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Unexpected Electronic Properties of Micrometer-Thick Supracrystals of Au Nanocrystals

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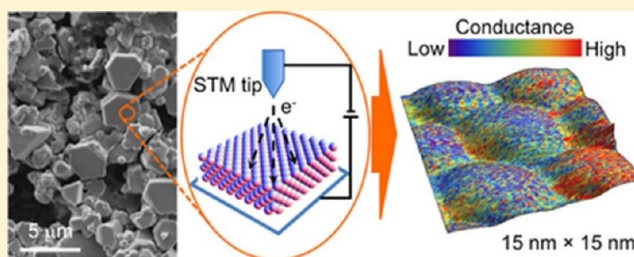
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S Supporting Information

ABSTRACT: We investigated the electronic properties of highly ordered three-dimensional colloidal crystals of gold nanocrystals (7 ± 0.4 nm), called supracrystals. Two kinds of Au supracrystals with typical thicknesses of 300 nm and 5 μ m, respectively, are probed for the first time with scanning tunneling microscopy/spectroscopy at 5 K revealing similar power law behavior and showing homogeneous conductance with the fingerprint of isolated nanocrystal. Potential applications evading the size-related risks of nanocrystals could be then considered.

KEYWORDS: Collective electronic properties, Coulomb blockade, Coulomb staircase, scanning tunneling microscopy/spectroscopy



The formation of well-defined colloidal nanocrystal films (so-called supracrystals) may promise new materials with tunable properties.^{1–6} Especially, the array of nanocrystals provides a model to study fundamentally the electron transport in an ordered mesoscopic system. Many efforts have been made by several groups to investigate the electronic properties of 1-, 2-, and thin 3-dimensional (3D) arrays^{7–17} and to elucidate the theory of electron transport in such systems.^{18,19} The fabrication of a thick (<1 μ m) 3D array has been reported.²⁰ However, up to now, due to the difficulty in fabricating large, thick, and well-defined supracrystals, the relevant investigation of the electronic properties for thick 3D nanocrystal assemblies was limited. Here, we present for the first time a scanning tunneling microscopy/spectroscopy (STM/STS) study at 5 K of highly ordered, thick 3D superlattices (up to 5 μ m thick) of 7 nm sized Au nanocrystals, protected with alkanethiol molecules ($C_{12}H_{25}SH$), as building blocks.

The Au nanocrystals are synthesized by using an organo-metallic route described in ref 21. The nanocrystals have a diameter of 7 nm with a very low size distribution (around 6%). 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 at the air–toluene interface and precipitates appear.²² The interfacial film, which is withdrawn using a tungsten ring, is deposited on highly oriented pyrolytic graphite (HOPG) substrate. The precipitates are collected and deposited on the HOPG substrate. By small-angle X-ray diffraction technique,²² it is observed that the nanocrystals involved in the interfacial film and in the precipitates are highly ordered in face-centered cubic (fcc) structure called supracrystals. Hence two simultaneous supra-

crystal growth mechanisms are involved when nanocrystals are dispersed in toluene and kept for seven days in a toluene-saturated atmosphere. At the air–toluene interface, well-defined layer-by-layer thick supracrystal films (scanning electron microscopy (SEM) image shown in Figure 1a), called interfacial supracrystals, are formed. In the meantime, a homogeneous growth takes place in solution with formation of randomly oriented, well-defined, thicker supracrystals with different polyhedral shapes (SEM image shown in Figure 1d), called precipitated supracrystals. Field emission scanning electron microscopy (FESEM) studies (Figure 1b,e) reveal a well-defined hexagonal arrangement of nanocrystals on the surface of both interfacial and precipitated supracrystals as illustrated by the fast Fourier transform (FFT) pattern shown in Figure 1b,e insets, respectively. This hexagonal arrangement corresponds to the {111} surface of the fcc structure. The thicknesses of interfacial and precipitated supracrystals are typically 300 nm and 5 μ m and composed of about 40 and 700 nanocrystal layers, respectively. As already mentioned, these supracrystals are extracted from the solution and transferred ex situ directly on HOPG substrate. The samples are then introduced into the STM chamber without any further treatment.

