Hydrogenation of HOPG-Supported Gold Nanoparticles: Surface or Volume?

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Abstract: The hydrogenation features of gold nanoparticles deposited on highly oriented pyrolytic graphite were determined, and composite nanostructures consisting of pure and hydrogenized gold were synthesized. Methods of scanning tunneling microscopy and spectroscopy have been successfully used to probe the bottom of the conductive band and to determine the shape of the electron energy barrier in hydrogenized gold. Considering models of surface and volume hydrogenation, we have shown that no hydrogen dissolution occurred in gold nanoparticles, but all changes in their electronic structure were associated with surface processes. The results of the quantum chemical simulation also corresponded with this conclusion.

Keywords: nanoparticles; gold; highly oriented pyrolytic graphite; hydrogen; adsorption; dissolution; scanning tunneling microscopy; scanning tunneling spectroscopy

1. Introduction

Nowadays, nanostructured materials are becoming the base for many catalysts. For example, low-temperature CO oxidation [1] and selective oxidative coupling of methanol to methyl formate [2] use gold nanoparticles as catalysts. Reactions such as selective isomerization of epoxides to allylic alcohols [3], benzylation of aromatics [4], and production of vinyl chloride and vinyl acetate monomers [5] are also based on the use of gold nanocatalysts. Among others, a very important reaction is catalytic hydrogenation, in which gold nanoparticles are also used: catalytic alkene hydrogenation [6], chemoselective hydrogenation of crotonaldehyde to crotyl alcohol [7], chemoselective hydrogenation of nitro compounds [8], and heterogeneous hydroformylation of olefins [9]. In cases when the hydrogenation process is assisted by hydrogen transfer, reactions such as reduction of carbonyl compounds [10,11] and the hydrochlorination of amines [12] and alkynes [13] were shown to occur in the presence of gold. In all these processes, an important role is played by the molecular hydrogen dissociative adsorption and the interaction of the surfaces of nanoparticles with nascent H atoms. For example, by means of TEM, calorimetry and XRD, it was found that the direct synthesis of water from molecular oxygen and hydrogen occurred at 383–433 K over silica-supported gold nanoparticles under a pressure of several kilopascals [14]. The conclusions of this work about the interaction of gold and hydrogen are supported by the corresponding DFT calculations and by results obtained for Al₂O₃-supported gold nanoparticles [15,16].

However, even for the model reactions in nanocatalytic systems based on gold, the elementary mechanisms remain unclear despite the long-term studies [17–24]. For example, in what form does hydrogen exist in gold-based nanosystems? Is it manifested only by surface adsorbate atoms? If not, it may be crucial, e.g., for the estimation of Au-H binding energy. Although hydrogen chemisorption on gold and the possibility of gold hydride
formation are undoubted today [25–27], there is still a lack of information on hydrogen solubility in gold [28].

Previously, adsorption of hydrogen has been found to change the electronic structure of gold nanoparticles [29]. Furthermore, the electron density distortions introduced by the hydrogen adatom were revealed to be local [30]. For the system of gold nanoparticles supported on highly oriented pyrolytic graphite, we experimentally showed that the gold–carbon interface was the preferred region for hydrogen adsorption [31]. Note that a long period of time is necessary for the transition of the system to the final stable state [31]. After the exposure of gold nanoparticles to hydrogen, one has to wait up to 25–30 h before stable STS results can be obtained. This long transition time may result from significant activation barriers for H atoms’ surface migration and for the structural rearrangement processes within the nanoparticles, which may include the diffusion of H atoms or synthesized AuH species in volume.

Based on the results of TPD experiments, some authors [32,33] suppose that subsurface hydrogen exists, which may form dimers with adsorbed H atoms and influence surface reactions. Unfortunately, due to the very small amount of active substance, it is impossible to carry out such experiments and to distinguish between adsorbed and dissolved hydrogen in the case of nanostructured catalytic systems. Lots of effective methods are used to study the catalytic properties of nanoparticles—calorimetry, mass spectrometry, photoelectron microscopy, and X-ray methods—but there is a great general problem in that they do not detect hydrogen at all. Additionally, the information provided by these methods is averaged over a large ensemble of nanoparticles in different states. As a result, it is impossible to find out how the local structural features of nanoparticles correlate with their chemical properties. Using probe methods—in particular, scanning tunneling microscopy and spectroscopy—can solve this problem, since their spatial resolution allows one to investigate chemical interactions between solid surfaces and gaseous reagents even at the level of single molecules and defects.

