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Observation of room temperature mono-electron phenomena on nanometre-sized CdS particles

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Abstract. A STM study of ultra-small cadmium sulphide particles formed in a bilayer of cadmium arachidate exposed to a hydrogen sulphide atmosphere is reported. Particles of nanometre size were identified as negative features inside the film after the reaction. Voltage–current characteristics of particles of different apparent sizes were measured by means of the microscope probe. The behaviour of the tunnelling current indicates the occurrence of a Coulomb staircase at room temperature and reveals a new phenomenon which shows the appearance of regions with negative resistance.

1. Introduction

In recent years [1], it has been proposed that a nanometre-sized semiconductor particles of cadmium sulphide inside Langmuir–Blodgett (LB) films of cadmium arachidate could be formed by exposing the LB films to gaseous hydrogen sulphide. The protons of H_2S protonate the headgroups of the arachidic acid and sulphur binds to cadmium. Further works on mercury sulphide [2] and lead sulphide [3] confirmed the general applicability of the approach for the formation of particles of sulphur salts of bivalent metals. Optical [1] and electron diffraction [1, 3] investigations on particles formed by this technique allowed their size to be estimated to fall within the range 5–20 nm.

Nanometre-sized objects are predicted to be suitable candidates to exhibit mono-electron phenomena [4] at room temperature. Coulomb blockade and Coulomb staircase [4] phenomena have been observed at low (liquid helium) temperature on particles of larger size [5, 6] and, by scanning tunnelling microscopy (STM), on conductive granules even at room temperature [7]. These phenomena, which occur when a small granule is separated from two electrodes by two tunnelling junctions, arise from the quantized increase in the average number of electrons occupying the granule with the increase in the bias voltage [8]. The presence of electrons in the granule provides an electric field which prevents a new incoming electron entering the granule until a suitable voltage biases the junction. Each quantized increase in the average number of electrons takes place whenever the voltage through the structure changes by a quantity e/C, where e is the electron charge and C is the capacity of the structure [4]. Such a quantized increase in the number of electrons in the 'island' results in a staircase behaviour of voltage–current characteristics [4].

Mono-electron phenomena takes place when the electrostatic energy ($e^2/2C$) exceeds the thermal excitation energy (kT) [9]. The classical approach for matching the previous requirements is to decrease the value of T, because there are technological limits in decreasing the value of C. CdS nanoparticles, however, are among the right candidates for overcoming this technological limit, because they can have capacitance values as small as 10^{-18} F and thus can display mono-electron phenomena at room temperature.

To build a suitable set-up for registering mono-electron phenomena, however, it is not enough to have ultra-small granules; it is also essential to provide a double-tunnelling barrier structure and to monitor voltage–current (V–I) characteristics through a single granule. STM could provide the possibility of imaging directly the structures formed by the described technique and measuring the V–I characteristics by placing the scanning probe over single particles [7, 10]. The simplified scheme of the measuring set-up is shown in figure 1.

2. Materials and methods

Arachidic acid was purchased from Sigma. Arachidic acid monolayers were formed at the surface of water containing 10^{-4} M $CdCl_2$. One bilayer of cadmium arachidate was deposited with a LB trough (MDT, Russia) [11] onto graphite substrate at the surface pressure of 28 mN m^{-2}

