Electronic Supplementary Material (ESI) for Environmental Science: Nano.
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Supporting Information

Top-Down Synthesis of Luminescent Microplastics and Nanoplastics by Incorporation of Upconverting Nanoparticles for Environmental Assessment

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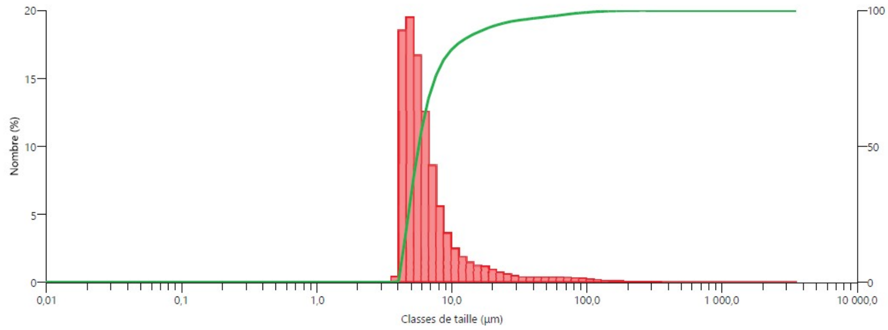
a)



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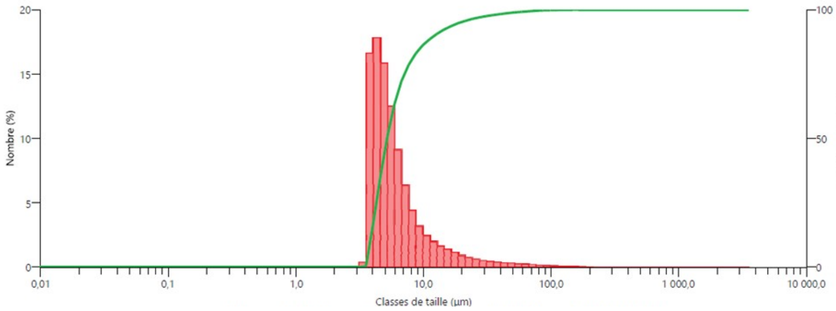

Figure S1. Granulometric analysis after cryogenic grinding, expressed as a percentage and cumulative percentage as a function of the size of a) the blank, where Dn(10)= 4.31 µm, Dn(50)=5.69 µm and Dn(90)=13 µm and b) the UCNP-doped particle, where Dn(10)= 3.82 µm, Dn(50)=5.18 µm and Dn(90)=12.3 µm. The distribution of the particles is not significantly different with or without incorporation of UCNPs. The parameter Dn(x) is the value in the size distribution, up to and including which x% of the total number of particles in the sample is included. Acronyms: upconverting nanoparticles (UCNPs).

