IMPACT OF PROTONATION ON THE STRUCTURAL AND ELECTRONIC PROPERTIES OF SINGLE-WALLED CARBON NANOTUBES

A VENUGOPAL RAO
Research Scholar
Department Of Chemistry
SJJT University
Rajasthan.

Dr.TUMATI SRINIVASARAO
Quality Assurance Manager
Satyadivis Pharmaceutical Pvt. Ltd.

Dr. DEEPAK PAREEK
Professor
Department Of Chemistry
SJJT University
Rajasthan.

ABSTRACT

Strong tube-tube van der Waal attractions that hinder the dissolution of single walled carbon nanotubes (SWNTs) as individuals have been overcome by the direct protonation of the tubes by super acids. The removal of electrons from the SWNT, leading to a fractional positive charge on the carbons in the protonated state, is reversible upon deprotonation. With increasing concentration of the solubilized nanotubes, anion-mediated attractions at lower concentrations and spatial constraints at high concentrations guide the transformation of the SWNT-acid system into a nematic mesophase. Amine-terminated self-assembled monolayers (SAMs) have been shown to selectively adsorb semiconducting single-walled carbon nanotubes (sc-SWNTs). A dissolution model is proposed wherein the solubilized tubes exist as protonated polycarbocations, charge balanced by corresponding conjugate base anions. Previous studies have shown that when deposited by spin coating, the resulting nanotube networks (SWNTnts) can be strongly influenced by the charge state of the amine (primary, secondary, and tertiary). When the amine surfaces were exposed to varying pH solutions, the conductivity and overall quality of the resulting fabricated networks were altered. Finally, differing SWNT solution volumes were used to compensate for adsorption differences and yielded identical SWNTnt densities on the various pH-treated samples to eliminate the influence of network density.

Keywords: *single walled carbon nanotubes (SWNTs), nanotube networks, SWNT-acid system, self-assembled monolayers (SAMs).*

INTRODUCTION

Herein, we provide a survey of some of the fundamental electronic and structural properties of SWCNTs with emphasis on their unique electronic properties. We start with a discussion of their structure and symmetries. We then discuss the metallic SWCNTs. Since the first discovery of multi-walled carbon nanotubes in 1991 and the successful preparation of single-walled carbon nanotubes in 1993 carbon nanotubes (CNTs) have rapidly become a research hotspot. Due to unique mechanical and thermal properties they have a broad application prospects in the field of materials science, optics, nanoelectronics, nanotechnology. Replacing some carbon atoms of CNTs by other elements like N can efficiently alter the electronic properties and come into being new applications. The relaxation structure of C3N single wall nanotubes (C3NSWNT) was reported to be independent of the chirality of nanotubes. C3NSWNT has higher thermal conductivity and is affected by its length, chirality, and uniaxial strain. And most of C3NSWNT are semiconductors with high Young's modulus. We then discuss the standard graphene sheet model (GSM) for SWCNTs, pointing out its successes and limitations when compared to more

sophisticated calculations. (A closely related approach to the standard GSM is the k·p scheme of Ando and co-workers from which many important results have been obtained. Next, we discuss some of the key nanotube experimental results with emphasis on the strong interplay between theory and experiment that this area has enjoyed. We then turn to some current fundamental issues awaiting resolution. Finally, we conclude with brief comments. Zigzag C3NSWNT with vacancy defects exhibited ferromagnetic spin alignment. The H atom adsorptions have significant effects on the electronic structure of C3NSWNT. The C3NSWNT is well suited for a hydrogen storage material.

LITERATURE REVIEW

Jorio A (2021) This study provides a broad overview of Raman spectroscopy to help readers better comprehend carbon nanotubes. First, a quick primer on Raman spectroscopy and how it relates to grapheme-based materials will be provided. In order to construct materials and systems that may possibly display Raman spectra, we shall further go into the specifics of altering and specifying nanotube characteristics. By using cutting-edge methods, it might improve Raman spectroscopy as a tool for studying CDs.

Manu and Abhas (2020) penned it in 2020. Nanoscale refers to an epoch a thousand times smaller than that of a human hair, and "nonmaterials" are substances that mimic the characteristics of such items. Nanoparticles' remarkable physical and chemical properties contributed significantly to their skyrocketing ascent to stardom. For the first time, nonmaterial's showed up in the field of nanoscience and nanotechnology. Innovations in the vast area of nonmaterial's research may cause a sea change in how many products are made. The study looks at how transportation vehicles are being improved technologically in every way, from speed to safety to how easy they are to operate. The article delves deep into the topic of novel uses of nonmaterial's, covering a wide range of topics such as improved engine fuel efficiency, nano-filters, nano-coatings, novel particles, and many more. More Nanoparticles, according to the study's authors, might make automobile components more efficient and lessen the environmental impact of transportation.

Krishnan (2020) despite being in its early stages, the automobile industry provides a fertile setting for innovative research and development. Due to their potential in gasoline component systems, we will examine the implications of carbon nanotubes for improved fuel economy "on the road." With an eye on its potential uses in automobile sector, this article provides a comprehensive overview of carbon nanotubes. Carbon nanotubes (CNTs) are an attractive reinforcing element for composite constructions, particularly those using polymers, and their aesthetically pleasing properties make them suitable for use in a wide variety of automotive applications. This could serve as a springboard for you to reach your ideal weight, I hope. Emerging production methods using CNTs have the potential to revolutionize the industry by constructing intricate, geometrical, or asymmetrical patterns and structures from cheap, readily available basic materials. Great efficiency and effectiveness could result from this.

Isao Yamaguchi (2019) the levels of prorogation was modulated by the feed ratios of Pyr-SO3H/PEI. To create

branching PEIs with sulfopyrenyl pendant groups, we found the following molar ratios of 1-pyrenesulfonic acid (Pyr-SO3H) to PEI: Pyr-PEI (1:1), Pyr-PEI (1:2), Pyr-PEI(1:3), and Pyr-PEI(1:4). As a result of treating single-walled carbon nanotubes (SWNTs) with Pyrenees-PEIs, soluble composites known as SWNT-Pyr-PEIs were produced. Throughout this process, the Pyrenees group was attached to the surfaces of the SWNTs. Photoluminescence (PL) and ultraviolet-visible (UV-vis) studies showed that the absorbance and PL intensity in SWNT-containing materials in SWNT-Pyr-PEI composites rose with increasing PEI percentages. The electrical conductivities of SWNT-Pyr-PEIs were determined through electron migration, and it was demonstrated that n-doping resulted in conductivities that were higher than those of pure SWNT.

Moustafa Ala-Eddin (2016) Carbon nanotubes (CNTs) are fascinating new materials with remarkable physiochemical capabilities and remarkable flexibility; these attributes have found applications in a wide range of industries, from medicine to consumer goods. Recently, there has been a lot of talk about how harmful CNTs are to both humans and ecosystems. The potential toxicity of carbon nanotubes (CNTs) to humans, other animals, and their embryos is believed to be heavily influenced by their physiochemical properties and the way they interact with living cells. Congruent with our findings, recent research has shown that CNTs kill cells in both humans and animals. This is so because CNTs alter genes that are involved in such processes as angiogenesis, adhesion, cell death, survival, and proliferation. Research on the effects of CNTs on embryonic development has shown contradictory results.

Single-walled carbon nanotubes (SWCNTs)

Single-walled carbon nanotubes (diameter < 3 nm) create a nano-sized electrical interface that is well suited for biosensing. Single-walled carbon nanotube suspension solutions have been utilized in various sensing techniques as well as in preparation for subsequent deposition on electrode surfaces. Additionally, various non-covalent and covalent SWCNT/electrode immobilization protocols (e.g. thiol linking, electrodeposition, and polymer encapsulation) have been utilized to immobilize SWCNTs onto electrode surfaces. These SWCNT-based biosensors have experienced improved sensitivity in numerous biosensing applications. Suspending SWCNTs in solutions can be a challenging task. The solubility of SWCNTs in de-ionized (DI) water is quite low (less than 0.1 mg/mL on sonication). The functionalization of SWCNTs with chemical groups increases the solubility in water. Modification with glucosamine increased the solubility in water to 0.1–0.3 mg/mL whereas modification with single-stranded DNA (ssDNA) can increase the solubility to 4 mg/mL.

Basic Electronic Structure

SWCNTs are a hollow and cylindrically shaped one dimensional (1D) graphitic carbon allotrope, characterized by an extended network of sp2 hybridized carbon atoms. SWCNTs are theoretically constructed by rolling up a graphene sheet with the hexagonal rings joining seamlessly into a cylinder at a certain chiral angle with respect to a plane

perpendicular to the tube's long axis. The way the graphene sheet is rolled up determines the diameter and the carbon-carbon bonding orientation with respect to the nanotube axis. Indeed, a huge diversity of different SWCNT structures can be constructed differing in length, diameter and the orientation of the hexagonal carbon rings with respect to the nanotube axis. Each SWCNT can thus be defined by its diameter and chiral angle which varies from 0° to 30°. More conveniently, a pair of indices (n,m), referring to equally long unit vectors at 60° angles to each other across a single hexagonal carbon ring can be used to describe the structure of each SWCNT type.

