Electron transfer processes on Au nanoclusters supported on graphite

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Abstract Electron transfer processes play an important role in surface chemistry. This paper presents results of a study of changes in resonant electron transfer processes, as a function of gold cluster sizes, on the example of electron transfer between Li^+ ions scattered on Au clusters on highly oriented pyrolytic graphite (HOPG). The gold nanoclusters were grown on lightly sputtered HOPG surface in order to obtain a wide coverage distribution of clusters. The growth of clusters was monitored by scanning tunneling microscopy. We found that electron transfer is much more probable on small clusters, whose lateral size is of the order of 2 to 3 nm and height in the 1-nm range, than on bulk Au or thin Au films. A comparison with Au clusters grown on the semiconducting titania did not reveal significant differences with HOPG.

Keywords Au · Clusters · Electron transfer · Charge exchange · Ion scattering

Introduction

Supported metal nanoparticles have attracted much attention because of their use in many fields such as heterogeneous catalysis, microelectronics, photonics, etc. The size, shape, and nature of the support affect the properties of the nanoparticles and can play a crucial role in determining their use in a particular application [1–3]. The size effects have been discussed in terms of morphology and electronic structure and questions of the interaction with the substrate have been addressed [1–3]. As a function of increasing size, the electronic

structure of the clusters evolves from the extreme case of the atomic structure of its constituent atoms to the formation of a system with molecular character, which progressively evolves to that of a band structure of the bulk metal. The molecular aggregate is characterized by an energy gap between occupied and unoccupied levels. The increase in size of the system progressively leads to the disappearance of this gap and transition towards the valence band structure of the metal. According to existing literature, the number of atoms that are necessary to induce this transition may range from several tens to several hundred [1–12]. These evolutions have been studied in a series of elegant scanning tunnel microscopy (STM) studies for various metal clusters on various substrates [4–12].

In recent years, special attention has been paid to gold clusters since the discovery made by Haruta et al. [13] that nanosized gold clusters on titania (TiO_2) exhibit unique catalytic properties. Maximum catalytic activity for these clusters was found to coincide with the metal to nonmetal transition occurring in clusters with a diameter of approximately 3.0 nm, as determined by STS cluster band gap measurements [9–11]. This cluster diameter also coincides with a cluster growth transition from the nucleation of flat, two-dimensional clusters, to their agglomeration into three-dimensional structures, as measured by STM.

In surface reactivity, electron transfer processes between atoms and molecules and the surface play a crucial role. Most surface science experiments, which deal with the study of either the kinetics of adsorption/desorption (e.g., in temperature programmed desorption) or with characterization of adsorbates or products of reactions in situ, do not provide information on the time-dependent dynamics of the electron transfer or on the effect of the surface on the electronic states of the approaching gas-phase particle (atom or molecule). Our objective is to obtain this information in experiments that involve atom or ion beam scattering in which the energy and charge state of particles are monitored. We can, thus, obtain quantitative information in

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controlled conditions that can serve as a basis for theoretical modeling. In this study, we therefore focused on this aspect in the interaction of ions with clusters, since information on electron transfer processes can be directly obtained. Here, we focus on resonant neutralization of Li^+ ions. Because the ionization potential of Li is small and comparable with the workfunction of many metals, we deal with electron transfer near the Fermi level also relevant in chemical reactions.

When dealing with reactivity of clusters, besides size effects, the question of the role of the support has been put forth. Our studies therefore focus both on the changes of electron transfer processes as a function of cluster size and for different types of substrates. Recently, we investigated [14] how electron transfer processes are affected as a function of growth of clusters on the example of neutralization of Li^+ ions on Au clusters grown on TiO_2 . It was found that significantly more efficient neutralization occurs on small clusters, with neutralization decreasing as the cluster size grew. Similar results have been obtained by another group [15]. Here, we extend this work to the case of Au clusters grown on highly oriented pyrolytic graphite (HOPG) to investigate in particular if any strong changes would be observed when going from the semiconducting TiO_2 to the conducting graphite.

Experiment

The scattering experiments are performed in an UHV system [16]. The system is equipped with a differentially pumped ion gun used for low-energy ion scattering LEIS and Ar sputtering, and a Li ion gun which uses a getter source. Time of flight measurements were made using a channel plate detector set at 45° with respect to the Li gun, so that the scattering angle of ions corresponds to 135° . The detector is placed at the end of a 124 cm long flight tube.

Our measurements on neutralization probabilities involve low Li^+ beam flux, pulsed beam time of flight measurements. This precludes ion implantation effects. This was, however,

regularly checked by performing the same type of measurement, e.g., at a given energy or a given coverage in different conditions, i.e., in the beginning or end of a series of measurements or for different coverage “steps.” We, thus, exclude that our results are affected by Li implantation.

