Optical spectroscopy of carbon nanotube-based hybrid materials

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Szeged
2015
Introduction

In the past three decades modern materials science has been absolutely defined by the results achieved in nanotechnology research. Carbon is one of the most common chemical elements in nature. The two best known allotropes of carbon are diamond that has tetrahedral structure, and graphite with layered structure. Both are built only by carbon atoms, but their physical properties are widely different.

A new era in carbon materials began in the middle of 1980s when the discovery and research of carbon nanostructures got into the center of interest and since then it has remained a challenging field in nanoscale science. These carbon nanostructures include: fullerenes – the most common one is the soccer ball-like molecule with the formula C_{60}; graphene – a single layer graphite that is a one atom thick plane of carbon; carbon nanotubes (CNTs) – theoretically they can be derived from a single layer graphite, if we consider it as a rolled up piece of graphene sheet. All of these nanostructures contain only sp^{2} hybridized carbon atoms and their electron system is similar, however due to the perturbation caused by the curvature, their physical and chemical properties differ highly. Owing to this diversity, the potential application fields also vary widely: microelectronics, optoelectronics, sensing applications, medicine, solar cells, energy storage, etc.

A multi-walled carbon nanotube (MWNT) is considered to be a coaxial assembly of cylinders of single-walled carbon nanotubes (SWNT), like a Russian doll, one within another. The separation between tubes is almost equal to that between the layers in natural graphite.

To each single-walled carbon nanotube can be assigned an \((n,m)\) pair of integer numbers, called chiral indices. The most interesting property of nanotubes is that they can be metallic or semiconducting merely due to the way the carbon atoms are arranged on their surface. From the chiral index this behavior can be deduced: if \((n - m)\) mod 3 = 0 then the nanotube is metallic, otherwise it is semiconducting. This means that in a common sample the metallic:semiconducting ratio is 1:2. This gives rise to one of the most promising applications of carbon nanotubes, which is the area of transparent conducting layers. Replacing indium tin oxide (ITO) is a very urgent issue that should be solved. Due to their better flexibility and being free of any heavy
metal content, carbon-based materials are among the best candidates. The possibility of separating carbon nanotubes by electronic type and thus gaining not only highly enriched semiconducting or metallic networks, but also extremely purified mixed samples, has broadened the interest in carbon nanotubes as transparent conductors.

With the aim of exploiting their peculiar electronic and structural properties, carbon nanotubes are being implemented more and more in the design of new materials for applications in several fields. The main attribute of the nanotubes is their high aspect ratio, which makes them perfect candidates to build nano-sized electric circuits or to use them in composites. Due to this, the chemistry on carbon nanotubes can be classified into two major groups: covalent and non-covalent functionalization. Regarding covalent functionalization: covalent sidewall chemistry and covalent chemistry at defect sites or open ends can be distinguished, respectively. Non-covalent functionalization involves: non-covalent surfactant adsorption, non-covalent polymer wrapping, molecular insertion into the SWNT interior and doping of carbon nanotubes, respectively.

Non-covalent functionalization of carbon nanotubes by polymers or aromatic systems is a rapidly emerging field. Its importance originates in the possibility of combining special (optical, electric) properties of the added molecules with the mechanical stability of nanotubes. Polymer wrapping of carbon nanotubes has become a general method. Originally developed in order to increase solubility, it is now used for various other applications. A special application is to use the polymers as interfaces between nanotubes and metallic nanoparticles.

Nowadays environmental issues reached significant proportions, which are pressing scientific solutions. For example, the detection and removal of metal ions from industrial liquid wastes is of pivotal interest for the community, because depending on their concentration, these metal ions can be very toxic. It is not surprising that carbon nanotubes – due to their exceptional versatility – have also been employed for environmental purposes, such as depolluting agents.
Objectives

Investigating changes in the electronic system of carbon nanotubes is the main purpose of my dissertation. These changes were achieved by non-covalent functionalization, covalent functionalization or doping, respectively. Therefore, my work is divided into three parts and discussed separately.

Crucial to all applications is an experimental tool to characterize the interaction strength between the nanotubes and the associated species. Led by this purpose, I have investigated a non-covalently functionalized carbon nanotube hybrid system. Poly(allylamine hydrochloride) (PAH) is a linear cationic polyelectrolyte with primary amine groups on the chain and is widely used as a "molecular glue" for attaching nanoparticles onto CNTs. Using optical – attenuated total reflection infrared (ATR-IR) – spectroscopy as characterization method, my goal was to understand how poly(allylamine) covers the surface of the single-walled carbon nanotubes.

