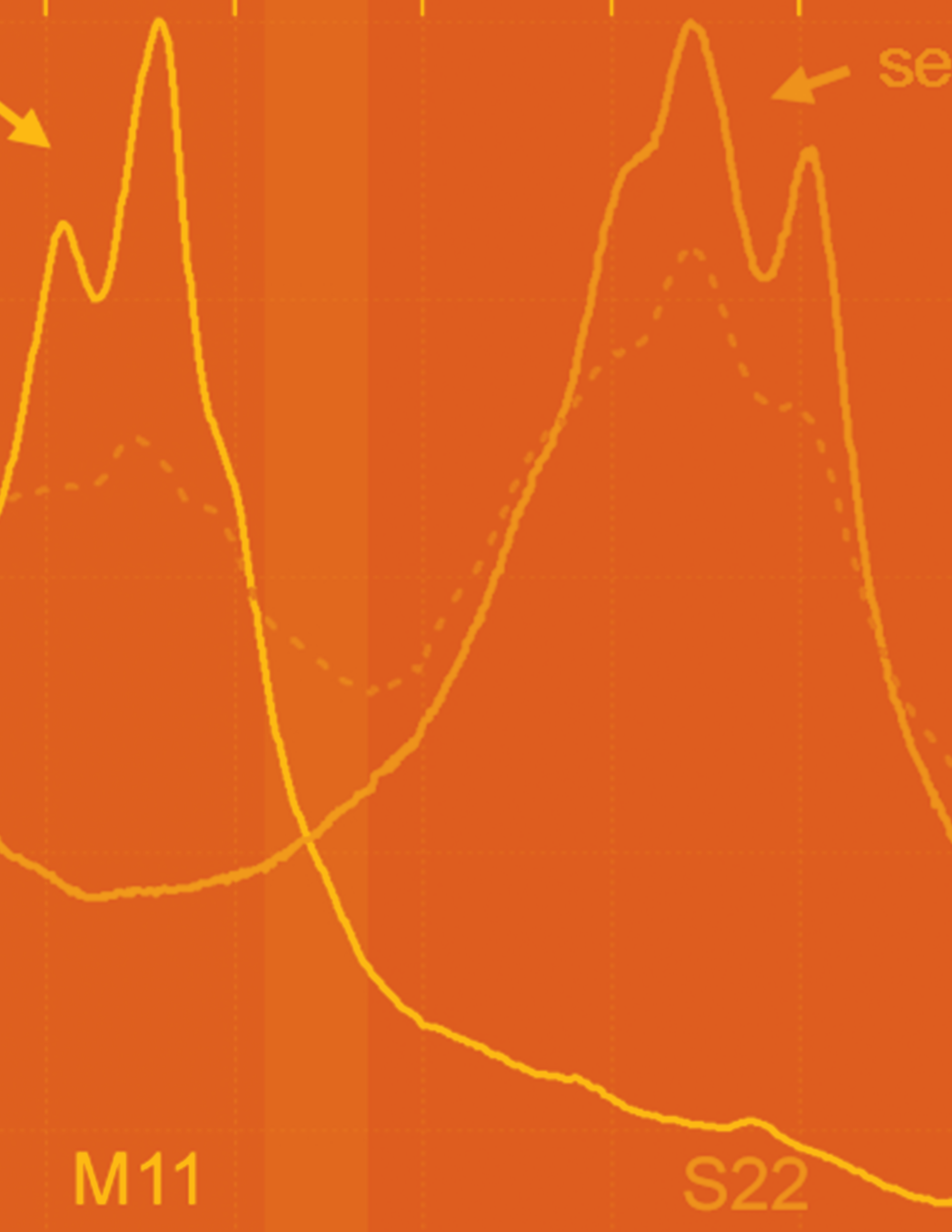

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Sorting of Arc Discharge–Produced Carbon Nanotubes by Electronic Structure in Density Gradients

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Abstract

Carbon nanotubes have been shown to behave as very effective conductors and semiconductors, but their electronic uses are limited by how well metallic and semiconducting nanotubes can be sorted. Recent investigations have shown an effective method of separating laser ablation–produced carbon nanotubes by electronic type. However, laser ablation nanotubes are no longer produced. This investigation of arc discharge carbon nanotubes has yielded some candidates for substitutes. Carbolex's nanotubes yield a high-purity semiconductor sorting. Carbon Solutions Inc.'s nanotubes show limited metallic sorting. These results can be used to further optimize the sorting process and to ultimately find a replacement for laser ablation–produced nanotubes.

