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Optical Interferometric Imaging of Sub-50 nm Semiconductor Nanoparticles

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Optically detecting individual nanoparticles (NPs) form a technical basis of numerous bio-chemical imaging techniques that are based upon the optical emission or scattering from NPs. For plasmonic NPs such as the ones made of silver or gold, strong scattering resonances at visible frequencies enable facile detection of individual particle as small as 30 nm. For strongly emitting semiconductor quantum dots, fluorescence detection enables easy detection at single photon as well as at single particle level. On the other hand, for other classes of NPs that are neither strongly scattering nor fluorescing (such as iron oxides, silicons, or polymeric NPs), sensitive optical detection is not straightforward. In this note, we demonstrate a simple yet sensitive optical detection of weakly scattering NPs. The technique is based on the coherent interference of scattering from NPs and the reflection from air-substrate interface, which optically "amplifies" the scattering signal. The detection sensitivity of the current method is compared with that of the conventional Raman-based detection.

The technique, which is schematically shown in Figure 1, is based on a generic epi-confocal scanning microscopy. A coherent laser beam (E_0) that is focused onto a nanoparticle on a flat substrate is both scattered by the nanoparticle to give a scattered field (E_{scat}), and is also reflected (E_{refl}) at the air-substrate interface. The objective lens collects the optical field that is a coherent sum of the two components ($E_{tot} = E_{scat} + E_{refl}$). The intensity of detected light is $I_{tot} = E_{tot}E_{tot}^* = |E_{tot}|^2 = |E_{refl}|^2 + |E_{scat}|^2 + 2|E_{refl}||E_{scat}|\cos\phi$, where the ϕ is the phase difference between the E_{scat} and E_{refl}. Under 1 mW of incident beam, the intensity of reflected light ($I_{refl} = |E_{refl}|^2$) is ~10 μW and is near-constant. On the other hand, the pure scattered intensity from a weakly scattering nanoparticle ($I_{scat} = |E_{scat}|^2$) is ~1 pW level. Thus the total detected intensity is approximately $I_{tot} \sim I_{refl} + 2I_{refl}^{1/2} I_{scat}^{1/2}$ cosf. The image contrast of the NP (*i.e.*, signal with and without the NP) is given by the interference term, $S_1 = 2I_{refl}^{1/2} I_{scat}^{1/2}$ cosf. For pure Rayleigh scattering from an NP without any interference, the signal intensity, and also the image contrast, is simply given by $S_2 = I_{scat}$. The ratio of the two is $S_1/S_2 \sim (I_{refl}/I_{scat})^{1/2} \sim 10^3$ or larger. In other words, simple interference "amplifies" the optically detected signal. Such interferometric advantage has been previously recognized,[1,2] but it has been primarily used for detecting small plasmonic nanoparticles. Below, we experimentally show that it can be also used for detecting small and/or weakly scattering dielectric (insulating or semi-conducting) NPs.

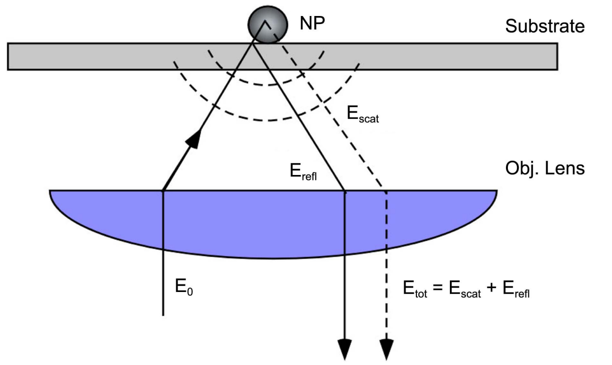

Figure 1. The scattering (E_{scat}) from a nanoparticle (NP), and reflection (E_{refl}) from the substrate, and the interference between the two.

As a generic weakly scattering NP, we employ TiO_2 NPs with diameters less than 50 nm sitting on a glass coverslip. We use the excitation light at the wavelength of 632 nm (2.0 eV), which is well-below the bandgap of the TiO_2 (~3.0 eV)[3]. Figure 2(a) is the image recorded at the Rayleigh wavelength, and the one shown in Figure 2(b) is the (Stokes) Raman scattering image of the same region monitoring the E_g phonon band of TiO_2. The two features are evident from the comparison. First, the nanoparticles and their aggregates appear as a negative contrast for Rayleigh image, which clearly shows the interferometric nature of the detected signal: if the Rayleigh images of NPs represent pure scattering from the nanoparticle alone, it should have a positive contrast. We believe that the sign of the image contrast will vary (negative or positive), depending on the phase difference, ϕ.

