# Photoelectron Spectroscopy of Ionic Liquids and Thin Films Made of Fullerenes and Their Application to Photoelectrochemistry

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Electrodes made of fullerenes and their derivatives and electrolytes containing ionic liquids (ILs) are used in the photovoltaic devices such as dyesensitized solar cells (DSSCs). Both electronic structures and mesoscopic mixing schemes of the materials are key issues which affect their efficiency and lifetime. These structures of materials can be investigated using a combined

study of spectroscopic and thermodynamic measurements.

#### 1. Fabrication of LB Film Electrodes of Sulfonated Fullerenes and Evaluation of Their Feasibility for the DSSCs

Carbon electrodes are candidates of substitutes for the Pt electrodes which are used in the most of present DSSC cells. To produce the carbon electrodes suitable for DSSC, we utilize the Langmuir-Blodgett (LB) technique and sulfonated fullerenes as building blocks. We first used stearic acid and

oleic acid to find out suitable conditions for producing thin and homogeneous LB films. We then fabricated the LB monolayers and multilayers of fullerene/fatty acid mixtures and the sulfonated fullerenes. We found that even the LB monolayers of sulfonated fullerenes have electrochemical reactant selectivity. We are trying to produce homogeneous multilayer films and examine the suitability for DSSC.

# 2. Stimulation Induced Phase Transition of Crystals of Salicylideneaniline Derivatives

Some crystals have solid phase transition induced by small energy such as mechanical forces and light irradiation. We have measured the Raman spectra of the crystals of salicylideneaniline derivatives before and after the phase transition. The Raman spectra were found to change gradually during the period of the phase transition. We will analyze the change of the Raman spectra and elucidate mechanisms of the transition. Knowledge on the phase transition induced by the small energy in three-dimensional space gives us clue to understand a key to control self-organization in two-dimensional films.

## Observation of 3-Dimensional Chemical Nano-Structures of a Cell Nucleus

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Computed tomography (CT) is a powerful technique to observe 3-dimensional (3D) structure of a sample without any destructive process. In regard to relationship between spatial resolution and transmittance, CT by using a scanning transmission soft Xray microscope (STXM) is a suitable combination. Moreover, this combination also enables to perform 3D

spectro-microscopy by changing energies of incoming X-rays.<sup>1)</sup>

3D distributions of DNA and protein in an isolated cell nucleus of a HeLa S3 at stage 0 (*i.e.* normal cell) were observed. The cell nucleus was fixed by glutaraldehyde and critical point drying without any additional staining. Since X-ray absorption spectra of DNA and protein show remarkable difference in N K-edge, 50 images stacks around N K-edge were acquired with rotating the sample 3.6° each (180° in total). The 3D distributions of DNA and protein were reconstructed after fitting each reference X-ray absorption spectra to the energy stacks. A projection image of 3D distribution of DNA and cross sectional images of distributions of DNA and protein are shown in Figure  $1^{(2)}$  Several cell nucleoli with high density and framework-like structures are clearly observed in Figure 1(b).

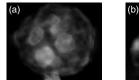






Figure 1. (a) A projection image of 3D distribution of DNA and cross sectional images of distributions of (b) DNA and (c) protein. Scale bar is  $2 \mu m$ .

#### References

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- T. Ohigashi, A. Ito, K. Shinohara, S. Tone, Y. Inagaki, H. Yuzawa and N. Kosugi, *Microsc. Microanal.* 24, 400–401 (2018).