Photochemically-Induced Heterogeneous MnO_2 Formation on Plastic Substrates

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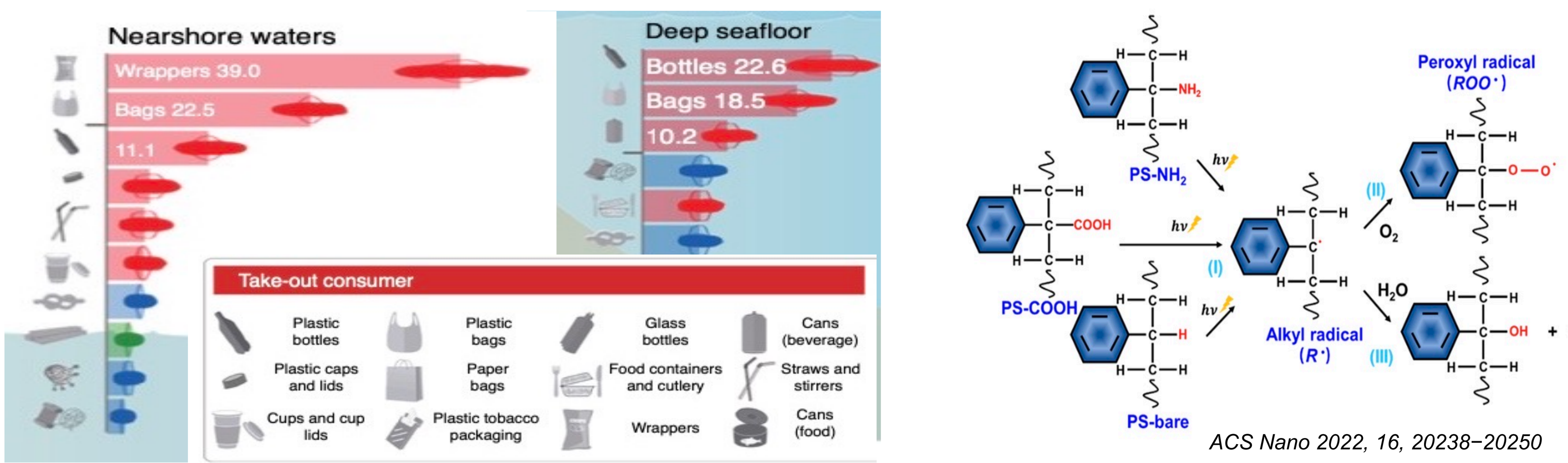
Introduction

- Most plastic wastes ended up in the ocean are takeout consumer items, *e.g.*, **PET** (Polyethylene Terephthalate), **PS** (polystyrene), **PP** (polypropylene), and **HDPE** (high-density polyethylene).
- Plastics not only **adsorb** heavy metals and organic pollutants, but acting as **source for reactive oxygen species (ROS)** when illuminated



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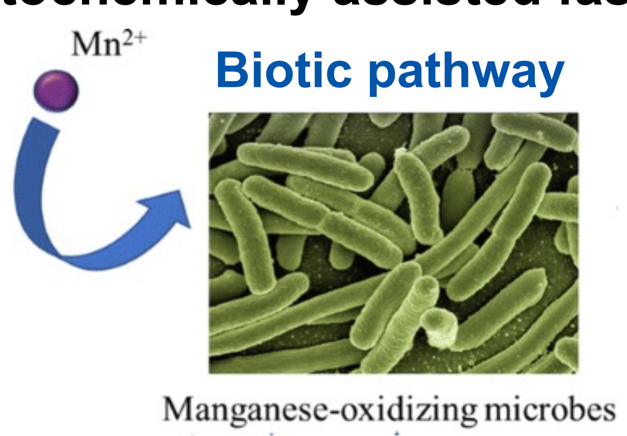
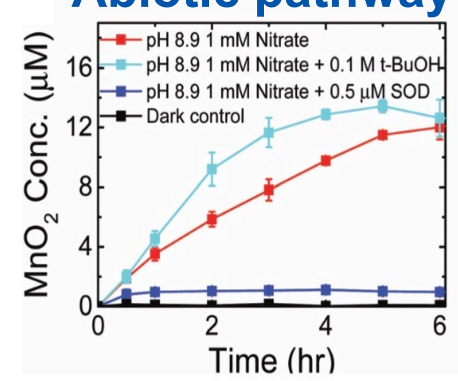
Environmental significance of Manganese (Mn) and Mn oxides

- Second most **abundant** heavy metals near Earth's surface.
- Mn (hydr)oxides are highly **reactive** minerals.
- **High oxidation** and **adsorption** capabilities.
- Various phases with tunnel or layered structures.

