Inside and Outside: X-ray Absorption Spectroscopy Mapping of Chemical Domains in Graphene Oxide

Luis R. De Jesus, ‡[1] Robert V. Dennis, ‡[1] Sean W. Depner, ‡[1] Cherno Jaye,[2] Daniel A. Fischer,[2] and Sarbajit Banerjee*[1]

[1]Department of Chemistry, University at Buffalo, The State University of New York, Buffalo, New York 14260–3000
[2]Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

Supporting Information

Preparation of Graphene Oxide

Graphene oxide was synthesized using the modified Hummers method[1] utilizing natural flake graphite from Bay Carbon Inc. (Michigan, USA). Briefly, graphite was oxidized using $KMnO_4$ and H_2O_2 and the expanded graphite oxide was exfoliated to yield graphene oxide. The synthesis of graphene oxide has been detailed in our previous work.[2] A graphene oxide solution in deionized water was vacuum filtered through a silicon nitride TEM window with ca. 2 μm holes and 3 μm spacing between holes. The silicon nitride membrane has a thickness of 50 nm and a window size of 0.5 mm × 0.5 mm. A single flake of few-layered graphene oxide was identified using transmission electron microscopy and further characterized by STXM and Raman spectroscopy. Ensemble NEXAFS measurements were performed on graphene oxide from the same batch as was vacuum filtered through the silicon nitride membrane by preparing a free-standing GO paper by vacuum filtration through a nitrocellulose membrane as described in previous work.[2]

Scanning Transmission X-ray Microscopy

STXM data was collected at spectromicroscopy beamline 10ID-1 of the Canadian Light Source, Saskatoon, SK, a 2.9 GeV third-generation synchrotron light source. The STXM end-station is equipped with an elliptically polarized undulator source (APPLE II) and a slitless entrance-plane grating monochromator. Incoming X-rays were focused using a Fresnel lens zone plate including an order-sorting aperture to eliminate unwanted diffraction orders.[3] The optical design allows for high flux in transmission geometry and yields a spatial resolution of ~30 nm. Plane grating monochromators with 250-line mm^{-1} and a 500-line mm^{-1} were used for the C and O K-edge measurements, respectively. A pixel size of 30 nm was used with a 1 ms dwell time at each pixel location. The areas of interest were raster scanned through the focal point of the X-ray beam, and transmitted beam intensities were measured at the detector. Energy scans were performed stepwise through regions of interest with typical resolving power ($\Delta E/E$) of 2×10^{-4} to acquire sequences of images denoted as image stacks. The image stacks were analyzed using Jacobsen's Principal Components Analysis (PCA) suite and aXis2000 (available free for non-commercial applications at http://unicorn.mcmaster.ca/aXis2000.html).[4] Principal component analysis was used to orthogonalize and noise-filter the spectral features of the STXM image stacks. This involves deconvoluting the spectra into discrete abstract orthogonalized components that each represent a linear combination of spectral signatures from multiple chemical species. Subsequently, cluster analysis (as a pattern matching mode) was used to classify pixels by spectral similarity to extract average spectra with improved signal-to-noise characteristics across the given cluster. The graded contributions of the orthogonalized spectral components at each pixel were also determined, allowing for construction of maps indicating their relative abundance at each pixel within the area of interest.[5,6] Application of this multivariate analysis method allows for nanoscale visualization of chemical speciation (such as in Fig. 3B) by reconstructing images from eigenspectra in complex samples without requiring *a priori* knowledge of reference spectra of the different chemical species. The angle dependence cutoff was set to the point just before the highest pixel contribution. This approach eliminates thickness variations and allows for mapping of variations in chemical signatures.[5]

Transmission Electron Microscopy

TEM images were acquired using a JEOL 2010 instrument operating at 200kV using the same Norcada grids as noted above.

Raman Spectroscopy

The Raman spectrum of the graphene oxide flake was acquired in back-scattered mode using a Horiba Jobin-Yvon Labram HR system with 514.5 nm laser excitation using an edge filter for Rayleigh line rejection and an Andor Peltier-cooled CCD camera. The spectrum was acquired using a 600 lines mm^{-1} grating yielding a resolution of 1.5 cm^{-1}.

NEXAFS Spectroscopy

Carbon K-edge NEXAFS experiments were performed at National Institute of Standards and Technology (NIST) beamline U7A of the National Synchrotron Light Source at Brookhaven National Laboratory. A 600 lines/mm toroidal spherical grating monochromator was used yielding an energy resolution of approximately 0.08 eV. The entrance slits were set to 30 μm × 30 μm. The spectra were acquired in partial electron yield (PEY) mode using a channeltron electron multiplier detector with an entrance grid bias set to -150 V to enhance surface sensitivity and limit noise. A charge compensating electron gun was used to neutralize the effects of sample charging. The PEY signals were normalized using the incident beam intensity obtained from the photoemission yield of a freshly evaporated Au grid with 90% transmittance placed along the path of the incident X-ray beam to eliminate the effects of beam fluctuations and monochromator absorption features. The C K-edge spectra were calibrated to an amorphous carbon mesh with a π^* transition at 285.1 eV. Pre- and post-edge normalization of the data was performed using the Athena suite of programs.

REFERENCES

(1) Hummers, W. S.; Offeman, R. E. Preparation of Graphitic Oxide. *J. Am. Chem. Soc.* **1958**, *80*, 1339.

(2) Dennis, R. V.; Schultz, B. J.; Jaye, C.; Wang, X.; Fischer, D. A.; Cartwright, A. N.; Banerjee, S. Near-edge X-ray Absorption Fine Structure Spectroscopy Study of Nitrogen Incorporation in Chemically Reduced Graphene Oxide. *J. Vac. Sci. & Technol. B* **2013**, *31*, 41204.

(3) Zhou, J. G.; Wang, J.; Sun, C. L.; Maley, J. M.; Sammynaiken, R.; Sham, T. K.; Pong, W. F. Nano-scale Chemical Imaging of a Single Sheet of Reduced Graphene Oxide. *J. Mater. Chem.* **2011**, *21*, 14622–14630.

(4) Jacobsen; Wirick; Flynn; Zimba Soft X-ray Spectroscopy from Image Sequences with Sub-100 nm Spatial Resolution. *J. Microsc.* **2000**, *197*, 173–184.

(5) Lerotic, M.; Jacobsen, C.; Gillow, J. B.; Francis, A. J.; Wirick, S.; Vogt, S.; Maser, J. Cluster Analysis in Soft X-ray Spectromicroscopy: Finding the Patterns in Complex Specimens. *J. Electron Spectrosc.* **2005**, *144–147*, 1137–1143.

(6) Lerotic, M.; Jacobsen, C.; Schäfer, T.; Vogt, S. Cluster Analysis of Soft X-ray Spectromicroscopy Data. *Ultramicroscopy* **2004**, *100*, 35–57.