# Raman spectra and optical trapping of highly refractive and nontransparent particles

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(Received 26 April 2002; accepted for publication 10 June 2002)

We measured the Raman spectra of single optically trapped highly refractive and nontransparent microscopic particles suspended in a liquid using an inverted confocal laser-tweezers-Raman-spectroscopy system. A low-power diode-laser beam of $TEM_{00}$ mode was used both for optical trapping and Raman excitation of refractive, absorptive, and reflective metal particles. To form a stable trap for a nontransparent particle, the beam focus was located near the top of the particle and the particle was pushed against a glass plate by the axial repulsive force. Raman spectra from single micron-sized crystals with high index of refraction including silicon, germanium, and $KNbO_3$, and from absorptive particles of black and color paints were recorded. Surface-enhanced Raman scattering of R6G and phenylalanine molecules absorbed on the surface of a trapped cluster of silver particles was also demonstrated. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1497437]

Detection and identification of microscopic particles using micro-Raman spectroscopy have been attractive to materials science, biology, and medicine.[1] As an effective analytical tool, micro-Raman spectroscopy uses a focused laser beam to illuminate the micron-sized particles, and then collects the scattered light from which Raman spectra can be obtained. The molecular composition and structure information of the particles can be obtained from the positions, intensities, and linewidths of the Raman peaks in the spectra. When the particles are dispersed in a liquid, such as colloid particles and motile biological cells, the conventional micro-Raman spectroscopy becomes less effective because the particles will randomly move in and out of the illuminating micro-probe beam due to Brownian motion. In this case, the particles under study have to be immobilized with either physical or chemical methods.

Optical tweezers have been used to capture and hold dielectric and biological particles using a focused laser beam based on the gradient force.[2,3] The particles that can be stably trapped by single-beam optical tweezers ($TEM_{00}$ mode) are limited to be transparent (or with very low absorption) and the index of refraction of the particles should be slightly greater than that of the surrounding medium. Once a particle is trapped at the focus of the laser beam, Raman spectroscopy can be conveniently performed and provides fingerprints for the identification of the particles in an aqueous solution without the need of immobilization. Optical tweezers have been combined with Raman spectroscopy for the studies of living biological cells[4] and microdroplets,[5,6] which are almost transparent and with low relative index of refraction. For those particles that have high index of refraction and high coefficient of reflection and absorption, such as metallic particles, it is difficult to achieve stable trapping with a single Gaussian beam since in this case the gradient force will be exceeded by the enlarged scattering force, which points in the direction of the incident laser beam and tends to repulse the particles from the laser beam.[2] Several schemes have been developed to confine metal particles and absorptive particles, including two-dimensional trapping by a $TEM_{01}$-mode laser beam,[7,8] high-order Laguerre–Gaussian beam,[9] and circularly scanning beam.[10] These methods rely on the repulsive scattering force to trap the nontransparent particles in the dark central minimum of the effective doughnut beam. Metal particles have also been confined in two dimensions with a fixed Gaussian beam at an off-axial position based on the attractive force arising from a creeping wave,[11] or at an off-focus position when the laser beam focus is located near the bottom of the particle.[12] The combination of Raman spectroscopy with optical trapping for highly refractive and nontransparent particles has not been demonstrated yet.

In this letter, we report on the demonstration of Raman spectroscopy of single optically trapped highly refractive and nontransparent particles in a liquid using an inverted confocal laser-tweezers-Raman-spectroscopy (LTRS) system. In our system, a fixed Gaussian beam ($TEM_{00}$ mode) generated from a low-power diode laser at 785 nm was used both for optical trapping and Raman excitation. Various micron-sized particles including silicon, germanium, and $KNbO_3$ microcrystals that have a high index of refraction, black and color paint particles that have high absorption, and metal particles that have high reflection, were trapped in water and Raman spectra from these particles were measured.

