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Probing hotspots of plasmon-enhanced Raman scattering by nanomanipulation of carbon nanotubes

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Abstract

We present a two-step procedure to probe hotspots of plasmon-enhanced Raman scattering with carbon nanotubes (CNTs). Dielectrophoretic deposition places a small CNT bundle on top of a plasmonic Au nanodimer. After ‘pre-characterizing’ both the nanotubes and dimer structure, we subsequently use the tip of an atomic force microscope to push the bundle into the plasmonic hotspot located in the 25 nm wide dimer gap, characterize its location inside the gap, and observe the onset of plasmon-enhanced Raman scattering. Evidence for the activation of the CNT’s double-resonant D-mode by the near-field of the plasmonic hotspot is discussed.

Keywords: plasmon-enhanced Raman scattering, carbon nanotubes, plasmonic hotspot nano-manipulation

(Some figures may appear in colour only in the online journal)

1. Introduction

Metallic nanostructures enable the localization of electromagnetic waves into nanoscale volumes far smaller than the wavelength of light at optical frequencies [1, 2]. The electromagnetic wave couples to the collective excitation of electrons in the metal nanostructure known as a localized surface plasmon resonance (LSPR). This leads to a strong enhancement of the local near-field at the metal surface. When two nanostructures are closely spaced, coupling of the confined LSPRs (at certain polarizations) leads to a collective excitation across both, generating particularly strong field enhancement in the gap between them. Such a region is termed a plasmonic hotspot. The field enhancement varies considerably within and around such a plasmonic hotspot and may differ by several orders of magnitude over tens of nanometers [1–4].

One of the most spectacular applications of LSPRs is plasmon-enhanced Raman scattering, where the incident light and that inelastically scattered from an object inside a plasmonic hotspot is greatly enhanced [5, 6]. Plasmon-enhanced

Raman scattering has enabled the detection of single molecules and offers great potential for studying the fundamental aspects of light–matter interactions as well as biological and chemical sensing applications [7–17].

A recurring problem in quantifying plasmon-enhanced Raman scattering are small geometric variations between plasmonic structures of the same design, which may strongly alter the enhancement experienced by a Raman scatterer that is nominally located at the same position inside a corresponding plasmonic hotspot [18, 19]. It is therefore desirable to probe the plasmon-enhanced Raman scattering enhancement at different locations in and around one plasmonic hotspot using the same Raman scatterer. Kusch *et al* recently suggested reading out the plasmon-enhanced Raman scattering enhancement at a plasmonic hotspot via the Raman signal of a sharp Si-tip of a scanning near-field optical microscope [20]. The spatial extent of the tip, however, masks subtle variations of the enhancement on the nanometer scale. Similar restrictions apply to molecules, the traditional probe for plasmon-enhanced Raman scattering, because their exact location and orientation inside a plasmonic hotspot are impossible to control and, more importantly, cannot be altered. A nanoscale Raman scatterer that probes the enhancement in and around a plasmonic hotspot is therefore highly desirable.

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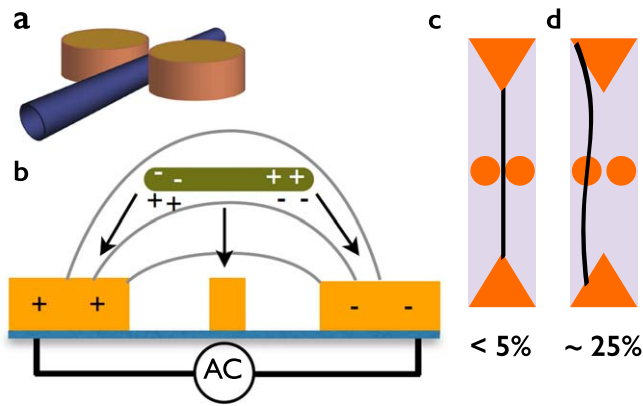


Figure 1. (a) Schematic of a CNT at the plasmonic hotspot in a nanodimer gap. (b) AC voltage drives the nanotubes in solution to deposit between the electrodes, where the plasmonic dimers are located. Based on reference [24], DEP has a yield $< 5\%$ for nanotubes passing through the gap, as in (c), and $\sim 25\%$ for nanotubes crossing one of the discs forming the dimer, as in (d).

