

Full Articles

Interaction of hydrogen and oxygen on the surface of individual gold nanoparticles*

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Adsorption properties of gold nanoparticles on pyrolytic graphite were studied. Water molecules are formed due to the consecutive adsorption of hydrogen and oxygen on the nanoparticle surface. The energies of bonds between chemisorbed hydrogen, water, and gold were determined.

Key words: nanoparticles, gold, adsorption, oxygen, hydrogen.

Bulky gold is usually considered as an inert metal. However, the physicochemical properties of gold nanoparticles differ substantially from those of bulky samples. The catalyst based on gold nanoparticles can be very efficient in CO oxidation.¹ Gold nanoparticles exhibit catalytic properties also in other reactions.^{2–10} Various factors contribute to the enhanced activity of gold when going to nanosized particles. Among those

are dimensional quantization, nanoparticle charge caused by interaction with the support, and a increase in the fraction of low-coordinated gold atoms with a decrease in the particle size.^{11–13} The question about the reason for the activity of gold nanoparticles remains disputable.

In this work, we present the results of studying the interaction of hydrogen with oxygen on the surface of single gold nanoparticles supported on highly ordered pyrolytic graphite (HOPG) by the laser electrodispersion method.¹⁴

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Experimental

An ultra-high vacuum research complex consisting of a scanning tunneling microscope (STM) Auger and mass spectrometers, and facilities for the preparation of samples and STM tips to experiments (ion gun, manipulators, and a gas storage and feeding system) was used for the study. The basic pressure in the system was $P = 2.6 \cdot 10^{-10}$ Torr.¹⁵

Amorphous gold nanoparticles supported on the HOPG surface by the laser electrodispersion (LED) method were used in experiments.¹⁴ The degree of coverage of the HOPG surface with nanoparticles was determined by the exposure time in a flow of dividing gold droplets and varied within 0.1–0.9 monolayer. In most cases, a uniform (on a large scale) coating consisting of separate nanoparticles was formed on the surface.

Morphological features of the surface of the samples and their electronic structure were studied on an Omicron scanning tunnel microscope (Germany) using the standard topographic "constant current" mode and scanning tunnel electron-vibrational spectroscopy. This method provides the diagnosis of the elemental composition and electronic structure of the layer of particles adsorbed on the particle surface from specific features of the volt-ampere curves of the STM tunneling current, $I = I(V)$.¹⁶

Tips made of the polycrystalline tungsten wire by electrochemical etching in an 0.1 *M* aqueous solution of KOH were used for topographic and spectroscopic measurements in STM. The tips were placed in ultra-high vacuum chamber and subjected to additional purification: argon ion bombardment ($E = 500$ – 1000 eV, $I = 1$ – 1.5 nA) to eliminate the surface oxide. In the further examination only the tips that made it possible to obtain atomic resolution on the HOPG surface and reproducible S-shaped volt-ampere curves of the STM tunnel current typical of the tunneling contact of pure metals was used.

The elemental composition of the studied samples was determined using the data of both spectroscopic measurement in STM and studies by an Omicron SMA-100 Auger spectrometer (Germany) of the cylindrical mirror type. At all stages of experiment, the composition of the gas medium in the ultrahigh vacuum chamber was monitored using a HAL301 quadrupole mass spectrometer (Great Britain). The desired gas (oxygen or hydrogen) with the pressure up to $P = 1.3 \cdot 10^{-6}$ mbar was fed to the chamber in order to study the interaction of the nanoparticles with gas-phase reagents. The exposure of the sample was measured in Langmuir units (L), $1 \text{ L} = 1.3 \cdot 10^{-6} \text{ mbar s}^{-1}$. The temperature of the sample during exposure to this or another gas was 300 K.

