

Nanoscale Fluorescence Imaging Using a Single-Wall Carbon Nanotube

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Abstract: A single-wall carbon nanotube attached to an AFM probe is used for near-field optical imaging of 20 nm diameter fluorescent spheres and 5 nm diameter CdSe quantum dots.

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Compared with conventional AFM probes, single-wall carbon nanotubes (SWCNTs) have remarkable electrical and mechanical properties [1]. Their small diameter, high aspect ratio, mechanical robustness, electrical conductivity and selective chemical reactivity provide great advantages for ultrahigh-resolution imaging and manipulation at the nanoscale [2]. Coupled with end-selective chemical and biological functionalization, the SWCNT-AFM expands the capabilities of these tools beyond topographical imaging applications [3]. In this paper, we report nanoscale fluorescence imaging of 20 nm diameter fluorescent spheres and 5 nm diameter CdSe quantum dots with SWCNT probes. SWCNTs are grown on a silicon substrate with an iron catalyst via chemical vapor deposition (CVD). Vertically oriented tubes are lifted off the surface via van der Waals forces as the AFM probe scans over the growth substrate in tapping mode [2, 4]. Fig. 1(a) shows a typical force curve of a SWCNT attached to an AFM probe. The red curve traces the deflection of the AFM cantilever as the tip approaches a clean surface while the blue line traces the subsequent retraction. The protrusion-length of the SWCNT is given by the distance between the kink in the approach curve (point A) and the location where the cantilever starts to deflect (point B), ~40 nm in this case. The diameter of the SWCNT can be estimated from AFM images of prone nanotubes and quantum dots obtained using the SWCNT tip. From these measurements, we estimate the diameter of the SWCNT-AFM tips to be 3-5 nm.

The experimental scheme of the fluorescence imaging is given in detail in our previous report [5]. A radial-polarized laser beam at 543 nm was focused from below using an oil-immersion objective lens (N.A. = 1.4). The SWCNT tip was aligned into the focus of the laser and the sample is raster-scanned through the focus spot under the tip. The polarization of the optical field within the focus is predominantly axial; this is needed for tip-induced enhancement of the excitation intensity. Fluorescence emission was collected by the same objective and detected by an avalanche photodiode. Fig. 1(b) shows a fluorescence photocount image of a 20 nm diameter fluorescent latex sphere excited with the axial-polarized laser beam when the fast scanning axis is from left to right (trace) while figure 1(c) corresponds to a right-to-left scan (retrace). When the SWCNT approaches the sphere from the left, as shown in Fig. 1(b), the fluorescence is suppressed within a crescent-shaped region that opens to the right. Conversely, when the tip approaches from the right, as shown in Fig. 1(c), the crescent opens to the left. Fluorescence quenching is a well-studied phenomenon that can occur when a metal surface is brought into close proximity with an excited fluorophore, thereby providing non-radiative de-excitation paths that lead to a reduction in the fluorescence lifetime and a concomitant reduction in the fluorescence emission rate. Statistically, two-thirds of the SWCNTs grown on the CVD substrate should exhibit semiconductive, rather than metallic, behavior. We tested about 15 SWCNT-AFM tips and all of them cause a reduction, rather than an enhancement, in the detected fluorescence signal. In contrast, previous studies using silicon AFM probes showed dramatic fluorescence

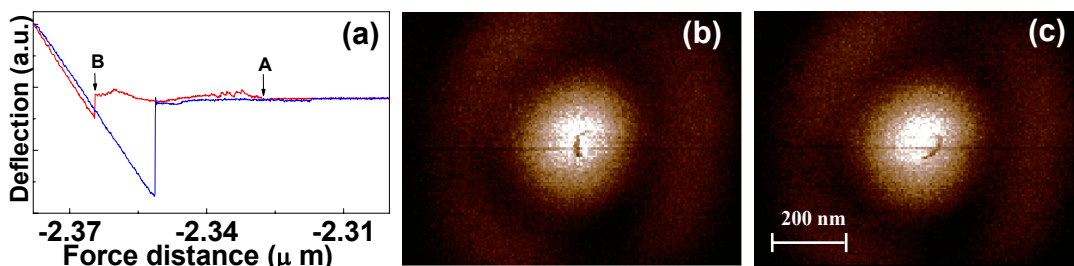


Fig. 1. (a) Deflection of the AFM cantilever as the AFM probe approaches the surface. (b) and (c) Fluorescence photocount images of a 20 nm diameter latex fluorescent sphere scanned with a SWCNT AFM probe. Panel (b) corresponds to a left-to-right fast scan axis (trace) and panel (c) corresponds to a right-to-left scan (retrace).

