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Endohedral Functionalization of Metallicity-Sorted Single-Walled Carbon Nanotubes †

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Abstract: We performed endohedral functionalization of high-purity metallicity-sorted semiconducting and metallic single-walled carbon nanotubes (SWCNTs) with a mean diameter of 1.4 nm with silver chloride (AgCl) by the method of capillary filling with the melt. The AgCl-filled SWCNTs were investigated by high-resolution scanning transmission electron microscopy and spectroscopic techniques, such as Raman spectroscopy, X-ray photoelectron spectroscopy and ultraviolet photoelectron spectroscopy, which were combined to study comprehensively the modified electronic properties of the filled SWCNTs. The data revealed a downshift of the Fermi level of the nanotubes upon filling, i.e., a p-doping of SWCNTs.

Keywords: single-walled carbon nanotube; metallicity-sorting; filling; electronic properties

1. Introduction

Single-walled carbon nanotubes (SWCNTs) have attracted ever-increasing attention from the research community due to their extraordinary physical and chemical properties and unique one-dimensional structure. This makes them promising candidates for various applications, including nanoelectronics, energy storage, sensors and nanomedicine.

In recent years, chemical functionalization methods were developed for the modification of the electronic properties of SWCNTs. Among these methods, the endohedral functionalization of SWCNTs is a promising method for the controllable doping of nanotubes, because a large variety of substances with appropriate physical and chemical properties can be introduced inside SWCNTs. The encapsulation of electron donors and acceptor substances inside SWCNTs opens the way for tailoring the electronic properties of nanotubes for specific applications [1].

In this contribution, we performed the filling of high-purity semiconducting and metallic SWCNTs with a mean diameter of 1.4 nm with silver chloride (AgCl), which is an insulator and potential electron acceptor and which melts at moderate temperatures, by the method of capillary filling with the melt, and we investigated the electronic properties of the filled SWCNTs.

2. Materials and Methods

In the synthesis procedure, the SWCNT buckypapers and AgCl were sealed inside a quartz ampoule under high vacuum; the quartz ampoule was heated in a tube furnace to a temperature that exceeded the melting point of salt by 100 °C (555 °C), kept at this temperature for 6 h and slowly cooled to room temperature. The filling of the SWCNTs was analyzed by high-resolution scanning transmission electron microscopy (HR STEM), and the electronic properties of the filled nanotubes were studied by spectroscopic techniques, such as Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS).

3. Results and Discussion

HR STEM confirmed the filling of the semiconducting and metallic SWCNTs and the formation of 1D nanocrystals of AgCl. XPS confirmed the chemical composition of the encapsulated compound. A detailed analysis of Raman spectra of the pristine and filled SWCNTs allowed the investigation of filling-induced changes in the electronic properties of SWCNTs. The radial breathing mode (RBM) and G-bands of Raman spectra were fitted with individual components. The analysis of the RBM-band testified to the alteration of relative intensities of the components, which was attributed to the changes in their resonance conditions. The analysis of the G-band revealed upshifts of the components of the filled SWCNTs and the changed profile of the band of the metallic SWCNTs. This indicated the doping of nanotubes by the encapsulated AgCl [2,3]. The direction of charge transfer in the filled metallic SWCNTs was determined by XPS. The observed downshift of the C 1s XPS peak of the filled nanotubes as well as its broadening were attributed to the p-doping of the SWCNTs accompanied by the charge transfer from the nanotubes to the inserted AgCl. The detailed information on the doping-induced shift of the Fermi level of the metallic SWCNTs upon their filling was obtained by UPS. The UPS spectra of the filled SWCNTs demonstrated the downshift of the π-resonance, which was a direct confirmation of the downshift of the Fermi level of the nanotubes by 0.36 eV [3].

4. Conclusions

To summarize, we encapsulated AgCl inside semiconducting and metallic SWCNTs and studied the electronic properties of the filled SWCNTs. We revealed a downshift of the Fermi level of the nanotubes upon filling, i.e., a p-doping of SWCNTs. The obtained results showcase the potential of precise Fermi level engineering of SWCNTs by filling their channels and achieving high doping levels, which is a key step toward applications of endohedrally functionalized nanotubes.

Author Contributions: M.V.K. performed the synthesis, characterization of the filled SWCNTs and data analysis. C.K. assisted in the Raman spectroscopy investigations. O.D. and T.P. performed the XPS measurements. A.M. obtained the HR STEM data. K.Y. provided help with the sorting of SWCNTs. D.E. supervised the research work. All authors have read and agreed to the published version of the manuscript.

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