Imaging the structure, symmetry and surface-inhibited rotation of polyoxometalate ions on graphene oxide

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Extracting structural information routinely and dynamically from single molecules remains a significant challenge in spite of recent advances in this field. While it has been possible to produce atomically resolved images of static or moving molecules by either scanning tunneling microscopy (STM) or atomic force microscopy (AFM), the structural features produced are imprecise unless highly stringent experimental procedures are applied. Another approach has been to image molecules mounted within carbon nanotubes by low voltage, aberration corrected transmission electron microscopy (AC-TEM). For example, functional groups tethered to fullerenes and the structure of D_{5d} symmetry C_{80} or I_h symmetry $Er_3N@C_{80}$ molecules can be imaged at 80 keV using this approach. However this methodology is limited by the internal van der Waals surface of the host tubules, which restricts both the size of the molecules that can be imaged and also constrains their *in situ* motion. A new prospect is presented by the imaging of molecular-scale species on atomically thin 2D supports such as graphene or graphene oxide (GO).[1] These substrates do not exhibit the steric constraints of nanotubes and provides a periodic support that acts as both an *in situ* calibration and also a crystalline basis for tracking molecular motion.

In this presentation, we show how molecular-scale low-symmetry polyoxometalate anions can be imaged on GO by low-voltage AC-TEM, enabling static and dynamic imaging studies to be performed with precision. Imaging studies were performed on discrete C_{2v} $[\gamma\text{-SiW}_{10}O_{36}]^{8-}$ lacunary Keggin ions, a lower symmetry molecular species than the O_h symmetry $[W_6O_{19}]^{2-}$ ion previously imaged within carbon nanotubes.[2] Polyoxometalates (POMs) are a diverse family of compounds based on assemblies of metal oxide polyhedra with potential applications in medicine, catalysis, electrochemistry, nano-scale devices and as building blocks for more mesoscale superstructures. Lacunary Keggin ions differ from 'full' Keggin ions (e.g. $[\alpha\text{-PMo}_{12}O_{40}]^{3-}$) in that they have a reduced number of polyhedra per anion, exposing a reactive structural defect or 'lacuna' on the POM surface, and form lower symmetry structures that can exhibit greater catalytical activity and a tendency to align preferentially on electrode surfaces. Observing the behaviour of these ions on GO has revealed surface behaviour not previously reported for other ultra-thin TEM supports.

Atomic-resolution imaging of discrete $[\gamma\text{-SiW}_{10}O_{36}]^{8-}$ lacunary Keggin ions dispersed onto monolayer graphene oxide (GO) was achieved by 80kV aberration corrected transmission electron microscopy. Under low electron beam dose, individual anions remained stationary for long enough that a variety of projections of discrete C_{2v} symmetry $[\gamma\text{-SiW}_{10}O_{36}]^{8-}$ anions was observed and structural information extracted with ca. ± 0.03 nm precision. Unambiguous assignment of the orientation of individual ions with respect to the point symmetry elements was determined. The ion was imaged along its two-fold C_2 axis (Fig. 1(a)-(e)) or orthogonally with respect to one of two non-equivalent mirror planes (i.e. σ_v). Continued electron beam exposure of a second ion imaged orthogonal to σ_v (Fig. 2(a)) causes it to translate and/or rotate in an inhibited fashion so that the ion can be viewed in different relative orientations. The inhibited surface motion of the anion, which is in response to H-bonding-type interactions (Fig. 2(b)), reveals an important new property for GO in that it demonstrably interacts far more strongly with supported molecules than other ultrathin supports, including graphene. This behaviour indicates that GO has more in common with similar substrates used in imaging techniques such as AFM and STM and this feature also sets it apart from other support films used in transmission electron microscopy.