Industrial liquid wastes can be very toxic depending on the metal ion concentration, thus detection, sensing, and removal of these metal ions is of pivotal interest for the community. In the second part of my work, I have studied a new supramolecular approach generated for trapping transition-metal cations using multi-walled carbon nanotubes. The goal was to improve the reversibility and selectivity of the interactions between carbon nanotubes and M$^{2+}$ ions. The suspension of this new hybrid structure turns into nanotube aggregates, when metal ions are added. To obtain this aggregation and thus trapping the metal ions, the ligand ought to be covalently bound to the carbon nanotube. I was applying optical spectroscopy technique to confirm this condition.

The last part of this dissertation is related to the investigation of optical and conducting properties of separated metallic and semiconducting single-walled carbon nanotubes, and then the comparison of these characteristics to an ultrahigh purity reference (mixed) sample was performed. For this purpose, wide-range (far infrared through ultraviolet) optical measurements were performed on self-supporting nanotube thin films and transport measurements on transparent nanotube networks. In order to improve the conductivity and avoid chemical reactions at defects, mild doping was used and its effect was studied. Two questions have led this work: which kind of carbon nanotubes should be used to obtain the best transparent conducting properties for substituting ITO; and which kind of carbon nanotube is the most stable against accidental doping?
Methods

Different measurement techniques require different sample preparation processes. During my work I was mainly using powder samples and self-supporting thin films.

If we are interested in the degree of functionalization of the carbon nanotubes, the vibrations appearing in the mid-infrared range (400-4000 cm\(^{-1}\)) need to be investigated. Attenuated total reflection infrared (ATR-IR) spectroscopy is the best choice for measuring samples in powder form, because this technique possesses two major advantages: on one hand, there is no need for further sample preparation, on the other hand, the whole measured quantity of the sample can be recovered, due to the fact that this is a non-destructive procedure.

To accomplish wide-range transmission measurements, transparent free-standing carbon nanotube thin layers are the most suitable. The absence of substrate provides the possibility to use the same sample in every frequency range, without applying complicated multilayer optical models. These samples are prepared using a vacuum filtration method, where the thickness of the film can be varied by the amount of filtered nanotube suspension. This method produces homogeneous nanotube layers. The filter can be dissolved in acetone and the remaining nanotube film can be transferred onto the sample holder, which is usually a graphite disc with a hole and the nanotube layer is stretched over this hole. For thickness measurements, the layer can be placed on a Si wafer, and for transport measurements, on a quartz substrate. Finally, heat treatment under dynamic vacuum is used to remove the solvent from the samples. The wide-range spectra were obtained using three different spectrometers: a UV-VIS spectrometer and two Fourier transform infrared interferometers in the FIR-MIR and NIR range, respectively.

Atomic force microscopy (AFM) measurements were applied to determine the thickness of the nanotube thin layers that serves as an input parameter in the Kramers-Kronig calculations performed to evaluate the optical conductivity from the transmission spectra. Four point van der Pauw method was used to measure the sheet conductivity of the different carbon nanotube transparent thin layers stretched on quartz substrate.
New scientific results

1. I studied the poly(allylamine hydrochloride)-covered carbon nanotube hybrid system. Using optical spectroscopy technique, I showed that in alkaline medium the surface of nanotubes is non-covalently functionalized by the polymer and this wrapping is so tight that the evanescent field of the nanotube’s surface combined with the vibrations of the adsorbed matter, invokes surface attenuated infrared absorption. Since this polymer is applied often as a molecular glue between nanotubes and metallic nanoparticles, its interaction strength with the nanotubes is essential [P1].

2. Using attenuated total reflection infrared spectroscopy, I proved the success of the covalent functionalization of multi-walled carbon nanotubes with 4-(11-azidoundecyl)pyridine. The disappearance of the starting reagent’s azide band confirms the formation of a covalent bond between the reagent and the nanotube. This hybrid system behaves as a new supramolecular catcher for trapping transition-metal ions in liquid wastes. Without this covalent interaction, the trapping of metal ions is impossible, because the attached ligand is responsible for catching and removing the contamination from the liquid waste [P2].

3. I have investigated electronic type separated single-walled carbon nanotube based transparent thin film conductors. Applying wide-range optical and transport measurements, I found that if charge doping is used to increase the dc conductivity, separation of nanotubes is not necessary. After mild nitric acid doping, the non-separated (mixed) sample shows the best conductivity and this result proves that although intertube connections play a crucial role in increasing conductivity, they do not dominate transport properties of high-quality thin nanotube networks [P3].

4. Based on a recently introduced figure of merit, I have shown that a nitric acid doped mixed carbon nanotube network with thickness in a certain range is a promising alternative for replacing ITO as transparent conductor for technological applications using visible light [P3].
Publications


The publications below are not related to the subject of this Dissertation:


