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CATALYSIS  
AND NANOTECHNOLOGIES

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## Adsorption, Catalysis, and Reactions on the Surfaces of Metal Nano-oxides

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**Abstract**—Nanomaterials based on metal oxides are considered. Special attention is given to adsorption, because this step determines physicochemical properties of nanostructured materials. The main processes are considered that occur on the surface of metal nano-oxides in the course of adsorption and the nature of chemoresistance. A model is presented that explains the increasing sensitivity of semiconductor sensor materials with a decrease in the grain size. The potential of the use of metal and metal oxide nanoparticles in catalysis and photocatalysis is discussed. Examples are given for the selective synthesis of  $\alpha$ -mercaptopyridine on the surface of  $\text{TiO}_2$  with supported silver nanoparticles with a diameter of  $<1$  nm. Possible problems that might appear when nanoparticles are used in large-scale manufactures are discussed. Promising examples of the use of magnesium and calcium oxide nanoparticles for the destruction of toxic substances, specifically 3,3-dimethyl-2-butylmethylphosphoxofluoride and dichloroethyl sulfide at room temperature are analyzed. The method of cryoformation is considered that makes it possible to create new nanomaterials for use in catalysis, in gas sensors, and for modifying pharmaceuticals to reach a higher biological activity.

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### INTRODUCTION

In the natural sciences, notions have evolved about the crucial and strident development of nanoscience and nanotechnology. Nanoscience comprises basic research on physics, chemistry, biology, and medicine of small-scale particles that are smaller than 100 nm [1]. Materials, substances, devices, and instruments based on these particles are the main subject of nanotechnology. The characteristic feature of the true nanostate is the dependence of the fundamental properties of the substance on the size and shape of particles that constitute the substance. These dependences are called a size effect and reveal themselves in chemical reactions as a distinct feature of nanochemistry [2, 3].

Along with the qualitative changes in the properties and reactivity with changes in the number of atoms in a particle, the dependence on the structure is also important. This is due to self-organization during the formation of a nanoparticle. Particles with the same number of atoms may have different properties. Thus, one can speculate about the size-and-structure effect in nanochemistry, where particles with sizes of 1–10 nm undergo most interesting, new, and unusual transformations. The dependence of physical and chemical properties on size is most pronounced in this range of sizes, and surface properties dominate over bulk properties. Particles of this sort have many uncompensated bonds, high reactivity, and a reserve of energy, which is used in ordinary chemical transformations. The high activity of metal nanoparticles is related to the problems of synthesis, organization, sta-

bilization, toxicity, experimental reproducibility and scale-up of syntheses. Each of the above problems is worth being considered separately and should be taken into account in the practical implementation of the results of basic research. Special attention should be given to the questions of usability of the particles obtained, materials based on them and their cost. However, in our opinion, in nanotechnology, and specifically in nanochemistry, basic research and applied studies are closely related. Multiple functions and novelty of ideas in nanoscience and nanotechnology lead to the situation when almost any basic research work may find practical use and any practical application requires serious basic research.

Currently, nanopowders of various oxides find active use: unlike metals, oxides are more stable. According to [4] and analysis of literature data, 80% of annual production of nanopowders is the production of silica, alumina, and titania, and 20% is the production of oxides of other metals, mostly iron, zinc, copper, magnesium, and certain rare and rare-earth elements. Annual production of  $\text{SiO}_2$  is  $>25000$  t with an overall value of \$15 billion. The production of titania nanopowder is 5000 t with an overall value of \$0.5 billion. The production of zinc oxide is 2000 t, and the annual production of magnesia 1000 t. Of metals, the production of nanoparticles of nickel and copper is 32% (1500 t). The production of tungsten and molybdenum oxides is 500 t; the production of iron oxide, alumina, and titania is  $>1500$  t. A compound that is most widely used is mixed tungsten–cobalt carbide:

~600 t (\$200 million). Almost half of the powders produced have sizes <30 nm and have a high degree of homogeneity and purity. The consumption of oxide nanopowders is determined by their usefulness and cost. Thus, 1 kg of zinc oxide nanopowder costs \$75, and zirconia nanopowder costs \$1500. Information on oxide nanopowders produced in Russia was reported in [4].

Metal nanoparticles can be considered as two-phase multiple-layer systems with a nucleus and high specific surface area, which is affected by various factors and largely determines the properties of nanoparticles, their chemical, sensor, and catalytic activity in the subsequent transformations.

In air nanoparticles of most metals are covered by an oxide layer. Depending on the conditions and properties of a metal and its oxide, the thickness of the oxide layer varies from several monolayers to the state when the whole particle consists of the oxide.

Metal oxides are chosen for this review because they are well studied and have wide applications in the synthesis of various materials. Metal nanochemistry has been analyzed in detail in [3].

This review considers specific features and possible applications of various oxides in nanochemistry and nanotechnology using examples. The main attention is given to adsorption as a step that determines the further chemical activity of nanoparticles. Catalysis, chemical transformations with the participation of metal nano-oxides, and some problems of the use of nonequilibrium states and low temperatures for the modification and micronization of drugs are also briefly considered.

## ADSORPTION

Adsorption is one of the main processes in the synthesis and use of nanomaterials because of the considerable influence on the physical and chemical properties of nanosystems. For instance, the adsorption of stabilizing ligands on the surface of active nanoparticles leads to their greater stability (e.g., covering nanoparticle with carbon). Surface modification with molecules that have a certain structure and functional groups makes it possible to obtain biocompatible materials or increase the sensitivity of gas sensors to some gases [5]. Adsorption is one of the main chemical processes and it has been considered in detail in textbooks and monographs. We will briefly discuss certain features of adsorption on oxide *n*-type semiconductors that are usually used as sensor materials. Analysis of general regularities makes it possible to categorize the specifics of various applications of metal oxide nanoparticles.

Currently, many publications are devoted to the creation of nanomaterials with a high sensitivity to various compounds. Most often laboratory studies are carried out under conditions that are far from real. Possible changes in the composition of air, humidity,

and temperature are usually neglected. As a result, although there are a lot of wonderful laboratory results, there are very few commercial sensors for real applications.

The reasons for the high sensitivity to a certain substance or gas and the accompanying low selectivity are related to the principle of metal oxide sensor action. Available problems can be overcome if one deeply understands the nature of processes occurring on the surface of these materials.