Introduction

Today's technological world is dominated by one word: miniaturization. Miniaturization — the process that will allow scientists to bring the futuristic ideas shown in the movies to the present reality — is key in industry because smaller means faster. A good example of the trend is the semiconductor industry. Smaller transistors on processors mean more transistors can fit on a chip, which in turn means faster processing speeds. However, chip manufacturers are already pushing the limits of conventional silicon. Carbon nanotubes could replace silicon in these applications, since they are capable of functioning at the molecular scale — a scale where silicon ceases to function.[1]

Carbon nanotubes exhibit two types of electronic behavior. Metallic nanotubes can be used to carry very large current densities,[2,3] and semiconducting nanotubes can be switched on and off as field-effect transistors.[4,5] Unfortunately, there are no methods of producing pure metallic or semiconducting nanotubes. Current commercial methods — arc discharge, laser ablation, and chemical vapor deposition — each yield both electronic types. Calculations show that if distribution of chiralities is random, two-thirds of the nanotubes produced are semiconducting and one-third metallic.[6] Clearly, this is a hurdle that must be addressed because the presence of both electronic types leads to neither good conductivity nor a switching ratio for effective use in industry.

Nanotubes are produced by one of three methods: chemical vapor deposition (CVD), arc discharge, and laser ablation. For the purposes of sorting by electronic structure, uniform geometry is desired. CVD nanotubes have many defects and, therefore, are not desired for the sorting process. In the laser ablation method, a laser pulse vaporizes a graphite target, generating a carbon gas that forms the carbon nanotube. Laser ablation produces very uniform single-walled nanotubes with a controlled diameter range. However, the process is extremely costly, due to the requirement of expensive lasers. The arc discharge method utilizes two graphite rods spaced closely together. A high current is run through the graphite electrodes, causing a spark that vaporizes some of the graphite and creating carbon nanotubes. This method is most commonly used because it produces relatively defect-free nanotubes with a diameter range easily controlled with a catalyst.

Arc discharge–produced nanotubes were chosen for their low defects as well as similar diameter range to the laser ablation nanotubes. In order to directly compare the purity of the sorting process, the exact methods and parameters used to sort the laser ablation nanotubes in previous experiments[7] were repeated.

Background

Carbon nanotubes are macromolecules of carbon, analogous to a graphite sheet rolled into a cylinder. However, they form in many different structures, or chiralities. Nanotubes can have a variance in twist and diameter, due to chiral vector. Chirality, in turn, determines the Fermi point, which specifies the electronic type. Also, chirality determines the optical absorbance of the carbon nanotube. Each chirality has a unique absorption peak, allowing for analysis of electronic type using spectrophotometry. Figure 1[7] shows the metallic and semiconducting sorting of laser ablation–produced carbon nanotubes. In laser ablation, as well as any similar-diameter nanotube, the semiconductor 22 and 33 bands are located on the outside of the spectra, while the metallic 11 transition is located in the middle. There is very little overlap, allowing for clearly distinguishing semiconductor from metallic structures.

