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Research Article

In Situ Raman Spectroscopy of COOH-Functionalized SWCNTs Trapped with Optoelectronic Tweezers

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Optoelectronic tweezers (OETs) were used to trap and deposit aqueous dispersions of carboxylic-acid-functionalized single-walled carbon nanotube bundles. Dark-field video microscopy was used to visualize the dynamics of the bundles both with and without virtual electrodes, showing rapid accumulation of carbon nanotubes when optical virtual electrodes are actuated. Raman microscopy was used to probe SWCNT materials following deposition onto metallic fiducial markers as well as during trapping. The local carbon nanotube concentration was observed to increase rapidly during trapping by more than an order of magnitude in less than one second due to localized optical dielectrophoresis forces. This combination of enrichment and spectroscopy with a single laser spot suggests a broad range of applications in physical, chemical, and biological sciences.

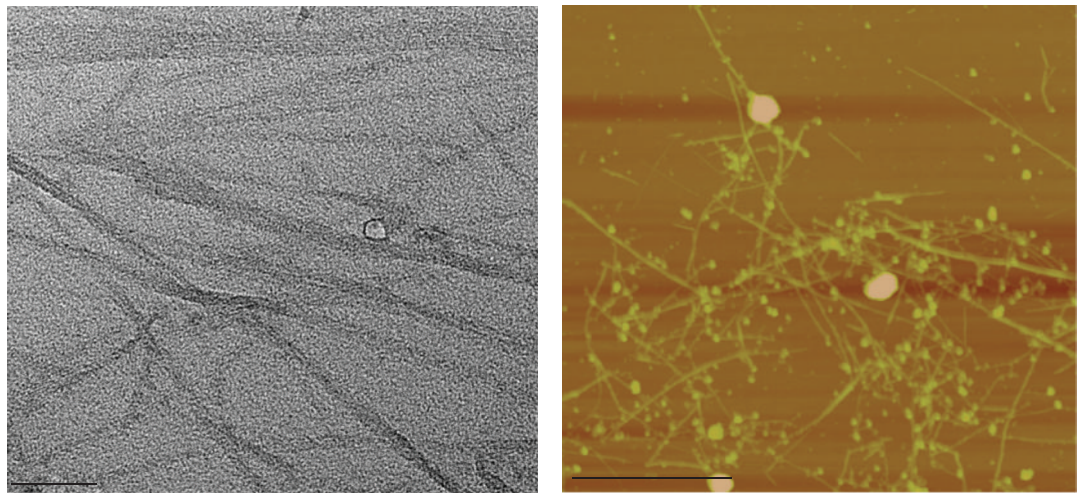
1. Introduction

One persistent challenge in molecular sensing is the enriching of candidate analytes to concentrations high enough for detection. Optoelectronic tweezers (OET) recently have been used as a versatile platform for trapping objects such as polystyrene spheres, living cells [1], and solid-state nanowires [2], and both [3] single- and [4] multi-walled samples of carbon nanotubes using 100,000x less optical power than single-beam laser traps. Based on a combination of dielectrophoresis and optical image patterning, OET has the unique capability of massively parallel localization of organic and inorganic nanoscale structures for both direct visualization and spectroscopic characterization. In this paper, we use carboxylic-acid- (COOH-) functionalized single-walled carbon nanotubes as a model system to demonstrate analyte enrichment by over an order of magnitude with a low-power OET trapping laser that serves simultaneously as a Raman spectroscopic probe.

