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Sensor for detection of water presence in gaseous mixtures based on gold nanoparticles stabilized by sodium citrate

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ABSTRACT

The adsorption properties of organic–inorganic sensitive films formed by gold nanoparticles dropped from sodium citrate solutions of different concentrations are investigated using mass-sensitive (QCM) sensors. The obtained sensitive layers, composed of discontinuous assembly of gold nanoparticles and sodium citrate film have demonstrated several special adsorption properties. The most interesting among them are (i) the reverse dependence of the sensitivity on the initial colloid solution concentration, (ii) the difference of the response value for alcohols and water (the sensitivity to water is more than one order higher than to alcohols) and (iii) the character of water adsorption curves (the presence of two stages of adsorption with different kinetics). The physical mechanism of water adsorption on the citrate–gold surface is considered to be concerned with the presence of two processes: adsorption and diffusion of water molecules along the surface of citrate to the gold nanoparticles. Gold nanoparticles in this case serve as drains for water molecules. The results obtained can be applied for the development of sensors for the detection of water presence in gaseous mixtures of different nature.

1. Introduction

Gold nanoparticles are widely used for the development of sensitive coatings for chemical sensors [1–14]. Nanostructured layers have number of advantages making them of particular interest in this field. The adsorption properties of nanostructured films depend on their surface morphology, characteristic dimension of particles, packing etc.

Although pure gold nanoparticles can be used as sensor coatings [5], there are many reports, where they are modified by different organic compounds. Indeed, the development of mixed organic–inorganic nanostructured layers opens wide possibilities for the creation of sensors with well-defined adsorption properties.

A brief overview of state of the art in this field is given below.

A film of three-dimensional (3D) structures made of gold nanoparticles linked with bifunctional (thiol–thiol or thiol–carboxyl) molecules of saturated hydrocarbons was used for fabrication of chemoresistors [6,7]. There were detected different volatile molecules at a concentration level of several hundreds ppm.

The advantages of using amines as nanoparticles modifiers are demonstrated in [8].

The effect of organic coating of a nanoparticle on its sorption capacity was studied in [9]. The authors used thiols of four types to modify the gold particle surfaces and tested ten different volatile molecules in two measurement modes: chemoresistance (CR) and QCM. It was noted that the ratio between the signals, CR/QCM, depends appreciably on the type of thiol covering the nanoparticle surface: this ratio is 1.9 for 4-methoxythiolphenol and 16.9 for octanethiol. Thus, the type of organic coating affects the sensitivity to adsorption of volatile organic molecules; this can be used to control the detection specificity.

The authors of [10] have grafted colloidal gold nanoparticles to a thin polymer film of *n*-butylamine deposited onto the surface of metal electrode of a quartz crystal microbalance (QCM). Such a surface contains many amines affined to gold surface. As a result, the whole surface was tightly coated with gold nanoparticles and it was used successfully for detection of antibodies in solutions.

The gold nanoshells 20 nm in diameter on the base of polystyrene spheres were obtained in [11] by mixing aqueous suspensions of polystyrene spheres properly, HAuCl4 and sodium citrate. These shells were modified with horseradish peroxidase and were used as a sensitive indicator of hydrogen peroxide.

To form a continuous film of gold particles on glass surface, the printing technique was applied [12]. At first, the surface was coated with bifunctional molecules to form a surface sulphur layer; then a layer of functionalized gold nanoparticles was deposited onto it.

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In the chemoresistor mode, the samples demonstrated sensitivity to adsorption of organic molecules at a level of ppm and tens of ppm.

Gold nanoparticles are most often produced in a liquid by reduction of chloroauric acid (H[AuCl$_4$]). After dissolving H[AuCl$_4$], the solution is rapidly stirred while a reducing agent is added. This causes Au^{3+} ions to be reduced to neutral gold atoms. As solution becomes supersaturated, gold starts to precipitate gradually in the form of subnanometer particles. The rest of the gold atoms stick to the existing particles, and, if the solution is stirred vigorously enough, the particles will be fairly uniform in size. To prevent the particles from aggregating, some sort of stabilizing agent is added. They can be functionalized with various organic ligands to make organic–inorganic hybrids with advanced functionality [13]. More recently, the above method was refined in [14] for organic solutions, where one can easily perform functionalization of gold nanoparticle surface.

The main efforts of researchers are concentrated on the obtaining of rigidly linked 3D networks of gold nanoparticles. In this case, the nanoparticles on the surface are packed rather close (with spacing between nanoparticles being from several nm up to several tens of nm). Now the most popular procedure for obtaining of nanoparticles is that based on Au–S covalent bonding strength [13]. However, the Au–S bonding is not very unique. For instance, the authors of [15] demonstrate that some other functional groups (CN, NH$_2$) have very high affinity to gold atoms as well. One of the benefits of such approach is the possibility of making water solutions with different nanoparticles concentrations. This allows creation of thin films with different characteristic distances between gold nanoparticles. The concentration of gold nanoparticles in mixed sensitive layer can serve as an additional means of film's adsorption properties controlling.