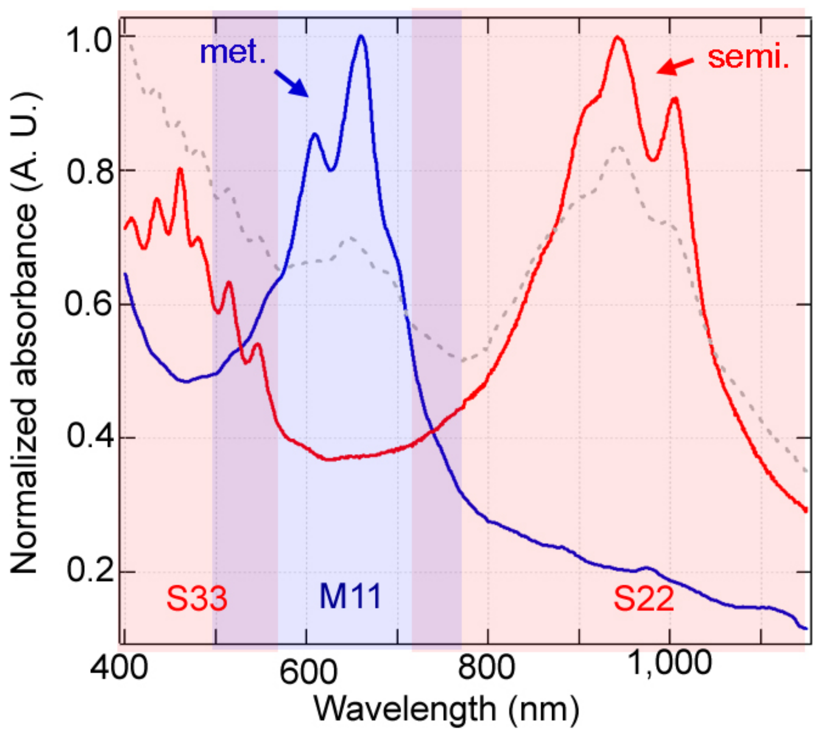

Figure 1: Optical absorbance spectra for metallic (blue) and semiconductor (red) sortings of laser ablation–produced nanotubes.

In 2005, Arnold, Stupp, and Hersam discovered a method of sorting single-walled carbon nanotubes (SWCNT) by diameter in density gradients.[8] Since then, an adaptation of this method has been used to successfully separate metallic and semiconducting electronic types from laser ablation–produced nanotubes.[7] It uses SWCNT encapsulated in sodium cholate and sodium dodecyl sulfate surfactants instead of DNA. This method yielded results of greater than 90% sorting by electronic structure.

As stated above, single-walled arc discharge–produced nanotubes were chosen for their similar properties to those of laser discharge nanotubes. The specific sources used in this investigation were obtained from Carbolex Inc. (as processed), NanoLab, and Carbon Solutions Inc. (CSI). The manufacturer-stated diameter range and purities,[9,10,11] in comparison with experimentally determined parameters of laser ablation–produced nanotubes,[7] are shown in Table 1. Carbolex nanotubes appear to be the most promising because they have relatively high purity and the same typical diameter as the previous laser ablation source. The nanotubes of NanoLab and Carbon Solutions have unknown average diameters. However, these companies use very similar arc discharge processes and catalysts, so the diameters should be similar to the Carbolex and Laser nanotubes.

Approach

For the encapsulation and isolation of arc discharge–produced nanotubes, sodium cholate (NaCh) was used, due to its success with laser ablation–type SWCNT. The nanotubes were prepared by ultrasonication in a 2% weight/volume solution of NaCh and centrifugation for 14 min at 54k rpm.

In the density gradient, Sigma-Aldrich iodixanol medium was used as the primary density component. A 1.5 mL, 60% iodixanol underlayer was placed