Carbon Nanotubes for Bioimaging

SWNTs usually have some optical properties. For example, semiconducting SWNTs have NIR photoluminescence properties with low autofluorescence. The intrinsic photoluminescence can penetrate the deep tissue beyond 1 mm in the NIR region. These properties made SWNTs an ideal material for NIR photoluminescence imaging. CNTs can also be used for Raman or photoacoustic imaging. Synthesized phospholipid-polyethylene glycol (PL-PEG)-coated SWNTs by sonicating SWNTs with sodium cholate followed by surfactant exchange. They thought this method was much better than directly sonicating SWNTs with PL-PEG, because the exchange process resulted in less damage.

Structure of Carbon Nanotubes

Single walled carbon nanotubes are an allotrope of sp2 hybridized carbon, similar to fullerenes. The structure can be thought of as a cylindrical tube comprised of 6-membered carbon rings, as in graphite. The cylindrical tubes may have one or both ends capped with a hemisphere of the buckyball or fullerene structure. An understanding of SWNT structure requires familiarity with the concept of nanotube chirality, since the chirality of a SWNT dictates many of its properties. A concept known as a Chirality Map, illustrated in has been developed as a tool for understanding chirality and its implications. A SWNT can be envisioned as a sheet of graphite one atom thick rolled into a tube. The chirality describes both the orientation and diameter to which the sheet is rolled. Each SWNT on the chirality map is defined by two integers, (n,m). As indicated previously chirality defines many of the properties of the individual SWNT. For example, SWNT shown on the chirality map in blue are metallic in nature. These are tubes where n=m (armchair) or n - m = 3i, (where i is any integer.) Those depicted in yellow are semiconducting, displaying different band gaps depending on the length of the chiral vector.

RESEARCH METHODOLOGY

Being insoluble in water and most organic solvents, isolated SWNTs float on top of it all with the help of a dispersion agent. The bio-molecules and surfactants were first dispersed in a solution using ultrasonication. Afterwards, the nano-tubes were suspended in the fluid using high-speed centrifugation. We tested several combinations of SWNT precursor, dispersing agent, and processing conditions to perfect our mix, as proper dispersion is critical for molecular analysis. In order to assess the quality of the SWNT suspensions, we used fluorescence quantum yield determination, absorption spectroscopy, and fluorescence spectroscopy. Carbon nanotube-containing compounds may take on an almost infinite

variety of shapes, sizes, hilarity states, and lengths. While the many different SWNT structures lead to a great number of permutations, they also make it more difficult to research and build the unique capabilities shown by each moiety. The samples have a tendency to clump together while getting ready for optical study because the SWNTs have large van der Waals contacts on their sidewalls, which amounts to around 500 eV/µm of contact. The resolution of absorption properties and the intensity of fluorescence are both diminished by aggregation. Because they tend to cluster into complex networks and don't have any surface functional groups, carbon nanotubes are very water resistant. With the probable exception of N-methylpyrrolidone, SWNTs have poor solubility in water and the majority of organic solvents. We can see the operation of this here.

RESULTS AND DISCUSSIONS

Fluorescence Intensities of Single Molecules

A photoluminescence spectrum of a single CdTe/ZnS quantum dot (QD) with dimensions of 40 nm FWHM and an emission wavelength of 705 nm. On the inside, a regular glowing image showed up. As seen in the light emission from a single quantum dot exhibits fluorescence intermittency, which is defined as an on/off blinking pattern. Blinking is a clear indication of fluorescence from a single quantum dot, thus by tracking the nanoparticles' time traces; we could verify that we were investigating individual particles.

Table 1: Raw Fluorescence Intensities and Absorption Cross Sections for SWNTs and QDs

(6,4) SWNTs	**(9,1) SWNTs**	**(8,3) SWNTs**	**(6,5) SWNTs**	**CdTe/ZnS QDs**
E_{22}(nm)[a]	693	663	567	-
E_{11}(nm)[a]	912	952	975	-
average fluorescence intensity (counts)[b]	188	203	183	263
counts/power (counts/mW)	147	159	143	2023
average QY (%)	2.9	3.0	2.9	-
estimated σ_{633nm} (cm^2)[c]	7×10^{-15}	7.5×10^{-15}	7×10^{-15}	2.6×10^{-15}
σ_{E11}(cm^2)[c]	-	-	1×10^{-13}	-

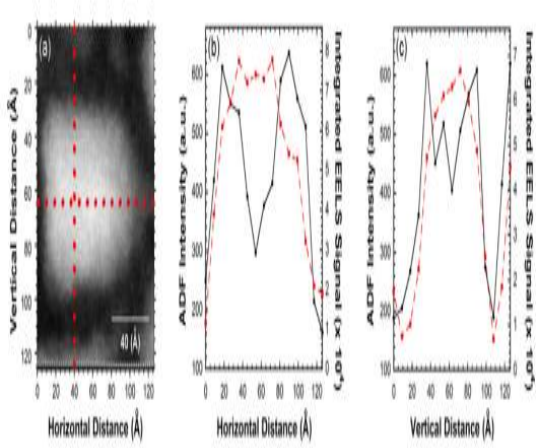
Writing standards: Fluorescence intensities were adjusted based on the effectiveness of detecting peak emission wavelength and excitation intensity.