The mechanism of optical trapping of a nontransparent particle with a Gaussian beam can be understood from Fig. 1. Consider a black spherical particle that completely absorbs the incident light rays in all directions. Due to the absorption, a repulsive force that pushes the particle in the direction of the incident light ray will be generated. If the focus of the beam is located near the top of the sphere and the sphere is symmetrically located in the beam axis, as shown in Fig. 1(b), the net repulsive force in the transverse direction will be zero. If the sphere is shifted to the right of the beam axis

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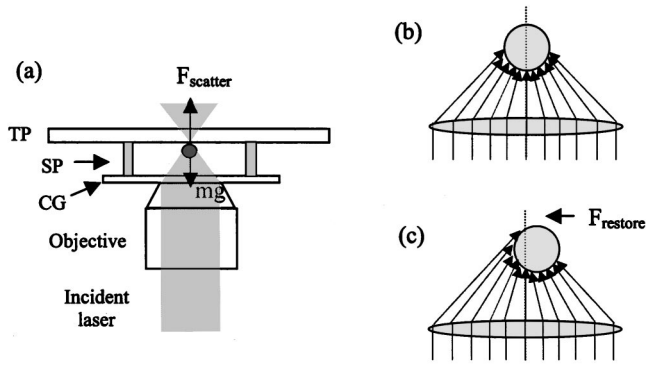


FIG. 1. (a) Optical trapping of a nontransparent particle when the laser focus is located near the top of the particle. TP - top glass slide; SP - spacer; CG - cover glass. (b) The transverse repulsive force equals zero when the nontransparent sphere locates in the beam axis. (c) The repulsive force pushes the particle toward the beam axis when the sphere is shifted to the right.

due to the Brownian motion, as shown in Fig. 1(c), the light flux absorbed by the sphere area in the right-hand side of the beam axis is larger than that in the left-hand side. The repulsive force from the right-hand side is then larger than that from the left-hand side. So, the net transverse repulsive force tends to pull the sphere toward the beam axis if the sphere is located off axis, acting as a restoring force. In both cases, a net repulsive force $F_{\text{scatter}}$ in the axial direction pushes the particle upward and the particle moves up until the top glass slide, where $F_{\text{scatter}}$ is equal to the sum of the particle's gravity force *mg* and the glass contact force. Therefore, a stable three-dimensional trap can be formed for the absorptive particles. Similar analysis shows that a stable trap can be also formed for metal particles[9,12] and highly refractive particles when the beam focus is located near the top of the particles.

The experimental setup of our LTRS system was described previously.[4] A circularized beam from a laser diode at near 785 nm is spatially filtered and then introduced in an inverted microscope equipped with an objective (100×, numerical aperture=1.30) to form a single-beam optical trap. The sample holder was made of a top glass slide, a spacer of 50 $\mu$m-thickness, and a bottom cover glass. A nontransparent particle can be selectively trapped under the top glass slide by the repulsive force when the beam focus is located near the top of the particle. The backscattered light from the trapped particle is collimated with the same objective lens and passes through a 200 $\mu$m confocal pinhole aperture to reject most of the off-focusing Rayleigh scattering light. Two interference notch filters are used to remove most of the on-focusing Rayleigh scattering light. The Raman scattering light is then focused onto the entrance slit of an imaging spectrograph equipped with a liquid-nitrogen-cooled charged-coupled detector.

Figure 2 shows the Raman spectra of single trapped particles with high index of refraction in water. Silicon (Si), germanium (Ge), and potassium niobate ($KNbO_3$) microcrystals are of importance in semiconductor and nonlinear optics manufacturing. They have very high indexes of refraction in visible-near-infrared regions, i.e., $n \sim 3.4$ for Si, 4.0 for Ge, and 2.3 for $KNbO_3$. We prepared the microcrystals by grounding a piece of pure materials into powders and then the powders were diluted with distillated water. The shape of

