

Supplementary Information

Freezing-induced microplastic degradation in anoxic Fe(II)-containing solution: the key role of Fe(IV) and •OH

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This PDF file includes:

Figures S1 to S10.

Table S1.

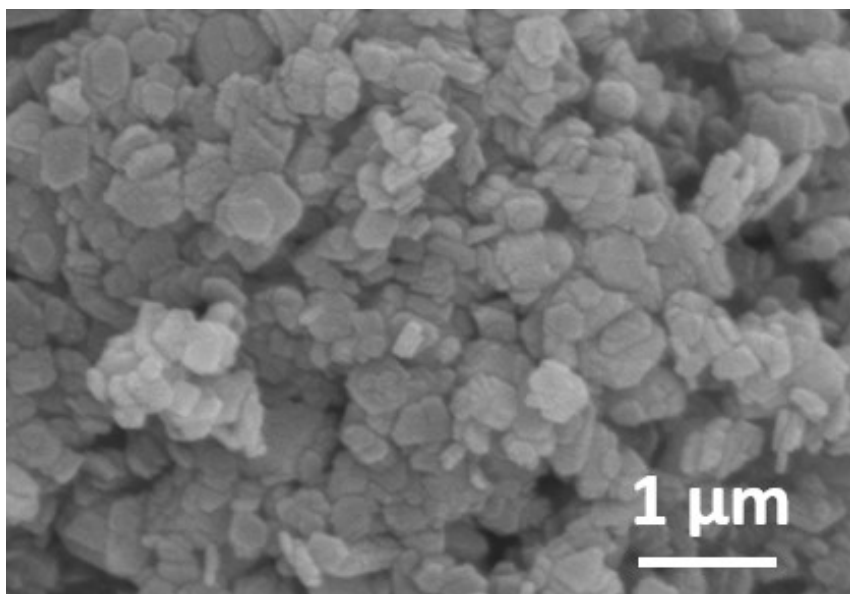


Fig. S1 SEM image of PS-Fe(II)-I after 12d of reaction.

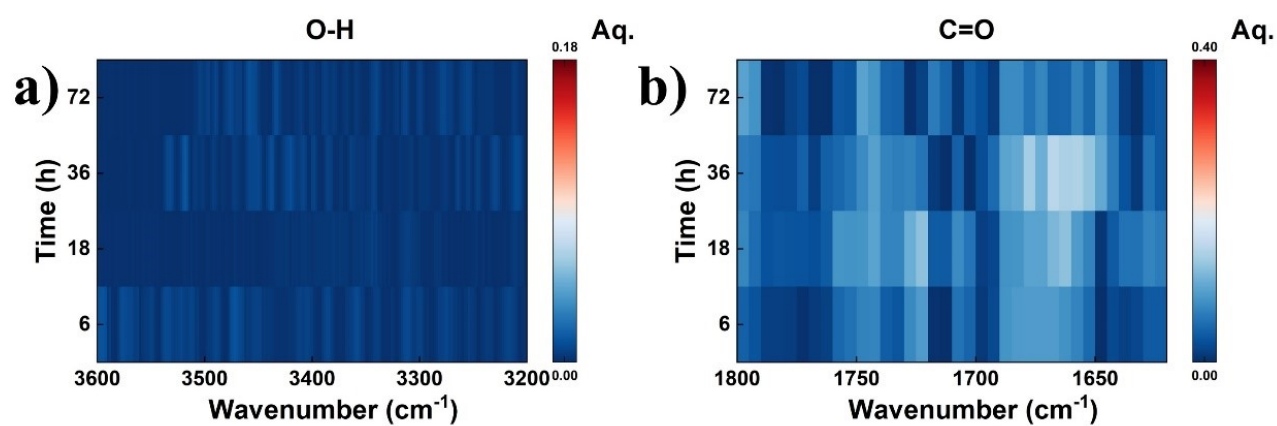


Fig. S2 Heat mappings of a) -OH and b) C=O functional group analyzed by FT-IR for PS-Fe-I after reaction of 6 h, 18 h, 36 h and 72 h.