The main purpose of this work is to determine if the hydrogenation process takes place over the surface or in the volume of gold nanoparticles. This paper presents the results of an experimental study of composite nanoparticles based on pure and hydrogenized gold. The conclusions are proven by numerical simulation of the energy stability of a complex based on gold nanoclusters and dissolved atomic hydrogen.

2. Experimental Section

2.1. Synthesis, Exposition and STM/STS Measurements

Nanoparticles were synthesized on the surface of highly oriented pyrolytic graphite (HOPG) with angular spread of the c-axes of the crystallites being 0.8° [34] by the impregnation-precipitation method. An aqueous solution of chloroauric acid, HAuCl₄, with a concentration of 5 mg/L was used as a precursor. The precursor solution was applied to a cleaned surface of HOPG (AIST-NT, Moscow, Russia), which looked like vast atomically smooth C(0001) terraces. After drying the solution, the sample was placed in an STM chamber (Omicron NanoTechnology, Taunusstein, Germany), where it was calcined under ultrahigh vacuum (UHV) conditions at a temperature of 600–750 K for 8 h. The residual gas pressure did not exceed 2 × 10⁻¹⁰ mbar. During calcination, the precursor solution decomposed [35]:

\[
2\text{HAuCl}_4 \cdot 3\text{H}_2\text{O} \xrightarrow{345–450 \text{K}} \text{Au}_2\text{Cl}_6 + 2\text{HCl} + 6\text{H}_2\text{O} \quad (1)
\]

\[
\text{HAuCl}_4 \cdot 3\text{H}_2\text{O} \xrightarrow{345–450 \text{K}} \text{HAuCl}_2(\text{OH})_2 + 2\text{HCl} + \text{Cl}_2 + \text{H}_2\text{O} \quad (2)
\]

Gaseous HCl and Cl₂ were pumped out of the chamber. Further decomposition of solid gold-containing compounds occurred according to the following scheme [35]:

\[
\text{Au}_2\text{Cl}_6 \xrightarrow{450–505 \text{K}} 2\text{AuCl} + 2\text{Cl}_2 \quad (3)
\]

\[
4\text{HAuCl}_2(\text{OH})_2 \xrightarrow{450–505 \text{K}} 4\text{Au} + 8\text{HCl} + 2\text{H}_2\text{O} + 3\text{O}_2 \quad (4)
\]
Thus, the selected temperature provided full decomposition of the precursor and formation of metal gold on the HOPG surface.

The experiments were carried out using a scanning tunneling microscope (UHV VT STM, Omicron NanoTechnology, Taunusstein, Germany) under UHV conditions. This allowed us to avoid uncontrolled changes in the chemical composition of the samples due to residual gases. The tungsten STM tips used for the experiments were prepared by standard methods and treated by argon-ion sputtering under UHV conditions. In the experiments, we only used those tips that showed a reproducible S-shaped curve of the volt-ampere characteristic (VAC) when scanning HOPG. Such a VAC is typical for metal–metal tunnel nanocontacts [36–40].

H₂ adsorption under 1 × 10⁻⁶ mbar of pressure was studied at 300 K. After pumping H₂ out of the chamber, STM spectroscopy experiments were performed to investigate the structure of Au nanoparticles modified by H₂. The exposure value was measured in Langmuir, where 1 L = 1.33 × 10⁻⁶ mbar·s.

2.2. Numerical Simulation

To check the energy stability of a complex based on gold nanoparticles and dissolved atomic hydrogen, quantum chemical simulation was carried out within the framework of density functional theory (DFT) using software package OpenMX-3.7 (OMX) [41]. All the calculations were carried out in a generalized gradient approximation (GGA) using the PBE functional without regard for spin polarization. The GGA-PBE approximation met the requirements of the study since the main focus was on calculating the changes in the projected density of states (PDOSs) for the atoms of the model with various hydrogen atom positions. The atomic bases in OMX are specified using localized functions—pseudoatomic orbitals. In accordance with the results of test calculations, we used the s4p3d2f2-set with 17 valence electrons (N_{val}) and a cutoff radius (R_{cut}) of 9 Å for Au atoms. The more accurate set of s3p2-set, N_{val} = 1 and R_{cut} = 7 Å was used for H atoms.

3. Results and Discussion

3.1. Measurements

According to the results of the STM measurements, most of the gold nanoparticles on the surface of the HOPG were arranged on terrace edges and other graphite surface defects. The shape of the nanoparticles was oblate spheroidal. The lateral size distribution was at its maximum in the range of 4–8 nm, while the average height of the nanoparticles was approximately 1.5–2 nm. In Figure 1a, one can see the image of single gold nanoparticles deposited on the surface of HOPG. The STS measurements (Figure 1b) revealed that nanoparticles and graphite have similar VACs. The curve’s shape was of the S-type, which is characteristic for tunnel junctions formed by metals.

