Russian Chemical Reviews **76** (11) 1013 – 1022 (2007) © 2007 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2007v076n11ABEH003735

Nanomaterials for sensors

V E Bochenkov, G B Sergeev

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Abstract. Publications of the past five years dealing with nanomaterials used as sensors for determination of gases are analysed. Peculiarities of the production of chemoresistive nanosensors based on semiconducting oxides, carbon nanotubes and polyaniline are outlined. The main application fields of gas sensors are considered. Prospects for the use of quasi-one-dimensional nanomaterials such as nanorods, nanotubes and nanobelts as the materials in sensor units are discussed. The bibliography includes 114 references.

I. Introduction

Nanoscience deals with fundamental problems of natural science on the nanoscale; its results are implemented in nanotechnologies as nanodevices, nanosystems, new substances and nanomaterials.[1, 2]

Nanoparticles are highly reactive; this is why, in the absence of stabilising media, they are studied in high vacuum or at low temperatures. Under conditions of ultralow temperatures, unusual chemical reactions were carried out and different reactivity of metal atoms, clusters and nanoparticles of different sizes was demonstrated.[3] The use of low temperatures and the joint condensation of vapours of different compounds led to the development of methods for the cryogenic formation of nanosystems with the gas-sensitive and sensor properties.[4] Studies in the field of cryochemistry play the important role in the development of nanochemistry.[5] Nanotechnologies are also beginning to use cryogenic freeze-drying.[6]

Preparation of materials with sensor properties and the development of the corresponding instruments based on these materials is an important problem. After the terrorist act of September 11, 2001, the USA sharply raised financing of the field of nanoscience devoted to sensors and correspondingly reoriented their research policy. New sensor materials are of great social and economic importance. According to the Business Corporation Company, the total sum obtained by the USA from nanosensors sold in 2004 was ~$ 190 million. The annual increase in the sale volume of nanomaterial-based sensors is 26% and the total sum from their sale will reach 592 million to 2010. The annual gain in the sale volume was 53% for gas sensors and 32% for biosensors. According to the 'Nanomaterials Research' Journal, the total sale of all types of sensors will reach $ 2.5 billion in 2010.

The diversity of sensors developed for different fields of science, technology, and industry as well as their properties, preparation techniques and application areas were surveyed in the monograph [7] and the following review papers:

— control over volatile combustion products in industry,[8]
— analysis of exhaust gases of cars,[9]
— quality inspection of foodstuffs,[10]
— peculiarities of using the polyaniline gas sensors,[11]
— using the plasmon resonance in biosensorics,[12]
— sensors for ammonia detection,[13]
— preparation and chemoresistive properties of nanostructured materials,[4]
— materials for environmental monitoring.[14]

In this study, attention is focused on the materials and sensors used in the determination of combustible and toxic gases, volatile organic compounds and in the diagnostics of certain diseases. In our opinion, at present the demand for such sensors is the highest. They are required for the prevention of technological disasters and terrorist attacks, in the environmental protection and the human health care. All these problems are currently central in Russia.

This review considers the problems associated with the use of low temperatures in the synthesis of new gas-sensitive nanomaterials for sensors. Physical and chemical methods of the formation of sensor systems and certain general properties of gas-sensitive materials are discussed. For the most part, chemoresistive sensor materials that change their properties upon adsorption of a particular substance are considered. In contrast to other reviews on the related subjects (*e.g.*, see Refs 4, 15), in the analysis of properties of nanomaterials for sensors special attention is paid to the peculiarities of their synthetic methods of their synthesis, and certain general problems of nanosensors are discussed in relation to the detection of ammonia.

II. Physicochemical properties of nanomaterials for sensors

Nowadays, nanoparticles and nanomaterials are coming into extensive use in the development of sensors.[4, 8 – 14] However,

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Received 25 June 2007
Uspekhi Khimii **76** (11) 1084 – 1093 (2007); translated by T Ya Safonova

recently published monographs on sensors [16, 17] described the use of nanomaterials only briefly and fragmentarily.

Nanomaterials to be used as sensors should exhibit sensitivity, selectivity and stability. The size dependence of nanoparticle properties forms the basis for the development of highly sensitive sensor devices. Certain problems associated with the dependence of the sensitivity of sensors on the size and shape of nanosystems, the ligand type and the response mechanism were considered in several reviews.[4, 15]

In this review, the methods of preparation of gas-sensitive nanomaterials are conditionally divided into physical and chemical. A method used for the formation of nanoheterogeneities in materials at low temperatures, *i.e.*, cryosynthesis, is considered separately.

1. Physical and chemical methods of synthesis of sensor nanomaterials

Physical methods of preparation of gas-sensitive nanomaterials include, *inter alia*, different versions of vacuum deposition that employ the resistive, laser and electron-beam evaporation and magnetron sputtering. As a rule, these methods are used in the preparation of metal-oxide semiconducting nanosystems and metal nanoparticles deposited on different substrates.

Operation of gas sensors is based on the variations in the resistance (conductivity) of chemoresistive materials under the effect of the analysed gas. At present, the majority of sensors for the gas analysis employ semiconducting materials. As a rule, the operation of these materials requires elevated temperatures.

Metal-oxide semiconducting nanomaterials are the most thoroughly studied sensor materials — they were the subject of a considerable number of publications devoted to methods of synthesis [18–20] and mechanisms of sensor response.[18, 21, 22] This is why we do not consider in detail metal-oxide nanomaterials (with the exception of new types of sensors based on nanowires, nanobelts and nanotubes).

Chemical methods of synthesis of sensor nanosystems include their conventional synthesis in solutions and the chemical synthesis in the gas phase. The former is used in the production of materials based on self-assembled nanoparticles of noble metals coated with alkanethiols and in the preparation of gas-sensitive polymeric films. The latter method is actively employed in the synthesis of materials based of carbon nanotubes.