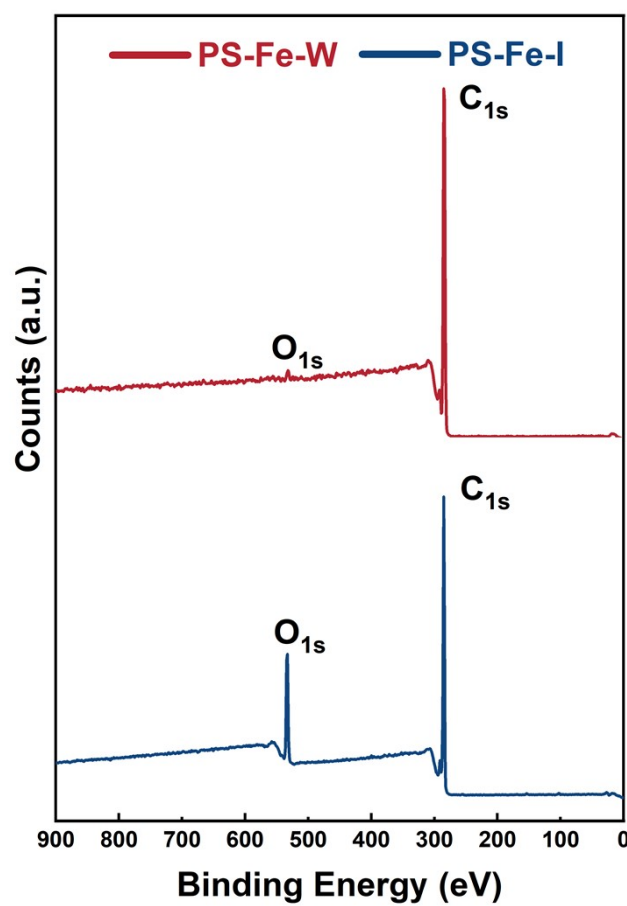


Fig. S3 XPS spectra of PS-Fe-W and PS-Fe-I after the degradation reaction for 36 h.

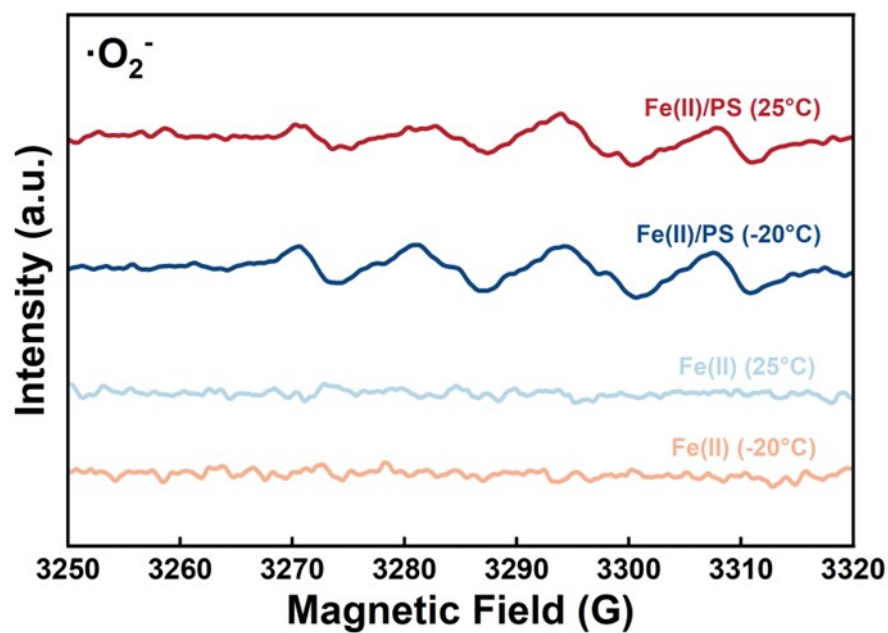


Fig. S4 EPR spectra of $\cdot\text{O}_2^-$ in PS frozen (-20°C , Fz.) and aqueous (25°C , Aq.) Fe (II) solutions after 36 h. $\text{Fe(II)} = 100\ \mu\text{mol/L}$, $[\text{PS}] = 25\ \text{mg/L}$.

