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Editor's choice

The temporal evolution process from fluorescence bleaching to clean Raman spectra of single solid particles optically trapped in air

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ABSTRACT

We observe the entire temporal evolution process of fluorescence and Raman spectra of single solid particles optically trapped in air. The spectra initially contain strong fluorescence with weak Raman peaks, then the fluorescence was bleached within seconds, and finally only the clean Raman peaks remain. We construct an optical trap using two counter-propagating hollow beams, which is able to stably trap both absorbing and non-absorbing particles in air, for observing such temporal processes. This technique offers a new method to study dynamic changes in the fluorescence and Raman spectra from a single optically trapped particle in air.

1. Introduction

Solid particles, such as bioaerosols, mineral dust, soot, carbon black, metal flakes, and so forth, are ubiquitous in atmospheric and local environments, and they play important roles in air quality, climate change, human health, etc. Compared to the well-controlled liquid droplets in a laboratory, solid particles involve more complex processes due to their irregular shape, diverse morphology, large surface-to-volume ratios, etc. Inferring their fundamental physical and chemical properties at the single-particle level is the key to understand the complicated compositions and heterogeneous processes [1]. A single solid particle can be isolated by placing it on a substrate or levitating it in air using optical trapping (OT), electrodynamic balance (EDB) devices, or acoustic levitation [1–3]. Among the various single-particle trapping techniques, optically trapping particles in air has unique advantages, such as no interference from substrates or liquid medium, no pre-charging required, high flexibility for particle manipulation, and the capability to trap a wide range of particles with different materials from non-absorbing to strongly absorbing substances, sizes from nanometers to tens of micrometers, morphologies ranging from solid microspheres to irregular, loosely packed clusters, and physical phases including liquid, solid, or mixed. The OT technique has been increasingly adapted in recent single particle studies [4–15].

Raman spectroscopy, especially when combined with optical trapping, is a widely used analytical tool for reagentless and non-destructive characterization of micrometer-sized particles [16]. The Raman scattering signal can be excited and collected from a great variety of particles despite their materials, sizes, morphologies, phases, or temperatures. Since spectral fingerprints of the chemical functional groups or molecules can be obtained from the Raman spectra, Raman spectroscopy is able to characterize selectively and monitor dynamically the chemical properties of single particles. For example, Raman spectroscopy was applied to investigate the heterogeneous process of single optically trapped solids under controlled relative humidities [10], and the precise size change of single optically levitated droplets during evaporation [17]. However, the spontaneous Raman scattering, which is the simplest form of the Raman signals, is typically weak and often in company with strong fluorescence emissions, especially for biological particles. Fluorescence is a double-edged sword, which, on one hand, can be used as a fast method to count or classify single biological aerosols. The intrinsic laser-induced fluorescence (LIF) from single particles can be spectrally dispersed and analyzed [18], or simply detected via the total fluorescence emissions [19]. Several biomolecules, such as flavin, tryptophan, tyrosine, and so on, have specific fluorescence characteristics, which can be used to distinguish and classify bioaerosols [20]. On the other hand, the strong fluorescence often obscures the weak spontaneous Raman signals and makes the chemical characterization of single particles a challenging task. Several fluorescence-quenching methods have been applied to improve the signal-to-noise ratio of Raman spectra from single particles. Surface-enhanced Raman spectroscopy (SERS) [e.g., 21] can quench the fluorescence and enhance the Raman scattering as much as ten orders of magnitude,

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but it requires metal nanospheres (silver, gold, etc.) or special manufactured substrates as efficient quenchers. Using longer excitation wavelengths (633 nm, 785 nm, etc.) is also a common way to avoid excitation of strong fluorescence [22,23], but the molecules excited by a longer wavelength also have much weaker Raman scattering, as the Raman intensity is proportional to inverse fourth-power of the excitation wavelength [23]. Long-time irradiation using mercury lamps, ultraviolet or visible lasers can photochemically bleach fluorescent molecules in the particles deposited on a substrate [22,23], but the bleaching process either takes a long time (minutes to hours) or induces partial or complete damage to the particle.