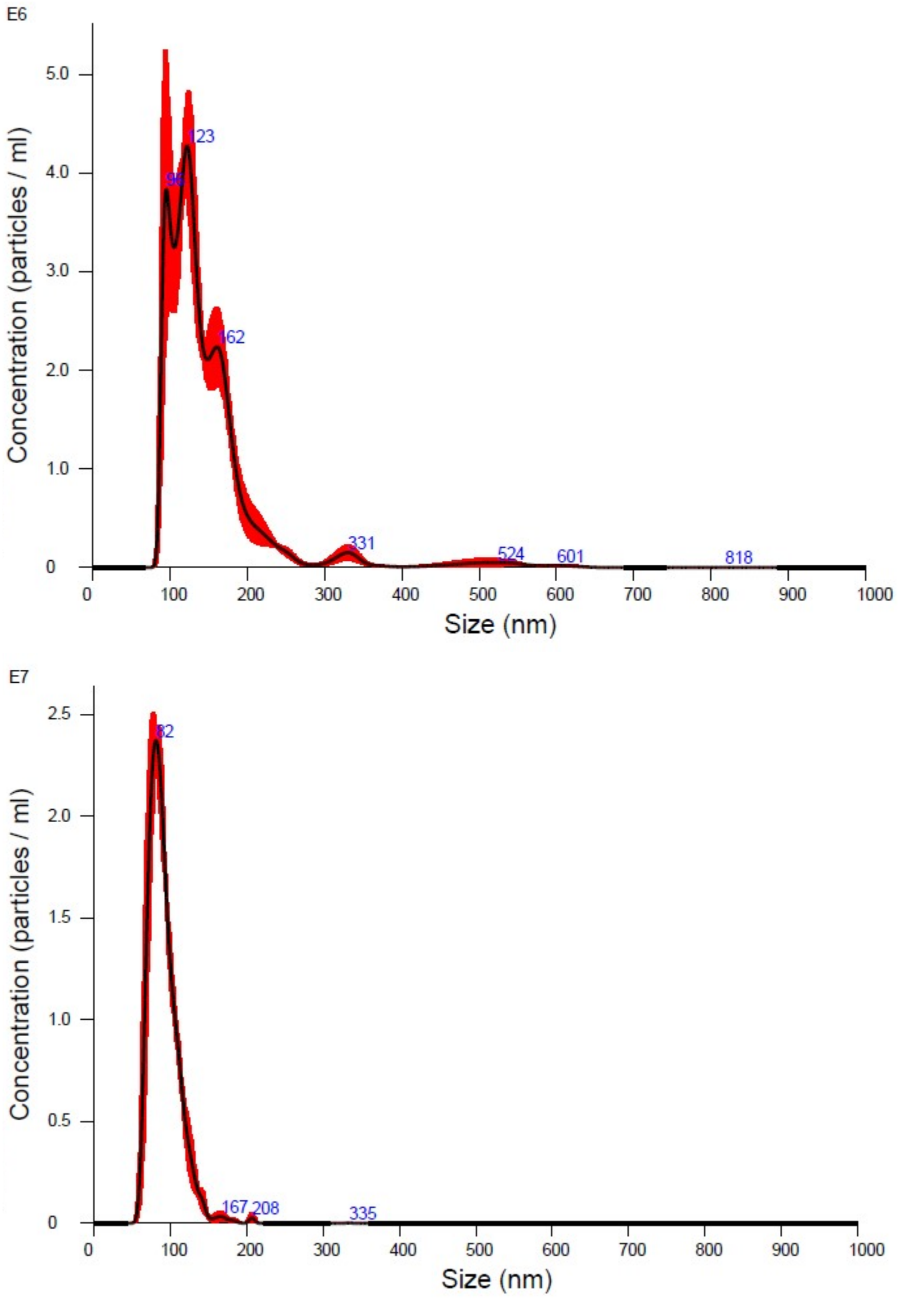

Figure S2. Size distributions of Blank-Upcon-PE and nano-Upcon-PE obtained by nanoparticle tracking analysis (NTA). Data are presented as the average concentration per size over three measurements. For Blank-Upcon-PE, the values obtained were Dn(10)= 96.9 nm, Dn(50)=130.9 nm and Dn(90)=201.4 nm, and b) for nano-Upcon-PE, Dn(10)= 70.8 nm, Dn(50)=87.9 µm and Dn(90)=117.3 nm. The distribution of the particles is not significantly different with or without incorporation of UCNPs. The parameter Dn(x) is the value in the size distribution, up to and including which x% of the total number of particles in the sample is included. Acronyms: upconverting nanoparticles (UCNPs).