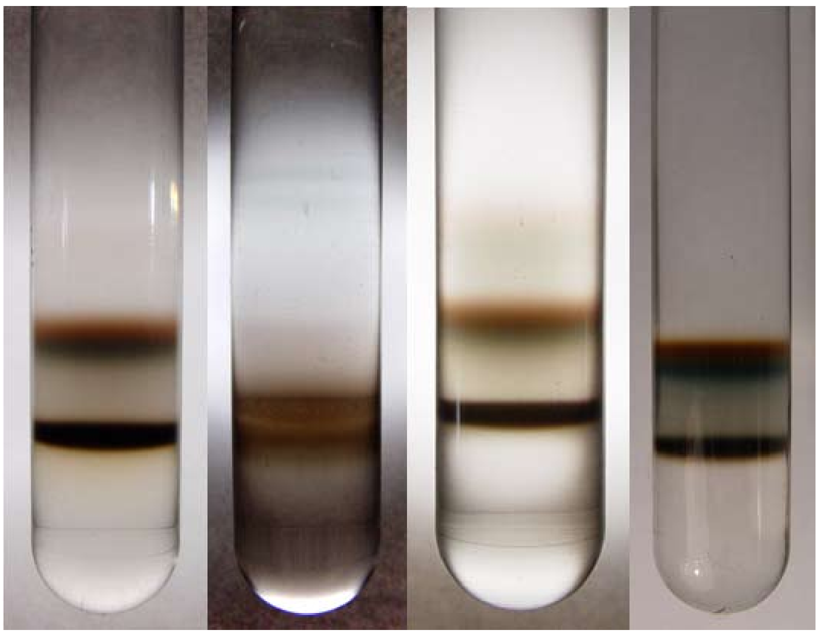

Figure 2a: Semiconductor separations of Carbolex, NanoLab, CSI, and laser nanotubes, respectively.

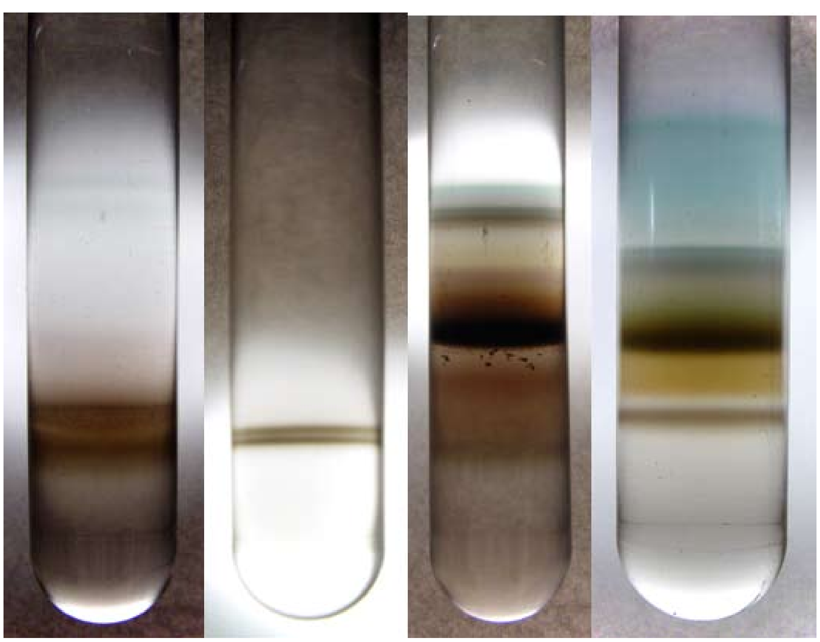

Figure 2b: Metallic separations of Carbolex, NanoLab, CSI, and laser nanotubes, respectively.

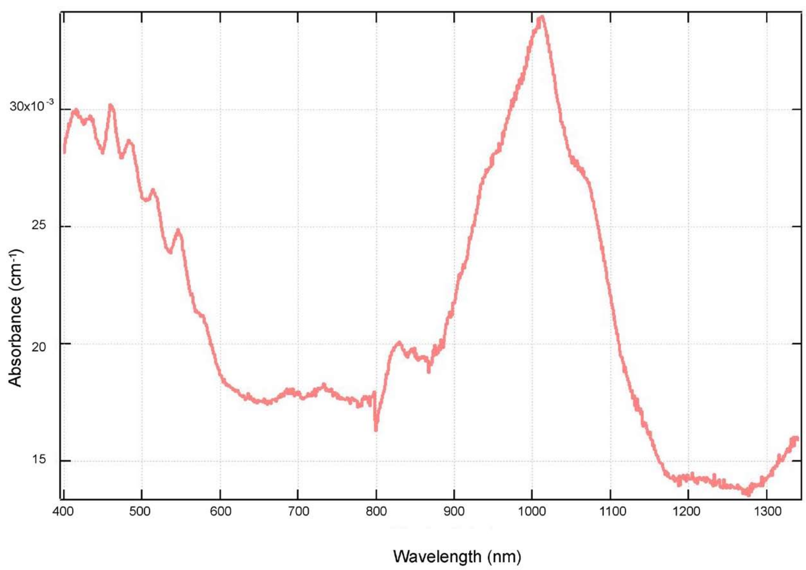

Figure 3: Optical absorbance spectra of Carbolex's semiconductor separation.

