Cathodoluminescence spectro-microscopy of carbon nanotube forests

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Abstract

Cathodoluminescence microscopy is a technique that studies light emitted from materials that have been stimulated by an electron beam. By scanning an electron probe instead of a light probe, the diffraction limit of visible light can be overcome and spatial resolution better than 10nm can be obtained. In this study we share preliminary results from cathodoluminescence microscopy used to study thermal conductivity of vertically aligned arrays of multiwall carbon nanotubes, also known as carbon nanotube forests (CNTFs).

We report the first ever measurement of cathodoluminescence from carbon nanotubes isolated from substrates, and establish that the bulk of the cathodoluminescence is generated by the nanotubes themselves, not impurities such as catalyst nanoparticles. We also investigate the signatures of the carbon nanotube spectra and try to relates its features to local excitation such as interband optical transitions, excitons, plasmons. CNTFs have previously been shown to sustain heat localization with temperature gradients over 10 K/um, and the individual tube-level spatial resolution afforded by cathodoluminescence microscopy allows us to narrow down the conduction channels that allow these temperature gradients.

References

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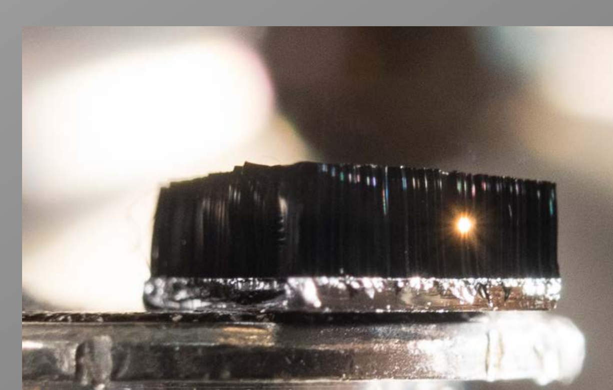
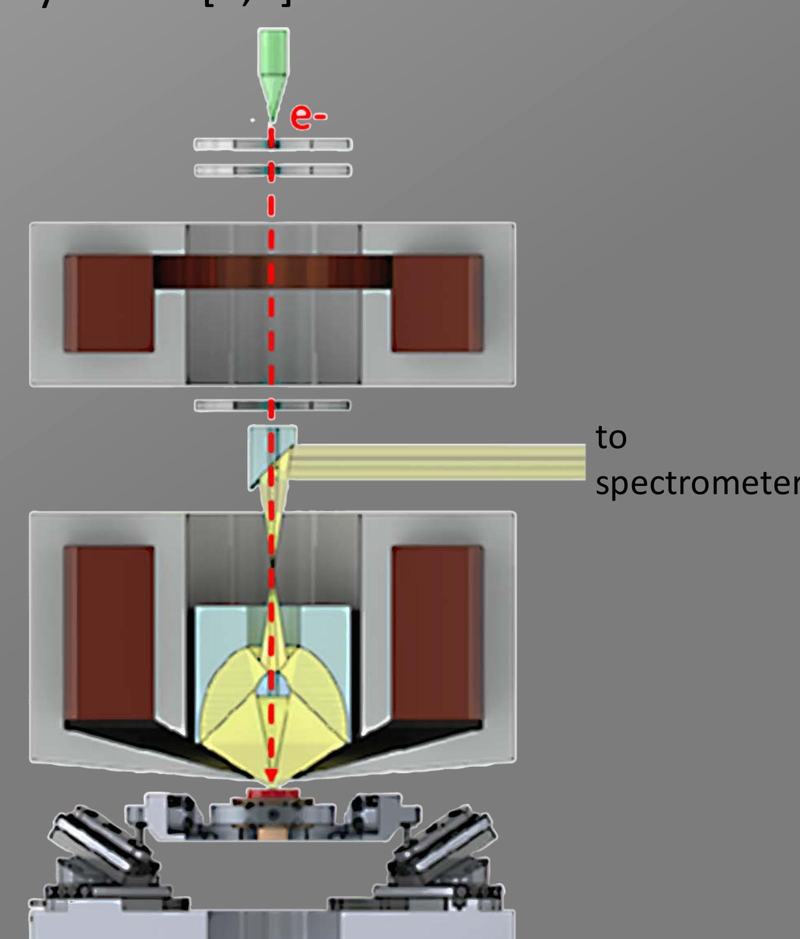
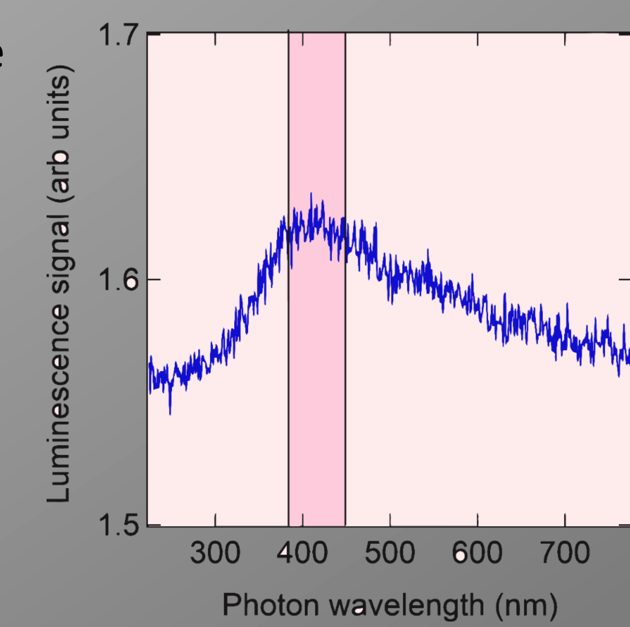
Carbon nanotubes and thermal conductivity

