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Cathodoluminescence imaging for characterising micro and nanoplastics

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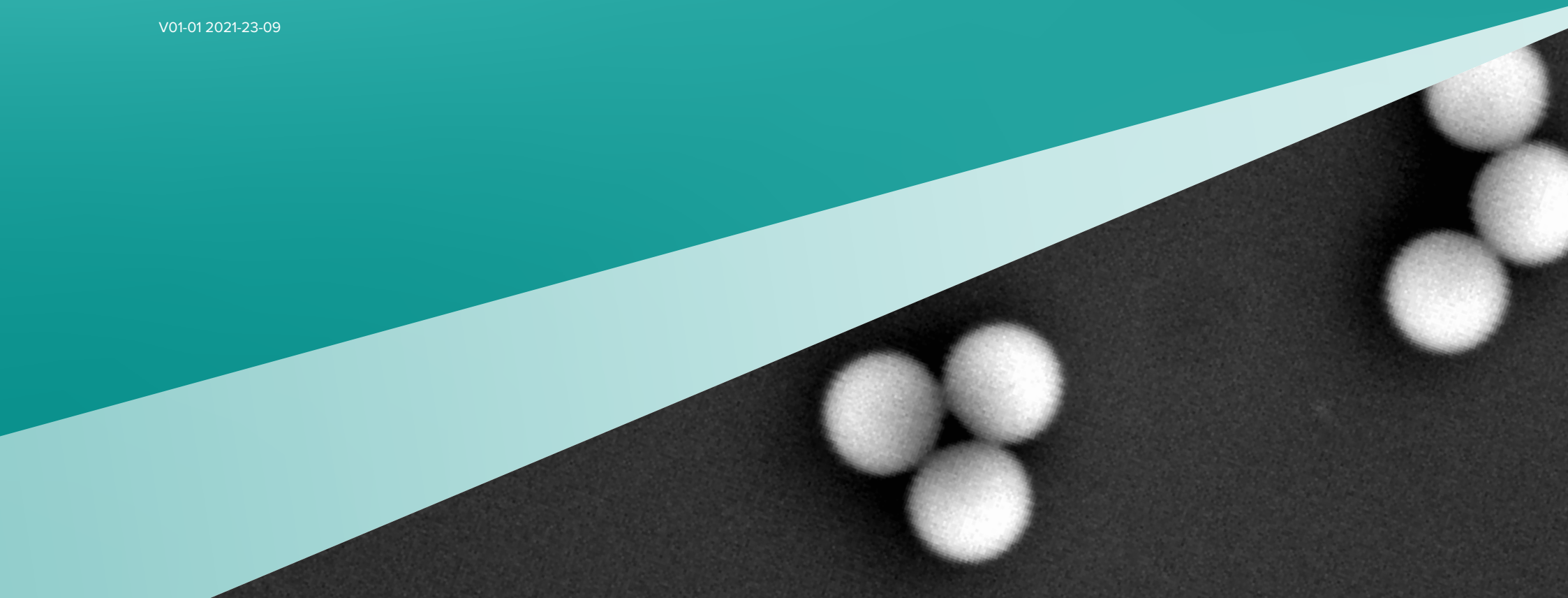

Cathodoluminescence imaging for characterising micro and nanoplastics

Plastics find wide use in our daily lives, with over 300 million tonnes [1] of plastics being produced every year, of which about 40% is single use plastic. A lot of this ends up in the marine environment, by direct deposition by bumans, through drainage systems, etc. Over time, under UV exposure, the plastic debris undergo photooxidation and become brittle [2]. This brittle plastic is exposed to the elements like wind and water, which cause it to form micro (1 µm – 1 mm) and nano particles (<1 µm). Moreover, micro and nanoplastics are also explicitly manufactured for cosmetics, paints, adhesives, etc. These particles are ingested by marine wildlife [3, 4], and eventually, humans, seriously endangering them. Studies have also found that microplastics can act as vectors for heavy metal poisoning or adhere to chemical additives, which are then released and damage nearby tissue [2, 5, 6]. The toxicity of nanoplastics is often unknown, as their properties are size-dependent and can vary greatly from those of the bulk material. Studying micro and nanoplastics has therefore become important as well as urgent.