enhancement and no evidence of quenching [6, 7]. We are investigating three possible causes of this apparent discrepancy: 1) metallic-type SWCNTs are preferentially lifted off the CVD substrate; 2) photo-induced charge carriers impart metallic behavior even to semiconductive tubes; and 3) the signal reduction is not quenching but rather a redirection in fluorescence emission (away from the collection solid angle) caused by strong antenna-like coupling between the vertically-oriented nanotube and the fluorophores within the sphere.

The same SWCNT-AFM probe was also used to image single quantum dots (QDs) with diameters of ~ 5 nm. Figures 2(a) and (b) show the trace and retrace fluorescence image of a single QD, respectively. In this case, the diameters of the SWCNT and the QD are comparable and we observe a solid circular region of nearly complete fluorescence suppression. Fig. 2(c) shows the signal profile along the designated axis in the trace image. The width of the dark region is ~ 20 nm, which is significantly larger than the diameter of either the SWCNT or the QD. This suggests that the mechanism responsible for the suppression of fluorescence acts over a distance of ~ 10 nm. We note that the fluorescent spheres carry a net negative charge, whereas the QDs do not. The difference in target particle diameter and charge may help explain the peculiar crescent shape of the suppression region for the trace and retrace images of the 20 nm diameter fluorescent spheres. We are investigating the possibility that the relatively large size of the fluorescent spheres, coupled with their net charge, leads to a mechanical or electromagnetic interaction between the SWCNT and the sphere that causes the nanotube to bend during imaging [5]. Since the direction of the bend should depend on whether the nanotube is scanned over the sphere from left to right or right to left, the region of mechanical contact between the nanotube and the sphere will be essentially inverted for these two cases. This could affect the details of the fluorescence suppression process leading to the observed crescent shapes.

In summary, we have demonstrated nanoscale fluorescence imaging of single fluorescent particles using SWCNT AFM probes. In the near future, we will continue to investigate the fluorescence suppression mechanism through measurements of the conductivity of the nanotubes and their optical response as a function of excitation wavelength and polarization. These studies will provide deeper understanding of our present results.

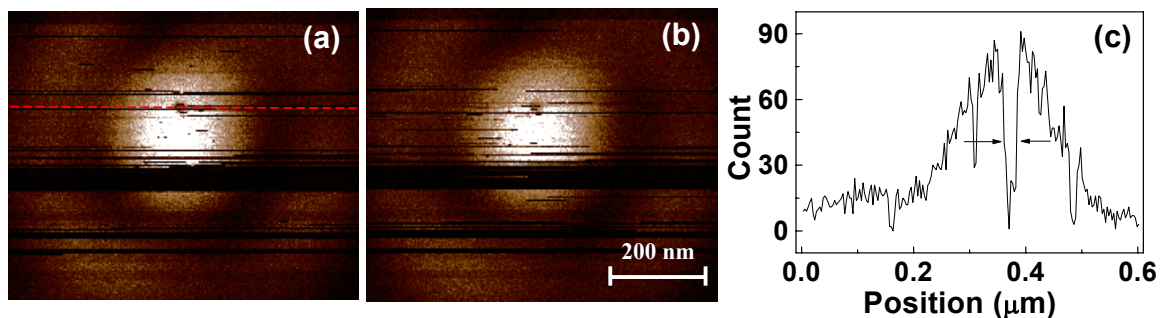


Fig. 2. Fluorescence photocount images of an isolated CdSe quantum dot (5 nm diameter) scanned with a SWCNT AFM probe. (a) Trace image; (b) Retrace image; (c) Cross line of trace image.

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