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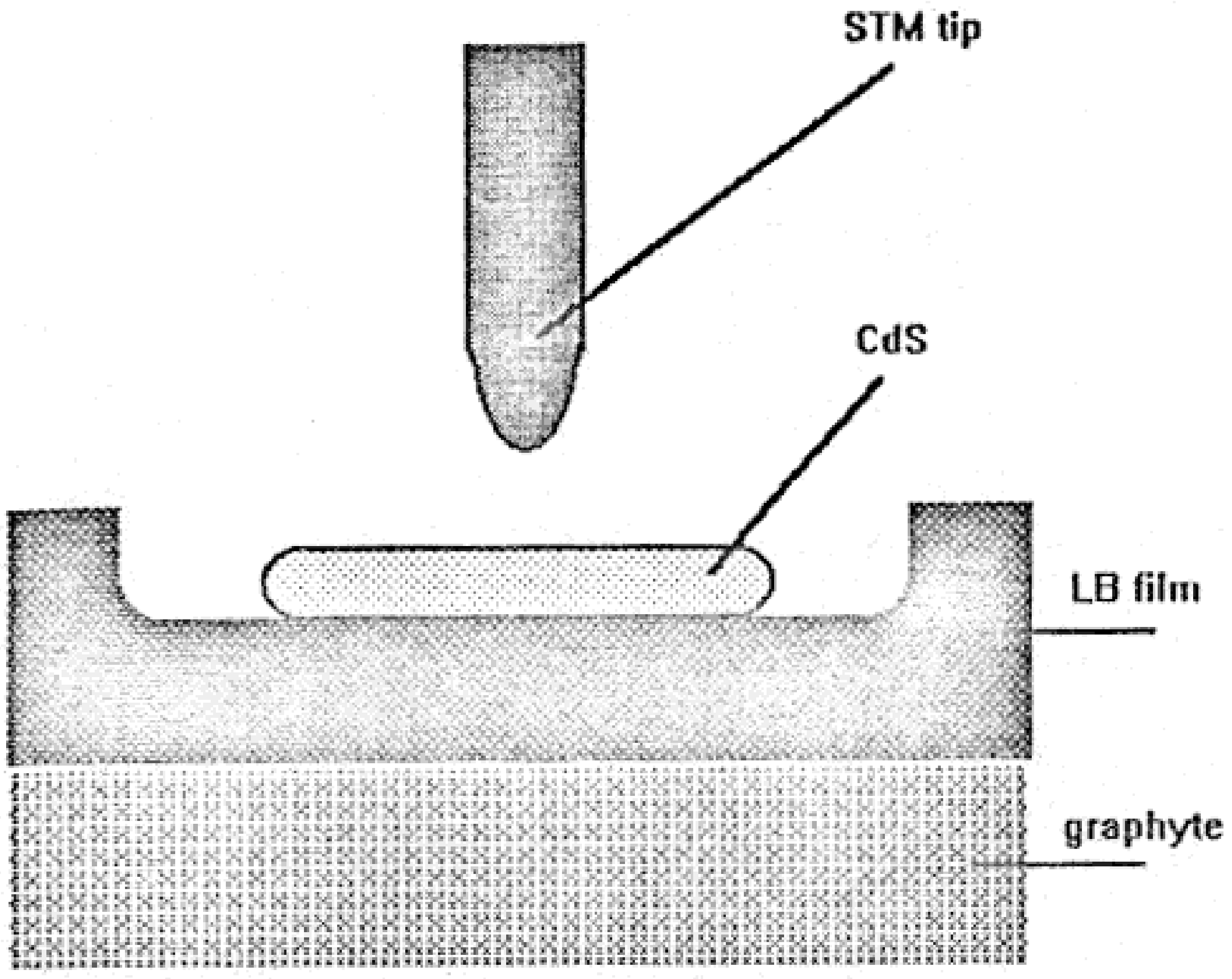


Figure 1. The scheme of the experimental set-up for measuring STM V–I characteristics.

by the LB technique [12]. The samples were exposed to gaseous H_2S for 15 min.

