Insight into Two-Dimensional MoS$_2$ by Raman and DFT Study

Mark Waterland
Massey University, New Zealand
E-mail: M.Waterland@massey.ac.nz

Abstract

Two-dimensional nanostructures have attracted attention for their unique physical properties and electronic structure and their enhanced catalytic activity. For MoS$_2$ nanoribbons the most active catalytic sites are located at the edges of the two-dimensional nanosheets, while in graphene, functionalisation at the edges allows functionalisation with minimal perturbation of the sp$^2$ graphene lattice. Vibrational spectroscopy, and Raman spectroscopy in particular is recognised as a valuable technique for characterising two-dimensional nanostructures. In this work we use IR and Raman spectroscopy to characterise the edges of these nanostructures. The low proportion of edge atoms requires increased sensitivity and selectivity and we demonstrate how plasmon resonance provides the necessary enhancement for graphene nanoribbons.

We show how silver nanoparticles preferentially locate at the edges of graphene nanoribbons. The nanoparticles enhance both infrared and Raman intensities and we show how surface-enhanced infrared absorption spectroscopy (SEIRAS) provides spectroscopic evidence for edge functionalization. A quantum field theory treatment of IR absorption is used to suggest that resonance enhancement of graphene IR modes occurs under SEIRAS conditions.

Preliminary results from DFT calculations show zigzag and armchair fragments should have distinct spectral features in the IR spectrum. We compare these calculations with SEIRAS spectra of two samples taken from the same HOPG starting material that show distinct spectral features that we attribute to differences in edge structure.

The Raman cross-section of modes associated with MoS$_2$ edges is sufficiently strong to generate observable features in the spectra of MoS$_2$ nanostructures that may be associated with defect modes. We show that as the fraction of edge atoms in a sample is increased (either by mechanical fracturing or ultrasonic methods) new features appear in the MoS$_2$ spectra that suggest the defects are strongly associated with edge structures. These tentative assignments are supported by ab initio calculations of the vibrational modes of a series of MoS$_2$ nanostructures. The modes are strongly resonantly enhanced with near infrared excitation which allows for mode assignments.

Keywords: graphene, SEIRAS, defect modes, MoS$_2$, resonance Raman