

Absorption Spectroscopy as a Powerful Technique for the Characterization of Single-Walled Carbon Nanotubes

Authors

Dr. Ivo Stemmler

PerkinElmer GmbH
Rodgau, Germany

Dr. Claudia Backes

ZMP Institute of Advanced Materials and Processes
University of Erlangen-Nuremberg
Fuerth, Germany

Introduction

In the exploding field of nanoscience and nanotechnology, carbon nanotubes have attracted considerable attention owing to their unique mechanical and electronic properties for a broad field of potential applications.

Carbon nanotubes (CNTs) belong to the family of synthetic carbon allotropes and are characterized by a network of sp^2 hybridized carbon atoms. The one dimensional (1D) carbon nanotubes can thus be queued between their zero dimensional relatives fullerenes and the two dimensional (2D) relative graphene. The structure of nanotubes has first been described as helical microtubules of graphitic carbon in 1991 by Iijima, who generated the novel material by an arc discharge evaporation process originally designed for the production of

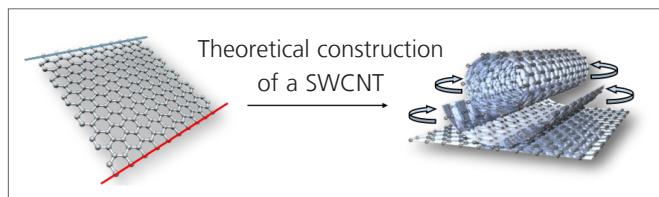


Figure 1. A SWCNT is a hollow cylinder of a rolled-up graphene sheet.²

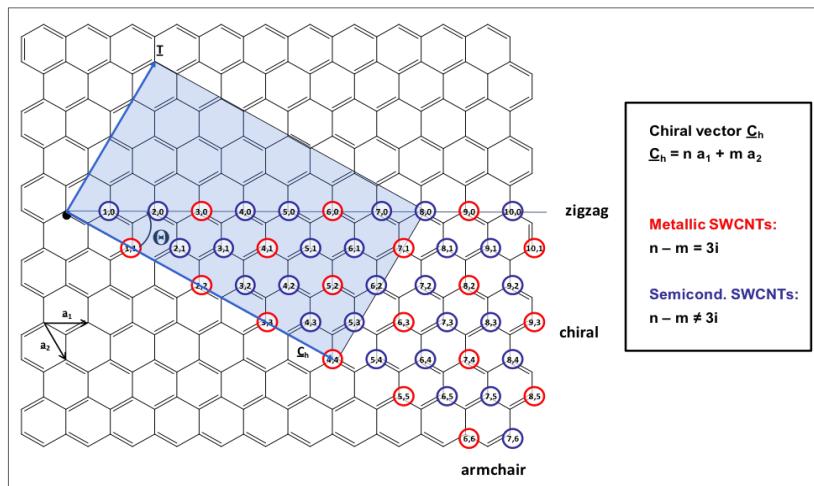


Figure 2. Schematic representation of the unrolled graphene layer of a carbon nanotube with the unit cell vectors a_1 and a_2 , which define the chiral vector C_h . The colored rectangle displays the unit cell of the (4,4)-SWCNT. Metallic (n,m)-SWCNTs are indicated by the red circles, semiconducting species by the blue circles, respectively. SWCNTs exhibit metallic behavior, when $n-m$ is a multiple of three. All other nanotubes are semiconducting.²

fullerenes.¹ CNTs are theoretically constructed by rolling up a graphene sheet into a cylinder with the hexagonal rings joining seamlessly.

Depending on the way the graphene sheet is rolled up (classified by their chirality and the so-called (n,m)-indices, see Figure 2), a huge diversity of single-walled carbon nanotube (SWCNT) structures can be constructed differing in length, diameter and roll-up angle, which defines the orientation of the hexagonal carbon rings in the honeycomb lattice relative to the axis of the nanotube. In addition, carbon nanotubes possess unique electronic properties, as they exhibit either metallic or semiconducting behavior - depending on the (n,m)-indices.