Photochemically assisted fast abiotic oxidation of Mn by Nitrate



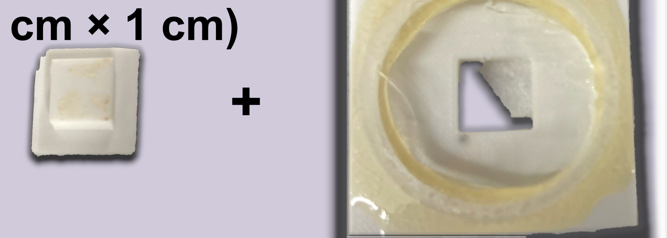


Scientific Questions: Can PET promote the oxidation of surrounding redox-active transition metal (Mn^{2+}) under illumination? Will Mn oxidation occur on the surface (heterogeneous) or in the bulk (homogeneous)? What is the mechanism behind it?

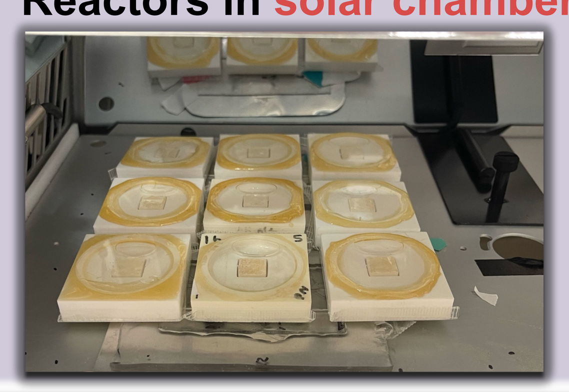
Materials and Methods

Plastic film on stage
PET
PS
PP
HDPE
(1 cm × 1 cm)

0.1 mM $MnCl_2$
Borate Buffer (10 mM)
pH = 8.9 ± 0.05



Reactors in solar chamber

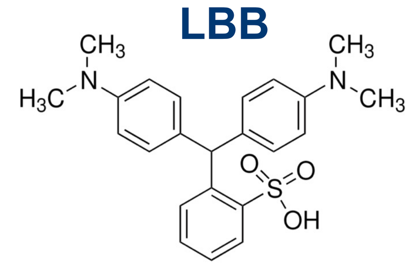


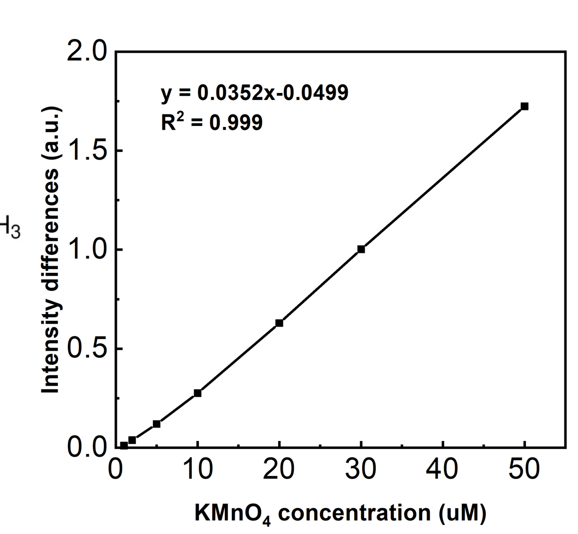
Measurement of Mn oxides concentration

Leucoberbelin blue I (LBB)

