Hydrogen Peroxide Solid-State Sensors

Review Article

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Abstract: The determination of trace amounts of hydrogen peroxide is very important in medical, environmental, pharmaceutical, and biological fields as well as in food and textile industry due to a wide spectrum of antibacterial properties, low toxicity and ecological purity. It is necessary to determine the concentration of hydrogen peroxide (H_2O_2), not only in chemical and industrial processes (for example, disinfection), but also as an intermediate product of an enzyme reaction in biochemical processes). Therefore, the development of sensors for determination of the H_2O_2 concentration is important and attracts interest of chemists, physicians, industrial engineers, etc. Several techniques have been developed for a reliable and sensitive determination of H_2O_2 such as chemiluminescence, spectrophotometry, fluorimetric and colorimetric detection, liquid chromatography, optical interferometry. These techniques are complex, expensive and time consuming.

Earlier hydrogen peroxide sensors made from organic materials. Now electrochemical sensors are mainly used. In recent years, nanotechnology progress is promoted advance in the field of manufacturing of the H_2O_2 sensors. New sensors for H_2O_2 vapor have been developed using a semiconductor. For example, metal oxides, carbon nanotubes and graphene can be used. Nanostructured sensors for detection of hydrogen peroxide vapors were developed recently. All these versions of sensors and their main characteristics are reported in this review.

1. Introduction

The determination of trace amounts of hydrogen peroxide is important in medical, environmental, pharmaceutical, and biological fields as well as in food and textile industry due to a wide spectrum of antibacterial properties, low toxicity and ecological purity. It is necessary to determine the concentration of hydrogen peroxide (H₂O₂), not only in chemical and industrial processes (for example, disinfection, wastewater treatment), but also as an intermediate product of an enzyme reaction in biochemical processes (for example, glucose determination). Therefore, a hydrogen peroxide sensor can be also used as an intermediate transducer for other biosensors.

However, pure H_2O_2 at large concentrations is explosive under certain conditions (for example, in the presence of transition metals). Therefore, concentrated solutions of H_2O_2 can cause burns in the case of the contact with skin, mucous membranes and respiratory tract. H_2O_2 is subsumed under the category of matters those are dangerous for man with certain maximum permissible concentration. Therefore, the development of sensors for determination of the H_2O_2 concentration in the environment is important and attracts interest of chemists, physicians, industrial engineers, etc. The H_2O_2 stable sensors can be used in in various fields of the industry

and analytical chemistry, for the environmental control, in clinical diagnostic. In biology and physiology, H_2O_2 has been recognized as a gesturing molecule for precise and prompt determination of oxidative stress that can be associated with different kinds of chronic diseases such as Alzheimer's, atherosclerosis, lungs injury, cardiovascular diseases, parasitic infections, diabetes, cancer and so on. It is not only a byproduct of numerous oxides in various biological functions, but also a requisite mediator in biomedical, pharmaceutical, food and environmental analysis. In living systems, its massive accumulation is detrimental for normal growth of cells and is engendered by the oxidative mitochondrial functions, incomplete reduction of oxygen and metabolic reactions occurring in live cells [1, 2]. It is noteworthy that H_2O_2 and other reactive oxygen species play a critical role in proliferation, physiological intracellular signaling transduction, straddling development, abiotic anxiety influences, response to lethal attacks, relocation and distinction of healthy cell [3]. Nevertheless, the excessive production of H_2O_2 in cellular environments causes its penetration to other cellular compartments and is extremely pathogenic to living organisms [4, 5]. Therefore, the determination of exact level of H_2O_2 [6].

Several techniques have been developed for a reliable and sensitive determination of H_2O_2 such as chemiluminescence, spectrophotometry, fluorimetric and colorimetric detection, liquid chromatography, electroanalytical and optical interferometry [7-12]. These techniques are complex, expensive and time consuming. Now electrochemical sensors are mainly used [11-15]. A large range of materials such as ferric hexacyanoferrate (Prussian blue) and other metal hexacvanoferrates, metallophthalocvanines and metalloporphyrins, transition metals and metal oxides have been employed for the manufacture of these sensors. The advantages of these sensors are simplicity of manufacturing, good response and capability of control in a real time. In recent years, nanotechnology progress is promoted advance in the field of manufacturing of the H_2O_2 electrochemical sensors. For example, carbon nanotubes and graphene can be used either as substrates with high specific area for catalytic materials or as electrocatalysts by themselves [16-18]. H_2O_2 serves as a disinfectant for medical equipment and surfaces as well as for sterilizing surgical instruments. Therefore, the correct selection of the H_2O_2 concentration during the sterilization of the equipment technological surfaces and also control of the H₂O₂ content in air after completion of disinfection cycle are very important. Note that the process of chemical decontamination can be carried out in two different ways: the first one is the wet approach using water or any other solutions of H₂O₂ (certain concentration) and the second one is the dry method using H_2O_2 in vapor phase [19]. Therefore, the development and manufacturing of stable and reproducible sensors sensitive to H_2O_2 vapors are extremely required [20-22]. The checking of H₂O₂ vapors phase is also crucially significant in connection with counterterrorism efforts. The sensors sensitive to H₂O₂ vapors may find application in the detection of peroxide-based explosives. The most used method is based on the determination of the concentration of H_2O_2 vapors after cooling down and being absorbed in the water. The near infrared spectrophotometry was used for the monitoring of the concentration of H_2O_2 vapors in the course of sterilization [20].

