Aligned carbon nanotubes as polarization-sensitive, molecular near-field detectors

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Abstract

Aligned SWCNT arrays because this would cause all of the optical antenna | plasmonics

Optical antennas (1–4) are the analogs for light of radio frequency dipole antennas. Recently, they have been of scientific and technological interest for their ability to enhance and localize electromagnetic radiation (5–11). A gold or silver nanoparticle of any shape, e.g., a nanosphere, a nanorod, or a nanoprism, serves as an optical antenna owing to the oscillation of the conduction electron plasma (Mie resonances) (12, 13). The near fields generated by metallic nanostructures offer some intriguing features such as polarization control of single-molecule emission (14, 15). A polarization-sensitive nanoscale probe that does not perturb the near fields generated by optical antennas would be invaluable for studying these features. To this end, we have explored the properties of aligned single-walled carbon nanotubes (SWCNTs) (16), quasi-1-dimensional molecules that are formed by rolled-up single graphene sheets. Depending on their chirality, SWCNTs can be either metallic or semiconducting (17). Both varieties, however, exhibit Van Hove singularities in their electronic band structures, allowing for resonant absorption and scattering of light (18). Resonant Raman (19) and Rayleigh (20) spectroscopic studies of single SWCNTs have demonstrated the strong polarization-dependence of these phenomena. Optical absorption of SWCNTs is strongly suppressed when the polarization of light is perpendicular to the nanotube axis (20, 21). This suppression is attributed to the depolarization effect (21), i.e., the “antenna effect” (22, 23). A parallel external field will induce charges only at the extremities of the SWCNT similar to an antenna, whereas a perpendicular field would induce charges in the SWCNT walls that would, in turn, cancel the external field.

Because Raman scattering from SWCNTs depends on the polarization of the exciting field, SWCNTs can be used as polarization-dependent nanoscopic near-field “detectors.” With this approach, we have directly imaged the distribution of transverse near fields generated by gold nanodisk antenna arrays via surface-enhanced Raman scattering (SERS) from the SWCNTs with the excitation laser polarization perpendicular to them (Fig. L4). Using SWCNTs as Raman antennas requires perfectly aligned SWCNT arrays because this would cause all of the SWCNTs to respond in concert to a particular polarization determined by the alignment direction. Recent advances in SWCNT synthesis (24, 25) allow us to realize the proposed idea.

Near-field scanning optical microscopes are widely used in imaging of subwavelength features in various material systems and nanostructures. For a variety of applications, polarization-sensitive near-field probes can provide valuable information on the nature and symmetry of the imaged nanoparticles and emitters. Conventional near-field optical microscopy lacks in-plane polarization sensitivity. Here, we use aligned single-wall carbon nanotubes as polarization-sensitive molecular scale probes to image the transverse near-field components of an optical Hertzian dipole antenna. Because of the Raman “antenna effect” in carbon nanotubes, only the near-field components along the nanotube axis are detected. These findings demonstrate that aligned carbon nanotubes can be used as polarization-sensitive near-field detectors.

Fig. 1 B and C shows the calculated local field generated along the x axis around a gold nanodisk antenna upon illumination by a plane wave polarized along the x and y directions, respectively. A commercial finite integration technique (FIT) code (CST Microwave Studio) is used for solving the 3-dimensional antenna problem. The nanoantenna array on a quartz substrate is illuminated with a plane wave of wavelength 633 nm propagating in the z-direction. In the near zone of the nanodisk antenna, all 3 electric field components exist, as it would be for any dipole. For a subwavelength dipole the near zone electric field is given as

\[ \vec{E} = (3\hat{n}(\vec{n} \cdot \vec{p}) - \vec{p})/r^3, \]

where \( \vec{n} \) is the unit vector along r, the radial distance from the dipole (26). For a dipole moment \( \vec{p} \) along the x axis, Eq. 1 has all x, y, and z components. Because our nanodisk antenna is much smaller than the wavelength of the incident light, it can be treated as a Hertzian dipole, which has the near-field distribution given by Eq. 1. The in-plane parallel x component and transverse y component of the near fields generated by the antenna array are comparable in strength (Fig. 1). To image these 2 different polarization components, one needs a polarization-sensitive near-field “detector” that would not perturb the near fields of the nanodisk antenna. Here, we propose and demonstrate the use of aligned SWCNTs as near-field probes. Fig. JD shows a scanning electron microscope (SEM) image of a typical structure that comprises gold nanodisks fabricated around aligned SWCNTs.

