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Nanostructured materials for CBRN detection

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Abstract: Nanomaterials are gaining significance in technological applications due to their chemical, physical, and mechanical properties and enhanced performance when compared with their bulkier counterparts. The synthesis of nanostructured materials has led to a significant increase in properties (thermal, optical, electrical, magnetic, mechanical) as well as the discovery of materials with new properties due the fact that at the nanoscale the materials have a high surface area Most applications of nanomaterials in sensors are related to their synthesis. In this paper we report recent trends in applications of various nanomaterials such as nanoparticles, carbon nanotubes, nanowires and graphene to detect CBRN agents.

Keywords: nanostructured materials, CBRN, sensors, detection, applications

1. Introduction

Chemical, biological, radiological and nuclear (CBRN) risks add a new dimension to possible terrorist attacks, accidents, natural disasters and / or pandemics due to transnational effects and the causing of large numbers of casualties [1].

The EU's long-term involvement in CBRN programs began with the declaration of the Ghent European Council of 19 October 2001, which focused on combating terrorism "in all its forms and throughout the world", in direct response to the attacks of 11 September 2001. in New York, preceded by the conclusions of the Laeken European Council of 13-14 October 2001.

The EU CBRN Action Plan, presented by the European Commission in June 2009 and adopted by the Council of Europe in November 2009, is divided into three sections: prevention, detection, preparedness and response. It is essential to recognize the importance of all three of these aspects in addressing CBRN materials to ensure the correct implementation of risk assessment studies, responses and control measures. The general objective of EU CBRN policy is "to reduce the risks of CBRN and the damage it causes to the citizens of the European Union" and must be achieved by "minimizing the possibility of CBRN incidents, as well as by limiting their consequences, in case of in which such incidents would occur". Continuous proliferation and uncontrolled dissemination of nuclear or radioactive technologies and materials, the existence on the territory of various states of chemical, biological, radiological or nuclear mass destruction (CBRN), the possibility of making Radiological Dispersion Devices ("dirty bomb"), the existence industrial targets with nuclear, biological and / or chemical risk on the national territory, or on that of other states, the possibility of carrying out terrorist activities that include CBRN means, increasing the risk of CBRN events as a result of natural disasters, is a series of factors of direct threat to the population, territory and environmental factors, with major socio-economic effects in the medium and long term.

2. Nanosensors: type, classification

A sensor is a device that detects a variable amount, usually electronically, and converts the measurement into specific signals. The most important requirements of the sensors are diversity, sensitivity, accuracy of the extracted information, selectivity and stability [2]. Nanosensors are applied for monitoring physical and chemical phenomena in hard-to-reach regions, detecting biochemicals in cellular organs, measuring nanoscopic particles in industry and the environment. Chemical detectors are used in applications for:

a) Industry: leak detection, food quality control
b) Environment: air and water quality
c) Military field: anti-terrorist applications
d) Aerospace: chemical analysis of soil and atmosphere constituents

Nanosensors are detection devices with at least one of their detection dimensions up to 100 nm. The nanostructured materials used in the production of nanosensors are: nanomatic-scale wires (high detection capacity), carbon nanotubes (very large surface area), thin films, nanoparticles and polymer nanomaterials [2].

2.1. Classification of nanosensors

As illustrated in Table 1. and in Figure 1, Nanosensors can be classified according to their energy source, structure and applications [3].

1. Regarding the energy source: acording this, nanosensors are classified:

a) active nanosensors that need a power source, such as a thermistor, and
b) passive nanosensors in which they do not exist a source of energy.

2. Based on structure: there are four types of sensors classified on the basis of structure, namely:

a) optical nanosensors,
b) electromagnetic nanosensors and
c) mechanical and / or vibrational.

Table 1. Classification of nanosensors – adapted by [2]

Optical Mechanical Stimuli	Properties
Thermal	Position, acceleration, stress, voltage, force, pressure, mass, density, viscosity, moment, amplitude of the sound wave torque, phase, polarization, speed
Electric	Absorbance, reflectance, fluorescence, luminescence, refractive index, light scattering
Magnetic	Temperature, flow, thermal conductivity, specific heat
Chemicals	Charging, current, potential, dielectric constant, conductivity
Biological	Magnetic field, flux, permeability
Optical Mechanical Stimuli	Components (identities, concentrations, states)
Thermal	Biomass (identities, concentrations, states)

3. Application-based classification: four types of sensors are identified based on the application:

a) chemical sensors,
b) implementable nanosensors,
c) electrometers,
d) biosensors.