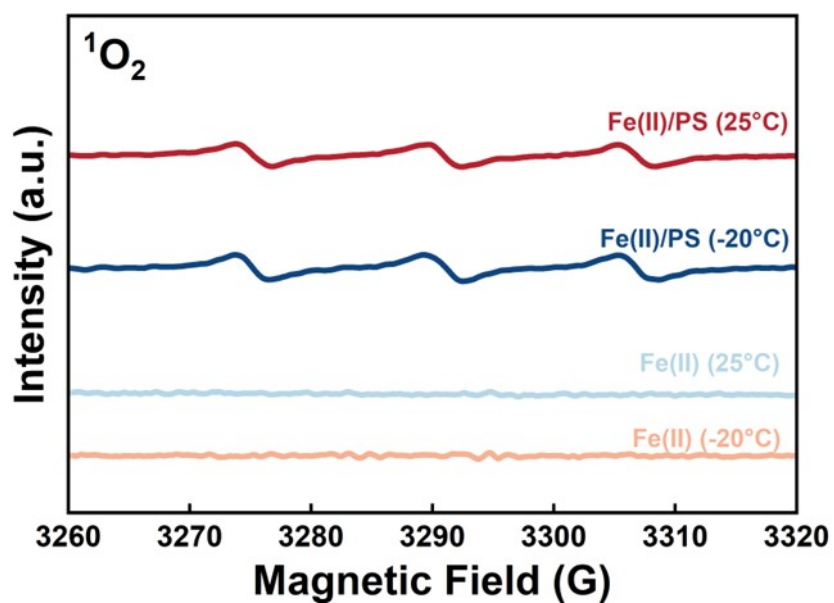


Fig. S5 EPR spectra of $^1\text{O}_2$ in PS frozen (-20 °C, Fz.) and aqueous (25 °C, Aq.) Fe(II)-containing solution after 36 h. Fe(II) = 100 $\mu\text{mol/L}$, [PS] = 25 mg/L.

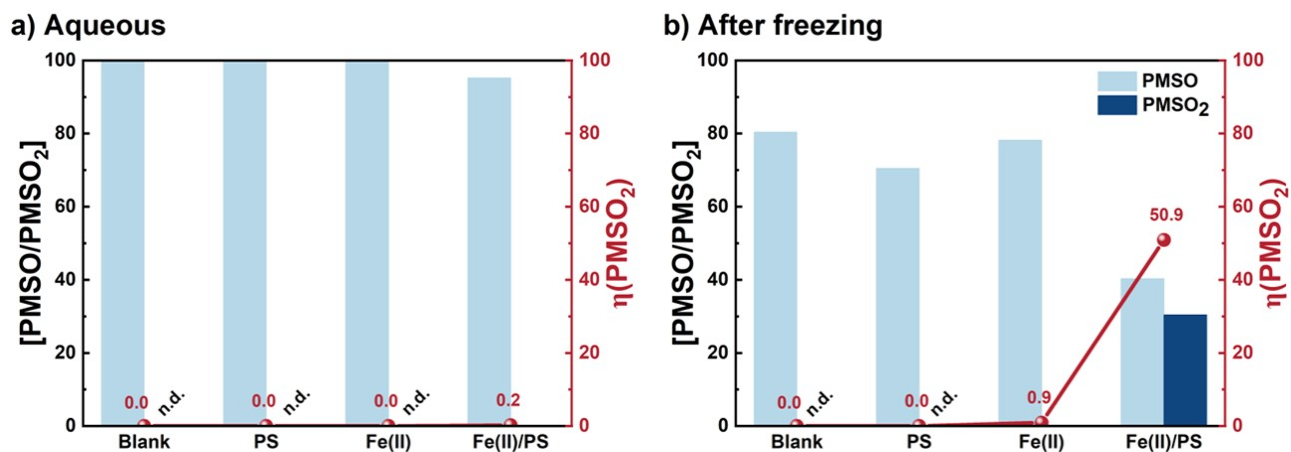


Fig. S6 PMSO degradation, PMSO₂ formation and $\eta(\text{PMSO}_2)$ a) before freezing and b) after freezing in a blank, PS solution, Fe(II) solution, Fe(II) and PS solution. $[\text{Fe(II)}]_0 = [\text{PMSO}]_0 = 100 \mu\text{mol/L}$, $[\text{PS}] = 2.5 \text{ mg/L}$, freezing temperature = -20°C , freezing time = 36h.

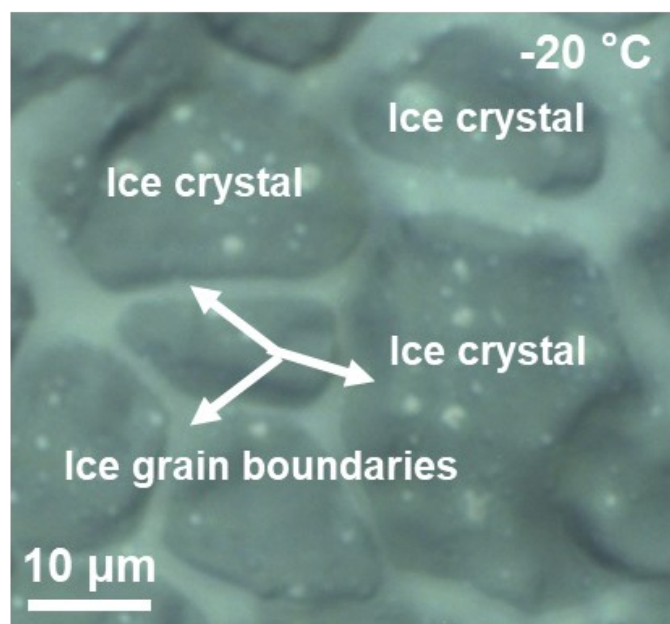


Fig. S7 Confocal Raman microscopy test of PS-Fe-I at -20°C.

