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Supporting Information

Water promoted the photo-oxidation and -mineralization of ¹⁴Cpolystyrene nanoplastics

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Synthesis of [β-¹⁴C]-styrene

 $[\beta^{-14}C]$ -malonic acid (1.5 × 10⁷ Bg, 2.1 × 10⁹ Bg mmol⁻¹, 99% radiochemical purity) was 50-fold diluted with non-labeled malonic acid (0.0362 g) and dissolved in pyridine (1 mL) in a 25 mL flask equipped with a magnetic stir bar and reflux condenser. Piperidine (177 µL) and benzaldehyde (0.1128 g, 1.065 mmol) were added to the flask. The mixture was heated at 105 °C for 14 h, acidified with 20 mL HCl (1 M), and extracted with ethyl acetate (9 times, each 15 mL). After drying over anhydrous Na₂SO₄ and rotary evaporation to 0.5 mL, the mixture was loaded onto a preparative thin layer chromatography (TLC) plate. TLC was performed on silica gel 60 plates with fluorescence indicator. Analytical (3 cm \times 10 cm \times 0.2 mm) and preparative (20 cm \times 20 cm \times 2 mm) plates (GF254; Qingdao Hailang Factory, Qingdao, China) were used. Preparative TLC plates were pre-treated by eluting the plates in ethyl acetate. The plates with loaded samples were developed in *n*-hexane: ethyl acetate: formic acid (100:100:1, by volume). An imaging scanner (Typhoon Trio+; GE Healthcare, Fairfield, USA) was used for autoradiography of the developed plates. The bands of cinnamic acid ($R_{\rm f} = 0.67$) were scraped from the plates and extracted with ethyl acetate (seven times, each 15 mL), resulting in $[\beta^{-14}C]$ -cinnamic acid $(1.2 \times 10^7 \text{ Bg}, 4.2 \times 10^7 \text{ Bg} \text{ mmol}^{-1}, 99.99\%$ radiochemical purity) with a radiochemical yield of 82.8%.

The above [β -¹⁴C]-cinnamic acid was 10-fold diluted with non-labelled cinnamic acid and the total 3 mmol cinnamic acid was added to a 25-mL flask containing silver acetate (0.0096g, 0.6 mmol) and K₂CO₃ (0.0124 g, 0.9 mmol). After gentle flushing

the vessel with nitrogen gas to replace the headspace, degassed *N*,*N*dimethylacetamide (DMAc) (4 mL) was dropwise added by syringe and the resulting mixture was stirred at 160 °C for 8 h. Then, it was allowed to cool down to room temperature, diluted with *n*-hexane (2 mL), poured into aqueous NaOH solution (1 M, 10 mL), and extracted repeatedly with *n*-hexane (5 times, each 4 mL). The organic extracts were combined and washed successively with aqueous NaHCO₃ (50 g L⁻¹, 4 mL) and saturated brine (4 mL), dried over anhydrous Na₂SO₄, and rotary evaporated to 1 mL, resulting in [β -¹⁴C]-styrene (4.2 × 10⁶ Bq, 99.99% radiochemical purity) with 33.7% yield.

Characterization of synthesized ¹⁴C-PS nanoplastics

Scan electron microscopy (SEM). The morphological analysis was performed with a Field Emission Gun-SEM (Quanta 250 FEG, FEI, Oregon, USA). Samples were sputtering with gold before observation.

Dynamic Light Scatter (DLS). The hydrodynamic diameter and its distribution of nanoplastics were measured with a DLS (Zetasizer Nano ZS-90, Malvern Instruments, UK). The samples were suspend in deionized water and dispersed for 10 min by ultrasonic before measuring.

Fourier-transform infrared spectroscopy (FT-IR). Products were pretreated by tableting with KBr and measured in transmission mode on a Nexus 870 spectrometer (Nicolet, Massachusetts, USA). The spectra of PS samples were obtained with a 1 cm⁻¹ resolution in the wavenumber range of 400–3600 cm⁻¹.

Nuclear Magnetic Resonance (NMR) spectroscopy. The NMR was performed

on a DPX-500MHZ spectrometer (Bruker, Germany) with Tetramethylsilane (TMS) as internal standard and CDCl₃ as the solvent.

Molecular weight determination. The number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index ($PDI = M_w / M_n$) of molecules of nanoplastics were measured by gel permeation chromatography (GPC) (PL-GPC120; Agilent Technologies, USA) with a refractive index detector. Two tandem gel columns of polystyrene, PL-gel MIXED-B (10 µm, 300 mm × 7.5 mm) and PL-gel MIXED-C (5 µm, 300 mm × 7.5 mm), were used, with tetrahydrofuran as a mobile phase running at 1.0 mL min⁻¹ and 40 °C. The columns were calibrated using polystyrene standards (Polymer Source Inc., Dorval, Canada).



Fig. S1 The variation of leachates amount in the water washed ¹⁴C-PS nanoplastics from treatment of UV in air. In order to analyze the transformation products in treatment of UV in air, 10 mL nanopure water was added to wash the ¹⁴C-PS nanoplastics in air treatment. After shaking for 5 min, the ¹⁴C amount was detected and then sampling at 30 min, 60 min and 720 min respectively. No significant increase was observed after 5 min indicated that 5 min was enough to wash out all the products in ¹⁴C-PS nanoplastics.



Fig. S2 Scanning electron microscope (SEM) image of synthesized ¹⁴C-PS (A) and the hydrodynamic diameter of synthesized ¹⁴C-PS in distilled water determined by DLS. The average size range was 250 ± 88 nm, with a PDI of 0.31.



Fig. S3 FTIR spectra of standard (A) and synthesized (B) PS. The indicated numbers are characteristic peaks of PS.



Fig. S4 ¹H NMR spectra of standard (A) and synthesized (B) PS. Peak area was showed at the bottom of the peaks.



Fig. S5 ¹³C NMR spectra of standard (A) and synthesized (B) PS.



Fig. S6 FTIR spectra of ¹⁴C-PS nanoplastics before (black line) and after 48 h of UV irradiation in water (red line) and in air (blue line).



Fig. S7 UV spectra of leachates from ¹⁴C-PS nanoplastics after 48 h of UV irradiation in water (red line) and in air (blue line) as well as blank (black line). The absorption at 220 nm may be associated with carboxylic and aromatic chromophores.