The chemiresistive films made from organic p-type semiconducting phthalocyanines metalized with elements of p-, d-, and f-blocks were sensitive to H_2O_2 vapors [18]. An amperometric sensor for detection of H_2O_2 vapors made of an agarose-coated Prussian-blue modified thick-film screen-printed carbon-electrode transducer was investigated [21]. It was reported about organic single-wire optical sensor for H_2O_2 vapors made of organic core/sheath nanowires with wave guiding core and chemi-luminogenic cladding [22].

A new type of concentration sensor for H_2O_2 vapor has been developed in [21] by making use of a semiconductor. Output from the vapor sensor has been shown to have a good linear relationship with the logarithm of the concentration of H_2O_2 vapor. Concentration of H_2O_2 vapor introduced into the sterilization chamber was kept constant. The hydrogen peroxide sensor has been calibrated and standardized by using the standard H_2O_2 vapor whose concentration has been determined by calculating partial pressure of H_2O_2 over the water- H_2O_2 solution. It indicated that the sterilization by H_2O_2 vapor can be validated as precisely as steam sterilization by measuring and controlling the concentration of hydrogen H_2O_2 peroxide vapor using a combination of the H_2O_2 concentration sensor and the vapor generator. Influence of temperature and humidity has also been studied. Hydrogen peroxide bio-decontamination Bioquell equipment is proposed [www.bioquell.com].

2. Hydrogen Peroxide Sensors using organic materials

Possibilities of monitoring of vapour phase hydrogen peroxide (VPHP) decontamination process were investigated by group headed by P. Kačer [20, 28].Polymer matrix based methylene blue sensors based on its spectra changing in VPHP were developed.

A novel nonenzymatic H₂O₂sensor has been fabricated and investigated in paper [29]. By dispersing copper nanoparticles onto polypyrrole (PPy) nanowires by cyclic voltammetry (CV) to form PPy-copper nanocomposites on gold electrodes. It was proved [29] that the PPy-copper nanocomposite showed excellent catalytic activity for the reduction of H₂O₂. The sensor showed a linear response to hydrogen peroxide in the concentration range between 7.0×10^{-6} and $4.3 \times 10^{-3} mol \cdot L^{-1}$ with a high sensitivity, and a detection limit of $2.3 \times 10^{-6} mol \cdot L^{-1}$. Experiment results also showed that the sensor had good stability.

A low cost sensor for measuring the concentration of H₂O₂ in liquids utilizing spectrometric method was developed in [30]. The sensor was tested using various concentrations of a peroxidase enzyme immobilized on a glass substrate. H₂O₂ can be catalyzed by peroxidase and converted into water and oxygen. The transmission intensity is strongly related to the H₂O₂concentration. The measurement range for H₂O₂ is from 5×10^{-5} % to 1×10^{-3} % (0.5 ppm to 10 ppm) and the results show high linearity. This device can achieve a sensitivity and resolution of 41,400 (photon count/%) and 3.49×10^{-5} % (0.35 *ppm*), respectively. The response time of the sensor is less than 3 min and the sensor can be reused for 10 applications with similar performance.

The possibility for improving of analytical performances for nanostructuring of Prussian blue (PB) have been reported in [12]. It is possible by electrodeposition of nanostructured PB films. Analytical performances of the resulting PB based nanoelectrode arrays have been studied in course of H₂O₂detection. The value of sensitivity for sensors was $0.2A \cdot M^{-1}cm^{-2}$, which is more than for electrodes modified by PB electrodeposited through liquid crystal template. Detection limit was $10^{-8}M$ and a linear calibration range was extending over six orders of magnitude of H₂O₂ concentrations, which are the most advantageous analytical performances in hydrogen peroxide electroanalysis. H₂O₂ acts as a powerful oxidizing agent, so it could be applied in many organic compound synthesis reactions [31].

3. Hydrogen peroxide sensors made from metal oxides

A glassy carbon and indium tin oxide (ITO) electrodes have been modified in [32] with the nano TiO₂–Au–KI film by the adsorption of TiO₂ nanoparticles on the electrodes followed with the electrochemical depositions of nano Au and KI film. Further the nano TiO₂–Au–KI film modified ITO was examined. From the microscopic results, the adsorbed nano TiO₂ particles size were found in the range of 70-100nm. Here the electrochemical depositions of nano Au were formed as a flower shape were in the size range of 230nm to 1mcm. The electrochemical behavior of nano TiO₂–Au–KI film has been examined in different pH solutions. The linear range of detection for H₂O₂ oxidation using nano TiO₂–Au–KI film was found as 1×10^{-5} to $1\times10^{-4}M$ and 1×10^{-9} to $1\times10^{-7}M$ in CV and differential pulse voltammetry (DPV) techniques. Differential pulse voltammograms of nano TiO₂–Au–KI film are shown in Fig. 1. It shows the DPVs of nano TiO₂–Au–KI film (pH=7 PBS) for the different concentrations of H₂O₂. Here the DPVs were



Fig.1. Differential pulse voltammograms of nano TiO₂–Au–KI film modified GCE in pH=7 (containing $1\times10-3M$ KI) with various concentration of H₂O₂ (a–g) 0, 1×10^{-9} , 5×10^{-9} , 1×10^{-8} , 2×10^{-8} , 5×10^{-8} and 1×10^{-7} M.

recorded by sweeping the potentials in the range of 0-0.9V at pulse amplitude of 50mV, and a scan rate at $50mVs^{-1}$. Here the DPVs were recorded in the concentration range of 1×10^{-9} to $1\times10^{-7}M$ H₂O₂, respectively. Curve a–g in Fig. 1 shows the well-defined and stable anodic peak current curves for H₂O₂ oxidation. These anodic DPV curves confirm the H₂O₂ oxidation process on the TiO₂–Au–KI film modified GCE. Further the oxidation peak currents of H₂O₂ increases linearly with the increasing concentration of H₂O₂, respectively. The inset of Fig. 1 shows the current vs. concentration plot for the electrocatalytic oxidation of H₂O₂.