Aligned single-wall SWCNT arrays are grown on single crystal quartz wafers by using a chemical vapor deposition technique (24, 25). A photolithographically patterned thin Fe film (<0.2 nm) is used as a catalyst. The growth was performed at 925 °C at atmospheric pressure. Carrier gases, Ar (10 sccm) and H2 (10 sccm), flow into the chamber through an ethanol bubbler. After 20 min, the growth process is terminated. The average diameter and the length of the SWCNTs grown by this process are 1.5 nm and 100 μm, respectively (Fig. S1).

We fabricate the gold nanodisk arrays by a standard bilayer e-beam lithography process. First 2 layers of e-beam resist are...
spincast on the substrate, followed by a 5-nm-thick Cr evaporation to avoid charging during e-beam writing. After the removal of the Cr layer and development of the resist, 35 nm of Au is evaporated after a 3-nm Ti adhesion layer. Then the nanodisks are revealed with a lift-off process. Arrays are fabricated both in periodic and quasiperiodic Penrose lattice arrangements (SI Text and Fig. S2) (27). Atomic force microscope (AFM) image of the fabricated square array structure is shown in Fig. 2A. The good alignment between the nanodisk antennas and the SWCNTs is visible in Fig. 2A. The nanodisks in these arrays have a diameter of 130 ± 10 nm (Fig. 2B) and the array period is chosen to be 300 nm.

We characterized the localized surface plasmon resonances of our 100-μm × 100-μm nanoantenna arrays by far-field reflection measurements (28). An incoherent white light source is collimated and then sent through a broadband polarizer and a long-working-distance, N.A. 0.55, microscope objective onto the arrays. The reflected light is then collected back through the same objective and fiber-coupled into a spectrometer. Each spectrum is corrected for the background and the wavelength dependence of the light source by normalizing to the reflection of the quartz substrate itself. Fig. 2C shows the reflection spectrum of the square nanodisk array for polarizations parallel and perpendicular to the axes of the SWCNTs. The resonance wavelengths for the nanodisk arrays do not change significantly with the polarization. Note that we have chosen array parameters such that the plasmonic resonance wavelength lies between the laser excitation line and the G-band Raman line (Fig. 2C).

We use a sample scanning confocal optical microscope fiber-coupled to a sensitive spectrometer for Raman measurements of the SWCNTs. The 633-nm line of a He–Ne laser is expanded and sent through a holographic laser line cleanup filter and focused on to the sample by a 0.9 N.A. 100× objective. Reflected light is collected back through a long-pass filter to suppress the excitation beam. A representative surface-enhanced resonant SWCNT Raman spectrum from the square array for laser polarization parallel to the SWCNT is shown in Fig. 2D. The radial breathing mode (RBM), the defect induced mode (D) and the tangential stretching mode (G) are all identified (21). The hump-shaped background is due to the photoluminescence from the gold nanoantennas (29).

The SEM image in Fig. 3B shows the Raman enhancement along the y direction generated around a single nanodisk optical antenna in a square array for illumination polarized parallel (B) and perpendicular (C) to the SWCNT assumed oriented along the x direction. The nanodisk thickness, the nanodisk diameter, and the period of the array are 35, 130, and 300 nm, respectively. The red arrow shows the polarization of the incident plane wave. The color scale is the same for both B and C. (D) Exemplary SEM image of the coupled system of the aligned SWCNT antennas and the gold nanodisk antenna array.

Fig. 1. Schematic representation of the polarization-sensitive SWCNT near-field detector configuration. (A) Shown is a schematic of the spatial distribution in the vicinity of the metallic nanodisks of the near-field amplitude along the x direction, when the laser is polarized normal to the SWCNT. (B and C) Calculated near-field amplitude distribution along the x direction generated around a single nanodisk optical antenna in a square array for illumination polarized parallel (B) and perpendicular (C) to the SWCNT assumed oriented along the x direction. The nanodisk thickness, the nanodisk diameter, and the period of the array are 35, 130, and 300 nm, respectively. The red arrow shows the polarization of the incident plane wave. The color scale is the same for both B and C. (D) Exemplary SEM image of the coupled system of the aligned SWCNT antennas and the gold nanodisk antenna array.