Changes in the electrophysical properties of a semiconductor under the action of adsorption of gas molecules are primarily due to the formation of charged chemisorbed oxygen molecules [6]. The transition of chemisorbed species into the charged state is accompanied by changes in the surface charge. The formation of a charge on the semiconductor surface leads to band bending [7]. Depending on the type of a semiconductor and the chemical nature of the adsorbate, the surface layer may be depleted or enriched in the main charge carriers [8]. In the adsorbate–adsorbent systems, two types of equilibria can be observed: (1) transition of all chemisorbed species into the charged state and (2) equation of the Fermi level of the adsorbent to the energy level of chemisorbed species. The former exists at low coverages and the latter is possible at high coverages [9]. In both cases, in the semiconductor surface layer, a region of spatially distributed charge is formed. Changes in the energy levels of an *n*-type semiconductor in anionic chemisorption is shown in Fig. 1.

The region of the spatially distributed charge is characterized by the width *l* and by the surface potential  $qV_s$  [11, 12].

$$qV_s = q^2 N_O^2 / 2\varepsilon\varepsilon_0 N_d, \quad (1)$$

where  $N_O$  is the surface concentration of oxygen ions,  $N_d$  is the concentration of donors in the bulk of oxide,  $qV_s$  is the value of band bending near the surface,  $q$  is the elementary charge,  $\varepsilon_0$  is the dielectric permittivity of vacuum, and  $\varepsilon$  is the dielectric constant of the semiconductor.

The charge on the surface affects the conductivity of thin layers of a semiconductor. Depending on the composition of the medium, the coverage of specific surface sites may vary and this leads to a change in the electric conductivity. This is called a chemoresistive effect and reveals itself as the sensitivity of semiconductors to gases. A relative change in the electric conductivity of the structure upon the exposure to the gas to be analyzed compared to the electric conductivity in the reference gas or the slope of the dependence of electric conductivity on the concentration of the gas is used as a measure of the sensitivity to this gas [13]. Air or nitrogen is usually used as reference gas.

Gases may act as oxidants or reducing agents depending on their effect on the conductivity of the semiconductor. Oxygen is a typical example of an oxidant. The interaction of many gases with the solid sur-

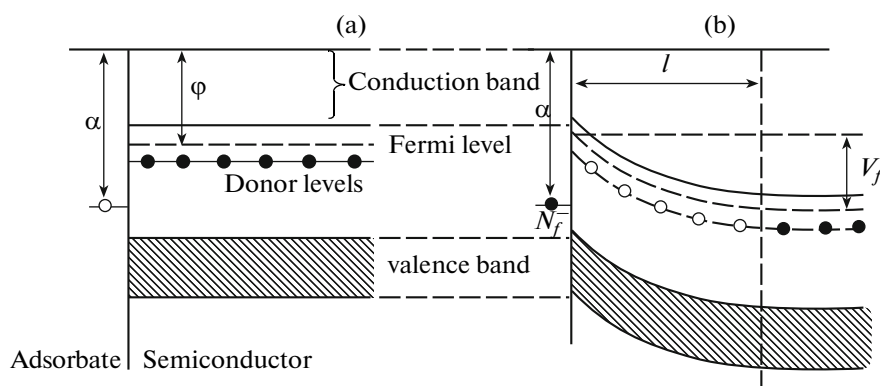


Fig. 1. Anionic chemisorption on the  $n$ -type semiconductor (a) before and (b) after chemisorption [10].

face is due to the presence of adsorbed oxygen molecules. Oxygen can be chemisorbed on the surfaces of semiconductors mostly in the form of ions  $O^{2-}$ ,  $O^-$ , and  $O_2^-$  [14]. Some oxides do not adsorb oxygen. In this case, lattice oxygen participates in the interaction between the surface and the gas phase. The existence of different forms of oxygen ions is associated with heating the surface [12]. Depending on temperature, oxygen may localize different amounts of electrons from the conduction band of semiconductors. This sort of capture leads to changes in the position of the Fermi level on the surface [15].

Gases that are reducing agents are hydrogen, carbon monoxide, hydrocarbons, alcohols, etc. In many cases, these gases or their mixtures are interesting for the designers of gas sensors.

The adsorption of reducing gases leads to various processes on the surface of  $n$ -type semiconductors:

(1) Molecules or atoms of a reducing gas are adsorbed on the surface of  $n$ -type semiconductors as donors and inject electrons into the bulk. Adsorption can be accompanied by the dissociation of molecules;

(2) Molecules of the adsorbed substance may bind lattice oxygen on the surface in a chemical reaction, and the concentration of donors in the bulk may change because of the vacancy diffusion into the bulk of a semiconductor; and

(3) The reducing agent may react on the semiconductor surface with chemisorbed oxygen and return localized electrons to the conduction band.

The dominance of one of the above mechanisms depends on temperature, pressure, and the composition of the medium. For instance, the conductivity of tin oxide with platinum additives increases in the hydrogen atmosphere at  $<400$  K [16], which corresponds to the first mechanism. The model of redox reactions explains the experimental results on the interaction of tin oxide with reducing gases [17]. An XPS study of the Pt/SnO<sub>2</sub> surface showed the absence of adsorbed oxygen ions [18]. It has been suggested that the sensitivity to gas was due to a change in the

number of surface defects in the presence of a reducing agent. A mechanism of the influence of the reducing gas on the region of the surface charge and, consequently, on the electric conductivity of a semiconductor through interaction with chemisorbed oxygen was proposed for the reaction between carbon monoxide and tin oxide [19].

In the same adsorbate–adsorbent system, the mechanism of gas sensitivity may change when conditions change. For instance, with an increase or decrease in the semiconductor surface temperature. The effect of hydrogen and carbon monoxide on the electric conductivity of gallium oxide in the absence of oxygen and the form of the temperature dependence were considered in relation to the first two mechanisms, each dominating in its own temperature range [20]. In the general case, the chemisorption of the reducing gas usually leads to a decrease in the potential barrier on the  $n$ -type semiconductor surface and to an increase in the conductivity.