Note that in the measured voltage range the tunneling current observed on the nanoparticle was slightly higher than that on graphite in its absolute value. In other words, the nanoparticles’ local conductivity exceeded the graphite conductivity. The system behaves in such a way due to the fact that, for metal nanoparticles, the density of states in the vicinity of the Fermi level exceeds that of semimetal structures such as HOPG. The chlorine compounds and other residual impurities on the surface of the sample were absent according to the results of elemental analysis: Auger spectrum demonstrates energy maxima at 272 eV corresponding to carbon, and 69, 141, and 160 eV to gold. Signals of other elements are inappreciable. In our previous experiments [31], the result was the same.
Exposing the sample to hydrogen resulted in a significant perturbation of the local electron density of nanoparticles. The change in the electronic structure of nanoparticles due to their interaction with H₂ (200 L) is shown in Figure 2. As these data show, after the exposing the sample to hydrogen equal to 200 L, an area appeared on the nanoparticle periphery where the local electronic structure was different from that of the metal. VAC curves measured in this area have a region of zero current. For STS experiments, the width of the zero-current region coincides with the dimension factor with the band gap of the material under the STM tip—that is, after exposure to hydrogen, we could observe two different areas on the surface of the gold nanoparticle: the central area with metal a structure, and the peripheral area with a semiconductor structure.

According to the data above, nanoparticles with composite structures formed after the exposure of HOPG-supported gold nanoparticles to hydrogen. Note that STM/STS methods are sensitive to the electronic structure of the nanoparticle surface. Thus, the following question arises: how does the observed electronic structure (on the surface) correlate with the inner atomic structure of the hydrogenized nanoparticle (in the volume)? We can
consider two possibilities. The first is that hydrogen dissolves in the gold nanoparticle, so an interface is formed in the volume of the nanoparticle between the semiconductor and the metal (Figure 3a). The second is that hydrogen forms only surface and subsurface layers, while the nanoparticle core remains a metal (Figure 3b).

![Figure 3.](image)

**Figure 3.** Variants of the inner atomic structure of hydrogenized gold nanoparticles on HOPG: (a) dissolution of hydrogen atoms in gold; (b) formation of surface and subsurface layers of hydrogen atoms.

In the case of hydrogen dissolution, HOPG-supported gold nanoparticles with peripheral semiconducting areas can be described as junctions with a metal-semiconductor-metal (MSM)-type structure. Indeed, carbon and gold with metal electronic structures are separated from each other in some volume by hydrogenized gold with a semiconductor structure. Due to charging effects at the interfaces between pure and hydrogenized gold and between hydrogenized gold and carbon, the form of the potential barrier will change, and the observed band gap of hydrogenized gold will also change. Let us consider this process.

A contact potential is well known to exist between two dissimilar metal electrodes separated by a narrow gap or a semiconductor layer (Figure 4). In asymmetric junctions, in which the gap between the electrodes is less than 100 Å, such contact potential results in intrinsic electric fields of extremely high strength. The magnitude of such a field \( F_{in} \) (V/Å) is:

\[
F_{in} = \frac{\psi_2 - \psi_1}{s},
\]

(6)

where \( s \) — the thickness (in angstroms) of the layer of hydrogenized gold and \( \psi_1 \) and \( \psi_2 \) are the work functions (in eV) of carbon and gold electrodes, respectively. The form of the barrier between the electrodes is trapezoidal, and its height changes. So, we can say that the height of the barrier edges—at the interfaces between hydrogenized gold and carbon and between hydrogenized gold and pure gold—are related as follows:

\[
\phi_2 = \phi_1 + s \cdot F_{in} = \phi_1 + \psi_2 - \psi_1 = \phi_1 + \Delta \psi,
\]

(7)

where \( \Delta \psi = \psi_2 - \psi_1 \). The height of the barrier \( \phi(x) \) between the electrodes is readily deduced as

\[
\phi(x) = \phi_1 + \frac{\Delta \psi x}{s}.
\]

(8)

Due to the charging effects, gold and carbon electrodes influence the energy of the electron located within the space between them. As a result, the height and width of the potential barrier between the electrodes is reduced, since the image potential makes its corners rounded. Using the mirror image methods [42], we can calculate the image force potential \( V_i(x) \) as

\[
V_i(x) = -\frac{\varepsilon^2}{8\pi\kappa} \left\{ \frac{1}{2x} + \sum_{n=1}^{n=\infty} \left[ \frac{ns}{(ns)^2 - x^2} - \frac{1}{ns} \right] \right\},
\]

