Supplementary Information

Local Infrared Spectral Measurement System for the Inspection of Independent Nano-plastic Particles in Water-based Solutions

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The supplementary information includes 3 tables and 2 figures in 15 pages.

Table S1 The advantages and disadvantages of each method for collecting nanoscale plastic particles.

Methods	Advantages	Disadvantages	References
Collection by local laser-induced generation of microbubbles Microbubbles are generated by laser focused heating of the interface between the substrate and the solvent. Marangoni convection is induced, and particles are collected at the microbubble interface.	● Enables concentration and accumulation at desired locations. ● Applicable for efficient microscopy measurements. ● Marine samples can be used in practice. ● Experiments can be performed with a few µl of liquid sample.	● Heat sensitive samples are difficult. ● Mixed particles are difficult to separate.	[1-4]
Centrifugation The method of separating molecules of different densities by rotating them in solution (in the rotor of a centrifuge) at high speed around an axis.	● High yield. ● High purity depending. ● Reproducible. ● Well, established.	● Requires batch processing. ● Bulky. ● Relatively expensive.	[5-8]
Membrane Filtration (MF) The single feed stream is passed through a membrane system, which separates it into two separate streams called permeate and reverse osmosis. The four types of MF are known as reverse osmosis, nanofiltration, ultrafiltration, and microfiltration, in order of increasing pore size.	● No Chemicals. ● Highly efficient contaminant removal. ● Easily combined with other processes.	● Cost to fabricate. ● Harmful chemicals. ● Membrane fouling. ● Maintenance and repair.	[9-15]
Field Flow Fractionation (FFF) The method of separation using the interaction between the solute and the external force applied to the flow path.	● High separation capacity. ● Excellent versatility. ● Simultaneous measurements possible. ● Applicability to a wide variety of samples over a wide mass size range. ● Flexibility to target specific problem areas. ● High reproducibility.	● Compromise between resolution and speed in optimization. ● High cost. ● Low equipment requirements. ● Small production scale.	[15-17]
Cloud Point Extraction (CPE) Separation techniques used for extraction and preconcentration of analytes from sample matrices. CPE is based on phase separation caused by the aggregation of surfactant micelles in aqueous solution above a temperature called the cloud point.	● Low cost. ● Easy to operate. ● Can be combined with analytical techniques. ● high extraction efficiency can be obtained. ● Sample clean-up.	● Large volume of samples required.	[18-22]
Pressurized Fluid Extraction (PFE) A new sample extraction method using liquid solvents at high temperature and pressure to prepare samples suitable for analysis by gas chromatography or	● Reduced extraction time. ● Solubility and diffusion of target compounds at high temperatures.	● Destructive. ● All plastics of different sizes are extracted. ● Expensive laboratory equipment required.	[22-24]

liquid chromatography.	● Extraction cost reduction. ● Simple.	● To avoid matrix-dependent efficiency, variables must be thoroughly optimized.	
Alkali-assisted Thermal Hydrolysis (ATH) A technique to accelerate hydrolysis of plastics (polyester, polybutylene terephthalate, polycarbonate) with ester or carbonate bonds in the molecular chain by using an aqueous alkaline solution and high heat to break them down.	● Thermal and Alkaline. ● Quantification of PET and PC. ● Transport, useful for assessing potential impact.	● Applicable only to PET and PC with ester groups in the main chain. ● Difficult to apply extensively. ● Hydrolysis causes loss of the original size and morphology of the plastic pieces.	[22, 25-28]
Emulsions A liquid in which one liquid with low mutual affinity is dispersed in the other liquid in particulate form: hydrophobic emulsions (W/O), hydrophilic emulsions (O/W), and complicated emulsions which are (W/O/W) and (O/W/O).	● Hydrophobic interactions allow them to be adsorbed on micro and nanoplastics. ● Extraction of a wide range of plastic sizes.	● Relatively large volumes of oil are required for highly efficient extraction. ● Cost inefficient. ● Limited by the release of surfactant molecules, Fe^{2+}/Fe^{3+} ions, and related substances from magnetic particles. ● Particle agglomeration.	[29-32]

Table S2 The advantages and disadvantages of each method for visual analyzing nanoscale plastic particles.