Results and Discussion

An experiment consisted of three stages, each including exposure of supported nanoparticles to molecular hydrogen, deuterium, and oxygen and heating in ultrahigh vacuum. It has earlier been shown¹⁷ by studies of the shape, structure, and electronic structure of individual gold nanoparticles that they are spheres 2–3 nm in diameter, contain no impurities, and have the metallic type of conductivity; the conductivity of gold nanoparticles exceeds that

of graphite.* Specific features of the HOPG surface covered with gold nanoparticles are shown in Fig. 1. Figure 1, *a* presents a topographic pattern on which lighter points correspond to elevated regions of the surface. Figure 1, *b* shows the profile of the sample along the line indicated in Fig. 1, *a*, whereas Fig. 1, *c* shows the volt-ampere curves of the tunnel current measured on the HOPG (curve 1) and on the gold nanoparticle (curve 2). The volt-ampere curves are S-shaped, which is characteristic of the nanocontact formed by the conductors.

Hydrogen adsorption. In order to study the interaction of nanoparticles with hydrogen taking its isotope deuterium as an example, we measured the volt-ampere characteristics of the STM tunnel current at different points on the nanoparticle surface directly during gas feeding to the ultra-high vacuum chamber. A volt-ampere characteristics measured on exposing the surface to deuterium is presented in Fig. 2 (curve 1). As can be seen from this figure, the shape of the curve changes and a band gap with a width of 1.5–2 eV appears. A change from the S-shaped volt-ampere curve measured on the same nanoparticles before experiment (see Fig. 1, *c*) to the curve in Fig. 2 means that hydrogen is adsorbed on nanoparticles even at room temperature, unlike adsorption on bulky gold. The observed jumps of the tunnel current are not occasional: they caused by a change in the surface state due to hydrogen adsorption and migration over the nanoparticle surface. The exposure of gold nanoparticle in deuterium was 2000 L. After sample storage in ultra-high vacuum for 16 h, it was found that the current jumps disappeared from the volt-ampere curves (see Fig. 2, curve 2) but the region of the band gap persisted.

To estimate the energy of the bond between gold and deuterium atoms, the HOPG sample containing gold nanoparticles was heated in a ultrahigh vacuum vacuum to $T = 500$ K for 45 min. No substantial changes were observed on the volt-ampere curves measured after heating. These results make it possible to estimate the energy of the bond between deuterium and gold using the Frenkel' formula

$$t = t_0 \exp[E/(RT)],$$

where t is the duration of adatom residence on the surface at temperature T , t_0 is the pre-exponential factor

* In this case, the terms of solid state physics (conductivity band and band gap) are used for nanoparticles (restricted systems) in the following meaning: in rather dense discrete spectrum of electronic states ($\Delta E < kT$, where ΔE is the distance between the levels), the distance between the highest occupied (HOMO) and lowest unoccupied (LUMO) levels, E_{HL} , satisfies the condition $E_{\text{HL}} \gg kT$. The conductivity of the STM nanocontact containing nanoparticles is determined by the spectrum of states of this particle, which forms, in the above indicated case, the volt-ampere characteristic of the tunnel current with the zero-current region, the size of which corresponds to E_{HL} , i.e., to the region with the zero density of states in the vicinity of the Fermi level.