The HOPG single crystal is a 1-mm thick, $10 \times 10 \text{ mm}^2$ plate. The sample was cleaved in air with a scotch tape and then attached to a Ta plate, and mounted on a XYZ rotary manipulator. It was heated through a combination of radiation and electron bombardment using a tungsten filament positioned behind it. Before the measurements, it was degassed by heating to 600°C .

The chamber is equipped with a Knudsen cell metal evaporation source, and a quartz crystal microbalance. The deposition rate was generally varied between 0.01 and 0.1 eq mL (where 1 eq. mL=1 monolayer; corresponds to $1.4 \times 10^{15} \text{ atom/cm}^2$) as in our previous work [14].

In order to get an idea of the characteristics of the growth of gold clusters, some STM measurements were performed. The STM experiments were carried out in a separate setup [17], equipped with a variable-temperature STM (Omicron VT-STM) using polycrystalline W tips. The STM chamber is coupled with a second one, equipped with a LEED/Auger system and an Ar sputter gun. The same evaporator was used on both setups.

Results and discussion

Before presenting the results of the study of neutralization on Au clusters, we first briefly describe the results of the STM investigation of the characteristics of cluster formation on HOPG. On pristine HOPG, it is well known that clusters do not form on defect-free HOPG planes, but rather cluster along step edges. This was also verified in our experiments. In order to induce growth over the whole surface of graphite, it is necessary to induce defects that act as nucleation sites. Here,

Fig. 1 **a** STM image of a slightly bombarded HOPG surface showing defects (white spots). **b** Line profiles of a single defect after 0.8 eq ML Au deposition and after 3.2 eq ML Au deposition. **c** 3D view of the surface after 3.2 eq ML Au deposition

we bombarded HOPG with an Ar ion beam to induce defect formation, examined characteristics of the defects formed, and then deposited Au and examined the gold clusters.

Figure 1a shows an STM image of a pristine HOPG surface bombarded for a few seconds with a 1.5 keV Ar⁺ beam for 5 s. The white spots correspond to ion-induced damages presumably in single collision events. We see a fairly evenly distributed defect size distribution. Figure 1b shows a line profile along one of the defects in the STM image. In the STM image, the defects look like small protrusions, with an apparent mean height of ~0.2 nm and a lateral dimension (FWHM) of about 2 nm.

When gold is evaporated onto this surface, one observes an increase in size of these structures. Figure 1b shows the evolution of cluster heights as deposition proceeds. Since one cannot monitor the height evolution of a specific cluster, the profiles are taken from arbitrary clusters that are representative of these evolutions. After deposition of 0.8 eq ML of Au, the mean height and width of the structures is about 0.5 and 2.2 nm. For 3.2 eq ML Au deposition, the height increases to about 2 nm and the width is of the order of 2.5 nm. Thus, the clusters grow significantly in height but in the lateral dimensions, it did not increase very significantly.

As the Ar ion beam dose increases, we first observe the formation of a series of isolated, but clustered, defects with an average lateral dimension of the defect cluster in the 8 to 15 nm range. In this case, after 3.2 eq ML Au deposition, we observe clusters that are about 3-nm high and with similar lateral dimensions. In this case, gold clusters are first formed on the individual isolated defects and then coalesce into the larger cluster. At much higher ion fluence, the number of clustered defects increases. The size of the Au clusters is the same as mentioned above for the intermediate Ar ion fluence.

The experiments on Li ion neutralization involve a time of flight scattering study, which allows us to *separate scattering on gold clusters and substrate* as shown in Fig. 2a and also to obtain separately spectra for scattered ion and neutrals (Fig. 2b) and hence determine the *cluster-specific neutralization probability*.

Results of measurements performed as a function of Au evaporation onto a sputtered HOPG surface are shown in Fig. 3. We observe that generally, *more efficient neutralization*

Fig. 2 a Schematic diagram of scattering configuration. b TOF spectrum of Li scattering on Au clusters on HOPG. Vertical lines indicate the areas for integration to derive the neutral fraction

Fig. 3 Neutral fraction dependence on gold clusters on sputtered HOPG as a function of increasing Au coverage. The horizontal bar on the right indicates the value of the neutral fraction obtained on a Au(111) surface obtained after a very large evaporation. The red triangles summarize data (14) for scattering on Au clusters on TiO₂

occurs in the initial stages of deposition as compared to the case of large deposition doses and thin film formation. Initially, at the lowest deposition stages, a slight increase of neutralization occurs followed by a slow decrease for more than 2 eq ML deposition. Because in these experiments we do not perform ion scattering on STM previewed clusters on the same setups, we can only correlate trends between microscopy and scattering experiments, for similar Au deposition fluxes. By comparison with the results of the STM data, it would appear that neutralization is most efficient for cluster heights of the order or less than 1 nm, which would correspond to clusters of few atomic layers. This result would qualitatively concord with the observation that the reactivity of clusters is highest for clusters of about 2 to 3 atomic layers [6–12]. For large Au deposition, the results tend to that of a thin Au film, for which as may be seen, neutralization is much smaller.