Contrary to what is expected, these thick supracrystals are conductive enough to be investigated by using STM/STS. All the STM/STS experiments are carried out with a chemically etched tungsten STM tip at 5 K on a commercial setup

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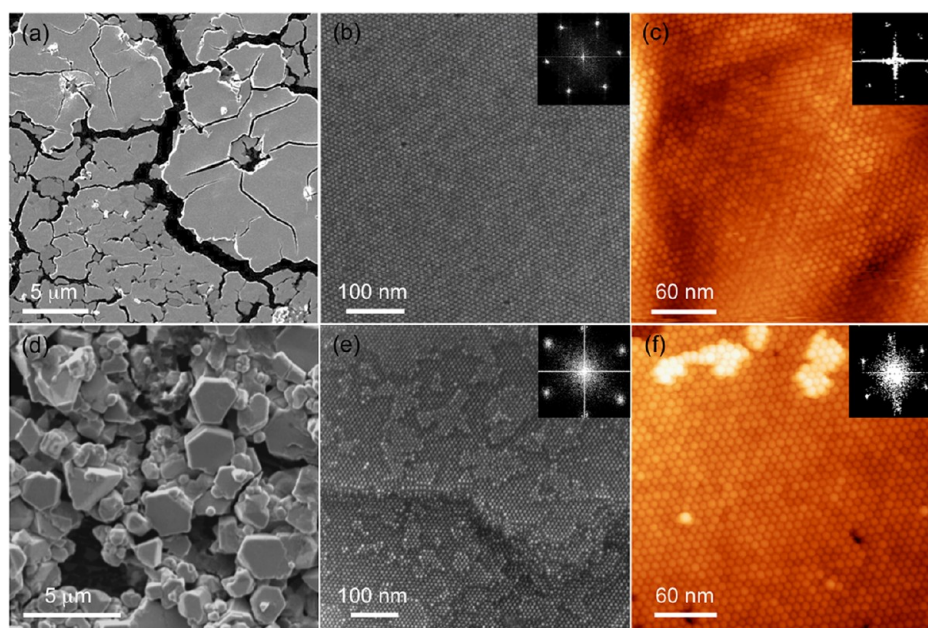


Figure 1. Typical scanning electron microscopy (a,d), field emission scanning electron microscopy (b,e), scanning tunneling microscopy (c,f) images for interfacial (a–c) and precipitated (d–f) supracrystals. The topographic STM images are obtained at 5 K with a bias voltage of 2.5 V and a current set point of 50 pA in (c), and 5 V, 150 pA in (f). Insets in panels b, c, e, and f show the corresponding fast Fourier transform patterns.

(Omicron Nanotechnology) under ultrahigh-vacuum conditions (base pressure $<10^{-11}$ Torr). In our configuration, the sample is grounded, that is, the occupied states of the sample are detected when a positive bias voltage is applied on the tip. Data analysis and image processing were performed using MATHEMATICA and the WSxM programs.²³

Typical topographic STM images of interfacial and precipitated supracrystals are shown in Figure 1 panels c and f, respectively. These STM images show a clear hexagonal arrangement of nanocrystals on the surface of the supracrystals. The corresponding FFT patterns (Figure 1c,f insets) show well-defined hexagonal features similar to those of FESEM images (Figure 1b,e insets). Especially, for the precipitated supracrystals the STM image (Figure 1f) show clearly some defects, such as vacancies, adsorbed nanocrystals and small pieces of stacking layers, which can be also observed in the FESEM image (Figure 1e). It is worth noting that the topographic STM image of the interfacial supracrystal shown in Figure 1c is obtained with a bias voltage of 2.5 V. However, the precipitated supracrystals (thicker) are imaged at a higher bias voltage, for example, 5 V (Figure 1f) and some STM images have been taken up to 9 V. Such a high voltage suggests that the potential drop between the STM tip and the first nanocrystal layer of the supracrystals is not equal to the applied voltage but is instead markedly reduced due to the highly resistive nature of the films. In a standard STM experiment with a tip in front of a simple metallic surface, at 9 V the junction would be in strong field-emission regime and the field-emitted electrons would certainly damage severely the sample. In our case, the nanocrystals are coated with thiol molecules, which play the role of a dielectric barrier, and the nanocrystals act as voltage dividers. Hence the current passes across the supracrystalline network via tunneling between nanocrystals. Such a process confers a very high resistivity to the supracrystal^{7,24} and a large voltage drop across the layers appears. Then, the voltage drop between the STM tip and the first nanocrystal layer of the supracrystal is much lower than the applied voltage, in particular in the case of the

precipitated supracrystals. Of course, the voltage drop through the film increases when the number of nanocrystal layers increases explaining why imaging the very thick precipitated supracrystals needs higher voltages as compared to the much thinner interfacial supracrystals.