In the present work we study the adsorption properties of mixed organic-gold nanoparticles sensitive layer. The nanoparticles were made by reduction of chloroauric acid, with addition of sodium citrate.

Water solutions with different gold and sodium citrate concentrations were obtained and used for thin films preparation. The dependence of films sorption properties from the concentration of the solution was investigated using quartz crystal microbalance sensors.

2. Experimental procedure

Quartz crystal microbalance sensors (QCM) based on AT-cut quartz resonators with resonance frequency of 10 MHz were used.

To obtain colloidal gold solution, we used chloroauric acid (Aldrich, USA), tri-sodium citrate dihydrate (Merck, Germany), and water (double-distilled in a quartz distiller). The colloidal gold solution was prepared in accordance with the procedure described in [15]. All preparations were made in glass as far as we found that colloidal solution can coagulate being in contact with some plastics (tubes or pipette tips). 50 ml of 1 mM solution of HAuCl$_4$ was boiled in a glass flask with vigorous steering on magnetic mixer. Then 5 ml of 38.8 mM *freshly prepared* solution of sodium citrate at room temperature was quickly added into the vortex. Colour of the mixture changed from light yellow to a dark red within a minute, showing formation of nanoparticles. The solution was cooled down slowly with steering, then transferred to a dark bottle and stored at +4 °C. According to optical absorption spectra the solution was stable at least for two month.

As a control coating 3.53 mM solution of sodium citrate without nanoparticles was used.

The solutions with gold particle concentrations of $1.3 \times 10^9\ \mu l^{-1}$, $0.72 \times 10^9\ \mu l^{-1}$ and $0.5 \times 10^9\ \mu l^{-1}$ were prepared. Gold nanoparticles were fixed at the surface of silver electrodes of QCM by dropping from the solution. A solution drop (1 μl) was put on the surface of silver electrode and spread uniformly over the whole its area (of ~0.5 cm^2). The film obtained was dried in a flow of dry argon for 5 h. After this, the samples were accumulated in a sealed argon-filled vessel.

The same procedure was used to obtain control sensors coated by citrate film without nanoparticles. 3.53 mM sodium citrate solution was used instead of colloidal gold solution, the same dilutions as in the previous case were performed.

Presence of gold nanoparticles on the silver surface was determined with atomic force microscopy (AFM). Shown in Fig. 1 is the AFM pattern of a film formed from the solution with the highest concentration of nanoparticles ($1.3 \times 10^9\ \mu l^{-1}$). One can see that the nanoparticles vertical size is 16–18 nm. This value is close to the results obtained in [15] with transmission electron microscopy. The distance between nanoparticles is about hundreds of nm.

The sensors were formed from solutions of three different concentrations of gold nanoparticles and sodium citrate. Sensors were placed in a flow-through cell. Liquid analyte (water, ethanol, methanol, and isobutyl alcohol) was placed in a closed vessel. The saturated vapour accumulated over the liquid surface was transported by gas-carrier (argon) to the measurement cell with sensors. The QCM oscillations frequency changes caused by the adsorption of analyte's molecules were detected according [16].

3. Results and discussion

Shown in Fig. 2 are the responses of sensors with different coatings (formed from the colloidal gold solutions of three different concentrations) to ethanol and water. Fig. 2a presents the kinetics of ethanol adsorption. (We performed the same measurements also for isobutyl and methanol. The character of responses to these analytes is similar to that in the first case, so they are not presented here.) One can see that three adsorption curves are close to those of Langmuir-type. The response values are rather small (the response of the most sensitive sensor is about 60 Hz). Special attention must be given to the reverse sequence of the curves in Fig. 2a in amplitude: the biggest response is demonstrated by the coating with the lowest concentration of gold nanoparticles.

Fig. 2b presents the responses of the same sensors to water vapour. In this case, the sensor sensitivity is much higher than to alcohols. The response is about 1200 Hz for the most sensitive coating (that with the lowest concentration of gold nanoparticles). In this case, the sequence of the curves (reverse dependence on the nanoparticle concentration) is the same as for alcohols.

The feature of the responses to water is the presence of two stages of adsorption, with different kinetics and values. In the course of the first stage, the sensor frequency variation is 60–90 Hz, while on the second stage the response is 400–1200 Hz. This may indicate the presence of two adsorption mechanisms for water molecules. One of them starts with some delay, after the concentration of adsorbed molecules reaches a certain threshold value.

On Fig. 3 the amplitudes of response of the same sensors to ethanol, methanol and isobutyl alcohol (Fig. 3a) and water (Fig. 3b) are presented.

The reverse dependence of sensitivity on gold nanoparticles concentration on the surface is typical for all the analytes considered. At the same time, the sensors demonstrate extremely high sensitivity (over 1000 Hz) to water only.

The sensitive layers of our sensors involve two substances, namely, a gold nanoparticles and sodium citrate. To determine the role of each of the above components in adsorption processes at the surface, measurements with sensors coated by sodium citrate without gold nanoparticles were performed. In this case, the same