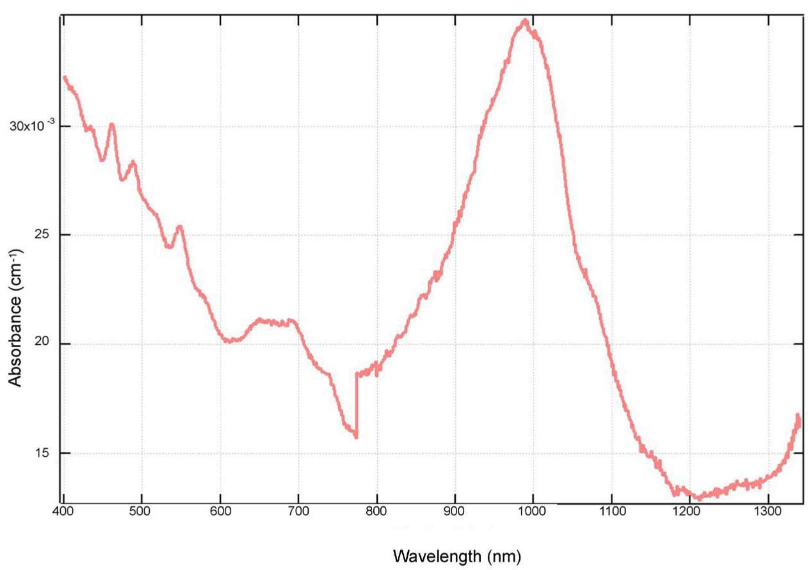

Figure 4: Optical absorbance spectra of NanoLab's semiconductor separation.

at the bottom of the centrifuge tube. A 5 mL density gradient was formed on top of the underlayer using a linear gradient maker from Hoefer Inc. A 0.88 mL carbon nanotube layer was infused into the density gradient using a syringe pump. A purely aqueous solution overlayer was slowly placed over the gradient to fill the centrifuge tube. Sodium dodecyl sulfate (SDS) was used as a cosurfactant throughout the centrifuge tube in the same ratio as in previous laser separations[7]; 2% weight/volume solutions of NaCh and SDS were used. In Table 2, parameters for the semiconductor and metal separations are listed. These are the same parameters as those of the previous laser separations. These solutions were centrifuged for 12 hr at 45k rpm.

After centrifugation, samples were fractionated using the BioComp Instruments Gradient Fractionator. Fractions ranged from 0.5 mm to 2.5 mm in size. These fractions were then analyzed using a spectrophotometer. Optical absorbance spectra were taken from 400 nm to 1,340 nm.

Results and Discussion

Qualitative results can be seen in Figures 3, 4, and 5.

The Carbolex semiconductor separation is very similar to the laser ablation separation. However, the peak heights indicate that its laser ablation separation had a considerably higher yield. This is another large factor in industrial applications because a higher yield lowers the cost, since less initial material is required to obtain the same amount of nanotubes sorted by electronic type.

The results indicate that there is a diameter range difference between the Carbolex, NanoLab, CSI, and laser ablation nanotubes. This can be seen with the shift in peaks in separations. From the laser separation, the S22 peak is located at 950 nm. However, the Carbolex and CSI separations show a peak closer to 1,000 nm, indicating that the Carbolex and CSI diameters are larger than that of laser ablation nanotubes. NanoLabs shows a diameter closer to laser ablation than CSI or Carbolex, but also considerably larger.

