Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Supporting information

Cross over between anti- and pro-oxidant activities of different manganese oxide nanoparticles and their biological implications

Xiumei Jiang [†], Patrick Gray [†], Mehulkumar Patel [‡], Jiwen Zheng [‡], Jun-Jie Yin [†*]

[†] Division of Analytical Chemistry and Division of Bioanalytical Chemistry, Office of Regulatory Science, Center for Food Safety and Applied Nutrition, U.S. Food and Drug Administration, College Park, Maryland 20740, United States

[‡] Division of Biology, Chemistry and Materials Science, Office of Science and Engineering Laboratories, Center for Devices and Radiological Health, U.S. Food and Drug Administration, Silver Spring, Maryland 20993, United States

* Corresponding author: Junjie.Yin@fda.hhs.gov

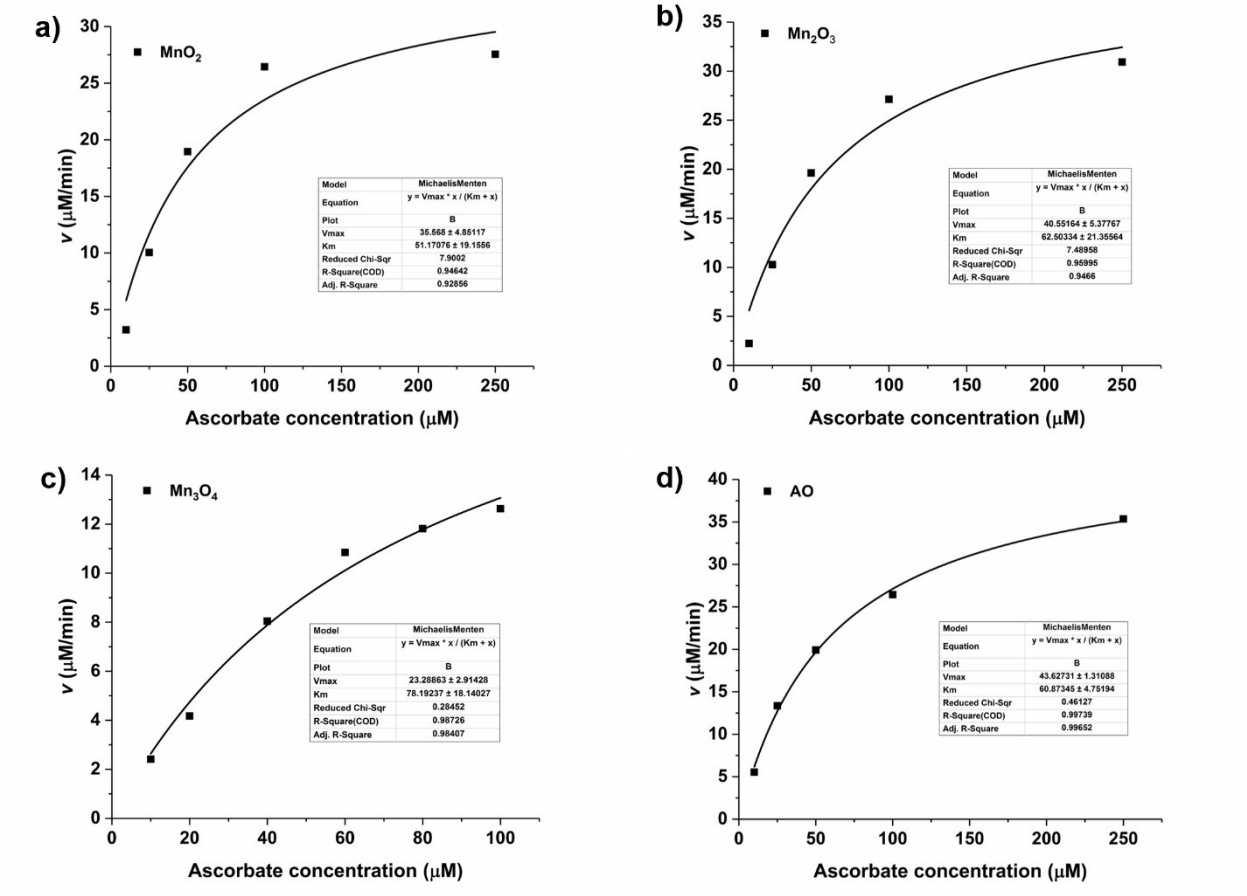

Figure S1. Characterization of the catalytic kinetics of ascorbate oxidase-like activities of MnO_x NPs. Michaelis-Menten curves for (a) MnO_2, (b) Mn_2O_3, and (c) Mn_3O_4 NPs and (d) ascorbate oxidase (AO). The concentration of MnO_x NPs are 100 μM, AO concentration is 1 U/ml and the ascorbate concentration varied from 10 to 250 μM.