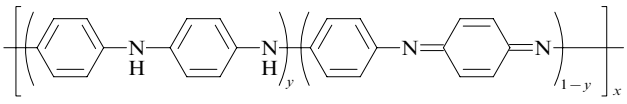
Metal nanoparticles stabilised with organic molecules and the materials based on them are interesting due to their unique properties and the possibility of their application as gas sensors. Metal nanoparticles are stabilised by monolayers of alkanethiol derivatives.[23, 24] The organic coating prevents aggregation of particles and affects their physicochemical properties.[25]

One of the first studies that employed gold nanoparticles coated with a thin octanethiol film as the sensor† units considered the effect of vapours of volatile organic substances on the film conductivity. It was found that the film conductivity remained virtually unchanged under the action of propanol and water vapours and decreased when subjected to action of toluene and trichloroethylene vapours.[26] For toluene, the detection limit was several molecules per million. Later, materials sensitive with respect to vapours of polar solvents were synthesised.[27] The conductivity in such systems was discussed in terms of two possible mechanisms, namely, the electron tunnelling between metal nuclei and the hopping mechanism of conduction *via* thiol molecules. Changes in the charge distribution in a system with the adsorption of vapours of volatile substances give rise to the sensor response. Moreover, it was assumed that the swelling of organic matrices upon adsorption of a solvent vapour may influence the film conductivity that is related to the variations in the distance between metal particles.[28]

When manufacturing chemoresitive thin films based on metal nanoparticles coated with thiol derivatives, it is necessary to know the dependences of the material conductivity on the particle radius, the distance between particles and the dielectric permittivity of the medium. The effect of the distance between nanoparticles of gold and a gold–silver alloy on the conductivity and sensitivity of films was studied.[29] For the first time, certain α,ω-dithiols and dicarboxylic acids with different numbers of CH_2 units ($n = 3–18$) were used in addition to decanethiol for the fixation of interparticle distances. It was shown that the sensitivity of samples with respect to vapours of hexane, toluene and benzene depends on the number n of CH_2 units in the spacer chain. This dependence has a sigmoid form, where the largest changes in the sensitivity fall to the n range from 9 to 13.

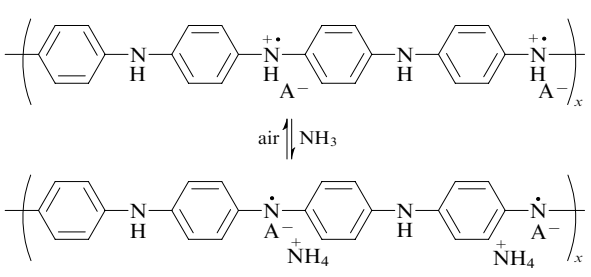
Conducting polymeric films [30] synthesised by chemical methods display the following advantages over metal-oxide sensors: the possibility of operation at room temperature, high sensitivity and short response times. Conducting polymers can be synthesised by chemical and electrochemical reactions, their molecular structure is changed by co-polymerisation or modification of functional groups.[30]

Attention of scientists was always attracted to the development of the so-called synthetic metals, *i.e.*, conducting materials based on organic compounds. The interest in such compounds increased with the discovery of conduction in polymers.‡ Different modifications of polyaniline were used most extensively as the sensor materials.



Polyaniline samples can have different shapes and acquire different colours depending on the y value. This makes it difficult to carry out their reproducible synthesis and measure their conductivity. Protonated forms (or salts) of polyaniline have the highest conductivity that reaches $15\ \Omega^{-1}\ cm^{-1}$ (Ref. 31), which is much lower than the metal conductivity ($10^3\ \Omega^{-1}\ cm^{-1}$).

The methods of preparation of polyaniline films, the mechanism and features of their modification with different inorganic and organic compounds were analysed.[11] Their modification involved the use of acids (HA), where A = Cl, HSO_4, ClO_4. The sensitivity of modified polyaniline films placed, *e.g.*, in the ammonia atmosphere changed as a result of protonation and deprotonation.[32, 33]



† Nowadays, solutions containing alkanethiol-stabilised gold and silver nanoparticles can be purchased from suppliers of chemicals.

‡ For this discovery, A J Heeger, A D MacDiarmid and H Shirakawa were awarded the Nobel Prize-2000 in chemistry.

Table 1. Sensitivity of polyaniline films with respect to different gases depending on the preparation method.

NO_2	H_2S	SO_2
Spin-coating		
+ + (4 ppm)	+ + + (4 ppm)	+ + (2 ppm)
Thermal deposition		
+ + (2 ppm)	+ (10 ppm) irreversible	+ (10 ppm)

Note. In parentheses, the gas concentration is shown. Symbols +, + + and + + + designate the relative value of response.

Table 1 shows the sensitivity of non-modified polyaniline films synthesised by different methods with respect to different gases.

It was noted [34] that polyaniline is insensitive with respect to carbon dioxide or methane; the same paper reports the results of studies of the polyaniline film conductivity (in nitrogen atmosphere, at room temperature) as a function of its thickness and the method of preparation. The conductivity of polyaniline synthesised by thermal evaporation was $10^{-10}\,\Omega^{-1}\,cm^{-1}$. This was higher as compared with samples synthesised by the spin-coating method. The higher conductivity of films obtained by the thermal deposition was associated with the predominant presence of *N*-phenyl-*p*-phenylenediamine blocks in the sample. The other method produced a mixture of *N*-phenyl-*p*-phenylidenediamine and quinonediimine blocks, which interrupted the sequence of conjugated double bonds. It was demonstrated [35] that polyaniline films containing polyvinyl alcohol may be used in the analysis for carbon dioxide. Composites based on polyaniline and copper particles were used in the analysis for chloroform.[36]

Incorporation of palladium particles into polyaniline was accomplished.[37] Examination of the ability of different surfaces to change the conductivity of deposited polyaniline films has shown that the deposition rate of polyaniline on a hydrophobic surface was higher as compared with hydrophilic films. Similar dependences were obtained [38, 39] for thiol-modified silicon and gold surfaces, respectively. The conductivity of films on hydrophobic surface was higher; however, the adhesion of films to hydrophilic surfaces was stronger. The use of polyaniline as the material chemoresistive towards different gases faces the problems associated with stability, selectivity and response times that are typical of all gas sensors.