From the above results, it shows that the nano TiO_2 –Au–KI film modified GCE is effective for the electrocatalytic oxidation of H_2O_2 in nanomolar concentration range by using DPV techniques.

The practical applications of nano TiO₂–Au–KI film was evaluated by analyzing the real samples such as antiseptic and contact lens cleaner solutions containing H₂O₂.

Structurally integrated metal oxide intercalated layered double hydroxide (LDH) nanospheres (NSs) hybrid material has been of considerable current interest [33]. A new type of MnAl LDH wrapped CuO (CuO@MnAl LDHs) NSs by anchoring CuO nanoparticles (NPs) with MnAlLDHs via a facile co-precipitation and hydrothermal approach was reported. Its practical application as high-efficient electrocatalyst towards H₂O₂ reduction for biological application was explored. The integration of n-type spinel of CuO and p-type semiconductive channels of MnAl LDHs can accelerate electron transfer at breakdown voltage of p-n junction. Owing to the synergistic effect of the high surface area of CuO NPs, superb intercalation features of semiconductive MnAl LDHs for encapsulating NSs, and their intrinsic p-n junction characteristics, CuO@MnAl NSs have exhibited excellent electro-catalytic activity towards the reduction of H₂O₂. When implemented in electrochemical sensor system, the CuO@MnAl NSs modified electrode displays high nonenzymatic sensing performances towards H₂O₂, detection limit, good selectivity and long-term stability.

Hollow-sphere Co₃O₄ nanoparticles were successfully synthesized [34-41]. It is found that the as-prepared Co₃O₄ nanoparticles possess uniform hollow spherical structure with many voids on the surface. It is worth noting that the high density of metal sites, the ordered arrangement of Co, as well as the uniform crystal size and regular morphology resulting in an excellent accessibility of Co. The resulting Co₃O₄ hollow sphere was exploited as an electrocatalyst for sensitive H₂O₂ detection in an alkaline medium. The Co_3O_4 hollow sphere modified glassy carbon electrode exhibited a fast response time (within 3s). a high sensitivity of $120.55 \mu A/mM(959.79 m kA \cdot m M^{-1} cm^{-1})$, a broad linear range from 0.4mM to 2.2mM, a detection limit of 0.105 mM(S/N=3), and good stability and selectivity, suggesting its excellent performance towards H_2O_2 detection [34].

Rapid, reproducible, cost-effective approaches for the detection of H_2O_2 has been developed in [42] based on the change of localized surface plasmon resonance (LSPR) peak of Au nanorods (NRs). A method for detecting the concentration of H_2O_2 based on the change of LSPR of Au NRs was developed. H_2O_2 can etch Au NRs due to higher standard redox potential. The absorption spectra showed that various ratio of LSPR peaks is proportional to the concentration of H_2O_2 , which suggested that Au NRs can potentially serve as a new sensor for the detection of H_2O_2 .

4. Hydrogen peroxide sensors made from metal oxides and graphene

A new electrocatalyst, MnO_2 /graphene oxide hybrid nanostructure was synthesized for the detection of H_2O_2 [43]. The MnO_2 /graphene oxide based electrodes showed high electrochemical activity for the detection of H_2O_2 in alkaline medium. Manganese dioxide (MnO_2) is a kind of attractive inorganic material and can catalyze the electrocatalytic ability towards H_2O_2 [19,20]. The GO/MnO₂ electrode presents high sensitivity, low potential and long-term stability towards the detection of H_2O_2 . Amperometric response of the graphene oxide/ MnO_2 electrode to H_2O_2 is shown in Fig. 2.



Fig. 2. Amperometric response of the graphene oxide/MnO₂ electrode upon addition of H₂O₂ at −0.3 V.
(b) The corresponding calibration curve between the current response and concentration of H₂O₂.

The preparation of NiO/graphene (NiO/GR) nanocomposite for determination of H₂O₂ was reported in [44]. The electrocatalytic behaviors towards H₂O₂ are investigated by cyclic voltammetry and chronoamperometry in alkaline aqueous solution. High electrocatalytic activity toward the oxidation of H₂O₂ was observed with detection limit of $0.7664\mu M$, high sensitivity of $591\mu A \cdot mM^{-1}cm^{-2}$, a wide linear range of 0.25 - 4.75mM.

A novel nonenzymatic, amperometric sensor for H_2O_2 was developed in [45] based on an electrochemically prepared reduced graphene oxide (RGO)/zinc oxide (ZnO) composite. RGO/ZnO composite was fabricated on a glassy carbon electrode (GCE) by agreen route based on simultaneous electrodeposition of ZnO and electrochemical reduction of graphene oxide (GO). The electrochemical performance of the RGO/ZnO composite modified GCE was studied by amperometric technique, andthe resulting electrode displays excellent performance towards H_2O_2 at-0.38 Vin the linear response range from 0.02 to 22.48mM, with a correlation coefficient of 0.9951 and short response time (<5s). The proposed sensor also has good operational and storage stability with appreciable anti-interfering ability. Note that graphene and graphene oxide are very promising materials for manufacturing of other chemical sensors (see, for example, papers [46-53]).