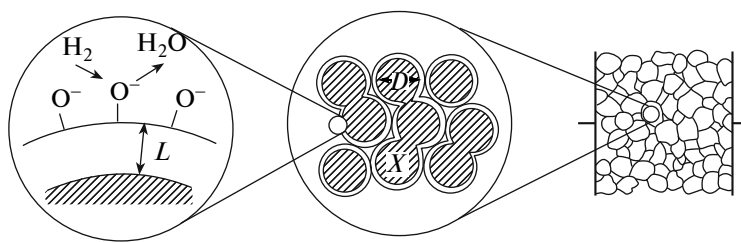
Gas-sensitive materials based on tin dioxide are best studied and widely used. Nevertheless, studies with the goal of achieving their better selectivity, stability, and sensitivity are continued [21–23].

#### DEPENDENCE OF THE SELECTIVITY ON THE GRAIN SIZE

The sensitivity of semiconductor materials increases with a decrease in the size of crystallites for rather small particles [24]. Figure 2 shows a sensitive layer on the surface of metal oxide semiconductor grains.

A typical example of the dependence of SnO<sub>2</sub> sample sensitivity to adsorption of 0.08% H<sub>2</sub> and 0.08% CO on the diameter of grains is shown in Fig. 3 [24].

Because in the formation of the region of spatially distributed charge the bulk of semiconductor is depleted with charge carriers only for the thickness  $L$ , three mechanisms of conductivity control are possible (Fig. 4). For the large crystallites, the size of particles is  $D \gg 2L$ , and the conductivity in the system is deter-



**Fig. 2.** Gas-sensitive layer on the surface of semiconductor grains:  $L$  is the zone of surface charge,  $D$  is the size of particles, and  $X$  is the size of isthmuses.

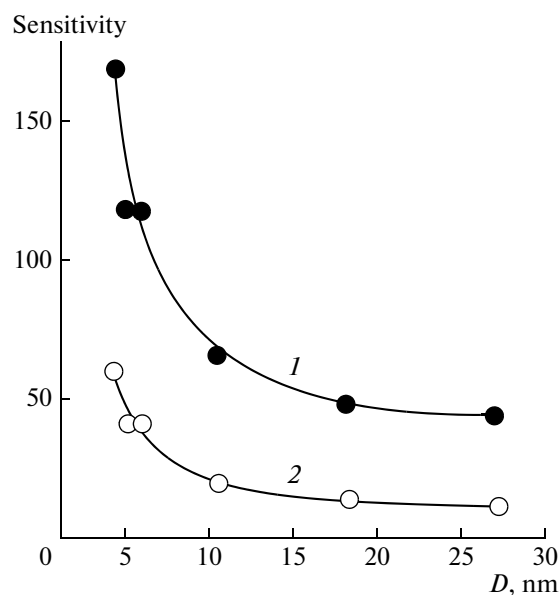
mined by the Schottky double barriers, which appear at the points of grain contact. The sensitivity is almost independent of  $D$ , and the conductivity is determined by the width of the potential barrier at the grain boundaries [12, 25]. When  $D = 2L$ , each electronic channel in the isthmus is rather small and can affect the resistance. Because the number of isthmuses is much greater than the number of contacts between the grains, they determine the resistance of material and lead to the appearance of the size dependence of gas sensitivity. When  $D < L$ , each grain is completely captured by the region of spatially distributed charge. In this case, electron transport in any part of the particle is determined by the surface charge. The conductivity of such a system depending on the oxygen partial pressure was calculated in [26].

Thus, by decreasing the size of particles, one can increase the sensitivity of semiconductor materials. A critical review of the known methods for the formation of thin films for their use as gas-sensitive materi-

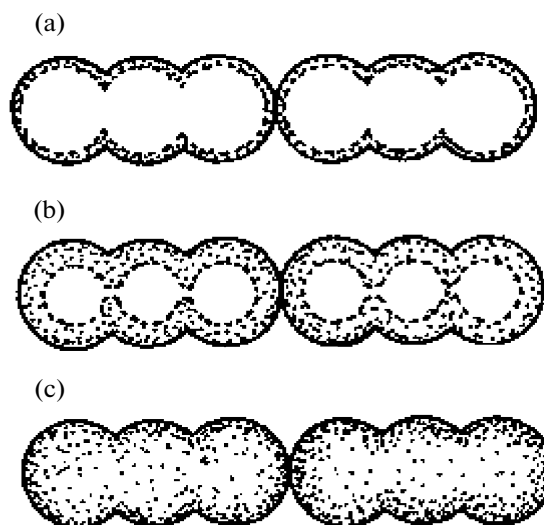
als, as well as oxide nanomaterials of the new type is given in [27, 28]. Quasi-one-dimensional nanomaterials, such as oxide nanotubes, nanoribbons, and nanofilaments, have a potential for use as sensitive layers in gas sensors [28].

### EFFECT OF WATER VAPOR ON THE CONDUCTIVITY OF SEMICONDUCTOR LAYERS

The presence of water vapor in the atmosphere leads to a greater surface conductivity of  $\text{SnO}_2$  samples [12]. In this case, the sensitivity to CO increases [29] and the sensitivity to hydrocarbons decreases [30]. When the surface temperature is between 100 and  $200^\circ\text{C}$ , water molecules physically adsorb on the surface of tin dioxide via the formation of hydrogen bonds or hydroxyl groups. Thermal desorption and IR spectroscopy were used to show that, at  $t > 200^\circ\text{C}$ , adsorbed water molecules appear on the surface.



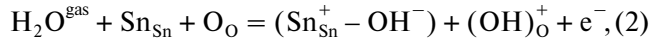
**Fig. 3.** Dependence of the gas sensitivity of  $\text{SnO}_2$  to (1) 0.08%  $\text{H}_2$  and (2) 0.08% CO in air at  $300^\circ\text{C}$  on the size of crystallites ( $D$ ) [24].



**Fig. 4.** Effect of the grain size on the mechanism of conduction in metal oxide gas-sensitive layers. Hatched region corresponds to the high resistance and nonhatched regions correspond to the low resistance; control: (a)  $D \geq 2L$ , by the grain boundaries; (b)  $D = 2L$ , by isthmuses; and (c)  $D < 2L$ , by grains.

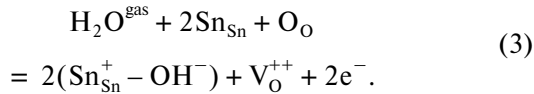
Hydroxyl groups may form by the redox reaction in which the OH group with its electron pair appears bound by a Lewis acid site (Sn) and a hydrogen atom reacts with either lattice oxygen (a Lewis base) or an adsorbed oxygen molecule.