Hydroxyl radical generation activity of MnO_x NPs

The spin trap DMPO was used to detect hydroxyl radical (•OH) generation in the reaction of MnO_x NPs and H_2O_2. The spin adduct DMPO/•OH yields a typical ESR spectrum with a relative intensity of 1:2:2:1. The instrument settings for hydroxyl radical measurement are 20 mW microwave power, 1 G modulation amplitude, and 100 G scan range.

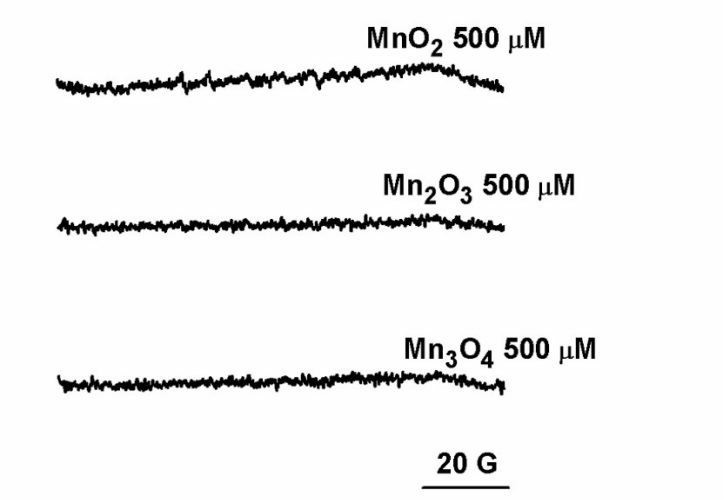

Figure S2. No hydroxyl radical was detected in the reaction of MnO_x NPs and H_2O_2. The concentrations are MnO_x 500 μM and H_2O_2 20 μM. The ESR spectra were recorded 5 min after the reaction started.