Let continue short description of H_2O_2 sensors using graphene and graphene oxide. The catalytic activity of N-doped graphene toward a peroxidase substrate oxidation in the presence of H_2O_2 is presented in [53]. In addition, the activity was compared with that of metallic nanoparticles decorated-graphene, achieved either by catalytic chemical vapor deposition with induction heating or by chemical reduction of graphene oxide (GO). From all investigated graphene-based nanomaterials, the highest activity was exhibited by N-doped graphene and gold nanoparticles supported on chemically-reduced graphene oxide. The steady state kinetic of the two nanocomposites was carried out in order to evaluate their peroxidase-mimetic activity. Doping the graphene surface with nitrogen atoms led to a nanomaterial with a better affinity toward H_2O_2

compared to the natural enzyme (horseradish peroxidase). Additionally, the systematic study of the catalytic activity for a variety of graphene-based nanomaterials offered important findings for designing new nanomaterials with peroxidase-like activity. The sensing applications presented here are offering a useful comparison of the peroxidase-like ability of a large variety of graphene-based nanomaterials. The results are showing that the oxidation of benzidine derivatives in the presence of H₂O₂ by graphene nanocomposites is mainly due to the known catalytic activity of the superficial metallic nanoparticles and/or the residual functional groups existing in the chemically obtained graphene based composites. Moreover, in comparison with natural enzymes, doping the graphene surface with nitrogen atoms (N-Gr) led to the formation of a promising platform for building new enzyme mimic nanomaterials.

Graphene oxide nanoribbons (GONRs) were synthesized in the work [54] via the longitudinal unzipping of multi-walled carbon nanotubes (MWCNTs) nanoparticles with the aid of strong oxidants. The MnO2/reduced graphene oxide nanoribbons (MnO2/rGONRs) composites were fabricated by means of a reproducible and single-step hydrothermal co-reduction of KMnO4 and GONRs.MnO2/rGONRs exhibited high electrochemical response toward H₂O₂.

The developed nonenzymatic electrochemical sensor exhibited well-defined amperometric response towards H₂O₂ in a wide linear range of 0, 25 - 2245M (see Figure 3), and a detection limit of 0.071M(S/N=3) could be obtained. The proposed sensor displayed excellent electrochemical analytical performance, acceptable reproducibility, high accuracy, and great anti-interference ability.



Fig. 3. The corresponding calibration curve of the $MnO_2/GNRs/GCE$ in the H_2O_2 concentration range of 0.25–2455 M.

Au nanoparticles and reduced graphene oxide (r-GO) co-modified TiO_2 nanotube arrays (TNTs) were prepared in [55] by a facile and green strategy based on the electro-deposition technology for detecting H_2O_2 , O2 and nitrite. A highly ordered TiO_2 nanotubes was synthesized based on anodic oxidation method, and Au nanoparticle sand reduced graphene oxide were electro-deposited on the membrane to fabricate an electrochemical electrode. The established Au/r-

GO/TNTs electrode is as a novel electrode system for H₂O₂ detection with a quick response H₂O₂ at -0.3V with a high sensitivity (1011.35 $mA \cdot M^{-1}cm^{-2}$), wide linear range (0.01–22.3mM), low detection limit (0.006mM), good stability and enzyme-like selectivity. In addition, it holds great promise to the preparation of electrochemical sensing and biosensing platform based on the electrocatalytic behaviors of different kinds of important electroactive compounds such as dissolved O₂ and nitride ion. As is demonstrated in [55], r-GO sheets are uniquely advantageous to serve as a conductive support to uniformly anchor Au nanoparticles with well-defined size and shapes, in which the agglomeration of Au nanoparticles in common electrode is avoided. Based on the particular architecture and novel performance, the Au/r-GO/TNTs hybrid could be an extremely promising candidate applicable for a wide range of electrochemical sensing and biosensing applications.

Series of FeVO₄ materials with different morphologies were prepared in [56] through a facile hydrothermal method and were studied as peroxidase mimics. The different pH values during the preparation process led to different crystal structures, morphologies and peroxidase-like activities of the as-prepared FeVO₄ products. FeVO₄₋₄ NBs exhibited the best intrinsic peroxidase-like activity compared to other FeVO₄ materials owing to its nanobelt structure combined with a large BET specific surface area. Because of its excellent peroxidase mimic activity of FeVO₄₋₄ NBs, a novel ultrasensitive system for optical detection of H₂O₂ was established, and the detection limit of H₂O₂ could reach 0.2mM. Besides, FeVO₄₋₄ NBs exhibited from its chemical stability and magnetic property. This work provides a novel, fast response, low cost, accessible and highly sensitive system for visual detection of H₂O₂.

A novel TiO₂-encapsulated Au (Au@ TiO₂) yolk-shell nanostructure was synthesized in [57] via a method, in which the TiO₂ nanotubes could effectively restrain the aggregation and growth of Au nanoparticles and supply more active sites and high surface areas for biocatalytic reactions. Based on the highly efficient peroxidase-like activity of Au@TiO₂, an effective method for colorimetric detection of H₂O₂ and glucose was established. Considering numerous advantages including reduced aggregation, good chemical stability and high catalytic activity available by the present Au@TiO₂ with unique structure, designing other yolk-shell nanostructures with exact function orientation using a similar strategy may also be very promising in the application of biocatalysis and bioassays.

