The imaging properties of polyoxometalate ions on curved graphene

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Recently we have demonstrated that polyoxometalate (POM) ions, formed from various assemblies of tungsten oxide polyhedra, and of the form $[W_6O_{19}]^{2-}$ or $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ can be imaged by conventional and aberration corrected transmission electron microscopy (AC-TEM) when supported either within carbon nanotube capillaries[1] or on monolayer graphene oxide.[2,3] These experiments have permitted the observation of small structural distortions within individual anions[1] and have also enabled for the first time the direct visualization of the surface interaction of POMs with hydroxyl functionalities on the surface of graphene oxide.[2] Critical to these studies has been a detailed understanding of the imaging properties of both the respective anions and also the specimen supports which inevitably produce a strong contribution to the composite contrast of both specimen and support.

What is perhaps less well understood is the contribution that the imaging properties of supported molecular scale species supported on ultrathin carbon monolayers (or within nanotubes) can make to the understanding of the local curvature and other morphological features of supporting material. In this, the experimentally imaged polyoxometalates are well-placed to make a significant contribution in that their image contrast both as a function of relative orientation[1,2] and also defocus[1] can readily be simulated. As in certain projections these anions offer either single or pairs of heavy tungsten atoms (Z=74) arranged parallel to the electron beam, the image contrast due to these anions is quantitative and can be used as a measure of local focusing conditions. As the local specimen height and electron microscope objective lens defocus are complementary, the relative focusing properties of individual polyoxometalate anions as a function of relative height can also be simulated and in principle can be used as a local probe for height variation and curvature within a strictly monolayer support film.[4] In this study we therefore assess the imaging properties of individual polyoxometalate ions as a function of the local height of a monolayer support film, in this instance graphene carbon.

For these studies, a version of the transmission electron microscope image simulation code based on the multislice method was implemented in Mathematica 8. This allows the program to take advantage of the recent advances in GPU computing to increase the calculation speed for massively parallel problems and increase the accuracy over previous multislice simulations using the enhanced computing power available. This removes the restrictions inherent in some simulation codes on either the number of atoms that can be simulated or the resolution of the images that can be produced; additionally there are no limits on either the sample size or shape. The simulation can take an input file specifying the positions of all the atoms within the sample and produce a simulated TEM image from the sample with control over aperture size, defocus, spherical aberration, two and three fold astigmatism, accelerating voltage and specimen tilt among others. This is done by splitting the sample into numerous slices perpendicular to the direction of the electron beam, and then calculating the projected atomic potential for each slice. The electron wave can then be successively transmitted through each slice and propagated through a vacuum to the next slice to calculate the wave function upon exiting the sample.

Simulations of individual polyoxometalate anions were then produced for small sections of graphene supporting a single anion (i.e. either the lacunary $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ Keggin ion or the $[W_6O_{19}]^{2-}$ Linqvist ion) in order to evaluate the effects of objective lens defocus on the anion, the relative orientation of the respective anion (i.e. Figs. 1(a)-(h)) and the coefficient of spherical aberration (set to 0.02 mm in order to reproduce an aberration-corrected TEM). As can be seen, we see that the local imaging characteristics of a given anion in a given orientation vary as a function of defocus. Given the variation in contrast as a function of defocus, we would expect that performing the complementary operation of simulating a graphene film with applied curvature and then varying the local height of the anions would produce a similar progression in contrast and this indeed the case (i.e. Figs. 2(a)-(c)). In this second set of simulations we find a commensurate variation in the image contrast due to both the specified polyoxometalate anions (and the $[W_6O_{19}]^{2-}$ ion in two distinct orientations) as a function of their orientation with respect to the imaging electron beam and also as a function of relative height on the film. Although we have deliberately exaggerated the local curvature of the theoretical graphene monolayer support, we find a sufficient variation in the local contrast of the anions between height differences of 2-5 nm that it ought to be able to image this difference for experimental curved graphene films.

References

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[4] J. Sloan et al., submitted.