2. Materials and Methods

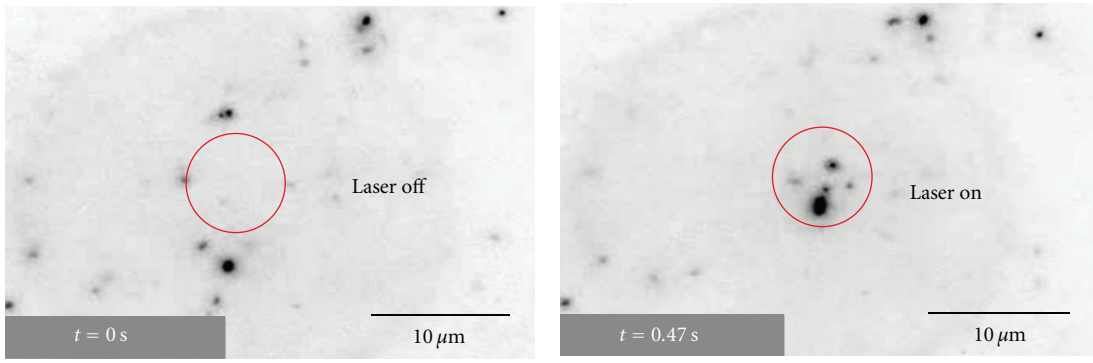
2.1. Carbon Nanotube Sample Preparation. COOH-functionalized carbon nanotubes have been used as a surfactant-free alternative for aqueous SWCNT suspensions, with the hydrophilic COOH-surface functional groups serving as a means to suspend the nanotubes on polar solvents such as water [5]. In this work, COOH functionalized SWCNTs (P3, Carbon Solutions, Inc., ~4 atomic % COOH-functionalization) were dispersed as made in Milli-Q deionized water, bath-sonicated for 30 min, and centrifuged for 30 min at 16,000 g to remove large bundles and other metallic catalyst particles yielding a semitransparent solution.

2.2. Carbon Nanotube Sample Characterization. Transmission electron microscopy (JEOL CM-300) and atomic force microscopy (Veeco) were used to characterize the physical dimensions for the nanotube bundles. Atomic force microscopy measurements provide a diameter distribution



(a) (b)

Figure 1: Characterization of COOH-functionalized SWCNTs used in this study. (a) Bright-field transmission electron micrograph. Scale bar = 50 nm. (b) Atomic force micrograph of SWCNTs on an aminopropylesilane-coated mica wafer. Scale bar = 1 μm.



(a) (b)

Figure 2: Dark-field EMCCD video microscopy of optoelectronic trapping of COOH-SWCNTs with laser off (a) and on (b) at an AC bias of 15 Vpp, 100 kHz. Images are inverted to enhance visibility of faint light scattering from SWCNT bundles. The laser line (Ar^+, 488 nm) is blocked by a holographic notch filter.

for the carbon nanotube bundles ranging from 2 to 11 nm, and lengths ranging from 0.1 to 2 μm (Figures 1(a) and 1(b)), with a mean bundle diameter of 6.4 ± 2.4 nm.

2.3. Dark-Field Imaging with Optoelectronic Tweezers. OET chambers were fabricated as reported previously [1], and images were collected during trapping with a Nikon Eclipse LV150 microscope equipped with long working distance dark-field objective lenses. Dark-field optical microscopy was used [6] to image aqueous suspensions of SWCNT bundles with a video-rate, thermoelectrically cooled, back-illuminated electron multiplying charge-coupled device camera (Andor, iXon). Standard chamber depths were fixed with double-sided adhesive tape with a standard thickness measured at 75 microns with a hand-held micrometer. During darkfield imaging, the trapping was performed with an argon-ion laser using the 488 nm emission line. The laser power was measured to be 100 μW focused to a spot size of 5 microns. The laser spot is filtered from the dark-field image using a holographic notch filter.