(9)
If we consider the hydrogenation process to be the formation of surface and subsurface layers of atomic hydrogen, the system should be described in another way. The surface of pure gold is covered with a thin layer of hydrogenized gold, and its real electronic structure is unknown. The observed band gap in this case is a result of complicated interactions between the electronic structures of hydrogenized and pure gold. Of course, the edge factors for such hydrogenized spots on the gold surface will influence the observed band gap, but interaction with the gold core will be the key factor. The local band gap will be the same, regardless of whether it was measured on the top of a fully hydrogenized gold nanoparticle or on the semiconducting ring on the nanoparticle periphery.

**Figure 4.** Energy diagram for gold and carbon electrodes separated by a semiconductor layer of hydrogenized gold.

where $e$—the electronic charge, $x$—the distance within the hydrogenized gold measured from the interface with carbon, $\varepsilon_0$—the free space permittivity, and $K$—the dielectric constant of the semiconductor. In a more convenient form, one can approximate this expression for the image force as follows:

$$V_i(x) = -\frac{0.795 e^2}{16\pi K\varepsilon_0 x(s-x)}.$$

(10)

Hereinafter, the use of electron volts and angstroms as energy and measurement units will be more convenient for us; thus, Formula (10) becomes

$$V_i(x) = -\frac{2.86 s}{K x(s-x)}.$$

(11)

The true barrier $\psi_i$ is a result of combination of the image potential $V_i(x)$ and the trapezoidal barrier. It is a function of distance within the electrodes:

$$\psi_i(x) = \phi_1 + \frac{\Delta \psi x}{s} - \frac{2.86 s}{K x(s-x)} \text{ eV.}$$

(12)

Thus, in the case of a gold structure with a peripheral semiconductor area, the true barrier will depend on the visible thickness of the semiconducting ring.

If we consider the hydrogenation process to be the formation of surface and subsurface layers of atomic hydrogen, the system should be described in another way. The surface of pure gold is covered with a thin layer of hydrogenized gold, and its real electronic structure is unknown. The observed band gap in this case is a result of complicated interactions between the electronic structures of hydrogenized and pure gold. Of course, the edge factors for such hydrogenized spots on the gold surface will influence the observed band gap, but interaction with the gold core will be the key factor. The local band gap will be the same, regardless of whether it was measured on the top of a fully hydrogenized gold nanoparticle or on the semiconducting ring on the nanoparticle periphery.
In the above case of synthesized composite nanoparticles, these rough estimations show that conclusions about the atomic structure of hydrogenized gold can be obtained from the data on the local electronic structure—namely, band gap edges—within the surface of the semiconducting ring.

3.3. Barrier Symmetry Analysis

What factors does the barrier shape depend on in MSM structures? According to Formula (12), the edges of the observed barrier do not coincide with the edges of the electrodes. From the equation \( \varphi_i(x_{1,2}) = 0 \), we found the observed barrier thickness \( \Delta s = x_2 - x_1 \), which is less than the semiconductor’s real thickness.

The shape of the barrier also depends on \( K \). For \( \Delta s = 20 \text{ Å} \) and various \( K \) values, we observed changes in the barrier shape, symmetry, and maximum location (Figure 5). For \( K = 1 \), the barrier is smooth and low, it looks symmetric, and its maximum is close to the center of the semiconductor layer \( (\lambda_{\text{max}} \approx \Delta s/2) \). The larger \( K \) is, the higher the barrier. Its form tends to be more trapezoidal, and its maximum shifts significantly towards the electrode with a higher work function.

![Figure 5. Barrier height \( \varphi_i(x) \) in the MSM structure according to Formula (12) for \( \Delta \varphi = 0.5 \text{ eV}, \Delta s = 20 \text{ Å} \) and various \( K \) values. Plots are shifted along the X axis to make the edges of observed barriers coincide for various \( K \) values.](image_url)

In our previous work [31], we showed that the hydrogenation of gold nanoparticles starts at the gold–carbon interface. Due to diffusion, there is a hydrogen concentration gradient in gold-based semiconductor, which also affects the barrier parameters. If the concentration is low, the material behaves more like a metal, and its \( K \) is higher. The converse is also true: the higher the hydrogen concentration is, the lower the \( K \). Thus, the barrier is sharp and trapezoidal close to the surface of the gold electrode and smoother close to the
carbon surface. Nevertheless, even with the diffusion factor, the barrier stays asymmetric, and its maximum shifts significantly towards the surface of pure gold.

