

# FILLING OF SINGLE-WALLED CARBON NANOTUBES WITH LEAD HALOGENIDES

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## INTRODUCTION

Single-walled carbon nanotubes (SWCNTs) attract ever increasing attention of researchers in fundamental science. They possess extraordinary physical and chemical properties and unique one-dimensional structure<sup>[1]</sup>. As-synthesized nanotube samples represent mixtures of nanotubes with different atomic structures and electronic properties<sup>[2]</sup>. However, fundamental research requires the SWCNTs with homogeneous properties.

To controllably modify the electronic properties of SWCNTs, several methods were established. They include the covalent and noncovalent modification of the outer surface of SWCNTs, substitution of atoms in the SWCNT walls by other atoms, intercalation of bundles of SWCNTs and filling of internal channels of SWCNTs<sup>[3]</sup>. Among these methods, the filling of SWCNTs is a promising approach of tailoring the electronic properties of SWCNTs, because the channels of nanotubes can be filled with different substances<sup>[4]</sup>. The SWCNTs were filled with metals and non-metals, inorganic compounds (metal halogenides, metal chalcogenides, metal oxides), molecules (fullerenes and their derivatives, metallocenes, metal acetylacetonates).

Here, we perform the filling of SWCNTs with lead halogenides (PbCl<sub>2</sub>, PbBr<sub>2</sub> and PbI<sub>2</sub>). We investigate the filling ratio of SWCNTs by high-resolution scanning transmission electron microscopy (HR STEM) and the modified electronic properties of SWCNTs by spectroscopic techniques (Raman spectroscopy and X-ray photoelectron spectroscopy (XPS)).

## EXPERIMENTAL

The SWCNTs synthesized by the arc-discharge method (1.4 nm ArcSO type, Meijo-Nanocarbon Co.) were used as starting material. The SWCNT ends were opened by annealing in air at 500°C for 30 min. After that the SWCNTs and powders of lead halogenides were put into a quartz ampoule, evacuated (10<sup>-6</sup> mbar) and sealed. The ampoule was heated in a tube furnace until a temperature 100°C above the melting point of each lead halogenide: 601°C for PbCl<sub>2</sub>, 471°C for PbBr<sub>2</sub> and 502°C for PbI<sub>2</sub>, kept at this temperature for 6 hours and cooled at rates of 0.05-1.5°C/min to obtain one-dimensional crystals of the salts.

The HR STEM imaging was conducted using a Nion UltraSTEM 100 microscope operated at an accelerating voltage of 60 kV. Samples were prepared by drop casting dispersions of filled SWCNTs in isopropanol onto carbon-coated gold grids. Raman spectroscopy measurements were performed using Horiba Jobin Yvon LabRAM HR800 spectrometer equipped with a tuneable ArKr laser (Coherent Innova 70c) (458, 488, 514, 531, 568 and 647 nm) and a HeNe laser (633 nm). The measurements were performed directly on the buckypapers. The experimental accuracy is 2 cm<sup>-1</sup>. The Raman spectra were fitted to Voigtian and Fano peaks and the area intensities were calculated with PeakFit v4.12. XPS spectra were measured with a SPECS spectrometer equipped with a monochromatized AlK<sub>α</sub> (1486.6 eV) X-ray gun (μFocus 350 μm) and a hemispherical Phoibos 150 WAL analyzer. Buckypapers (5 mm × 5 mm) were mounted on a sample holder using double-sided carbon tape. The pass energies for detailed and survey XPS scans were 30 and 100 eV, respectively.

## RESULTS AND DISCUSSION

The HR STEM data proves the filling of SWCNTs with lead halogenides. Figure 1 presents an example of image of bundles of SWCNTs filled with lead iodide. The filling ratio differs for different lead halogenides. According to the XPS data, the filling ratio is maximal in the case of  $\text{PbI}_2$  and minimal in the case of  $\text{PbBr}_2$ .

Raman spectroscopy and XPS testify to p-doping of SWCNTs by the encapsulated compounds. The strong modifications of radial breathing mode and G-bands of Raman spectra are observed. They include shifts of the peaks and changes in their relative intensities. The C 1s XPS spectra demonstrate shift of the peak towards lower binding energies, which is caused by increasing the work function of SWCNTs as a result of a downshift of the Fermi level of SWCNTs due to the charge transfer from the nanotubes to the encapsulated salts. Both Raman spectroscopy and XPS data prove that the doping efficiency differs for different lead halogenides. The effect is strongest for  $\text{PbI}_2$ , followed by  $\text{PbCl}_2$  and  $\text{PbBr}_2$ .

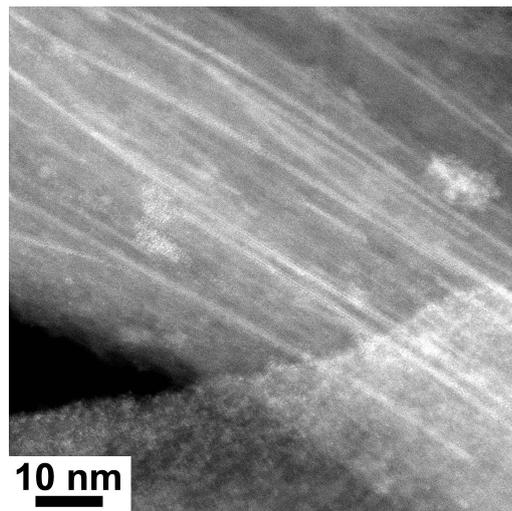
There are several factors that influence the doping level of filled SWCNTs. Firstly, the doping level depends on the chemical and physical properties of the encapsulated compounds. There is a gradual change in the properties of lead halogenides, such as anion radius and electron affinity of halogen, in the line  $\text{PbCl}_2$  -  $\text{PbBr}_2$  -  $\text{PbI}_2$ . However, this does not explain the observed variation of the doping level of SWCNTs. Secondly, the doping level depends on the filling ratio of SWCNTs. The XPS investigations showed that the nanotubes have different filling ratios with different lead halogenides. This is in line with the observed differences in the doping efficiency of SWCNTs.

## CONCLUSION

To summarize, the SWCNTs were filled with one-dimensional nanocrystals of  $\text{PbCl}_2$ ,  $\text{PbBr}_2$  and  $\text{PbI}_2$ . The filling of SWCNTs was confirmed by HR STEM. Raman spectroscopy and XPS proved that lead halogenide nanocrystals result in p-doping of the nanotubes accompanied by a downshift of the Fermi level of SWCNTs. The doping level varies for different lead halogenides: the doping effect is the largest for  $\text{PbI}_2$  and the smallest for  $\text{PbBr}_2$ .

## REFERENCES

- [1] Saito R, Dresselhaus G, Dresselhaus MS (1998) Physical properties of carbon nanotubes. Imperial College Press, London
- [2] Joselevich E, Dai HJ, Liu J, Hata K, Windle AH (2008) Carbon nanotube synthesis and organization. In: Jorio A, Dresselhaus G, Dresselhaus MS (eds) Carbon nanotubes: topics in applied physics, vol 111. Springer, Berlin, pp 101–164
- [3] Kharlamova MV (2013) Electronic properties of pristine and modified single-walled carbon nanotubes. *Phys Usp* 56:1047–1073
- [4] Kharlamova MV (2016) Advances in tailoring the electronic properties of single-walled carbon nanotubes. *Prog Mater Sci* 77:125–211



**Figure 1:** The HR STEM image of lead iodide-filled SWCNTs.