A novel strategy to synthesize elegant Au@TiO₂ yolk-shell nanostructures used as peroxidase-like enzymes was developed. Their applications for colorimetric detection of H₂O₂and glucose were investigated. Benefited from the effective combination of high controllable technology involved in ion sputtering and atomic layer deposition, the prepared Au@TiO₂ nanocomposites had uniform morphology with well-dispersed Au nanoparticles confined in TiO₂ nanotubes. The Au@ TiO₂ exhibited remarkably decent intrinsic peroxidase-mimic activities and was highly dependent on the pH, temperature and the concentration of reactants.

Nanozymes, as the next-generation artificial enzymes, have attracted wide interest in recent years [58]. Compared with natural enzymes, nanozymes, with their advantages of high stability against denaturing, low-cost, easy storage and treatment are attractive and promising candidates in chemical sensing, immunoassay development, cancer diagnostics and therapy, and environmental protection [59]. At present, a large number of nanoparticle (NP) artificial enzymes have been constructed to mimic natural enzymes, including iron oxide-based NPs with peroxidase and catalyze-like activities [60, 61], cerium oxide-based nanomaterials with oxidase, catalase and

SOD mimetic properties [62, 63], cobalt oxide ones that are peroxide and catalase mimics [64,65], copper oxide and manganese dioxide nanomaterials that display oxidase-like activity [66, 67], vanadium pentoxide peroxidase mimics [68],and metal/bimetal-based [69] and carbon-based NPs [70] with oxidase, peroxidase, and SOD mimetic activity.

A new V₂O₅ nanozymes-based colorimetric assay has been developed for H₂O₂ and glucose detection. Under the optimal reaction conditions, the method showed good responses toward H₂O₂ with a linear range from 1 to 500M. The result shows that the proposed assay method for H₂O₂ and glucose based on V₂O₅ nanozymes has a wide linear range, and is simple, fast, and sensitive.

5. Hydrogen peroxide sensors made from carbon nanotubes

Our investigations of gas sensors made from different metal oxide composites with carbon nanotubes (CNTs) [71-77] have shown the following:

1. Use of pristine CNT as sensors does not promising.

2. Functionalization of CNTs can be made with organic materials. Hyper sensibility and selectivity of detection of CO₂, NH₃, O₂, Cl₂, HCl, dimetyldimetylphosphate observed by CNT nanocomposites, covered with polyethylene, polyanylyne and polypyrrol.

3. CNTs, decorated with Pd, Rh, Au and Ni nanoparticles are suggested for detection of H₂S, CH₄, H₂, CO, O₃, C₆H₆, NH₃, NO₂, and C2H5OH up to their ppb level.

4. Special interest is attended to investigation of possibilities of manufacture of CNT functionalized (decorated) with different metal oxide composites. Most of its are carried out by CNT, decorated with SnO₂. Modifications of such nanosensors surface with precious metals led to remarkable improve of the sensitivity and selectivity of sensors.

5. Sensibilisation of CNT- SnO₂ composites in water solutions of Ru (OH) Cl₃ leads to high response to hydrogen as well as to synergistic effect during detection of isobutene and the lowering of temperature of pre-heating of work body of sensors up to $150 - 200^{\circ}C$. Such sensors are sensitive also to vapors of VOC gases (acetone, toluene, ethanol and methanol) at approving the same temperatures of pre-heating.

6. Thin film (including 1D film) nanosensors of ethanol vapors were manufactured on the base of CNT-Fe₂O₃ solid solutions. Sensors of H₂, NO_x and CO were manufactured from CNTs with cobalt oxide, Co_{1-x}N_xFe₂O₄, CuO and WO₃.

7. Substantial interest invokes research and development of nanosensors working without preheating of their work body (at room tmperature). 10%- SnO₂–CNT nanocomposit sensor detected ammonia and NO₂. Doping of CNT with N and B and its synthesis with metal oxide SnO₂ allowed dramatically increase the conductivity of the nanosensor and response to CO and NO₂. Nanosensors made from Co₃O₄- SnO₂ and Pt/TiO₂/CNT were sensitive to H₂, NH₃ and O₃ on the 20 ppb level of gas concentration.

8. Nanosensors made from all mentioned composites CNT-metal oxides had lowest response and shorter times.

9. It is clear that the doping of metal oxides with CNTs lead to greater sensitivity to gases, better speed to response of nanosensors and a lowering of temperature of pre-heating of their work body (up to room temperature, when the pre-heating is not necessary). Possible mechanisms of the response of developed sensors to gases are discussed. Doubtless, that different type of conductivity of CNTs and metaloxides, change in the work function (higth of potential barrier), modulation of

formed heterujunctions should be take into account at the analysis of complicate processes and phenomena in gas sensitive structures reported above.

Nanostructured Sensors for Detection of Hydrogen Peroxide Vapors (VPHP) were presented in [78]. The sensor chip with sensors on it was sat in the ambient air. When the output of H_2O_2 mixture blow to the sensors, the change of resistances was multiplexed and recorded. The recorded response curve shows 1) the base resistance of sensors during the pure carrier gas exposure and then 2) the change of the resistance due to the sensor response to the H_2O_2 while the syringe pump injected the saturated H_2O_2 of 50% H_2O_2 in water with different pump rates for different concentrations. The sensor response is from pristine carbon nanotubes interact with the H_2O_2 molecules. There are 3 replicates of the H_2O_2 exposure sat each concentration. The repeatability is varied from 0.21% to 0.47% for different concentrations in terms of standard deviation calculated from 3 repeat responses. The response time included the sample injection time is in seconds to the full responses for all the exposures and the recovery time are also in seconds. This fast response enables reported sensors for high throughput airport security inspection. The quick response to the H_2O_2 injection and reach to the full response enables the accurate measurement for low false alarm rate.