Three mechanisms have been proposed that explain an increase in the conductivity of SnO<sub>2</sub> in the presence of water vapor [12]. According to the first mechanism, OH group with an oxygen atom from lattice oxygen plays the role of the electron donor:



where (Sn<sub>Sn</sub><sup>+</sup> - OH<sup>-</sup>) is the isolated hydroxyl group and (OH)<sub>O</sub><sup>+</sup> is a hydroxyl group bound by the surface. The reaction involves the hemolytic dissociation of water on the surface and the reaction of neutral hydrogen atom with lattice oxygen, which is usually in the 2<sup>-</sup> state. The OH group formed may be ionized and become an electron donor for the conduction band of the semiconductor.

Taking into account the second mechanism, one considers the possibility of the reaction between a hydrogen atom and lattice oxygen, and the hydroxyl group thus formed may bind to tin atom. In this case, oxygen vacancy is ionized by providing an additional electron:

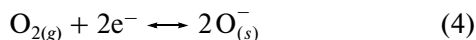


The third mechanism takes place at low temperatures and is related to the competition between water and oxygen molecules for the same adsorption sites. In equilibrium conditions, some of the active sites are occupied by water molecules and the concentration of chemisorbed oxygen decreases, which leads to the lower surface charge. The results of studies using diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) provides evidence in favor of this mechanism in the form of information on the state of the surface and adsorbate at a given temperature and in a certain medium [29, 31].

### ADSORPTION RESPONSE KINETICS

Profiles  $S(T, C_{\text{gas}})$  of changes of sensor response with the temperature and concentration of the gas to be determined differ from system adsorbate-adsorbent to another. The most frequent bell-shaped temperature dependence of the response with a maximum at  $S_M$  at temperature  $T_M$ . This dependence is explained by the processes of adsorption and by the first-order reaction, both depending on temperature [32].

The process of oxygen adsorption in the ionic form



can be described by the equation:

$$\begin{aligned} \frac{d}{dt} N_{\text{O}} &= k_{\text{ads}} \rho_{\text{O}_2} N_{\text{C}}^2 \exp\left(-\frac{2E_{\text{ads}}}{k_{\text{B}} T}\right) \\ &- k_{\text{des}} N_{\text{O}}^2 \exp\left(-\frac{2E_{\text{des}}}{k_{\text{B}} T}\right), \end{aligned} \quad (5)$$

where  $N_{\text{O}}$  is the surface concentration of oxygen ions;  $N_{\text{C}}$  is the concentration of vacant sites;  $\rho_{\text{O}_2}$  is the oxygen partial pressure;  $k_{\text{ads}}$ ,  $k_{\text{des}}$ ,  $E_{\text{ads}}$ , and  $E_{\text{des}}$  are the rate constants and the activation energies of adsorption and desorption.

In the case of the reaction with the reducing gas on the oxide surface, one can add the additional term:

$$R_e = L N_{\text{O}} k_0 \exp\left(-\frac{E_a}{k_{\text{B}} T}\right), \quad (6)$$

where  $L$  is the surface coverage with the molecules of reducing gas and  $k_0$  and  $E_a$  are the rate constant and the activation energy of the reaction.

In the pseudo-steady-state conditions, the equation can be rewritten as follows assuming electron tunneling near the surface:

$$0 = k_{\text{ads}} \rho_{\text{O}_2} n_{\text{D}}^2 - k_{\text{des}} N_{\text{O}}^2 - L N_{\text{O}} k_0 \exp\left(-\frac{E_a}{k_{\text{B}} T}\right). \quad (7)$$

The analytical solution to this equation gives us the surface concentration of oxygen ions:

$$\begin{aligned} N_{\text{O}} &= \left\{ L k_0 \exp\left(-\frac{E_a}{k_{\text{B}} T}\right) \right. \\ &+ \left. \sqrt{\left[ L k_0 \exp\left(-\frac{E_a}{k_{\text{B}} T}\right) \right]^2 + 4 k_{\text{ads}} k_{\text{des}} \rho_{\text{O}_2} n_{\text{D}}^2} \right\} / (2 k_{\text{des}}). \end{aligned} \quad (8)$$

In the absence of the reducing gas (at  $L = 0$ ), this expression takes the following form:

$$N_{\text{O}}^{\text{air}} = \sqrt{\frac{k_{\text{ads}}}{k_{\text{des}}} \rho_{\text{O}_2} n_{\text{D}}^2}. \quad (9)$$

The depth of the surface charge zone is

$$l = N_{\text{O}} / n_{\text{D}}. \quad (10)$$

Therefore, for the oxide layer with width  $D_s$ , we have the expression for the sensor signal:

$$S(T, C_{\text{gas}}) = \frac{R_{\text{air}}}{R_{\text{gas}}} - 1 = \frac{D_s - l_{\text{gas}}}{D_s - l_{\text{air}}} - 1, \quad (11)$$

where  $l_{\text{air}}$  and  $l_{\text{gas}}$  are the depths of the spatially distributed charge in air and in the presence of the reducing gas, respectively.

Thus, the apparent bell-shaped dependence of the sensor signal on temperature is explained by the combination of adsorption and chemical reactions of adsorbate on the oxide surface. The experimental tem-

perature dependences of the sensor signal in the framework of the above model make it possible to determine the activation energies of adsorption and oxidation reaction.

Based on the available ideas about adsorption on semiconductor Nano-oxides, the Laboratory of Low-Temperature Chemistry at the Department of Chemistry of Moscow State University has developed an original method for the preparation of nanostructured gas-sensitive materials, which is low-temperature vapor deposition in vacuum with further oxidation [33, 34]. This method is based on the vacuum condensation of metal vapor on the constant-temperature support at 80–300 K. Cooling the support leads to a substantial decrease in the mobility via diffusion at the instant of deposition. Therefore, the formation of column-like structures is possible in the course of condensation, and this is due to the attraction between atoms approaching the support and deposited clusters. In further controlled annealing, the structure is decomposed and metal particles are formed on the nonwetable support.