Carbon nanotubes (CNTs) overcome some of these limitations and have recently emerged as a promising alternative to probe and quantify plasmon-enhanced Raman scattering on the nanoscale as their one-dimensional nature allows us to experimentally obtain the exact location and orientation within a plasmonic hotspot [21–28]. Interfacing CNTs with rationally designed hotspots, on the other hand, remains a challenge. We recently demonstrated the benefit of using directed dielectrophoretic assembly (DEP) to place CNTs precisely into the plasmonic hotspot at the ~ 25 nm gap of gold nanodimers, figure 1(a), and observed a 10^3 – 10^4 enhancement of the Raman intensity [24, 25]. More importantly, CNTs are perhaps the only nanoscale object that is able to probe plasmon-enhanced Raman scattering enhancement at different locations in a plasmonic hotspot, as the location and orientation of a nanotube can be purposefully altered by nanomanipulation [29, 30].

Here we demonstrate a two-step scheme that combines dielectrophoretic deposition of CNTs with tip-based nanomanipulation to probe plasmon-enhanced Raman scattering outside and inside the plasmonic hotspot of a gold nanodisc dimer. With the tip of an atomic force microscope (AFM) we push a small CNT bundle, deposited on one of the discs forming the dimer by dielectrophoresis, into the dimer gap. We determine the position of the nanotube bundle inside the hotspot and verify the onset of plasmon-enhanced Raman scattering by an 100-fold Raman enhancement of the nanotube’s G-mode, an inverted polarization behaviour and the spatial localization of the Raman signal after nano-manipulation. Beyond quantifying plasmon-enhanced Raman scattering, the proposed scheme will enable the realization of nanotube-nanoplasmonic experimental systems that were previously not accessible.

2. Experimental

The sample fabrication and dielectrophoretic deposition process follows the procedures described in references [24, 25]. In short, arrays of dimers and electrodes for DEP were

fabricated on a SiO_2 (90 nm) on Si substrate by electron beam lithography using a LEO 1530 Gemini FEG SEM and a Raith Elphy Plus Lithography System. Metallization was carried out by evaporating 5 nm Cr + 40 nm Au followed by lift-off in an ultrasonic bath. The dimers are located between electrode pairs (distance $\sim 1 \mu\text{m}$) with sharp tips for directed dielectrophoretic deposition. During directed dielectrophoretic deposition, a droplet of ultrapure, unsorted CNTs (www.nanointegris.com) in aqueous solution is placed on top of the arrays and a kHz AC voltage is applied between the electrodes [31, 32]. Initial AFM characterization after DEP was performed using an Park Systems XE 150 AFM. Nanomechanical manipulation was performed using a Bruker Dimension Icon AFM using Bruker TAP150A probes with cantilevers with a nominal stiffness of 5 N m^{-1} . All imaging was performed in non-contact mode. Raman characterization was performed using Horiba Yobin Ivon XploRa ($\lambda = 532 \text{ nm}$) and Witec alpha300 ($\lambda = 633 \text{ nm}$) single grating spectrometers using $100\times$ objectives (NA 0.9), and piezo stages for spatial mapping. To measure the polarization, we rotated the sample by 90° . We used integration times up to 10 s and laser powers between 1 mW (532 nm) and $50 \mu\text{W}$ (633 nm). The luminescence background from the Au nanostructures was subtracted for all Raman spectra.

3. Results and discussion

We fabricated arrays of dimer structures consisting of two closely spaced nanodiscs by electron beam lithography on top of a SiO_2/Si substrate. The dimer’s dimensions (cylinders with diameter ~ 100 nm, height 45 nm, separated by a gap of ~ 25 nm) were chosen to provide resonant enhancement for $\lambda = 633$ nm excitation polarized along the dimer axis [24, 33, 34]. The strongest coupling to the high-intensity near-field occurs for a nanotube placed inside the plasmonic hotspot at the nanoscale gap of the dimer [1, 2]. We realized such an interface for plasmon-enhanced Raman scattering of CNTs using directed dielectrophoretic deposition from solution as described in detail in [24, 25]. Dielectrophoretic forces drive the nanotube to deposit between electrodes where we have placed the plasmonic dimers, see figure 1(b). Ideally the CNT the electrode tips in a straight line and passes through the gap as shown in figure 1(c). This ideal configuration, however, has a yield below 5%. A scenario where the nanotube does not connect the electrode tips directly and crosses one of the discs forming the dimer as shown in figure 1(d) is much more likely ($\sim 25\%$) but does not provide significant Raman enhancement. It is therefore the ideal starting point for the two step procedure proposed in this work, because it allows us to characterize the CNT and its Raman signatures before it is interfaced with the plasmonic hotspot at the dimer gap.

