1555 Microsc. Microanal. 21 (Suppl 3), 2015
doi:10.1017/S1431927615008557 Paper No. 0776

Thickness mapping of freestanding Ionic Liquid films using Electron Energy Loss Spectroscopy in the TEM.

A.E. Ribbe, P. Kim, D. Hoagland, T.P. Russell

Department for Polymer Science & Engineering, University of Massachusetts Amherst, Amherst, Massachusetts 01003 USA

One of the biggest challenges in Electron Microscopy in fluids is to overcoming the limitation of the high vacuum requirements. To observe the dynamics of fluid samples, sophisticated fluid cells have been developed that typically use 25 nm Silicon Nitride membranes with a separation of ~ 200 nm [1]. Recently it was demonstrated that graphene can be used to trap liquids for TEM observation [2] which improves resolution substantially due to the negligible scattering contribution of the graphene layers. However, sample sizes are quite small, ~ 100 nm in diameter.

Ionic Liquids (IL) [3] recently found application in Cryo-TEM for visualization of polymers morphologies [4] or nanoparticle assemblies [5]. The ability to perform room temperature TEM [6] measurements is enabled by the very low vapor pressure. Recently HRTEM studies showing a microstructure in ILs have been shown [7].

We here describe the shape of IL films that can be used as a medium to investigate nanoparticle dynamics n TEM and SEM by using Electron Energy Loss Spectroscopy (EELS) thickness mapping. Lacey carbon, which has an average hole diameter of ~2 μm. and a thickness of 20-30 nm [8] provided the most reliable support for IL films. The rather large hole size distribution allows for the random generation of an array of different IL film geometries i.e. thickness, diameter and surface curvature.

IL (TEGO1) thickness maps where acquired using a JEOL JEM-2200FS EFTEM with in-line omega-type electron energy loss filter. First, the local thickness of the IL film was determined using EELS with a small filter entrance aperture at various locations, as marked in Figure 1. Absolute thicknesses were calculated using the log-ratio method: $t/\lambda = \ln(I_t/I_0)$ where I_t and I_0 are the total spectrum the zero-loss intensities, t is the film thickness and λ is the mean free path of the IL. Subsequently, an uncalibrated thickness map was acquired in energy filtered (EFTEM) imaging mode by calculation of the log-ratio-image of an unfiltered and zero-loss filtered bright field image. The absolute thicknesses determined by EELS were then used to calculate an absolute thickness map using a 2D gray value profile of the uncalibrated thickness map, as illustrated in Figure 2.

The shape of the individual free-standing IL films depends mainly on the thickness of the respective hole. While films < 100 nm appear to have convex shape with thicknesses of smaller than 20 nm in the center, films with t> 100 nm are generally concave, with up to 300 nm thickness in the center. Recently we described particle motion in IL films on solid substrates by SEM [9]. This work expands our experiments to free standing IL films and we will demonstrate that IL films can be utilized in both SEM and TEM to study particle dynamics as for example Brownian motion.

---

[1] de Jonge, N., Ross, M.F. “Electron microscopy of specimens in liquid” Nature Nanotechnology”, 6, 695-704 (2011).

[2] Yuk, J.M., Park, J., Ercius, P., Kim, K., Hellebusch, D.J. “High-Resolution EM of Colloidal Nanocrystal Growth Using Graphene Liquid Cells” Science, 336, 61-64 (2012).
Michael F. Crommie,1,2,6 Jeong Yong Lee,3† A. Zettl,1,2,6† A. Paul Alivisatos2,4

[3] Welton, T., “Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis“, Chem. Rev. 99, 2071-2083 (1999).

[4] Simone, M., Lodge, T.P., “Micellization of PS-PMMA Diblock Copolymers in an Ionic Liquid” Macromol. Chem. Phys., 208, 339–348, (2007).

[5] Dalaver, H. et al. “Cryo-transmission electron microscopy of Ag nanoparticles, grown on an ionic liquid substrate” Mater. Res., 25(7), 1264-1271 (2010).

[6] Maddikeri, R., Colak, S., Gido, S.P., Tew, G.N. “Zwitterionic Polymersomes in an Ionic Liquid: Room Temperature TEM Characterization” Biomacromolecules, 12(10), 3412–3417 (2011).

[7] Chen, S., Kobayashi, K., Kitaura, R., Miyata, Y., Shinohara, H. “Direct HRTEM Observation of Ultrathin Freestanding Ionic Liquid Film on Carbon Nanotube Grid” ACS Nano, 5(6), 4902 (2011).

[8] Karlsson, G. “Thickness measurements of lacey carbon films”, Journal of Microscopy, 203/3, 326-328 (2001).

[9] Ribbe, A.E., Kim, P., Hoagland, D., Russell, T.P. “Diffusion Processes in Ionic Liquids Observed via low voltage Scanning Electron” Microscopy and Microanalysis, 18(S2), 1618-1619 (2012).

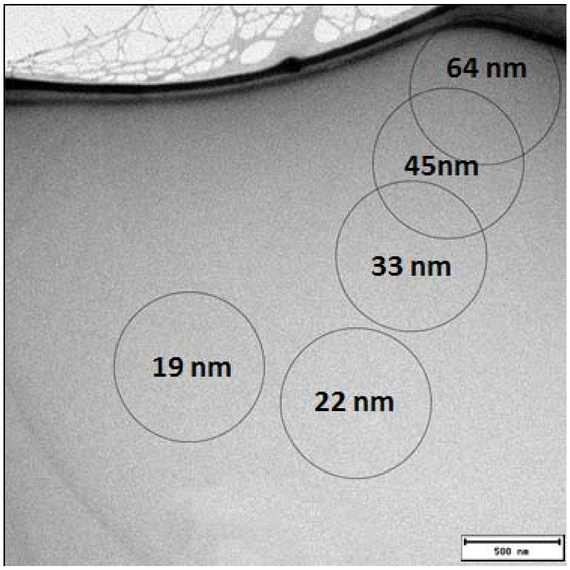

Figure 1: Zero-loss filtered bright field image of TEGO1 and filter entrance aperture locations for EELS thickness determination.

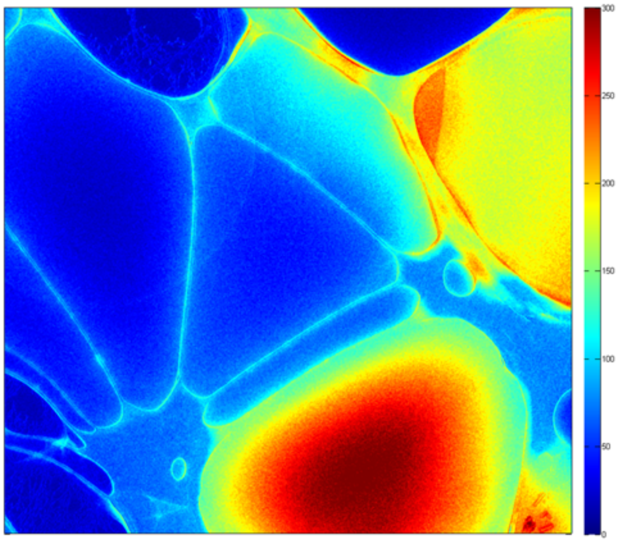

Figure 2: Absolute thickness map of TEGO1 suspended on lacey carbon. Color scale in nm; image size 11µm x 11µm.