***Optical nanosensors.* -** Optical sensors are able to monitor chemical analysis. They depend on the optical properties of nanomaterials. They can be applied in various fields, such as chemical industry, biotechnology, medicine, environmental sciences and human protection.

The first reported optical nanosensor was based on fluorescein which is trapped in a polyacrylamide nanoparticle and was used to measure pH. In practice, fluorescent sensors are particles that include at least one binding component and photoactive units. The luminescence phenomenon is a process by which a fluorophore absorbs light with a certain wavelength, which is followed by the emission of a quantity of light with an energy corresponding to the energy difference between the ground and the stimulated states. [2]

The most basic type of optical nanosensor is that of a molecular fluorescent paint probe inside a cell reported by Sasaki et al. The advantage of this basic approach is to minimize physical disruption of the cell. However, a disadvantage of the free dye is the inherent chemical interference of the dye-cell due to protein binding, cell sequestration and toxicity. Another method is known as labeled nanoparticles which consists of a reporter molecule attached to the outside of the nanoparticles. The major difference between the labeled nanoparticles and the free dye method is the solid state and the fluid nature of the former and the latter, respectively.

Similar to the free dye, the labeled nanoparticles flow freely and the reporter molecules are in contact with the intracellular components. Externally labeled particle sensor types have been used for intracellular detection, but retain the similar disadvantages of using free fluorescent dyes because the signal is derived from receptor molecules that are not isolated from the cellular medium. [3]

Fiber optic nanosensors. - Fiber optic nanosensors have the potential to analyze important cellular processes in vivo. The first submicron fiber optic nanosensor is attributed to Tan et al. The interaction between the target molecule (A) and the receptor (R) is designed to produce a physicochemical disturbance that can be converted into an electrical signal or other measurable signal:

$$R + A \rightarrow RA + \text{measurable signal.}$$

This measurable signal is then taken up by the optical probe and transmitted to the database. The disadvantages associated with the chemical interference of the color cell in the colorless method are overcome due to the distance of the optical fiber arm between the surrounding and the sensitive area. Another advantage of the optical nanosensor is that the minimum level of invasion has been reached.

Figure 1. Classification of nanosensors [5]

Electromagnetic nanosensors. **-** There are two types of sensors in the category of electromagnetic nanosensors, based on their detection mechanisms:

1. Monitoring by measuring electric current.
2. Monitoring by measuring magnetism.

Electricity measurement. **-** The advantage of this approach is the methodology without labels compared to the use of dyes. Geng et al investigated the interaction between hydrogen sulfide gas molecules and gold nanoparticles. In each detection cell, the chromium electrode and the gold electrode, source and drain. A typical width of the gap of approx. 40-60 nm were made between the two electrodes. Au nanoparticles are randomly placed over the gap area. The formation of the sulfur coating inhibits the transfer of charge "e" from one nanoparticle to another, ie the so-called jump phenomena. By using current and voltage on chromium and gold electrodes in the existence of an applied electric field, the electron jump was determined [3]

Magnetism measurement. These magnetic nanosensors have been designed to detect specific biomolecules, such as; proteins, enzymatic activity and pathogens (eg virus) with low sensitivity in the femtomolar domain (0.5 ± 30 fmol). Magnetic nanosensors are composed of magnetic nanoparticles (iron oxide). When these magnetic nanoparticles bind to the intended molecular target, they form stable nanoassemblies. This leads to a corresponding decrease in the spin-spin relaxation time (T2) of the surrounding water molecules, which can therefore be detected by magnetic resonance imaging (NMR / NMR) techniques [2]

Mechanical nanosensors. Mechanical nanosensors have comparative advantages over optical nanosensors and electromagnetic nanosensors for detecting nano-scale mechanical properties. There are several types of mechanical nanosensors, such as CNT-based fluid shear sensors and console nanomechanical sensors. Binh et al. proposed the oldest mechanical nanosensor for monitoring the vibrational and elastic properties of a nanosphere attached to a conical console. The role of mechanical sensors is essential for application in nanodevice components and nanoscale subassemblies in microelectronic devices. [5]

4. Classification of sensors according to their applications

Chemical nanosensors. This type can be applied to analyze a single chemical or molecule. Several different chemical optical nanosensors were used to measure properties such as pH and different ion concentrations.

Nanosensors. This type is used in the military or in other forms of national security, such as Sniffer STAR. It is characterized by a lightweight, portable chemical detection system that combines a nanomaterial for sample collection and a concentration with a micro electromechanical detector.