None of the aforementioned fluorescence quenching studies has used a single particle isolated from substrates or bulk samples, except for very limited reports [24–26]. Kaiser et al. [24] observed the fluorescence-suppression phenomenon in single optically levitated droplets, which contained dioctyl phthalate (DOP) doped with a fluorescence dye (coumarin 6), a type of monomer, or a type of engine lubricant. As compared with the bulk liquid materials in a cuvette, the single droplets facilitated effective fluorescence suppression. Laucks et al. [25] used an EDB device to levitate a single bioaerosol (pollen) and measured weak Raman bands on top of a strong fluorescence background. In that work, although the laser bleaching of fluorescence was applied, no obvious bleaching effect was observed. In a very recent work, Wang et al. [26] measured Raman spectra of single optically trapped bioaerosols in air, and weak Raman peaks from the C—H stretching at 2940–3030 cm^{-1} were observed for four different types of pollens. The weak Raman bands were imposed on a strong fluorescence background, and also, no obvious fluorescence bleaching effect was found in the Raman spectra from single optically trapped bioaerosols. To obtain clean Raman spectra from single solid particles that contain fluorescent materials remains to be explored.

In the present work, we report the observation of the entire temporal evolution process (the transition from the strong fluorescence to clean Raman spectra) from a single solid particle optically trapped in air. Two types of dye-doped polyethylene (PE) microspheres and one type of pure PE microspheres, corresponding to strongly, weakly, and non-absorbing materials, were stably trapped for the observation. The optical trap is formed using two counter-propagating hollow beams at 532 nm. The dynamic photo-bleaching processes are monitored by both the Raman and imaging systems. We show the fluorescence from the trapped particle is effectively bleached within a short period of time (seconds) as compared to tens of minutes to hours when the particles are placed on a substrate.

2. Experimental description

Fig. 1(A) shows the configuration of the optical trapping-Raman spectroscopy (OT-RS) system. Briefly, a continuous-wave (CW) 532 nm laser beam (Gaussian beams (Near TEM_{00})) was split into two and converted to hollow beams using a pair of axicons (cone angle = 170°, Thorlabs) before being focused by two micro-objectives. The hollow optical trapping region was formed by the two focused counter-propagating hollow beams (CPHB). The separation distance between the two foci determines the size of the hollow trapping region, and the laser power is related to the robustness of the trap. The single particles were introduced via a syringe needle and trapped in a quartz cuvette between the two micro-objectives, which is detailed in Fig. 1(B). This CPHB trap is able to stably trap diverse types of particles including strongly, weakly, and non-absorbing microspheres or irregularly shaped particles. The capability of trapping both transparent and absorbing particles in air using a single optical configuration was demonstrated only recently by Redding and Pan [27]. Practically, we found that the laser power is a more vital factor in order to be able to trap both transparent and absorbing particles in the CPHB trap. Three types of particles: rhodamine B doped, fluorescent green, and pure PE microspheres (size = 10–30 μm, Cospheric), can be stably trapped for hours or longer in the CPHB trap with proper laser power. Typically, the trapping beam power delivered into the

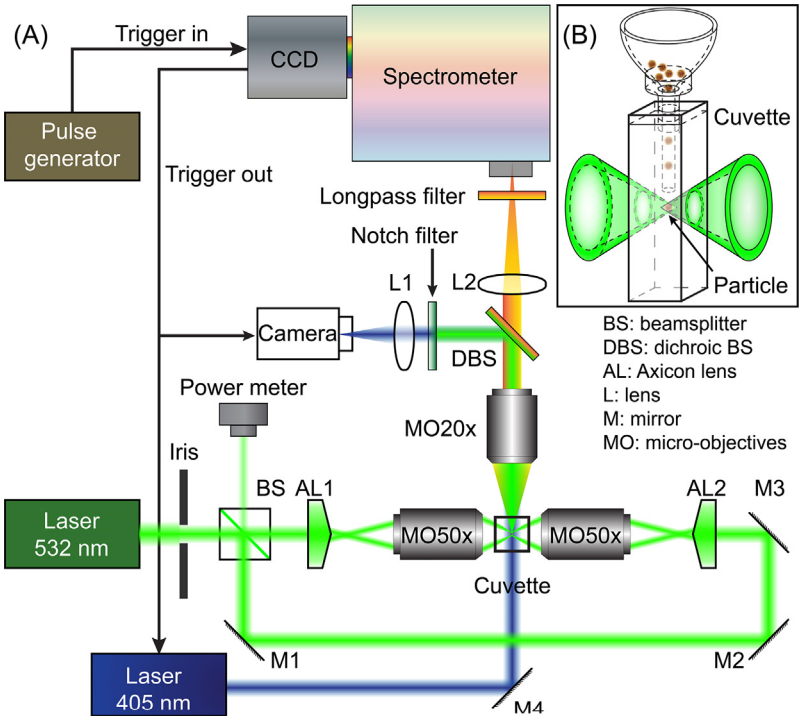

Fig. 1. The experimental setup. (A) The OT-RS system based on two counter-propagating hollow beams for trapping and characterizing both absorbing and transparent particles. (B) The detailed particle introduction setup and the hollow optical trap.