Carbon nanotubes are the promising material for gas sensors. They are synthesised by several methods, which can be classified into two groups associated with the use of either high or moderate temperatures. The former group includes the methods that employ arc discharge, the second group comprises the catalytic chemical vapour deposition.[40]

One of the first gas sensors based on carbon nanotubes could detect low concentrations of NO_2 and NH_3 at room temperature.[41] This result served as an impetus for the further experimental [42, 43] and theoretical [43, 44] studies of the sensitivity of carbon nanotubes with respect to gases. Particularly, it was shown [45] that materials synthesised upon the deposition of carbon nanotubes on tin(IV) oxide substrates were chemoresistive with respect to NO_2. For multi-walled carbon nanotubes with external diameters of ~ 30 nm, a linear dependence of their response on the ammonia concentration in the range of 5–200 ppm at 25 °C was revealed.[42] The response time was 3 min; however, to recover its performance, a sensor should be annealed at 250 °C for 6 h.

To enhance the sensitivity of carbon nanotubes, their surface was modified with metal particles,[46, 47] covalently bound functional groups, polymers and even DNA molecules.[48] This provided an increase in the selective adsorption of particles of a certain kind due to their interaction with functional groups or as a result of acceleration of catalytic processes on the surface of metal nanoparticles. Carbon nanotubes modified with palladium nanoparticles exhibited sensitivity with respect to hydrogen for its content in the range from 50 to 10 000 ppm at room temperature.[49]

Single-walled nanotubes functionalised with poly(*m*-aminobenzenesulfonic acid) demonstrated the detection limit at a level of 5 ppm (Ref. 50). The use of a polyaniline coating allowed the record-breaking detection limit for ammonia of 50 ppb to be reached.[51]

In the gas detection, it was proposed [52, 53] to use carbon nanotubes as the anode in ionisation detectors. Due to the high field intensity, vertically aligned carbon nanotubes allowed the breakdown potential to be substantially reduced. This made it possible to use such detectors in portable gas analysers and gas chromatographs. The advance in the synthesis of vertical carbon nanotube forests promotes the development in this field.[54]

2. Cryosynthesis

The use of low temperatures in the production of nanostructured materials is first of all associated with the possibility of limiting the diffusion mobility of particles and, as a consequence, decreasing the sizes of growing aggregates.

Cryochemical technologies were successfully employed in the preparation of small-size particles [6] that can be used in the production of gas-sensitive materials. Thus samples of nanograin tin(IV) oxide synthesised by chemical deposition followed by cryogenic freeze-drying were chemoresistive with respect to carbon monoxide.[55]

Based on fundamental studies in the field of low-temperature chemistry,[56] a new approach to the synthesis of nanostructuried gas-sensitive materials has been developed, namely, the low temperature deposition of metal vapour in vacuum followed by oxidation.[57]

Figure 1 illustrates the essence of this method, which consists of the vacuum condensation of metal vapour on a substrate kept at a temperature from 80 to 300 K. Cooling of the substrate considerably decreases the diffusion mobility in the deposition. As a result, columnar structures can be formed in the moment of condensation as a result of the attraction of the approaching atoms to the already deposited clusters. The subsequent controlled annealing destroys the structure to afford spherical particles on the oxide substrate non-wettable by the metal.

The introduction of oxygen makes it possible to form materials with certain nanostructures and chemical compositions, particularly, with nanograins of the core–shell structure that are connected with bridges. The control over the deposition parameters such as the rate and the temperatures of the substrate and the evaporator allows one to govern the structure of synthesised condensates and chemically modify the surface of grains. Low-temperature deposition made it possible to synthesise lead nanoparticles sensitive with respect to ammonia and water vapours.[58, 59] From our viewpoint, the sensitivity of such systems is due to the formation of a percolation structure of lead nanoparticles with the size of ~ 50 nm coated with semiconducting oxides. Oxide bridges between the metal particles are responsible for the overall conductivity of the material and the manifestation of the chemoresistive effect.

The chemoresistive properties of materials also depend on the changes in their microstructure and porosity. This was taken into account in a method of low-temperature co-condensation with an additional component (*e.g.*, an inert gas), which is removed from the system on annealing. Thus the structure of thin lead films was affected by its co-condensation with carbon dioxide.[60] It was shown that the roughness of the

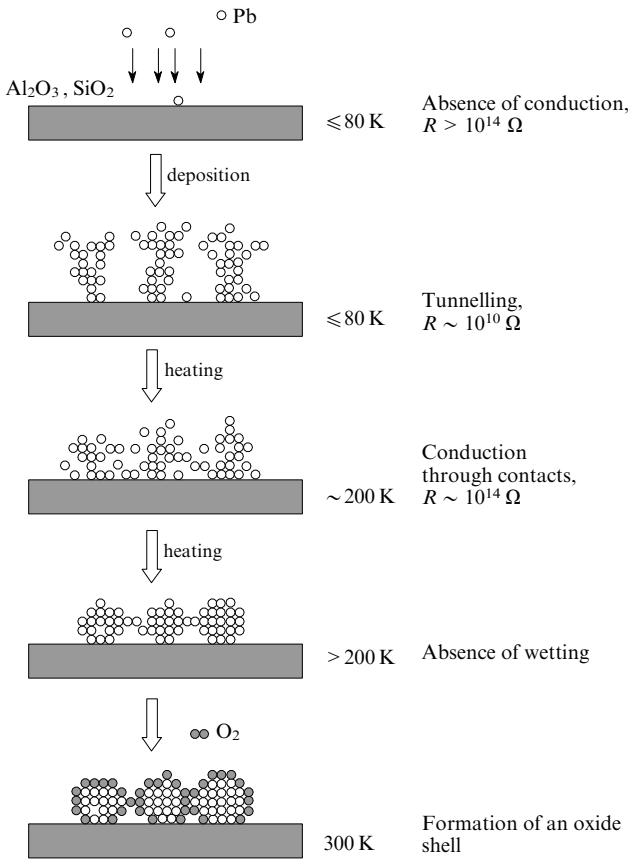


Figure 1. A model of cryogenic formation of gas-sensitive metal condensates on non-wettable substrates.[57]

resulting films was higher as compared with lead films untreated with carbon dioxide. The noted fact allows one to consider the co-condensation – annealing method as promising for the preparation of materials with well-developed surface areas.