In carbon nanotube science, significant hurdles — such as controlled production and purification, the intrinsically low solubility and polydispersity with respect to electronic type, length and diameter — had and still have to be overcome in order to tap their potential in industrial applications. Nonetheless, a broad spectrum of proof of principle devices has been developed, as carbon nanotube functionalization enabled their dispersion, processing and separation. For example, metallic SWCNTs are particularly interesting as

conductive coatings useful for applications such as touch screens, flexible displays, printable electronics, thin film photovoltaics, transparent electrodes, supercapacitors, and nanowires due to their outstanding current-carrying capacities and the ballistic conductivity along the CNT axis. The semiconducting SWCNTs have found applications in field effect transistors, switching, sensing.

Owing to their extraordinary stiffness, bending strength and high aspect ratio, carbon nanotubes are also ideal candidates for reinforcing polymers.

Use of UV/Vis/NIR spectroscopy

In addition to the difficulties in processing and functionalizing SWCNTs, researchers have also been challenged by the search for reliable SWCNT characterization techniques enabling the detailed investigation of unmodified and processed nanotube samples. In this regard, UV/Vis/NIR absorption spectroscopy has proven to be a powerful tool in SWCNT characterization, making high information density related to the physical and electronic properties of the SWCNT sample accessible through a readily available and inexpensive technique.

In absorption spectroscopy, the optical transitions of the SWCNTs are probed, which arise from so-called van Hove singularities (energy levels with significant high density of states) that are caused by rolling-up the 2D graphene sheet into a 1D carbon nanotube (Figures 1 and 2).³ The electronic density of states of a semiconducting nanotube is exemplarily depicted in Figure 3. By absorption of light, the electrons in the van Hove singularities of the valence band are elevated to the corresponding energy levels in the conduction band (denoted as S_{11} and S_{22} in the case of the semiconducting SWCNTs). In principle, the same process happens in the case of metallic SWCNTs. However, the spacing between the van Hove singularities is larger so that only M_{11} transitions can be probed in the UV/Vis region.

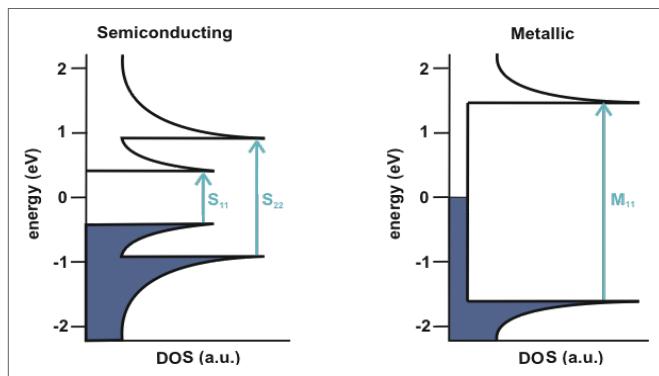


Figure 3. Schematic representation of the electronic density of states of a semiconducting (left) and metallic (right) SWCNT and the possible transitions between the van Hove singularities.

Most conveniently, the optical properties of the SWCNTs are measured from dispersed/solubilized samples in transmission mode. In this regard, the discovery of SWCNT dispersion with the aid of physisorbed surfactant molecules that stabilize the nanoobjects was a major breakthrough.⁴ The sample preparation involves ultrasonication of the nanotubes in aqueous surfactant solution followed by centrifugation to remove large particulates that were not efficiently solubilized. The ultrasonication provides the energy to overcome the mutually high van der Waals attraction of the SWCNTs, while the surfactant stabilizes the exfoliated/individualized nanotubes. The simplest surfactants are classical detergents such as sodium dodecyl benzene sulfonate (SDBS). More recently, highly efficient surfactants with an aromatic anchor were designed.