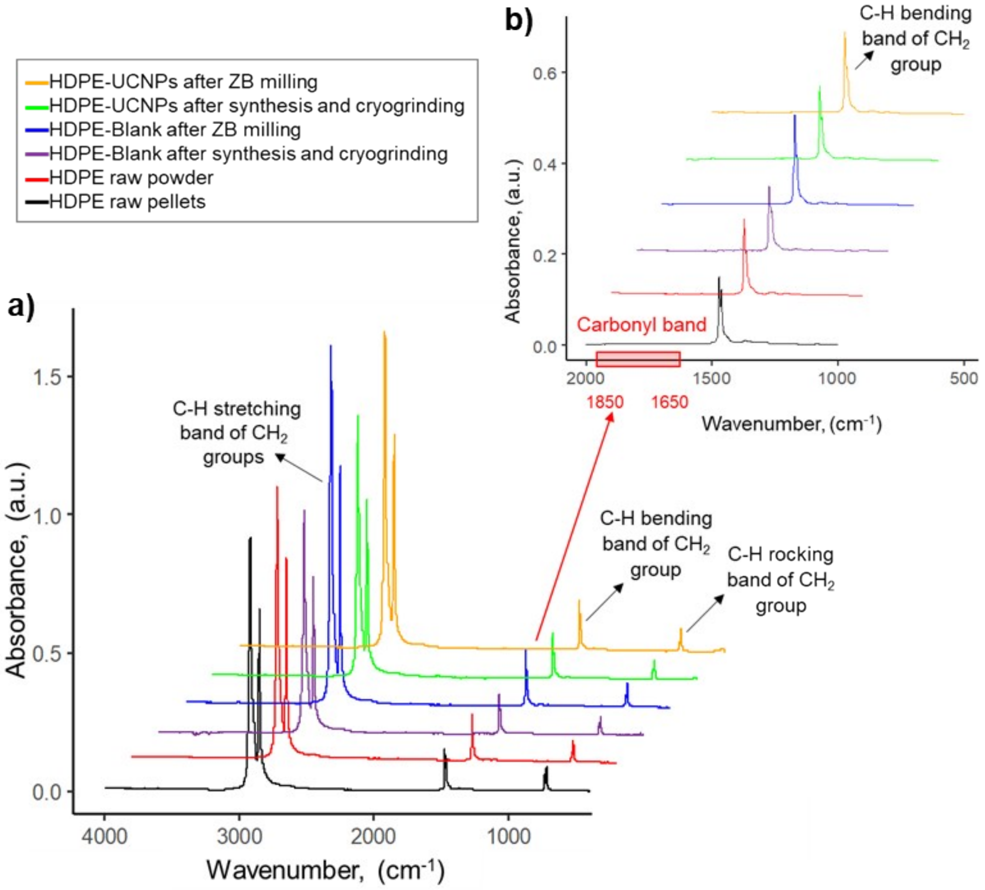

Figure S3. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) of raw PE and at different stages of particle synthesis were recorded using a Thermo Nicolet 6700 spectrometer equipped with a diamond crystal attenuated total reflectance accessory and a deuterated triglycine sulfate (DTGS) detector. Background and sample spectra were recorded as the average of 16 scans in the spectral range of 650–4000 cm^{-1} at a resolution of 4 cm^{-1}. Recorded data were corrected to obtain transmission-like spectra using the ATR Thermo correction (the refractive index considered as 1.5). The carbonyl signal for all analyzed samples was integrated in the 1650-1850 cm^{-1} region. a) FTIR spectra of raw PE material and Blank-PE and Upcon-PE samples recorded after every processing step of MP synthesis (synthesis of bulk material, cryogenic grinding, ZB milling); b) zoom around the carbonyl region, showing the absence of a carbonyl band, which signifies that no oxidation occurs for PE during the synthesis of MPs.