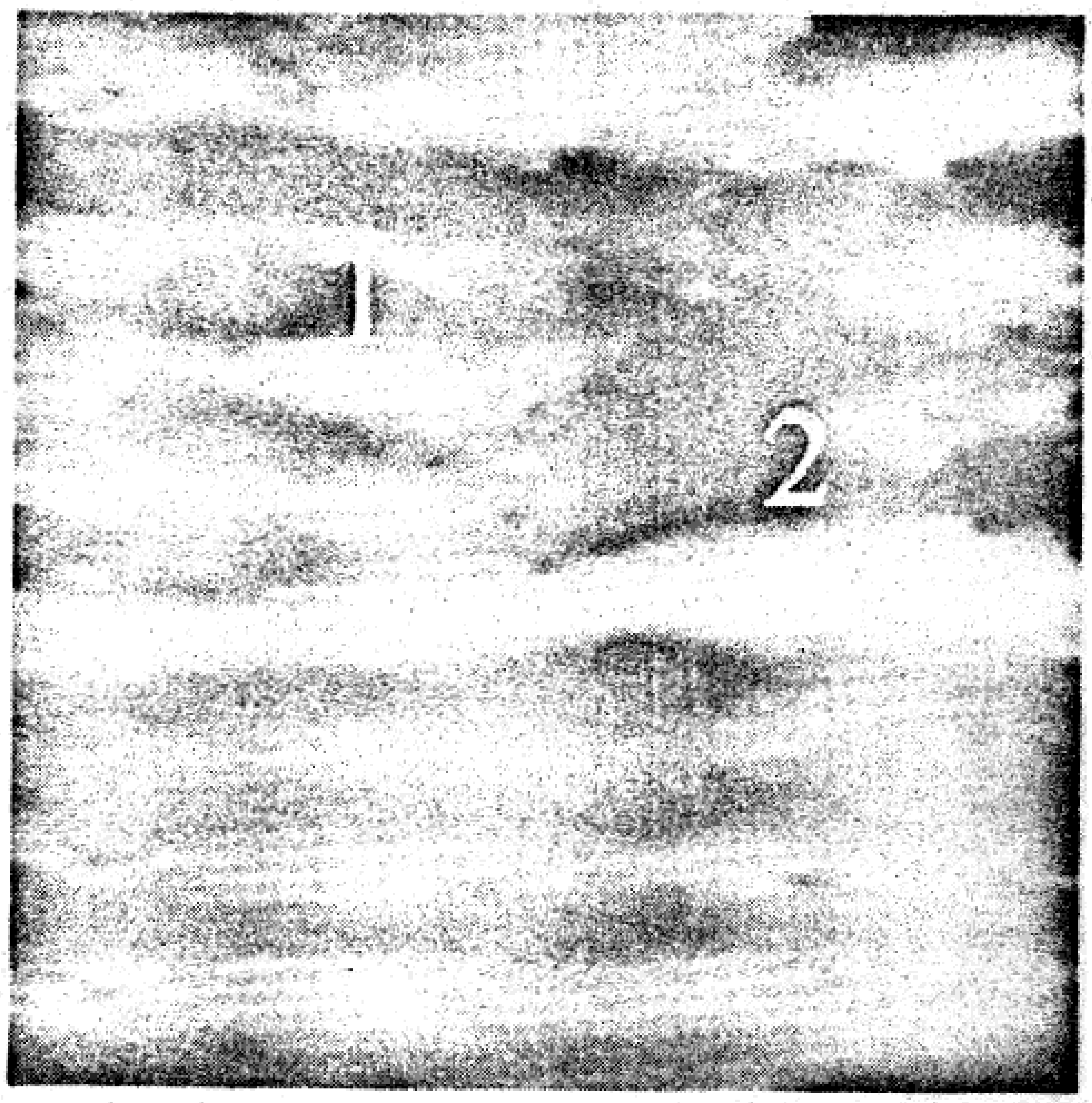
STM (MDT, Russia) [13] imaging was performed in constant current mode, using Pt–Ir (90–10) tips. For registering V–I characteristics the tip was placed above the chosen granule, maintaining a chosen value of tunnelling current; then, feedback was switched off and the voltage was swept, recording the corresponding tunnelling current.

3. Results and discussion

STM analysis of different areas of several samples showed similar features, some of which are presented in figures 2 and 3 from the top view and in a three-dimensional representation, respectively. In all cases, it is possible to distinguish features shaped like wells in a corrugated matrix; sometimes they are isolated, sometimes preferetially arranged along lines. Their size, typically in the range 5–10 nm, matches well the size of CdS particles formed by the above-described procedure, as estimated by optical absorption spectra [1] and by electron diffraction [3]. This comparison allows one to suggest that the wells in the images could be related to CdS particles formed in a LB film of arachidic acid (for example particles could lie inside the wells). This fact is in agreement with general concepts derived from previous data [9] obtained by ellipsometry [1] and x-ray analysis [3] and with the suggestion that the initial two-dimensional arrangement of cadmium atoms in the film can be preserved to a certain extent in the final film after the reaction. The reaction process disturbs strongly the structure of the film, resulting in an increased corrugation of the arachidic acid matrix, at least in some regions surrounding the particles. Taking into account the hydrophilic properties of CdS [14], we can suppose that the matter in the bilayer is re-distributed after the reaction in such a way that CdS particles are not covered by the arachidic acid molecules. These considerations can account for negative features that are visible in the STM images and therefore could be related to CdS particles.

Two typical trends of V–I characteristics obtained upon placing the scanning probe above the wells shown

(*a*)



