Electronic properties probed by scanning tunneling spectroscopy: From isolated gold nanocrystal to well-defined supracrystals

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Scanning tunneling microscopy and spectroscopy at 5 K have been used to determine the electronic properties of 7-nm dodecanethiol-passivated Au nanocrystals in three different configurations: isolated nanocrystal, self-organized thin films (few nanocrystal layers), and large three-dimensional well-defined thick films (over 30 nanocrystal layers) called supracrystals. The electronic properties of both thin and thick well-ordered supracrystals are analyzed in scanning tunneling spectroscopy geometry through $dI/dV$ curves and conductance mapping at different bias voltages. The single particles exhibit a typical $dI/dV$ curve with a Coulomb gap of $\sim 360$ meV and a Coulomb staircase. The $dI/dV$ curve of the thin supracrystals presents a Coulomb blockade feature $\sim 100$ meV narrower in width than that of the single nanocrystal but without well-defined staircase. On the contrary, the thick supracrystals exhibit a $dI/dV$ curve showing a large Coulomb gap with a Coulomb-staircase-like structure. Generally, the conductance mapping is found to be very homogeneous for both supracrystals. Nevertheless, for some bias voltages, inhomogeneities across individual nanocrystals appear. Additionally, some of these inhomogeneities seem to be related to the supracrystal surface morphology. Finally, these slight variations in the conductance mapping across individual nanocrystals embedded in the supracrystal are discussed in terms of high degree of nanocrystal ordering, low nanocrystal size distribution, and nanocrystal crystallinity.

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I. INTRODUCTION

The control of the assembly processes of nano-objects into highly ordered structures still remains a challenging problem for nanoscience and nanotechnology.1,2 Systems of nanoparticles or biomolecules, assembled into periodic structures, are found in many natural systems, such as atomic and molecular solids, opals, bacterial colonies, etc. The ability to assemble “artificial atoms,” such as nanocrystals (NCs), into ordered structures is expected to create a novel class of “artificial solids” such as supracrystals.3,4 Periodic structures can be obtained in the form of films or perfectly faceted colloidal crystals.5,6 Close-packed NC solids connected with linker molecules are also exciting new materials for their potentially novel electronic properties.7,8 The ordered NC arrays exhibit a wide range of fascinating architectures with emerging physical properties different from those of classical crystalline solids.9,10 In order to manipulate them and optimize their elaboration, one has to understand the properties of these materials. In particular, the control of the packing uniformity and interparticle distances has led to important advances in our understanding of fundamental charge transport phenomena.11–13

Transport measurements and electronic properties of more or less ordered NC assemblies have been extensively studied.14–22 The fact remains that these studies involved single NC, monolayer, or few NC layers. Moreover, most of these studies used contact electrode measurements in planar geometry. Here, we illustrate the evolution of electronic properties from isolated NCs to quasi-two-dimensional (2D) supracrystal (thin film of a few NC layers, thickness $< 30$ nm), and in turn to a three-dimensional (3D) face centered cubic (fcc) supracrystal (over 30 NC layers, thickness of $\sim 300$ nm).

For this purpose, we use scanning tunneling microscopy and spectroscopy (STM/STS), which allows us to measure the electronic signatures of individual NC embedded at the surface of supracrystals while, in addition, to acquire information on the overall electronic behavior of the thick and thin supracrystals. Note that in our previous paper, the electronic properties of micrometer-thick supracrystals are briefly reported.23

II. EXPERIMENTAL SECTION

The Au NCs are synthesized by using an organometallic route described in the previous paper.24 They are coated by dodecanethiol molecules (C$_{12}$H$_{25}$SH) and dispersed in toluene. The colloidal solution is maintained under saturated toluene vapor. After 7 days, a film appears at the air-toluene interface.25 This film is withdrawn by using a tungsten ring from the solution and transferred ex situ directly on highly oriented pyrolytic graphite (HOPG) substrate. The samples are then introduced into the STM chamber without any further treatments. STM and STS measurements were performed with a commercially available low-temperature ultrahigh vacuum setup (Omicron Nanotechnology) at a base pressure in the $10^{-11}$ Torr range. For maximum stability and reproducibility, all measurements were performed at 5 K. Cooling is achieved by means of a cold finger. Chemically etched tungsten tips were used. STM topographic imaging (800 $\times$ 800 data points) of supracrystals on HOPG substrate was performed in constant current mode. Simultaneously with the topographic image, $I$-$V$ curves were recorded with an open feedback loop in the current imaging tunneling spectroscopy mode26 with a grid size of 200 $\times$ 200 points. Then, maps of conductance are obtained numerically from these grids at selected values of
the tunneling voltage. Image processing was performed with the WSXM program and a MATHEMATICA program adapted in our laboratory. All experiments were repeated several times with different NC batches, and the results presented in this work were representative and consistent with the more comprehensive data set.