3. Sensitivity and selectivity

The sensitivity of semiconducting nanomaterials is determined by two basic factors, namely, the ratio of the surface area (S) to the volume (V) and the ratio of the Debye screening length (L_D) to the effective radius of conducting channels (R). All other conditions being the same, the larger the S/V and L_D/R ratios the higher the material sensitivity.

Numerous studies of thin nanostructured SnO_2 films showed that the sensitivity of samples with respect to detected gases dramatically increased as the grain size decreased to several nanometers.[61–64] A systematic analysis of the size dependence of the sensitivity of SnO_2 samples can be found in Ref. 65. Problems of the selectivity of nanostructurised gas-sensitive materials and the possibility of their use in the analysis of multicomponent gas mixtures.[66]

A conventional method aimed at the enhancement of sensitivity and selectivity of semiconducting metal-oxide nanomaterials consists of doping samples with metal nanoparticles, *e.g.*, palladium,[67] platinum,[68] gold,[69,70] silver.[65,71] Thus the deposition of palladium nanoparticles on the surface of tin dioxide nanowires led to the increase in the sensitivity of such a system with respect to oxygen and hydrogen. This is explained by the increase in the concentration of O^- anions due to the acceleration of dissociation of oxygen molecules on palladium particles.[72] In turn, the size of dopant nanoparticles also affects the sensitivity of nanomaterials with respect to gases. It was shown that with a decrease in the size of silver particles deposited on tin dioxide particles, the sensitivity of this system with respect to ethanol vapours increased.[73]

Recently, to enhance the sensitivity of chemoresistive materials, quasi-one-dimensional nanomaterials such as nanowires, nanorods and nanobelts came into use in addition to films.[15,74–77] To a certain degree, this was associated with the development and investigation of such structures.[78,79] Their use allows one to substantially lower the detection limits, because as compared with films, the conductivity of a one-dimensional nanosample responds to a smaller amount of the adsorbate.

As an example, we consider the mechanism of the sensor response of silver oxide nanowires to ammonia and hydrogen chloride vapours (Fig. 2).

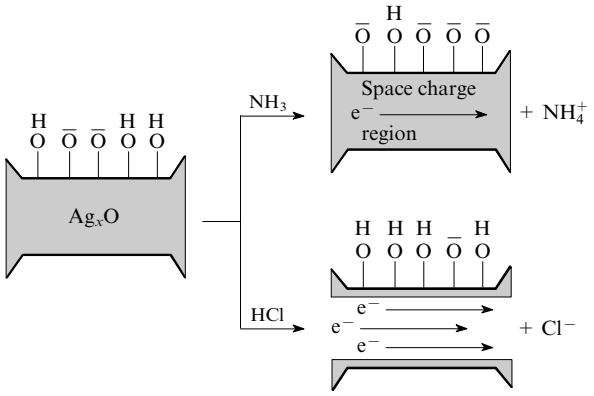


Figure 2. Scheme of a presumed mechanism of the Ag_xO response to ammonia and hydrogen chloride at room temperature.[80]

The proposed mechanism takes into account that, at room temperature, the oxide surface is coated by hydroxyl groups.[80] With the adsorption of ammonia and amines, these groups are deprotonated to form a negatively charged surface layer, which prevents the transport of electrons and favours an increase in the wire resistance. The effect of acid vapour leads to protonation of surface hydroxyl groups and, as a consequence, reduces the resistance.

A comparison of properties of nanowires and thin granulated films formed by silver particles connected with oxide bridges has evidenced the higher sensitivity of nanowires.[81] A qualitative model explaining this effect is shown in Fig. 3.

The adsorption of ammonia molecules increases the resistance of contacts between silver nanoparticles. For films, a change in the resistance of several contacts merely changes the route of electron transport (Fig. 3 *a*). For nanowires, 'blocking' of a single contact can substantially decrease the conductivity of the whole wire (Fig. 3 *b*). Thus, the adsorption of the same amount of substance will induce a greater change in the nanowire conductivity as compared with a thin film, which is the case in practice. It was shown [82–84] that tin dioxide nanowires exhibit sensitivity with respect to low concentrations of CO.

New types of nanomaterials for sensors were discussed in a review. [85]

Sensitivity of sensors can additionally be increased by designing one-dimensional objects connected with bridges that control the conductivity of the whole nanosystem. A comparative study of how straight SnO_2 nanowires ~100 nm thick and segmented nanowires with a diameter of ~500 nm formed by segments ~80 nm long and 10 nm thick respond to the addition of 0.4 ppm hydrogen have shown that the signal was higher for segmented wires although their

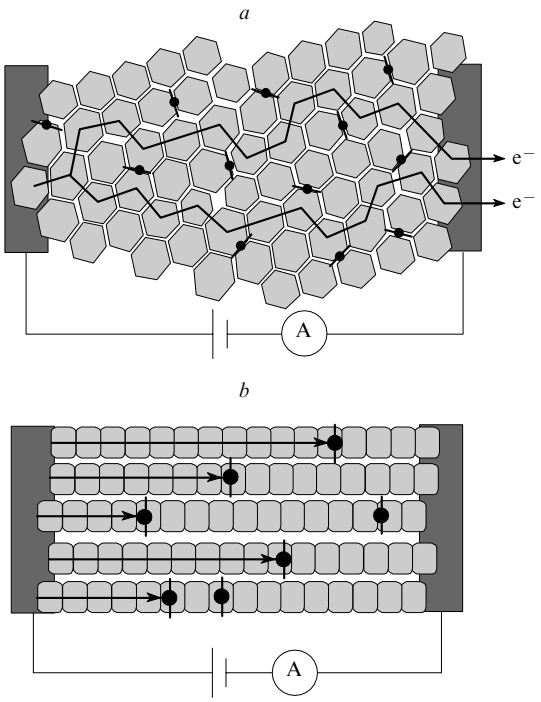


Figure 3. Model illustrating the changes in conductivity upon adsorption of ammonia on oxidised surface of silver particles (*a*) thin films and (*b*) nanowires.[81]

average radius several times exceeded that of straight nanowires.[86]