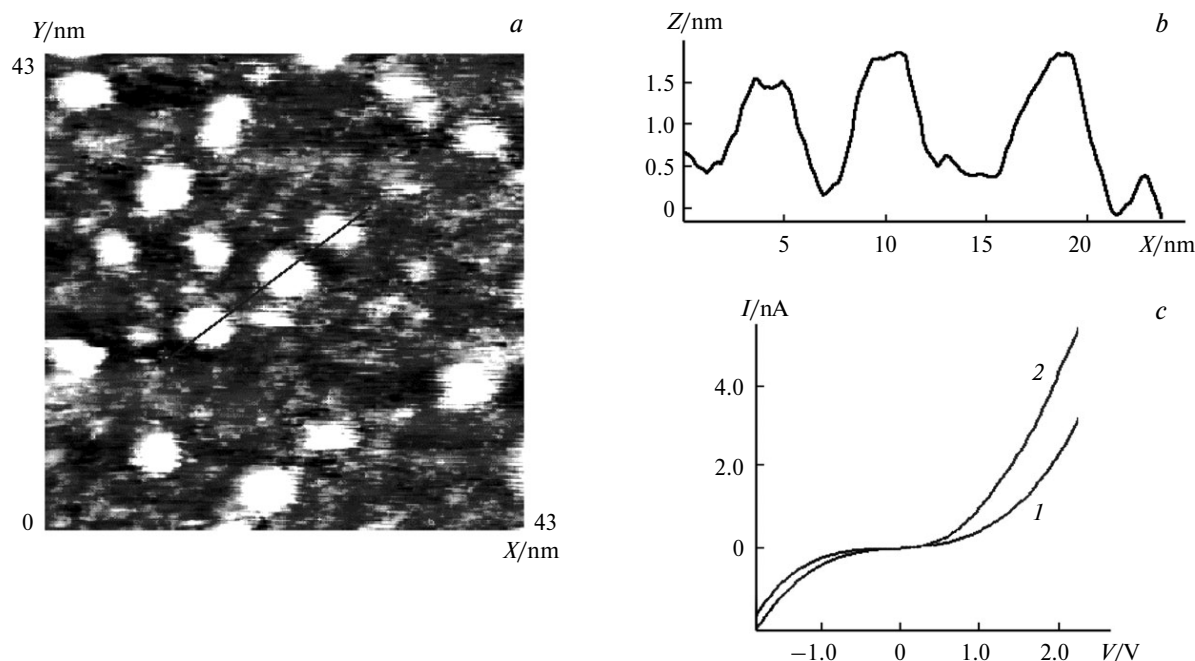


Fig. 1. (a) Topographic image of gold nanoparticles, (b) profile along the line indicated on the topographic image, and (c) volt-ampere curves measured in the HOPG region free of nanoparticles (1) and on the gold nanoparticles (2).

(10^{-13} – 10^{-12} s), and E is the bond energy (bond energy between gold and deuterium atoms is ≥ 1.6 eV).

The appearance of the band gap on the volt-ampere characteristics of the STM tunnel current measured on gold nanoparticles after hydrogen adsorption was observed for the first time. The question about the possibility of transition from the metallic type of conductivity of the nanoparticles to the semiconducting type for hydrogen adsorption on metal was earlier considered theoretically. The results of quantum chemical calculations for a plutonium single crystal covered with hydrogen were described.¹⁸ The calculations were performed using the full-potential linearized augmented plane-wave (FLAPW) method taking into account local spin density (LSDA) and the generalized gradient approximation (GGA) method taking account Hubbard's parameter U (LSDA + U and GGA + U , respectively). The used method makes it possible to take into account the Coulomb interaction between 5f-electrons of the metal atoms. For the quantitative ratio between plutonium and hydrogen atoms equal to 1 : 3, the band gap with a width of 0.26 eV was observed in the spectrum of the electronic states of the system.¹⁸

The experiments on deuterium adsorption on gold nanoparticles supported on the HOPG surface were described in the previous section. The interaction of the nanoparticles with hydrogen gives similar results. This suggests that hydrogen is dissociatively adsorbed on the gold nanoparticles and the energy of the bonds between the gold and hydrogen atoms is ≥ 1.6 eV. Such high bond energy can be explained by several reasons. Among these

are hydrogen penetration under the nanoparticle surface, the interaction with the low-coordination gold atoms, and charging of gold nanoparticles adsorbed on the HOPG surface. The latter assertion is confirmed by the quantum chemical calculations of the bond energy of oxygen adatoms with gold atoms in low-atomic clusters, which show that the bond energy increases upon charging of the cluster.¹⁹

Oxygen adsorption. It was established that molecular oxygen is not adsorbed directly on the gold nanoparticle. However, It was found that oxygen interacts with the gold nanoparticle pre-covered with deuterium or hydrogen.

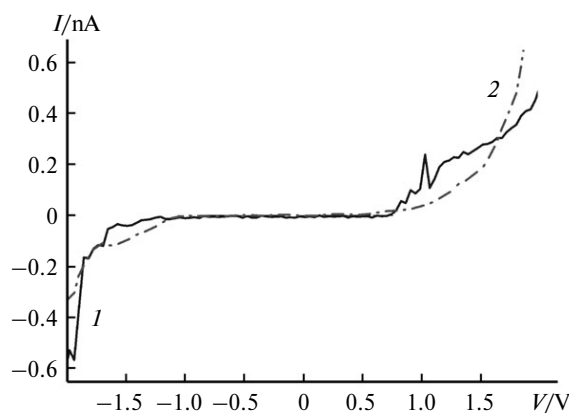


Fig. 2. Volt-ampere curves of the STM tunnel current measured during exposition to deuterium (1) and in 16 h after exposition to deuterium (2).