Within the different types of biological detection technologies developed, the field effect transistor (FET) has many advantages, such as; ultrasonic detection, mass production capacity and low cost production. The main devices based on FET are: transient ion with sensitive field effect (ISFET), silicon nanowire, organic FET, graphene FET and semiconductor compound FET.

Rai et al. studied wearable nano-biosensors based on textiles. This type can detect neurological signals and identify abnormalities for the diagnosis of targeted neurological and cardiovascular disorders.

Biosensors. Microfluidic (bi-sensor-on-chip) or (lap-on-chip) biosensors are essential for the development of robust and care-efficient diagnosis. The integration of microfluidic and biosensor technologies offers the ability to fuse chemical and biological components into a single platform and offers a new approach to biosensitization applications, such as portability, availability, real-time detection, unprecedented accuracy and simultaneous analysis of different analyzes in -one device. Das et al. nucleic acid detection (CFNA) technique, which are present at significant levels in the blood of cancer patients. [5]

3. Oxidic nanomaterials with detection properties

Most applications of nanomaterials in electrochemical sensors are related to their use as a substrate / transducer (or immobilization platform). Of particular importance for such use are metal oxides, CNT and graphene, although the application of nanoparticles to build / modify the surfaces of transducers has proven to be effective in improving the performance of the sensor [4].

Metal oxides (MOX) have a wide range of electronic, chemical and physical properties that are often extremely sensitive to changes in the chemical environment. Most commercial solid state chemical sensors are based on properly structured and doped metal oxides (mainly SnO2 and ZnO) that are able to detect a variety of gases with high sensitivity, good stability and also low production costs. The fundamental detection mechanism for metal oxide gas sensors is based on the change in electrical conductivity due to charge transfer between surface complexes, such as O-, O2-, H + and HO- and interacting molecules. This process requires activation energy, so classic MOX sensors only work at high temperatures, generally above 200 ° C.

Many types of metal oxides, such as TiO2, Fe2O3, Al2O3, ZnO and SiO2, have been synthesized by sol-gel or hydrothermal reactions. Due to the change in its surface properties, which influence the bandgap energy of materials, a metal oxide has a significant advantage in several applications, such as catalysts, chemical sensors and semiconductors.

In metal oxides, although the layers of positive metal ions are always completely filled with electrons, theirs may not be completely filled. Semiconductor metal oxides can be either classified as type n, in which electrons are the majority charge carriers, or type p, in which the majority charge carriers are holes.

The electronic, physical and chemical properties of metal oxide can be modified by changing the size, structure, composition, stoichiometry and doping. However, the electronic structure of these materials is extended, being divided into two main categories, namely transition and non-transition metal oxides, where the latter comprises pre- and post-transition metal oxides. Transition metal oxides are known to have a small energy difference, which allows a rapid transformation between different shapes, however with unstable structures. Metal oxides with electronic configurations d0 and d10 are characterized as materials with stable properties. Configuration d0 is found in transition metal oxides, such as TiO2, V2O5, and WO3, while configuration d10 is found in post-transition metal oxides, such as ZnO or SnO2. As for pre-transition metal oxides, they are expected to be inert in many applications, as they have large band gaps, electrons and holes are difficult to form. In general, metal oxide nanoparticles have a high density of corner or edge surfaces [5]

The electronic properties of nanoparticles depend on their size, surface area, chemical composition and modification. Al2O3 modification with organic ligands can control the size of materials produced by process aggregation. The presence of organic compounds, such as ligands, can improve the different surface characteristics of nanomaterials. The different types of ligand monomers used can also have an effect on the structural characteristics of the material produced, as seen in the modification of Al2O3 with organic ligands, which controls the size of the materials produced by the aggregation process. This type of modification also offers different electrical characteristics. Electrical properties, such as electrical conductivity and dielectric constant, could be improved by the addition of barium titanate (BT) due to its perovskite nanostructures and piezoelectric properties. [4]

A more important feature of these materials is their biocompatibility in ensuring a very active surface. The surface of NPs can be easily modified by several reactions, such as the attachment of a polymeric chain, coupling agent or doping metal ions. Moreover, fatty acids can be used to modify the surface of nanoparticles with green approaches, such as Al2O3. [5]

This change in the surface of the nanoparticles can change the properties of the materials, for example, the change of Al2O3 with another type of fatty acid showed that the materials precipitated in a water solution due to the hydrophobicity of the modifier attached to the surface of Al2O3. Several organic compounds are used to modify the surface of nanoparticles. A modified surface using a functional organic group can also provide unique physical and chemical properties, such as specific binding target analyzes and high density. Several organic compounds that are used for such a surface modification of nanoparticles include epoxies, amines, thiols and anionic compounds [5].