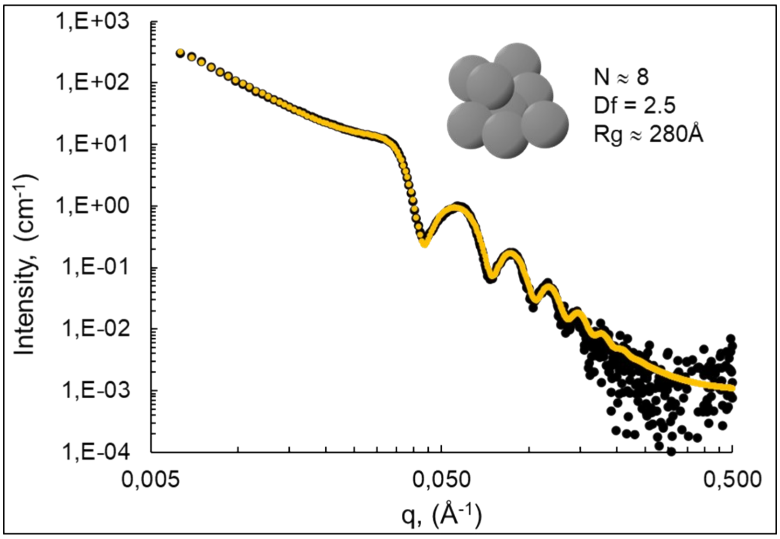

Figure S4: SAXS spectrum of UCNPs in solution. The experimental SAXS curve is plotted in Log I(q) as a function of Log q (black dots). The scattering curve can be described as the scattering of an aggregate object containing hard spheres. The fitting curve corresponding to the modeled SAXS curve is plotted in red dots for a model compatible with the SAXS data that was found to have the following physical parameters: number of nanospheres per cluster N = 8, fractal dimension Df = 2.5 and gyration radius Rg = 280 ± 10 Å.

Applied models for SAXS analysis

The SAXS curves can be described by the following equation written with the SASView program (SasView, http://www.sasview.org/):

$$I(q)_{global} = I(q)_{powerlaw} + I(q)_{sphere} * S(q)_{hardsphere} \qquad (1)$$

$$I(q)_{global} = Aq^{-P} + \frac{B}{V}\left[\frac{3V(\Delta\rho)(\sin(qr) - qrcos(qr)}{(qr)^3}\right]^2 * S(q)$$

where *A* and B are scaling factors, and the sphere is described by the volume *V*, radius *r* and contrast $\Delta\rho$. The nanospheres interact with each other, and the conditions where *S(q)* = 1 at small angles were not verified. The form factor S(q) is described here with a “hard sphere interaction model” described by Percus-Yevick (J.K. Percus, J. Yevick, J. Phys. Rev., 1958, 110, 1).

When UCNPs are distributed in the PE matrix, the scattering cross terms that reflect the interactions between the atoms of UCNPs and PE must be considered. However, we can apply the simplified model proposed in Equation (1) to describe Upcon-PE and a two-component model to describe the organization of PE MPs at large distances as follows:

$$I(q) = Aq^{-P} + \frac{C}{(1 + |q_0 - q|\xi)^m} \qquad (3)$$

where the second term represents a Lorentzian function to describe the interaction between the crystalline clusters inside the plastic matrix. q_0 is the position of the peak corresponding to the averaged distance separating the clusters (q_0 = 0.05 Å^{-1} ⇔ d = 125 Å).

The most interesting term is the exponential parameter P in Eq. (1) and (3), which describes the state of the particle surface. For both curves, this value is close to 3.7, corresponding to a slightly rough surface. The absence of a difference in the value of P suggests that the presence of UCNPs does not modify the state of the PE MP surface. Thus, these results suggest that UCNPs are absorbed inside the PE matrix.

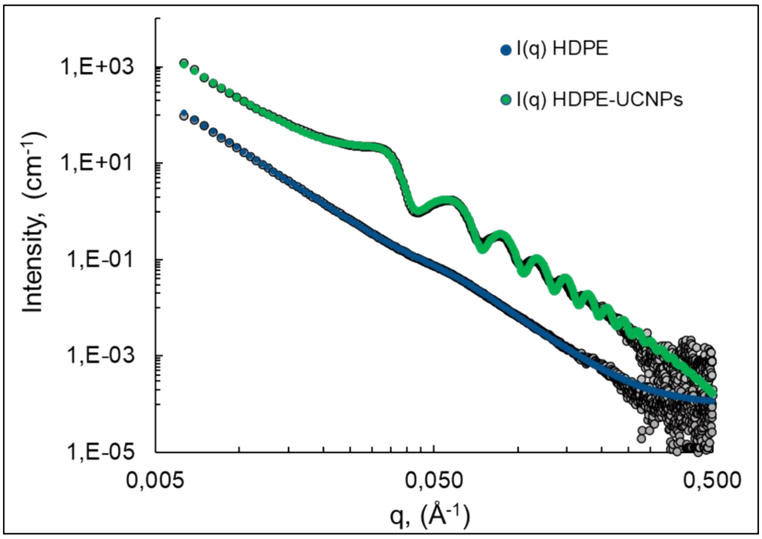

Figure S5. SAXS spectra of Blank-PE and Upcon-PE, along with superimposed fitting curves (blue and green, respectively). The experimental SAXS curves are plotted in Log I(q) as a function of Log q.