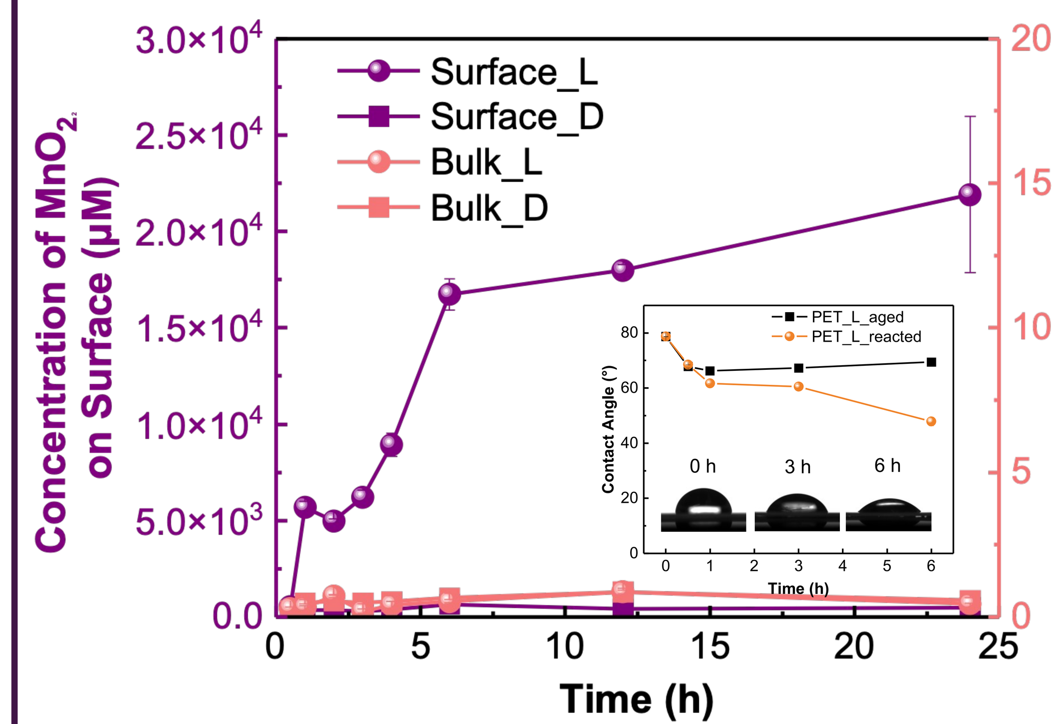
Colorimetric method:

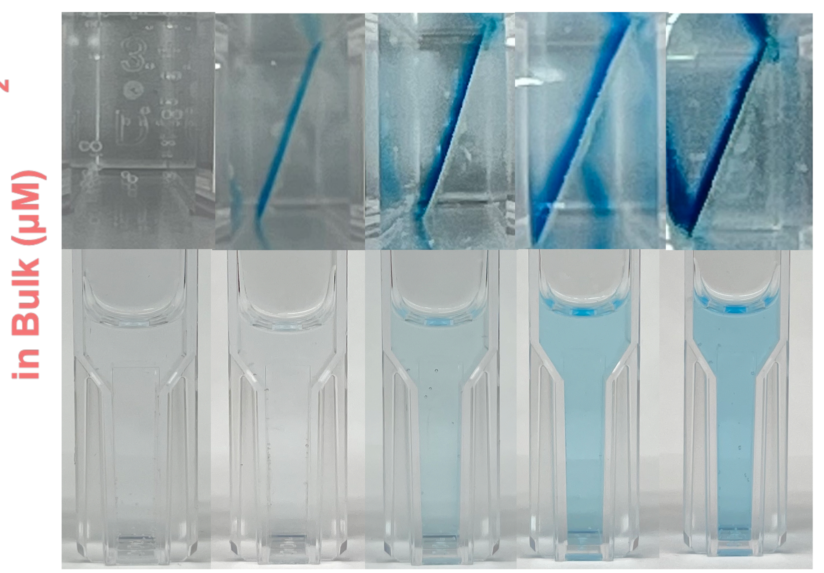
Mn(IV)→Mn(II), **colorless** LBB will be oxidized and turn to blue, oxidized LBB **(blue)** intensity is measured at 625 nm by **UV-vis**.