Local spectroscopic measurements were performed in order to gain some insight into the transport mechanism involved. Simultaneously with the topographic STM image, I – V curves in a grid of 200×200 points are recorded with an open feedback loop in the scanning tunneling spectroscopic mode.²⁵ All experiments were repeated several times with different STM tips, different spots on the sample, and the results presented in this work are representative and consistent with the more comprehensive data set. Some typical I – V curves averaged over 200×200 measurements are shown in the insets of Figure 2 panels a and b for interfacial and precipitated supracrystals, respectively. Obviously, the I – V curves show a symmetric feature with respect to zero bias voltage. Generally, asymmetry is observed in the shape of I – V curves for metallic materials at large bias voltages because the trapezoidal tunneling barrier is not symmetrical. The tunneling transparency is increased at large voltage and when the work functions of the tip and the sample are different, the transparency becomes strongly asymmetric at large bias voltage. When the bias is further increased and becomes comparable to the work functions, that is, in field-emission (Fowler–Nordheim) regime,²⁶ strong tip effect appears. It is easier for the tip to field-emit electrons than the opposite. In our case, as indicated previously, the voltage drop between the STM tip and the first nanocrystal layer of supracrystal is much lower than the applied bias voltage and is still in the low bias limit with a tunneling transparency that does not depend much on voltage. This stands for the symmetric I – V curves. For clarity, the I – V curves are plotted in log–log coordinates as shown in Figure 2a,b. The increase in the current with the applied voltage reveals power law dependence, that is, $I \propto V^\zeta$ when V is higher than a threshold voltage V_T . The scaling exponent ζ is related to the number of accessible

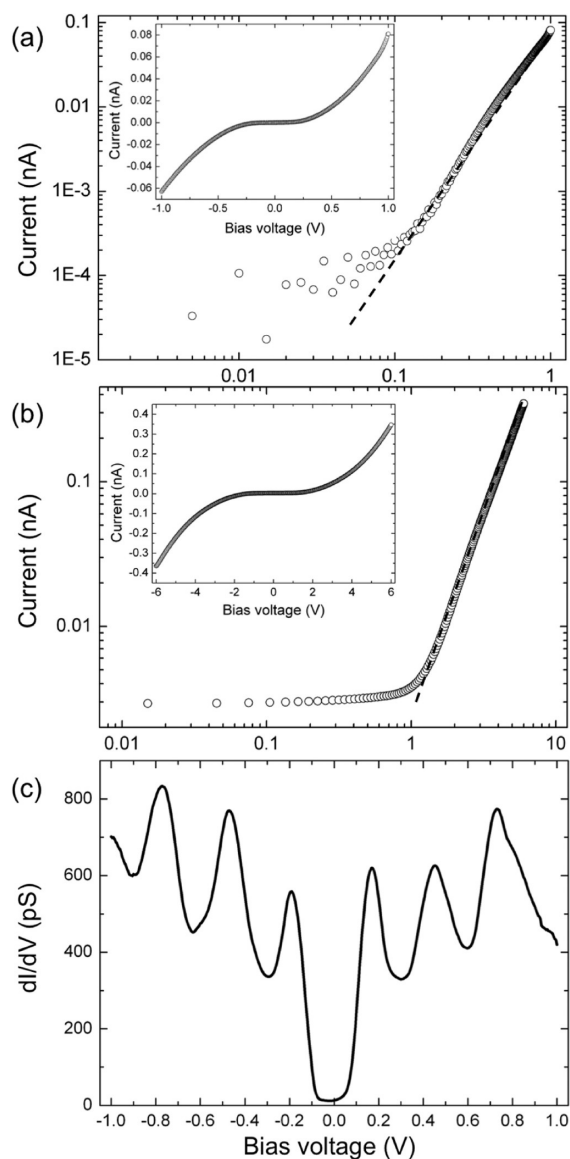


Figure 2. Log-log plot of average I - V curves on the surface of interfacial (a) and precipitated (b) supracrystals. The I - V curves reveal power law dependence, that is, $I \propto V^\zeta$ when V is higher than a threshold voltage V_T . The dashed lines are guide for the eyes. From several measurements, the scaling exponent (ζ) is about 3.3 and 3.7 for interfacial and precipitated supracrystals, respectively. The insets are the linear plots of the I - V curves. (c) The Coulomb staircase in the dI/dV curve (averaged from 126 individual curves measured at 5 K) of isolated Au nanocrystals adsorbed on the STM tip.