Some of the popular techniques [7 - 9] currently used for characterising plastic micro and nanoparticles are optical microscopy, Raman imaging, FTIR spectroscopy, gas chromatography, and SEM-EDX - all of which have advantages and disadvantages. For example, optical microscopy enable fast and easy visual inspection, but does not provide quantitative information. Raman imaging provides quantitative information, but is limited in resolution to about 1 µm. SEM-EDX is a high resolution technique, but only provides elemental composition. There is therefore no technique that is fast, easy to use, as well high resolution, capable of imaging particles of all sizes from nanometres into the microns or millimetres. Cathodoluminescence (CL) imaging is promising as an SEM-based high resolution optical technique that can overcome many of these disadvantages. The general understanding of the mechanism of CL generation from plastics [10 - 12] is bond cleavage by the electron beam, and the subsequent formation of luminescent polycyclic structures. The formation of radicals by the cleavage of aliphatic bonds may also lead to crosslinking, resulting in the generation of light under electron exposure. The amount of CL emission, as well as the particle morphology, are known to be affected by the electron dose the sample has received. By performing CL spectroscopy, making sure to remain in the regime where the morphology of the particles is intact, we have performed proof of principle measurements to characterise a variety of micro and nanoplastic materials.

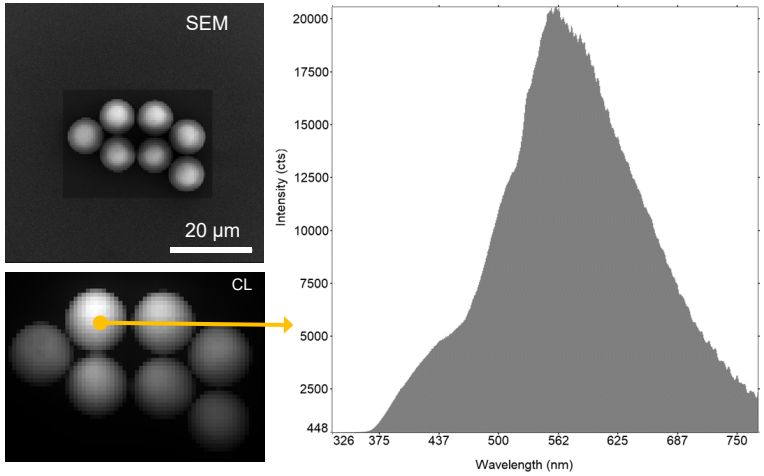

Figure 1 (left) SEM image, CL map (centred at 560 nm with a width of 50 nm) and CL spectrum for polystyrene beads, acquired at 20 keV and 100 ms dwell time.

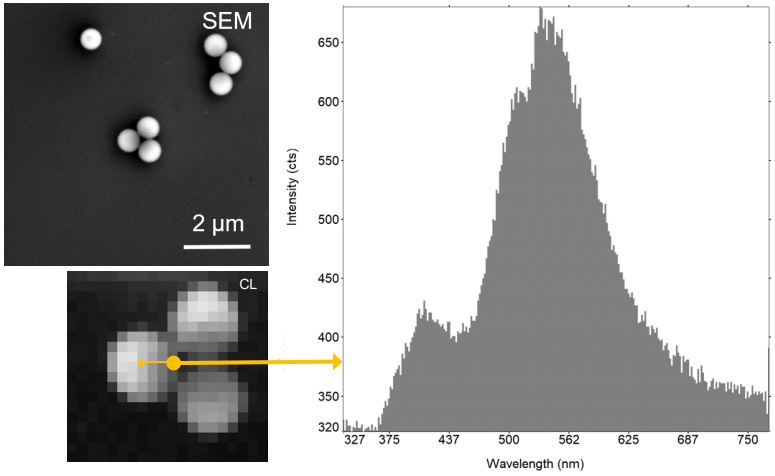

Figure 2 (right) SEM image, CL map (centred at 560 nm with a width of 50 nm) and CL spectrum for polystyrene beads, acquired at 5 keV and 300 ms dwell time.