We show an AFM phase image of such an initial scenario in figure 2(a). A small CNT-bundle (height ~ 7 nm, labelled CNT-B) crosses the left disc of a plasmonic dimer. The phase image is overlaid with a spatial map of the nanotube G-band just below 1600 cm^{-1} , the most prominent Raman feature in CNTs [35]. The corresponding Raman spectrum, taken with

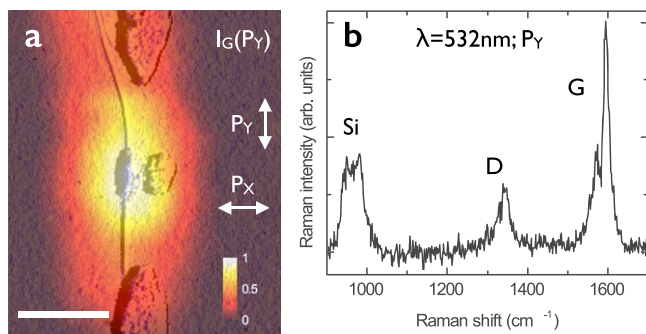


Figure 2. (a) AFM phase image of CNT-B overlaid with its integrated G-peak intensity for 532 nm and P_Y . The scale bar is 500 nm and the intensity normalized to the maximum G-mode intensity. (b) Raman spectrum acquired at the dimer. D-mode and G-mode of CNT-B and the second order Si peak are labelled in the spectrum.

the laser centred on the dimer, is shown in figure 2(b). The D-mode at $\sim 1350 \text{ cm}^{-1}$ indicates the presence of defects. It also appears in Raman spectra of CNTs dropcasted from the as purchased solution on a bare SiO_2/Si substrate and is therefore not caused by DEP [24, 25]. Both the energy of the excitation ($\lambda = 532 \text{ nm}$) and its polarization P_Y (perpendicular to the dimer) prevent plasmonic enhancement from the dominant dipolar LSPR of the dimer.

The spatial distribution of the integrated G-mode intensity $I_G(P_Y)$ in figure 2(a) matches that of CNT-B. We attribute the increased intensity around the dimer disc to a maximized overlap between CNT-B and the laser spot in combination with minor plasmonic enhancement from the disc's LSPR or due to electric field line crowding at the disc edges [1]. We did not observe a considerable signal for P_X , as the strong antenna effect in CNTs suppresses Raman scattering for polarizations perpendicular to the tube axis [35, 36]. For an excitation wavelength that overlaps with the dimer resonance ($\lambda = 633 \text{ nm}$), no Raman signal within our detection threshold was observed for both P_X and P_Y .

Before we discuss the nano-manipulation of CNT-B, we investigate more closely the topography of CNT-B and its interface with the dimer structure. A high-resolution AFM topography image is shown in figure 3(a). It confirms that CNT-B crosses the left nanodisc. Height profiles parallel to the dimer axis are shown in figure 3(c). They connect the dots of corresponding colour in figure 3(a), and are offset by 5 nm with respect to each other for clarity. On top of the dimer (green), CNT-B sits close to the edge of the left disc as indicated by the dashed vertical line. The AFM tip is insufficiently sharp to probe between the dimers. The tip sides as depicted in figure 3(e) are angled at 15° deg (left) and 25° (right) to the vertical. This leads to a slight asymmetry in the observed height profile at the sides of the discs. Close to the dimer edge (red), the CNT-B adheres to the disc wall and does not appear as a topographic feature. The tip, on the other hand, reaches to the bottom of the dimer gap. At distances of 20 nm (blue) and 100 nm (orange) away from the dimer, CNT-B adheres to the substrate at the same lateral x -position.