current paths through the supracrystals, and it depends on the supracrystal dimensionality.¹¹ For 1D and 2D arrays, ζ is predicted to be 1 and 5/3, respectively.¹⁸ The scaling exponent is expected to increase for 3D arrays due to the greater numbers of current paths even though this has not been theoretically demonstrated.¹¹ For our system, from several measurements, ζ is determined to be ~ 3.3 for interfacial supracrystals whereas ~ 3.7 values are found for precipitated supracrystals. The fact that the scaling exponents are comparable for the supracrystals having ~ 40 or ~ 700 nanocrystal layers seems to indicate that interfacial and precipitated supracrystals have similar transport mechanisms. The self-similarity of I - V curves is found when the bias voltage range is changed on the same spectroscopic spot, which is confirmed by a recent publication.²⁷ Moreira et

al. have demonstrated a similar power law dependence of the current with self-similarity by very low noise measurements of I - V characteristics over a large number of decades for electron transport in gold nanocrystal arrays.²⁷ Because of the self-similarity of I - V curves, V_T changes with the bias voltage scale. Consequently, V_T is not a relevant parameter while ζ is important for understanding the perpendicular electron transport in the supracrystals. Besides, isolated nanocrystals can be adsorbed on the STM tip during the scanning, which in turn form a double barrier tunneling junction between the tip and the substrate.²⁸ Figure 2c shows the oscillations in the dI/dV curve of such a double barrier tunneling junction, which are related to Coulomb staircases.²⁸⁻³⁰ Following the orthodox theory,³¹ R_1 (resistance between the tip and the adsorbed nanocrystal) and R_2 (resistance between the adsorbed nanocrystal and the substrate) are estimated to be 0.06 and 0.91 G Ω , respectively. Both R_1 and R_2 are significantly larger than the quantum resistance $R_Q = h/4e^2 \approx 6.5$ k Ω , which is critical for single electron tunneling, where h is Planck constant and e is elementary charge.³²

We carried out spectroscopic mappings (Figure 3) in order to measure the spatial variations in the electronic properties of the supracrystals. Conductance maps, $dI/dV(\vec{r}, V)$, were derived numerically from the I - V data on each spectroscopic grid point at selected values of the bias voltage. Figure 3a,b shows a conductance map at 0.45 V for the interfacial supracrystal and a map at 3 V for the precipitated one. The corresponding topographic STM images are shown in Figure 3 panels c and d insets. In order to observe the spatial variations of the conductance across a nanocrystal at different scales, the STM/STS images (Figure 3) have different sizes. Note that no obvious correlation between topography and conductance can be pointed out. The conductance maps show slight spatial variations at the nanocrystal scale as indicated in Figure 3a,b by the red and blue circles. Some nanocrystals can be clearly identified by their unique conductance. The dI/dV curves averaged from the regions delimited by the red and blue circles are illustrated by the red and blue curves in Figure 3c,d. For comparison, dashed lines in the plot illustrate the dI/dV curves averaged overall the surface. It is clear that from the dI/dV curves, a given nanocrystal exhibits a slight additional staircase-like modulation (red or blue lines) superimposed on the collective tunneling conductance background $dI/dV \propto V^{\zeta-1}$ (dashed lines). This modulation can be naturally associated with a Coulomb staircase through an isolated nanocrystal. Figure 2c shows a typical dI/dV curve of a single nanocrystal adsorbed on the STM tip, the blocking energy of 250 meV is comparable to the 300 meV observed in the interfacial supracrystal as shown in Figure 3c.

Then the collective electronic properties of supracrystals are associated with the fingerprint of its isolated component nanocrystals. For the precipitated supracrystals, faint Coulomb oscillations are also possibly observed but their characteristic energy is of the order of 2 eV instead of 250 meV for an isolated particle (Figure 3d). This is attributed to the large resistivity of the precipitated supracrystal that induced a large voltage drop through the multiple particle layers. Hence, the effective voltage drop between the STM tip and the first particle layer is strongly reduced and one has to apply large voltages in order that the effective voltage drop between the tip and the first nanocrystal become comparable to the Coulomb energy. Except for these weak Coulomb oscillations, the conductance maps are very homogeneous, in particular the

