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SCIENTIFIC REPORT (REFERENCE: COST-STSM-CM0601-04582)

Title: Nanoscale potassium islands and gold nanoparticles on graphite

Purpose of the visit

Hereby, I describe the scientific outcome of my Short Term Scientific Mission (STSM) during 29.03.-03.04.2009 in the group of Prof. Richard E. Palmer (Nanoscale Physics Research Laboratory) in the University of Birmingham.

I have recently worked in collaboration with Prof. Palmer's group concerning STM imaging of nanoscale potassium islands on graphite. By combining theory and experiments, we have explained that the observed bright rings around K islands are STM field-induced effects, and our work has been published in Physical Review Letters [1]. The purpose of this visit was to continue our fruitful collaboration (experiments and theory) on further topics. The first one concerns STM imaging of alkali metal monolayer islands (K, Rb, Cs) on graphite in the low coverage, dispersed (Wigner-type) phase (as discovered by Palmer and Li), which should display entirely different properties from the close-packed K islands. The work is performed as previously: experiments being carried out in Birmingham, while I and my local colleagues in Finland perform the theoretical work (electronic structure calculations, density functional theory). We also wanted to develop a complementary collaboration on AuNPs. Our work on AuNPs has attracted broad international attention [2,3] and the Birmingham group is currently deploying 3D atomic resolution electron microscopy to analyse the structure of the passivated Au38 cluster. A crucial question is how to compare quantitatively the experimental results with the simulations of different theoretical models. This is rarely attempted in electron microscopy and will be an important challenge.

Description of the work carried out during the visit

Our collaboration includes contributions from both experiments and theory. I am a theoretician and perform density functional (DF) simulations of electronic structure on various topics. Such calculations, that incorporate the electronic structure of the system of interest, are both cpu- and time-consuming and cannot be carried out in few days. The work plan of this visit was to analyze already measured STM and TEM data, plan related DF simulations, and discuss further experiments on these topics. No experiments were performed during this visit. In the following, I shall mainly present DF results that I have obtained after my visit for the dispersed phase of K atoms on graphite. Further

simulations are being performed, and I must emphasize that the DF simulations of this problem will take several months to complete.

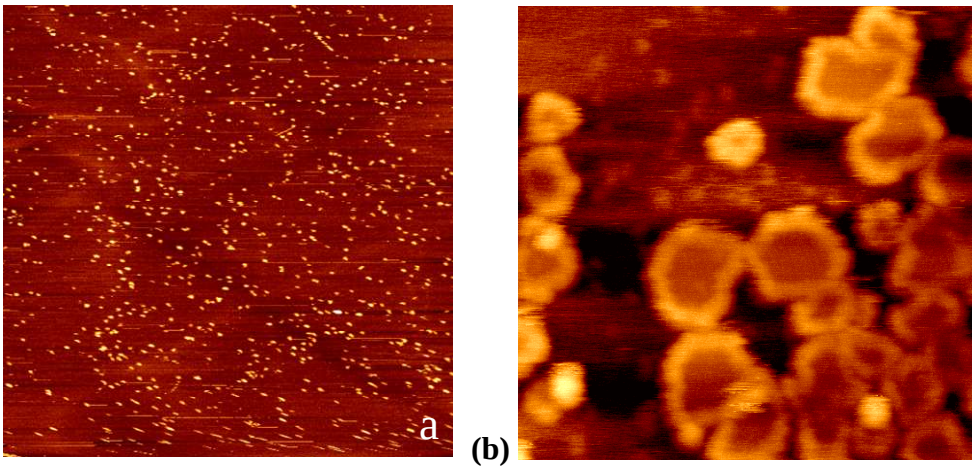

Figure 1. STM images of K islands on graphite. (a) Dispersed phase of K adatoms and clusters, and (b) nanoscale K islands and sparsely distributed K adatoms (weak features).

We reported earlier [1] that the observed bright rings around the nanoscale K islands in the STM images were caused by the measurement itself: The positively charged STM tip results in an electric field which is capable of attracting a significant portion of the electron density back to the adsorbate layer. The restored charge accumulates in the island perimeters [beaches, see Fig. 1(b)]. There are also other (unpublished) features of great interest in the K-graphite system. Further analysis of the measured STM images indicates that single K adatoms [dispersed (7x7) construction] appear much larger (1.5 nm, "supersized") in the image, as illustrated in Fig. 1(a). Another interesting feature is that at higher coverage, the dispersed phase regions are more likely to occur in the vicinity of the islands resulting in areas of very low coverage elsewhere. Our DFT calculation aim to shed light onto these observations, and further STM measurements are planned in order to achieve high-resolution images at low temperatures.

In addition, we are working on the electron microscopy measurements of small thiolate-protected gold nanoparticles (AuNPs). The system of interest is the $Au_{38}(SR)_{24}$ cluster whose structural determination is still lacking. Theoretical models have been proposed for the cluster geometry, and we have compared those with the recent TEM measurements. The preliminary results are encouraging as we are able to distinguish the most promising geometry, but further experiments are needed in order to obtain TEM images of higher resolution. These will be conducted in near future.

