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Change in the conductivity of single naked metallic clusters by ligation

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It is shown by scanning tunnelling microscopy current–voltage measurements that the ligation of Ag_n-clusters by excess (PPh_3) produces a tunnel system based on the resulting $Ag_n(PPh_3)_m$ clusters in which correlated single-electron tunnelling can be realized.

Cluster molecules on the surface of highly orientated pyrolytic graphite (HOPG) can be detected by scanning tunnelling microscopy (STM). Japanese scientists[1] have observed the randomly positioned clusters of Rh and Pt {$Rh_4(CO)_{12}$ and $[Pt_{12}(CO)_{24}][NEt_4]_2$} as scattered humps in STM images. We have obtained the similar results using other clusters: $Pt_5(CO)_6(PBu_3)_4$, $Pt_{17}(CO)_{12}(PEt_3)_8$, $Pd_{10}(CO)_{12}(PBu_3)_6$ and $[Fe_6C(CO)_{16}]^{2-}[NEt_4]^{2+}$; in all cases single free-lying clusters on the HOPG surface were observed. However, we believed that only results of topograpy and surface elemental analysis together with conformity of the average diameter of the hillock to the size of cluster, known from X-ray analysis, are insufficient proof that observed peculiarities of surface topography are actually clusters. We therefore carried out a number of additional experiments.

One possible use of STM, apart from topography studies, is correlated single-electron tunnelling (SET) in a 'tip–particle–substrate' system.[†] Earlier we have shown that in accordance with theory it is possible to achieve correlated SET through the cluster molecule with sufficiently less temperature restrictions.[4] In this work the current–voltage characteristics (CVC) of tunnel system based on the above cluster molecules on HOPG are studied. SET was observed at room temperature in a wide range of clusters.[‡] It was shown that CVC measured in different parts of surface differ greatly fom one another: the shape of the curve depends on whether the STM tip is located above a level surface area or above 'hump' (caused by cluster and/or cluster fragments). With a level surface no distinguishing features in CVC are observed except for the nonlinear current at a large voltage and certain asymmetry. In contrast, the CVC measured near the single peak shows a distinct blockade area at the origin of coordinates (BA, Figure 1) on

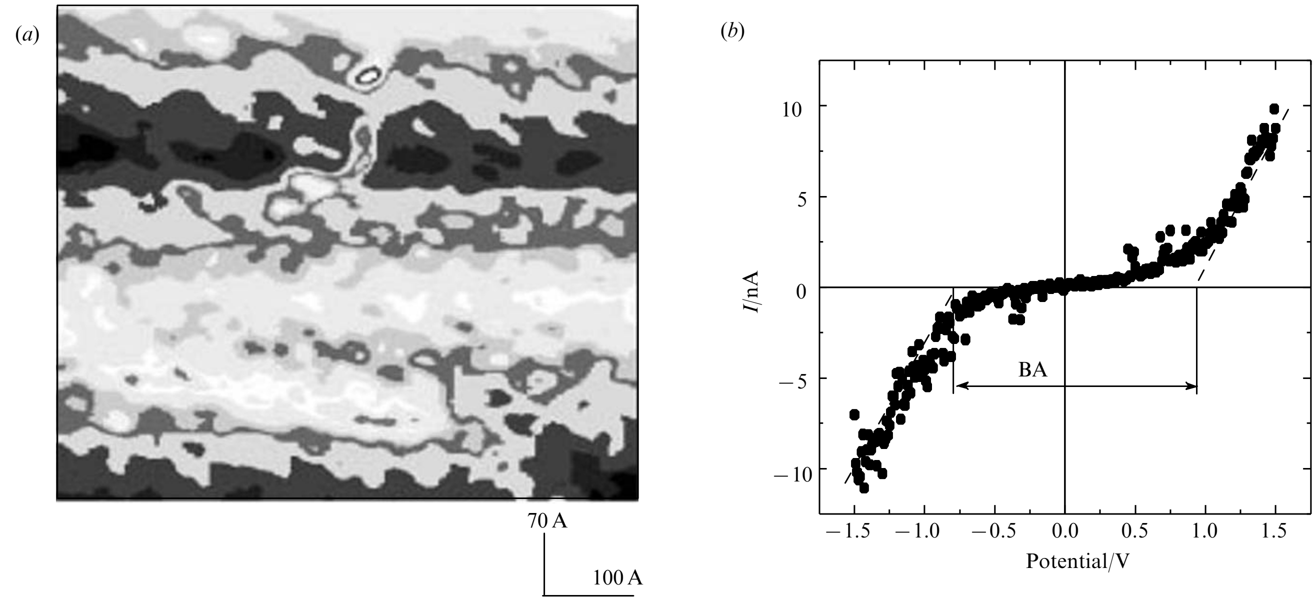

Figure 1 (*a*) Room temperature STM image of $Pd_{10}(CO)_{12}(PBu_3)_6$ clusters deposited on a HOPG surface where single clusters can be observed. Arrows indicate the position of the tip during the CVC recording. (*b*) Tunnel characteristic CVC of the cluster; BA — the blocade area.