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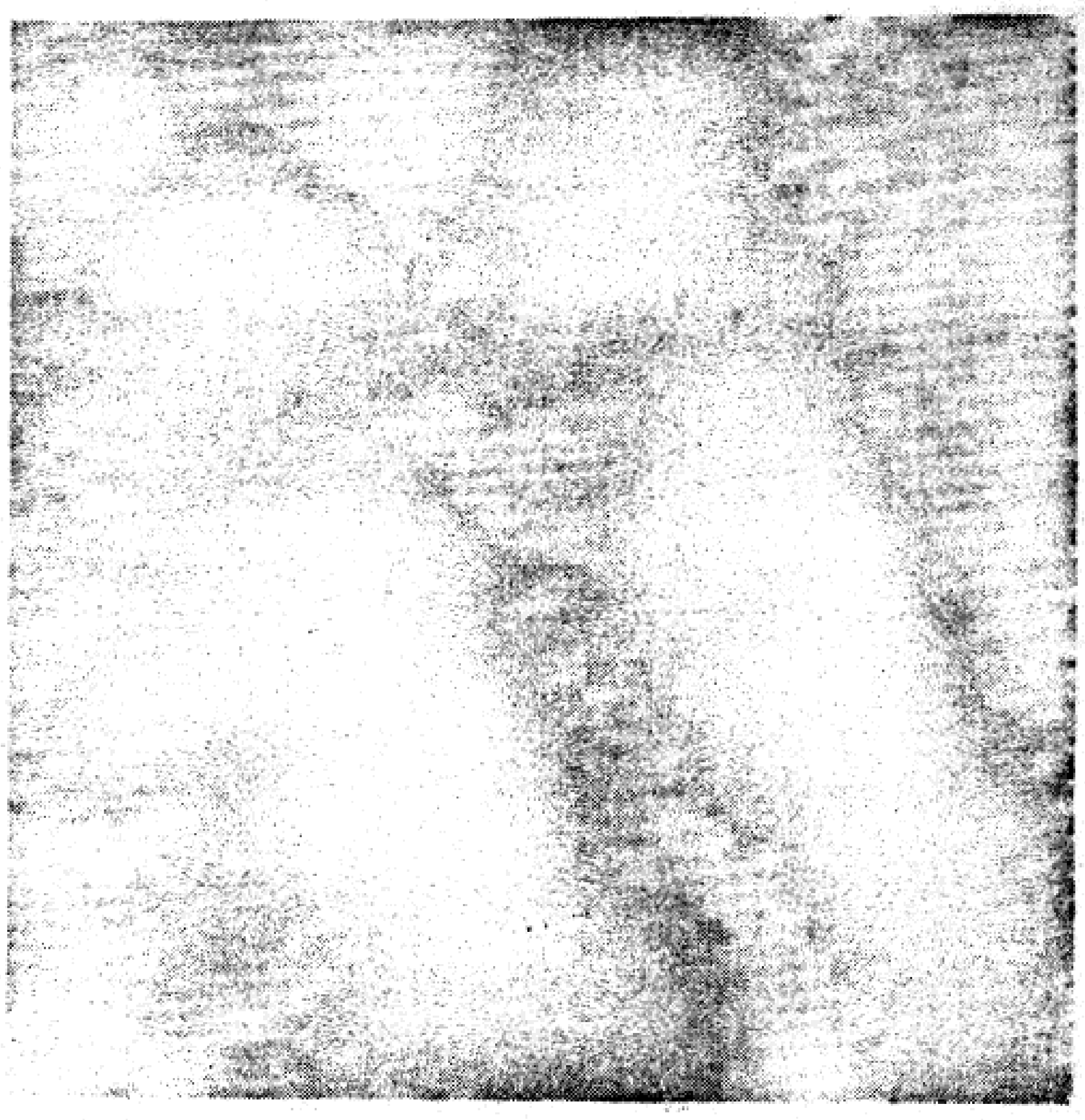

Figure 2. STM images of CdS granules inside a LB film of cadmium arachidate (top view). Imaging parameters V_t = 0.6 V (tip positive), I = 1.5 nA, scanning speed 12 Hz, image size (*a*) 51.2 nm×51.2 nm and (*b*) 40 nm×40 nm.

before (see figures 2 and 3) are shown in figures 4 and 5, whereas in figure 6 the typical characteristic measured outside the wells is reported. In particular, figure 4 reports a staircase behaviour that is typical for systems that display Coulomb staircase phenomena; in this case, a current of 0.5 nA was locked. By analysing the curve it was possible to estimate a voltage step of 0.3 V (see arrows) which corresponds, within the concept of the Coulomb staircase, to a capacitance value of 5.3×10^{-19} F. Such a value implies an electrostatic energy of the particle of 0.15 eV, which is higher than the thermal excitation at room temperature

