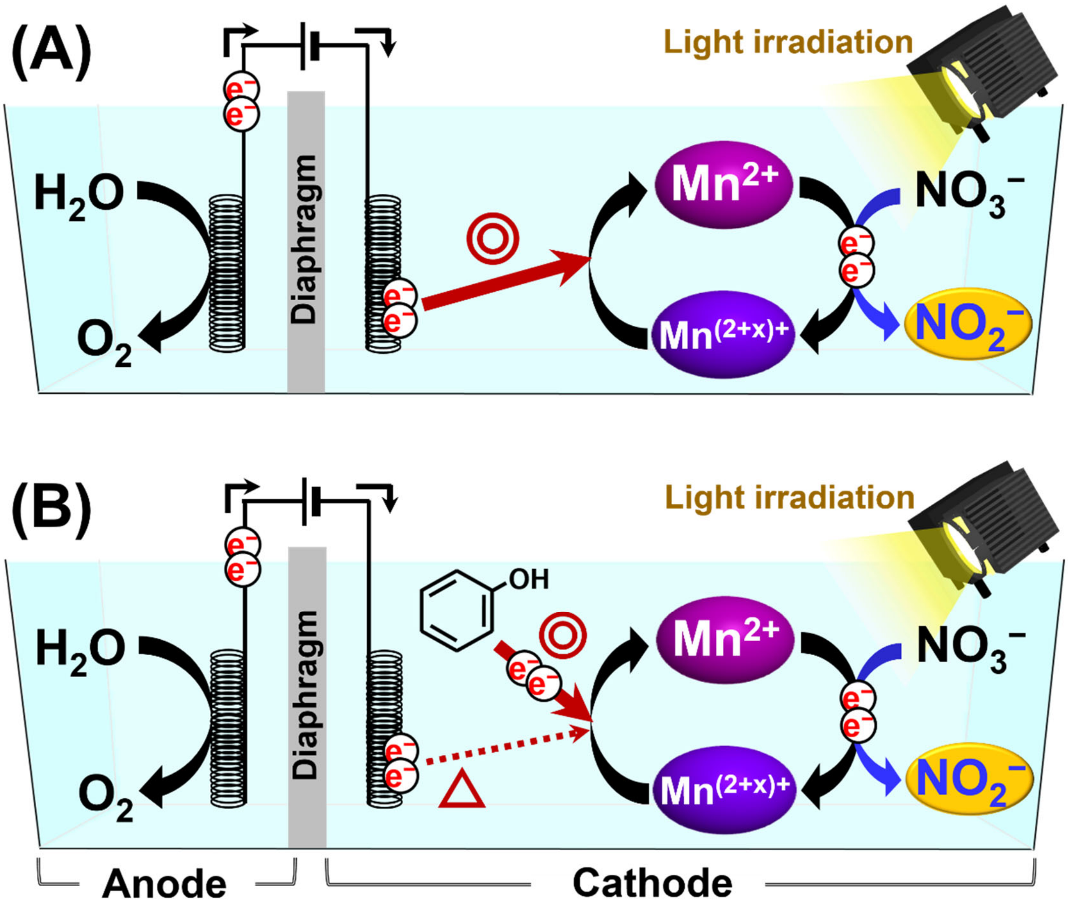

Fig. S4 Proposed mechanism of the photoelectrochemical properties on a Pt electrode under light irradiation in an $Mn(NO_3)_2$ aqueous solution (A) without and (B) with phenol.

The significant decrease in photoreduction current observed upon phenol addition can be attributed to this regeneration pathway. Specifically, under the applied electrochemical conditions (+0.5 V *vs.* Ag/AgCl) in this study, electron transfer from the electrode to $Mn^{(2+x)+}$ species is less favorable compared to the spontaneous electron donation from phenol. As a result, the phenol-derived electrons effectively outcompete the electrochemical electron transfer, leading to a suppressed cathodic current. This suggests that phenol facilitates Mn^{2+} regeneration *via* a non-electrode-mediated route, which is energetically more favorable under visible light irradiation.

The oxidation of phenol in this system proceeds not only to CO_2 but also *via* partial oxidation pathways leading to intermediate organic compounds, making the determination of a single redox potential challenging. However, the effective electron donation from phenol to $Mn^{(2+x)+}$ species is strongly supported by the observed suppression in photoreduction current upon phenol addition (Fig. 3), which is attributed to non-electrode-mediated Mn^{2+} regeneration.