Methods	Advantages	Disadvantages	References
Atomic Force Microscope (AFM) **A high-resolution type of scanning probe microscope that uses a sharp probe to perform raster scans to measure and visualize sample height, as well as to analyze electrical, magnetic, and mechanical properties such as friction and viscoelasticity.** The observation range: ~30 μm (the ultra-small size of nm is also possible.) A type of Scanning Probe Microscope (SPM).	● No sample preparation required. ● Low cost. ● No restrictions on measurement environment: air, liquid, vacuum, high/low temperature, etc. ● Non-destructive. ● Sample shape, height, and characteristics can be measured.	● Measurement of samples with low magnification or large irregularities is difficult. ● Narrow vertical measurement range. ● Sample analysis takes time. ● Careful handling of ultra-small tips is required.	[33-35]
Scanning Electron Microscope (SEM) A microscope that provides high-resolution observation of surface irregularities, particle shapes, and surface elemental analysis of nanoparticles, fine particles, film and substrate surfaces, composite materials, fiber shapes, pore structures, etc. by irradiating a sample surface with an electron beam and detecting the secondary electrons and reflected electrons generated.	● Provides great depth of focus. ● Larger area can be scanned. ● Clear, high-resolution images of particles. ● Available to be combined with other measurement techniques.	● Requires conducting samples and charging effect could be observed. ● High capital and maintenance costs. ● Requiring skilled operators. ● Prolonged sample preparation times. ● Long time and effort for analysis. ● Need special space requirements to avoid interference from electromagnetic and vibrational noise of neighboring instruments and activities.	[33-38]
Transmission Electron Microscope (TEM) A microscope that uses the difference in transmittance of electron beams irradiated on a sample to provide and observe information on the size, shape, localization, dispersion, agglomeration, etc. of particulate matter in a two-dimensional image.	● Images are high quality and detailed. ● Thin samples can be scanned. ● High-cost performance. ● Very high resolution (<0.1 nm). ● Possible to combine with other analytical techniques. ● Easy to operate with proper training.	● Images are black and white. ● Very time consuming to measure. ● Large and very expensive. ● Possible artifacts from sample preparation. ● Requires special training for operation and analysis. ● Electron-transparent sample with particle size of 100 nm or larger, withstands vacuum chambers, and must be large enough to	[33-39]

		fit in the chamber. ● Requires special housing and maintenance equipment.	
Scanning Tunneling Microscope (STM) Metallurgical microscope that observes and evaluates the surface properties of nanoparticles by detecting the tunneling current between the probe and the sample. A type of Scanning Probe Microscope (SPM).	● Very high-resolution images of conductors and semiconductors can be obtained. ● The probe tip can be made of wire. ● Inexpensive to purchase.	● Not usable on insulators. ● Must often be used under vacuum.	[40-43]
Photo-induced Force Microscope (PiFM) A scanning probe technique that provides images with spectral and spectral contrast very close to that of far infrared spectroscopy with spatial resolution in the nanometer range. The basis for this is the modern development of AFM.	● Non-destructive. ● Time and cost efficiency. ● Broad applicability to all types of sample analysis. ● Operation under ambient conditions. ● Domains are easily identified.	● The presence of moisture can attenuate the infrared signal. ● A significantly more complex sample–probe interaction. ● Sample pretreatment is required. ● The obtained spectra may not be comparable to conventional infrared analysis and should be carefully considered.	[33, 44-49]

Table S3 The advantages and disadvantages of each method for spectral analyzing nanoscale plastic particles.