The addition of oxygen at a certain moment of condensate evolution makes it possible to form materials with a certain nanostructure and a certain chemical composition, specifically with nanograins of the “nucleus–shell” type and with isthmuses between them. The control of deposition parameters (rate, support temperature, and evaporator temperature) allows one to control the structure of condensates and chemically modify the grains). Thus, in low-temperature vacuum deposition, lead nanostructures that are sensitive to ammonia and water vapors have been obtained [35, 36]. The detection threshold of ammonia was  $\sim 10^{-3}\%$ . In our opinion, the sensitivity of such systems is due to the formation of percolation structure of  $\sim 50$ -nm nanoparticles of lead covered with a  $\sim 1.5$ -nm-thick semiconductor oxide layer. Oxide isth-

muses between metal particles determine the general conductivity of the material and the presence of the chemiresistance effect.

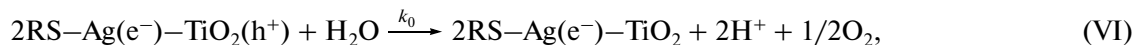
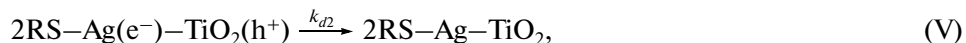
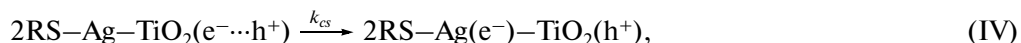
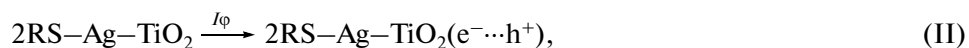
There is another way to affect the chemiresistance of materials by affecting the microstructure and porosity of the samples through the low-temperature cocondensation with the additional component (e.g., inert gas), which is removed from the system by annealing. To affect the structure of thin films of lead, cocondensation with carbon dioxide was used [37]. It was shown that the roughness of such films is higher than the roughness of lead films without carbon dioxide. Therefore, the method of cocondensation and annealing is promising for the creation of materials with a high surface area.

Other applications of nanomaterials as sensors have been considered in [5].

## CATALYSIS

Most of the catalytic reactions that are of interest for nanotechnologies are carried out using metal nanoparticles with various sizes. Metal oxides are applied less frequently. Therefore, we only consider several examples from photocatalysis.

The photocatalytic reduction of bis(2-dipyridyl) disulfide (RSSR) in 2-mercaptopyridine (RSH) by water on the surface of titania is selective. The process rate substantially increases if silver nanoparticles with a size of less than 1 nm are supported on  $\text{TiO}_2$  (0.24 wt %) [38]. Thiols are widely used in agricultural chemistry, petrochemistry, pharmaceuticals, and for the stabilization of metal nanoparticles. A study of RSSR adsorption, absorption spectra, and the effects of pH, exposure, the amount of supported silver, and temperature made it possible to propose the following reaction mechanism [38]:



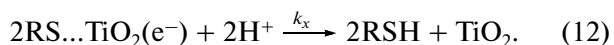
where  $K_a$  is the constant of equilibrium adsorption,  $I_4$  is the light intensity, and  $k$  is the intensity of light absorption.

In step (I), selective adsorption of RSSR on the surface of silver nanoparticles is accompanied by the cleavage of the S–S bond. In step (II), the excitation

of nanoparticles in the field of forbidden band of TiO<sub>2</sub> leads to the generation of the pair electron(e<sup>-</sup>)–hole(h<sup>+</sup>). Most of the electron–hole pairs recombine (steps (III) and (V)). In step (IV), charges are separated: silver nanoparticles accept an electron, and holes transfer to the TiO<sub>2</sub> support. The positive potential of the hole is sufficient for the oxidation of water and for the formation of H<sup>+</sup> and the O<sub>2</sub> molecule (step (VI)). In step (VII), the catalytic system is restored and RSH is formed. As a result, according to the authors, supported silver nanoparticles cause

- (1) The acceleration of RSSR adsorption;
- (2) The spatial separation of positions where silver particles are reduced and TiO<sub>2</sub> support is oxidized (i.e., the effect of charge separation); and
- (3) The selective adsorption of the oxidant (RSSR) and the reducing agent (H<sub>2</sub>O) in the sites for oxidation and reduction that stipulates the high selectivity of the process.

Comparison of the catalytic systems TiO<sub>2</sub> and Ag–TiO<sub>2</sub> showed that both of them are characterized by the same activation energies of the photocatalytic reduction. This points to the fact that the rate-limiting step in this multiple-step process is reaction (VI) rather than photocatalysis. When there is no silver, the scheme of RSSR reduction on TiO<sub>2</sub> is as follows:



In recent years, semiconductor nanoparticles find active use in catalysis and photocatalysis. The comparative catalytic activity of various nanosized particles of

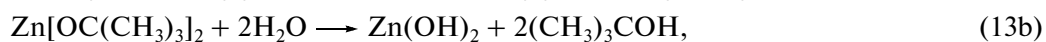
semiconductor oxides and sulfides is studied in polar (acetonitrile) and organic solvents [39]. The study was performed using the photooxidation of pentachlorophenol, which is a toxic substance used as a fungicide, bactericide, or wood preservative.

The use of metal and metal oxide nanoparticles in catalysis of large-scale chemical manufactures is not highly probable. This is related to the scaling factor and the cost. Scaling causes two problems: one is related to the preparation of the sufficient amounts of catalytic metal nanoparticles. The other is related to the phenomenon of having a selective process with a high yield in a nanoreactor and not having the same characteristics in a large-scale reactor. In our opinion, catalysis by nanoparticles will be most actively used for the synthesis of new useful compounds with unique properties in near future. The use of various nanoparticles in chemical reactions is along these lines.

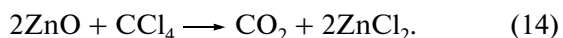
## REACTIONS

Oxide nanoparticles are widely used. The reactivity of metal oxides is lower than the reactivity of metals. Therefore, the formation of metal oxides is often used to stabilize metal nanoparticles. A number of reactions of interest in nanochemistry and nanotechnology have been recently carried out with metal oxide nanoparticles.