Highly ordered arrays of core–shell nanoparticles with metal cores and semiconductor shells was proposed as a new type of sensor materials.[87]

The increase in the sensitivity and selectivity of sensor nanosystems is the prime objective of scientists. The application field of sensors (especially oxide-based) can be extended by lowering the working temperature of gas-sensitive materials to room temperature. One of the ways to solve this problem may be the use of metal oxides in the form of quasi-one-dimensional materials. From our viewpoint, the development of systems with the higher selectivity should be based on the targeted synthesis of ligands capable of the selective interaction with the determined gases.

III. Certain application fields of sensors based on nanomaterials

Chemoresistive sensors are used in different fields of science and technology and in industry for the control over technological processes and the contents of toxic substances in air, water and soil. Below, certain fields of practical application of sensors are considered by the example of ammonia and several other gases and volatile organic substances. Attention is focused on the use of sensors in medicine.

1. Environmental monitoring

The environmental air and water contain large (and permanently growing) amounts of different impurities with wide concentration ranges. This stimulates the search for new versions of the use of metal oxides, which form the basis of conventional sensor materials. For example, a system comprising SnO_2, ZnO, WO_3, CuO and In_2O_3 was proposed for flow-through determinations of CH_4, CO, NO, NO_2, NH_3, SO_2 and H_2S at temperatures in the range of 200–400 °C.[88]

The environmental monitoring requires the knowledge of temperature dependence of the sensitivity with respect to the determined gas. The effect of temperature on the sensitivity of thin tin dioxide films manufactured by electron beam evaporation was explored for the determination of different concentrations of hydrogen, carbon oxide and ethylene, and the kinetics of their response was simulated.[89] It was shown that the minimum sensitivity and temperature are related to the energies of adsorption (E_{ads}) and activation (E_a). Being dependent on the nature of a gas, the adsorption energy determines the strength of its bonding with the oxide surface, whereas the activation energy determines a barrier that should be overcome to induce the surface oxidation. In turn, the quantities E_{ads} and E_a depend on the concentration of the analysed gas.

A cheap and relatively sensitive sensor for hydrogen was developed based on palladium nanowires deposited on the surface of highly oriented pyrolytic graphite.[90] The sensor operates at room temperature; its conductivity is two orders of magnitude higher in the presence of hydrogen than in its absence.

New sensors for ammonia and amines were developed. A new sensor based on V_2O_5 nanowires with extremely high sensitivity with respect to amines was described.[91] The high conductivity of wires makes it possible to use this sensor at room temperature. The limiting sensitivity, which was defined as a concentration at which the signal exceeds the noise by a factor of three, was <30 ppb for *tert*-butylamine. Sensitivity with respect to amines increased linearly as the humidity of the carrier gas increased to 60%. The conductivity depended on the position of the amine contact with vanadium wires. The selectivity of the sensor was determined by comparing its response to amine, ammonia, propanol and toluene following 5-min contacts. The highest sensitivity was exhibited towards ammonia and amine.

In air, sulfuric and nitric acids react with ammonia to form particles of ammonium sulfate and nitrate. These particles serve as nuclei for the formation of aerosols and smog in air over large cities. With the appearance of smog, the air temperature decreases due to the sunlight screening.

The ammonia content in air is usually 10–100 ppb and falls to several molecules per billion over the ocean. In the vicinity of livestock farms, the ammonia concentration can reach 10 ppm (Ref. 92). To determine ammonia in the atmosphere, response times of about a minute are sufficient; air is delivered to the sensitive material by jet systems.

A different situation is observed in the determination of ammonia in exhaust gases of vehicles or in air-conditioned passenger compartments. The ammonia content in exhaust gases should be determined at a level of ~ 8 ppm (Ref. 93). To prevent the appearance of odour in the passenger compartment, the ammonia concentration should be detectable at a level of no higher than 50 ppm with the sensor response time of several seconds.

Exhaust gases of engines operating on diesel oil contain high concentrations of NO and NO_2 (NO_x).[94,95] The amount of toxic nitrogen oxides can be reduced by their selective catalytic reduction[96]

$$4\,NO + 4\,NH_3 + O_2 = 4\,N_2 + 6\,H_2O.$$

The reaction is carried out by the injection of a controlled amount of ammonia into the exhaust system. In this process, the ammonia sensor should measure its concentrations of an order of magnitude of several molecules per million, have the response time within 1 minute and operate at elevated temperatures.[94]

Sensors based on zinc oxide nanorods with palladium particles deposited on the surface have demonstrated high

sensitivity with respect to hydrogen.[97] In a nitrogen flow with the hydrogen concentration varied from 10 to 500 ppm, the sensor determined concentrations < 10 ppm, was easily recoverable and did not respond to the presence of oxygen.

Nanorods of molybdenum oxide with the diameter from 50 to 300 nm and the length of 2–4 μm were used in sensors for the detection of carbon monoxide and ethanol at 200 °C. Carbon oxide was determined in amounts < 30 ppm (Ref. 98).