2.4. Raman Microscopy. Raman measurements were made with the 632.8 nm line of a helium-neon laser. Laser light was focused onto samples using a long working distance 20x near-IR corrected apochromatic objective lens (Mitutoyo). Scattered light was collected using the same objective and was focused onto a pinhole (to improve spatial resolution) before being collimated and directed into the spectrometer. A holographic filter (Kaiser Optics) was used to reject elastically scattered laser light. The spectrometer was a 0.3 m Jobin Yvon LabRam system equipped with 1,200 lines/mm and 1,800 lines/mm gratings. The detector was an LN2-cooled CCD (Roper Scientific). The system was calibrated

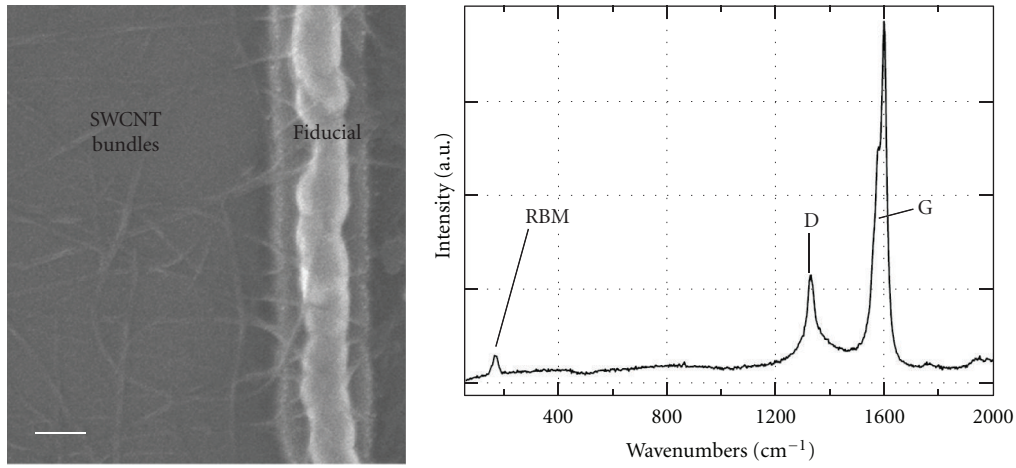


Figure 3: *Ex situ* characterization of COOH-SWCNTs following deposition with optoelectronic tweezers at high peak-to-peak voltages. (a) SEM image of SWCNT bundles deposited next to a Ti/Au fiducial marker. Scale bar = 100 nm. (b) Raman spectrum of deposited SWCNT bundles showing radial breathing mode (RBM), D, and G bands; a-Si background subtracted.

using a neon lamp. In all experiments, laser power was measured with a hand-held power meter.

3. Results and Discussion

When a 15 Vpp, 100 kHz trapping voltage is applied across the OET chamber, the SWCNTs are observed to move away from one another (Figure 2(a)) due to repulsive, in-phase dipole-dipole interactions. When the trapping laser is turned on, SWCNT bundles are observed to migrate into the laser spot (Figure 2(b)), agreeing with previous reports of positive dielectrophoresis forces for metallic SWCNTs [7] as well as with recent calculations for MWCNTs predicting forces in the range of piconewtons [4]. At high trapping voltages (20 Vpp, 100 kHz), the SWCNTs are observed to attach irreversibly to the a-Si surface. Electron beam lithography is used to pattern a grid of metallic fiducial markers (20 nm Ti, 50 nm Au) on top of the polished a-Si layer, which are then used to locate regions on the OET surface following Raman deposition experiments. Using scanning electron microscopy (SEM) (Figure 3(a)) and micro-Raman (Figure 3(b)) for *ex situ* characterization confirms that the deposited structures are indeed SWCNT bundles.

Single-beam laser tweezers have been used previously for three-dimensional trapping [8, 9], and Raman characterization [10] of SWCNT suspensions; however, they typically require several milliwatts of power to produce electric field gradients sufficient for trapping. Confocal micro-Raman measurements may also be performed with OET in an upright backscattering configuration. Generally, several hundred μW from the polarized 632.8 nm line of a CW He : Ne laser (Figure 4(a)) are focused to an area of $\sim 75\,\mu m^2$, yielding a maximum local irradiance of $<500\,W/cm^2$, which is more than sufficient to actuate the OET virtual trapping electrodes while simultaneously providing enough inelastically scattered photons for Raman spectroscopy. The focal point is positioned in the chamber with a motorized translation stage, using the Raman signal of the a-Si as a means of ensuring that the Raman focal volume coincides directly with the OET-trapping volume.

