

$= 3k$ (k is integer) , the tube is metallic ; but if $| m - n | = 3k \pm 1$, the tube is semiconducting . The nanotube diameter d is related to m and n as

In this equation , $a = 0.246$ nm is the magnitude of either unit vector a_1 or a_2 .

The situation in multi wall CNTs is complicated as their properties are determined by contribution of all individual shells ; those shells have different structures , and , because of the synthesis , are usually more defective than SWCNTs . Therefore , optical properties of MWCNTs will not be considered here .

== Van Hove singularities ==

Optical properties of carbon nanotubes derive from electronic transitions within one dimensional density of states (DOS) . A typical feature of one dimensional crystals is that their DOS is not a continuous function of energy , but it descends gradually and then increases in a discontinuous spike . In contrast , three dimensional materials have continuous DOS . The sharp peaks found in one dimensional materials are called Van Hove singularities .

Van Hove singularities result in the following remarkable optical properties of carbon nanotubes : Optical transitions occur between the $v_1 - c_1$, $v_2 - c_2$, etc . , states of semiconducting or metallic nanotubes and are traditionally labeled as S_{11} , S_{22} , M_{11} , etc . , or , if the " conductivity " of the tube is unknown or unimportant , as E_{11} , E_{22} , etc . Crossover transitions $c_1 - v_2$, $c_2 - v_1$, etc . , are dipole forbidden and thus are extremely weak , but they were possibly observed using cross polarized optical geometry .

The energies between the Van Hove singularities depend on the nanotube structure . Thus by varying this structure , one can tune the optoelectronic properties of carbon nanotube . Such fine tuning has been experimentally demonstrated using UV illumination of polymer dispersed CNTs .

Optical transitions are rather sharp (~ 10 meV) and strong . Consequently , it is relatively easy to selectively excite nanotubes having certain (n , m) indices , as well as to detect optical signals from individual nanotubes .

== Kataura plot ==

The band structure of carbon nanotubes having certain (n , m) indexes can be easily calculated . A theoretical graph based on this calculations was designed in 1999 by Hiromichi Kataura to rationalize experimental findings . A Kataura plot relates the nanotube diameter and its bandgap energies for all nanotubes in a diameter range . The oscillating shape of every branch of the Kataura plot reflects the intrinsic strong dependence of the SWCNT properties on the (n , m) index rather than on its diameter . For example , (10 , 1) and (8 , 3) tubes have almost the same diameter , but very different properties : the former is a metal , but the latter is a semiconductor .

== Optical absorption ==

Optical absorption in carbon nanotubes differs from absorption in conventional 3D materials by presence of sharp peaks (1D nanotubes) instead of an absorption threshold followed by an absorption increase (most 3D solids) . Absorption in nanotubes originates from electronic transitions from the v_2 to c_2 (energy E_{22}) or v_1 to c_1 (E_{11}) levels , etc . The transitions are relatively sharp and can be used to identify nanotube types . Note that the sharpness deteriorates with increasing energy , and that many nanotubes have very similar E_{22} or E_{11} energies , and thus significant overlap occurs in absorption spectra . This overlap is avoided in photoluminescence mapping measurements (see below) , which instead of a combination of overlapped transitions identifies individual (E_{22} , E_{11}) pairs .

Interactions between nanotubes , such as bundling , broaden optical lines . While bundling strongly affects photoluminescence , it has much weaker effect on optical absorption and Raman scattering .

Consequently , sample preparation for the latter two techniques is relatively simple .

Optical absorption is routinely used to quantify quality of the carbon nanotube powders .

The spectrum is analyzed in terms of intensities of nanotube @-@ related peaks , background and pi @-@ carbon peak ; the latter two mostly originate from non @-@ nanotube carbon in contaminated samples . However , it has been recently shown that by aggregating nearly single chirality semiconducting nanotubes into closely packed Van der Waals bundles the absorption background can be attributed to free carrier transition originating from intertube charge transfer .

= = = Carbon nanotubes as a black body = = =

An ideal black body should have emissivity or absorbance of 1 @. @ 0 , which is difficult to attain in practice , especially in a wide spectral range . Vertically aligned " forests " of single @-@ wall carbon nanotubes can have absorbances of 0 @. @ 98 ? 0 @. @ 99 from the far @-@ ultraviolet (200 nm) to far @-@ infrared (200 ?m) wavelengths .

These SWNT forests (buckypaper) were grown by the super @-@ growth CVD method to about 10 ?m height . Two factors could contribute to strong light absorption by these structures : (i) a distribution of CNT chiralities resulted in various bandgaps for individual CNTs . Thus a compound material was formed with broadband absorption . (ii) Light might be trapped in those forests due to multiple reflections .

= = Luminescence = =

= = = Photoluminescence (Fluorescence) = = =

Semiconducting single @-@ walled carbon nanotubes emit near @-@ infrared light upon photoexcitation , described interchangeably as fluorescence or photoluminescence (PL) . The excitation of PL usually occurs as follows : an electron in a nanotube absorbs excitation light via S22 transition , creating an electron @-@ hole pair (exciton) . Both electron and hole rapidly relax (via phonon @-@ assisted processes) from c2 to c1 and from v2 to v1 states , respectively . Then they recombine through a c1 ? v1 transition resulting in light emission .