Conclusions

This investigation of arc discharge carbon nanotubes as substitutes for laser ablation nanotubes has identified two possible candidates: Carbolex nanotubes for semiconductor sorting, and Carbon Solutions' nanotubes for metallic sorting.

To consider these sources comparable to laser ablation–produced nanotubes, however, much more optimization must be done. Further investigations can include improvements to the initial separation by adjusting the gradient concentration as well as the surfactant-cosurfactant ratio, and conducting multiple iterations of the separation process with concentration steps in between. With further improvements and multiple iterations, it is possible that these two candidates will yield separations that are as pure as laser ablation–produced nanotubes.

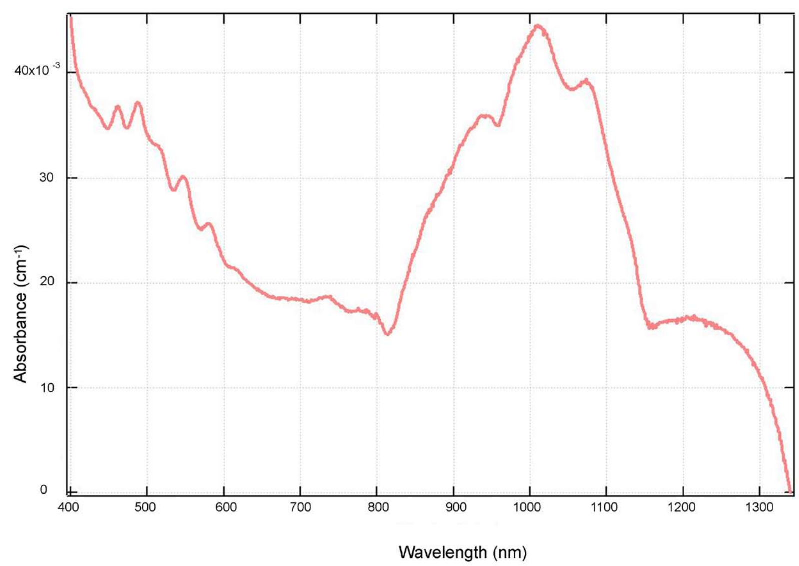

Figure 5: Optical absorbance spectra of CSI's semiconductor separation.

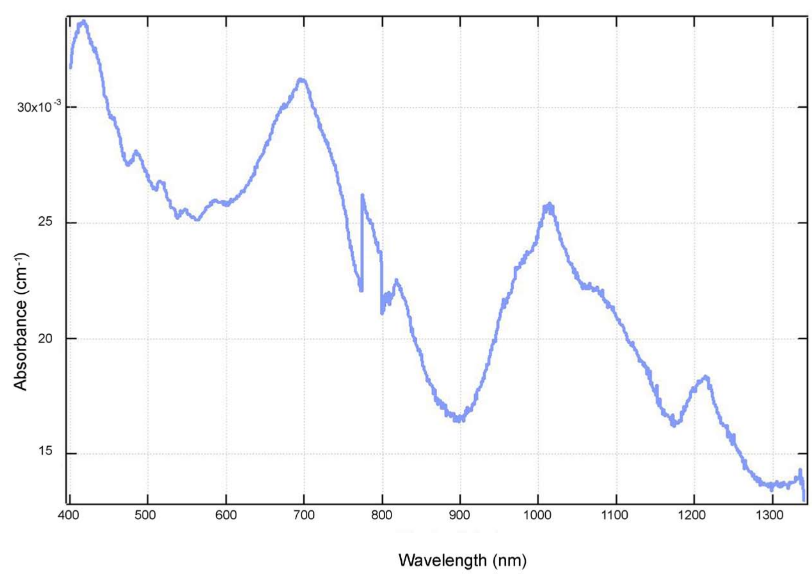

Figure 6: Optical absorbance spectra of Carbolex's metal separation.