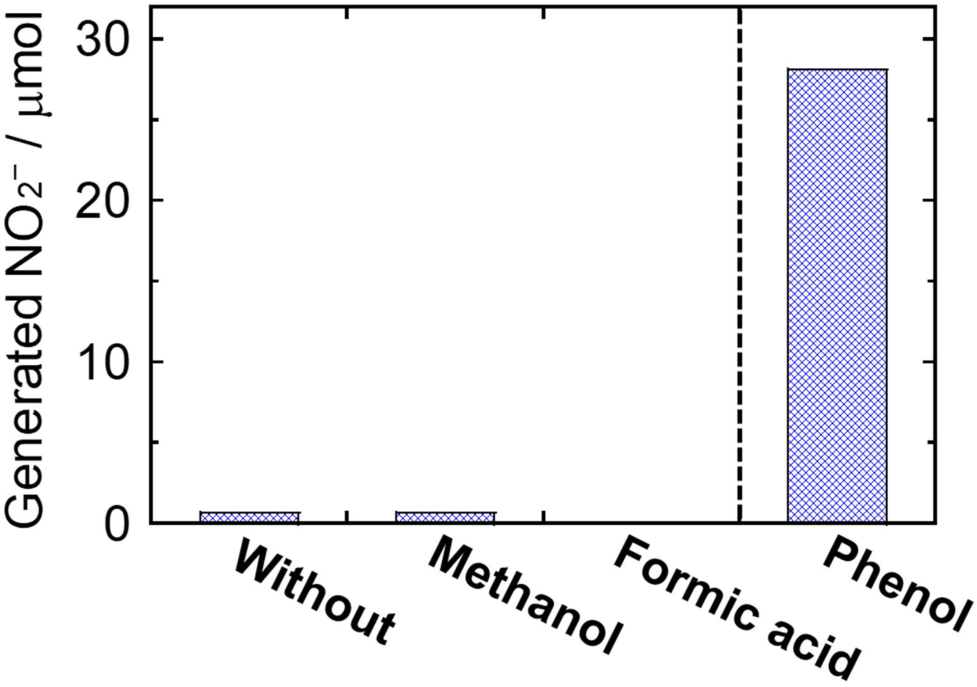

Fig. S5 Effects of the organic compound species on the reduction of NO_3^- to NO_2^- under visible light (λ > 420 nm) irradiation and ambient air conditions at 30ºC in an aqueous solution of $Mn(NO_3)_2$ and organic compounds (reaction time: 180 min).

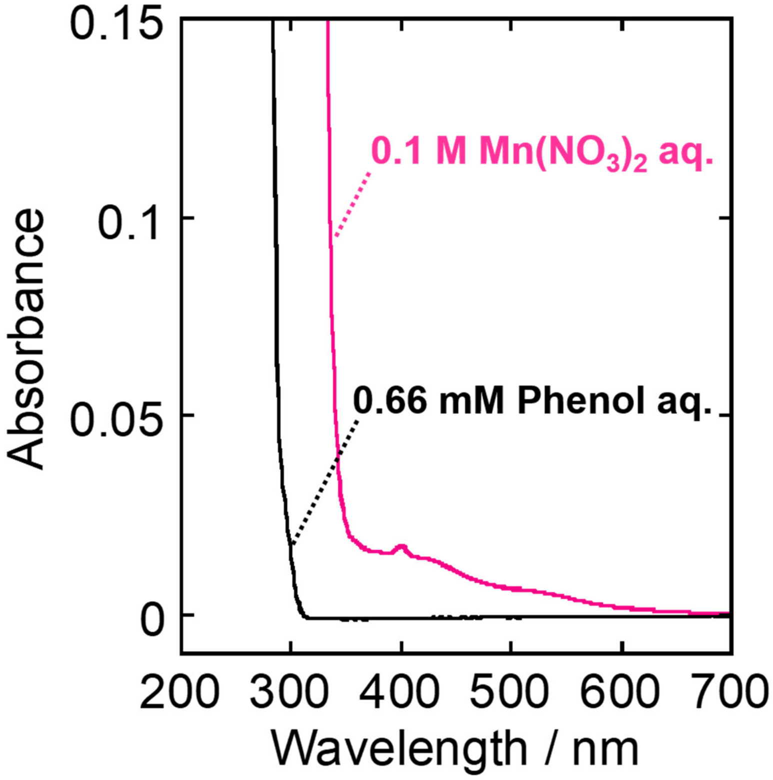

Fig. S6 UV-vis spectra of aqueous solutions of phenol (0.66 mM) and $Mn(NO_3)_2$ (0.1 M).