Optical and Raman spectroscopy of carbon nanotube-based hybrid materials

Ph.D. dissertation booklet

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Background

Carbon nanotubes have remarkable mechanical, electrical, and thermal properties. Molecules can be attached to the exterior of the nanotubes or encapsulated in the hollow one-dimensional inner cavity. Heterostructures, synthesized by noncovalent functionalization of the nanotubes, can preserve or improve the properties of the guest molecules without altering the intrinsic properties of the carbon nanotubes. These materials are referred to as carbon nanotube hybrids. The high mechanical stability and robustness make carbon nanotubes superior to various other hollow materials as nanocontainers or nanoreactors.

Hybrid materials made from two types of carbon-based conductors, carbon nanotubes and conducting polymers, are of considerable interest, because it is hoped that the interaction can improve the electrical conductivity, the mechanical stability, and the biocompatibility of the resulting system. Though various systems have been prepared and used in applications, generally little is known about the exact structure of the hybrids.

Combining nanotubes with fluorophores is compelling, since it would allow the synthesis of robust materials with tunable luminescent properties. Though several attempts have been made to produce such structures, only few types of luminescent hybrids were successfully prepared. [Yanagi 2006, Liu 2009, Loi 2010, Alvarez 2011, Battigelli 2013, Almadori 2014, Gaufrès 2014] The outer surface of the CNT nanocontainers can be functionalized without affecting the encapsulated species according to the needs of the applications. Functionalization can improve the processability of the hybrids or targeting molecules can be attached for biological applications. [Gaufrès 2014, Cambré 2015] In certain cases, the hybrids possess new, interesting properties due to the confinement of the guest molecules that are not present in the individual constituents, for example strong second-order nonlinear optical response. [Cambré 2015]

The concave interior of the nanotubes has very low chemical reactivity, providing a good environment for chemical processes. Structure and size of the final products can be tuned via the adjustable diameter of these nanoreactors. [Khlobystov 2011]

Aims

I studied both wrapped and encapsulated systems to gain deeper understanding of their structure. The chosen principal methods were infrared and Raman spectroscopy, because the attachment of various molecules is reflected in the vibrational spectra of the hybrid material.

1. In the case of conductive polymer-wrapped nanotubes I examined how vibrational spectra reflect the strength and type of the interaction between the constituents.

2. Interactions between the host nanotube and the guest species in encapsulated systems can cause changes in their electronic structure. I studied peapods (C_{60}@SWCNT[1]) and double-walled carbon nanotubes (DWCNTs). As peapods have a broad literature, results obtained on these samples helped us to optimize our characterization protocol for other types of encapsulated nanotube hybrids. In the case of DWCNTs I investigated the possibility of charge transfer between the inner and outer tubes.

3. Coronene was observed to form both stacked and ribbon alignment upon encapsulation in carbon nanotubes. While the former was suggested to be an ideal candidate as a fluorescent hybrid material [Okazaki 2011], the latter could be used for templated nanoribbon growth [Talyzin 2011a]. However, contradictions in the former spectroscopic and transmission electron microscopy results in the literature suggested that these structures are not well-defined. [Okazaki 2011, Talyzin 2011b] Molecules can interact both with the interior and exterior of the walls, and the elimination of reaction side products is

[1] guest@host, SWCNT = single-walled carbon nanotube

often challenging. My aim was to study how the encapsulated and adsorbed species can be distinguished according to their vibrational properties. Based on the gathered knowledge, my goal was to optimize the synthesis method to produce well-defined hybrid structures to study how the confined environment affects the polymerization of coronene, and how the interaction between the carbon nanotubes and the inner species influences the luminescent properties of the various hybrids.

Experimental methods

Owing to the complexity of carbon nanotube samples, there is no ideal characterization technique, the different techniques all have their benefits and drawbacks, and the combination of various methods has to be properly chosen for each specific problem. To study noncovalent functionalization and reactions inside and on the surface of nanotubes, I used Raman, optical absorption, and photoluminescence spectroscopy. Raman spectroscopy is an ideal tool to investigate changes in the nanotube vibrational modes caused by hybrid formation. While Raman spectroscopy can detect both encapsulated and adsorbed species, infrared spectroscopy can be used to investigate molecules attached to the outer wall of the nanotubes. Wide-range optical measurements can sensitively detect doping or chemical modification of the nanotubes. Photoluminescence spectroscopy was used to characterize the coronene-nanotube hybrids, as both coronene and its oligomers emit strong visible luminescence. In the case of these hybrids the work was supported by high resolution transmission electron microscopy investigations.

New scientific results

1. I have investigated the hybrid structures formed by polymerization of aniline, carbazole, and dopamine in the presence of carbon nanotubes. The conductivity of the polyaniline-nanotube and polycarbazole-nanotube hybrid electrodes was observed to improve significantly compared to the pristine carbon nanotube electrodes.