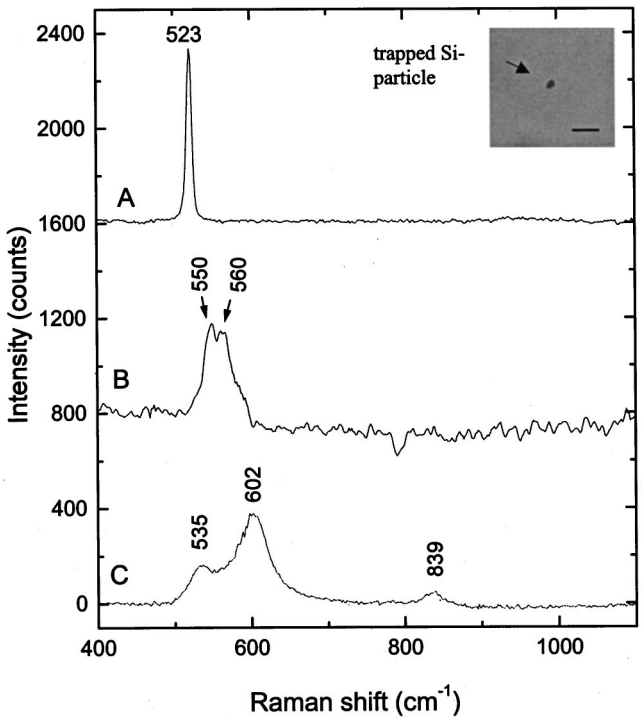


FIG. 2. Raman spectra of trapped particles with high index of refraction. Curve A is for a silicon crystal with an integration time of 2 s and an incident power of 6 mW; curve B is for a germanium particle; and curve C is for a $KNbO_3$ crystal with a 30 s acquisition time and 16 mW incident power. The inset photograph is the image of single trapped silicon particle with a scale bar of 5 $\mu$m.

the microcrystals is irregular and the effective index *m* of the microcrystals in water, defined as the index of the particle *n* divided by the index of water ($n_b=1.33$), is too high to trap with single Gaussian beam tweezers.[3] However, they can be trapped with our LTRS system and the Raman spectra can be obtained. Curve A is the Raman spectra observed from a trapped silicon particle of $\sim 2$ $\mu$m size, as shown in the inserted image. The characteristic band at 523 $cm^{-1}$ is assigned to Si I phase.[1] Curve B is the Raman spectra from a trapped germanium particle with the observed Raman band near 560 $cm^{-1}$. Curve C is the Raman spectra from a trapped $KNbO_3$ particle, in which Raman bands at 535, 602, and 839 $cm^{-1}$ are observed.

Figure 3 shows the Raman spectra of single trapped absorptive particles in water. The absorptive particles were made of powders grounded from a piece of dried black paint and other color paints that are often used for instrument and the vehicle's body painting. The size of the paint particles ranges from 0.5 to 10 $\mu$m with irregular shape. Curve A is the Raman spectra from a trapped black paint particle of $\sim 2$ $\mu$m size, whose image is shown as the inset. The black paint contains unknown materials that yield Raman bands at 1091 and 717 $cm^{-1}$. Curves B and C are the Raman spectra from a trapped ColorPlace paint particle (green color) and a trapped Krylon paint particle (red color), respectively. For these measurements, the integration time was 10 s and the laser power was 6 mW. Although we were unable to assign each Raman band due to the unknown molecular compositions of these commercial painting materials, the intrinsic difference in Raman spectra between different paints allows rapid identification of the existence of unknown paint par-

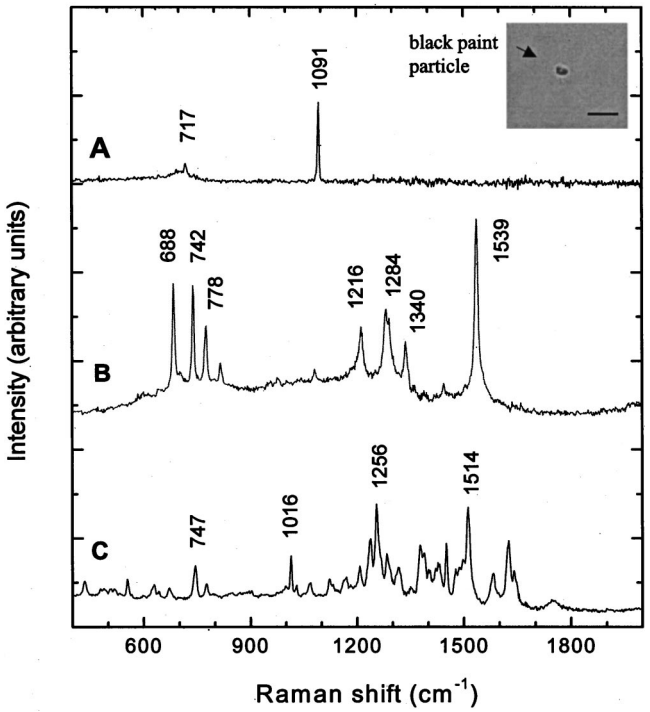


FIG. 3. Raman spectra of single trapped particles of absorptive color paints. Curve A is for a black paint; B for a ColorPlace paint (green); and C for a Krylon paint (red). Laser power, 6 mW; integration time, 10 s; scale bar of the image, 5 $\mu$m.