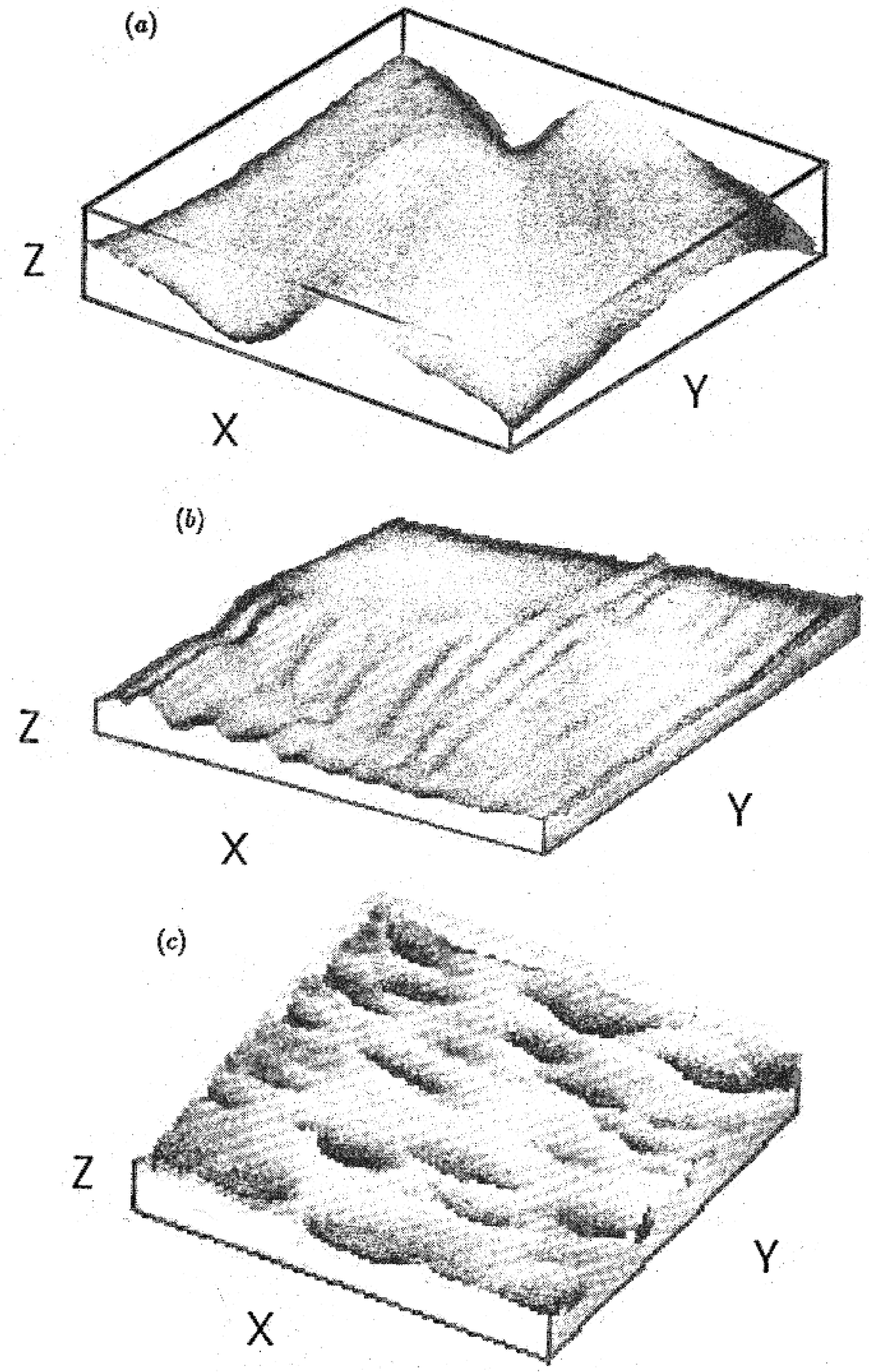

Figure 3. STM images of CdS granules inside a LB film of cadmium arachidate (three-dimensional view). Imaging parameters V_t = 0.6 V (tip positive), I = 1.2 nA, scanning speed 13 Hz, image size (*a*) 31 nm×31 nm and (*b*) 60 nm×60 nm and (*c*) 55 nm×55 nm.

(0.0258 eV). The fact, therefore, allows one also to predict mono-electron phenomena at room temperature from a theoretical point of view.

Results reported in figure 5 were registered by locking a tunnelling current value higher than in the previous case (1 nA instead of 0.5 nA). Regions with negative resistance which are not usually reported in the literature for the Coulomb staircase phenomenon appeared in these curves. However, several aspects of these curves are similar to those which characterize a Coulomb staircase, namely, equal steps in voltage values corresponding to the position of current steps. Moreover, there is a dependence of the voltage step width upon the particle size over which the tip was located. In fact, the curves b and d in figure 5(*b*) represent V–I characteristics obtained by placing the STM tip over the points marked 1 and 2 in figure 2. The curve acquired at the point labelled 1 (curve b in figure 5(*b*)), shows current oscillations generated in correspondance to constant voltage increases; V–I characteristics acquired at the point labelled 2 also show oscillating behaviour but with a different voltage step. This difference, together with the difference in the apparent size of the features labelled 1 and 2 in figure 2, could suggest the appearance of mono-electron phenomena.