2. Sensors in chemical industry

The use of sensors in chemical industry is discussed by the example of ammonia. Ammonia is synthesised from molecular nitrogen and hydrogen at high temperatures and pressures in the presence of catalysts. For the most part, it is used in the production of fertilisers and in certain chemical processes; large amounts of ammonia are still used in refrigerating units for foodstuff storage at temperatures below 0 °C.[99,100] At ammonia utilising plants, its leakage is possible; this is why such plants should be equipped with appropriate detection systems that allow one to prevent environmental contamination with ammonia. The maximum allowable amount of ammonia in the surrounding air should not exceed 20 ppm. Such a concentration is allowed to hold for a long time; for its detection, sensors with the response times of an order of magnitude of one minute may be used. The ammonia production is a high-temperature process; hence, sensors should withhold temperatures of up to 500 °C.

In recent years, keen attention has been paid to the development of new sensors for ammonia. Sensors based on silver oxide microwires were developed.[80] Nanowires of zinc oxide were prepared and their sensitivity with respect to ammonia at room temperature was studied (using quartz crystal microbalance).[101] The nanowires were synthesised by evaporation of zinc granules at 900 °C in air and then deposited onto the quartz crystal surface. It was found that with the increase in the thickness of layers, the absolute magnitude of response towards ammonia linearly increased. Samples were sensitive to ammonia in the concentration range from 40 to 1000 ppm. The response time was ~5 s. Sensors based on ZnO nanowires were stable and provided reproducible results.

Semiconducting oxides underlie the majority of sensors for ammonia used in the chemical industry. In such sensors, the signal is determined by the conductivity variations caused by the reaction of negatively charged oxygen species (O^-, O^{2-}) with the reducing gas on the sensor surface. To enhance the selectivity of oxide sensors, different doping additives were used, particularly, transition metals.

Figure 4 illustrates the dependence of the sensitivity of tungsten oxide with respect to NH_3 and NO on the addition of different metals.[102] These data were obtained at 350 °C in the analysis of exhaust gases of vehicles. The sensor systems, which in addition to SnO_2, employed WO_3 doped with gold and MoO_3, were capable of detecting ammonia in the concentration range from 1 to 1000 ppm.[103] Such sensors were used in the detection of ammonia losses in refrigerating units [104] and in the combustion of gases.[88]

Sensors for the determination of hydrogen, methane, carbon monoxide and hydrogen sulfide were developed by the deposition of metal particles with different catalytic activity on the surface of carbon nanotubes. The selective determination of these gases involved the use of a pattern-recognition method.[47]

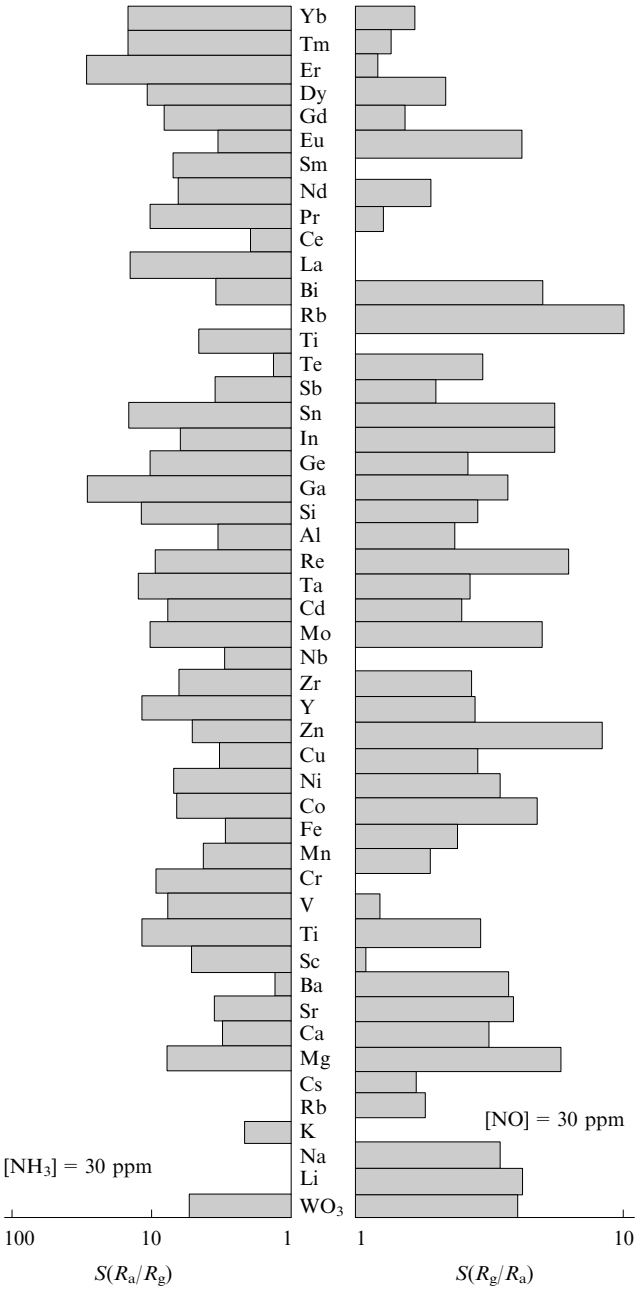


Figure 4. The effect of the introduction of 1 mass % of different dopants on the sensitivity of a gas sensor based on tungsten oxide with respect to ammonia and nitrogen monoxide.[102]
S is sensor response, R_a and R_g are the sample resistance in air and in the analysed gas atmosphere, respectively.

3. Sensors in biology and medicine

Nowadays, active studies are carried out aimed at the use of nanoparticles in biology and medicine. The problems to be solved in these fields of knowledge are closely interrelated; this is why they are often considered together. For biological and medicinal applications, nanoparticles that as a rule have hydrophobic stabilising shells should be transferred to aqueous solutions where the hydrophobic ligands are replaced by hydrophilic. For this purpose, it is necessary to use molecules that contain several functional groups of which some groups can be used for stabilisation of nanoparticles and the other should promote their modification and functionalisation.