Thus, adsorbed hydrogen prepares a "landing ground" for the further interaction with molecules from the gas phase. Figure 3 shows the volt-ampere characteristic of the STM tunnel current measured immediately after exposure to oxygen, 2000 L (curve 1). It is seen from Fig. 3 that the volt-ampere characteristic curve changed its shape. The value of band gap decreased to 0.5–1 eV. After storing in a ultrahigh vacuum for 24 h and heating to $T = 500$ K, the curves approaches in shape to the volt-ampere characteristic of diode (curve 2).

Repeated hydrogen adsorption. Hydrogen adsorption on the gold nanoparticle pre-covered with deuterium (hydrogen) and oxygen again results in the change of the volt-ampere curve of the tunneling current. A series of specific changes, in particular, local maxima appear in the curves, and the distances in the voltage axis between adjacent and "next nearest" maxima were 0.2 and 0.41 V (Fig. 4, *a*). The local maxima are arranged almost symmetrically relative to the coordinate origin, and curves 1 and 2 measured on different nanoparticles are very similar in the arrangement of local maxima and their intensity. Figure 4, *b* illustrates the method of measuring the distance between the local maxima.

Similar volt-ampere characteristics were obtained in control experiments for the consecutive adsorption on gold nanoparticles of deuterium, oxygen, and again deuterium. However, in this case, the distances between the maxima changed to be 0.13 and 0.27 V. The histograms of distribution of these distances for the first series of experiments (*a*) and the second (control) series (*b*) are shown in Fig. 5. In these histograms, the measured distances between the local maxima are put on the abscissa and the number of measurements are put on the ordinate. The distribution maxima correspond to the values of quanta of the electron-vibration excitation of the water molecule (bending vibration and vibration of the oxygen–hydrogen bond) with an accuracy to the dimensional coefficient. Thus,

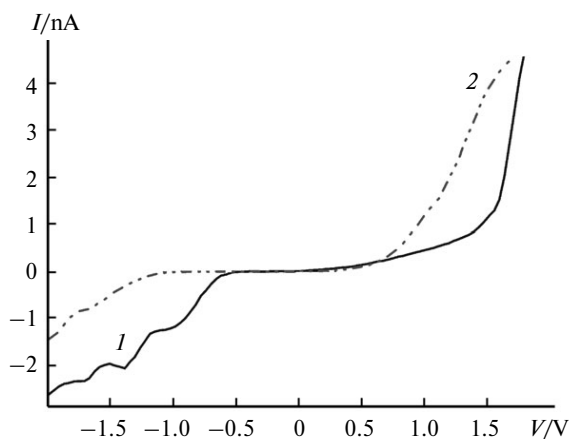


Fig. 3. Volt-ampere curves of the STM tunnel current measured immediately after contact with oxygen (1) and in 24 h after heating to $T = 500$ K (2).