Methods	Advantages	Disadvantages	References
Atomic Force Microscopy based Infrared Spectroscopy (AFM-IR) A technique in which light from a tunable infrared laser is irradiated onto a localized region of a sample and the resulting amplitude change in photothermal expansion of the sample is measured using the cantilever of an atomic force microscope to obtain IR absorption spectra and absorption images of individual independent particles with a spatial resolution on the 50-100 nm scale.	● Non-destructive. ● Fine spatial resolution below conventional optical diffraction limits for chemical analysis and compositional mapping. ● Morphological and chemical imaging. ● Point IR spectral acquisition. ● Direct correlation with FTIR. ● High accuracy. ● Ideal for organic and biological samples such as polymers, blends, and composites. ● Additional characterization such as hydrophobicity and conductivity of MP and NPs is also possible.	● Background interference. ● Signal enhancement by gold-coated probes and substrates. ● Decreased peak intensity compared to bulk IR spectrum. ● Sample preparation required. ● Sample characteristics (thickness, smoothness, thermal diffusivity, etc.) limit resolution and signal intensity.	[50-59]
Fourier Transform Infrared Spectroscopy (FTIR) A standard nondestructive analysis technique to identify synthetic polymers based on their characteristic molecular vibration spectra by creating interference waves using a fixed mirror and a moving mirror, shining them on the object, and measuring the transmitted or reflected interference waves by Fourier transform and infrared spectrum.	● Confirmation of the composition of the MPs. ● No false positive or negative data. ● Detection of small plastic particles (less of 20 μm) with μ-FTIR. ● Non-destructive analysis of materials. ● Four main analytical techniques for the use of FTIR (transmission, diffuse reflectance, true specular-adsorption and attenuated total reflection). ● The ability to identify FTIR spectra and reference spectra in the online library allows for easy identification of common types of polymers, along with detailed information on particle size.	● Wavelength radiation can be a limiting factor in detection. ● Time consuming to analyze all particles. ● High capital cost and limited accessibility. ● Requires skilled labor to manipulate spectra. ● Possibility of causing spectral shifts. ● Trace amounts of moisture in the sample can interfere with analysis.	[33-35, 58-59]

Thermal Analysis (TA) A group of techniques in which a property of the sample is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed. Five typical techniques: differential thermal analysis (DTA) to detect temperature and temperature differences, differential scanning calorimetry (DSC) to detect heat flow differences, thermogravimetry (TG (TGA)) to detect mass and weight changes, thermomechanical analysis (TMA) and dynamic mechanical analysis (DMA) to detect mechanical properties.	● Specific material information can be obtained by using any thermal analysis technique. ● Characterization of additives. ● Identification of many samples at once. ● Existing data libraries can be used for analysis.	● Destructive. ● Constrained to a variable temperature defined by a pre-set program. ● Dependent on sample melting temperature. ● Lack of specificity due to mixtures and multiple peaks. ● Requires references due to complex data. ● Quantitative analysis of each sample is not possible.	[33-35, 38, 59-60]
Raman Spectroscopy A non-destructive spectroscopic technique that provides structural information on macroscopic polymers based on the inelastic scattering of photons from a monochromatic light source (most commonly a laser).	● No false positive or false negative data. ● Non-destructive. ● Capable of analyzing solutions, gases, films, surfaces, solids, and single-crystal samples. ● Low sample volume requirements ● Allows evaluation of stereoregularity of polymers to be screened. ● Provides structural information that reveals the identity of polymers and the type of additives. ● Not affected by sample thickness or moisture.	● Low overall intensity. ● Sufficient sampling time required. ● Possible damage from focused excitation laser. ● Expensive equipment. ● Interference with additives and pigments. ● Sample purification. ● Limited resolution. ● Large sample throughput.	[22, 33-35, 61-63]
Surface-enhanced Raman Scattering (SERS) spectroscopy Surface-sensitive technology that uses plasmonic magnetism to enhance Raman scattering of molecules adsorbed on rough metal surfaces and nanostructures such as silica nanotubes.	● Increased sensitivity and selectivity over standard Raman spectroscopy. ● Chemical specificity. ● Non-destructive. ● Label-free analysis. ● Non-invasive. ● Performs under a variety of temperature and pressure conditions. ● Detects less than a single layer of analyte on a surface, even in complex mixtures.	● Difficult to operate. ● Further efforts are needed to improve data reproducibility, substrate stability, and substrate-analyte interactions. ● Requires coupling with nanoparticles. ● Requires tagging or immediate proximity to the molecule.	[33, 64-66]