Since various factors influence the optical properties of SWCNTs, absorption spectroscopy gives access to the following information:

- SWCNT sample composition
- Dispersion efficiency
- Degree of individualization (qualitatively)
- Evaluation of the sample purity
- Tracing interactions of dyes and SWCNTs
- Efficiency of separation procedures

A suitable UV/Vis/NIR spectrophotometer needs to deal with high absorbing (black carbon) liquids as well as with low absorbance values with best possible signal-to-noise ratio and low spectral bandwidths in Vis and NIR. By an experimental comparison with SWCNTs, it could be shown that the PerkinElmer LAMBDA™ 1050 Wide Band UV/Vis/NIR spectrometer showed the best performance available on the market and is the best choice for these kinds of experiments. The LAMBDA 1050 UV/Vis/NIR offers a double monochromator system with very low stray light and allows to analyze samples up to 8 Å (absorbance units) in Vis and NIR. With such a system, the sharp SWCNT peaks, which are superimposed on the high absorbing background, can still be precisely determined in the entire spectral region. The high signal-to-noise ratio also allows very low sample concentrations, e.g. down to 0.2 µg/mL⁻¹.

SWCNT sample composition

The electronic structure of a SWCNT is unique for every (n,m) kind of nanotube. Accordingly, absorption spectroscopy yields very valuable information of the composition of the nanotube sample.⁵ This is especially important due to the fact that nanotubes are always produced as mixtures of different diameters and electronic types. A typical absorption of SWCNTs dispersed in an aqueous solution of SDDBS is presented in Figure 4. In the UV/Vis region, the transitions of metallic SWCNTs are probed, while the semiconducting nanotubes are observed in the Vis and NIR region. Each peak in the spectrum corresponds to a specific SWCNT species as exemplarily indicated for the (7,5)-SWCNT. In general, the larger diameter nanotubes are characterized by pairs of van Hove singularities with a smaller energy gap yielding red-shifted peaks compared to smaller diameter nanotubes.

Dispersion efficiency

As has already been briefly mentioned, the dispersion of SWCNTs is a critical issue, as it enables solution-phase processing. Similar to the stacking of individual graphene layers in graphite, the van der Waals and π-π-stacking interactions are responsible for a strong attraction between individual SWCNTs. Accordingly, SWCNTs tend to form bundles (of up to 100 individual nanotubes) and can hardly be dispersed in the absence of surfactants that shield the nanotube surface. It is thus highly important to assess the performance of a surfactant using a readily available technique.

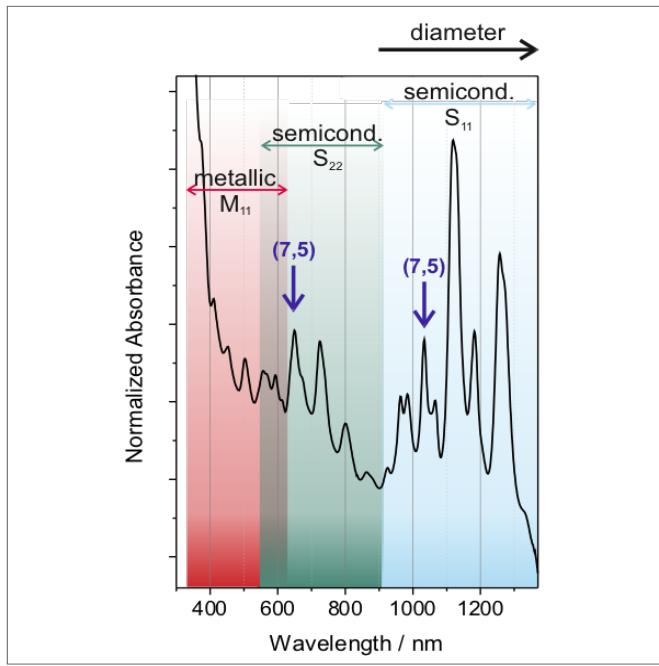


Figure 4. Typical absorption spectrum of a mixture of different SWCNTs dispersed in an aqueous solution of SDBS. The transitions of metallic and semiconducting SWCNTs are indicated by the shaded areas. The different peaks in the spectrum arise from different SWCNT species. In the case of semiconducting SWCNTs, one specific nanotube yields one peak in the S₁₁- and one in the S₂₂-regime, respectively as exemplarily shown for the (7,5)-SWCNT.²

In a first approximation, various surfactants can be screened and compared in their potential to solubilize nanotubes by sonicating the SWCNTs in the presence of the surfactant (usually at different concentration of both components), followed by (ultra) centrifugation. The ratio of the absorbance at a fixed wavelength before and after the centrifugation step represents the dispersion efficiency in %, as demonstrated in Figure 5a.⁶⁻¹² It should be noted that this value is to be considered semi-quantitative, as multiple factors (sonication power and time, centrifugation conditions) influence the dispersion efficiency. Nonetheless, it is very useful, especially when new surfactants are compared to a well known standard such as SDBS.

