



NITech - LFG joint workshop on carbon allotropes

Tuesday, February 14, 2017

Venue: seminar room 0.332, Institute of Particle Technology (LFG), Cauerstr. 4,
91058 Erlangen

10:00 – 10: 30 **Yosuke Ishii**, Low temperature structural changes accompanied with charge-transfer reaction of polyiodide ions encapsulated in single-walled carbon nanotubes

10:30 – 11: 00 **Thomas Nacken**, Top-down graphene production and quantitative analyses of graphene oxide

11:00 – 11: 20 **Keisuke Kurimoto**, Electrochemical properties of functional molecules encapsulated single-walled carbon nanotube

Low temperature structural changes accompanied with charge-transfer reaction of polyiodide ions encapsulated in single-walled carbon nanotubes

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Transparent conductive films such as indium tin oxide (ITO) or fluorine tin oxide (FTO) are in high demand for use in optoelectronic devices, including solar cells. However, ITO and FTO are expensive and inflexible. On the other hand, it has been expected that we can fabricate transparent, conductive, and flexible films by placing single-walled carbon nanotubes (SWCNTs) on the surface of transparent and flexible polymer films. Such nanotube-based transparent conductive films have a great potential to replace ITO and FTO. However, the conductivity of pristine SWCNTs is not sufficient for typical transparent conductive film applications. To improve the conductivity, doping of alkali metals (K, Rb) or halogen atoms (Br, I) into SWCNTs would be an effective technique. Among the doped SWCNTs, iodine-doped SWCNTs are particularly interesting. Iodine doping can lead to a reduction in current resistance of SWCNTs by an order of magnitude, and the iodine-doped SWCNTs are known to be air-stable charge-transfer compounds. However, it is not very easy to control iodine doping level by conventional doping methods. Recently, we found that iodine molecules can be encapsulated (here we write iodine molecule encapsulated in SWCNTs as I@SWCNTs) by an electrochemical method [1]. This method is very easy to control the doping level. We also found that iodine doping improves not only the conductivity but also the dispersibility of SWCNTs. Interestingly, I@SWCNTs were dispersed in water very well at low temperature.

In order to investigate the temperature dependence of I@SWCNT dispersion, we measured Raman spectra of SWCNTs encapsulating iodine molecules at low temperatures. Three kinds of SWCNTs having mean tube diameters of 1.0, 1.5 and 2.5 nm were used in this study. For electrochemical iodine doping, we fabricated three-electrode configuration cells: SWCNT working, Pt counter, and Ag/AgCl reference electrodes. Iodine-doping processes were investigated by in situ Raman scattering. The Raman measurements were performed using a micro-Raman spectroscopy system (JASCO) equipped with a temperature control stage (JHT 10036 L).

It was found by Raman measurements that G-band peak position of I@SWCNTs shifts toward higher wavenumber side with decreasing temperature. It indicates that charge transfer from SWCNT to iodine molecules increases with decreasing temperature. Raman peaks of polyiodine molecules and their overtone peaks were also observed in the low wavelength region. The peak at around 175 cm⁻¹ and its overtones are assigned to the Raman band of I⁵⁻, while the peak at around 110 cm⁻¹ is assigned to I³⁻. The presence of poly iodine molecules was also confirmed by XPS measurements. It is very interesting that the peak intensity ratio of the I⁵⁻ Raman band to the G-band of SWCNTs observed at around 1600 cm⁻¹ increased with decreasing temperature. It indicates that I⁵⁻ ion formation in SWCNTs by the reaction ($5I_2 + 5e^- \rightarrow I_5^-$) is promoted at low temperature [2]. On the meeting, I will discuss the structural changes of iodide ions in SWCNTs having different diameter with decreasing temperature.

Reference

- [1] H. Song, Y. Ishii, A. Al-zubaidi, T. Sakai, S. Kawasaki, Temperature-dependent water solubility of iodine-doped single-walled carbon nanotubes prepared using an electrochemical method, *Phys. Chem. Chem. Phys.* **15**, 5767-5770 (2013).
- [2] Y. Yoshida, Y. Ishii, N. Kato, C. Li and S. Kawasaki, Low-Temperature Phase Transformation Accompanied with Charge-Transfer Reaction of Polyiodide Ions Encapsulated in Single-Walled Carbon Nanotubes, *J. Phys. Chem. C* **120**, 20454-20461 (2016).

Electrochemical properties of functional molecules encapsulated single-walled carbon nanotube.

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Single-walled carbon nanotube (SWCNT) encapsulation systems have been paid much attention since the discovery of C₆₀ peapod in 1998. So far, several kinds of molecules (e.g. coronene, β -carotene, 9,10-dichloroanthracene, water, iodine) have been encapsulated into SWCNTs. This encapsulation system has many unique properties.

Today, I will talk about two kinds of our recent activity for SWCNT encapsulation systems. The first one is lithium- and sodium-ion battery electrode properties of organic molecules encapsulated in SWCNTs. In this study, we investigated physical and electrochemical properties of 9,10-anthraquinone (AQ) and 9,10-phenanthrenequinone (PhQ) molecules encapsulated in SWCNTs. We found that the encapsulated quinone molecules have good electrochemical activity and can store lithium- and sodium- ions reversibly. Interestingly, undesired capacity fading, which is a common problem of organic active electrodes used in lithium- and sodium-ion batteries, was diminished probably due to the large adsorption potential field in the nanopores of SWCNTs [1]. We also found that the PhQ@SWCNT electrodes works very well even at a low-temperature (0 °C) [2]. The second one is application for the cathode material for fuel cell. We found that some of encapsulation molecules enhance the catalytic activity of oxygen reduction reaction (ORR) on the outer surface of SWCNTs. This enhancement would be explained by the charge-transfer reaction between SWCNTs and encapsulated molecules.

Reference

- [1] Y. Ishii, K. Tashiro, K. Hosoe, A. Al-Zubaidi and S. Kawasaki. Electrochemical lithium-ion storage properties of quinone molecules encapsulated in single-walled carbon nanotubes. *Phys. Chem. Chem. Phys.*, 2016, **18**, 10411-10418.
- [2] C. Li, Y. Ishii, S. Inayama, and S. Kawasaki. An encapsulation strategy to convert carbon nanotubes into ion-size independent electrodes for low-temperature Na ion batteries. submitted.