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Reactive Oxygen Species-Mediated Photoaging Pathways of Ultrafine Plastic Particles under UV Irradiation

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Abstract : Reactive oxygen species (ROS) generation is considered as an important photoaging mechanism of microplastics (MPs) and nanoplastics (NPs). To elucidate the ROS-induced MP/NP aging processes in water under UV365 irradiation, we examined the effects of surface coatings, polymer types, and grain sizes on ROS generation and photoaging intermediates. Bare polystyrene (PS) NPs generated hydroxyl radicals (•OH) and singlet oxygen ($^1O_2$), while coated PS NPs (carboxyl-modified PS (PS-COOH), amino-modified PS (PS-NH_2)) and PS MPs generated fewer ROS due to coating scavenging or size effects. Polypropylene, polyethylene, polyvinyl chloride, polyethylene terephthalate, and polycarbonate MPs only generated •OH. For aromatic polymers, •OH addition preferentially occurred at benzene rings to form monohydroxy polymers. Excess •OH resulted in H abstraction, C-C scission, and phenyl ring opening to generate aliphatic ketones, esters, aldehydes, and aromatic ketones. For coated PS NPs, •OH preferentially attacked the surface coatings to result in decarboxylation and deamination reactions. For aliphatic polymers, •OH attack resulted in the formation of carbonyl groups from peracid, aldehyde, or ketone via H abstraction and C-C scission. Moreover, $^1O_2$ might participate in phenyl ring opening for PS NPs and coating degradation for coated PS NPs. This study facilitates understanding the ROS-induced weathering process of NPs/MPs in water under UV irradiation.

Keywords : microplastics, nanoplastics, photoaging, reactive oxygen species, surface coating
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