Tunnel volt-ampere characteristics for colloidal gold quantum dots under dissipative tunneling conditions

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Abstract. In this project the tunnel volt-ampere characteristics of colloidal gold quantum dots in a system of combined tunnel and atomic force microscopes were experimentally measured. It is assumed that ionic conductivity contributes for tunnel current the most. A qualitative comparison was made for tunnel volt-ampere characteristics and the theoretical probability curve of 2D-dissipative tunneling under influence of two local wide-band phonon modes. A qualitative agreement was found for theoretical and experimental curves, which indicates the possible contribution of the dissipative tunneling in the current through a quantum dot at the tip of a cantilever, which can be amplified in clusters ranging in size from 1 to 5 nm in thinner films.

1. Introduction

The electronic properties of ultrafine nanoparticles (UFPs) have been attracting researchers’ attention throughout several decades. Electronic structure and properties of UFPs differ sharply from those of bulk samples of metals. The properties of UFPs occupy an intermediate position between the individual atoms of metals and bulk samples. In particular, of the fundamental interest is the critical number of atoms in UFPs from which their properties are indistinguishable from those of bulk samples. In the UFP systems a number of fundamental physical effects can be observed, such as changes in the electronic structure of UFP due to size quantization and the associated changes in heat capacity, magnetic susceptibility [1–11]; effects of Coulomb blockade of electron tunneling through UFP, etc. [1–6]. The purpose of this work is to study the tunneling volt-ampere characteristics which were obtained for growing colloidal gold quantum dots in the system of combined atomic-force and scanning tunneling microscopes (AFM/STM), as well as to study the conditions of possible contribution of 2D-dissipative tunneling in the tunneling volt-ampere characteristics. It is necessary to make a qualitative comparison of a tunneling volt-ampere characteristic for a growing colloidal gold quantum dot in the combined AFM/STM system and a theoretical curve for the field dependence of the probability of 2D-dissipative tunneling under the influence of two local phonon modes.
2. Experimental part
The experimental part of the procedure partly corresponds to the method of authors from University of Kobe (Japan), published in [1]. The formation of gold particles in films of Au(III) – SiO\textsubscript{2}/TiO\textsubscript{2} is performed using an atomic force microscope. Topographic images of the film surface are recorded before the formation of gold nanoparticles without external electric field. Then a cantilever comes close to a certain surface point. Local ion reduction of Au(III) is performed by applying a negative potential to the indium oxide film with a cantilever as grounding. Ion reduction of Au(III) can be observed by cathode current in the volt-ampere characteristic and the current dependence on distance between the cantilever and the film surface. Formation of gold nanoparticles also occurs during the process of scanning a particular area by a cantilever while applying a negative potential to a film. The scanning speed and cycles are manipulated by changes in density and morphology of generated gold nanoparticles. In the Japanese authors’ experimental work [1], semispherical colloidal gold quantum dots grew only at a negative voltage, but in the experiment performed in this work, clusters of size up to 10 nm (figure 1) were formed at a negative voltage, while toroidal colloidal gold nanostructures were formed in a positive one (figure 2). The theoretical work was carried out based on the theory of dissipative tunneling using the instanton method. At the formation of colloidal gold clusters with size of above 10 nm in the combined system of AFM/STM, the main conductivity mechanism is assumed to be ionic. In this case, because the thickness of a gelatinous film is about 100 nm, the golden quantum dot grows up to the 100 nm size, when the dissipative tunneling mechanism is suppressed. Due to the diffusion drift, trivalent gold ions penetrate into the area of high field strength under the tip of a cantilever of AFM/STM, which stimulates the corresponding flow of electrons. Apparently, the mechanism of conductivity occurs if the film thickness is sufficiently large (100 nm) and the size of clusters is large as well (above 10 nm). On the other hand, the dissipative tunneling mechanism can be implemented in systems of sufficiently thin films (less than 10nm thick) and clusters of small sizes (from 1 to 5 nm).

