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Detection of microplastics and nanoplastics: Are Raman tweezers and enhanced Raman methods the solution for sub 20 µm particles?

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Abstract. Despite the significant progress in the detection of nano and small microplastics, the detection of such particles still faces problems caused by the limitations of current detection methods and instruments. Herein, we present the optical methods for detection of sub 20 µm microplastics. We introduce optical methods for the analysis of individual microplastics and the fabrication of a substrate using plasmonic particles to detect plastic nanoparticles. We summarize recent experimental activities involving the construction of portable Raman tweezers that can be used for optical trapping and analysis of microplastics with size from a few hundred nanometers to lower tens of micrometers. Optical trapping is complemented by another optical manipulation method: nanoimprinting of plasmonic nanoparticles that enables create the "active" aggregates that can be used for Surface Enhanced Raman Spectroscopy (SERS) detection in microfluidic circuits and as plasmon-enhanced thermoplasmonic concentrators for nanoscale particulate matter such as nanoplastics. The principle of nanoimprinting is based on the dominance of the scattering force (compared to the gradient force) for plasmonic particles, this force pushes the particles in the direction of propagation of the light beam. This phenomenon enables the preparation of an aggregate comprising of plasmonic particles that can serve as a substrate for SERS and as a source of the temperature gradient that is able to attract dielectric nanoparticles. In both cases, enhanced sensitivity is demonstrated, allowing the detection of nanoplastics/molecules of size/concentration orders of magnitude lower than what can be achieved by Raman spectroscopy. This study demonstrates that the combination of two optical manipulation techniques with Raman spectroscopy is capable of filling the technological gap in the detection of plastic particles ranging in size from a few tens of nanometers to 20 micrometers. This is an ideal solution for the detection of very small microplastics, which currently lacks a suitable technology.

1 Detection of microplastics

Degradation of plastic items results in the generation of various types of micro- and nanoplastics particles that represent high-concern environmental pollutants. Plastic objects smaller than 5 mm are generally referred to as microplastics. Small microplastics are defined as objects smaller than 20 microns and nanoplastics are defined as objects smaller than 1 micron. Detection of small microplastics suspended in marine and fresh water still faces major challenges due to the limitations of the current detection methods, especially for the elusive sub-1µm nanoplastic fraction (nanoplastics). Commonly used spectroscopic techniques, such as Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), fluorescence spectroscopy, are limited in the detection of microplastics mainly by spatial resolution and weak signal. Raman tweezers have the potential to overcome spatial limitations typically encountered when detecting small microplastic objects [1]. The working range of Raman tweezers encompasses sizes from few hundreds of nanometers to ca. 10 µm [2]. Here we would like to present preliminary activities in the construction of a portable version of the Raman tweezers for Raman analysis of individual microplastic particles floating in an aquatic medium. The fundamental configuration of the Raman tweezers setup is illustrated in Figure 1.

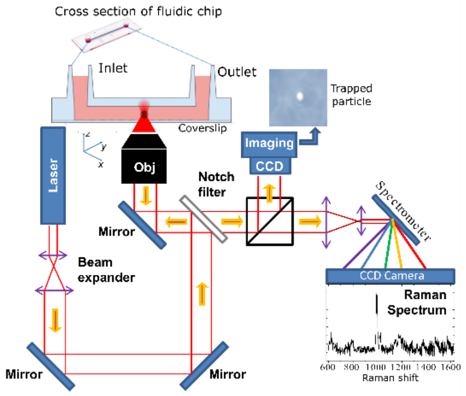

Fig. 1. The basic scheme of a Raman tweezers.

2 Detection of nanoplastics

Due to the volume dependence of the Raman scattering, the Raman signal expected from nanoplastics is to be 10^3 to 10^9 smaller than the one of microplastics. The use of enhanced spectroscopic techniques (or a combination of these methods) could help to overcome the detection limit for the detection of microplastics/nanoplastics. This is due to the increasing cross-section of the commonly used spectroscopy techniques. It has been demonstrated that the combination of Raman spectroscopy with substrates (or nanoparticles) that induce a surface plasmon

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resonances or localized surface plasmon resonances has been highly successful in recent years, both for enhancing the Raman signal (surface-enhanced Raman spectroscopy—SERS) and for enhancing spatial resolution (tip-enhanced Raman spectroscopy—TERS) [3-7]. Here we show optical pushing methods that induce a self-concentration of nanoplastics in an optical trap. The fundamental principle is based on the observation that the scattering force (in comparison to the gradient force) dominates for plasmonic particles. This force acts to propel the particles in the direction of the propagation of the light beam. The introduction of a barrier into the path of the laser beam focus results in the formation of an aggregate comprising plasmonic particles. By mixing plastic nanoparticles with gold nanorods we are able to create aggregates in which the nanoplastics located in the hot spots of the nanorods. The plasmonic aggregate can serve as a substrate for surface-enhanced Raman spectroscopy (SERS) and as a source of a temperature gradient that is able to attract further nanoplastics by thermophoretic effects. The basic principle of such a process is shown in Figure 2.

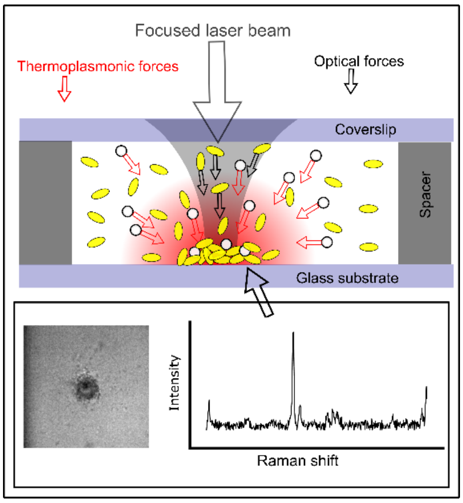

Fig. 2. Basic principle of nanoimprinting plasmonic particles by optical forces, followed by the formation of an aggregate that generates a temperature gradient that attracts the dielectric nanoparticles. a). The image of aggregate formed due to the plasmonic particles imprinting b). Raman spectrum of attracted nanoplastics due to the thermoplasmonic effect of the formed aggregate c).

In both instances, enhanced Raman scattering and sensitivity is demonstrated, allowing the detection of nanoplastics and molecules of size and concentration orders of magnitude lower than what can be achieved by Raman spectroscopy. The most recent findings indicate that optical printing may be employed to identify and detect nanoplastics in the range of lower tens of nanometers.

Summary

The combination of Raman tweezers and optical imprinting proves to be an effective method for detecting plastic particles below 20 µm with a lower detection limit of tens of nm. In addition, a portable version of the optical tweezers has been developed that allows direct analysis of microplastic particles in the area under investigation for plastic particles larger than a few hundred nanometers

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