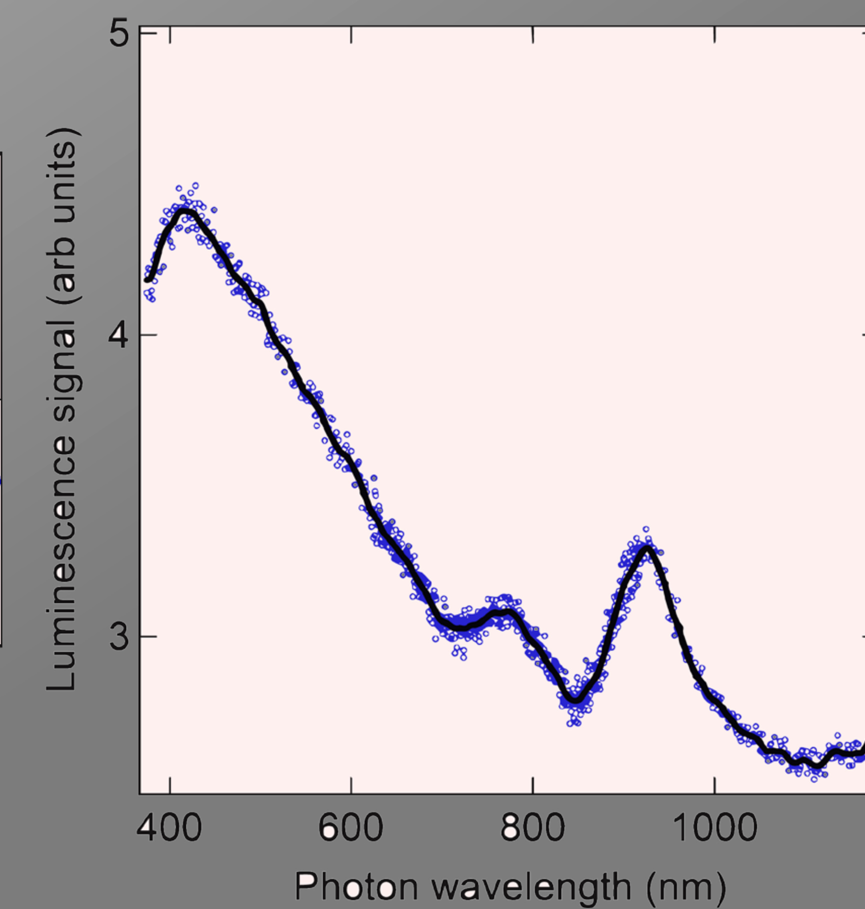
Since their discovery several years ago, carbon nanotube systems have provided an interesting medium to study mesoscopic physics with one-dimensional confinement in both electron and phonon transport. To highlight a particular phenomenon; arrays of vertically aligned multiwall carbon nanotubes, known as carbon nanotube forests (CNTFs), can be locally heated to temperatures over 2000 K while the surrounding material remains at ambient temperature (see photo below); with the localized spot being as small as 1mm. This phenomenon, dubbed the "Heat Trap", enables heating nanotubes to thermionic temperatures while maintaining the integrity of the underlying structure. The underlying physical principles responsible for the heat localization are not fully understood, however, nonlinear thermodynamic effects such as Umklapp scattering, as well as reduced dimensionality are believed to play a role [1,2].