As such molecules, amphiphilic polymeric molecules that are capable of transferring virtually any particle into aqueous media are used.[105] Their relative drawback is associated with the increase in the nanoparticle volume due to the formation of several stabilising layers. At the same time, the diversity of amphiphilic polymers makes it possible to introduce different

functional groups into shells of nanoparticles, bind the latter with bioactive molecules and use them as sensors.

When using nanoparticles, attention should be paid to the toxicity of nanosystems. Substances utilised in biology and medicine even if safe on the microlevel can become toxic on the nanoscale. Bearing this in mind, it is important to study the particle–cell interactions.[2] The adverse effect of nanoparticles on a cell can manifest itself as follows:

— a nanoparticle may oxidise the cell membrane; finding itself in the cell environment, a nanoparticle can behave as a toxic chemical that causes apoptosis,§ *i.e.*, the cell death;

— a nanoparticle captured by the cell membrane or adsorbed on its surface can become the reason for the impaired cell functions;

— a toxic effect can appear in the interaction of nanoparticles of different shapes (*e.g.*, spherical and fibre) in a cell.

Studies of the properties of CdSe nanoparticles and the CdSe/ZnS nanosystem have shown that the toxicity depends on the nanoparticle size, its surface coverage and the nature of functional groups bound with its surface.[106] Toxicity of CdSe particles was found in yet another study.[107]

Studies on the use of different types of quantum dots ¶ as the markers for cells, tissues, bacteria and viruses are actively progressing. As compared with organic dyes, quantum dots exhibit the higher photostability and sensitivity.

The ambiguity of views of scientists on the toxicity of nanoparticles does not reduce the number of publications on the use of these materials as the sensitive tags for sensors. Nanocrystals and especially quantum dots are the convenient markers that are unsusceptible to light bleaching and sufficiently biocompatible. Moreover, in cell fission, nanoparticles get to both new cells preventing the loss of the label. Particles CdS that exhibit fluorescence properties were grown on magnetic FePt nanoparticles. Such nanoformations can be delivered to any internal organ to follow the state of the latter.

For the same purpose, hybride nanoparticles and quantum dots covered with phospholipid biolayers (phospholipids are also parts of the membrane) were used.[108] Such nanosystems exhibit good luminescence properties, biocompatibility and can be used in the monitoring of cell transformations. For example, similar particles were introduced into frog's embryonal cells, which allowed scientists to follow the foetus development.†

Metal nanoparticles can be used in enhancing the sensitivity of a sensor for the determination of DNA. Thus detection of 5–10 DNA chains [109] involved the use of magnetic iron oxide nanoparticles and citrate-stabilised gold nanoparticles, which allowed the DNA detection with sufficiently high sensitivity. Figure 5 illustrates this process. In addition to using two metals, silver-coated electrodes were employed for the amplification of the signal from gold-modified DNA. Such a trick increased the light scattering (outlet signal), which allowed 10 chains or 500 zeptomoles (1 zmol litre^{-1} = 10^{-21} mol · litre^{-1}) to be detected. This method requires neither the use of enzymes nor great times and is relatively cheap. It also allows one to distinguish DNA molecules containing individual bases with the sensitivity of up to 10^{-18} mol litre^{-1}. The elaborated method was used in the detection of anthrax DNA.

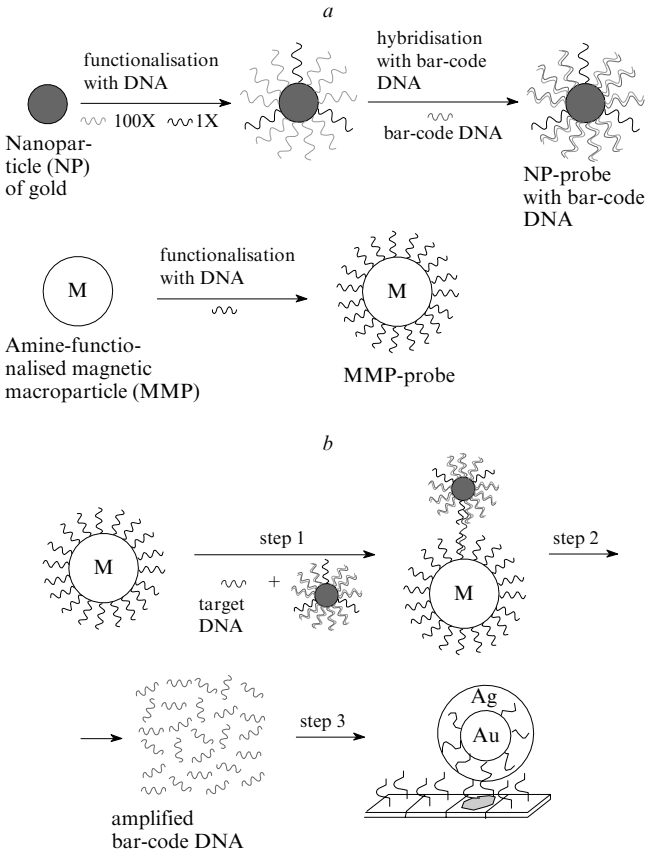


Figure 5. Scheme of operation of metal nanoparticles used in DNA detection.[109]
(*a*) Scheme of synthesis of probes based on nanoparticles and magnetic microparticles; (*b*) DNA amplification scheme: step 1 is the binding of the target DNA to functionalised DNA-NP and MMP probes, step 2 is the magnetic separation and decomposition of duplexes of bar-code DNA; step 3 is the determination and analysis of bar-code DNA. Target DNA (anthrax): 5′GGATTATTGTTAAATATTGATAAGGAT3′, bar code DNA: 5′AGCTACGAGTTGAGAATCCTGAATGAATGCGACG3′.

The development of the similarly fast and high-sensitive sensors is the burning problem for the prevention of terrorist attacks.