Degree of individualization

In addition to the dispersion efficiency that can be determined by absorption spectroscopy, the peak positions and pattern yield information about the quality of the dispersion, namely the individualization of the SWCNTs (rather than dispersion of bundles or aggregates). An example is presented in Figure 5b, which compares a raw dispersion of SWCNTs in aqueous SDBS to the same sample after ultracentrifugation. The centrifugation process removes nanotube bundles and aggregates so that the dispersion contains predominantly individualized nanotubes (but at a much lower concentration). For comparison, the spectra were normalized to the local minimum between the S₁₁ and S₂₂ transitions (at 920 nm). The difference in the pattern of the absorbance spectrum is striking, as the peaks arising from the SWCNT optical transitions are significantly sharper and more intense relative to the unspecific

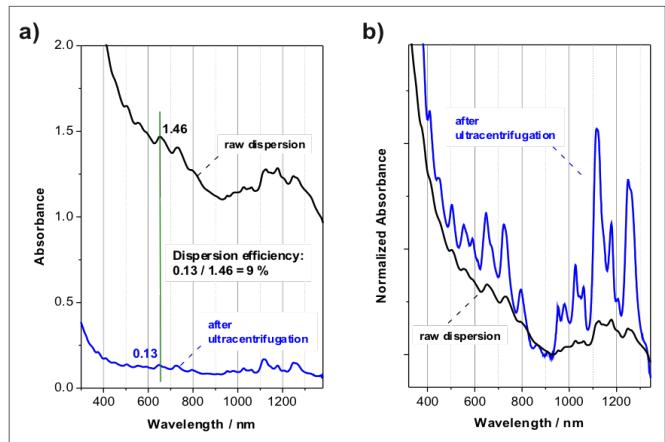


Figure 5. Absorbance spectra SWCNTs dispersed in an aqueous SDBS solution before and after ultracentrifugation. After ultracentrifugation, the sample is mainly composed of individualized SWCNTs, but at a much lower concentration: a) absorbance spectra with a pathlength of 1 cm; b) same spectra, but normalized to the local minimum.

absorbance background.⁴ Furthermore, the peaks in the raw dispersion are red-shifted, as the transitions are broadened and of lower energy when the SWCNTs are in van der Waals contact to each other. Thus, the peak position and relative intensity is an indicator for the degree of debundling in the sample, which is an important criterion for evaluating the quality of the SWCNT dispersion. An ideal sample would be characterized by a high carbon loading (high SWCNT concentration) with nonetheless high degree of individualization.

The effect of the degree of bundling and debundling can also nicely be demonstrated in the example presented in Figure 6. In this case, a nanotube raw dispersion was sorted by density gradient ultracentrifugation.¹³ This process¹⁴ enables the separation of individualized defect-free nanotubes (top fraction F1) from defective material (fraction F2) as well as nanotube bundles and impurities in fraction F3. The corresponding absorption spectra normalized to the local minimum are displayed in Figure 6. The bundled nanotubes and impurities are characterized by the absence of the characteristic nanotube transitions; only the strongly absorbing background is recorded. Defective nanotubes are collected in fraction F2. The characteristic nanotube peaks are superimposed on the background, however much weaker compared to the defect-free counterparts in fraction F1.