Original use of nanocrystalline zinc oxide was described in [40]. Zinc oxide was obtained by a modified sol–gel method via the following reactions:



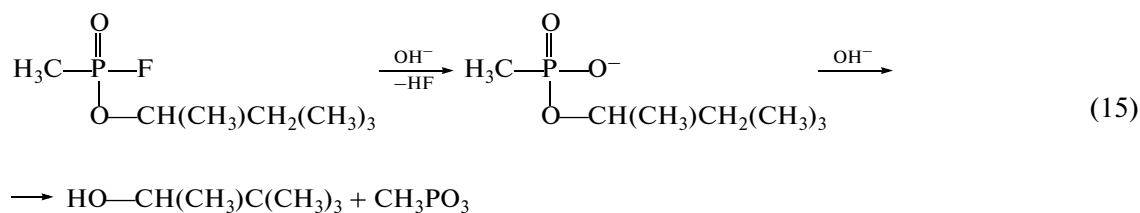
ZnO preparation included three steps: preparation, isolation, and activation of zinc oxide nanopowder. The latter process consisted of several steps of consecutive thermal treatment. First, the powder was slowly heated to 90°C and allowed to stay at this temperature for 15 min. Then, the temperature was gradually increased to 250°C, the sample was allowed to stay for 15 min and slowly cooled to room temperature. The resulting zinc oxide was in the form of crystalline nanoparticles with sizes of 3–5 nm and with a specific surface area of 120 m<sup>2</sup>/g. Zinc nano-oxide was used for the reaction



The process was performed at 250°C. CCl<sub>4</sub> was added to the reaction vessel in portions with 7-min intervals. CO<sub>2</sub> and unreacted CCl<sub>4</sub> was analyzed by gas chromatography. It was shown that nanocrystalline zinc oxide is more active than commercial samples. It

was also found that nanocrystalline zinc oxide efficiently adsorbs sulfur dioxide and dissociatively adsorbs diethyl-4-nitrophenyl phosphate, which is a toxic organophosphorus compound. In these processes, nanocrystalline zinc oxide is more active than commercial samples.

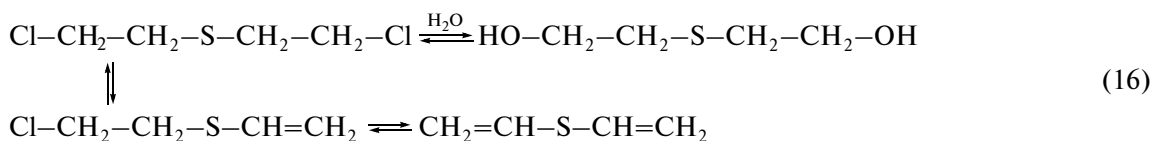
The high activity of nanocrystalline oxides was used in the reactions with compounds that find applications as chemical weapons. Nanocrystalline magnesium and calcium oxides readily react with organophosphorus compounds [41, 42]. For instance, 3,3-dimethyl-2-butylmethylphosphoxofluoride CH<sub>3</sub>–(O)P(F)O–CH(CH<sub>3</sub>)C(CH<sub>3</sub>)<sub>3</sub>, which is used as a nerve agent, reacts with nanocrystalline magnesia via the following scheme:



Magnesia abstracts HF to form  $\text{MgF}_2$  and  $\text{H}_2\text{O}$  and uses surface hydroxyl groups to convert the toxic compound into a nontoxic one.

Nanocrystalline oxides of alkaline earth metals have been successfully used for deactivating mustard

gas and other chemical weapons. The autocatalytic dehydrohalogenation of 2,2'-dichlorodiethyl sulfide on nanocrystalline calcium oxide was considered in [40, 42]. The reaction occurred via the following scheme

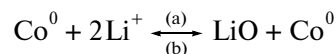
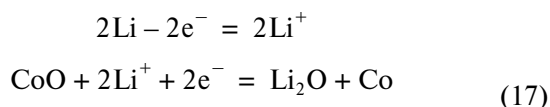


In this reaction, there is competition between dehydrochlorination with the formation of divinyl compound and the substitution of surface hydroxyl for chlorine. The reaction products were analyzed by the NMR method. In the products of decomposition of 2,2-dichlorodiethyl sulfide, one has found divinyl sulfide (~80%) and thioglycol and/or sulfonium ion (20%) with a hydroxyl group through which it probably binds to the surface of alkaline earth metal oxide. Besides mustard gas, the interaction of CaO with other organophosphorus compounds was studied. The kinetics of interaction of CaO with all compounds studied was characterized by the fast initial step and by the slow next step limited by diffusion.

In the above examples, nontoxic compounds were formed at room temperature, and the reaction rate was limited by the transfer of interacting substances. The presence of water in small amounts was favorable for detoxification, which is evidence for the promoting effect of hydroxyl groups on the oxide surface. Catalytic dehydrohalogenation occurred when calcium oxide nanocrystals and water were used.

An interesting application of nanoparticles of transition metal oxides was considered in [43]. The particles of Co, Ni, Cu, and Fe oxides with sizes of 1–5 nm were used as materials for electrodes in lithium batteries (the battery capacity was 700  $\mu\text{A h/g}$ ). In this case, the reactions of formation and decomposition of  $\text{Li}_2\text{O}$  and the respective oxidation and reduction of nanoparticles occur on CoO electrode nanoparticles.

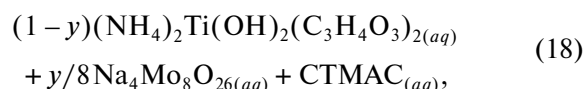
The scheme of reversible reactions can be written using CoO as an example:



Reaction (a) is probable and allowed by thermodynamics. Reaction (b) is unusual for electrochemistry.  $\text{Li}_2\text{O}$  has always been considered to be electrochemically inactive. Poisot et al. [43] failed at the electrochemical decomposition of  $\text{Li}_2\text{O}$  powder (mechanically ground powders of  $\text{Li}_2\text{O}$  and CoO were used). The possibility of reaction (b) is related to the participation of nanoparticles and an increase in their electrochemical with a decrease in the particle size.

The method of synchrotron radiation diffraction was used to find unusual structural states in the powder of zirconia nanoparticles [44]. It was shown that there may be two or three structures in a  $\text{ZrO}_2$  nanoparticle in the same time: monoclinic, tetragonal, and cubic. These kind of particles (called “centaurs”) suggest that various polymorphic transformations in a separate nanoparticle are possible.