Flow Cytometry (FCM) A technique for analyzing single particles or cells one at a time in a dynamic system in which the analyte passes through a detector in an aqueous solvent or buffer solution.	● Capable of detecting infectious disease pathogens in molecular biology and microbiology. ● Optional automated cell sorting by size and color. ● Fast analysis based on flow rate. ● Measure single cells or particles or large numbers of cells or particles. ● Simultaneous analysis of multiple parameters. ● Quantification of fluorescence intensity. ● Portable instrument.	● Very expensive and sophisticated equipment. ● Managed by highly trained professionals. ● Requires ongoing maintenance. ● Must be combined with secondary polymer detection techniques such as visual probabilistic network enveloping. ● Plastic agglomeration and sedimentation hinder identification. ● Intensive data generation. ● Interpretation of flow data is complex and labor intensive. ● Practical only for special applications. ● Requires warm-up, laser calibration, and cleaning after each use.	[58, 67-69]
Matrix-Assisted Laser Desorption/Ionization Time-Of-Flight Mass Spectrometry (MALDI-TOF/MS) **The device measures absolute molecular weight and performs structural analysis by uniformly applying an ionization aid called matrix to a thin sample of protein, peptide, or synthetic polymer, and ionizing the molecules contained in the matrix by laser irradiation.** MALDI is used as the ion source and TOF detector as the mass spectrometer.	● No need for trained operators. ● Complex polymers can be characterized. ● Wide detection mass range. ● Accurate and sensitive methods ● High throughput ● Easy sample preparation ● Cost-effective ● Automatic operation is possible.	● Time consuming. ● Cost prohibitive. ● Need to improve database width. ● No quantification. ● No particle guidelines for validation, implementation, and reporting of results.	[70-73]
Pyrolysis Gas Chromatography–Mass Spectrometry (Pyr-GC/MS) Multi-purpose system for extensive analysis of trace amounts of macromolecular substances and insoluble substances that cannot be directly introduced into the GC.	● High sensitivity. ● Minimal sample preparation is sufficient. ● Direct injection is possible depending on the environmental matrix. ● Can be used regardless of particle size. ● Identification of polymer type and	● Destructive. ● No information on physical shape of plastic fragments. ● Complex data processing. ● Possible variations in results for non-homogeneous samples. ● Fails to detect most inorganic constituents.	[33, 58, 74-77]

	estimated mass and additives. ● Can investigate materials and compounds not suitable for conventional GC-MS.		
Liquid chromatography–tandem mass spectrometry (LC-MS/MS) An analytical device in which analytes separated by liquid chromatography (LC) are ionized by a dedicated interface (ion source), the generated ions are separated by a mass spectrometer (MS) to dissociate and fragment specific mass ions, and those ions are detected by a mass spectrometer.	● High sensitivity. ● High detection speed. ● High specificity. ● High sensitivity. ● Wide dynamic range. ● Measurement of multiple steroids. ● Almost any compound that dissolves and ionizes in a liquid can be measured. ● Enables quantitative analysis of trace components because only specific masses can be selected and fragmented. ● Useful for structural analysis of trace components.	● Destructive in nature. ● No information on the number, size, color, or shape of plastic particles. ● Requires significant capital investment. ● Requires skilled operators. ● Time consuming sample preparation. ● Prone to experimental contamination. ● Complex data processing. ● Matrix co-extractables may suppress or enhance ionization potential. May require matrix-matched calibration for quantitation. ● Reproducibility is often not as good as LC-UV or other LC detectors when stable-labeled internal standards are not used. ● Limited use for polymers.	[78-81]