If hydrogenation of gold nanoparticles is a surface process, we should consider the observed local band gap as a result of the distortion of the initial metal structure under the influence of H atoms. Due to ring formation at low exposure, one can conclude that the surface concentration of H atoms decreases towards the top of the nanoparticle. When the surface concentration of the chemisorbed complex is high enough, a band gap is observed. Otherwise, it manifests itself only as a decrease in the local density of the electronic states without band gap formation. Thus, in the center of the hydrogenized spot, the observed band gap should reach its maximum value. In this case, the barrier will be symmetric.

3.4. Band Gap Mapping

Measurements of the extent of the zero-current region of the VAC curves at various points of the sample surface allowed us to observe the band gap changes within the semiconducting ring. During STS measurements, a positive or negative potential difference is applied to the vacuum gap between the sample and the STM tip. In the case of a semiconducting sample, the tunneling current will not flow until the Fermi level of the tip shifts above the upper (LUMO level) or under the lower (HOMO level) edge of the band gap of the sample material. Since the STM tip is grounded, the positive edge of the zero-current region coincides with the bottom of the conduction band, and the negative edge coincides with the top of the valence band of the semiconductor. Watching the positive edge of the VAC zero-current region at various points over the surface of our composite nanostructure, one can map the real barrier height and its changes within the semiconducting ring. Such a map is shown in Figure 6b.

![Figure 6. Single HOPG-supported gold nanoparticle after exposure to H2 (200 L): (a) topography image, (b) map of the barrier height with marked radial sections, (c-e) energy diagrams for barrier height along the selected radial sections α, β and γ.](image)

Figure 6 shows that the barrier along the radial section is quite symmetric, and its maximum height is 0.5–0.7 eV. The barrier’s edge is smooth in the area of the contact with pure gold. According to the estimations above, no hydrogen dissolution takes place, and all the observed phenomena occur over the surface of the gold nanoparticle, instead of in its volume.
3.5. Quantum Chemical Simulation

As an initial assumption, it is necessary to check whether atomic hydrogen can occupy an energetically stable position under at least one atomic layer of gold. For this, a hollow cluster of Au$_{12}$ with one filled icosahedral shell was taken as a model nanosystem, with one hydrogen atom placed at its center. This nanosystem is shown in Figure 7. In our previous works on the study of hydrogen adsorption on gold nanoparticles, a small cluster containing approximately 10 atoms was shown to be a good model of gold nanoparticles. This allows us to describe the electronic structure of nanoparticles and its changes during adsorption processes, as observed by STS measurements. Thus, it is possible to compare the calculated and experimental results [43].

![Figure 7. Au$_{12}$H nanosystem, consisting of an icosahedral shell of gold atoms and a central hydrogen atom.](image)

Optimization of the atomic structure of the resulting nanosystem, i.e., calculation of the energy minimum, showed that the position of a hydrogen atom inside a gold cluster is metastable. The most energetically stable atomic configuration of the Au$_{12}$H system is one with a hydrogen atom above the gold surface. A more detailed study of adsorption complexes based on small clusters of gold with hydrogen atoms has been carried out [30].

In addition, optimization of the Au$_{12}$H nanosystem with a central hydrogen atom in a fixed position was carried out, which demonstrated the possibility of the existence of this metastable structure. However, even a 0.1 Å displacement in the position of the hydrogen atom from the equilibrium position led to a transition from a metastable state to an energetically more favorable state. Thus, the hydrogen atom is pushed out of the gold cluster into an energetically more favorable state above the gold surface. This result is in accordance with the initial assumption that STS-observable changes in the electronic structure of gold nanoparticles are associated with surface phenomena and not with the dissolution of hydrogen in gold.

4. Conclusions

The experiments described above demonstrate that a semiconducting ring of hydrogenized gold is formed at the perimeter of HOPG-supported gold nanoparticles after 200 L exposure to hydrogen. STM/STS methods have been successfully used to determine the local electronic structures of these composite MSM nanoparticles. The bottom of the conductive band and the shape of the electron energy barrier were studied in the vicinity of the semiconducting ring. Considering the diffusion of H atoms, a rigorous model for hydrogenation in the volume gives a significantly asymmetric barrier, the maximum of which is shifted towards the surface of pure gold. The experimental results show that
the barrier is, in fact, symmetric and corresponds to the surface hydrogenation model. The results of quantum chemical simulation have also shown that, for hydrogen atoms, the state above the surface of a gold cluster is energetically more favorable than the state in the volume. Thus, the STS-observed changes in the electronic structure of gold nanoparticles are associated with surface hydrogenation and not with the dissolution of hydrogen in gold.

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