



A Review—Nanosensors and promising materials

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Abstract

Nanosensors are appliances manufactured at nano range which detect a physiochemical change and transform the detected changes to signals that can be measured. Nanosensors are very handy in detecting physiochemical changes, recognizing biomolecules and biochemical variations in tissues and detecting contaminating and dangerous substances present in our surroundings. Nanosensors can be categorized according to their, structure, energy source and applications. The nanomaterials used in manufacturing of nanosensors are Nanoscale wires (potential of high detection sensitivity), carbon nanotubes (high surface to bulk ratio and sufficiently high electron conductivity), metal and metal oxides nanoparticles, polymers and biomaterials are used as materials for nanosensors. The objective of this review paper is to facilitate an outline of nanosensors, materials used for their synthesis and pros and cons of various substances over each other.

1. Introduction :

Sensors are the appliances that recognize the change in any physical quantity like conductivity, resistance etc due to surrounding changes and convert those changes into electric/electronic signal. The main parameters characterizing a gas sensor are sensitivity; selectivity, stability, response time, recovery time, detection limit. Here we define these parameters briefly.

The sensitivity of a sensor for a particular gas is defined as

$$\gamma_{\text{gas}} = \frac{\partial x}{\partial c_{\text{gas}}}$$

Where ∂x represents change in measurable physical quantity and ∂c_{gas} represents change in concentration of gas.

The selectivity (E) of a sensor is equal to the ratio of the sensitivity of particular gas concentration to be detected and the maximum sensitivity to mixture of gases.

$$E = \frac{\gamma_{\text{gas}}}{\max(\gamma)_{\text{alltogethergases}}}$$

The stability of the sensor response is a characteristic which measures replication of the sensitivity and selectivity with time..

Detection limit is the lowest concentration of gas that can be measured by the sensor under testing environment.

Response time is the time it takes for the sensor to respond to a step concentration change. Recovery time is the time it takes for the signal to return to its initial value after a step concentration change.

Nanosensors owing to their miniature size has considerable advantage in ailment treatment and sample collections. The nanostructured materials utilized in development of nanosensors are carbon nanotubes, nanoscale wires, thin films, nano particles and polymer nanomaterials [1]. Carbon-based nanomaterials are utilized in observing gas molecules, food additives, antibodies and toxic pesticides [2]. Metal oxide nanowires are utilized owing to their easy manufacturing process and chemical stability.

The goal of this review article is to illustrate an overview of classifications of nanosensors, comparing the characteristics and main differences among the various categories in addition to different nanomaterials used.

2. Categorisation :

Nanosensors can be categorized according to its energy source, structure and applications.

1. According to energy source, nanosensors are classified as (a) active nanosensors that need an energy source such as a thermistor, and (b) passive nanosensors where no energy source is needed, such as a thermocouple.
2. On the basis of application sensors are of four types namely electrometers, biosensors, chemical sensors and deployable nanosensors.
3. As per structure type nanosensors are of three types namely optical nanosensors, mechanical nanosensors and electromagnetic nanosensors.

3. Nanomaterials for nanosensors:

Nowadays, nanostructures from metal, metal oxide, carbon nanotubes, graphene have been analyzed for chemiresistive sensing applications. The small size and high surface to volume ratio of nanomaterials are key factors which put them above traditional bulk films.

3a. Metal and noble metals nanomaterials.—

Metal nanoparticles have unique physical and chemical properties which have been widely applied for many applications. Various metals such as Au, Pt, Pd, Ag, Cu, Co, including rare earth metals have been employed for sensing[3]. Metal nanoparticles-based sensors provide a strong potential with increasing both sensitivity and selectivity via tuned signal amplifications. The design of the metal nanoparticles, bio-functionalized nanoparticles and nanocomposites have attracted research focused on nanosensors. Advanced numerous analytical methods were developed for environmental monitoring and food safety applications. Noble metals with outstandingly resistant to corrosion and oxidation even at elevated temperatures include the metals of groups VIIb, VIII and 1b of the second and third transition series of the periodic table i.e. rhodium (Rh), ruthenium (Ru), palladium (Pd), silver (Ag), osmium(Os), iridium (Ir), platinum (Pt), and gold (Au) [4].

3a.1. Gold nanoparticles.—

Gold nano wires (GNWs) can be used as important building blocks for nanotechnology because of their excellent physiochemical properties. As for unusual gold nanostructures, 70% of the gold atoms of ultrathin GNWs are at the surface, which make them an excellent nanoelectrode candidate in electrochemical applications, such as pressure sensors, DNA detector, interconnects and nanoelectrodes . The inclusion of gold nanoparticles in modified electrodes facilitates the electron transfer between the transducer and biomolecules leading to better bioanalytical performance when redox enzymes and heme proteins are presented [5]. Gold nanoparticles have been also widely used by virtue of their optical properties. For example, mercury traces have been detected by ultraviolet–visible spectroscopy using gold nanoparticles functionalized with complementary DNA sequences, which are intensely colored and are present as colloidal dispersion. Das et al.[6]. studied the behavior of gold nanoparticles as nanocatalysts for electrochemical protein detection. According to the work conducted by Yuan et al.[7]. Au nanoparticles are ultrasonically added to a carbonitride/graphene to form Au NPs/carbon nitride/graphene composite based electrochemical sensors. The interaction between Au NPs and GN/C3N4 allows improved charge transfer and provides effective catalytic effects and thus enhanced sensitivity. This material was used for sensitive detection of chloramphenicol and ciprofloxacin antibiotics in food.