   (a) I observed the attenuation of the in-plane infrared-active vibrations of polyaniline and polycarbazole upon hybrid formation with carbon nanotubes. I showed that the attenuation can be explained by the surface attenuated infrared absorption (SAIRA) effect, caused by the interaction between the polarizable π-electron network of the nanotubes and the vibrations of the molecules. Based on the observed changes I suggested that polyaniline and polycarbazole develop stronger interaction with the nanotubes than the melanin, resulting in a tight coating. [P1]

   (b) I showed that the strength of the SAIRA effect correlates with the conductivity results: hybrids where the nanotubes are more tightly wrapped by the polymer show larger increase in electrical conductivity upon hybrid formation. [P2]

2. I followed the process of C_{60}@SWCNT preparation and its transformation to DWCNT. I used Raman spectroscopy to confirm the successful encapsulation of C_{60} molecules and the inner tube formation. Based on the simultaneous decrease of the intensity of the nanotube transitions in the optical conductivity spectra, I concluded that there is no significant charge transfer between the outer and inner nanotube in DWCNTs. The observed changes can be explained by the localization of the charges. [P3]

3. I studied various hybrids prepared from coronene and carbon nanotubes. Based on the comparison of the vibrational and luminescent

properties of the different heterostructures, I was able to distinguish between the encapsulated and adsorbed species.

(a) I showed that high temperature vapor filling of coronene results in the formation of dicoronylene on the nanotube surface. The carbon surface has a catalytic role in the dimer formation. [P4, P5]

(b) I showed that the formation of the adsorbed by-product can be eliminated by lowering the filling temperature. Encapsulation of coronene using nanoextraction from supercritical CO_2 results in well-defined coronene@SWCNT structure, free from adsorbed oligomers. [P4, P5]

(c) I showed that coronene can be polymerized inside SWCNTs starting from a stacked alignment. The polymerization results in the formation of inner nanotubes via nanoribbons. This method produces GNR@SWCNT[2] structures having a clean outer surface. [P5]

(d) I showed that the photoluminescence of coronene in both stack and ribbon form is quenched inside the nanotubes. [P5]

Related publications

[P1] K. Kamarás, B. Botka, Á. Pekker, S. Ben-Valid, A. Zeng, L. Reiss, and S. Yitzchaik, "Surface-induced changes in the vibrational spectra of conducting polymer-carbon nanotube hybrid materials," *Physica Status Solidi B*, vol. 246, no. 11–12, pp. 2737–2739, 2009.

[P2] S. Ben-Valid, B. Botka, K. Kamarás, A. Zeng, and S. Yitzchaik, "Spectroscopic and electrochemical study of hybrids containing conductive polymers and carbon nanotubes," *Carbon*, vol. 48, no. 10, pp. 2773–2781, 2010.

[2]GNR = graphene nanoribbon

[P3] B. Botka, Á. Pekker, Á. Botos, K. Kamarás, and R. Hackl, "A systematic study of optical and Raman spectra of peapod-based DWNTs," *Physica Status Solidi B*, vol. 247, no. 11–12, pp. 2843–2846, 2010.

[P4] B. Botka, M. E. Füstös, Gy. Klupp, D. Kocsis, E. Székely, M. Utczás, B. Simándi, Á. Botos, R. Hackl, and K. Kamarás, "Low-temperature encapsulation of coronene in carbon nanotubes," *Physica Status Solidi B*, vol. 249, no. 12, pp. 2432–2435, 2012.

[P5] B. Botka, M. E. Füstös, H. M. Tóháti, K. Németh, Gy. Klupp, Zs. Szekrényes, D. Kocsis, M. Utczás, E. Székely, T. Váczi, Gy. Tarczay, R. Hackl, T. W. Chamberlain, A. N. Khlobystov, and K. Kamarás, "Interactions and chemical transformations of coronene inside and outside carbon nanotubes," *Small*, vol. 10, no. 7, pp. 1369–1378, 2014.

Other publications

[P6] Á. Botos, A. N. Khlobystov, B. Botka, R. Hackl, E. Székely, B. Simándi, and K. Kamarás, "Investigation of fullerene encapsulation in carbon nanotubes using a complex approach based on vibrational spectroscopy," *Physica Status Solidi B*, vol. 247, no. 11–12, pp. 2743–2745, 2010.

[P7] K. Kamarás, Á. Pekker, B. Botka, H. Hu, S. Niyogi, M. E. Itkis, and R. C. Haddon, "The effect of nitric acid doping on the optical properties of carbon nanotube films," *Physica Status Solidi B*, vol. 247, no. 11–12, pp. 2754–2757, 2010.

[P8] H. M. Tóháti, B. Botka, K. Németh, Á. Pekker, R. Hackl, and K. Kamarás, "Infrared and Raman investigation of carbon nanotube-polyallylamine hybrid systems," *Physica Status Solidi B*, vol. 247, no. 11–12, pp. 2884–2886, 2010.

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