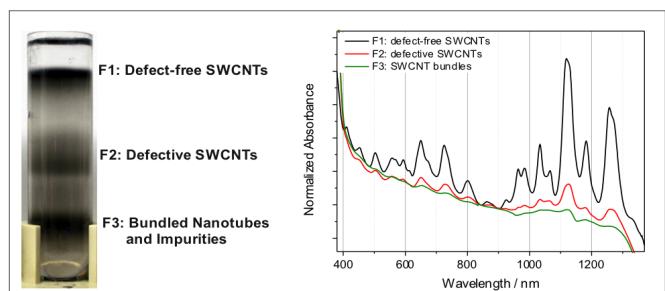


Figure 6. Left: centrifugation vial after separating individual defect-free nanotubes from defective counterparts and bundles. Right: the difference in the material composition is reflected in the absorbance spectra.¹³

Evaluation of the sample purity

As indicated in Figure 6b, the ratio of the nanotube peaks (resonant area) to the non-resonant background depends on the sample purity and structural integrity of the nanotubes.^{15,16} Defect-free and pure nanotubes typically have a resonant ratio of 0.15 (within the region marked by the shaded area in Figure 7), while the resonant ratio of raw dispersions typically is in the range of 0.03.¹³ With the sorting methodology described above,¹³ the resonant ratio of perfect, defect-free nanotubes can be determined. The as-obtained resonant ratio can be used as a reference system for the quantification of the amount of defect-free nanotubes in a given nanotubes sample (usually being a mixture of defect-free nanotubes, defective species and amorphous carbon).

This is a crucial factor, as other methods (such as thermogravimetric analysis) only capture the amount of non-carbon impurities such as catalyst particles, or do not allow for a quantification. On the basis of the resonant ratio, absorption spectroscopy, in combination with clever sorting techniques such as ultracentrifugation, enables precise quality monitoring. For the commercially available HiPco SWCNTs, it was found that approximately 20% (0.03/0.15) of the carbon-based material is attributed to structurally perfect and intact nanotubes.

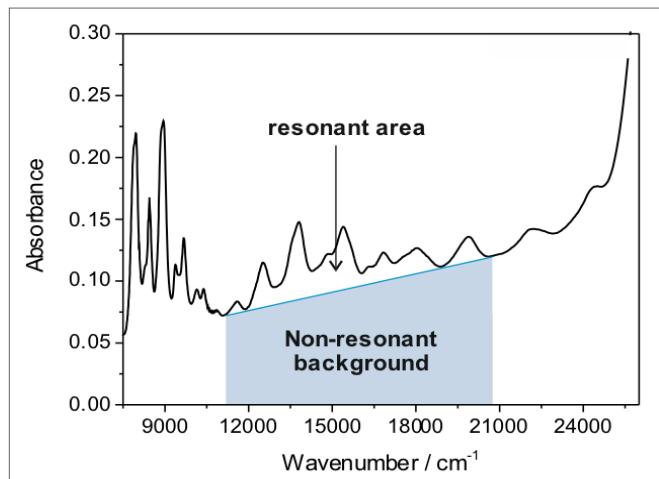
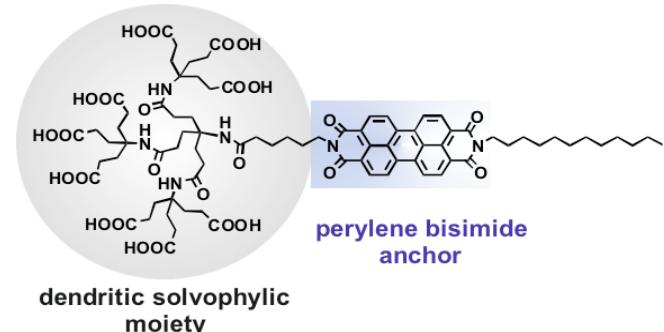


Figure 7. The ratio of the resonant area of the characteristic SWCNT peaks to the nonresonant background yields information about the sample purity and structural integrity. Defect-free and pure nanotubes typically have a resonant ratio of 0.15 (within the region marked by the grey shaded area), while the resonant ratio of raw dispersions is typically in the range of 0.03.