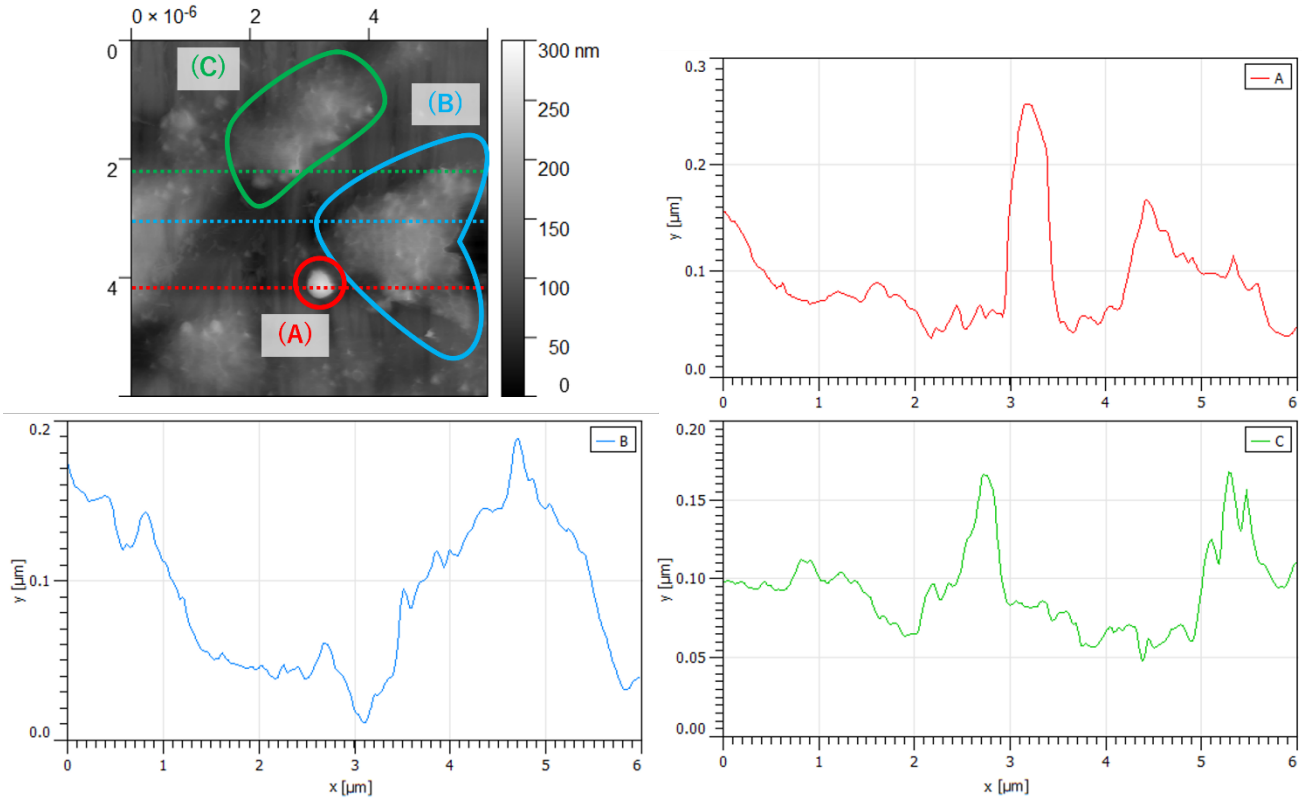

Fig.S1 The height profiles of (A) LDPE-NPs of about 300 nm diameter (B) LDPE-MPs.1 (C) LDPE-MPs.2

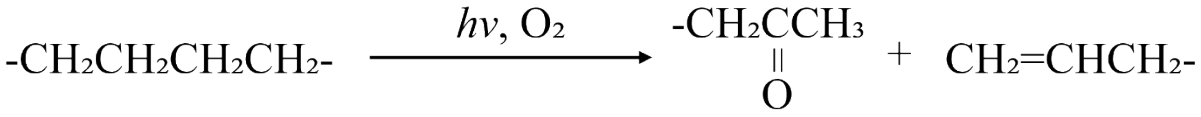

Fig.S2 An example of a possible decomposition reaction scheme. [82-89]

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