When Raman spectra are taken from the COOH-SWCNT dispersions, signal levels are low due to both the low concentration of tubes in solution and defects within the carbon lattice that decrease the inelastic scattering cross-section [11]. Raman spectra are acquired both with and without the OET-trapping voltage (6 Vpp, 100 kHz) at both the a-Si/fluid interface (Figure 4(a)) and $\sim 20\,\mu$m above the a-Si. Once the trapping voltage is applied, the in-plane E_{2g} stretching mode at 1591 cm^{-1} collected from the a-Si/fluid interface shows an 18-fold increase based on a ratio of integrated 1591 cm^{-1} peak areas. The enhancement exists both when compared to the case with the trapping voltage off, and with the voltage on, but with the focus $\sim 20\,\mu$m above the a-Si surface (Figure 4(b)). The signal enhancement is reversible, depending only on whether the laser is present to generate inhomogeneous lateral electric trapping fields. When the AC field is turned off, the signal relaxes to the background level, suggesting that trapped SWCNTs become free to diffuse through solution in agreement with dark-field images (Figure 2).

4. Conclusion

In conclusion, we report here the first demonstration of simultaneous trapping and micro-Raman spectroscopy of SWCNT materials with OET, providing a versatile means for locally concentrating dilute samples, therefore, enhancing the detected Raman signals by over an order of magnitude. This signal enrichment can potentially be combined with other Raman enhancement techniques such as surface-enhanced Raman spectroscopy (SERS) to create more sensitive Raman probes. OET is unique in that a few hundred

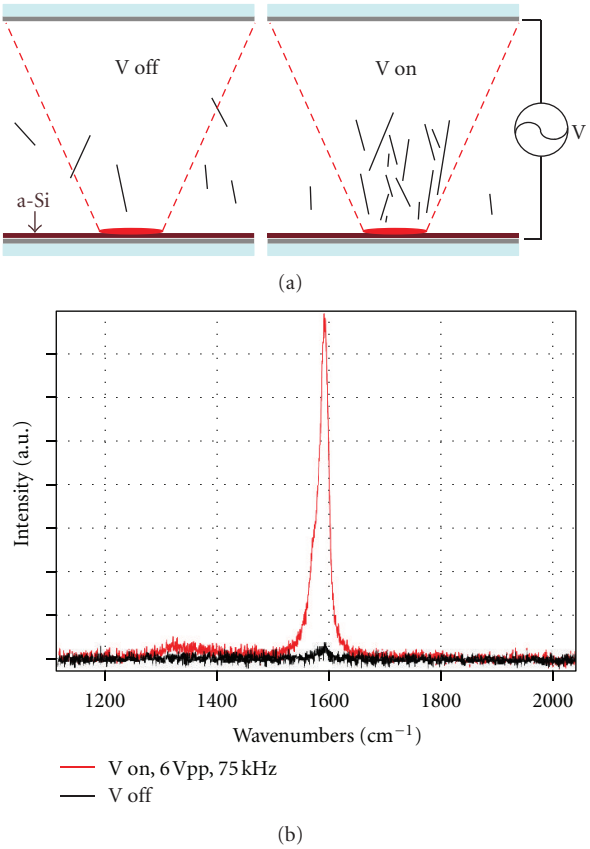


Figure 4: Enhanced Raman signal from COOH-SWCNTs trapped with OET. (a) Schematic of micro-Raman experiment and (b) Raman spectrum (480 W/cm^2, 60 s) with (red) and without (black) OET-trapping bias of 6 Vpp, 75 kHz.

micro-Watt laser intensities can be used to enrich the local analyte concentration while simultaneously producing inelastically scattered photons for sample characterization. This combination of enrichment and spectroscopy with a single laser spot suggests a broad range of applications in physical, chemical, and biological sciences. Finally, these results will help guide future experiments with isolated single-walled carbon nanotubes.

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