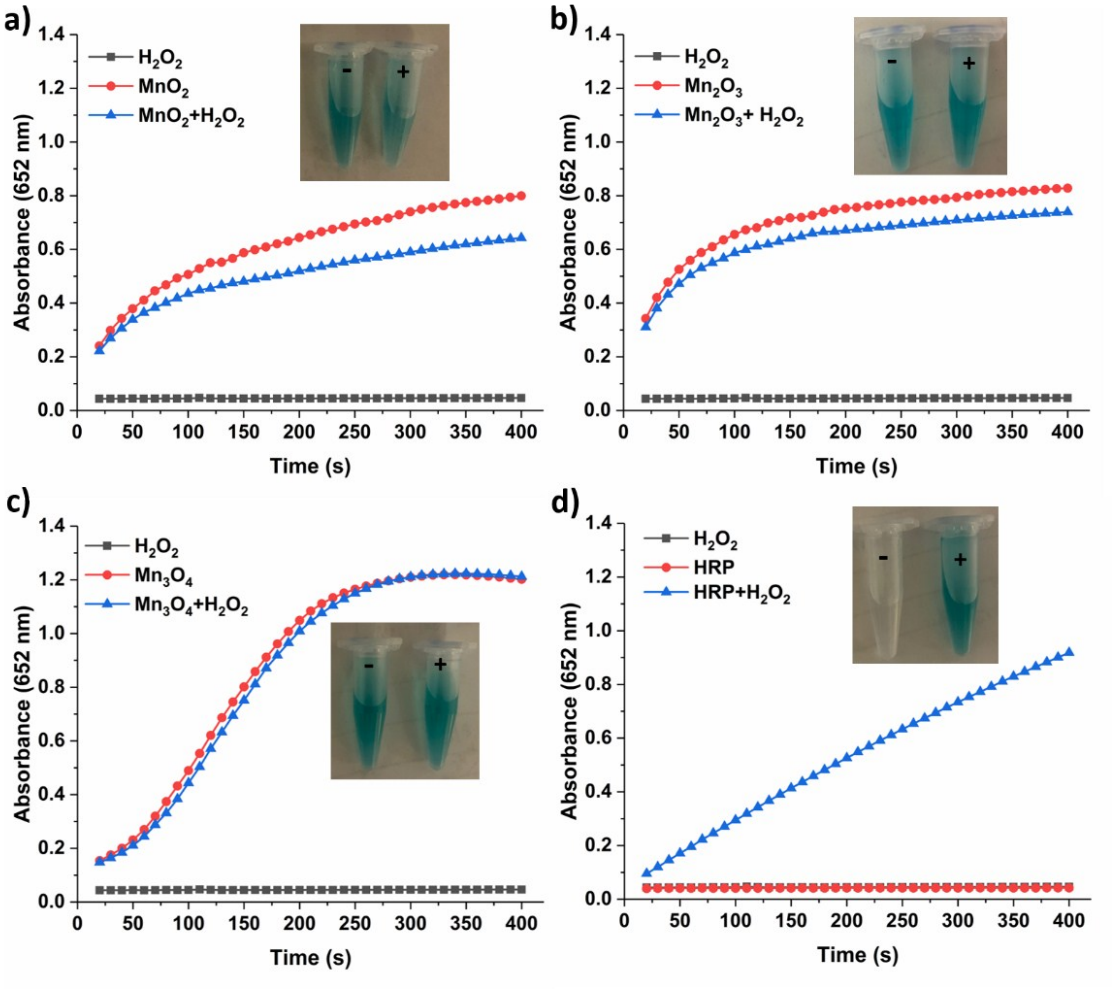

Figure S3. MnO_x NPs exhibit no peroxidase-like activity. Reaction-time curve of TMB catalyzed by (a) MnO_2, (b) Mn_2O_3, (c) Mn_3O_4, and (d) HRP in the presence or absence of H_2O_2. The absorbance at 652 nm was monitored 20 s from the reaction started and recorded every 10 s for 400 s. The concentrations are: TMB 0.1 mM, MnO_2 50 μM, Mn_2O_3 20 μM, Mn_3O_4 100 μM, HRP 50 ng/mL, H_2O_2 0.1 mM. The reaction take place in 0.2 M HAc-NaAc buffer at pH 3.5. Inserted photographs indicate the color of the TMB oxidation/peroxidation reaction. The +/- indicate with/without H_2O_2, respectively.

Hydroxyl radical scavenging activity of MnO_x NPs

In order to determine whether MnO_x NPs scavenge hydroxyl radical, we used Fenton reaction (20 μM H_2O_2 and 20 μM $FeSO_4$) to generate hydroxyl radicals and mix with MnO_x NPs. The instrument settings are 20 mW microwave power, 1 G modulation amplitude, and 100 G scan range.

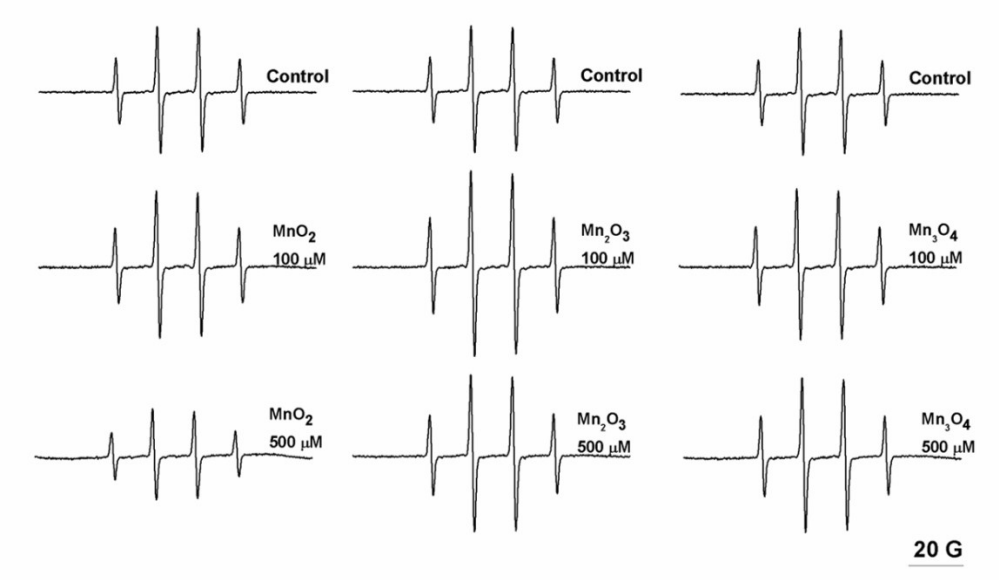

Figure S4. MnO_x NPs exhibit no hydroxyl radical scavenging activity. The hydroxyl radical was generated by the Fenton reaction, including $FeSO_4$ (20 μM) and H_2O_2 (20 μM) and mixed with different MnO_x NPs (100 μM, 500 μM). The spin trap DMPO (50 mM) was used to trap hydroxyl radicals in the reaction. The spectra were recorded 5 min after the reaction started.