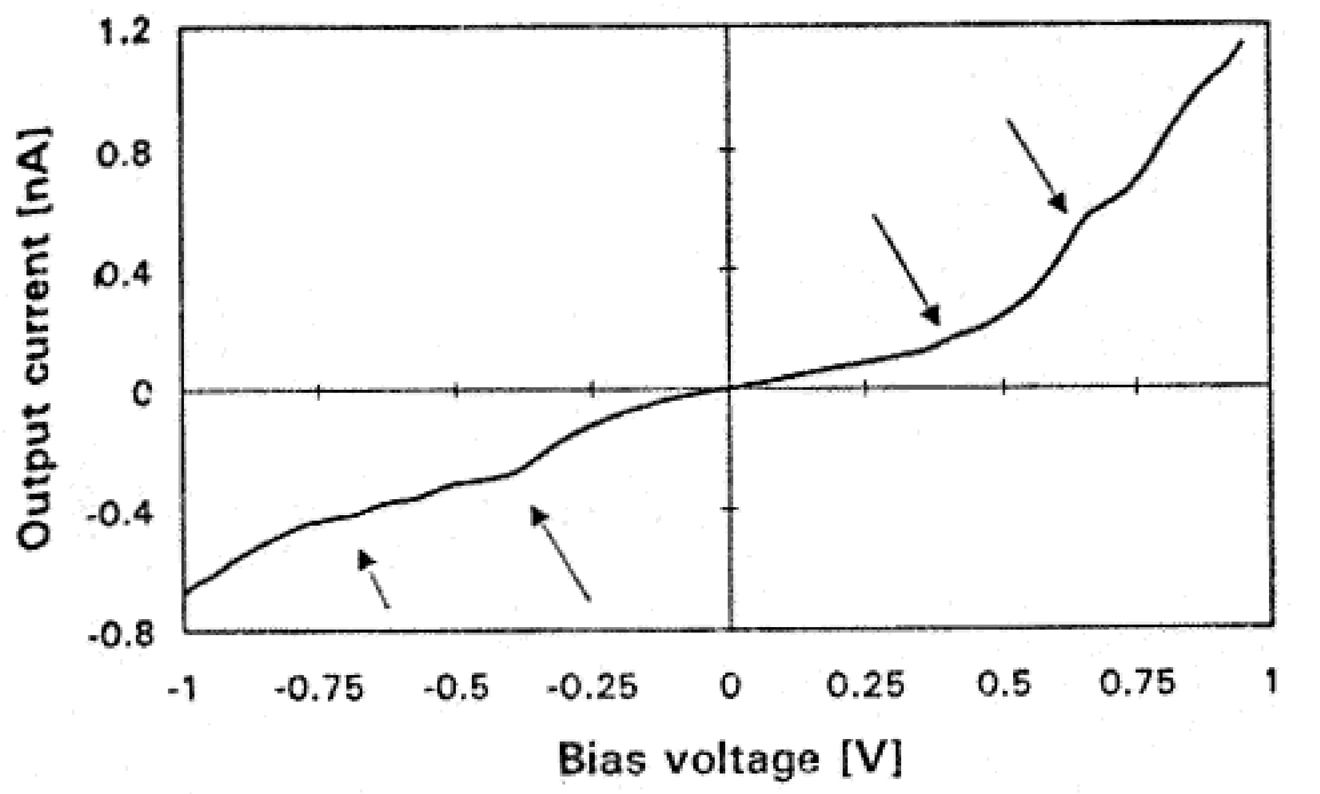

Figure 4. STM V–I characteristics showing staircase behaviour. The tip was placed above the particle, locking a current I = 0.5 nA.

