STM investigations of nanoscale materials

Characterisation of surfaces and polyoxometallate substrates deposited onto them

Tom Hopper*, Dr. Andrew Pike, Dr. Bee-Min Goh Chemical Nanoscience Laboratory, School of Chemistry

t.hopper@newcastle.ac.uk
Student Number: 120228504
Course: F103 MChem with Hons in Chemistry

Newcastle University

Introduction & aims

The **scanning tunnelling microscope (STM)** is a tool used by chemists and materials scientists to image surfaces and probe their electrical properties. In the right conditions, images of individual atoms can be obtained.

Polyoxometallates (POMs) are anions composed of metal and oxygen atoms. They are of interest in the fields of materials science and catalysis.

Aims:

- To become able to operate the STM and develop an appreciation for **scanning probe microscopy (SPM)** techniques
- To test the ability of STM and other SPM techniques in resolving atomic resolution images of POM arrays on conductive surfaces

Background

The STM works on the principle of **quantum tunnelling**. In classical physics, a particle will have to gain enough energy to overcome a potential barrier. However, in quantum physics, the Heisenberg Uncertainty Principle states that quantum-scale objects such as electrons have a large uncertainty associated with their position (and momentum). The electron exhibits wave-like behaviour and can tunnel through the barrier and appear on the other side, without ever having to gain the energy needed in the classical system.

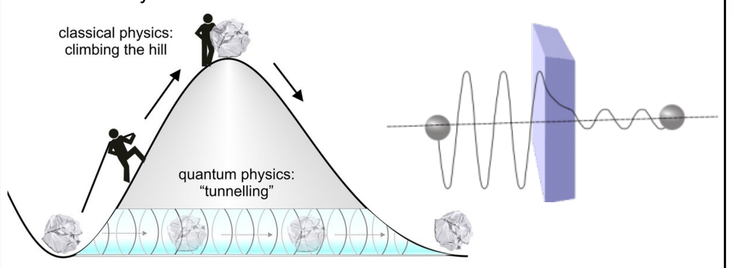

Figure 1. Left: Representation of classical vs. quantum system
Right: Wave-function of a particle tunnelling through a potential barrier

In terms of the STM, the "barrier" is the gap or vacuum between the tip and sample. By applying a potential difference (**bias**) between the tip and conductive sample, electrons pass between them. This movement of charged particles generates a **current**.

In **constant height mode**, the vertical position of the tip remains unchanged, and the image of the surface is obtained from changes in the current as the tip scans along the sample and encounters variations in the topography of the surface.

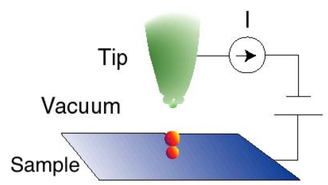

Figure 2. Diagram of STM tip scanning a surface

STM probes are typically made from Pt/Ir alloy, and are consequently quite expensive. To obtain a good image, the tip of the STM probe should be sharp. In principle, at the very edge of the tip should be a single atom. This is difficult to achieve by mechanical cutting.

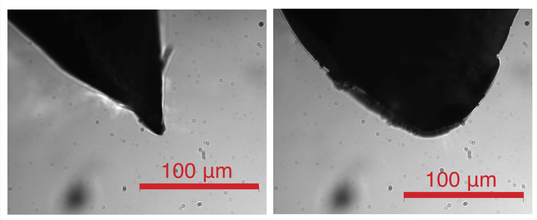

Figure 3. Images of sharp and blunt STM probes (left and right respectively), taken with an optical microscope at 40× magnification

Surfaces & substrates

Initially, ferrocenyl substrates on silicon were to be imaged. This was difficult for a beginner. Silicon is **semiconductive** and needs a high bias for successful imaging. The high voltage applied to the samples oxidised the surfaces before any features could be identified.

A different surface was selected. **Highly Oriented Pyrolitic Graphene (HOPG)** has a very distinctive honeycomb pattern of carbon atoms arranged in six-membered rings. This surface is much less susceptible to oxidation and can be imaged at a lower bias.