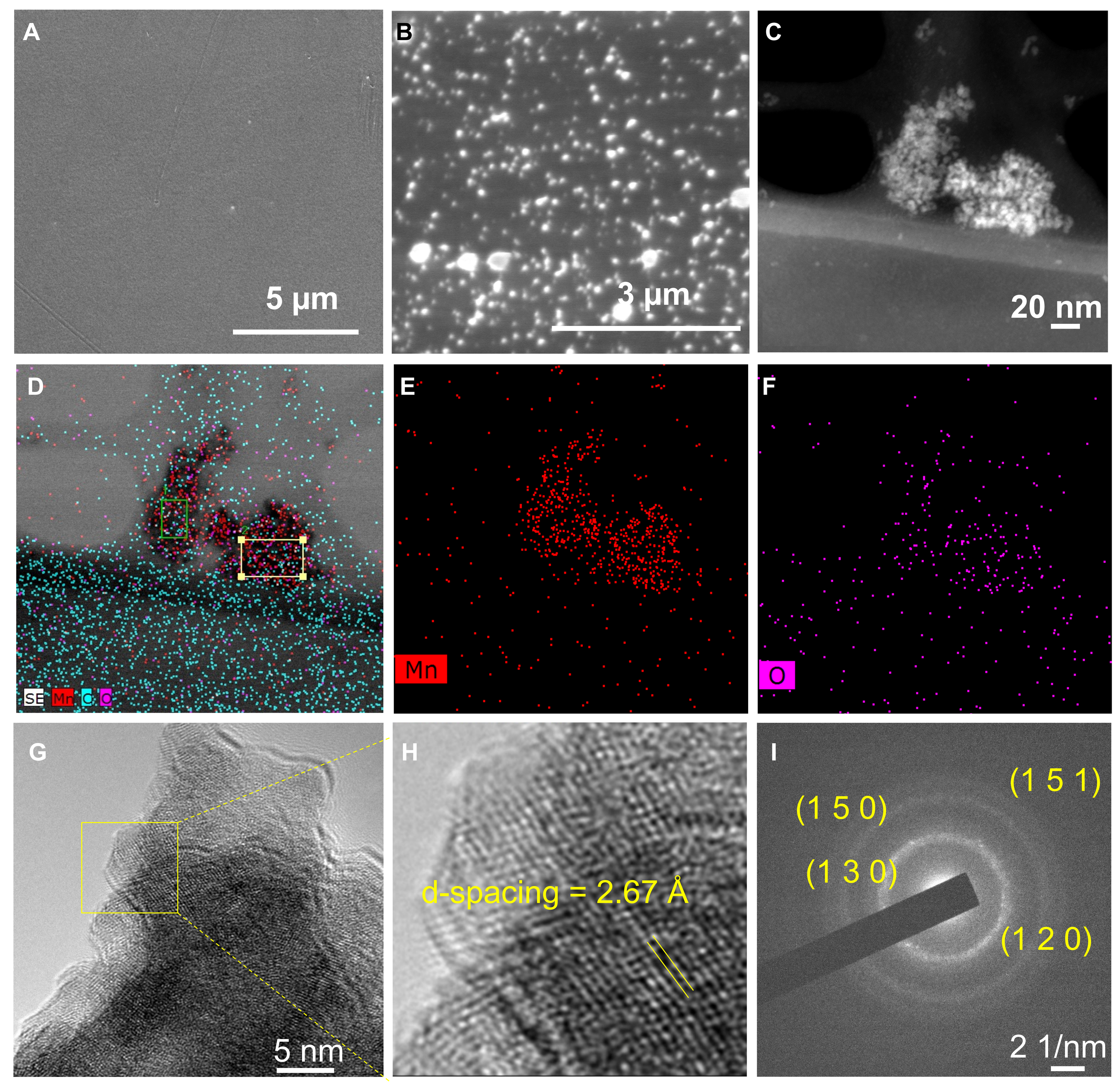


Heterogenous Ramsdellite (R-MnO_2) formed on PET surface under illumination



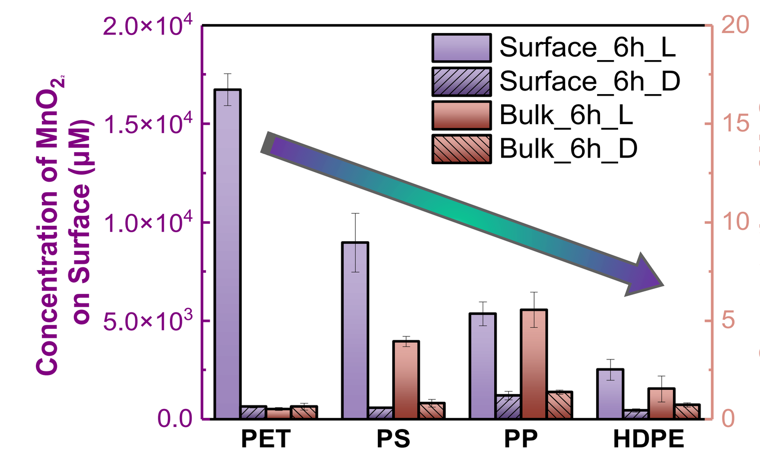


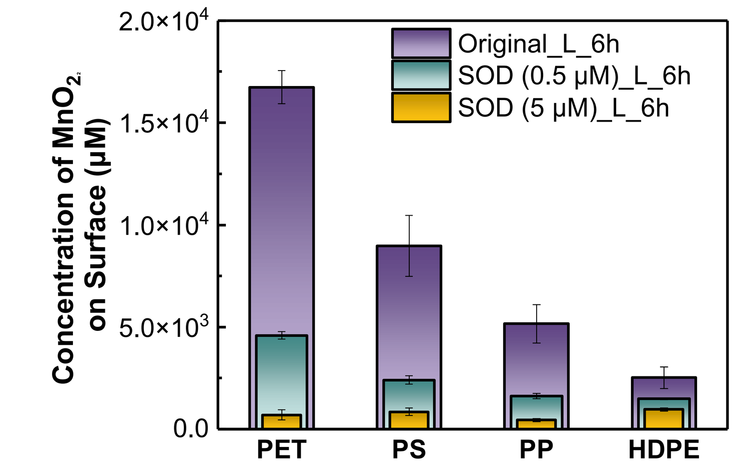
- **Light-induced fast abiotic Mn oxidation occurred heterogeneously on the PET surface, rather than homogeneously.**
- **Mn oxide formation decreased the hydrophilicity of PET surface.**