To move CNT-B into the gap, we ramped the tip into a chosen point on the dimer disc—to the left of CNT-B/dashed lines in figures 3(c), (d)—until a deflection setpoint of 50 nm was reached. This value corresponds to a downward force F_D of approximately 200–300 nN. While maintaining the downward force, the tip was slowly (50 nm s^{-1}) moved laterally 150 nm across the dimer gap to a second chosen point on the right nanodiscs, bottom figure 3(e), and retracted. The tip was then immediately used in tapping mode to image the dimer and CNT, figure 3(b). We achieved the same resolution as in figure 3(a) prior to the nanomanipulation—the observed profile of CNTB is the real profile convoluted with the tip apex profile—which shows that the tip did not measurably blunt while in contact with the surface.

The topography in figure 3(b) reveals that CNT-B was moved to the right such that it passes through the dimer gap. We will now deduce the exact configuration of the nanotube in the gap by comparing the corresponding height profiles in figure 3(d) to those taken before moving CNT-B in figure 3(c). On top of the dimer (green), CNT-B has been removed from its previous location (dashed line). At the dimer edge (red), CNT-B appears as a feature in the gap at a height of $\sim 25 \text{ nm}$, preventing the tip from imaging the gap region below. Around 20 nm away from the dimer (blue), CNT-B has been shifted to the right to accommodate for its new location at the dimer gap without building up strain. Further away from the dimer (orange), no changes in the tube's position have occurred.

The observed topography before and after nanomanipulation indicates that CNT-B is moved to a position suspended at a height of 25 nm in the gap. At first, the tip pushes CNT-B across the left disc's surface, thereby overcoming the adhesion of the CNT-B on the sides of the disc and on the substrate. The tip then enters the dimer gap to maintain F_D and carries the tube into the gap. The tip then retracts from the gap while the nanotube slips off and remains inside the gap. The position of CNT-B at a height of around 25 nm is in good agreement with the penetration depth of our tip with 25° side angle and a gap width of 25 nm. Note that during imaging in tapping mode, along the dimer axis the tip only reaches 10 nm into the gap, figure 3(e), and is therefore unable to probe CNT-B. This limitation also applies for mapping out the enhancement arising from a plasmonic dimer through the Raman signal of a Si-tip mounted on a scanning probe microscope as recently suggested by Kusch *et al* [20].

The observation of plasmon-enhanced Raman scattering from CNT-B after nanomanipulation confirms that we have successfully interfaced CNT-B with the plasmonic hotspot in the dimer gap. Figure 4(a) shows Raman spectra of CNT-B measured on the dimer with $\lambda = 633 \text{ nm}$ for both P_X (red) and P_Y (blue). The Raman intensity for P_X dominates the spectrum, and is a clear sign of enhancement due to near-field from the dipolar LSPR of the dimer structure. The signal is much stronger than for the non-resonant case ($\lambda = 532 \text{ nm}$), where we did not observe any signal for P_X . It is also stronger than for P_Y , along the CNT-axis, compare figure 2(b). We have previously identified this inverted polarization behaviour