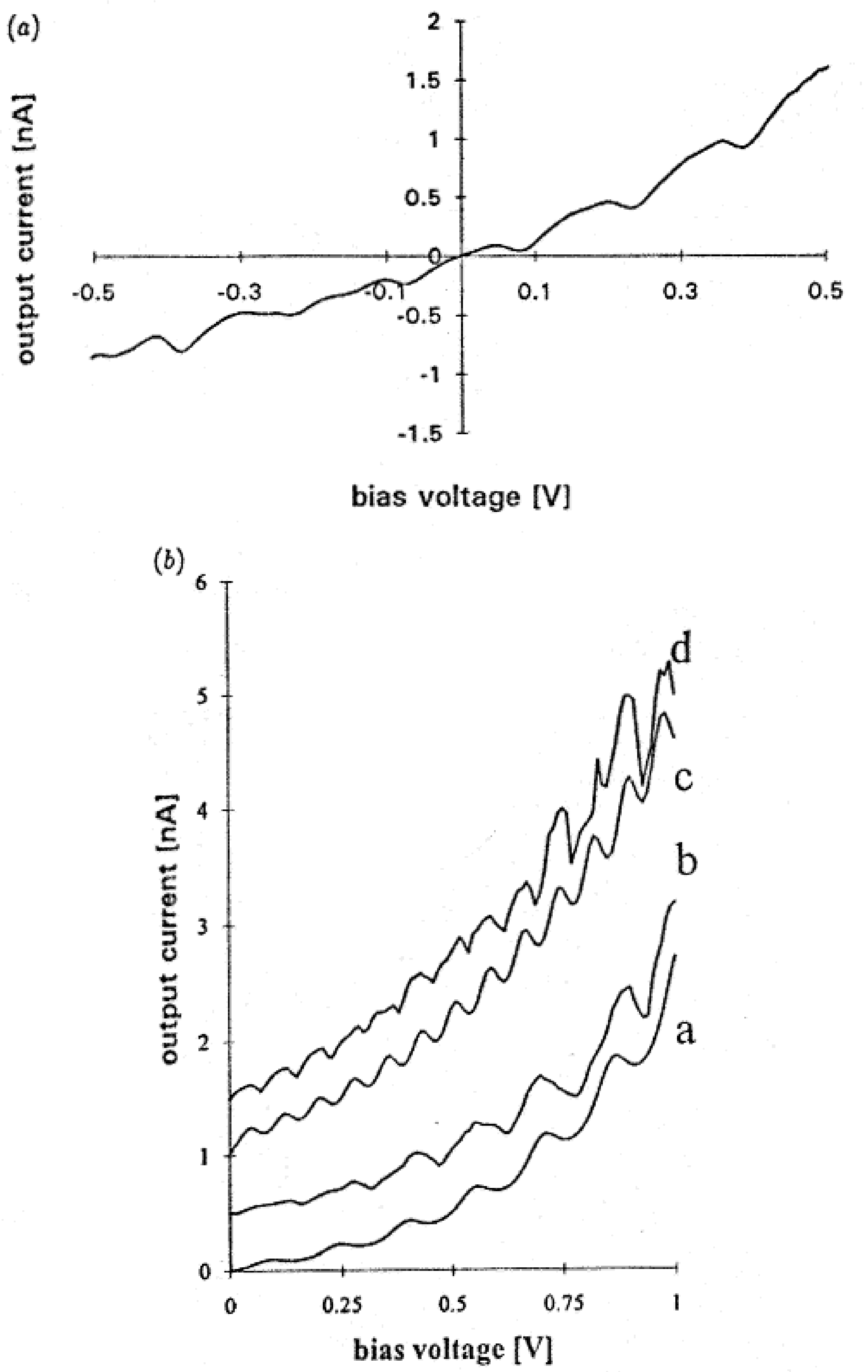

Figure 5. STM V–I characteristics showing negative resistance regions (a). The data acquired on the well at positions 1 (curve b) and 2 (curve d) in figure 2(a) are shown in (b). Curves a and c correspond to best fits. The curves are shifted relative to each other by 0.5 nA. The tip was placed above the particle, locking a current I = 1.0 nA.

Nevertheless, the appearance of regions characterized by negative resistance is generally not typical for the Coulomb staircase phenomenon. However, several works reported similar features both theoretically [15] and experimentally [16, 17].