The data for neutralization on gold clusters on HOPG is compared with that for the TiO₂ substrate studied previously [14]. We observe a fairly similar neutralization for the HOPG case. Note that this comparison is based on equivalent Au coverage, but in the TiO₂ case, it was also noted from AFM

Fig. 4 Schematic diagram of the behavior of the Li (2 s) level near a metal surface, illustrating the upward shift due to the image potential and downward trend near the surface as predicted in recent calculations. On the left a schematic view of a metal band structure, a situation with a bandgap and one with only discretized states

images that cluster sizes corresponding to greatest neutralization were for clusters of about 2 to 3 nm lateral dimensions.

As may be seen in both studies, we found that as Au deposition increased, the Li neutral fraction tended to a gold thin film limit, which in the case of TiO_2 had been identified with a Au(111) surface.

At present, it is difficult to give a reliable interpretation of these results. The results of this study need to be put into the perspective of a complex problem related in general to alkali ion neutralization on metal surfaces. While alkali neutralization on bulk metal surfaces seemed well understood [18–20], recent experiments [21–24] revealed very wide discrepancies with predictions of these “standard” jellium-like models of metals using a rate equation approach to describe neutralization. It was indeed found, as may also be seen in the Au thin film limit of Fig. 3, that on high workfunction surfaces, neutralization is still occurring, whereas the usual models would preclude this. Indeed, in these models, it is assumed that near the surface Li(2 s) level is upward shifted due to image potential effects, and Li is ionized as schematized in Fig. 4. Electron capture then occurs at large distances from the surface, when the Li (2 s) level lies below the Fermi level for atom surface distances greater than Z_F . For Au(111) [22, 24] with a workfunction of 5.4 eV, this would only occur at very large distances where the interaction with the surface is very weak, and therefore significant neutralization was not expected.

Initially it was thought [22] that the higher neutralization may be related to such features [25, 26] as projected band gap and surface states for (111) surfaces. However, this anomalously large neutralization appeared to be quite general and not restricted to a given type of surface [16, 24]. More recent theoretical studies show that near the metal surface, the Li(2 s) level actually lies below the Fermi level [24, 27] for some distance less than Z_C , and hence at small distances Li can be neutralized. Therefore, as opposed to the “standard” picture, one does not deal with the neutralization of an ion, as it recedes from the Au surface, but rather a more complex situation involving also neutral atoms that, as they recede from the surface, are first ionized and then neutralized. In the case of a very thin cluster, one could ask the question if the ion would feel the substrate and whether the effective neutralization may be different, although in the case of the present experiment, no significant differences between TiO_2 and HOPG can be noted.

Secondly, it appeared that adiabatically [24], at small velocities, the charge on Li tends to unity (neutral atom), and hence at low velocities neutralization is efficient [24], as opposed to what was expected in the standard descriptions. In a very recent calculation, this seems to be related to a much larger Li (2 s) level width [28] than predicted by earlier DFT calculations [19, 20, 23]. Another possible problem may be that a rate equation approach for determining the level populations, used in such descriptions, may not be suitable for a situation where the atomic level stays close to the Fermi level

for large atom-surface distances. Finally, the latest descriptions do not take into account properly the specifics of the band structure of the metals mentioned above.

Thus, it is clearly difficult to make definitive statements regarding the cluster case. Clearly, the electronic structure of the cluster should play a role. It is possible that, as suggested in some works [9–12], cluster reactivity may correspond to metal–non-metal transitions and opening up of a bandgap in the cluster electronic structure. This as well as appearance of quantized states, due to confinement [5], would obviously affect electron capture and loss probabilities; capture or loss would, e.g., be inhibited in the bandgap region, and the description of it would need to be different. In the case of *discrete states*, non-resonant velocity-dependent charge transfer processes [29–31] may play a role as for dielectric surfaces and should be treated using a *molecular description*, as this has been done also for ionic solids [32, 33]. Finally, it has also been suggested [14] that perhaps defect sites on the cluster or interaction with adatoms, atoms at kinks, and boundaries may somehow play a role. In earlier experiments [14], a test of such effects was made by roughening a Au(111) surface by prolonged bombardment, but no difference with the pristine surface was observed.

To summarize, in this work, we observed that Li ion neutralization on Au clusters grown on sputtered HOPG was more efficient than on bulk gold surfaces and was most efficient on small clusters. The results are fairly close to those obtained on Au clusters on TiO_2 . We have also noted a very similar trend on clusters on chains of clusters on pristine HOPG and on clusters grown on alumina films, but these results are beyond the scope of this brief paper. Further theoretical efforts on the description of alkali ion neutralization on bulk metals and for the case of supported clusters would be most welcome.

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