Recently, great interest is given to the preparation and physicochemical properties of hybrid nanomaterials of the nucleus–shell type and to particles that involve two or three different metals. New nanocrystalline hybrid materials of the nucleus–shell type, such as  $\text{TiO}_2$  and  $\text{MoO}_3$  are studied [45]. Particles of  $\text{TiO}_2-(\text{MoO}_3)_x$  were prepared by the conucleation of metal oxides on the micelle surface. The reaction stoichiometry was described by the equation





where CTMAC is cetyltrimethylammonium chloride and  $y = 0.57$ .

In the materials obtained, the energy of photoabsorption correlates with the particle size. With a decrease in the size of  $\text{TiO}_2\text{-MoO}_3$  particles from 8 to 4 nm, the energy of absorption decreased from 2.9 to 2.6 eV. For comparison, the energies of forbidden bands of compact  $\text{TiO}_2$  and  $\text{MoO}_3$  are 3.2 and 2.9 eV, respectively. The resulting materials are more efficient in the photocatalytic oxidation of acetaldehyde compared to conventional titania produced by Degassa (France).

Metallic nanorods with diameters of 30–50 nm based on copper, silver, and gold have been synthesized. New publications appear that report the synthesis of nanorods with diameters of 5–60 nm and with a length of  $>10\ \mu\text{m}$  based on  $\text{BaTiO}_3$  and  $\text{SrTiO}_3$  [46],  $\text{TiO}_2$  [47], and  $\text{SnO}_2$  [48]. The synthesis of nanorods and nanotubes based on various oxides was considered in [48].  $\text{VO}_2$  is the subject of intensive studies. Polycrystalline nanorods have been synthesized [49]. It has been also possible to synthesize metastable vanadia nanostrips [50] and crystalline nanowires with an average width of 60 nm and a length of  $>10\ \mu\text{m}$  [51]. The method of high-temperature evaporation in a flow of argon with further condensation was used for the synthesis of nanowire from vanadia [52].

To apply metal nanoparticles in optical and electronic devices, it is necessary

(1) to make reliable electric contacts between individual nanoparticles;

(2) to determine the characteristics of electromagnetic interactions between particles in symmetric well-organized aggregates of nanoparticles; and

(3) to understand chemical properties of nanoparticle surface and its effect on the optical and electron properties of these species.

Some approaches to solving these problems were considered in [53].

Recently, an interest in chemical transformations with the participation of nanoparticles with various sizes is shifted toward biology and medicine. It is believed that the use of nanoparticles will make it possible to create new forms of medicines, develop new efficient methods of their transport to the organs, and develop original intrusive methods of diagnosing diseases.

The creation of new medicinal substances is a long and expensive process. Therefore, doctors set a high value on discovering new curative properties of the known preparations. Correspondingly, the producers of medicines set a high value on modifying and improving of biopharmacological properties.

The Laboratory of Low Temperatures at the Faculty of Chemistry of Moscow State University proposed a new original method for modifying medicines [54] based on the methods of cryochemistry and making it possible to micronize available medicinal sub-

stances, obtain new polymorphic structures, improve bioaccessibility, and give new physicochemical properties to the known substances.

Methods developed for changing physicochemical properties of medicinal substances are based on the use of nonequilibrium metastable states of the matter, solid phases and low temperatures. Vapors of initial substances are condensed on the cold surface and form metastable states. Under certain regimes of heating, nanosized structures are formed with physicochemical properties differing from those of the initial sample. Particles of the substances studied with sizes of 10–500 nm were obtained without solvents. Cryomodification was applied to widely used medicines: Carvedilol, Gabapentin, Glibenclamide, Metronidazole, and Fluticasone Propionate. Some problems and prospects of nanochemistry were analyzed in [55].

## CONCLUSIONS

Consideration of the fundamental features of adsorption, catalysis, and chemical transformations of metal nano-oxides and their applications allowed us to formulate some general conclusions.

For the development of nanochemistry and nanotechnology, it is important to understand specific features of nanoparticle surfaces, the processes of nanoparticle growth, aggregation and self-organization. The chemical and catalytic activity and gas sensitivity of metal nanoparticles with the oxides shells are determined by the size of the nucleus and the thickness of the shell. The development of nanomaterials with a high sensitivity and selectivity requires the knowledge of mechanisms of processes in the adsorption–desorption of molecules of substances to be determined and possible admixtures.

Metal nano-oxides may be of interest in photocatalysis, specifically in the carrying out of reactions such as selective synthesis of  $\alpha$ -mercaptopyridine or the oxidation of pentachlorophenol. The application of catalysis by nanoparticles is promising for the synthesis of new compounds with valuable and unique properties.

Chemical reactions of oxide nanoparticles can be used for the development of technologies for the utilization of toxic waste. The reactions of magnesium and calcium oxide nanopowders with 3,3-dimethyl-2-butylmethylphosphoxofluoride and mustard gas and the reaction of zinc with carbon tetrachloride proved to be efficient at room temperature.

Cryochemical methods make it possible to affect the chemical composition and size characteristics of nanostructured materials due to a substantial decrease in the diffusion mobility of atoms and molecules after deposition from the gas phase. These approaches can be promising in the development of new nanomaterials for gas sensors, catalysts, and for the modifications of medicinal preparations.