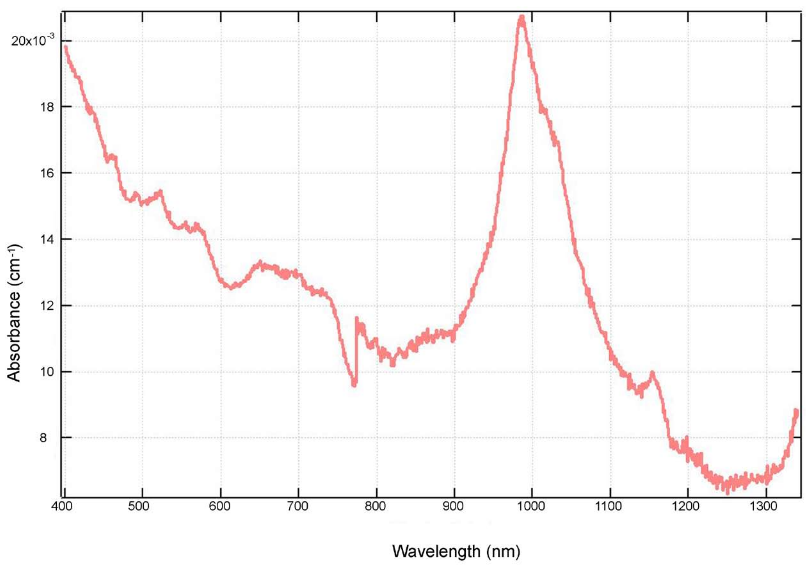

Figure 7: Optical absorbance spectra of NanoLab's metal separation.

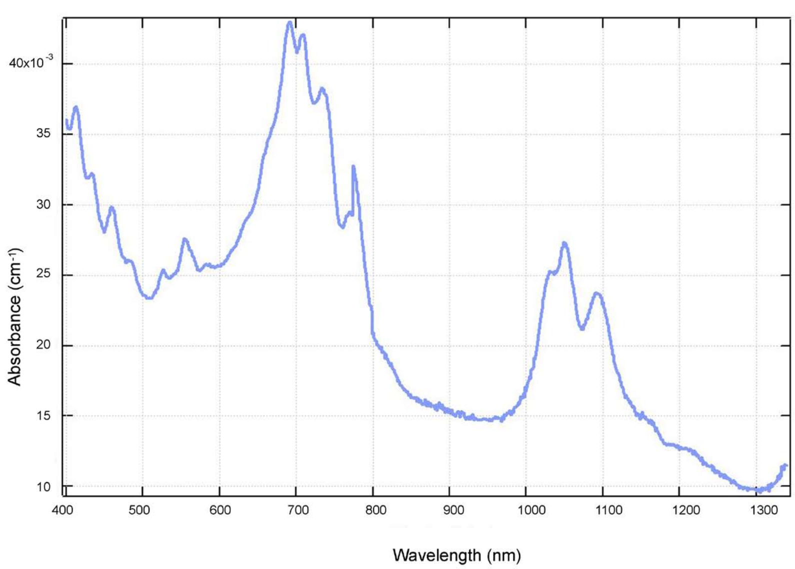

Figure 8: Optical absorbance spectra of CSI's metal separation.

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(11) http://carbonsolution.com/products/products.html

	Carbolex Inc.[9]	NanoLab[10]	Carbon Solutions Inc.[11]	Laser ablation[7]
Diameter range (nm)	not specified	1.0 to 1.5	not specified	1.1 to 1.6
Typical diameter (nm)	1.4	not specified	not specified	1.4
Purity (volume %)	50% to 70%	40%	40% to 60%	not determined

Table 1: Diameter range, typical diameter, and purity of nanotubes of Carbolex Inc., NanoLab, and Carbon Solutions Inc. as stated by the manufacturer and of laser ablation nanotubes as experimentally determined by M. S. Arnold and associates.

	SDS:NaCh ratio throughout	Underlayer density (% iodixanol)	Gradient bottom density (% iodixanol)	Nanotube layer density (% iodixanol)	Gradient top density (% iodixanol)	Overlayer density (% iodixanol)
Semiconductor	1:4	60	15	27.5	30	0
Metal	3:2	60	20	32.5	35	0

Table 2: Gradient-layer densities and surfactant ratios for semiconductor and metal separations.