[†] For a detailed introduction to this subject see refs. 2 and 3.

[‡] In our experiments microscope Nanoscope 1 used for topography and CVC measurements at $T = 300$ K. STM-images were made by constant current mode, usually at a tunnel current of 500 pA and a voltage of 500 mV. Current–voltage characteristics of the tunnel system based on the clusters were measured at the broken feedback loop of the STM by the usual technique, described elsewhere (see for example, ref. 2).

[§] The samples were prepared by the following procedure: HOPG fragments were split along in layers in saturated solutions of the clusters. It was expected that the main part of the interlayer energy (16.8 J mol^{-1}) will be used for the sorption of the clusters. The samples were prepared for measurement after usual washing and drying procedures.

[¶] For this purpose the silver clusters in naphthalene matrix with average diameter 40±10 A (LAS), obtained by reduction of the silver salts by lithium naphthalenide were used. In this case the samples were prepared in the same manner as the above samples but the suspension of silver clusters from the dissolution of the naphthalene matrix in hexane was used instead of the cluster solution.

[††] Metallic (or close to it) conductivity nature of the 'naked' clusters is well established both theoretically and separately, experimentally. So, IP of cluster Ag_{55} (*d ca.* 12 A) is 6.1 eV, but the width of conductivity band is evaluated to be 5 eV, the value of the IP rather quickly approaches the work function of the electron for bulk silver (4.3 eV) with increasing cluster size.[6]