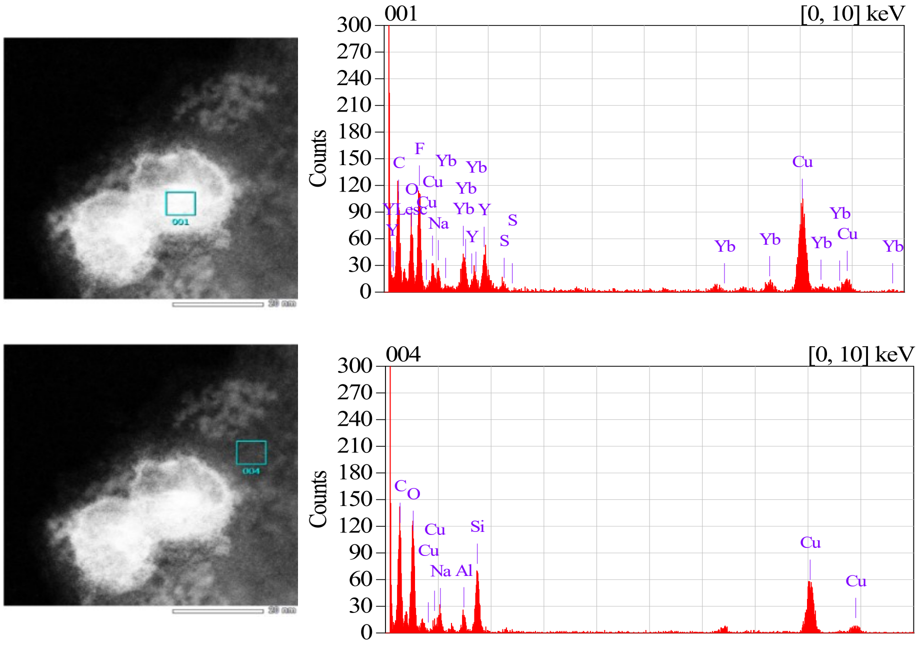

Figure S6. TEM image and energy-dispersive X-ray spectra of Upcon-PE nanoparticles. The box indicates where the measurement was taken on UCNPs (top) and on the PE matrix (bottom). Fluorine, yttrium, and ytterbium were detected in UCNPs but were not present in the PE matrix.

Table S1. The thermal stability of the samples was analyzed using thermogravimetric analysis (TGA). The apparatus was a TGA/SDTA 851 Mettler Toledo device. Approximately 15 mg of each sample was placed in 150 µL aluminum pans with a pierced cover. The analysis was performed from 30 to 900 °C at a heating rate of 10 °C/min under a nitrogen atmosphere with a rated flow of 40 mL/min. For each sample, a blank (analysis with empty crucible) was carried out under the same conditions as for the sample. All samples were analyzed in duplicate.

Sample	Mass, (mg)	T_{peak}, (°C)	Mass loss, (%)	Residue, (%)
PE raw powder	15.31	483	100.8	-0.8
Blank-PE	15.45	483	100.7	-0.7
Upcon-PE	15.84	481	94.3	5.7

Table S2. The average zeta potentials were measured in 10 mM NaCl at a native pH of 7.8 for the micrometric particles and at pH 7.5 for the nanometric particles.

	Zeta potential (mV)
µ-Blank-PE	-71 ± 7
µ-Upcon-PE	-73 ± 8
nano-Blank-PE	-56 ± 11
nano-Upcon-PE	-62 ± 10