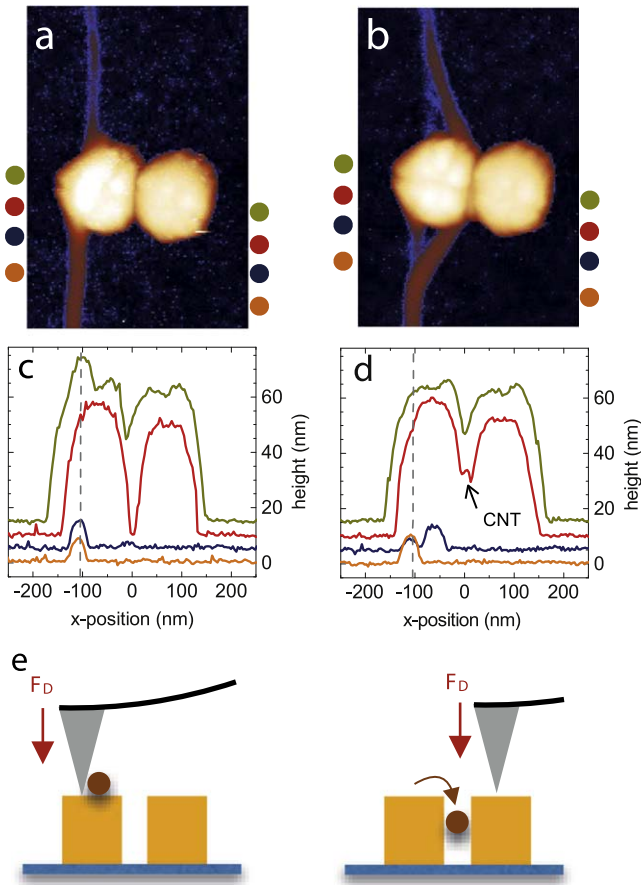


Figure 3. (a) AFM topography of CNT-B crossing the left dimer disc. (b) AFM topography after nanomanipulation. (c) and (d) show AFM height profiles across the locations indicated by the coloured dots in (a) and (b) respectively, confirming that the CNT bundle forming CNT-B has been pushed into the gap. (e) The downward force F_D holds down the tip while it is moved across the dimer, thereby moving CNT-B into the plasmonic hotspot at the gap.

as a clear sign of plasmonic enhancement from CNTs in dimer hotspots [24, 25].

The spatial distribution of the G-mode signal for P_X is shown in figure 4(b). It is strongly localized in space and shows the point-like character of the Raman enhancement arising from the hotspot in the dimer gap. Compared to P_X , the relative magnitude of the enhanced signal for P_Y and its localization, figure 4(c), may seem surprising. It originates from a minor plasmonic enhancement that couples favourably to CNT-B because the near field is polarized parallel to the axes of the tubes forming CNT-B. This is in stark contrast to the Raman intensity for P_X that scales only with the projection of the near field polarization on the tube axis [24, 33], explaining the relative intensities in figure 4(c). From the inverted polarization behaviour and signal localization presented in figures 4(b) and (c), we estimate 2.7×10^2 as the lower limit of the enhancement factor of the G-mode, for details see reference [24].

The D-mode is the dominant feature in our plasmon-enhanced Raman scattering spectra, figure 4(b). The ratio I_D/I_G is typically regarded as a measure for the defect

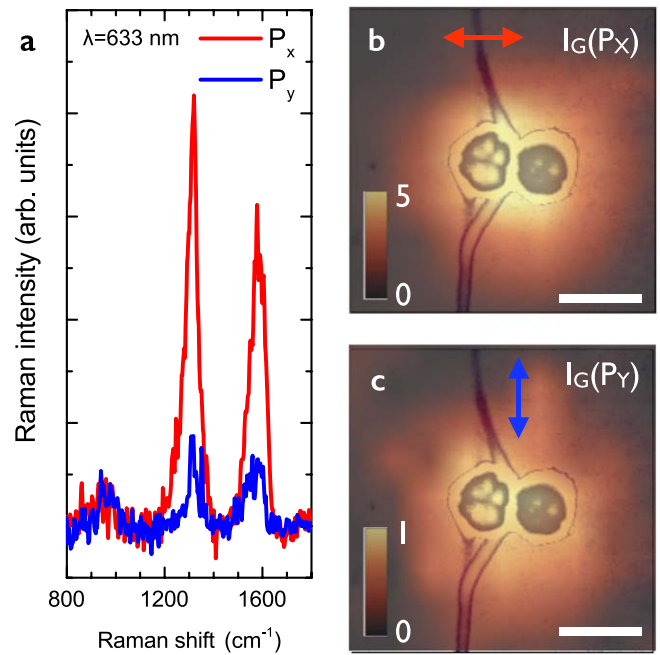


Figure 4. (a) plasmon-enhanced Raman scattering spectra from CNT-B after nanomanipulation for P_X (red) and P_Y (blue). Au photoluminescence has been subtracted from the spectra. (b) and (c) show Raman maps of the integrated G-mode intensity I_G for P_X and P_Y , respectively. They are overlaid with the AFM topography from figure 3(b). The scale bar in (b) and (c) is 200 nm.