References

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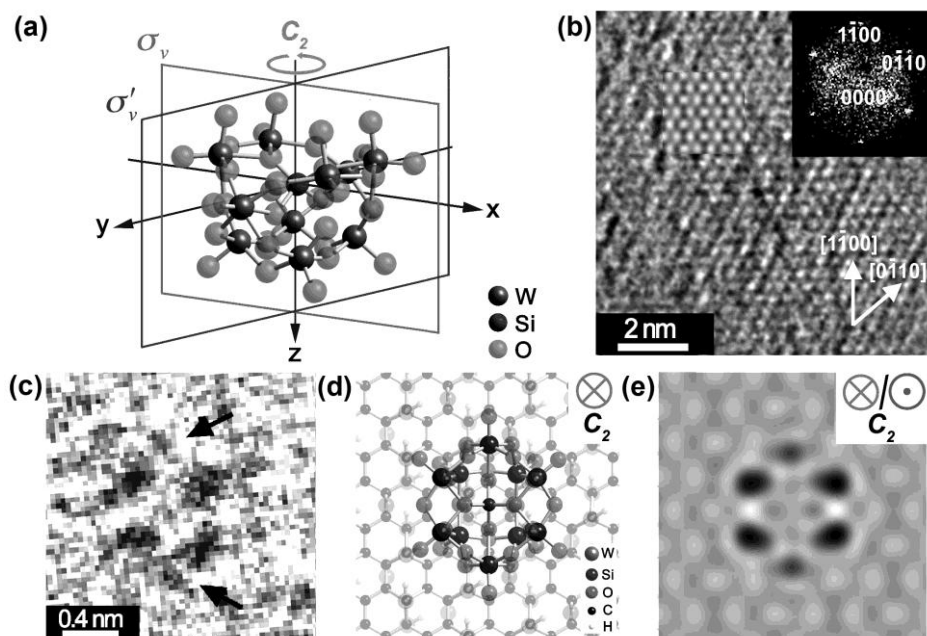
Figures

Figure 1. (a) Perspective view of the $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ ion with the C_2 axis and non-equivalent σ_v and $\sigma_v{}'$ planes indicated. **(b)** HRTEM image of monolayer GO with indexed FFT and inset image simulation based on an ordered GO model[24]. The lattice vectors are indicated at the bottom right. **(c)** $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ ion imaged approximately along C_2. The two arrows indicate diffuse contrast due to the two single WO_6 octahedra on the periphery of the anion. **(d)** Structure model of a single $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ ion viewed along C_2 mounted on GO. **(e)** HRTEM image simulation produced from the model in **(d)**. The contrast is identical regardless of whether the anion is viewed along $\otimes$ or $\odot$ with respect to z or situated above or below the GO support.
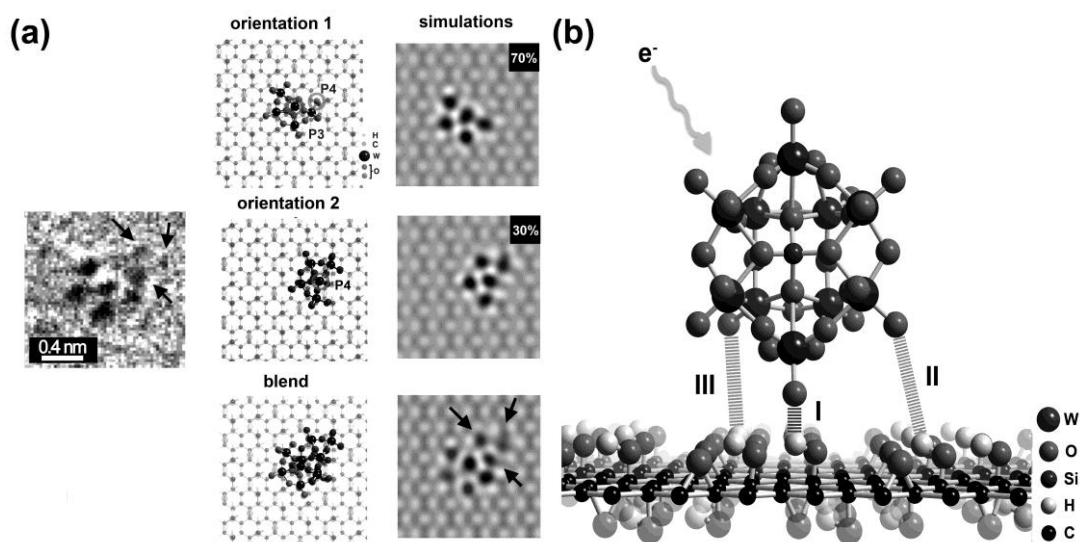

Figure 2**(a)** 0.8 s exposure HRTEM image (left) of a single $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ ion supported on monolayer GO. The main black spots correspond to strongly scattering W_2 atom columns. The indicated weaker spots correspond to a secondary orientational state of the anion captured during the exposure. The models (middle column) and simulations (right column) show how these two orientations are 'blended' to produce the final image. **(b)** Perspective schematic depiction of the proposed H-bonding interactions (**I-III**) which constrain the motion of the $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ ion on GO.