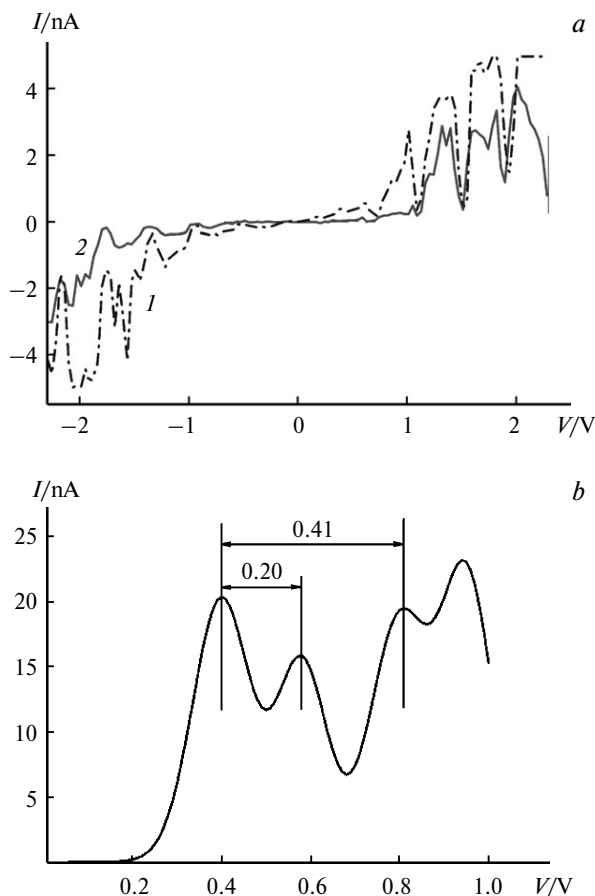


Fig. 4. Volt-ampere curves of the STM tunnel current: (*a*) experimental curves (1 and 2) measured after the repeated hydrogen adsorption on different gold nanoparticles and (*b*) the method of measuring distances between the local maxima.

water molecules are formed due to the consecutive adsorption of hydrogen, oxygen, and again hydrogen and then their interaction on the surface of single gold nanoparticles. A reference can be made to a series of theoretical works^{20,21} describing the modeling of the interaction of gold clusters with oxygen and hydrogen in which the geometric and electronic structures of the adsorption complexes were calculated by the density functional theory (DFT). It was shown that the formation of water molecules is also a favorable process for the combined adsorption of hydrogen and oxygen.

To approach the question of the nature of the experimentally observed local maxima on the volt-ampere curves of the STM current during adsorption, it is necessary to consider the model of two-center resonance electron tunneling.¹⁶ If the region of classically forbidden electron motion contains two scattering (trapping) sites, then the resonance component of the tunneling current is determined by the expression¹⁶

$$I = \text{const} W_{12} (\Gamma_{\text{in}} + \Gamma_{\text{out}}) / \{ [E_1(V) - E_2(V)]^2 + (\Gamma_{\text{in}} + \Gamma_{\text{out}})^2 \},$$

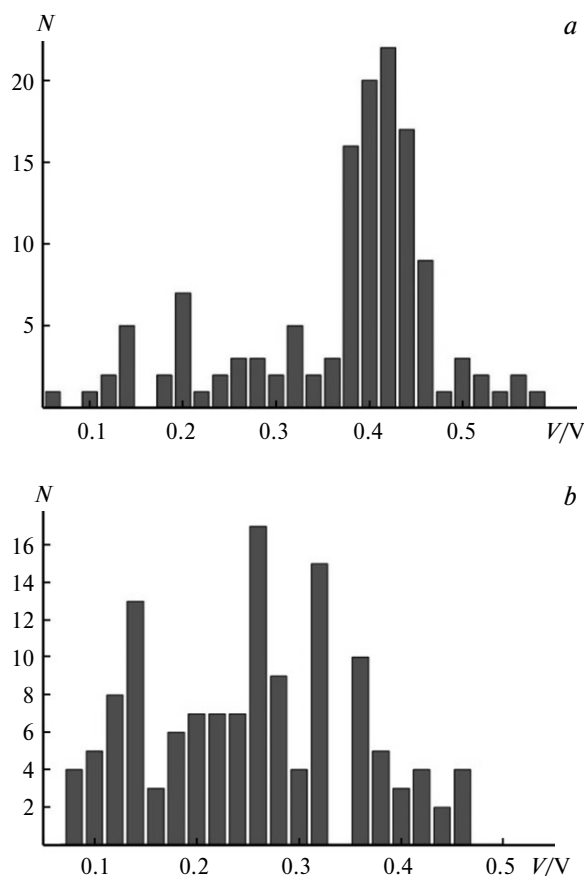


Fig. 5. Histograms of distributions of the number of distances between the local maxima on the volt-ampere curves of the tunnel current for the first (a) and second control series of experiments (b); N is the number of measurements.

where $E_{1,2}(V)$ are the energy levels of the sites, $\Gamma_{\text{in,out}}$ are the probabilities of transitions, and W_{12} is the probability of the intersite transition. Taking into account vibrational degrees of freedom, we obtain $E_{1,2}(V) = E_0(V, R) + \eta\omega(n + 1/2)$, where $E_0(V)$ is the ground state of the level, ω is the characteristic vibrational frequency, and n are natural numbers.