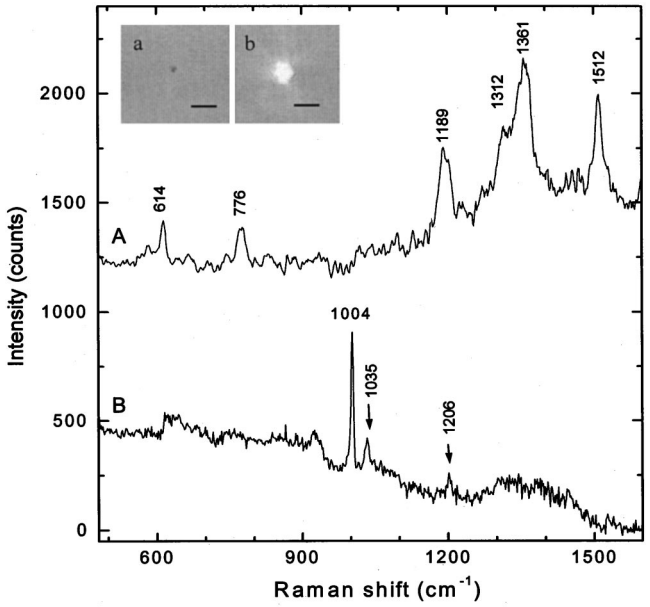


FIG. 4. Surface-enhanced Raman spectra of R6G (curve A) and phenylalanine molecules (curve B) observed from a trapped cluster of silver particles. The inset is the image of the trapped sliver cluster recorded with a filter (image a) and without the filter (image b). The scale bar is 5 $\mu$m.

ticles. This might be very valuable for police to recognize and identify the vehicles involved in car crashes and accidents.

The LTRS system also allows trapping metal particles of micron size and enables observation of surface-enhanced Raman spectra of organic or biological molecules adsorbed on the surface of the trapped metal particle. Figure 4 shows the Raman spectra of rhodamine 6G (R6G) and phenylalanine (Phe) molecules adsorbed on the surfaces of single trapped silver clusters. The silver particles in water were prepared with a laser ablation method using a yttrium–aluminum–garnet pulsed laser[13] and R6G or Phe solution of 1 $\mu$M concentration was added in the silver colloids for 1 h incubation. At this concentration, Raman spectra either from R6G or Phe bulk solution cannot be observed with an integration of 5 s and a laser power of 6 mW at 785 nm. However, as a clump of silver particles was trapped, Raman spectra from R6G (curve A in Fig. 4) and Phe (curve B) were easily observed due to the surface enhancement effect. Since the trapped silver particle was highly reflective, a low-pass filter (BG39) was used to block the scattered laser line before entering the video camera. The observed characteristic bands of R6G at 614 $cm^{-1}$, 776 $cm^{-1}$, 1189 $cm^{-1}$, 1361 $cm^{-1}$, and 1512 $cm^{-1}$ are identical to those of the published surface-enhanced Raman scattering spectra within the spectral resolution.[14] The characteristic bands at 1004 $cm^{-1}$ (aromatic ring) and 1035 $cm^{-1}$ were clearly observed in the Raman spectra of Phe. It should be noted that the trapped silver clusters were observed to randomly rotate inside the laser trap so that we did not observe extremely high surface enhancement effect as in Ref. 14 due to the position fluctuations of the ''hot'' particles.

In summary, we have demonstrated the combination of Raman spectroscopy and optical trapping for highly refractive, absorptive, and reflective particles in a liquid using a confocal LTRS system. Micron-sized nontransparent particles were trapped and excited with a single Gaussian beam that produces a restoring (repulsive) force under the condition that the beam focus was located near the top of the particle. Raman spectra from single trapped microcrystals of Si and Ge semiconductor materials and $KNbO_3$ nonlinear material were obtained. Surface-enhanced Raman scattering from R6G and Phe molecules was observed from trapped silver microclusters. We also demonstrated effective trapping and Raman spectra for the identification of absorptive paint particles. The LTRS system may be applied as a valuable analytical tool for semiconductor manufacturing, wastewater detection, and paint identification.

Y. L. acknowledges the funding support from the College Research Award and the Research/Creative Activity grant from East Carolina University.

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