- **Thicker and darker blueness showed heterogeneous MnO_2 formation on the illuminated side of PET with time.**

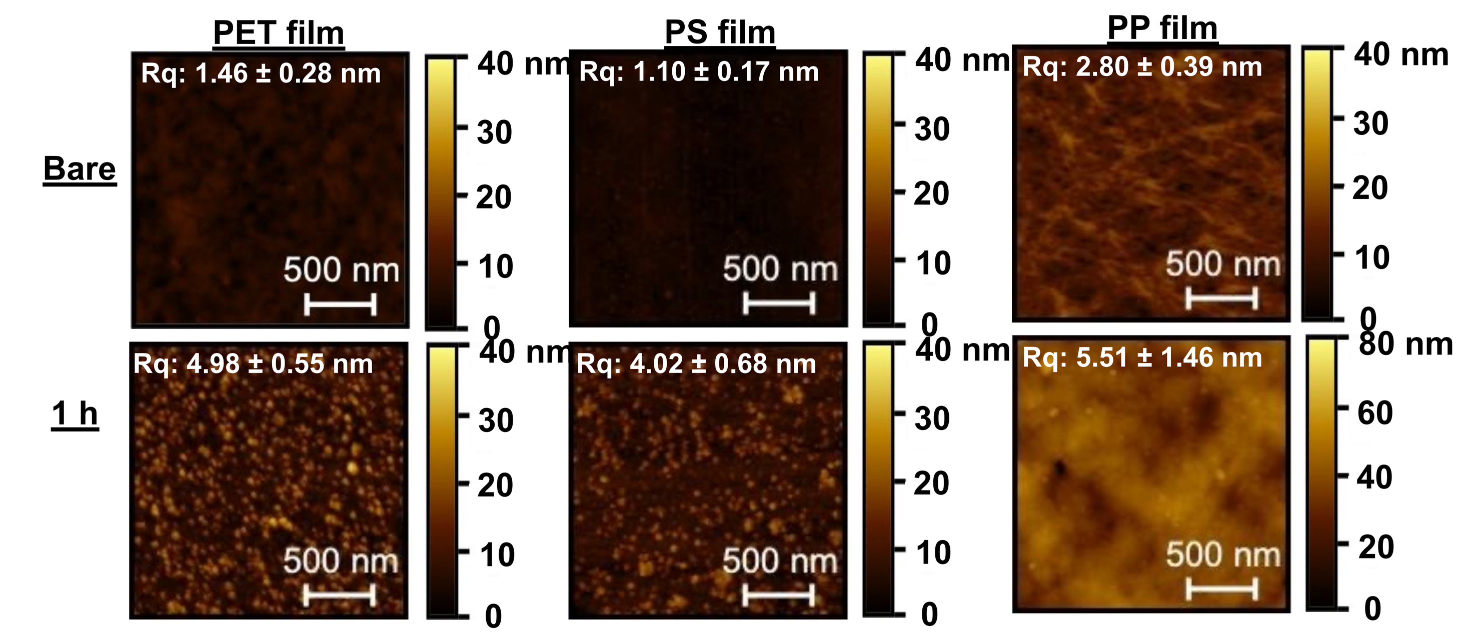


- **Nano-size Mn oxide aggregates had an average particle size of 120 ± 80 nm.**
- **Polycrystalline phase of Mn oxides as Ramsdellite (R-MnO_2), with interplanar d-spacings of 3.2 Å, 2.6 Å, 1.7 Å, and 1.5 Å, corresponding to the (1 2 0), (1 3 0), (1 5 0), and (1 5 1) planes.**

