東京大学大学院工学系研究科 総合研究機構
第17回「次世代電子顕微鏡法」講演会
2024年2月2日 14:00 – 15:00 ハイブリッド開催

Studying the chemistry and electronic properties of encapsulated molecular and atomic systems with monochromated STEM-EELS

Quentin M. Ramasse[1,2], Demie Kepaptsoglou[1,3]

[1]SuperSTEM Laboratory, Daresbury
[2]Schools of Physics, Astronomy & Chemical and Process Engineering, University of Leeds, UK
[3] Department of Physics, Engineering and Technology, University of York, UK

There have been great strides in recent years in the development of high-resolution dose-controlled electron microscopy methodologies for studying beam sensitive materials systems at high resolution. New and improved hardware, such as advanced aberration correctors and monochromators, as well fast direct or hybrid electron detectors or beam 'choppers' have widened the range of applicability of these techniques. State-of-the-art monochromated electron energy loss spectroscopy (EELS) in the scanning transmission electron microscope (STEM), in particular, offers the ability to map materials and atomic structures with an angstrom size electron beam and an energy resolution for EELS under 5meV. However, atomic and single molecular systems remain challenging objects for electron microscopy, especially when attempting to study their chemistry or electronic structure using EELS, an inherently dose-intensive technique. Here, we report on how encapsulated molecular and atomic systems provide ideal containers, or 'nano test-tubes', to study chemical reactions and electronic interactions in some of the most challenging materials systems. The diameter of encapsulating carbon nanotubes and the irradiating electron dose can be used in conjunction to control chemical reaction rates between the molecules and the encapsulating containers, as well as bond dissociation in the encapsulated structures. This approach was demonstrated in the cases of perchlorocoronene molecules [1], or of individual diatomic HF molecules isolated within fullerene cages [2]. The steric and electronic constraints imposed by the encapsulating tubes can also be used to form novel material phases with unique electronic properties, such as recently identified 'pico-perovskite' structures. These smallest conceivable halide perovskites were imaged and mapped using STEM-EELS [3], revealing a wealth of hitherto unknown crystalline structures whose electronic properties were further investigated using ab initio methods, based on these experimental observations. However, the mostly conducting nature of carbon-based containers can occlude electronic structure information in EELS experiments. Wide-band-gap BN nanotubes, in contrast, offer the promise of directly measuring the electronic or optical response of individual encapsulated nanostructure, while the more complex interactions with the host chemistry offer new avenues of investigation [4,5].

[1] K.L.Y. Fung *et al.*, *Phys. Chem. Chem. Phys.***25**, 9092 (2023)
[2] J. Biskupek *et al.*, *ACS Nano* **14**, 11178-11189 (2020)
[3] R. Kashtiban *et al.*, *Advanced Materials* **35**, 2208575 (2023)
[4] J.W. Jordan *et al.*, *J. Am. Chem. Soc.* **145**, 1206-1215 (2023)
[5] I. Cardillo-Zallo *et al.*, *ACS Nano*, in press (2024)

東京大学
次世代電子顕微鏡法
社会連携講座

主催: 「次世代電子顕微鏡法」社会連携講講座
e-mail: ishikawa@sigma.t.u-tokyo.ac.jp