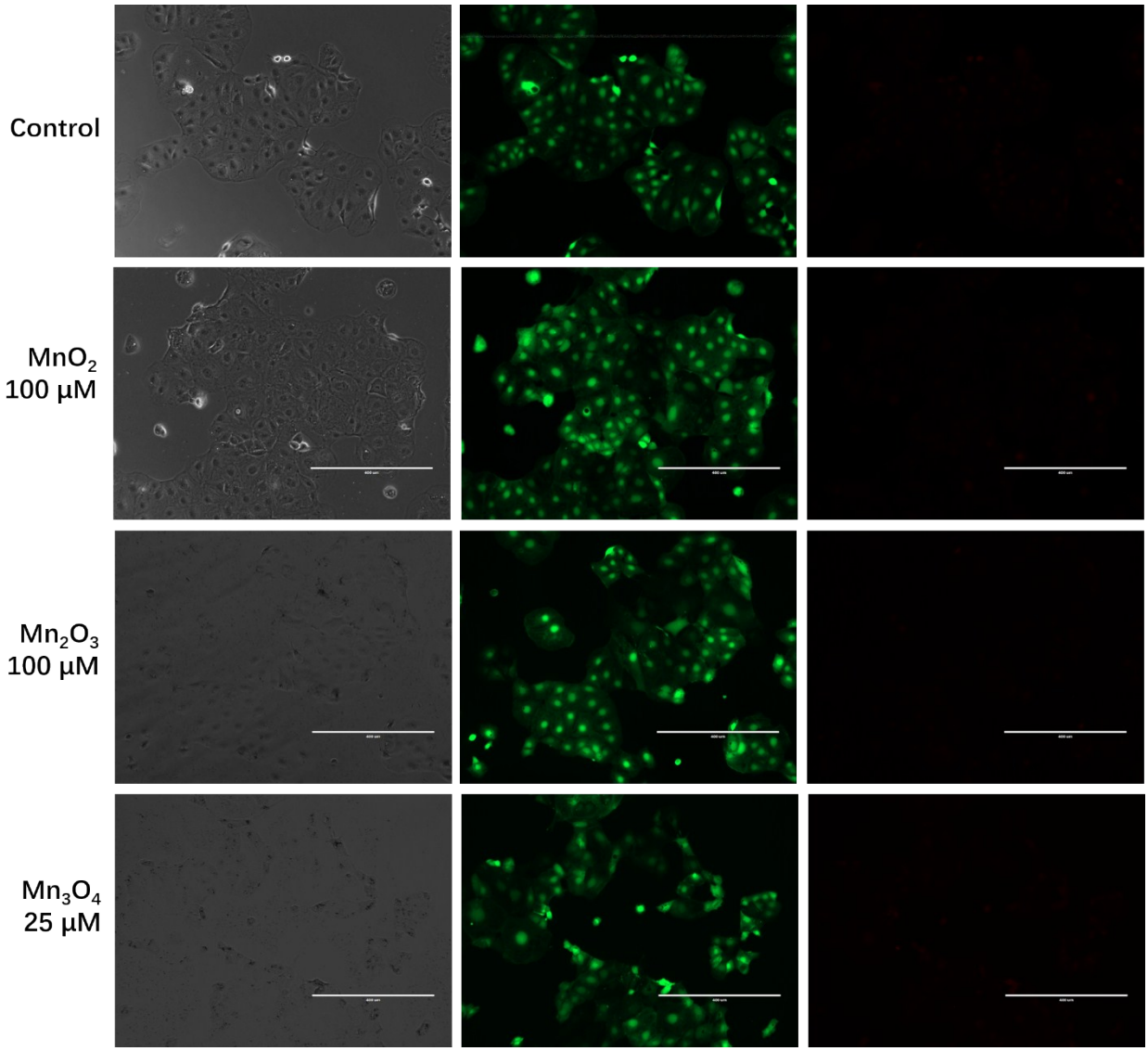

Figure S5. Live-dead cell staining of Caco-2 cells after exposure to different MnO_x NPs for 24 h. Live cells were stained with calcein-AM (2 µg/ml) (green color) and dead cells with propidium iodide (PI, 2 µg/ml) (red color) for 30 min. The images were taken at 100 × magnification. Scale bars are 400 µm.