Tracing interactions of dyes and SWCNTs

A significant share of SWCNT research is devoted to understanding interactions of molecules with the carbon surface (non-covalent functionalization). In this regard, absorption spectroscopy offers the possibility to trace the interaction of dyes with the nanotube surface. Recently, it has been found that the SWCNTs can be very efficiently dispersed and individualized in aqueous solution by amphiphilic perylene bisimide derivatives, such as the one displayed below.^{2,8,12,17}



The aromatic core of the nanotube (the perylene bisimide) exhibits a pronounced interaction with the aromatic backbone of the nanotube and thus serves as anchor to the sidewall. The dendritic unit, with its carboxylic acid functionalities, provides the water solubility of the system.

The adsorption of the perylene bisimide core to the nanotubes can be evidenced by absorption spectroscopy, as the pattern and peak position of both the nanotubes and the perylene derivative significantly change (see Figure 8). Due to its amphiphilicity, the perylene molecule is strongly self-aggregating in aqueous solution, yielding an absorption spectrum with a more pronounced $0\rightarrow 1$ transition compared to the $0\rightarrow 0$ transition (Figure 8b). When the dye anchors to the nanotube surface, the micelles are broken and a monomeric perylene fingerprint is observed (superimposed on the nanotube spectrum). However, in contrast to monomeric perylene bisimide molecules in solution, the peaks are red-shifted due to the interaction with the nanotube.

Similarly, the SWCNT transitions are altered (red-shifted and broadened), when the dye is adsorbed in comparison to a spectrum of nanotube in detergent solution. This is best visualized when the perylene is replaced from the nanotube scaffold by the addition of SDBS (blue trace in Figure 8). After the replacement, the nanotube and perylene absorbance peaks are shifted to lower wavelengths and appear sharper. In perfect agreement, the perylene signature of self-aggregated structures is obtained in the UV/Vis region.

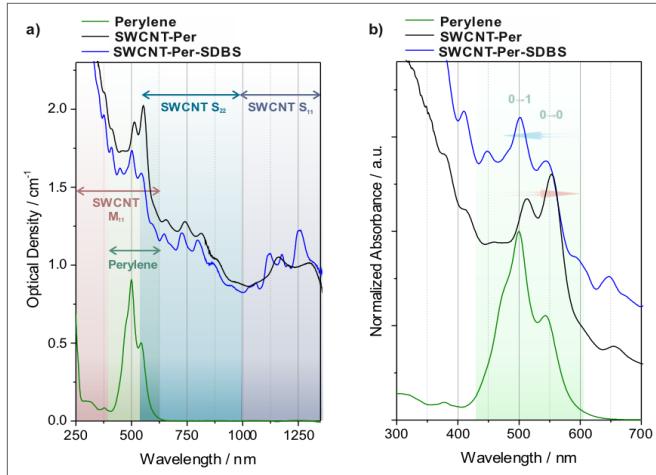


Figure 8. Absorption spectra of SWCNTs dispersed in an aqueous solution of a perylene bisimide dye. a) As recorded spectra where the characteristic transitions of semiconducting SWCNTs (S_{11} and S_{22}) and metallic SWCNTs (M_{11}), as well as the perylene transitions are indicated. b) Magnified view of the perylene transitions. The spectra are normalized to the strongest perylene transition and offset for clarity. The replacement of the dye from the nanotube surface by addition of SDBS can be followed by the respective absorption spectra (black trace: perylene adsorbed to SWCNTs, blue trace: same sample after substitution of perylene by SDBS).⁸

The pronounced interaction of the dye and the nanotube can thus very efficiently be evidenced by absorption spectroscopy. This observation can also be exploited to determine an ideal ratio of nanotube to dye, where the concentration of free surfactant is minimal.

Efficiency of separation procedures

In the past years, a broad variety of techniques have been elaborated in order to separate carbon nanotubes by diameter, electronic properties, length and even type.^{2,18,19} Since the sorting usually occurs in solution, absorption spectroscopy has evolved to a main characterization tool to evaluate the effectiveness of sorting. The major advantage is presented in the fact that both metallic and semiconducting SWCNTs can be probed, in contrast to emission spectroscopy that can only be applied in the case of semiconducting species.