![Figure 1. Topography (left) and a current image (right) of the surface area of the film before the modification (before the formation of a colloidal gold cluster). The voltage between the probe and the sample is 0.5 V.](image-url)
3. Possible conductivity mechanisms and qualitative comparison with the experiment

Indeed, the ion conductivity mechanism can be interpreted as a trivalent gold ion drift, initially equally distributed throughout the volume of a gel film in high external electric field at the needle of the cantilever, followed by the process of hemispherical cluster formation. This ion conductivity mechanism will prevail over the tunnel one, when the electric field of positive ions of gold $E^*$ exceeds the value of the external electric field $|E_\text{ext}|$, or $R_0/d > U/d |E^*| - 1$, where $R_0$ – the cluster radius, $L$ – the gel film thickness, $d = L - R_0$ (the distance from the top of the cluster to the tip of the cantilever), $U$ – the voltage of an external electric field. The reverse inequality correlates with the mechanism of tunneling current, and the previously proposed model of 2D-dissipative tunneling [11] becomes relevant.

![Figure 2](image)

**Figure 2.** Topography (left) and current image (right) of the surface area of the film after the modification (formation of toroidal nanostructure under the tip of a cantilever) at a positive voltage.

The potential difference between the probe and sample is $+0.5$ V.

For subsequent qualitative comparison with the experimental volt-ampere characteristics, we calculated the probability of 2D-dissipative tunneling using the one – instanton approach in the case of parallel movement of tunneling particles under influence of two local phonon modes in the wide band in the non-oscillatory mode. This probability can be defined as $\Gamma = \exp(-S^*)$, where $S^* = S/(a_\omega)$. Using the results of our works [5, 7–11], we can derive the following general formula for the action $S$ as a function of parameters $\tau_1$ and $\tau_2$ (instanton centers or barrier breakthrough timings):

$$
S = 2a(b+a)(\tau_1 + \tau_2)\omega^2 - \frac{\omega^2(a+b)^2(\tau_1 + \tau_2)^2}{\beta} - \frac{\omega^2(a+b)^2(\tau_1 - \tau_2)^2}{(\omega^2 - 2\alpha)\beta} - \frac{2\omega^2(a+b)^2}{\beta} \sum_{n=0}^{\infty} \left( \frac{\sin\nu_n \tau_1 + \sin\nu_n \tau_2}{\nu_n^2 + \omega^2 + \xi_n^2} + \frac{\sin\nu_n \tau_1 - \sin\nu_n \tau_2}{\nu_n^2 + \omega^2 - 2\alpha} \right),
$$

(1)
where \( \zeta_n \) is determined taking into account the influence of two local wide-band phonon modes

\[
\zeta_n = v_n^2 \frac{C_2}{\alpha \zeta (\alpha^2 + v_n^2)} + v_n^2 \frac{C_2}{\alpha \zeta (\alpha^2 + v_n^2)};
\]

\( a, b \) – positions of the double-oscillator potential minima along one of the parallel tunneling coordinates in the absence of external electric field; \( v_n \) – the Matsubara frequencies \( \nu = \frac{2\pi n}{\beta} \), \( \beta = \frac{\hbar}{kT} \) – the return temperature, \( \omega \) – the frequency of a two-well oscillator along the coordinates of tunneling; \( \omega_2, \omega_3 \) – the frequencies of the local phonon modes, normal to the tunneling coordinate, \( \alpha \) – the coefficient of the interaction of the parallel tunneling electrons in the dipole-dipole approximation.

The influence of the electric field on the asymmetric two-well oscillator potential along one of the parallel tunneling coordinates can be represented as:

\[
\tilde{U}(q) = \frac{\omega_2^2}{2}(q-a)^2 \theta(q) + \left[ \frac{\omega_0^2}{2}(q+a)^2 - \Delta I \right] \theta(-q) - |e|E_q,
\]

where the parameter \( \Delta I = \frac{\omega_0^2}{2}(a^2 - b^2) \) determines the original asymmetry of potential in absence of the field. In the external electric field, the value of the asymmetry of the two-well oscillator potential, as is well known, changes proportionally to the magnitude of the field.