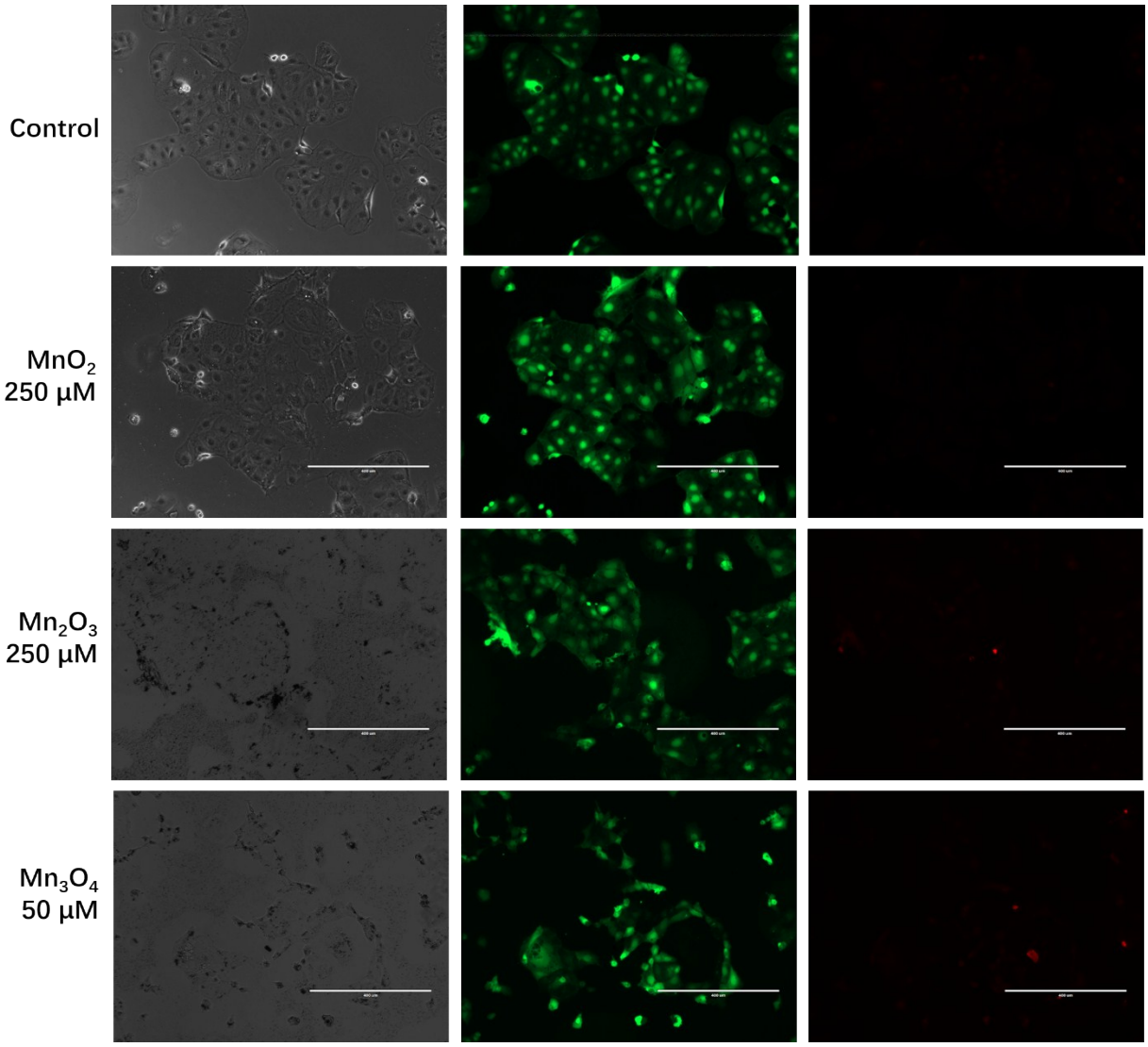

Figure S6. Live-dead cell staining of Caco-2 cells after exposure to different MnO_x NPs for 24 h. Live cells were stained with calcein-AM (2 µg/ml) (green color) and dead cells with PI (2 µg/ml) (red color) for 30 min. The images were taken at 100 × magnification. Scale bars are 400 µm.