Figures

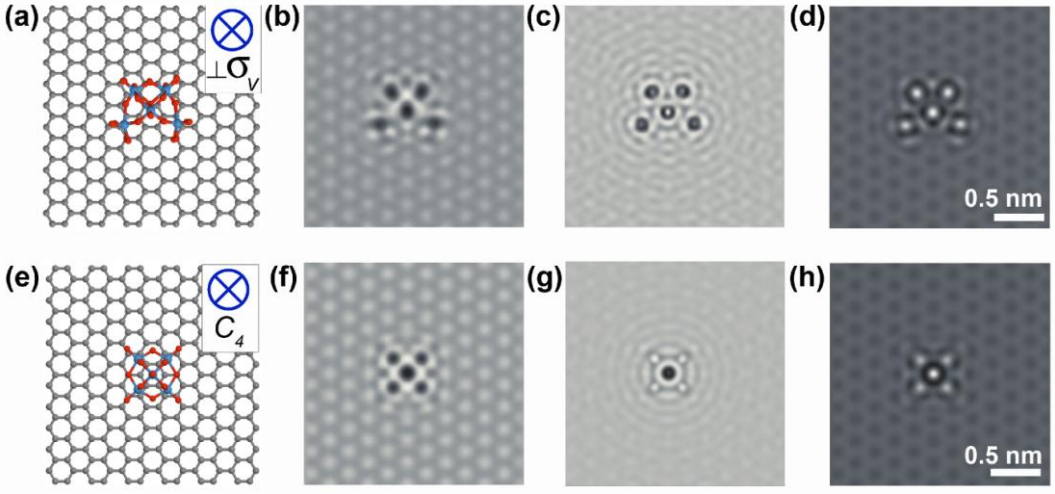

Figure 1. (a) *Composite structure model of the $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ lacunary Keggin ion mounted on graphene projected in a direction orthogonal to its σ_v mirror plane which is arranged parallel to the supporting graphene plane.* ***(b)*** *Underfocus image simulation of (a) (C_s = 0.02 mm and Δf = -5 nm).* ***(c)*** *At focus image simulation of (a) (C_s = 0.02 mm and Δf = 0 nm).* ***(d)*** *Over focus image simulation of (a) (computed with C_s = 0.02 mm and Δf = +5 nm).* ***(e)*** *Composite structural model with the $[W_6O_{17}]^{2-}$ Linqvist ion projected along its C_4 rotation axis with the graphene support arranged with its plane orthogonal to the axis and the electron beam direction.* ***(f)*** *Underfocus image simulation of (e) (C_s = 0.02 mm and Δf = -5 nm).* ***(g)*** *At focus image simulation of (e) (C_s = 0.02 mm and Δf = 0 nm).* ***(h)*** *Over focus image simulation of (e) (C_s = 0.02 mm and Δf = +5 nm).*

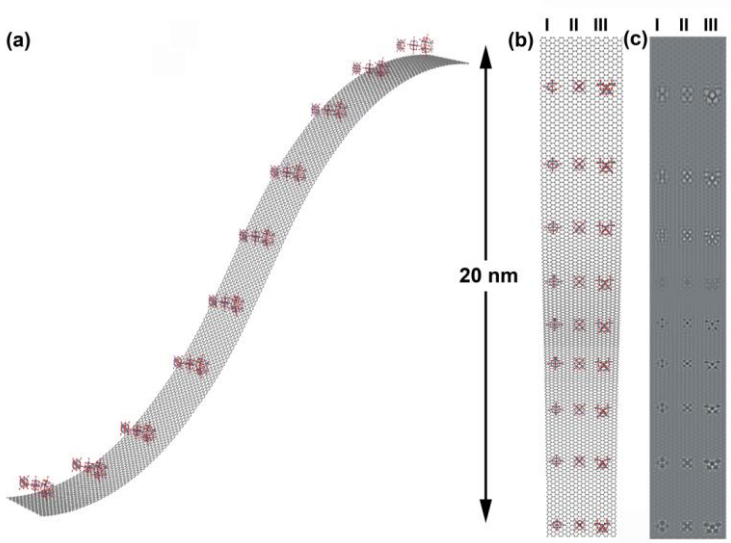

Figure 2 ***(a)*** *Schematic view of a curved graphene sheet with a height of 20 nm with both $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ lacunary Keggin ions and $[W_6O_{19}]^{2-}$ Linqvist ions arranged at different heights on the curved sheet.* ***(b)*** *Top down projection of the sheet in (a) showing effectively columns of $[W_6O_{19}]^{2-}$ Linqvist ions projected along C_2 (i.e.. column* ***I****) and C_4 (i.e. column* ***II****) and also the the $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ lacunary Keggin ion arranged with its σ_v mirror plane arranged orthogonal to the electron beam direction (i.e. column* ***III****). Because of the deliberately exaggerated curvature of the graphene sheet, the respective orientations of the anions have been adjusted so that the relevant projections are aligned parallel to the electron beam direction (c). Optimum focus image simulation of the model in (b).*