Description of the main results

A. STM images of alkali metal monolayer islandson graphite: dispersed phase of K

The interaction between the K adatom and the surface can be illustrated by the electron density redistribution upon K atom adsorption, and the results are shown in Figures 2 and

3. These plots have been produced by calculating the electron density of a separated K adatom and graphite substrate, and subtracting those from the electron density of the bound system. The system comprises one K atom in a (7x7) construction (hexagonal periodic boundary condition) and four graphene layers (392 C atoms). The K atom prefers the hollow site in the middle of graphite hexagon and the surface separation is 2.72 Å, as observed in our previous work for the (4x4) construction [4].

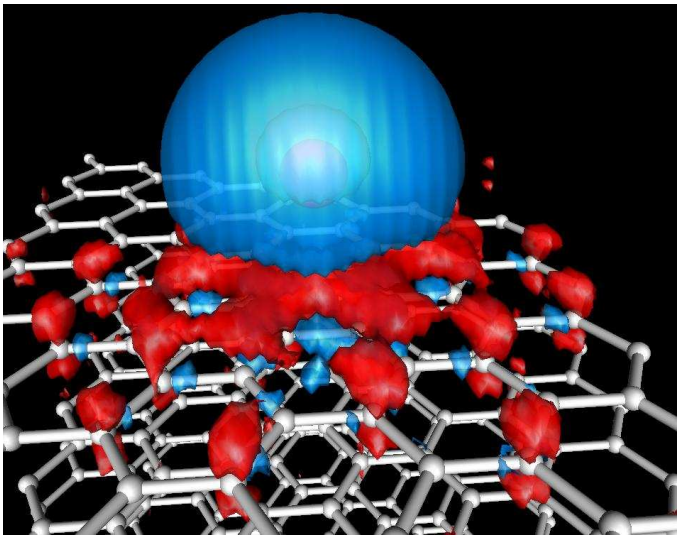

Figure 2. Electron density accumulation/depletion isosurfaces of a K adatom on graphite (density difference values ±0.0005 e/a_0^3). Color key: Red, accumulations; blue, depletion.

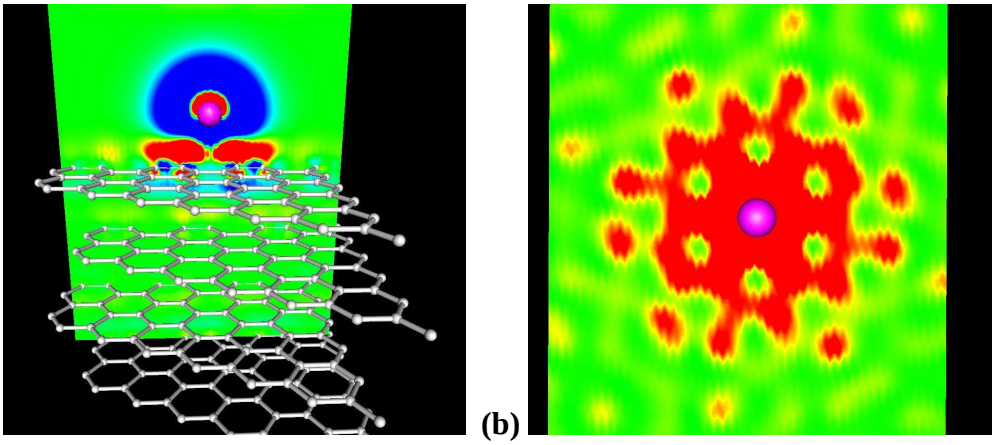

Figure 3. Cutplane representations of the charge density redistribution. Color key: Red, accumulations; blue, depletion.

Figures 2 and 3 illustrate a sizable charge transfer from the K atom to the substrate. The numerical value is 0.5-0.9*e* depending on the method of evaluation. Nevertheless, it is clear that K is highly cationic (depleted 4s electron), and that the charge is mainly transferred to the topmost graphene layer (carbon p_z-orbitals). The lateral cutplane image in Fig. 3(b) shows that the area of charge transfer is sizable with ~1 nm diameter. This

may be related to the observed STM effect, and further calculations for producing theoretical STM images are in progress.