concentration in nanoscale graphitic materials [35]. For CNT-B, it increased from 0.43 (532 nm, P_Y) before the nanomanipulation to 0.61 (633 nm, P_Y) and 1.22 (633 nm, P_X) in the presence of enhancement. For bulk quantities of our CNT starting material and for small CNTs bundles deposited directly into the dimer gap by DEP, the I_D/I_G ratio increases upon changing the excitation wavelength from 532 to 633 nm, see [24]. Therefore, the increase in I_D/I_G for P_Y is intrinsic to the CNTs used in this work and not caused by nanomanipulation. Did moving CNT-B, however, induce structural defects at tube segments now located at the plasmonic hotspot, which could explain the increase in I_D/I_G from 0.61 (633 nm, P_Y) to 1.22 (633 nm, P_X)? Previous studies showed that moving CNTs by AFM does not damage the nanotubes [37, 38]. Yano and co-workers moved CNTs with an AFM tip and subsequently characterized them by tip-enhanced Raman spectroscopy [39]. They did not observe any defects at the manipulated tube segments while probing with a spatial resolution of 20 nm, comparable to the localized nature of the enhancement in this work. As we were moving a bundle of CNTs, any stretching of the bundle due to nanomanipulation can be relaxed by interfacial sliding between tubes in the bundle which occurs at a much lower force than the introduction of structural defects within the nanotube [40]. We further exclude radiation-induced damage because we used low powers (50 μW) when acquiring the plasmon-enhanced Raman scattering spectra at $\lambda = 633$ nm.

In the light of these studies, we argue that the increase in the relative D-mode intensity in our plasmon-enhanced Raman

scattering spectra is not caused by structural defects. Instead, it is a consequence of the strongly localized nature of the near-field in the plasmonic hotspot. Two recent studies observed a strong D-mode for defect-free graphene interfaced with a single plasmonic hotspot [34, 41]. It was suggested that the confinement of the light fields in space provides the necessary momentum to excite non-vertical optical transitions. This activates the double-resonant Raman process that gives rise to the D-mode in graphene without requiring a real defect for momentum conservation [42, 43]. As the D-mode in CNTs has the same origin as in graphene [35, 36], we argue that the strong D-mode in the plasmon-enhanced Raman scattering spectra of CNT-B also arises from the localized near-field at the hotspot. This interpretation explains the factor of two different in the experimentally observed I_D/I_G ratios for P_Y and P_X . The near-field is less localized for P_Y than it is for P_X , resulting in a smaller—or more likely negligible—plasmon-induced contribution to the D-mode.

The two-step approach combining directed dielectrophoretic deposition and nanomanipulation presented here will find use beyond probing plasmon-enhanced Raman scattering from plasmonic dimers. It will allow to place CNTs into truly nanoscale gaps (≤ 5 nm) of bowtie antennas or plasmonic nanoclusters, which provide the electric field strengths necessary to observe phenomena such as the field gradient effect in plasmon-enhanced Raman scattering [44–46]. The low yield of placing CNT directly in such narrow gaps by DEP makes this technique impractical. Using directed dielectrophoretic deposition to carry the nanotubes close to the hotspots followed by nanomanipulation as described here, however, will achieve the desired interface.

4. Conclusions

In conclusion, we suggest directed dielectrophoretic deposition of CNTs followed by tip-based nanomanipulation to probe plasmon-enhanced Raman scattering from nanoscale plasmonic hotspots. With the tip of an atomic force microscope, we pushed a small CNT bundle 25 nm into the gap of an Au nanodimer. Its location at the hotspot was confirmed directly by atomic force microscope and indirectly by plasmon-enhanced Raman scattering. We observed a 10^2 enhancement of the nanotube's G-mode that was strongly localized in space in combination with an inverted polarization behaviour. Given the ability to characterize the nanotube beforehand, the strong D-mode after nanomanipulation was interpreted as a signature of plasmonic enhancement rather than being caused by structural defects while moving the nanotubes. Our two-fold scheme will allow the reliable placement of CNTs into nanoscale gaps of plasmonic structures and thereby enable experiments previously not accessible.

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