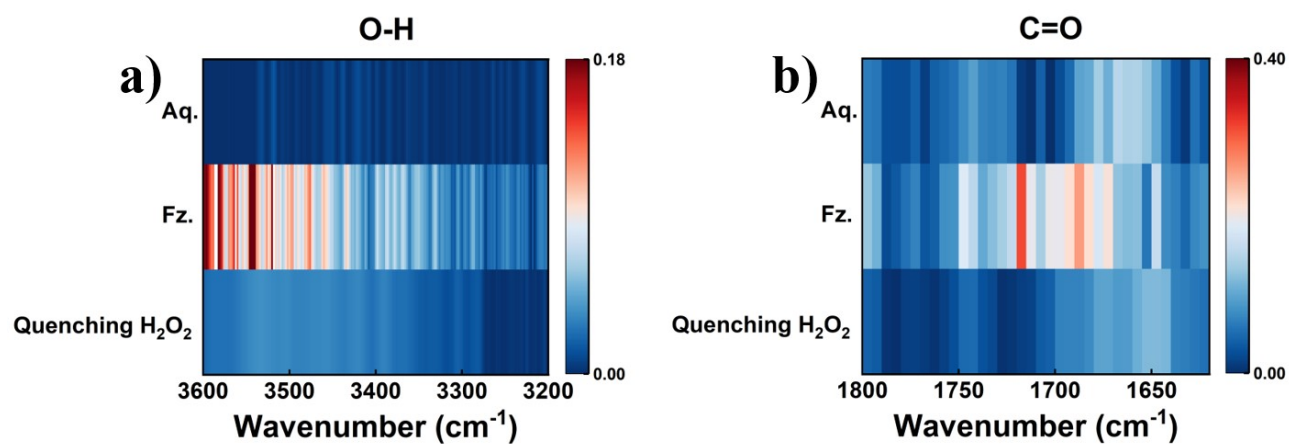


Fig. S8 Heat mappings of a) -OH and b) C=O regions in FT-IR spectra by quenching H_2O_2 after 36 h degradation in water and frozen ice.