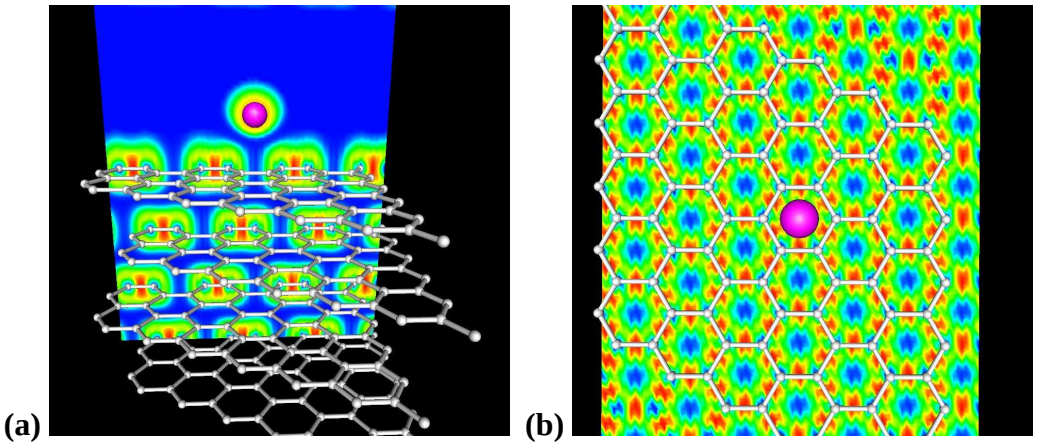

Figure 4. Electron localization function (ELF) of K adatom on graphite. Color key: Red, localization (covalent bonding); green, metallic bonding (homogeneous electron density); and blue, no overlap.

An alternative way to inspect the chemical interaction is to plot the electron localization function (ELF) which is shown in Figure 4. The ELF is defined as the measure of finding two electrons in the same location and its value ranges from 0 (no overlap) to 0.5 (metallic bonding) and to 1.0 (covalent bonding). The covalent C-C bonds (electron pairs) are visible in Figure 4 as red areas, and the green ring around the K atom is a sign of metallicity. Clearly, there is no chemical bonding between the K atom and graphite (intermediate blue region) and the adsorbate-substrate interaction can be characterized as purely ionic.

B. Electron microscopy of thiolate-protected AuNPs: $Au_{38}(SR)_{24}$ on amorphous carbon

The measured TEM images indicate that the $Au_{38}(SR)_{24}$ nanoparticle has a prolate overall shape, and that some Au atoms are separated as “satellites” from the main body of the cluster. This is fully consistent with the recent observations on other thiolate-protected AuNPs, where part of the Au atoms are lifted from the metallic core to the ligand shell [2,3]. According to theory, the most promising candidate up-to-date for the $Au_{38}(SR)_{24}$ geometry is shown in Figure 5. The cluster shape is indeed prolate, and it comprises a core of 23 Au atoms with two face-sharing icosahedra. The remaining 15 Au atoms (orange) participate in the 9 capping S-Au-S oligomers (6 long and 3 short units). Based on this geometry, the simulated TEM images resemble the measured ones closely. However, the varying cluster orientation is problematic in the experiments as the cluster can stick in many ways on amorphous carbon, and one plan is to repeat the TEM measurements on defect-free graphite. This would enforce the prolate clusters to lie in parallel along the surface, which would reduce the number of rotational degrees of freedom down to two and make the comparison with theory easier.

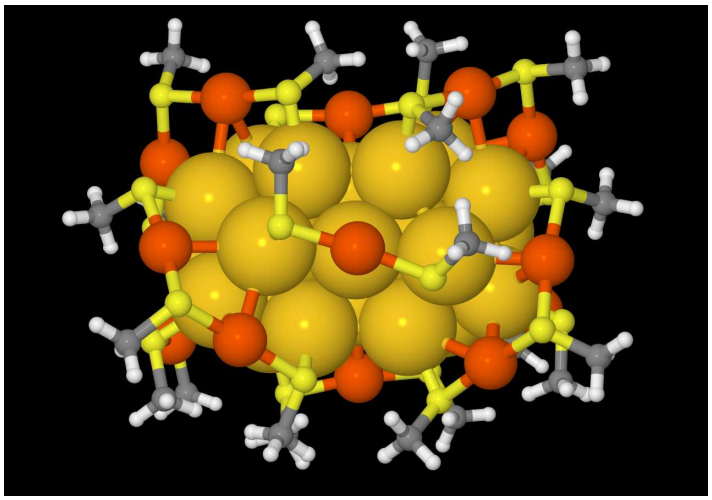

Figure 5. Putative ground state geometry of $Au_{38}(SR)_{24}$ nanoparticle ($R=CH_3$). Color key: Gold, Au in the core; orange Au in the ligand shell; yellow, sulfur; grey, carbon; and white, hydrogen.

Future collaboration and publications with the host institution

The work described here is still in progress. We consider that both topics, STM imaging of dispersed phases of K and AuNP electron microscopy, are potential projects for high-impact journals. Further calculations will be performed within the next three months and new STM and TEM experiments are planned to be carried out. Collaboration on other topics is also likely. One potential project would be the modeling of cluster-surface collisions of Au nanoparticles together with TEM measurements.

References:

1. F. Yin, J. Akola, P. Koskinen, M. Manninen, and R.E. Palmer, *Bright Beaches of Nanoscale Potassium Islands on Graphite in STM Imaging*, Phys. Rev. Lett. **102**, 106102 (2009).
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