Recently, metal nanostructures, metal oxide, carbon nanotubes, graphene, have been widely explored for chemoresistive detection applications. The small size and large ratio of surface area to volume of nanomaterials offer more advantages for detecting more than traditional bulk films.

One-dimensional (1D) nanostructures provide an excellent system for the electrochemical detection of environmental pollutants. Resistant (conductometric) gas sensors based on nanostructured metal oxide semiconductors such as SnO2, In2O3, ZnO, TiO2, WO3 and NiO play an important role in detecting environmental pollutants such as explosive / toxic gases and volatile organic compounds (VOCs).

The operating principles of the gas sensor are based on the variation of the resistance (electrical conductivity) caused by the change of the test gas molecules on the surface of the electrodes. Numerous research activities have been carried out on the design and production of hierarchical metal oxide nanostructures due to their smaller size and characteristic load carriers, in order to improve the sensitivity and limit of detection. [2]

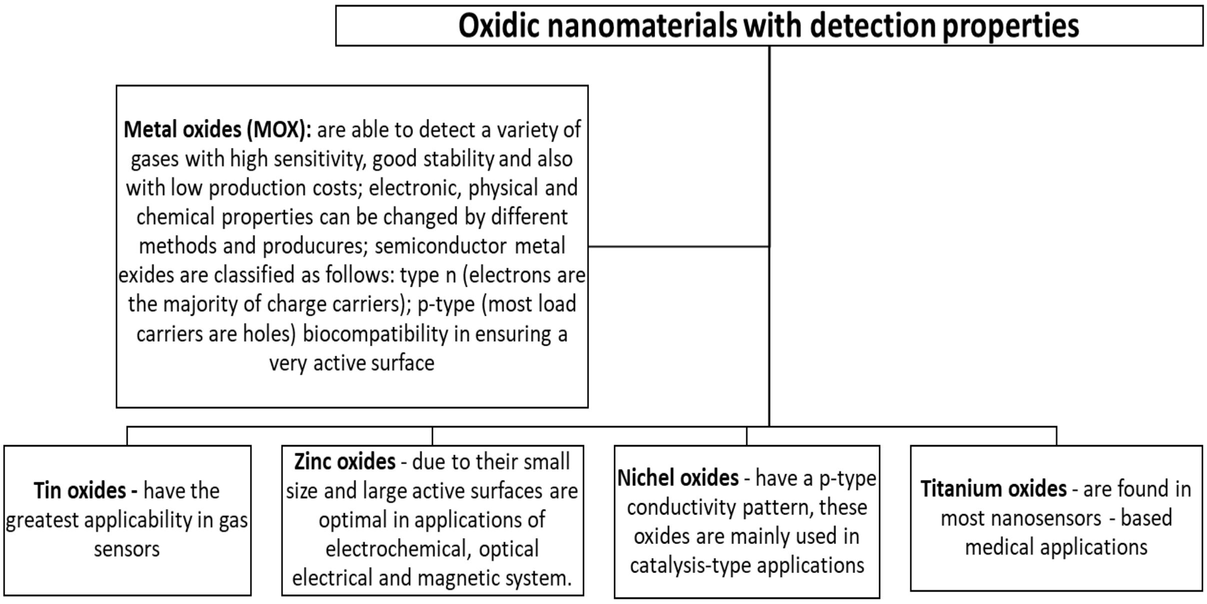

Figure 2. – Types of oxidic nanomaterials

Tin oxides. SnO2 nanoparticles are one of the most applied detection materials for gas sensors. Khong et al.81 investigated a hierarchical SnO2 / ZnO nanostructure for high performance ethanol sensors. Compared to the empty NO SnO2 sensor, hierarchical nanostructures have a higher sensitivity to ethanol gas, with better selectivity for interfering gases such as NH3, CO, H2 and CO2.

According to Pan et al., The SnO2 electrodeposite with the addition of polyethylene glycol (PEG), as a surfactant. This surfactant led to the formation of spherical SnO2 nanoparticles. The obtained sensor showed better gas detection performance than those built of SnO2 prepared without the assistance of the surfactant.

The combination of SnO2 and reduced graphene oxide (rGO) has been studied for the simultaneous and selective electrochemical detection of ultra-trace heavy metal ions in drinking water. The results satisfied the World Health Organization (WHO) well.