III. RESULTS AND DISCUSSION

Au NCs coated with dodecanethiol are characterized by an average diameter of 7 nm and a size distribution of 6% [Fig. 1(a)]. A careful study shows that these NCs are composed of a large amount of single-domain crystals, whereas others are mainly multiple-twinned particles (MTPs) with very few polycrystals [Fig. 1(b)]. Because of the low size distribution, the NCs are able to self-order in well-defined supracrystals [Figs. 1(c) and 1(d)] with a thickness of ∼300 nm, corresponding to ∼30 NC layers. The small-angle x-ray scattering (SAXRD) pattern [inset of Fig. 1(c)] shows a very bright reflection normal to the substrate, indicating that the NC arrangements are always oriented with (111) as the basal plane on the substrate sharing a common crystallographic axis normal to the substrate. A long-range ordering within crystalline domains with a fcc structure is also found. As seen in Fig. 1(d), by tilting the sample, the supracrystal has sharp edges. However, very thin supracrystals of a few NC layers close to the large supracrystals can be observed as indicated by the arrows in Fig. 1(c). This is how we distinguish between thick and thin supracrystals. Figure 2(a) shows a typical STM image of a thick supracrystal similar to those shown in Figs. 1(c) and 1(d). Such STM images are obtained at relative low current, between 50 and 150 pA. Surprisingly, these highly stable thick supracrystals can be imaged at bias voltages up to 9 V. Figure 2(a) shows that the NCs are highly ordered in a hexagonal network as confirmed by the Fourier transform pattern having a sixfold symmetry [inset of Fig. 2(a)]. The typical STM image of thin supracrystals is shown in Fig. 2(b). It is clear that there are a few NC layers in this thin supracrystal on the HOPG surface. The surface of thin supracrystal also presents a hexagonal NC array.

Before considering the thin and thick supracrystals, we will first exhibit the electronic transport through a single NC. During the STM tip scanning, isolated NC can be stuck to the tip. Such an event is reflected in the STM image by more or less narrow strips [Fig. 2(b)]. The corresponding $dI/dV$ spectra taken within strips in areas 1 and 3 show a curve with a gap surrounded by some oscillations. Such characteristics are known to be the signature of Coulomb blockade and Coulomb staircase. In contrast, outside the strips, the spectrum in region 2 [curve 2 in Fig. 3(a)] exhibits the $dI/dV$ spectrum of HOPG with the expected “V shape.” In the following, the width of the Coulomb gap is determined approximately by the distance between the kinks in the $dI/dV$ curve at positive and negative biases. From curves 1 and 3, we measure that the...
FIG. 3. (Color online) (a) The tunneling spectra show the Coulomb blockade and Coulomb staircase: Average $dI/dV$ curves of isolated Au NCs (curves 1 and 3) taken inside regions 1 and 3 of Fig. 2(b), respectively. Curve 2 is the average $dI/dV$ curve taken inside region 2 of Fig. 2(b) and corresponding to the expected “V shape” of HOPG. Inset: (left) schematic diagram of Coulomb blockade system where a NC is adsorbed on the STM tip and (right) the equivalent circuit of the double-barrier tunneling junction. (b) The experimental $dI/dV$ curve is fitted using the orthodox theory at different temperatures, 5 and 100 K, respectively. The parameters used in the orthodox theory are given in the inset.

width of the Coulomb gap of a single NC junction is around 360 meV, demonstrating that the tip-particle HOPG junction presents a single-electron transport mechanism. It means that the charging energy of one electron exceeds the thermal kinetic energy and that the tunneling resistance of the junction ($R_T$) is significantly larger than the quantum resistance ($R_Q = h/4e^2 \approx 6.5 \, \text{k} \Omega$). The typical tunneling spectrum of an isolated NC deposited on HOPG substrate, forming a double-barrier tunnel junction as illustrated in the inset of Fig. 3(a), is simulated by using the orthodox theory. The best fit at 5 K (dashed line) of the experimental data (dot) is obtained by assuming that $C_1 \approx C_2$ and $R_1 < R_2$ [see the values in the inset of Fig. 3(b)]. Although this fit reflects the main features of the experimental curve, it is not possible to reproduce perfectly the experimental curve at 5 K. Note that both experimental and simulated spectra present shifts and asymmetries indicating effects of a fractional residual charge $Q_0$ on the tunneling junction. One can improve the fitting by using an effective temperature of around 100 K [solid line in Fig. 3(b)] in the orthodox model. This temperature increase could have a physical origin since it has been reported that some local heating or an inelastic contribution to the tunneling current could occur for such a double-barrier tunnel junction made of dodecanethiol molecules.