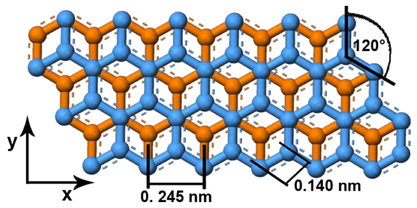

Figure 4. Diagram of a two-layer HOPG lattice with various dimensions labelled[1]

A more suitable substrate had to be selected. **Keggin type POMs** were selected for their distinctive size and packing and also ease of deposition.[2] The general molecular formula of the POM anions is $[XM_{12}O_{40}]^{3-}$ where X is a heteroatom and M is a metal (Mo or W). Two of these Keggin POMs were analysed, both containing phosphorus, but with different metals and counter-ions; $(TBA)_3[PMo_{12}O_{40}]$ in MeCN (TBA = tert-butylammonium) and $H_3[PW_{12}O_{40}]$ in H_2O. These POMs were drop-cast as 0.01 M solutions onto freshly cleaved HOPG surfaces, and allowed to dry for about an hour.[3]

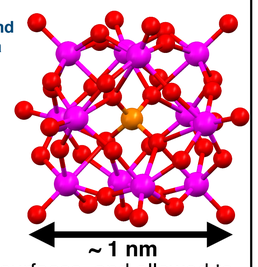

Figure 5. Ball and stick model of a Keggin anion

Phosphorus

Oxygen

Molybdenum or tungsten

STM Analysis

Figures 6 and 7 show the distinctive honeycomb pattern of HOPG. The blue dots indicate the approximate positions of carbon atoms in a six-membered ring. The **atom-to-atom distance** (length of a C-C bond) and **lattice constant** (diameter of a six-membered ring) are labelled. The literature values for these parameters are 1.42 Å and 2.46 Å respectively,[1,4] which agree with the measurements in Figures 6 and 7. Figure 7 is inferior in quality to Figure 6. The STM is very sensitive to vibrational, sonic and electronic **interference**. Various shielding apparatus are used to minimise this noise. Ideally, the experiment would be performed in a vacuum at very low temperatures. Even then, controlling the **feedback** is largely a matter of trial and error.

Figure 8 shows the HOPG surface after treatment with $(TBA)_3[PMo_{12}O_{40}]$. At first glance, there is a cubic array of features which are obviously too small to be the POM. It was assumed that these features were cations sitting on the aromatic rings, but **cross sectional analysis** revealed that the features had a diameter of around 0.179 nm. This is too small to be the counter-ion TBA, and still too small to be sodium, which is used in the synthesis of the POM. Inversion of the image reveals it is just bare HOPG, as shown in Figure 9. This inversion effect is believed to arise from the high bias and current used to image the POM relative to the bare HOPG samples.[5]

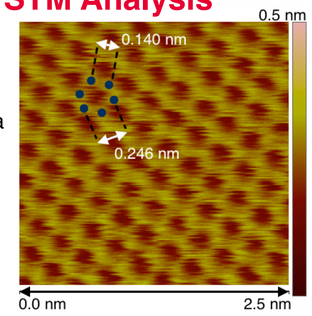

Figure 6. Reference STM image of bare HOPG recorded by Dr. Goh
Scan rate: 30.5 Hz
Current set point: 0.96 nA
Bias: 10 mV

Atom to atom distance = 0.140 nm
Lattice constant = 0.246 nm

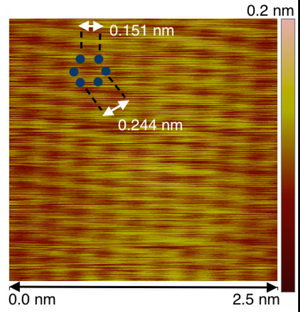

Figure 7. 2.5 nm x 2.5 nm STM image of bare HOPG
Scan rate: 8.72 Hz
Current set point: 2.50 nA
Bias: 150 mV

Atom to atom distance = 0.151 nm
Lattice constant = 0.244 nm

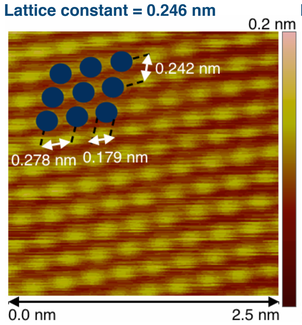

Figure 8. Image of HOPG surface after deposition of 0.01 M $(TBA)_3[PMo_{12}O_{40}]$
Scan rate: 61.0 Hz
Current set point: 5.00 nA
Bias: 300 mV

Lattice constants: 0.278 nm, 0.242 nm
Diameter of feature: 0.179 nm

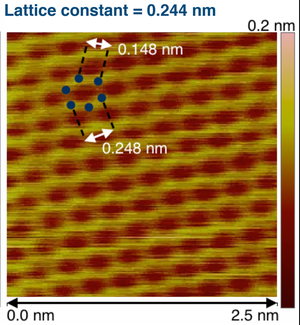

Figure 9. Inverted image of Figure 8. The array still seems more regular in some directions than others, however a honeycomb pattern can still be seen, and the dimensions of the labelled "six-membered ring" are very similar to those measured for the bare HOPG samples in Figures 6 and 7

AFM Analysis

Because the STM study of the POM was inconclusive, AFM was employed to confirm that the POM was deposited onto the surface. The **atomic force microscope (AFM)** works in a similar way to the STM, but the tip-surface interaction responds to intermolecular forces, as opposed to current. Hence a conductive surface is not necessary.