Zinc oxides. Due to their excellent electron transfer rate, ZnO nanostructures are able to evoke the hidden electrochemical capacity of biomolecules and facilitate their direct electrochemistry depending on their excellent electron transfer rate. High surface / volume ratio, non-toxic, low cost, chemical stability, environmental characteristics and higher electronic communication than their bulk material are the main advantages of ZnO nanostructures. For example, ZnO is a suitable candidate for potential applications in gas detection due to its thermal / chemical stability, good oxidation resistance, high biocompatibility and high conductivity.85.86 ZnO is known as an n-type semiconductor with a wide energy band. of 3.37 eV which can be used at high operating temperatures of approximately 200 ° C - 450 ° C.

In the gas sensor, especially in ZnO-based sensors, the morphology of the detection materials has an important role on their gas detection properties. ZnO nanostructures have the ability to rise at low temperatures, with many different morphologies, including wires, rods, tubes and the shape of the flower. Flower-shaped ZnO nanostructures have been synthesized using different methods of oxidation, reduction, decomposition and electrode position due to their interesting structure, shape and properties. They have potential applications in electrochemical, electrical, optical and magnetic devices. These applications are due to the low density, large active surface and surface permeability of these nanostructures.

In general, there are many methods for synthesizing ZnO nanostructure methods, such as vapor phase transport, magnetron spraying, laser ablation, wet chemical methods, including simple solution, and hydrothermal and / or microwave treatment, depending on their application. Microwave-assisted synthesis is considered a simple and fast technique that has been used for many years for a variety of applications. The sensitivity and / or selectivity of sensors, such as the optical, electronic and magnetic properties of ZnO, can be significantly affected by additives.

Akshaya Kumar applied the simple hydrothermal approach for the growth of ZnO nanorodes for the synthesis of the pH sensor based on interdigitated electrodes (IDE). The sensor showed −1 −10. This type of pH sensitivity of 1.06 nF in the field of pH 4 sensors presents a convenient and inexpensive device for measuring pH in water.

The most common ammonia sensors are based on metal oxides such as ZnO, TiO2, CuO, SnO2, In2O3 and WO3. Schottky diodes based on AlGaN / GaN heterostructures (HEMT) functionalized with ZnO nanorods were able to detect ammonia in the range of 0.1-2 ppm in the temperature range 25 ° C - 300 ° C. [6,7,8]

Nickel oxides. NiO nanostructures are p-type conductivity model semiconductors. They are widely used in many applications, such as catalysis, battery electrodes, and gas sensors. The flower-like morphology of NiO could enhance the electrochemical activity of the electrode and provide a larger contact area between the active material and the electrolyte. They have better electrochemical properties than conventional materials. The experimental results indicated the high sensitivity of rose-like NiO nanoparticles for the detection of formaldehyde gases. [7]

Titanium oxides. TiO2 nanostructures can also be used on electrochemical sensors for medical and pharmaceutical applications. A range of proteins was immobilized in nanoporous TiO2 film electrodes. This technique has been used successfully to develop electrochemical and optical biosensors. Li and his colleagues investigated the performance of TiO2 nanostructures to capture biomolecules such as cytochrome c, myoglobin and hemoglobin and studied the direct electrochemistry of these proteins [9,10].

Ardakani et al. Carbon paste electrodes modified by the addition of TiO2 nanoparticles and meso-tetrakis (3-methylphenyl) cobalt porphyrin, used to determine levodopa in the presence of carbidopa. The DPV investigation technique of the differential pulse voltammetry showed the efficient electrocatalytic activity of the modified electrodes in decreasing the anodic overpotential for oxidation of levodopa and the complete resolution of its anodic wave from carbidopa.

4. Conclusions

This article presented the types of nanomaterials used to develop sensors and transducers for the detection of chemical, biological, radiological and nuclear risks. Based on the chemical, mechanical or electrical characteristics of these nanomaterials, the nanosensors used for CBRN detection were classified.

The classification of nanosensors was made taking into account all the characteristic parameters: the energy source that is used, the type of structure (optical, mechanical, magnetic and / or electromagnetic, etc.), but also according to their field of applicability.

This review can be the starting point for the correct choice of nanomaterials and for the optimal design of nanometric sensors that are used in the fields of security, on generaly, and biological security (detection of viruses, pathogens), radiological security (detection of radioactive substances) and for detection of chemical leaks, in particular.

A novelty presented in this article represents the classification of oxide nanomaterials that can be used in the design of chemical sensors, exemplifying the electrical, physical and chemical properties of different types of metal nanooxides.

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