Now, if these isolated NCs are organized in quasi-2D films (see Experimental section) as thin supracrystals [Fig. 1(c)], they are well observed by STM as shown in Fig. 2(b). Figure 4(a) shows another typical 160 nm × 160 nm STM image of this thin supracrystal. On the left side of Fig. 4(a), NCs are organized in a hexagonal array forming a thin supracrystal that is located against a defect of HOPG (dark border) imaged on the right side. The average $dI/dV$ curve of the substrate [curve A in Fig. 4(b)] taken inside the circle A [Fig. 4(a)] shows the typical spectroscopic signature of HOPG. In the same way, the average $dI/dV$ curve of the NC network [curve B in Fig. 4(b)] taken inside the circle B [Fig. 4(a)] demonstrates a symmetrical Coulomb gap. The width of the Coulomb gap is of the order of 250 meV, a bit smaller than that of the single NC observed in Fig. 3(a). Moreover, no sharp Coulomb staircase is observed above the gap. Both features are certainly due to a collective behavior of the NCs forming the thin supracrystal and their interactions with the substrate. The conductance map associated to the thin supracrystal, at 0 mV, is finite valued. It appears to be very homogeneous with a lower average conductance than that of HOPG. The Coulomb gap is of the order of 250 meV, a bit smaller than that of the single NC observed in Fig. 3(a). Moreover, no sharp Coulomb staircase is observed above the gap. Both features are certainly due to a collective behavior of the NCs forming the thin supracrystal and their interactions with the substrate. The conductance map associated to the thin supracrystal, at 0 mV, is finite valued. It appears to be very homogeneous with a lower average conductance than that of HOPG. However, we could expect that it is an effect of direct tunneling between the tip and the substrate without passing through the NCs. The dielectric layer of the thiols capping the NCs lowers the
tunneling barrier compared to vacuum and then allows some electrons to pass directly between the tip and the surface. At 300 mV [Fig. 4(d)], outside the gap, the contrast is still very homogeneous and inverted compared to that in Fig. 4(c). In order to observe some singularities in the conductance of thin supracrystal, the bias should be close to the gap edge. Indeed, in Figs. 4(d) and 4(e) (80 and 300 mV, respectively), we note that there are some variations at the NC scale at the border between thin supracrystal edge and HOPG. For instance, at 80 mV [Fig. 4(e)], the conductance map reveals some singularities at the NC scale with low conductance [blue spot inside circle C in Fig. 4(e)].

These singularities are concentrated at the border between thin supracrystal edge and HOPG, but they are also seen far from this border. The averaged conductance curves of these singularities (circles C and D) are shown in Fig. 4(f) (curves C and D). The Coulomb gap width associated to these spots is ~100 meV larger than the one averaged on the NC network taken inside circle B [Fig. 4(b)]. Furthermore, Figs. 4(c)–4(e) show a marked change in the conductance for NCs close to the edge of the thin supracrystal. This gap enlargement may be due to the fact that NCs at the edge have fewer neighbors than those far from the edge. This is in good agreement with the fact that the average Coulomb gap width of the thin supracrystal is reduced compared to that of a single NC. When the number of neighbors is increased, the capacitance associated with the junction is increased, and therefore the Coulomb energy is reduced. The gap enhancement at the supracrystal edge might also be due to an accumulation of single-crystalline NCs at the edge. This is well observed from the transmission electron microscopy (TEM) pattern observed in the supracrystal with few NC layers. Figure 1S shows the bright (a) and dark (b) field TEM images with appearance of very homogeneous NCs (either totally bright or dark) at the edge of the film and heterogeneous NCs forming monolayers. Figure 1S(c) points out the region of such nanocrystallinity segregation. Other experiments recently carried out in our group with Au NCs show nanocrystallinity segregation with formation of supracrystals composed exclusively of either single-domain NCs or MTPs. Although the conductance of thin supracrystals is very uniform throughout, we still can find some areas where the conductance varies markedly from one NC to its neighbor [Fig. 5(a)]. Figure 5(a) shows a conductance map superimposed on the corresponding 3D topographic STM image (26 nm × 26 nm). As shown in Fig. 5(a), the NC labeled as A has a conductance clearly lower than one of its neighbors labeled as B, which is in turn lower than one of its neighbors labeled as C. The corresponding $dI/dV$ curve, taken over all of each NC, shows that the Coulomb gap width does not change. From the STM image shown in Fig. 5(a), the NC size can not be assigned to the change in the conductance between A, B, and C NCs. By comparing the STM [Fig. 5(a)] and TEM [Fig. 5(b)] images, these differences in the conductance could be attributed to a change in the nanocrystallinity during the supracrystal formation, i.e., either a single crystalline, or a MTP, or a polycrystalline NC as labeled by 1, 2, and 3, respectively, in Fig. 5(b).