Figure 9 sketches the absorption spectra that are yielded after an efficient separation, which is based on the selective interaction of different DNA sequences that wrap around the nanotubes depending on their structure, so that separation by ion exchange chromatography is accessible.²⁰ The separation process allowed for the extraction of 12 different nanotube species that could clearly be identified by their characteristic absorption spectra.

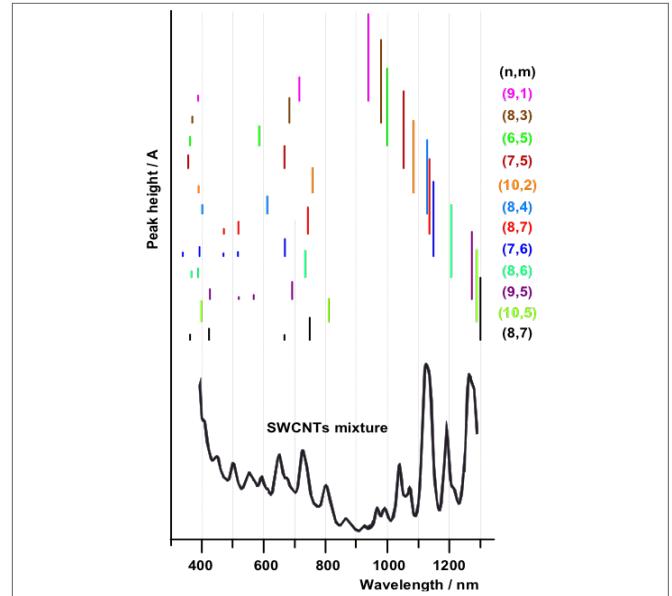


Figure 9. Schematic representation of the absorption spectra of sorted SWCNTs adapted from reference.²⁰ The separation of 12 individual SWCNT species enabled the assignment of the absorption peaks to the various species in a mixture of nanotubes (top spectrum).

Conclusion

In summary, UV/Vis/NIR absorption spectroscopy has evolved to a very powerful characterization tool of carbon nanotube dispersions and has thus contributed a significant share to the insights on nanotube purity, functionalization and sorting that were elaborated the past years.

Table 1. Typical parameters for the acquisition of SWCNT absorbance spectra

Parameter	Condition
Range	200-1380 nm (in water)
Increment	1 nm
Detector and monochromator change	810 nm
Lamp change	319 nm
PMT (UV/Vis detector)	Slit 2.5 nm; Integration time 0.24 s (for dilute samples)
InGaAs (NIR detector)	Slit servo; Gain 9; Integration time 0.24 s (for dilute samples)