The responses to H_2O_2 may be due to the partially (weak) oxidation of carbon nanotubes by H_2O_2 molecules. The calibration curve of the sensor response vs. the concentration of H_2O_2 shows that the response is proportional to the logarithmic concentration of H_2O_2 . This relationship reveals that there is a charge transfer interaction between the carbon nanotubes and the H_2O_2 molecules. The pristine carbon nanotubes as a sensing material for H_2O_2 detectionhave selected. From sensor testing results, it shows the sensor response time was in seconds, gives clear sensing signal to 50 ppm H_2O_2 in air at room temperature, recovered very fast for reuse in the field. With a reduction of the noise, our sensor should be able to detect 1ppm and lower.

Silver particles were patterned on flexible and transparent single-walled carbon nanotube (SWCNT) films using the electrochemical deposition method, and these patterned silver particles were then used as electrodes to detect H₂O₂ [79]. The sizes and densities of silver particles were tuned by varying the patterned design and the preparation conditions. Field emission scanning electron microscopy revealed that the patterned silver particles were homogeneously distributed on the SWCNT films (AgPs-SWCNT), with an average size of 150–200 nm. The AgPs-SWCNT sensor had excellent electrocatalytic activity for detection due to the unique electrocatalytic properties of the silver particles and the good conductivity of the SWCNT film. The amperometric response of the electrode was rapid (within 2 s), sensitive to a wide linear range of H₂O₂ concentrations from 0.016mM to 18.085mM, had high sensitivity and a low detection limit (2.76_M) for H₂O₂. Moreover, the AgPs-SWCNT film sensor was selective for H₂O₂ and was stable over a long period of time.

6. Nanostructured Sensors for Detection of Hydrogen Peroxide Vapors

Solid-state VPHP sensors made from doped metal oxide ZnO<La> and SnO₂<Co> were prepared in [80] for detection of H₂O₂ vapors. Ceramic targets made from metal oxide ZnO doped with 1 at.% La or SnO₂ doped with 2 at.% Co were synthesized by the method of solid-phase reaction in the air. The following program of annealing for the compact samples of ZnO<La> was chosen: rise of temperature from room temperature up to $1300^{\circ}C$ for three hours, soaking at this temperature during four hours, further decrease in the temperature for three hours prior to room

temperature. The annealing of the compacted samples $SnO_2 < Co>$ was carried out at $500^{\circ}C, 700^{\circ}C, 1000^{\circ}C$ and $1100^{\circ}C$ consecutively, soaking at each temperature during five hours. Then, the synthesized compositions were subjected to mechanical treatment in the air in order to eliminate surface defects. Thus, smooth, parallel targets with a diameter ~ 40 mm and thickness ~ 2nm were manufactured. The prepared ZnO<La> and SnO₂<Co> targets had sufficient conductance and were used for deposition of nanosize films. Multi-Sensor-Platforms (purchased from TESLA BLATNÁ, Czech Republic) are used as substrates. The platform integrates a temperature sensor (Pt 1000), a heater and interdigitated electrode structures with platinum thin film on a ceramic substrate. Heater and the temperature sensor are covered with an insulating glass layer.

Gas sensitive layer made from ZnO doped with 1 at.% La or SnO₂ doped with 2 at.% Co was deposited onto the non-passivated electrode structures using the high-frequency magnetron sputtering method.

The measurements of the manufactured sensors response (the sensor resistance changes under the H₂O₂ vapors influence) were carried out at different concentrations of H₂O₂ vapors. The sensor work body temperature was varied from room temperature up to $350^{\circ}C$. All measurements were carried out at the sensor-applied voltage of 0.5V. The thicknesses of the ZnO doped with 1 at.% La and SnO₂ doped with 2 at.% Co films were equal to 30nm and 160nm, respectively. The average size of nanoparticles was equal to 18.7nm for both compositions. The sensors manufactured by us are resistive. The operation of this type of sensors grounds on the changes in the electrical resistance of gas sensitive semiconductor layer under the influence of H₂O₂ vapors due to an exchange of charges between molecules of the semiconductor film and adsorbed H₂O₂ vapors.

The gas sensing properties of the prepared resistive type gas sensors made from doped metal oxide films under the influence of VPHP were investigated using a computer-controlled static gas sensor homemade test system (see [77]). The sensor was placed in a hermetic chamber. A certain quantity of the H₂O₂ water solution (10*mg*) was injected in the measurement chamber. Different concentrations of HPV (from 100 *ppm* up to 4000 *ppm*) were reached in the chamber depending on the percentage content of the H₂O₂ water solution.

The measurements of the manufactured sensors' electrical resistance under the VPHP influence were carried out at different operating temperatures. The platinum heater located around the active surface of the sensor on Multi-Sensor-Platform ensures a necessary temperature of the working body. The sensor on alumina substrate is placed on the heater which allows to rise temperature of the sensor's working body. All measurements of the electrical resistance were carried out at 0.5V DC voltage applied on sensor's electrode.

The typical response-recovery curves obtained in result of these measurements for sensors with $Zn_{0.9929}La_{0.0071}O$ sensitive layer are presented in Fig. 4. These films were deposited on alumina substrate during 15 minutes (Fig. 4a) and 30 minutes (Fig. 4b) and their thicknesses were equal to 80*nm* and 210*nm*, respectively. These characteristics demonstrate the change in the sensor's electrical resistance under the influence of 1800*ppm* VPHP at different operating temperature.