The observed phenomena can be explained starting

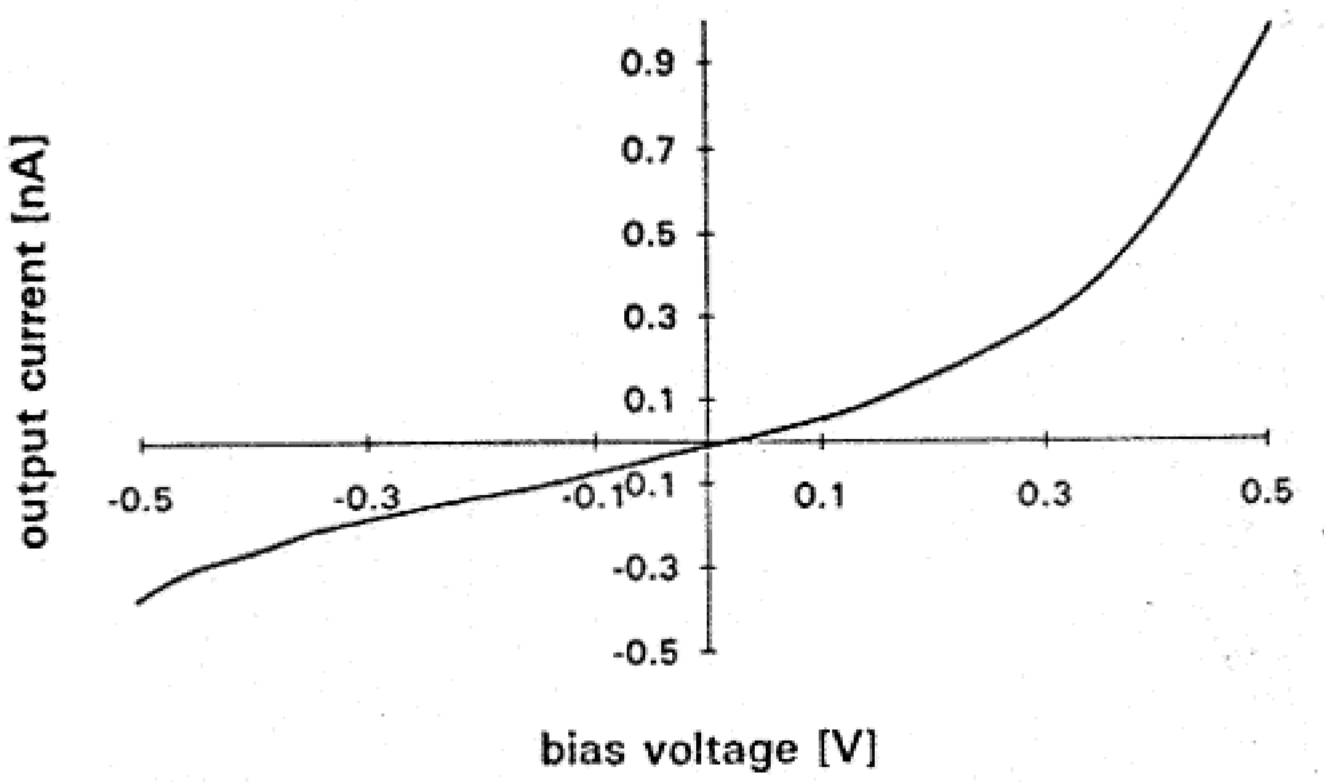

Figure 6. STM V–I characteristics acquired outside apparent particles.

from the consideration that different behaviours in the V–I characteristics of the same granule (staircase and negative resistance) are measured when different values of current are locked by the STM feedback. This fact implies, of course, that different tip–granule distances are attained in the two cases. By considering the structure as a two-barrier system, we can suggest that one barrier, namely that between graphite and granule, is fixed (cannot be varied) whereas the second can be adjusted by locating the vertical position of the tip. From these considerations, we can conclude that, by varying the locked current, we change the asymmetry of the structure.

Asymmetry of the structure is one of the basic parameters which enters when dealing with the Coulomb staircase phenomenon. Let us consider the case of an asymmetric structure in which one barrier is larger than the other. Upon applying the bias voltage to the structure, we induce electron tunnelling through the smaller barrier. In this case the electron will tunnel back from the granule to the electrode with a very high probability until the bias voltage matches the threshold value e/C. At this point one additional electron charges the granule. This event also allows tunnelling through the second barrier to take place. Thus, there is a fixed value of current through the whole structure until one more electron charges the granule.

In the case of rather symmetric systems, these considerations can no longer be considered valid. In fact, tunnelling probabilities now become of the same order for both barriers. Therefore the total current through the system is governed by both barriers. Before reaching the threshold value e/C, a normal tunnelling current through both junctions is present. This is a reason why a marked suppression of the conductivity around zero bias voltage was not observed. When the bias voltage matches e/C the charge existing in the granule unbalances the voltage distribution through the junctions, avoiding new ingress of the electrons to the granule and facilitating their drain. This behaviour could be the reason for the appearance of regions with negative resistance in the measured V–I characteristics.

Starting from these considerations, the fitting of experimental curves was performed taking into account two-barrier systems in which bias voltage is re-distributed along the structure when a successive electron enters the granule ($V_{bias} = ne/C$). The results of the fitting are shown in figure 5.

4. Conclusions

CdS nanocrystals were synthesized in a fatty acid bilayer. STM imaging allowed one to estimate their sizes. Voltage–current characteristics were measured over these particles by means of STM. A quantized increase in the current at the bias voltage, indicating the occurrence of mono-electron phenomena, has been registered. The characteristics demonstrate two kinds of behaviour, a step-like one and one with negative resistance, corresponding to different values of the locked current.

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