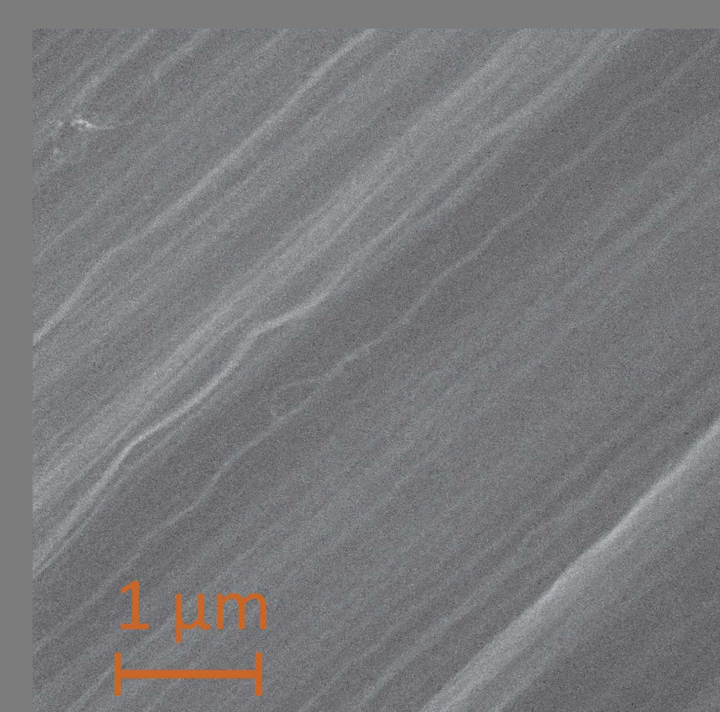
While cathodoluminescence microscopy is often used as a characterization technique for metals and semiconductors [3], as well as a tool for defect analysis in commercial nanopatterned devices, the only direct observation of cathodoluminescence from carbon nanotubes so far has been from carbon nanotubes embedded in a substrate [4]. Since properties such as phonon transport in nanotubes can be heavily affected by interaction with the substrate environment, it is desirable to study light emission from nanotubes with as few substrate interactions as possible. The schematic figure above illustrates the Attolight™ cathodoluminescence apparatus. An electron beam of user-defined electron energy is focused down to a several nanometer sized spot. The light emission stimulated by this electron beam is collected and analyzed using a grating spectrometer and visible photodiode, with sensitivity between 400nm-1200nm of photon wavelength. The secondary electrons from the sample are also collected. The sample sits on a XY-stage which can be scanned to obtain an image from the collected light emission and secondary electron signals.



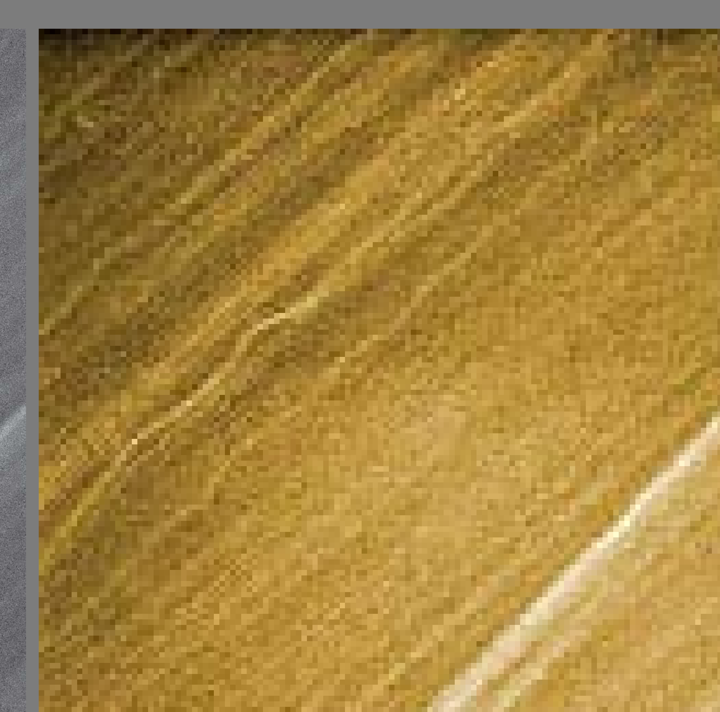


Light emission spectrum

The figure above and right shows the typical emission spectrum of light emitted from the CNTF sample with a 5 kV incident electron beam collected in a mode where spatial resolution was traded for high spectral resolution. The spectrum shows several broadband features over nearly the entire detection range, in particular, a broad high energy feature with a peak at 3 eV (410 nm), as well as narrower features at lower photon energies 1.6 eV (780 nm), and 1.3 eV (950 nm). The spectrum above and left shows the same emission spectrum, but collected in a mode where spectral resolution was traded for high spatial resolution. Light was collected from the highlighted band of the spectrum shown to form the luminescence image below.