No excitonic luminescence can be produced in metallic tubes . Their electrons can be excited , thus resulting in optical absorption , but the holes are immediately filled by other electrons out of the many available in the metal . Therefore , no excitons are produced .

= = = Salient properties = = =

Photoluminescence from SWCNT , as well as optical absorption and Raman scattering , is linearly polarized along the tube axis . This allows monitoring of the SWCNTs orientation without direct microscopic observation .

PL is quick : relaxation typically occurs within 100 picoseconds .

PL efficiency was first found to be low (~ 0 @. @ 01 %) , but later studies measured much higher quantum yields . By improving the structural quality and isolation of nanotubes , emission efficiency increased . A quantum yield of 1 % was reported in nanotubes sorted by diameter and length through gradient centrifugation , and it was further increased to 20 % by optimizing the procedure of isolating individual nanotubes in solution .

The spectral range of PL is rather wide . Emission wavelength can vary between 0 @. @ 8 and 2 @. @ 1 micrometers depending on the nanotube structure .

Excitons are apparently delocalized over several nanotubes in single chirality bundles as the photoluminescence spectrum displays a splitting consistent with intertube exciton tunneling .

Interaction between nanotubes or between a nanotube and another material may quench or increase PL . No PL is observed in multi @-@ walled carbon nanotubes . PL from double @-@ wall carbon nanotubes strongly depends on the preparation method : CVD grown DWCNTs show

emission both from inner and outer shells . However , DWCNTs produced by encapsulating fullerenes into SWCNTs and annealing show PL only from the outer shells . Isolated SWCNTs lying on the substrate show extremely weak PL which has been detected in few studies only . Detachment of the tubes from the substrate drastically increases PL .

Position of the (S22 , S11) PL peaks depends slightly (within 2 %) on the nanotube environment (air , dispersant , etc .) . However , the shift depends on the (n , m) index , and thus the whole PL map not only shifts , but also warps upon changing the CNT medium .

== Applications ==

Photoluminescence is used for characterization purposes to measure the quantities of semiconducting nanotube species in a sample . Nanotubes are isolated (dispersed) using an appropriate chemical agent (" dispersant ") to reduce the intertube quenching . Then PL is measured , scanning both the excitation and emission energies and thereby producing a PL map . The ovals in the map define (S22 , S11) pairs , which uniquely identify (n , m) index of a tube . The data of Weisman and Bachilo are conventionally used for the identification .

Nanotube fluorescence has been investigated for the purposes of imaging and sensing in biomedical applications .

== Sensitization ==

Optical properties , including the PL efficiency , can be modified by encapsulating organic dyes (carotene , lycopene , etc .) inside the tubes . Efficient energy transfer occurs between the encapsulated dye and nanotube ? light is efficiently absorbed by the dye and without significant loss is transferred to the SWCNT . Thus potentially , optical properties of a carbon nanotube can be controlled by encapsulating certain molecule inside it . Besides , encapsulation allows isolation and characterization of organic molecules which are unstable under ambient conditions . For example , Raman spectra are extremely difficult to measure from dyes because of their strong PL (efficiency close to 100 %) . However , encapsulation of dye molecules inside SWCNTs completely quenches dye PL , thus allowing measurement and analysis of their Raman spectra .

== Cathodoluminescence ==

Cathodoluminescence (CL) ? light emission excited by electron beam ? is a process commonly observed in TV screens . An electron beam can be finely focused and scanned across the studied material . This technique is widely used to study defects in semiconductors and nanostructures with nanometer @-@ scale spatial resolution . It would be beneficial to apply this technique to carbon nanotubes . However , no reliable CL , i.e. sharp peaks assignable to certain (n , m) indices , has been detected from carbon nanotubes yet .

== Electroluminescence ==

If appropriate electrical contacts are attached to a nanotube , electron @-@ hole pairs (excitons) can be generated by injecting electrons and holes from the contacts . Subsequent exciton recombination results in electroluminescence (EL) . Electroluminescent devices have been produced from single nanotubes and their macroscopic assemblies . Recombination appears to proceed via triplet @-@ triplet annihilation giving distinct peaks corresponding to E11 and E22 transitions .

== Raman scattering ==

Raman spectroscopy has good spatial resolution (~ 0 @.@ 5 micrometers) and sensitivity (single nanotubes) ; it requires only minimal sample preparation and is rather informative . Consequently ,

Raman spectroscopy is probably the most popular technique of carbon nanotube characterization . Raman scattering in SWCNTs is resonant , i.e. , only those tubes are probed which have one of the bandgaps equal to the exciting laser energy . Several scattering modes dominate the SWCNT spectrum , as discussed below .

Similar to photoluminescence mapping , the energy of the excitation light can be scanned in Raman measurements , thus producing Raman maps . Those maps also contain oval @-@ shaped features uniquely identifying (n , m) indices . Contrary to PL , Raman mapping detects not only semiconducting but also metallic tubes , and it is less sensitive to nanotube bundling than PL . However , requirement of a tunable laser and a dedicated spectrometer is a strong technical impediment .

== Radial breathing mode ==