Doped Single-Walled Carbon Nanotubes for Flexible Thermoelectric Applications

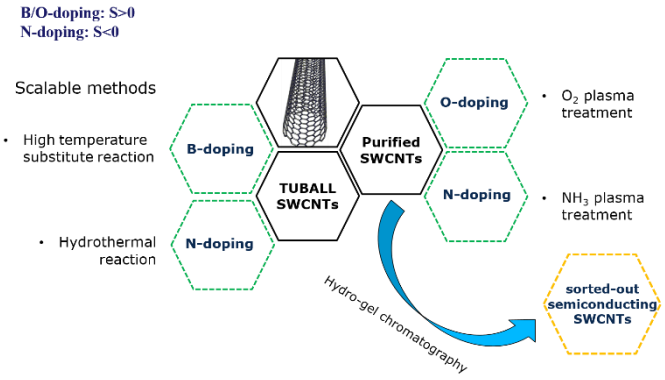
Liu Ye[1]
Vyacheslav Khavrus[1,2],
Mirko Nitschke[3],
Viktor Bezugly[1],
Gianaurelio Cuniberti[1]

[1] Institute for Materials Science, TU Dresden, Hallwachsstr. 3
01069 Dresden, Germany
[2] IFW Dresden, P.O. Box 270016, D01171 Dresden, Germany
[3] Leibniz Institute of Polymer Research Dresden, Hohe Str. 6, 01069 Dresden, Germany

ye.liu@nano.tu-dresden.de

Single walled carbon nanotubes (SWCNTs) have a high potential as flexible thermoelectric (TE) materials owing to their high charge carrier mobility, light weight and outstanding mechanical properties [1]. Recently, purified semiconducting SWCNT films showed TE properties comparable to commercial Bi_2Te_3 alloys [2]. Doping is a crucial step towards TE application of SWCNTs, not only for maximizing their thermoelectric power factor (S2σ), but also for providing n-type nanotubes that are demanded for TE devices (pristine SWCNTs are p-type materials due to oxygen/water absorption). Here doping as well as ambient effects on the TE properties of SWCNTs are investigated. We performed post-synthesis large-scale boron (B-) and nitrogen (N-) doping for commercial unsorted SWCNTs, by high temperature substitutional reaction and hydrothermal reaction, respectively. The maximum achieved dopants concentration were 0.5 at.% for substituting B atoms and 0.4 at.% for quaternary N atoms for B-SWCNT and N-SWCNT samples, respectively. By boron doping, we were able to enlarge both electrical conductivity (up to 250000 S/m) and Seebeck coefficient (up to 30 µV/K) of pristine SWCNTs that ended up at the increase of the power factor to ca. 120 µW/mK². On the other hand, a high amount of oxygen absorbed on N-doped SWCNTs is found to be the main obstacle for achieving negative Seebeck coefficient in ambient conditions.

As an alternative route towards improving TE properties of carbon nanotubes, semiconducting (sc-) SWCNTs were sorted out by gel chromatography, and thin sc-SWCNT films were prepared. By separating semiconducting-only nanotubes, Seebeck coefficient of SWCNT samples has been dramatically increased up to 120 µV/K. Then, the sc-SWCNT films were doped by oxygen or



ammonia plasma treatment. The treatment with oxygen plasma caused further increase of Seebeck coefficient up to 160µV/K. Ammonia plasma treatment led to a noticeably higher nitrogen-to-oxygen ratio in sc-SWCNTs than in case of the hydrothermal treatment. The films of N-doped sc-SWCNTs are n-type semiconductors with extremely low negative Seebeck coefficient.

Thus, doping of SWCNTs, especially in combination with sorting-out of sc-SWCNTs, leads to a dramatic enhancement of TE properties of carbon nanotubes. It can be expected, that hybrid composites made of doped SWCNTs and polymers may provide a new avenues for the development of optimal materials for flexible TE applications.

References

[1] Zhao, Weiyun, et al. "Flexible carbon nanotube papers with improved thermoelectric properties." Energy & Environmental Science 5.1 (2012): 5364-5369.

[2] Nakai, Yusuke, et al. "Giant Seebeck coefficient in semiconducting single-wall carbon nanotube film." Applied Physics Express 7.2 (2014): 025103.