Fig. 4. Response-recovery curves observed under the influence of 1800 ppm VPHP (42-45 % RH) measured at different operating temperatures for the Zn_{0.9929}La_{0.0071}O sensors with films thicknesses of 80 nm (a) and 210 nm (b).

As a result of the measurements of sensing charcteristics, the sensor response was calculated as the ratio R_{HPV}/R_{air} , where R_{HPV} is the sensor electrical resistance in the VPHP atmosphere and R_{air} is the sensor resistance in the air without VPHP. The results of such calculations of response for the SnO₂<Co>sensor are presented in Fig. 5. These measurements were carried out under the influence of 100 ppm VPHP at different working body temperatures.

The results of investigations of the dependence of the sensor response on operating temperature for sensors with the La-doped ZnO gas sensitive layer are presented in Fig.6. The concentration of target gas was 1800 ppm in these measurements. At relatively low operating temperature $(150^{\circ}C)$, the best response was observed for the structure with larger contents of impurity $(Zn_{0.9853}La_{0.0147}O)$. At higher temperatures, sensor with more thick film shows larger response. Probably a longer sputtering time allows obtaining a thicker film with more perfect structure. Besides the roughness of the films' surfaces is the same since these sensitive layers were made under identical conditions. However, the working volume and, accordingly, the number of H₂O₂ molecules participating in the charge exchange process are larger for a thicker film.



Fig. 5. Response-recovery curves observed under the influence of 100 ppm HPV (42-45 % RH) measured at different operating temperatures for the SnO₂<Co> sensor. Dependence of the sensor response on operating temperature (in insert).



Fig. 6. Dependence of the response to 1800 ppm of VPHP on operating temperature for the Zn_{0.9929}La_{0.0071}O sensors on alumina substrate with films thicknesses of 80 nm (1) and 210 nm (2) and for the sensor with Zn_{0.9853}La_{0.0147}O films deposited on Multi-Sensor-Platform (3).

Note, the electrical resistance of the prepared ZnO<La> sensors has changed in order of magnitude under influence of VPHP starting at operating temperature of $100^{\circ}C$. However, a longer time needed for recovery of the sensors parameters at such temperature. The pulsed rise in the working body temperature needed for decreasing of the recovery time of the investigated sensors. The response and recovery times were determined when the time required for reaching the 90% resistance changes from the corresponding steady-state value of each signal. For SnO₂<Co> structure both the response and recovery times were equal to 5 minutes at the temperatures more than $200^{\circ}C$. For the ZnO<La> sensors the response and recovery times were an average equal to 6-8 minutes and 10-12 minutes, respectively, at the operating temperatures more than $200^{\circ}C$. The real response times may be less than the mentioned values. This is because, as was already noted, 10mg of an aqueous solution with a certain percentage content of H₂O₂ is injected in measuring chamber in order to obtain the appropriate concentration of VPHP. The response time of the sensor, calculated from the moment when the H₂O₂ water solution is injected in the chamber until the maximum response reaches 90%, also includes the time necessary for the complete evaporation of the aqueous solution.

As shown in Fig. 5 and Fig. 6, the sensor response decreases for both structures, when the temperature of working body exceeds some certain value ($250 - 300^{\circ}C$ and $200^{\circ}C$ for La-doped ZnO and Co-doped SnO₂ sensors, respectively). The amount of vapor molecules adsorbed on a surface and generally kept by Van-der-Waals forces (physical adsorption), decreases with the increasing of temperature. More intensive exchange of electrons between the absorber and the absorbed molecules takes place when the stronger chemical nature bond is established between them, originated at capping of electronic shells of both adsorbent and adsorbate atoms. The amount of chemisorbed centers increases with increasing of temperature. Desorption prevails over the adsorption when a temperature is increased above certain value and, therefore, the sensor response decreases. The temperature of the sensors made of ZnO<La> structure, above which the sensitivity decreasing occurs, is greater than for the sensors made of SnO₂<Co> structure. Probably, the chemical bonds between molecules of ZnO and H₂O₂ are stronger than that between molecules of SnO₂ and H₂O₂. The fact that the recovery time for sensors made of Co-doped SnO₂ is less than that for La-doped ZnO sensors also testifies above-mentioned.

As it has already been noticed, the H_2O_2 belongs to the type of materials dangerous for man after certain maximum permissible concentration. The permissible limit of exposure of 1.0 ppm has established by Occupational Safety and Health Administration (OSHA, USA) ([22, 25]. It is immediately dangerous for life and health when its concentration reaches 75 *ppm*. Therefore, it was necessary to investigate the gas sensing characteristics of prepared sensors made from doped metal oxide films at low concentrations of VPHP. Such measurements of the sensing properties of the prepared sensors with La-doped ZnO and Co-doped SnO₂ sensitive films deposited on Multi-Sensor-Platforms were carried out at less than 100 *ppm* concentrations of VPHP. The results of these investigations are presented in Fig. 7 and Fig. 8.

The measurements of the sensing characteristics of the sensors with $Zn_{0.9929}La_{0.0071}O$ sensitive layer to 10 ppm VPHP were carried out in the following way. Firstly, an atmosphere containing 10 ppm of VPHP was prepared in a laboratory model of an isolator. This VPHP concentration decreased by spontaneous decomposition of H₂O₂. When a reference device (Dräger Sensor® H₂O₂ HC) could not detect any VPHP, the ZnO<La>sensor was inserted into the model isolator. Then, the sensor responded immediately. When the maximum response was reached, the sensor was taken out into an atmosphere without any traces of VPHP. This process was repeated three times (Fig. 7a). In these studies, a voltage on sensor at direct current is used as a parameter for sensing characteristics. The measurements of the sensing characteristics under the influence of 75 ppm VPHP were carried out using the same way for the SnO₂<Co> sensors(Fig. 7b).