The electronic behavior of the thick supracrystals is very different from that of the thin supracrystals. The typical $I-V$ curves of well-ordered thick supracrystals exhibit a nonlinear behavior at 5 K (inset of Fig. 6) totally different from the reported one associated to the thin supracrystals [Fig. 4(b)]. The logarithmic plot (Fig. 6) shows a power-law dependence of tunneling current on bias voltage $I \propto V^\zeta$ with $\zeta \approx 3.3$ when the bias voltage is higher than 200 mV at 5 K. Similarly, for the thin supracrystal, there is also a power law but with a $\zeta$ equal to ~1.4. A typical 100 nm × 100 nm topographic STM image of
the thick, well-ordered supracrystal is presented in Fig. 7(a). The surface shows hexagonal NC packing. The $dI/dV$ map corresponding to the STM image at 800 mV [Fig. 7(b)] shows that the conductance is very homogeneous over all the surface. This homogeneity is related to the well-defined structure of the supracrystals. Note that, at 800 mV, a marked change in the conductance in large areas (three terraces) of the STM image is observed with lower conductance or higher conductance. Considering the three regions labeled by black, blue, and red circles in Fig. 7(b), the $dI/dV$ curves show a similar Coulomb gap [Fig. 7(c)] with a width nearly equal to that of a single NC junction (Fig. 3). However, a deeper analysis shows that the Coulomb gap in the black, blue, and red regions is slightly different. Au NCs are characterized by a size distribution of 6% and differ by their nanocrystallinity with a mixture of single-crystalline, multiple-twinned, and polycrystalline NCs. Because of this low size distribution, these singularities at the NC scale show a staircaselike structure in their $dI/dV$ curves, which may suggest that these NCs forming the supracrystal partially keep features of isolated NC (Fig. 3). The change in the staircase structure could be attributed to the interactions between NCs. Note that we can count more or less the same number of steps in both cases, in Fig. 7(d) and Fig. 3, respectively. This seems to indicate that these singularities at the NC scale, forming the thick supracrystals, and surrounded by a large number of NCs, behave as isolated NCs deposited on HOPG. Nevertheless, locally, because of the NC size distribution, these singularities could be NCs smaller or larger than 7 nm. This has been already observed by photoinduced emission with a marked change in the behavior of small NCs embedded in a NC monolayer.

IV. CONCLUSION

Electronic properties at 5 K of a 300-nm-thick supracrystal made of dodecanethiol-passivated 7-nm Au NCs and ordered in a fcc structure called supracrystals are investigated. The thick fcc supracrystals are sufficiently conductive to be investigated by STM/STS even if the coupling of the NCs within the supracrystal is weak. The $dI/dV$ curves show a gap with a width of about 310 meV and a clear staircaselike structure. The conductance maps are very homogeneous. However, some areas show a slight change in the conductance may be attributed to the nanocrystallinity segregation of NCs during the supracrystal formation. Furthermore, some local singularities at the NC scale are detected and correspond to NCs embedded in the supracrystal surface. These particular NCs mimic the behavior of isolated NCs deposited on HOPG. As with the thick supracrystal, the thin supracrystal exhibits a homogeneous conductance over the entire surface tested. Finally, at the edge of the thin supracrystal, the conductance differs from that observed on the overall supracrystal, indicating changes in the electronic transport of NCs either due to the lack of NC neighbors or the change in the nanocrystallinity.

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38See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.86.075409 for Fig. 1S.
39Y. Wan, H. Portales, and M.-P. Pileni (private communication).
40See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.86.075409 for Fig. 2S.