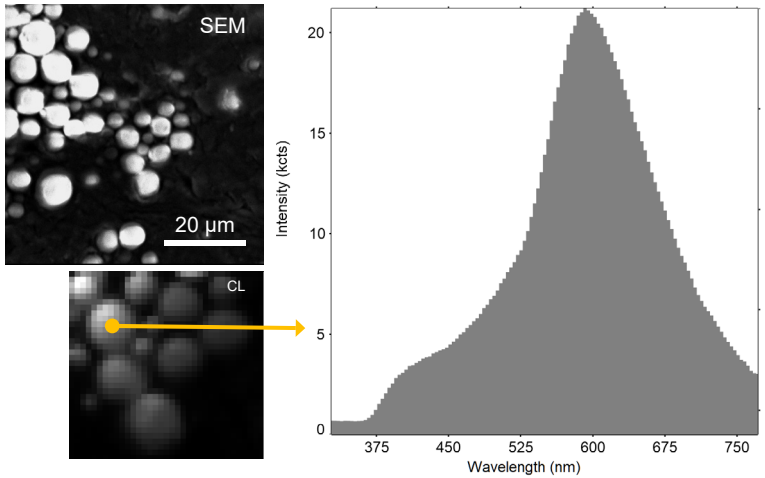

Figure 3 (left) SEM image, CL map (centred at 560 nm with a width of 50 nm) and CL spectrum for polyethylene beads of various sizes, acquired at 10 keV and 300 ms dwell time.

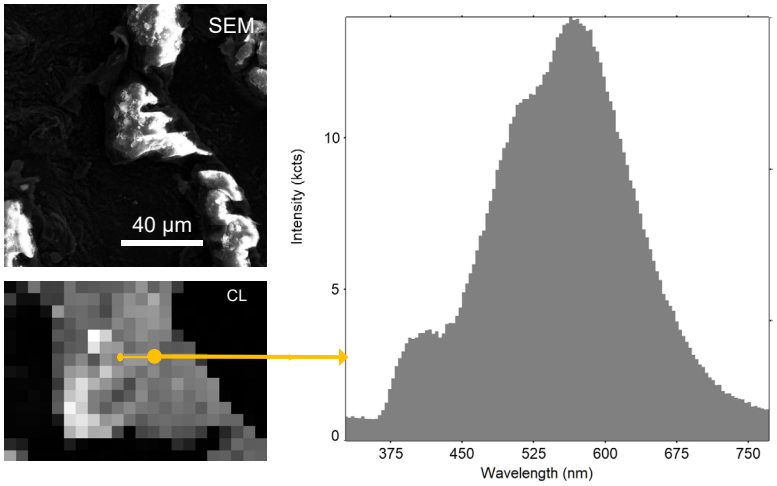

Figure 4 (right) SEM image, CL map (centred at 560 nm with a width of 50 nm) and CL spectrum for polypropylene, acquired at 10 keV and 300 ms dwell time.