Fig. 7. a) Response-recovery curves observed under the influence of 10 ppm VPHP measured at 220°C operating temperatures for the $Zn_{0.9929}La_{0.0071}O$ sensor and Dräger Sensor. b) Response-recovery curves observed under the influence of 75 ppm VPHP measured at 200°C operating temperatures for the SnO_2
<Co>sensor.



Figure 8. a) The temperature dependencies of voltage on sensor and sensitivity (V_{HPV}/V_{air}) for SnO₂<Co>sensor measured under the influence of 10 ppm VPHP (20-23 % RH) at 200°C operating temperature. b) The temperature dependencies of voltage on sensor and sensitivity (V_{HPV}/V_{air}) for Zn_{0.9929}La_{0.0071}O sensor measured under the influence of 100 ppm VPHP at 220°C operating temperature.

The temperature dependence of sensing parameter (or voltage on sensor) under the influence of 10*ppm* VPHP was investigated for the SnO₂<Co> sensors. For these measurements, the atmosphere in the "Peroxybox" system developed in the same Institute in Prague was controlled (0-10 ppm VPHP and 20-23% RH) and the sensor's temperature was changed. The final sensitivity was calculated as the voltage on sensor in "Peroxybox" system VPHP divided by voltage on sensor in the air V_{air} (Fig. 8a). The temperature dependence of sensing parameter under the influence of 100 ppm VPHP was investigated using the same way for the ZnO<La>sensors (Fig. 8b).

The investigations of the prepared sensors under the influence of low concentrations of VPHP showed that the sensitivity (V_{HPV}/V_{air}) to 10ppm of HVPHP was equal to ~2 for the ZnO<La>sensors at the working body temperature of $220^{\circ}C$. Note that the DrägerSensor® H₂O₂ HC reference device was not sensitive to 10ppm of VPHP (Fig. 7a). The investigations of the sensors sensitivity to very low concentrations (0-10 ppm) of VPHP showed that the structure made of SnO₂<Co> exhibits a response to 10ppm of VPHP at the operating temperature starting from $50^{\circ}C$ (Fig. 8a). The sensitivity to 10ppm of VPHP was equal to ~3 for the SnO₂<Co> sensors at the working body temperature of $200^{\circ}C$.

Fig. 9 presents the results of the investigations of the response at the different concentrations of VPHP for the prepared sensors. As can be seen in Fig. 9, the dependencies of sensor response on VPHP concentration have a linear character for all sensors. Due to the linear dependence of the response on concentration of target gas, it is possible to determinate of VPHP concentration in the environment.



Fig 9. Dependencies of the response on VPHP concentration measured at 150 °C operating temperature for Zn_{0.9929}La_{0.0071}O (a1), Zn_{0.9853}La_{0.0147}O (a2) and Sn_{0.9877}Co_{0.0123}O₂ (b) sensors.

So, it was found that both Co-doped SnO₂ and La-doped ZnO sensors exhibit a good response to VPHP starting at $100^{\circ}C$ operating temperature. Sensors made from SnO₂<Co> and ZnO<La> were sufficiently sensitive to 10ppm of VPHP. It was established that the dependencies of the responseon VPHP concentration at the operating temperature of $150^{\circ}C$ have a linear character for prepared structures and can be used for determination of VPHP concentration.

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Conclusions

The H₂O₂ stable sensors can be used in various fields of the industry and analytical chemistry, for the environmental control, in clinical diagnostic. A large range of materials such as ferric hexacyanoferrate (Prussian blue), metal hexacyanoferrates, metallophthalocyanines and metalloporphyrins, transition metals have been employed earlier. It is necessary now to involve new materials for the manufacture of small size sensors. Recently, linear response to hydrogen peroxide concentration range, high sensitivity, and low detection limit were reported for sensor made from copper and gold nanoparticles dispersed onto polypyrrole (PPy) nanowires. Hydrogen peroxide sensors made from metaloxides TiO₂, n-type CuO nanoparticles (NPs) with p-type semiconductive MnAl layered double hydroxide nanospheres and channels, hollow-sphere Co₃O₄ nanoparticles were reported. A new electrocatalyst, MnO₂/graphene oxide hybrid nanostructure, NiO/graphene and reduced graphene oxide / zinc oxide nanocomposites, reduced graphene oxide co-modified TiO₂ nanotube arrays, FeVO₄ nanobelt structures, TiO₂-encapsulated Au yolk-shell nanostructures iron oxide-based nanoparticles with peroxidase, V₂O₅ nanozymeswas synthesized and investigated as promising electrodes. Hydrogenperoxidenanosensorsfor detection of H₂O₂madefrom anotubes were presented. The Ag particles-SWCNT film sensor was investigated.

Vapor phase hydrogen peroxide sensors made from doped metal oxide ZnO<La> and SnO₂<Co> were prepared and investigated in details. It was found that both Co-doped SnO₂ and La-doped ZnO sensors exhibit a good response to VPHP starting at low operating temperature $(100^{\circ}C)$. Sensors made from SnO₂<Co> and ZnO<La> were sufficiently sensitive to low ppm of VPHP. It was established that the dependencies of the responseon VPHP concentration have a linear character for prepared structures and can be used for determination of VPHP concentration.

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