The requirements imposed upon the selectivity, precision and reliability of methods for the determination of clinically important metabolites as the indicators of the state of human health are gradually becoming more stringent. New versions of the detection of compounds associated with different diseases are being actively developed. One of such methods was used in the creatinine determination.[110] Creatinine, a common urine component, is also present in blood and muscles. Blood of a healthy person contains creatinine at a level of 35–140 μmol litre^{-1}. In kidney diseases or their transplantation, the creatinine concentration in blood serum and plasma may reach 1 mmol litre^{-1}.

Figure 6 illustrates the operation of a sensor by the example of creatinine determination. The main components of this system include the enzyme creatinite deaminase and a polyacrylamide hydrogel that contains spheres of polystyrene latex with diameter of 120 nm.

Under the action of the enzyme, creatinine is quickly hydrolysed to form hydroxide ion OH^-. In the second stage, 2-nitrophenol is added to the system by titration, which changes pH of the medium. Phenol deprotonation leads to hydrogel swelling due to an increase in the phenol solubility. As

§ Apoptosis is a phenomenon of programmed cell death accompanied by the appearance of typical cytological evidence (apoptosis markers) and molecular processes.

¶ Quantum dots are crystals of, as a rule, nanosize inorganic semiconductors that exhibit unique physical and chemical properties untypical of the same substances on the macroscale. Quantum dots may be bound to biological molecules by chemical bonds.

† In contrast to other studies, no mention was made on the toxicity of CdSe.[108]

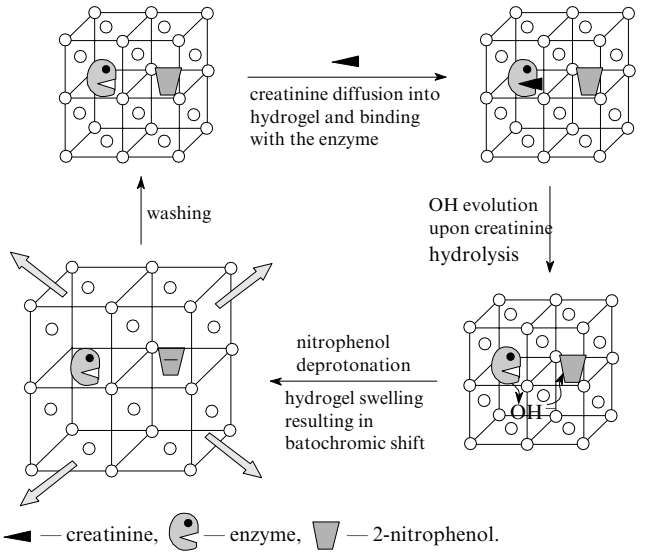


Figure 6. Illustration of operation of a sensor for creatinine.[110]

a result, with the increase in the creatinine concentration, the luminescence lines shift to lower energies, *i.e.*, the bathochromic shift is observed.

The spectral sensitivity of a sensor allows one to reliably determine creatinite concentrations in the range of 0.1 – 1 mmol litre^{-1}. With the aim of simplifying the creatinine determination, coloured calibration charts were proposed.[110] Such charts will allow patients to obtain information without using special instruments, which is of vital importance for those suffering kidney diseases.

The approach developed for the creatinine determination was used in designing a sensor for glucose.[111] Clinical tests have shown that such a sensor makes in possible to determine up to 0.15 mmol litre^{-1} glucose in solutions at 37 °C. The elaboration of such sensors is of great importance for diabetic patients.

Inhalation of air containing high ammonia concentrations can lead to pulmonary edema; once the ammonia concentration reaches 5000 – 10 000 ppm, death occurs in 5 – 10 min. Prolonged exposure in an atmosphere containing small ammonia concentration does not harm the health. This is due to the fact that ammonia is not accumulated in organisms. It is the metabolite of proteins and nucleic acids. Ammonia is removed from organisms with urine in the form of urea and ammonium salts. A small amount of ammonia is secreted by sweat glands.

In certain diseases, the organism contains an enhanced amount of ammonia, which can be found by the analysis of the exhaled air.[112] Such a test makes it possible to quickly diagnose stomach ulcer induced by the presence of bacteria *Helicobacter pylori*[113] or the urea imbalance inherent of kidney diseases. As little as several cubic centimetres of exhaled air are sufficient for the analysis with gas-sensitive sensors.[114]

Diagnosing of *Helicobacter pylori* is based on the urea conversion to ammonia and bicarbonate. Laying aside the complex processes that involve bacteria and lead to the ammonia synthesis, it should be noted that such analyses require sensors capable of the detection of < 50 ppb ammonia in the exhaled air in the presence of carbon dioxide in concentrations up to 3%.[112] The response time of such sensors should not exceed several minutes. To date, this problem is still unsolved. This example of the ammonia determination for the identification of *Helicobacter pilori* demonstrates all the complexity of problems faced by a designer of sensors for diagnosing diseases.

IV. Conclusion

The analysis of studies published in the recent years allows one to draw several general conclusions on the synthesis and application of nanomaterials in the development of new gas sensors. Two trends are clear, *viz.*, the development of sensors to be employed at room temperature and the use of new quasi-one-dimensional nanostructures (such as nanotubes, nanorods, nanobelts, nanowires, *etc.*) as the sensors.

Studies of size effects typical of substances in the nanostate should stimulate the further investigations of the sensor activity that depends on the surface-to-volume ratio, porosity, sample size and possible reactions with different oxygen forms on the sensor surface.

The use of quasi-one-dimensional materials and the production of hybrid systems require the refinement of mechanisms of the sensor sensitivity. Understanding of these mechanisms determines the successful use of new sensor materials. The following general requirements can be imposed upon virtually all sensor materials: the high sensitivity, selectivity, stability and safety. The other requirements to sensors differ depending on application fields and conditions. The development of nanoscience opens up new directions in the use of sensors, particularly, in the analysis of operation, identification, and safe performance of instruments and materials produced by nanotechnologies.

This review was written at partial financial support of the Russian Foundation for Basic Research (Project No 05-03-32 293) and the Grant of President of the Russian Federation for young Russian scientists, namely, candidates of sciences and their supervisors, (No. MK-4996.2006.3).

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