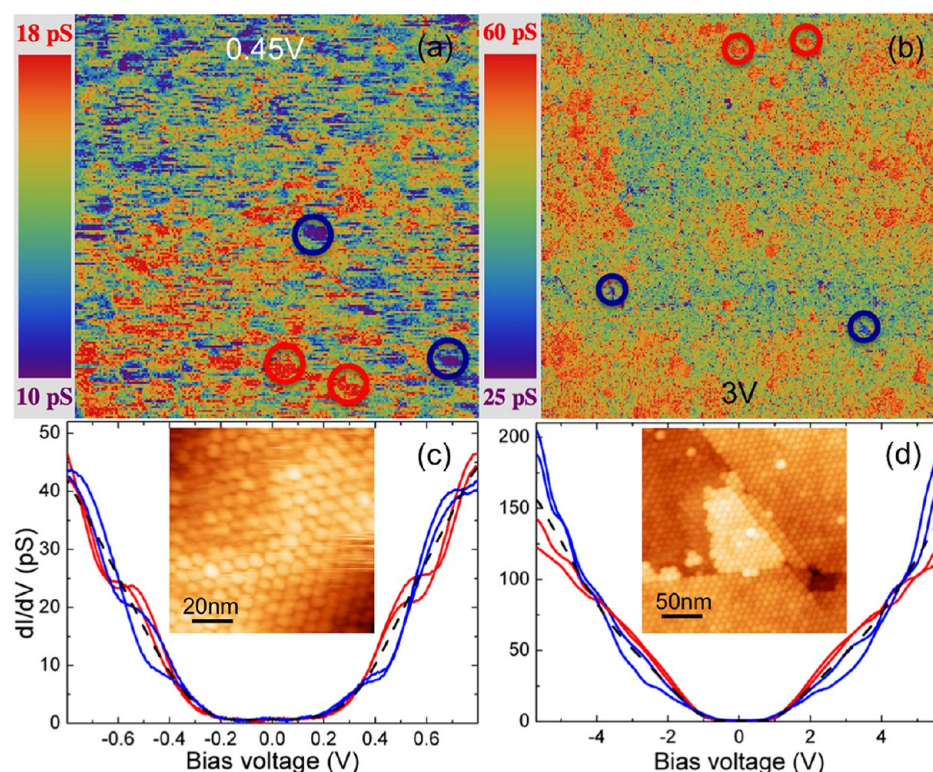


Figure 3. The conductance map at 0.45 V for interfacial (a) and at 3 V for precipitated (b) supracrystals. The fingerprint of isolated nanocrystals, that is, staircase-like structure, is found in the dI/dV curves (c,d) averaged from particular regions indicated by the red and blue circles on conductance maps (a,b). For both interfacial and precipitated supracrystals, the dI/dV curves averaged overall the surface are shown by dashed lines in (c,d). The insets in (c,d) show the topographic STM images corresponding to the conductance maps (a) ($100 \times 100 \text{ nm}^2$) and (b) ($250 \times 250 \text{ nm}^2$), respectively. These STM topographic images are obtained at 5 K with bias voltages and current set points at 2.3 V, 130 pA and 5 V, 200 pA, respectively.

underlying $dI/dV \propto V^{\zeta-1}$ conductance background. This homogeneity is attributed to both the high degree of nanocrystal ordering within the supracrystals and the low nanocrystal size distribution.

In conclusion, thick (up to $5 \mu\text{m}$) highly ordered supracrystals of 7 nm sized Au nanocrystals protected with alkanethiol molecules ($\text{C}_{12}\text{H}_{25}\text{SH}$) can be surprisingly well imaged by STM and investigated by STS at 5 K. The average I – V curves clearly show power law dependence $I \propto V^{\zeta}$ with a scaling exponent ζ larger than 3 indicating 3D multiple paths for tunneling through the supracrystals. For a given nanocrystal, the conductance exhibits a slight additional modulation superimposed on the collective conductance background that mimics the Coulomb staircase structure normally associated with an isolated nanocrystal. The observation of collective properties with the fingerprint of isolated nanocrystals makes it possible to benefit from the unique properties of nanocrystals while avoiding their size-related potential risks in future applications. But these superlattices also allow manipulating at a microscopic level the unique properties of nanocrystals.

■ ASSOCIATED CONTENT

● Supporting Information

Nanocrystal synthesis, fabrication of supracrystals, and supracrystal characterization are described in detail. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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