Fig. 2. Experimental characterization of coupled SWCNT and nanodisk arrays. (A) AFM image of the square antenna array. Alignment between the SWCNTs along the symmetry direction of the square nanodisk array is visible. The scan area is 2 × 2 μm. (B) Histogram showing the diameter distribution for the fabricated nanodisks in the square array. (C) Localized plasmon resonance spectrum of the antenna array for polarizations parallel (blue) and perpendicular (red) to the SWCNTs. The excitation (633 nm) and the Raman (G-band) lines are represented as vertical lines. (D) Exemplary SERS spectrum of a SWCNT and G-band Raman lines are labeled. Note the hump-shaped fluorescent background from the gold nanodisks.
nanodisks. Another factor reducing the enhancement is the averaging the Raman response to be averaged out spatially over the well-defined orientations that extend across the nanodisks, causing the Raman intensity by the Raman intensity from the pristine SWCNT. (C) Confocal Raman microscope (CRM) image of a 20-μm × 20-μm area with the laser polarization along the SWCNTs. This image is generated by spectrally integrating the intensity in the G-band for every pixel. G-band emission from SWCNTs that are not in contact with the gold nanodisks is visible for this polarization because of the “SWCNT antenna” effect. Surface enhanced Raman scattering is driven by the near-field distribution shown in Fig. 1B. (D) Same as C for perpendicular laser polarization. No Raman scattering from pristine SWCNTs is observed. For this case, surface-enhanced Raman scattering is driven by the transverse near-field component shown in Fig. 1C.

The measured enhancements (~20) are many orders of magnitude smaller than those achieved with metallic structures used for single-molecule Raman spectroscopy (31, 32). Unlike fluorescence, Raman scattering is not quenched at short distances from metals and decreases with increasing distance. In our configuration, there is a 3-nm Ti adhesion layer acting as an optically lossy spacer between the SWCNTs and the gold nanodisks, whereas in single-molecule studies, there is a physical contact with the gold nanoparticles.

We have thus far demonstrated that SWCNTs can be used to detect different polarization components of dipole near fields. The question to ask now is whether we can also extract some information on the spatial distributions or symmetries of these near fields. In conventional near-field microscopy (33), a probe is scanned over the optical near-field distribution of interest to map out the spatial extent of the former. In our configuration, both the probe (the SWCNT detector) and the object (the nanodisk antenna) are fixed on the quartz substrate. At first glance, it seems impractical to change the distance between the probe and the object. Nonetheless, the nanodisks are identical, and there is a slight misalignment between the SWCNTs and the nanodisk arrays. If we can find a SWCNT that crosses from one side of a row of nanodisks to the other (Fig. S3), we will have a distribution of lateral distances between the probe and the nanodisks. The aforementioned SEM imaging contrast aids us in finding such a SWCNT. Then by correlating the SEM images with the CRM images for different polarizations, we can retrieve spatial information on the near fields generated by the nanoantennas. Yet another caveat is that the whole section of the SWCNT lying in the confocal volume will contribute to the Raman signal, causing the latter to be spatially averaged.

To emulate the experimental situation, we have used the configuration shown in Fig. 4A. Because the SERS signal is approximately proportional to the fourth power of the near-field enhancement (33), we model the SWCNT as a detector that averages $|E|^4$ over its length along the $x$-direction. We then calculate the line-averaged field enhancement $\langle |E|^4 \rangle$ as a function of the distance $\Delta y$ between the SWCNT detector and the nanodisk center. Fig. 4B and C shows $\langle |E|^4 \rangle$ for parallel and perpendicular polarizations, respectively. Although our approach does not provide a 2-dimensional map of the near-field distribution, it nevertheless distinguishes the 2 distinct symmetries associated with the polarization components. An SEM image of a SWCNT that crosses 18 nanodisks is shown in Fig. 4D. The bright nanodisks are the indication of the physical contact between the SWCNT and the gold nanoantennas. The SWCNT touches the far-right bright nanodisk on the distance between the nanoantennas and the molecule of interest. Unlike fluorescence, Raman scattering is not quenched at short distances from metals and decreases with increasing distance. In our configuration, there is a 3-nm Ti adhesion layer acting as an optically lossy spacer between the SWCNTs and the gold nanodisks, whereas in single-molecule studies, there is a physical contact with the gold nanoparticles.

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bottom edge of the nanodisk and goes across the row of 18 nanodisks ending its physical contact at the top edge of the leftmost bright nanodisk. The CRM images corresponding to this region are shown in Fig. 4E and F for parallel and perpendicular laser polarizations, respectively. Fig. 4G compares the experimental results with the simulations. There is good qualitative agreement between the theory and the experiment. The symmetries associated with different polarizations are deduced by using our approach. The ratio of the measured field enhancements for the 2 polarizations is also consistent with the calculated values.

In summary, we have demonstrated both experimentally and theoretically that aligned SWCNTs can be used as polarization-sensitive near-field probes to image, by far-field microscopy techniques, the different polarization components generated by optical dipole nanoantennas. This work, which combines metallic nanoparticles and SWCNTs is likely to open up vistas in nanophotonics and plasmonics.

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