

# 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 dye-sensitized solar cells (DSSCs) to make a breakthrough in the field of renewable energy sources. Both electronic structures and mesoscopic mixing schemes of the materials are key issues which affect their efficiency and lifetime.

These structures 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

In the DSSCs, counter electrodes consist of Pt. The Pt electrode has some disadvantages such as cost and stability. Electrodes made of fullerenes and carbon nanotubes are

candidates of substitutes for the Pt electrodes. To produce the carbon electrodes, we utilize the Langmuir-Blodgett (LB) technique which has low burden on the environment. Additionally, the LB technique has ability to make ordered structure. We have fabricated the LB films using fullerenes and their amphiphilic derivatives. We succeeded in producing homogeneous films on ITO glass substrates. The produced LB film electrodes were diagnosed by electrochemical methods. We are now trying to apply photoelectron spectroscopy to understand the electronic structures of the films which is essential to the efficiency of photovoltaic devices.

## 2. Combined Study of Photoelectron Spectroscopy and Thermodynamic Measurements of ILs and Their Mixtures

We have just started a research subject to apply the combined study of spectroscopic and thermodynamic measurements to the ILs. This combined study will allow us to understand the extraordinary characteristics of the ILs and their mixtures.

# 3-Dimensional Spectro-Microscopy

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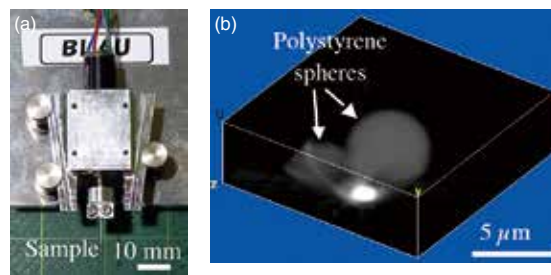


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Scanning transmission X-ray microscopy (STXM) can realize nano-scale 2-dimensional (2D) chemical state analysis without any destructive process, in combination of soft X-ray absorption spectroscopy with nano-focused X-ray beams obtained by using a Fresnel zone plate (FZP). This STXM technique can be extended to nano-scale 3D analysis based on a computed tomography (CT) method; however, the short working distance (typically, less than 0.5 mm) problem inherent in the FZP applied to the soft X-ray region has to be solved.

We designed a special compact sample cell for CT by using a two-phase stepping motor (shown in Figure 1(a)). As a feasibility test of this method, polystyrene spheres of diameter of 5  $\mu\text{m}$  were used as a standard sample, though 5  $\mu\text{m}$  is a little thicker than the focal depth of the present nano-focused beam. STXM images were successfully obtained with rotating the sample by 3.6° each, and 50 STXM images were acquired in total, where the photon energy was 280 eV and the dwell time

was 3 ms per a pixel. A reconstructed 3-dimensional volume image was obtained as shown in Figure 2. We will plan to apply this technique to  $\mu\text{m}$ -scale samples with heterogeneous chemical components.



**Figure 1.** (a) A sample cell for computed tomography and (b) 3-dimensional volume image of polystyrene spheres.

## Reference

- 1) G. A. Johansson, T. Tyliczszak, G. E. Mitchell, M. H. Keefe and A. P. Hitchcock, *J. Synchrotron Rad.* **14**, 395–402 (2007).