An AFM image of $(TBA)_3[PMo_{12}O_{40}]$ on HOPG was obtained but was too rough for accurate analysis. Instead, a smoother surface, mica, was selected. Figures 10 and 11 show the mica surface before and after deposition, respectively. It is clear that something is deposited onto the surface in Figure 11 from the presence of the "yellow" features. The vertical height of fifty features was measured, and a histogram was plotted. Statistical analysis reveals that the most of the features are between 0.400-0.499 nm tall, and the mean height is 0.520 nm. The actual diameter of the POM anion is 1.053 nm. These features are too small to be the POM anion.

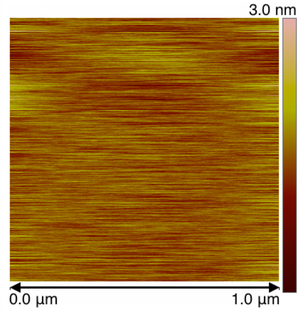

Figure 10. 1 μm x 1 μm AFM height image of bare mica surface

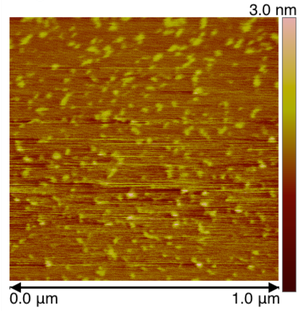

Figure 11. 1 μm x 1 μm AFM height image of mica surface after deposition of 0.01 M $(TBA)_3[PMo_{12}O_{40}]$

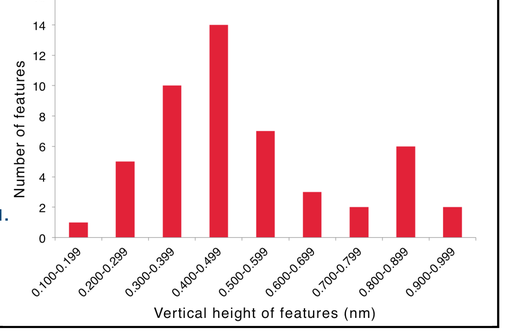

Figure 12. Histogram of vertical height of features against the number of features for the AFM image in Figure 11.
Mean height of features: 0.520 nm
Standard deviation: 0.204 nm
POM diameter: 1.053 nm

Conclusions & Future Work

- An understanding of STM and AFM techniques has been gained
- Silicon surfaces should be scanned with care to avoid oxidation of the surface
- Atomic resolution images of HOPG surfaces were obtained before and after the deposition of the POM $(TBA)_3[PMo_{12}O_{40}]$, however this POM could not be observed by STM. This requires further investigation
- AFM was used to investigate if the POM was deposited on a mica surface. Though something was deposited onto the surface, this species is unidentified
- Different POMs, i.e. $H_3[PW_{12}O_{40}]$, could not be analysed due to time constraints and because they gave very poor quality images

Acknowledgements & References

I would like to thank Dr. Andrew Pike and Dr. Bee-Min Goh for their continued support throughout the project, as well as Newcastle University for funding the scholarship. Special thanks are reserved for Dr. John Errington for his expertise regarding POMs, and his colleague Rebecca Short for depositing the POMs onto the surfaces.

1. PHYWE, Atomic resolution of the graphite surface by STM, http://www.phywe.com/index.php/fuseaction/download/lrn_file/versuchsanleitungen/P2532000/e/P2532000.pdf (Accessed October 2014)
2. M. S. Kaba, I. K. Song, D. C. Duncan, C. L. Hill, M. A. Barteau, *Inorg. Chem.*, 1998, **37**, pp. 398-406
3. M. S. Kaba, M. A. Barteau, W. Y. Lee, I. K. Song, *Appl. Catal., A*, 2000, **194**, pp. 129-136
4. S. H. Cohen, M. L. Lightbody, *Atomic Force Microscopy/Scanning Tunneling Microscopy 2*, Plenum Press, New York, 1997, pp. 77
5. G. Teobaldi, E. Inami, J. Kanasaki, K. Tanimura, A. L. Shluger, *Phys. Rev. B*, 2012, **85**(8), pp. 1-15