Resonance transitions occur due to three consecutive acts:

- electron transition from the contact with a negative potential to the nearest site with the probability Γ_{in} ;
- intersite transition to the site nearest to the contact with a positive potential with the probability W_{12} ;
- final transition to the contact with a positive potential with the probability Γ_{out} .

For some field strengths $V(z, R_1, R_2)$ depending on the vacuum gap z and site coordinates R_1 and R_2 , the condition $E_1(V, R_1) = E_2(V, R_2)$ is fulfilled, which opens the channel of two-center resonance tunneling and forms the local maximum in the volt-ampere characteristic of the tunnel current. When the condition $\omega\tau > 1$ is fulfilled (τ is the time of electron residence at the site), the resonance tunneling is accompanied by multi-quantum vibra-

tional transitions forming a set of equidistantly arranged local maxima on the volt-ampere characteristics. The distances between these maxima is $\Delta U \sim \eta\omega$. Two sites with similar electron vibrational characteristics, for example, two water molecules in the STM nanocontact, are necessary for the formation of symmetric local maxima. The one-dimensional scheme of two-center resonance tunneling is presented in Fig. 6.

Hydrogen or deuterium supported exclusively at the third stage of experiment is involved in water formation. Hydrogen adsorbed first on the nanoparticle does not participate in the formation of water molecules.

Heating the nanoparticles to $T = 550$ K for 3 h did not change the shape and arrangement of maxima on the volt-ampere curves, which makes it possible to estimate the lowest value of the bond energy between the gold atom and water molecule: ≥ 1.8 eV. The study¹³ of the interaction of hydrogen and oxygen with gold particles by adsorption microcalorimetry gave 251 kJ mol^{-1} (~ 2.6 eV) for the energy of the Au—OH bond consistent with our data.

A similar sequence of experiments on adsorption of hydrogen and oxygen isotopes on the gold foil did not lead to any substantial changes in the volt-ampere characteristics. This means that in accordance with expectation no adsorption occurred and bulky gold is inert.

Localization of the position of water molecules on the nanoparticle surface. The above presented study of hydrogen and oxygen adsorption and their interaction on the surface of single gold nanoparticles revealed the formation of water molecules. Similar measurements indicated sites of adsorption of water molecules (active sites) on the surface of single gold nanoparticles supported on the pyrolytic graphite surface. When measuring the spectroscopic

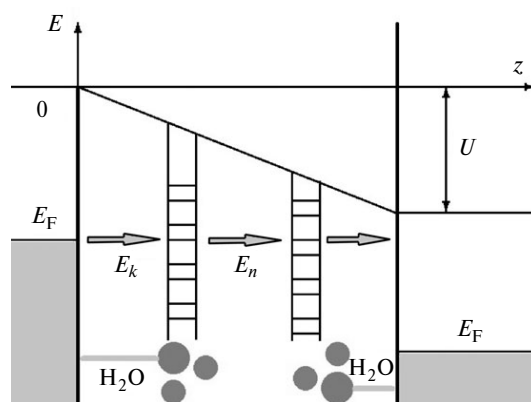


Fig. 6. One-dimensional scheme of electron tunneling in the STM nanocontact between the energy levels of water molecules adsorbed at the STM tip and gold nanoparticle. Designations: E is energy, E_F is the Fermi energy, E_k and E_n are the arbitrary energy levels of water molecules, U is the applied voltage, and z is the spatial coordinate; arrows indicate the direction of electron tunneling.

dependences directly above the sites of adsorption of water molecules, the tunnel current and intensity of specific features of the volt-ampere characteristics (local maxima) reached highest values (Fig. 7, curve 1). The shifts of the STM tip by 0.5 and 1 nm from this point significantly decreased the tunneling current and intensity of local maxima. Examples of the volt-ampere curves at these points are shown in Fig. 7 (curves 2 and 3, respectively). Thus, the sites of adsorption of water molecules and, hence, the positions of active sites on the surface of single gold nanoparticles were localized.