The phase difference again is influenced by the excitation wavelength and optical characteristics of the nanoparticle (scattering resonance for example). Secondly, not only does the Rayleigh image (Figure 2(a)) faithfully reproduces features of in Raman image (Figure 2(b)), but it also has significantly better signal-to-noise ratio (SNR) of the contrasts (With the same sampling time/pixel, the SNR of Rayleigh image is about 5 times larger than that of Raman image). For ex-

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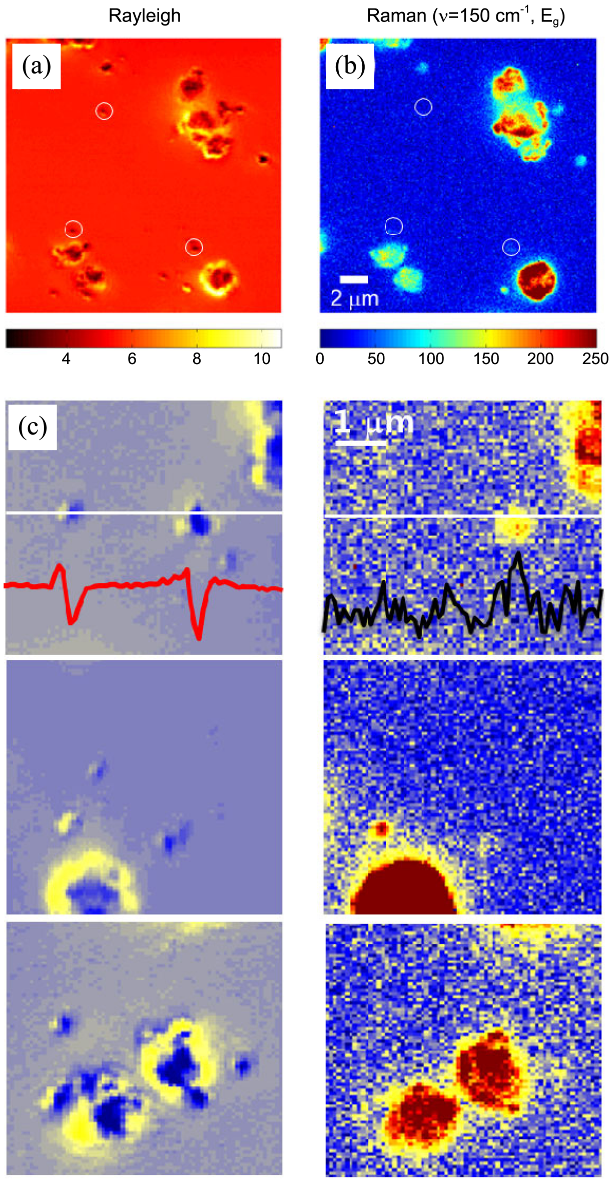

Figure 2. (a) Rayleigh reflection image of TiO_2 NPs dispersed on glass substrate. (b) Raman image (sampled at E_g phonon mode, 150 cm^{-1}) of the same region of the sample. Circles (white) in (a) and (b) point to the features that are readily shown in Reflection, but not in Raman images. (c) Zoom-in images of (a) and (b), showing the drastic SNR difference of the two. The line-profiles (red and black solid lines) of the top panels are sampled along the horizontal line indicated (white).

ample, some of the small features (marked as white circles in Figures 2(a) and 2(b), which are individual NPs, or a few number of NP aggregates) are readily shown in the Rayleigh image, whereas they are below the SNR limit of Raman mapping. The above two points are more clearly illustrated by the zoom-in images shown in Figure 2(c) and also the line-profiles.

To sum up, here we have demonstrated a simple yet sensitive Rayleigh reflection microscopy method that can detect small nanoparticles with moderate scattering cross sections. The technique only relies on the interferference of weak scattering from NPs and the reflection from substrate, and thus generally applicable to a general class of NPs. We believe that it can be easily improved (in sensitivity, selectivity, and temporal resolution) by employing multiple excitation wavelengths, wide-field illumination, and advanced interferometry techniques.

Experimental

The images (both the Rayleigh and Raman) are obtained by raster-scanning (with a piezo scanner, Physik Instrumente) and illuminating the sample surface with a focused laser beam of 632.8 nm light (HeNe laser) through a high-numerical aperture lens (NA 1.4, Olympus, oil immersion type). The collected light is detected by a CCD-based spectrometer. The sample is a TiO_2 powder (anatase, Aldrich) dispersed on a glass coverslip.

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