References

1. Iijima, S. Helical microtubules of graphitic carbon. *Nature* 354, 56-58 (1991).
2. Backes, C. *Noncovalent functionalization of carbon nanotubes: Fundamental aspects of dispersion and separation in water.* (Springer, 2012), ISBN 978-3-642-27581-4.
3. Saito, R., Fujita, M., Dresselhaus, G. & Dresselhaus, M. S. Electronic structure of graphene tubules based on C₆₀ fullerene. *Phys. Rev. B Condens. Matter* 46, 1804-1811 (1992).
4. O'Connell, M. J., Bachilo, S. M., Huffman, C. B., Moore, V. C., Strano, M. S., Haroz, E. H., Rialon, K. L., Boul, P. J., Noon, W. H., Kittrell, C., Ma, J., Hauge, R. H., Weisman, R. B. & Smalley, R. E. Band gap fluorescence from individual single-walled carbon nanotubes. *Science* 297, 593-596 (2002).
5. Bachilo, S. M., Strano, M. S., Kittrell, C., Hauge, R. H., Smalley, R. E. & Weisman, R. B. Structure-Assigned Optical Spectra of Single-Walled Carbon Nanotubes. *Science* 298, 2361-2366 (2002).
6. Ausman, K. D., Piner, R., Lourie, O., Ruoff, R. S. & Korobov, M. Organic Solvent Dispersions of Single-Walled Carbon Nanotubes: Toward Solutions of Pristine Nanotubes. *J. Phys. Chem. B* 104, 8911-8915 (2000).
7. Giordani, S., Bergin, S. D., Nicolosi, V., Lebedkin, S., Kappes, M. M., Blau, W. J. & Coleman, J. N. Debundling of Single-Walled Nanotubes by Dilution: Observation of Large Populations of Individual Nanotubes in Amide Solvent Dispersions. *J. Phys. Chem. B* 110, 15708-15718 (2006).
8. Backes, C., Hauke, F. & Hirsch, A. The Potential of Perylene Bisimide Derivatives for the Solubilization of Carbon Nanotubes and Graphene. *Adv. Mater.* 23, 2588-2601, doi:10.1002/adma.201100300 (2011).
9. Zhao, B., Itkis, M. E., Niyogi, S., Hu, H., Zhang, J. & Haddon, R. C. Study of the Extinction Coefficients of Single-Walled Carbon Nanotubes and Related Carbon Materials. *J. Phys. Chem. B* 108, 8136-8141 (2004).
10. Bergin, S. D., Nicolosi, V., Cathcart, H., Lotya, M., Rickard, D., Sun, Z., Blau, W. J. & Coleman, J. N. Large Populations of Individual Nanotubes in Surfactant-Based Dispersions without the Need for Ultracentrifugation. *J. Phys. Chem. C* 112, 972-977 (2008).
11. Nicolosi, V., Cathcart, H., Dalton, A. R., Aherne, D., Dieckmann, G. R. & Coleman, J. N. Spontaneous Exfoliation of Single-Walled Carbon Nanotubes Dispersed Using a Designed Amphiphilic Peptide. *Biomacromolecules* 9, 598-602 (2008).
12. Backes, C., Schmidt, C. D., Rosenlehner, K., Coleman, J. N., Hauke, F. & Hirsch, A. Nanotube Surfactant Design - The Versatility of Perylene Bisimide Derivatives. *Adv. Mater.* 22, 788-802 (2010).
13. Backes, C., Bosch, S., Mundloch, U., Hauke, F. & Hirsch, A. Density Gradient Ultracentrifugation on Carbon Nanotubes According to Structural Integrity as a Foundation for an Absolute Purity Evaluation. *ChemPhysChem* 12, 2576-2580, doi:10.1002/cphc.201100258 (2011).
14. Arnold, M. S., Green, A. A., Hulvat, J. F., Stupp, S. I. & Hersam, M. C. Sorting carbon nanotubes by electronic structure using density differentiation. *Nat. Nanotechnol.* 1, 60-65 (2006).
15. Itkis, M. E., Perea, D. E., Niyogi, S., Rickard, S. M., Hamon, M. A., Hu, H., Zhao, B. & Haddon, R. C. Purity evaluation of as-prepared single-walled carbon nanotube soot by use of solution-phase near-IR spectroscopy. *Nano Lett.* 3, 309-314 (2003).
16. Zhao, B., Itkis, M. E., Niyogi, S., Hu, H., Perea, D. E. & Haddon, R. C. Extinction coefficients and purity of single-walled carbon nanotubes. *J. Nanosci. Nanotechnol.* 4, 995-1004 (2004).
17. Backes, C., Schmidt, C. D., Hauke, F., Boettcher, C. & Hirsch, A. High Population of Individualized SWCNTs through the Adsorption of Water-Soluble Perylenes. *J. Am. Chem. Soc.* 131, 2172-2184 (2009).
18. Hersam, M. C. Progress towards monodisperse single-walled carbon nanotubes. *Nat. Nanotechnol.* 3, 387-394 (2008).
19. Martel, R. Sorting Carbon Nanotubes for Electronics. *ACS Nano* 2, 2195-2199 (2008).
20. Tu, X., Manohar, S., Jagota, A. & Zheng, M. DNA sequence motifs for structure-specific recognition and separation of carbon nanotubes. *Nature (London, U. K.)* 460, 250-253 (2009).

PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

For a complete listing of our global offices, visit www.perkinelmer.com>ContactUs

Copyright ©2013, PerkinElmer, Inc. All rights reserved. PerkinElmer® is a registered trademark of PerkinElmer, Inc. All other trademarks are the property of their respective owners.