Role of gold nanoparticle charging. The above presented experimental results revealed earlier unknown forms of hydrogen, oxygen, and water adsorption on gold nanoparticles that differ from those described for bulky gold in bond energy values. In our opinion, these effects are due to charging of gold nanoparticles on the HOPG surface. It

was found²² that the characteristic value of the electron work function from the surface of graphite single crystal is ~4.7 eV, whereas the electron work function from the gold single crystal ranges from 5.1 to 5.47 eV depending on the face structure. When two materials with different work functions and, hence, positions of the Fermi levels are in contact, the latter become equal. This equalization is accompanied by the electron transfer from the material with a lower work function to that with a higher work function. Gold nanoparticles supported on the HOPG surface attain a negative charge. At the same time, we carried out experiments on hydrogen and oxygen adsorption on the surface of the gold STM tip, which models the gold nanoparticle on bulky gold. Owing to the equality of the work functions of electrons, this particle is not charged and effects similar to those presented above were not observed in these experiments.

Thus, it is established that gold nanoparticles supported on the HOPG surface by the laser electrodispersion method are not inert. The lowest boundary of the energy bond between gold atoms and hydrogen chemisorbed on the nanoparticle surface was estimated as ≥ 1.6 eV. It is shown that the consecutive adsorption of hydrogen, oxygen, and re-adsorption of hydrogen on the gold nanoparticle surface results in the formation of water molecules on the nanoparticle surface. Adsorbed hydrogen is not preliminarily involved in the formation of water molecules but only changes the state of the nanoparticle thus providing the further interaction with molecules from the gas phase. The value of the bond energy of water molecules with gold atoms was estimated (≥ 1.8 eV). The unusual properties of gold nanoparticles arranged on the HOPG surface can be due to effects of charge transfer from graphite to gold because of the contact potential difference between gold and graphite.

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References

1. M. Haruta, T. Kobayashi, H. Sano, N. Yamada, *Chem. Lett.*, 1987, 405.
2. D. Thompson, *Gold Bull.*, 1999, **32**, 12.
3. A. Ueda, M. Haruta, *Gold Bull.*, 1999, **32**, 3.
4. D. Andreeva, *Gold Bull.*, 2002, **35**, 82.
5. D. A. H. Cunningham, W. Vogel, R. M. Torres-Sanchez, K. Tanaka, M. Haruta, *J. Catal.*, 1999, **183**, 24.
6. K. Tanaka, T. Akita, D. A. H. Cunningham, S. Tsubota, in *Structural Analyses and Characterization of Gold Catalysts*, Report of the Osaka National Research Institute, No. 393, 1999, Osaka, Japan, p. 11–35.