## REFERENCES

- Poole, C.P., Jr and Owens, F.J., *Introduction to Nanotechnology*, New York: Wiley, 2003.
- Ozin, G. and Arsenault, A., *Nanochemistry: A Chemical Approach to Nanomaterials*, Amsterdam: Elsevier, 2005.
- Sergeev, G.V., *Nanoshemistry*, Amsterdam: Elsevier, 2006.
- Petrinin, V., *Trudy VII Vserossiiskoi konferentsii "Fizikokhimiya ul'tradispersnykh (nano)-sistem"* (Proc. VII All-Russia Conf. on Physical Chemistry of Ultradispersed (Nano)Systems), Moscow: MIFI, 2006, pp. 10–14.
- Bochenkov, V. and Sergeev, G., *Usp. Khim.*, 2007, vol. 76, p. 1084.
- Vol'kenshtein, F., *Elektronnyye protsessy na poverkhnosti poluprovodnika pri khemosorbtsii* (Electron Processes on the Semiconductor Surfaces during Chemisorption), Moscow: Nauka, 1987.
- Morrison, S.J., *J. Phys. Chem.*, 1953, vol. 57, p. 860.
- Peka, G.P., *Fizika poverkhnosti poluprovodnikov* (The Physics of Semiconductor Surface), Kiev: Izd-vo Kievskogo Univ., 1967.
- Semiconductor Sensors in Physico-Chemical Studies*, Kupriyanov, L.Y., Ed., Amsterdam: Elsevier, 1996.
- Garner, W.E., *Chemistry of the Solid State* London: Butterworths Scientific Publications, 1956.
- Kocemba, I., *Electron Technology*, 1996, vol. 29, p. 372.
- Bârsan, N. and Weimar, U., *J. Electroceramics*, 2001, vol. 7, p. 143.
- Watson, J., *Sens. Actuator*, 1992, vol. 8, p. 173.
- Iwamoto, M., *Characterisation of Oxygen Adsorbates on Semiconductive Oxides*, Tokyo: Kodansha, 1992, vol. 4.
- Chemical Sensing with Solid State Devices*, Madou, M.J., and Morrison, S.R., Eds., London: Academic, 1991.
- Fryberger, T.B. and Semancik, S., *Sens. Actuator*, 1990, vol. 2, p. 305.
- Zemel, J.N., *Thin Solid Films*, 1988, vol. 163, p. 139.
- Gaggiotti, G., Galdikas, A., Kaciulis, S., et al., *Sens. Actuator*, 1995, vol. 25, p. 516.
- Windischmann, H. and Mark, P., *J. Electrochem. Soc.*, 1979, vol. 126, p. 627.
- Peti, F., Fleisher, M., Meixner, H., and Giber, J., *Sens. Actuator*, 1994, vol. 19, p. 573.
- Bârsan, N., Schweizer-Berberich, M., and Göpel, W., *Fresenius J. Anal. Chem.*, 1999, vol. 365, p. 287.
- Williams, D.E., *Sens. Actuator*, 1999, vol. 57, p. 1.
- Simon, I., Bârsan, N., Bauer, M., and Weimar, U., *Sens. Actuator*, 2001, vol. 73, p. 1.
- Yamazoe, N. and Miura, N., *Some Basic Aspects of Semiconductor Gas Sensors*, Tokyo: Kodansha, 1992, vol. 4, p. 19.
- Yamazoe, N., *Sens. Actuator*, 1991, vol. 5, p. 7.
- Kisin, V.V., Sysoev, V.V., Voroshilov, S.A., and Simakov, V.V., *Fiz. Tekh. Poluprovodn.*, 2000, vol. 34, p. 314.
- Sberveglieri, G., *Sens. Actuator*, 1995, vol. 23, p. 103.
- Bochenkov, V.E. and Sergeev, G.B., *Adv. Coll. Int. Sci.*, 2005, vol. 116, p. 245.
- Hahn, S.H., Bârsan, N., Weimar, U., et al., *Thin Solid Films*, 2003, vol. 436, p. 17.
- Schmid, W., Bârsan, N., and Weimar, U., *Sens. Actuator*, 2003, vol. 89, p. 232.
- Harbeck, S., Szatvanyi, A., Bârsan, N., et al., *Thin Solid Films*, 2003, vol. 436, p. 76.
- Ahlers, S., Müller, G., and Doll, T., *Sens. Actuator*, 2005, vol. 107, p. 587.
- RF Patent 2097751.
- Bochenkov, V.E., Chromium Coating and Electrophysical Properties of Discontinuous Films of Lead, *Cand. Sci. (Phys.-Math.) Dissertation*, Moscow: Moscow State University, 2004.
- Bochenkov, V.E., Zagorskii, V.V., and Sergeev, G.B., *Sens. Actuators*, 2004, vol. 103, p. 375.
- Bochenkov, V.E., Karageorgiev, P., Brehmer, L., and Sergeev, G.B., *Thin Solid Films*, 2004, vol. 458, p. 303.
- Shmanova, E., Bochenkov, V., Zagorsky, V., and Sergeev, G., *Mendeleev Commun.*, 2008, vol. 18, p. 8.
- Tada, H., Teranishi, K., Inubushi, Y., and Ito, S., *Langmuir*, 2000, vol. 16, p. 3304.
- Wilcoxon, J.P., *J. Phys. Chem. B*, 2000, vol. 104, p. 7334.
- Carnes, C. and Klabunde, K., *Langmuir*, 2000, vol. 16, p. 3764.
- Wagner, G., Bartram, P., Koper, O., and Klabunde, K., *J. Phys. Chem. B*, 1999, vol. 103, p. 3225.
- Wagner, G., Koper, O., Lucas, E., et al., *J. Phys. Chem.*, 2000, vol. 104, p. 5118.
- Poisot, P., Laurelle, S., Gruqeon, S., et al., *Nature*, 2000, vol. 407, p. 496.
- Shevchenko, V.Ya., Khasanov, O.L., Yur'ev, G.S., and Pakhomov, Yu.P., *Dokl. Akad. Nauk*, 2001, vol. 377, p. 797.
- Elder, S.H., Cot, F.M., Su, Y., et al., *J. Am. Chem. Soc.*, 2000, vol. 122, p. 5138.
- Urban, J.J., Yun, W.S., Gu, Q., and Park, H., *J. Am. Chem. Soc.*, 2002, vol. 124, p. 1186.
- Cozzoli, P.D. and Kornowski, A.W.H., *J. Am. Chem. Soc.*, 2003, vol. 125, p. 14539.
- Cheng, B., Russel, J.M., Shi, W., et al., *J. Am. Chem. Soc.*, 2004, vol. 126, p. 5972.
- Gui, Z., Fan, R., Mo, W., et al., *Chem. Mater.*, 2002, vol. 14, p. 5053.
- Liu, J., Li, Q., Wang, T., et al., *Angew. Chem., Int. Ed. Engl.*, 2004, vol. 43, p. 5048.
- Guiton, B.S., Gu, Q., Prieto, A.L., et al., *J. Am. Chem. Soc.*, 2005, vol. 127, p. 498.
- Dai, Z.R., Pan, Z.W., and Wang, Z.L., *Adv. Func. Mater.*, 2005, vol. 127, p. 9.
- McConnell, W.P., Novak, J.P., Brousseau, L.C., III, et al., *J. Phys. Chem. B*, 2000, vol. 104, p. 8925.
- RF Patent 2195264.
- Sergeev, G., *Nauka i Tekhnologii v Promyshlennosti*, 2005, vols. 3–4, p. 62.