SEM image



Luminescence image

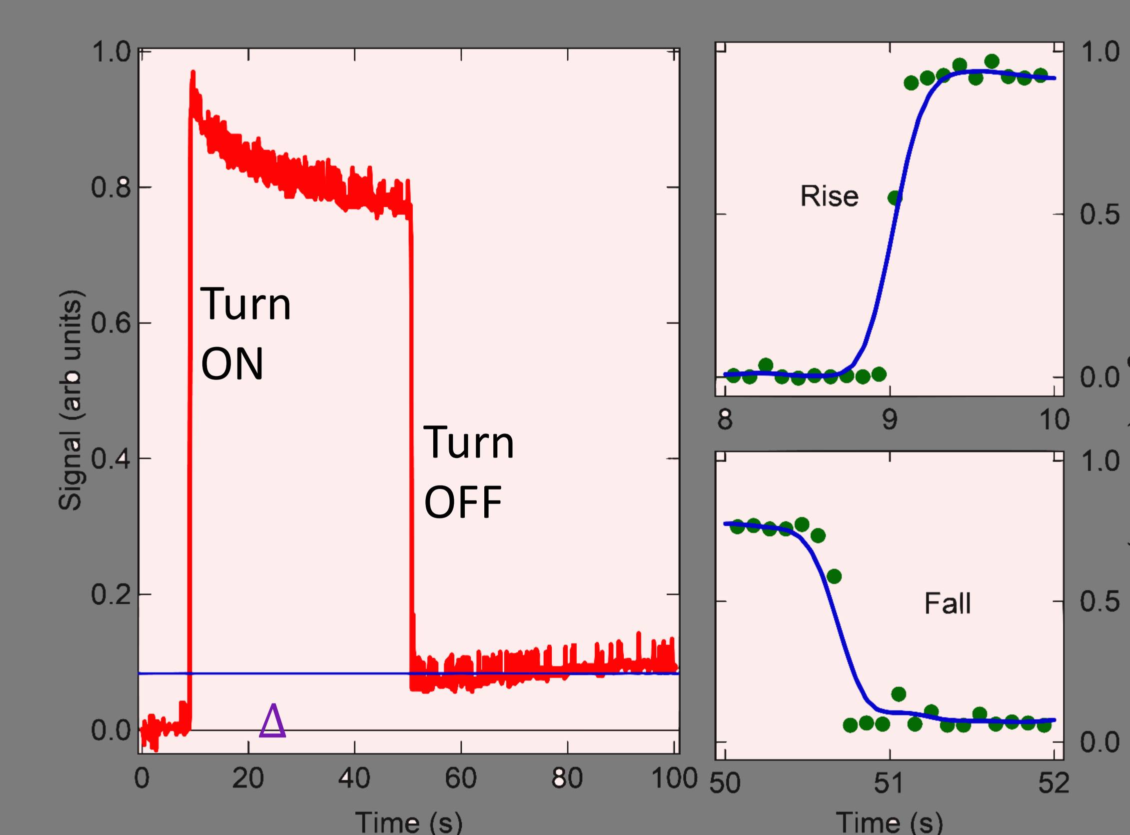
The intensity of the secondary electrons is plotted to form a conventional scanning electron microscope (SEM) image shown above and to the left, and can be compared directly with the luminescence image obtained from the intensity of light emission from the highlighted part of the spectrum. The agreement between these two images allows us to establish that the observed cathodoluminescence is generated directly by the nanotubes and not impurities such as catalyst nanoparticles.

Analysis

Understanding optical transitions and radiative properties in quasi one-dimensional materials like carbon, boron-nitride, and other nanotubes is crucial in providing a microscopic picture of dynamics in these materials and to their role in applications. Previous experiments using photoluminescence, embedded cathodoluminescence, and low energy EELS, have identified optical signatures including interband transitions, excitons, and plasmons.

Energy (eV)	System	Source	Technique
1.9, 2.2, 3.0	SWCNT	interband transitions	CL [4]
3.8, 5.3	BN-NT	defect state, exciton	CL [5]
1.4	SWCNT	two-photon emission	PL [6]
1.5	SWCNT	exciton	2ph-excit^{n} [7]
6.5	MWCNT	plasmon	EELS [8]

By juxtaposing with the data from literature in table above, we may interpret the 1.3 eV and 1.6 eV features in the CNTF data to correspond to interband optical transitions or exciton resonances. The broad 3 eV feature may seem to be too low in energy compared to plasmons, however we may interpret it as a plasmon resonance that has been redshifted and broadened due to proximity effects related to neighbouring nanotubes.



Temporal dynamics

We measured the cathodoluminescence response signal as a function of time with the electron beam turning off and on, as a crude indicator of the temporal response. Both the rise and fall times of the luminescence are faster than the response times of the detection mechanism, however, we note the existence of a long-time scale signal Δ that persists for several minutes after the electron beam is turned OFF.