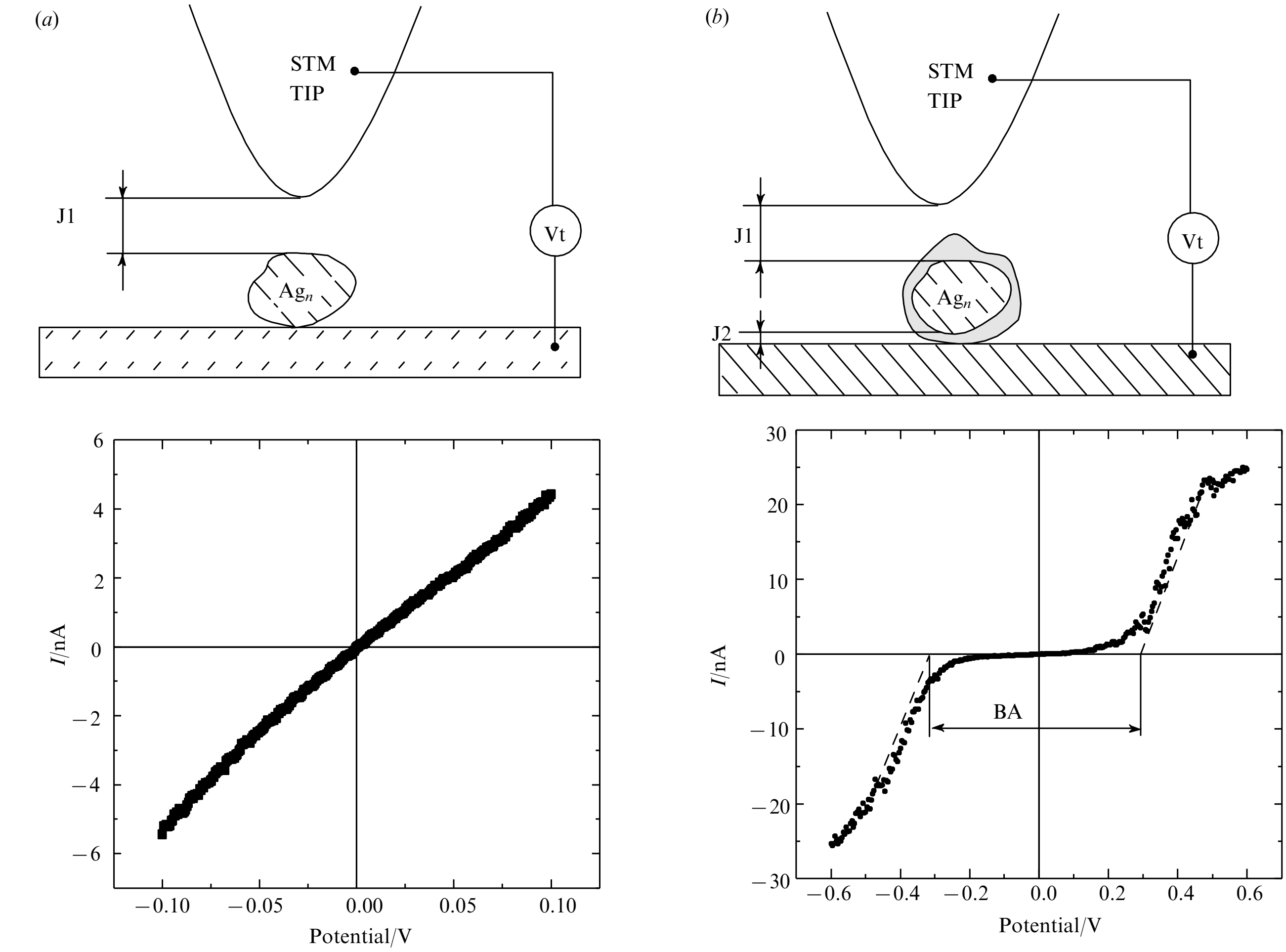

Figure 2 (*a*) CVC of the tunnel system 'tip–'naked' silver cluster (Ag$_n$)–substrate'. (*b*) CVC of the tunnel system 'tip–[Ag$_n$(PPh$_3$)]–substrate'.

which conductivity is drastically (more than 10 times) suppressed.[§] It is reasonable to suggest that according to the theory,[5] observed CVC's are associated with correlated single-electron tunnelling in the tunnel system 'tip–cluster (the closed, ligands insulated 'reservoir' of electrons)–substrate' formed at the location of the STM tip above the cluster.

The obtained results allowed us to assemble single clusters from the metallic core and ligands on HOPG surfaces. The samples were originally made by the deposition of 'nacked' silver clusters with average diameter 40±10 A on the freshly prepared HOPG surface.[¶] The above clusters are stable due to the interaction with the HOPG surface as a macro-ligand. In most cases topographic images have shown a large number of clusters, *i.e.* the graphite surface is largely covered by the silver. However, in many cases single free-lying clusters were observed on the HOPG surface of sizes 30–50×20–30 A. In addition larger roughness was observed which probably can be associated with cluster aggregation. The location of the STM tip above the single cluster allowed the CVC to be measured, Figure 2(*a*). The CVC in this case describes the electrical conductivity of the single tunnel junction 'tip–barrier (J1)–conductor' in which the role of the 'conductor' is the 'naked' metallic cluster deposited on the conductive substrate without any insulation (barrier-free), [Figure 2(*a*)].[††] If this is the case the distinction between the curves in Figure 1 (CVC of a two-barrier system) and Figure 2(*a*) (CVC of a one-barrier system) arises from differences in the nature of particles investigated: the ligands in the molecular cluster can serve as an a additional tunnel barrier between the metallic core and the substrate forming a two-barrier system in which the correlated tunnelling of electrons can be observed more easily than in one-barrier system. The following experiment was carried out to verify this and that the CVC in Figure 1 corresponds to the conductivity of the molecular cluster. A substrate, already containing the 'nacked' silver clusters [with a CVC like that shown in Figure 2(*a*)] was treated with an organic solution of PPh$_3$.[‡‡] The topography of the surface did not change but the CVC of the new clusters was considerably affected: the I–V curve [Figure 2(*b*)] has a region of strongly suppressed conductivity, closely resembling in Figure 1 (BA).[§§] The reason is that an insulating barrier in the form of ligands [Figure 2(*b*)] was formed around the metallic core and as a result single-electron tunnelling in the double-junction tunnel system 'STM tip–barrier (J1)–cluster–barrier (J2)–substrate'[¶¶] occurs. The theory of single-electronics[5] provides an approximate evaluation of the dimensions of the cluster on the HOPG surface from the size of the CVC area with suppressed conductivity (Coulomb blocade). Such an estimate gives a value of *ca.* 50 A, that closely agrees with the topography data and with the sizes of the silver clusters increased by the thickness of the ligand shell.

We have shown that ligand and core manipulations allow the generation of structures with unique physical properties. It provides the basis for work in the field of the creation of functional elements of single-electronic molecular devices for nanoelectronics.

‡‡ The HOPG samples with the silver clusters, obtained as above, were treated with a solution of PPh$_3$ in hexane and then were washed and dried.

§§ CVC's typical for the clean HOPG surface are observed at the location of the STM tip with the outside of the cluster.

¶¶ The drastic changes of the 'naked' metallic clusters resulted from 'immersing' them in the 'ligand medium' were repetedly noted (see, for example, ref. 7).

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