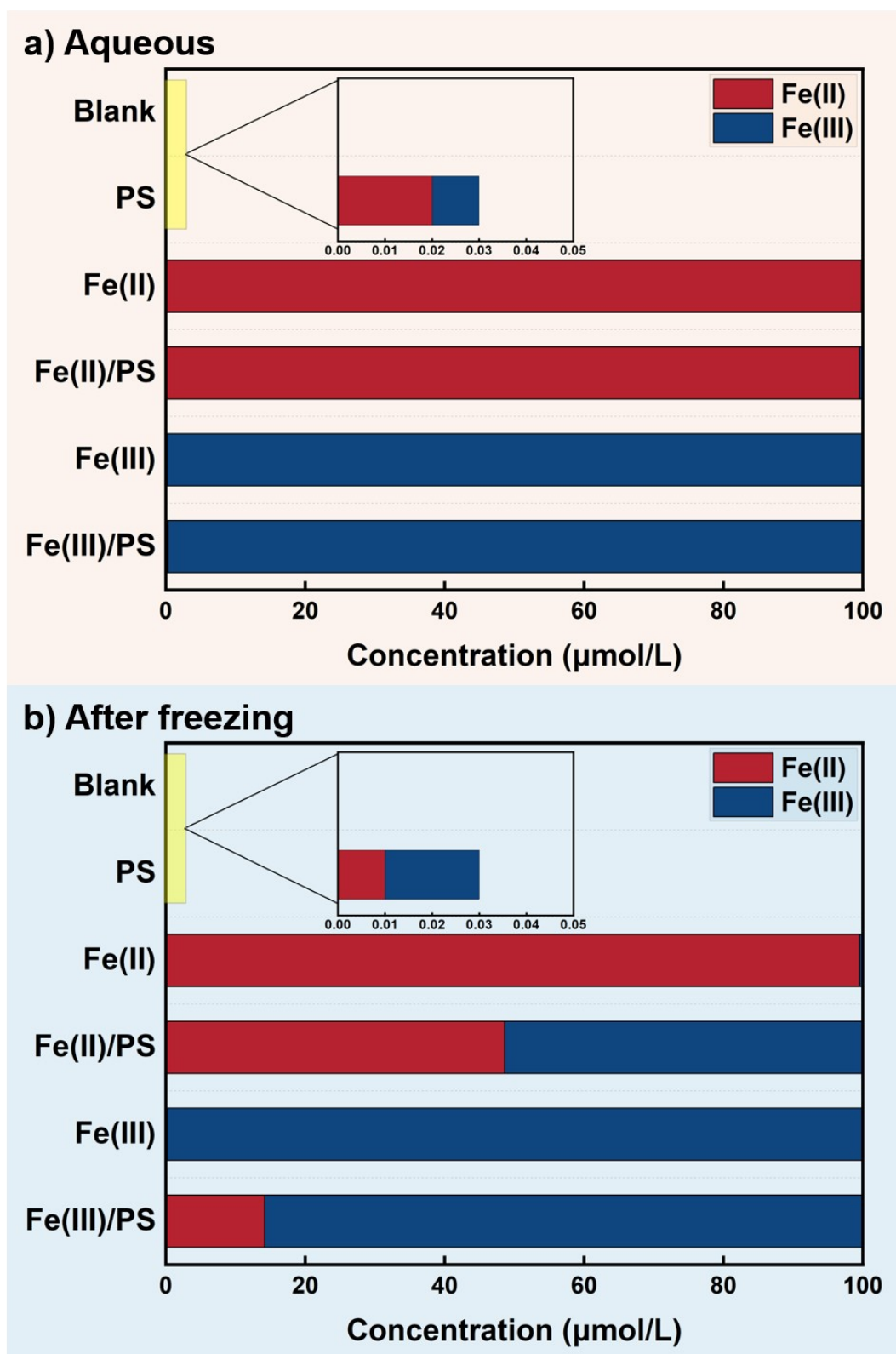


Fig. S9 The concentration of Fe(II) and Fe(III) a) before freezing and b) after freezing in a blank, PS solution, Fe(II) solution, Fe(II) and PS solution, Fe(III) solution, Fe(III) and PS. $[\text{Fe(II)}] = [\text{Fe(II)}] = 100 \mu\text{mol/L}$, $[\text{PS}] = 2.5 \text{ mg/L}$, freezing temperature = -20°C , freezing time = 36h.

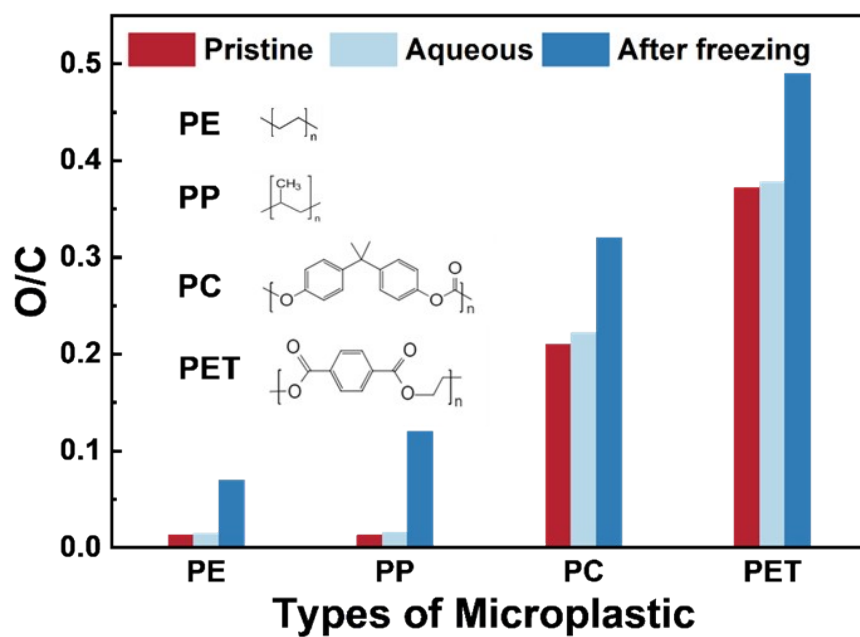


Fig. S10 Enhanced degradation of freezing polypropylene (PP), Poly ethylene (PE), polycarbonate (PC) and polyethylene terephthalate (PET).

Table S1 Determination parameters of PMSO and PMSO₂.

Organic Contaminant	Mobile Phase		Detection Wavelength (nm)	Flow Rate (mL/min)
	Water (%)	Acetonitrile (%)		
PMSO	72	28	230	0.13
PMSO ₂	72	28	230	0.13