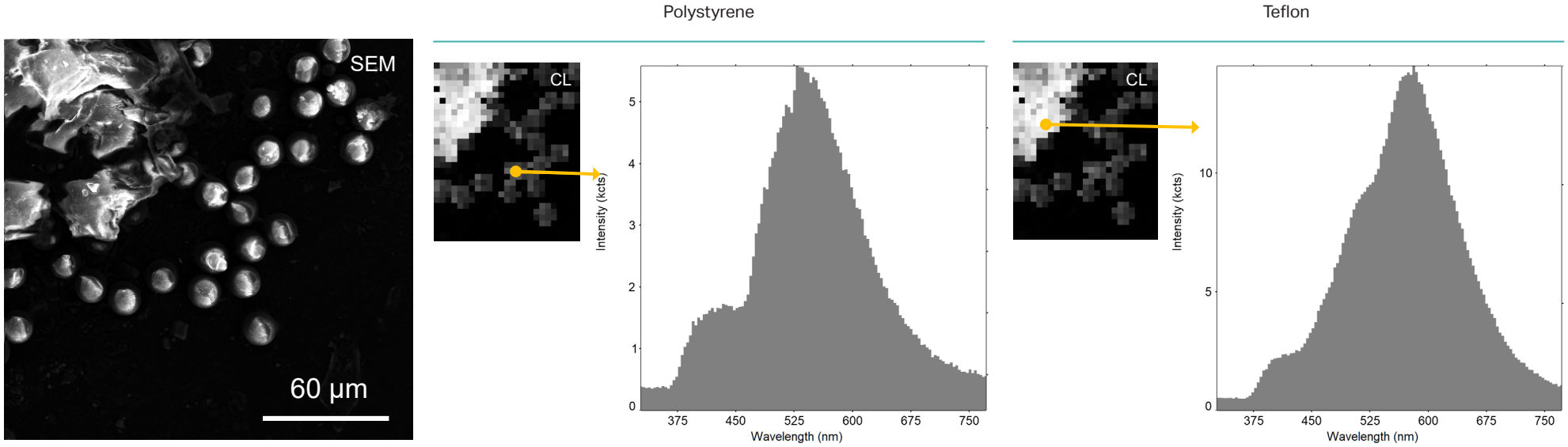

Figure 5 SEM image, CL map (centred at 560 nm with a width of 50 nm) and CL spectrum for a mix of materials, acquired at 10 keV and 300 ms dwell time.

Fig. 1 shows a CL spectral map of polystyrene beads 8 µm in size, collected on a standard SEM stub covered with carbon tape. Complete spectral information in the range 300-800 nm was acquired for every pixel in the CL map, and overlaid with the SEM image. A peak is visible in this material at around 560 nm, with a shoulder at around 430 nm. Since the beads were large, they were imaged at 20 keV, which would excite the bulk, with an exposure time of 100 ms. The high resolution of the technique is evident when imaging nanoparticles as shown in **Fig. 2.** The spectral map of 600 nm beads of the same material can be seen to have approximately the same peak positions as the 8 µm beads, but different peak widths and relative intensities. This is often the case for nanoparticles, whose properties can vary with size. For imaging these smaller particle, a beam energy of 5 keV was used, along with an exposure time of 300 ms. A few other materials that have been imaged in this study are polyethylene (**Fig. 3**) and polypropylene (**Fig. 4**), whose spectra also show characteristic CL peaks, as well as a mixture from which polystyrene and Teflon could be identified (**Fig. 5**). CL imaging is therefore a promising fast, high resolution technique for the characterisation of micro and nanoplastics.

One of the challenges is performing characterisation of low emission materials. Also, electron induced modification of plastic materials needs to be investigated in more depth, in order to determine the specific damage mechanisms in each of these materials, and determine suitable electron doses for imaging. For low-emission materials, in particular, higher electron doses may be necessary and such studies are very relevant. Furthermore, a thorough study is needed to create a database of spectra for different materials and particle sizes that will enable researchers to assign peaks and identify materials with confidence.

Samples courtesy

Samples courtesy of all figures, A. Valsesia, European Commission, JRC

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The SPARC Spectral system is a unique cathodoluminescense (CL) solution which allows you to acquire high-quality CL data in a fast and simple manner. The system is flexible, modular and can be customized according to your research needs.

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