PET best enhanced R-MnO_2 formation than PS, PP and HDPE

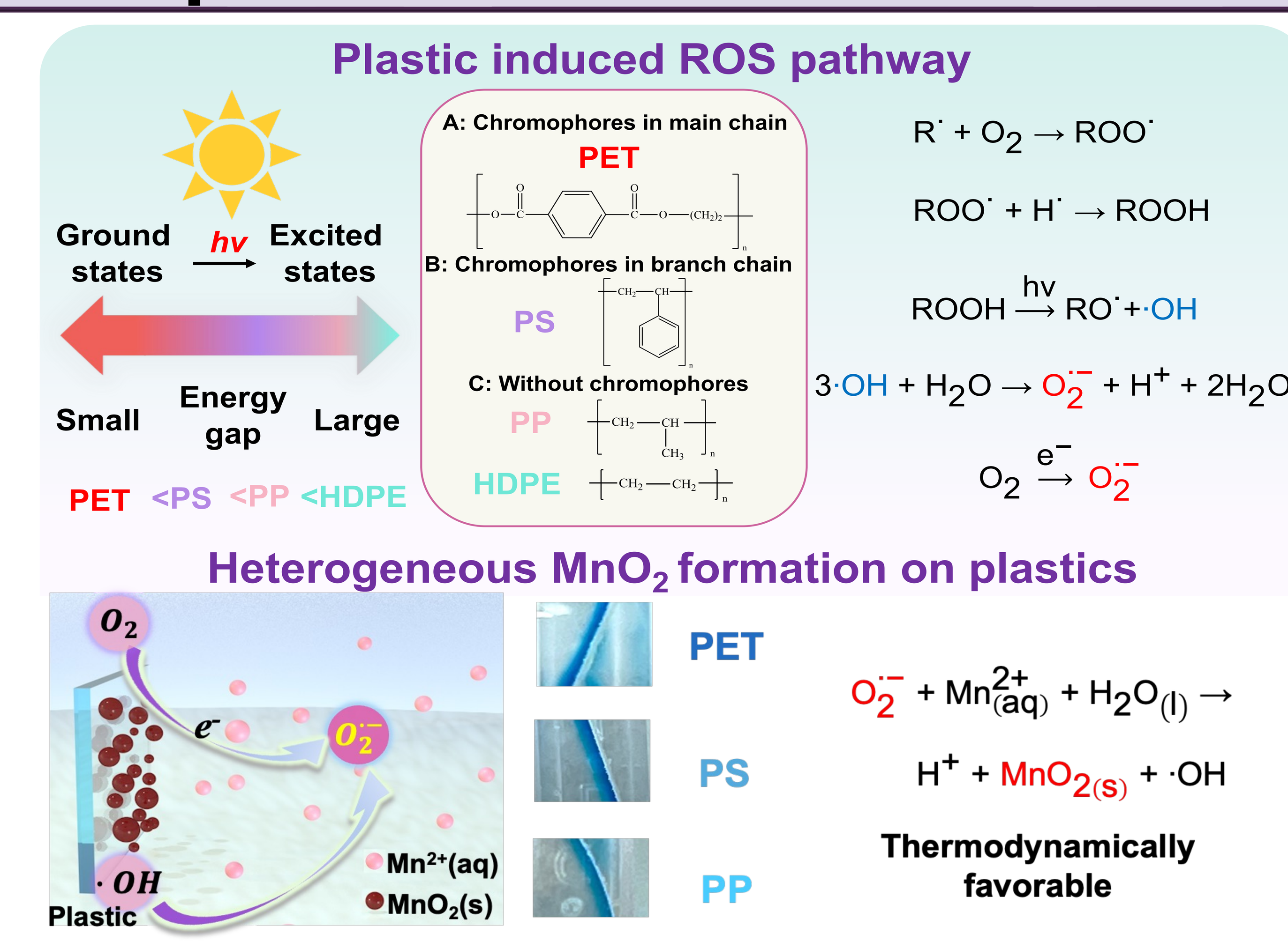






- **Plastics containing various chromophores all demonstrated the capacity to oxidize Mn^{2+}(aq) into MnO_2 on their surfaces. The performance was ranked as follows: PET > PS > PP > HDPE.**

$O_2^{\bullet-}$ is the main ROS induced from excited plastic surface for Mn oxidation



- **ROS induced from plastic surfaces can initiate redox reactions in surrounding environment.**
- **High oxidative ability and numerous redox sites of MnO_2 make it promising materials for in contaminants removal and supercapacitor applications.**