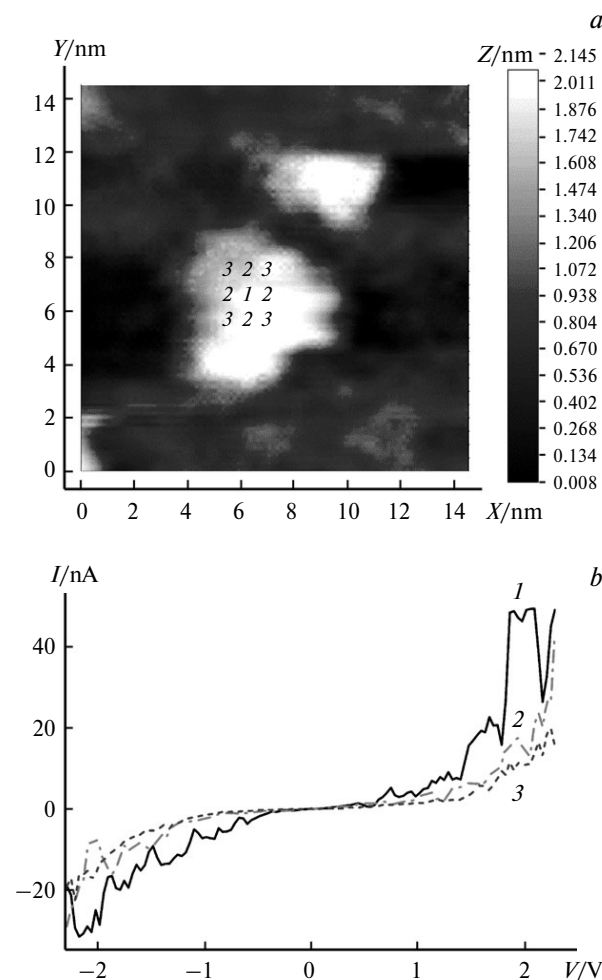


Fig. 7. Localization of the water molecules adsorbed on the gold nanoparticle surface: (a) topographic image of the gold nanoparticle, and numerals designate the points of measuring the volt-ampere curves; (b) examples of the volt-ampere curves of the tunneling current, and the number of the curve corresponds to the numeral mark on the topographic image.

7. D. Fischer, W. Andreoni, A. Curioni, H. Grönbeck, S. Burkart, G. Ganteför, *Chem. Phys. Lett.*, 2002, **361**, 389.
8. T. N. Rostovshchikova, V. V. Smirnov, V. M. Kozhevin, D. A. Yavsin, S. A. Gurevich, *Ros. Nanotekhnol. [Russian Nanotechnologies]*, 2007, **2**, 47 (in Russian).
9. S. A. Nikolaev, V. V. Smirnov, *Catal. Today*, 2009, 147S, S336.
10. B. Roldan Cuenya, *Thin Solid Films*, 2010, **518**, 3127.
11. J. T. Miller, A. J. Kropf, Y. Zha, J. R. Regalbuto, L. Delannoy, C. Louis, E. Bus, J. A. van Bokhoven, *J. Catal.*, 2006, **240**, 222.
12. T. V. W. Janssens, B. S. Clausen, B. Hvolbæk, H. Falsig, C. H. Christensen, T. Bligaard, J. K. Nørskov, *Top. Catal.*, 2007, **44**, 15.
13. C. T. Campbell, J. C. Sharp, Y. X. Yao, E. M. Karp, T. L. Silbaugh, *Faraday Discuss.*, 2011, **152**, 227.
14. V. M. Kozhevin, D. A. Yavsin, V. M. Kouznetsov, V. M. Busov, V. M. Mikushkin, S. Yu. Nikonov, S. A. Gurevich, A. Kolobov, *J. Vac. Sci. Techn. B*, 2000, **18**, 1402.
15. M. V. Grishin, A. K. Gatin, N. V. Dokhlikova, A. A. Kirsankin, V. A. Charitonov, B. R. Shub, *Russ. Chem. Bull. (Int. Ed.)*, 2013, **62**, 1525 [*Izv. Akad. Nauk, Ser. Khim.*, 2013, 1525].
16. F. I. Dalidchik, B. A. Budanov, N. N. Kolchenko, E. M. Balashov, S. A. Kovalevskii, *Zh. Eksp. Teor. Fiz.*, 2012, **142**, 1218 [*J. Exp. Theor. Phys. (Engl. Transl.)*, 2012, **142**].
17. M. V. Grishin, A. K. Gatin, A. A. Kirsankin, V. A. Khartanov, B. R. Shub, *Ros. Nanotekhnol. [Russian Nanotechnologies]*, 2013, **8**, 36 (in Russian).
18. J. Ai, T. Liu, T. Gao, B. Ao, *Comput. Mater. Sci.*, 2012, **51**, 127.
19. A. Franceschetti, S. J. Pennycook, S. T. Pantelides, *Chem. Phys. Lett.*, 2003, **374**, 471.
20. D. A. Pichugina, A. V. Beletskaya, N. E. Kuz'menko, A. F. Shestakov, *Rev. Adv. Mater. Sci.*, 2009, **20**, 48.
21. A. V. Beletskaya, D. A. Pichugina, A. F. Shestakov, N. E. Kuz'menko, *J. Phys. Chem. A*, 2013, **117**, 6817.
22. *Fizicheskie velichiny. Spravochnik [Physical Magnitudes. Manual]*, Eds I. S. Grigor'ev, E. Z. Meilikhov, Energoatomizdat, Moscow, 1991, p. 1232 (in Russian).

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