For the dimensionless quasi-classical action (because of the convenience of numerical comparison of theoretical and experimental curves), we make dimensionless designations:

\[
\epsilon = \epsilon' \omega = \left( \tau, -\tau \right) \omega; \quad \tau = 2\tau' \omega = (\tau_1, \tau_2) \omega; \quad \beta' = \beta \omega / 2; \quad \alpha' = 2\alpha / \omega; \quad b' = b / a, \quad b \geq a.
\]

Effect of the electric field can be accounted for by renormalization of the parameters: \( a = a_0 + |e|E / \omega_0^2 \), \( b = b_0 - |e|E / \omega_0^2 \). Then, the dimensionless semi-classical action takes the form:

\[
S' = \frac{S}{\alpha' \omega} = 2(b'^2 + 1)\tau - \frac{b'^2 + 1}{2\beta'} \frac{\epsilon'^2}{2(1-\alpha')} \frac{\omega'}{\beta'} \sum_{\nu} A_{\nu},
\]

where

\[
A_{\nu} = \frac{\sin^2 \nu \tau_1 \nu_1^2 (\nu_1^2 + \omega_1^2 + \zeta_1^2)}{\nu_1^2 (\nu_1^2 + \omega_1^2)} + \frac{\sin^2 \nu \tau_2 \nu_2^2 (\nu_2^2 + \omega_2^2 + \zeta_2^2)}{\nu_2^2 (\nu_2^2 + \omega_2^2)} + \frac{\sin^2 \nu \tau_3 \nu_3^2 (\nu_3^2 + \omega_3^2 + 2\alpha)}{\nu_3^2 (\nu_3^2 + \omega_3^2)} - \frac{\cos \nu \tau_1 \nu_1^2 (\nu_1^2 - \omega_1^2 + 2\alpha)}{\nu_1^2 (\nu_1^2 + \omega_1^2 - 2\alpha)} + \frac{\cos \nu \tau_2 \nu_2^2 (\nu_2^2 - \omega_2^2 + 2\alpha)}{\nu_2^2 (\nu_2^2 + \omega_2^2 - 2\alpha)} + \frac{\cos \nu \tau_3 \nu_3^2 (\nu_3^2 - \omega_3^2 + 2\alpha)}{\nu_3^2 (\nu_3^2 + \omega_3^2 - 2\alpha)}.
\]

The calculations of the presented sums were conducted by a method similar to the one considered by authors [5, 11]. The final form for the action \( S \) is very cumbersome, thus, it is not shown in this work. Figure 3 shows a qualitative comparison of the experimental volt-ampere characteristics for the clusters under the cantilever with the field dependence of the probability of 2D-dissipative tunneling.

In figure 3 one can see that the theoretical curve qualitatively corresponds only to one of the two experimental volt-ampere characteristics. Apparently, this is due to the fact that at the early stage of the cluster formation, the tunneling mechanism can still be seen in the diffusion drift. But, after the formation of the cluster greater than 10 nm, the dissipative tunneling mechanism is suppressed (curve 3 in figure 3). When using clusters with sizes greater than 10 nm (the thickness of a gel film
containing Au(III) ions is about 100 nm), the barrier-suppression wavelength becomes greater than the de Broglie one for tunneling particles, and the tunneling probability diminishes exponentially.

Figure 3. A qualitative comparison of the theoretical curve 1 for the field dependence of the probability of 2D-dissipative tunneling, obtained within the present model, and the experimental volt-ampere characteristic (curve 2) of a colloidal gold quantum dot under the cantilever of the AFM/STM system. Curve 3 describes the reverse tunnel current-voltage characteristic for a golden quantum dot with a size of about 100 nm when the dissipative tunneling mechanism is suppressed, and the ionic conductivity mechanism is dominated.

The “Cluster ripple” associated with the process of diffusion of trivalent gold ions drift, in our opinion, is reflected in the form of a “flicker” – chaotic noise oscillations in the volt-ampere characteristics.

4. Conclusion
Thus, in this experiment with the volt-ampere characteristics for colloidal gold clusters under the cantilever, the primary conductivity mechanism, when the forming cluster’s size is greater than 10 nm, is concluded to be ionic. The qualitative comparison of the tunneling volt-ampere characteristics for colloidal gold clusters in the AFM/STM system and the theoretical curve for the dependence of the probability of 2D-dissipative tunneling under influence of two local phonon modes shows the presence of a possible contribution of the dissipative tunneling in the tunneling current through a growing quantum dot at initial stages of growth. It is concluded that the ionic conductivity mechanism will prevail over the tunnel one when the magnitude of the voltage induced by the electric field of positive ions of gold exceeds the value of the external electric field voltage.
This theoretical model of 2D-dissipative tunneling does not allow to reveal flicker-like oscillations of volt-ampere characteristics. For these purposes, further development of the 2D-dissipative tunneling model with the account of the oscillating mode tunneling is needed.

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