At ambient temperature, the narrow width of the emission lines of isolated single-walled nanotubes (SWNTs) is about kBT, which is in agreement with the energy levels of certain nanotube configurations (n,m). Does not provide data for individual QDs, but rather a time trace of the same nanotube, which proves that SWNTs continuously produce photos table light. The average findings are shown in Table 1, while the raw fluorescence intensities of QDs and SWNTs respectively.

Absorption Cross Section of QDs

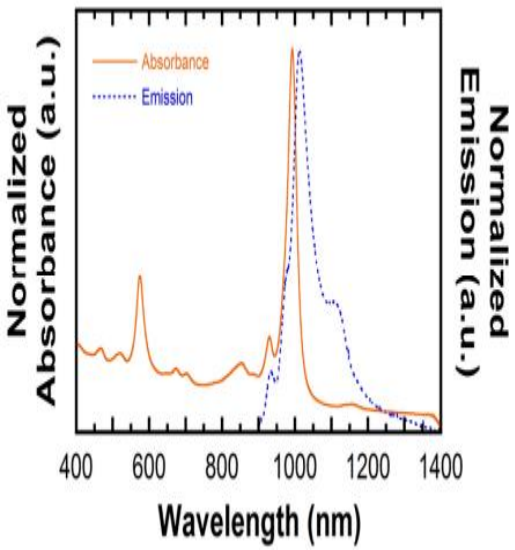
An ADF signal about 1.7 times stronger than the uncontrolled one is produced by

this configuration. As the sulphur concentration in the shell material increases, there is a positive correlation with the integrated EELS signal, which expands in a direction perpendicular to the electron beams longitudinal path. According to the quantum dot (QD) model, the integrated sulphur EELS signal should be smallest within the core and largest outside when the entire shell cross-sectional thickness (sulphur concentration) is highest.



Graph 1: a. using an annular dark field STEM, typical single quantum dots of CdTe/ZnS was imaged. The red horizontal dot in (b) and the vertical dot in (c) represent data points for sulphur EELS, respectively.

The challenging atomic EELS method was used to fabricate seven quantum dots (QDs). The results of the theoretical models that were applied to the EELS data are as follows: The shell is spaced 67.5 ± 2.9 Å apart from the core, which has a diameter of 47.9 ± 1.7 Å. A weighted average of these data is used to establish the effective QD diameter, which in turn yields the empirical estimates of an absorption cross section of 1.4 × 10-15 cm2.



Graph 2: Fluorescence (blue dotted line) and normalized absorbance (orange solid line) are shown in the spectra as a mixture of Como CAT-produced SWNTs suspended in DNA/H2O. Peaks at about 1000 nm indicate that the sample is likely rich in (6, 5) SWNTs.

The hard-rinsed samples were made by mixing 20 mM MgSO4 with the same amount of SWNTs, which had been diluted 128 times from the stock, and then waiting two hours. Following that, the cover slip was given 20 minutes to incubate after 5 µL of the sample was introduced to it. Next, we rinsed the film with five drops of water using a Pasteur pipette. The cover-slip was dried well before being placed in a mild nitrogen stream for about one minute. We made sure the topography and fluorescence measurements were accurate by pre-preparing the films without washing them.

CONCLUSION

Future ensemble studies will be able to build on our work, which analyzed the photo-physical characteristics of individual SWNTs and shed light on the excited state dynamics of these special molecules. Metal nanotubes, remaining bundles, defect sites, intersystem crossover to triplet

states, and fast scattering into non-radioactive dark states are some of the reasons for the poor ensemble QY of SWNTs. In addition to hilarity and diameter, several characteristics affect the quantum yield of ensemble samples. To further understand the apparently low SWNT QY, it may be helpful to review the four pillars of nanotube photo-physics. Furthermore, we provide prospective experiments that might go further into these topics. As stated in the dispersion agent connected to the SWNT causes changes in the fluorescence peaks and line widths, which may be either broadened or shortened. The excited state lengths of nearby individual nanotubes are impacted as well as the positioning of defect traps along the sidewall. Measuring the photoluminescence lifespan and single molecule fluorescence of SWNTs floating in various surfactants may help us understand the impact of these surfactants on SWNTs. Because, in contrast to far-field analyses that average over distributions of area dielectric environments, near-field optical approaches might allow the evaluation of small SWNT sections in a uniform micelle background. This is why the adsorption of molecules onto SWNT sidewalls is typically not uniform. Alternatively, optical measurements of SWNTs embedded in cage like compounds like Sarkosyl have been considered. These molecules provide a continuous dielectric environment around each SWNT.

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