3a.2. Silver nanoparticles :

Although silver exhibits many advantages over gold, such as higher extinction coefficients, sharper extinction bands, higher ratio of scattering to extinction, and extremely high field enhancements, it has been employed far less in the development of sensors, with the exception of sensors based on surface enhanced spectroscopies. The reason for this is the lower chemical stability of silver nanoparticles when compared to gold. Nevertheless, recent developments include means of protecting efficiently silver nanoparticles that offer far improved chemical stabilities. As a consequence, silver nanoparticles are rapidly gaining in popularity and several research groups have begun to explore alternative strategies for the development of optical sensors and imaging labels based on the extraordinary optical properties of these metal nanoparticles.

3a.3. Palladium nanoparticles.

Palladium nanoparticles are characterized by extensive catalytic and sensor applications towards gases, biomolecules and hazardous toxic molecules. The Pd nanoparticle based electrode materials exhibit high electrocatalytic activities towards various analytes. The abundance of Pd over other noble metals such as Au and Pt, makes it a cheaper substitute for designing of various electrochemical sensors [8]. The Pd based nanocomposites can improve the mass diffusion of the analytes. This in turn offered electron tunneling to enable the electron transfer between the active site and the electrode, leading to effective electrochemical sensing performance. He et al.[9] demonstrated sensitive hydrazine sensor fabricated by one-step electrodeposition of palladium–graphene nanocomposites (Pd–GENCs) on indium tin oxide (ITO). Mahmoudian et al.[10] have developed an electrochemical nitrate sensor based on

polypyrrole PPy (Pd NCs-PPy) coated Pd nanoclusters.. An electrochemical H₂O₂ sensor based on the polyvinylpyrrolidone coated Pd nanoparticles (Pd NCs-PPy), was developed by Sophia et al.[11]. The vinyl polymers PVP offers the capability to keep the well-established catalytic activity of the metal nanoparticles intact with the chemical stability and the affinity of PVP towards the Pd metal. According to research conducted by Tang and co-workers [12] palladium (Pd) nanoparticles were deposited on graphene using a new chemical method. Hydrogen sensors were fabricated using graphene decorated by Pd nanoparticles. The sensor showed a response of 5.88% for 1% H₂ at room temperature under purple light illumination.

3b. Metal oxide nanoparticles

Metal oxide thin films and nanoparticles have the advantages of very high surface area, low cost, and unique properties. Metal oxides (MO_x) have a wide range of electronic, chemical, and physical properties that are often highly sensitive to changes in the chemical environment. Most commercial solid state chemical sensors are based on appropriately structured and doped metal oxides (mainly SnO₂ and ZnO) that are capable of detecting a variety of gases with high sensitivity, good stability and also with low production cost. The fundamental sensing mechanism for the metal oxide-based gas sensors is based on the change in electrical conductivity due to charge transfer between surface complexes, such as O⁻, O₂⁻, H⁺, and OH⁻ and interacting molecules. This process requires an activation energy so that classical MO_x sensors are only functioning at high temperatures, generally above 200 °C [13]. These metal oxides nanomaterials with large surface area, high adsorptive capacity, unique electrochemical activity and stability are of important for the design and synthesizing of electrochemical sensors. The analytical performance of the metal oxide nanomaterial based sensor is affected the morphology, particle size, surface area and surface functionality [14]. The one dimensional (1D) nanostructures provide a great model system for electrochemical sensing of environmental pollutants. Resistive (conductometric) gas sensors based on nanostructured metal oxide semiconductors such as ZnO, TiO₂, WO₃ play an important role in detection of environmental pollutants such as explosive/toxic gases and volatile organic compounds (VOCs). The operation principles of resistive gas sensor are based on the variation of resistance (electrical conductivity) caused by the change of test gas molecules on the electrodes surface. Many research activities have been conducted on the design and production of the hierarchical metal oxides nano-structures due to their smaller size and characteristic charge carriers, in order to improve the sensitivity and detection limit [15,16].

3b.1. Tin oxides.

SnO₂ nanoparticle is one of the most applied sensing material for gas sensors. Khong et al.[17] have investigated a hierarchical SnO₂/ZnO nanostructure for high-performance ethanol sensors. As compared to the bare SnO₂ NWs sensor, the hierarchical nanostructures higher sensitivity towards ethanol gas with better selectivity for interfering gases such as NH₃, CO, H₂, and CO₂. The combination of SnO₂ and reduced graphene oxide (rGO) was studied for the simultaneous and selective electrochemical detection of ultra-trace heavy metal ions in drinking water. The results were well satisfying for World Health Organization (WHO).

3b.2. Zinc oxides

Due to their excellent electron transfer rate, ZnO nanostructures are able to evoke the hidden electrochemical ability of biomolecules, and facilitate their direct electrochemistry according to their excellent electron transfer rate [18] High surface to volume ratio, non-toxic, low cost, chemical stability, eco-friendly and high electron communication features than their bulk material are the main advantages of ZnO nanostructures. For instance, ZnO is a proper candidate for potential applications in gas sensing due to its thermal/chemical stability, good oxidation resistance, great biocompatibility and high conductivity. ZnO is known as an n-type semiconductor having a wide band gap energy of 3.37 eV which can be used at high working temperatures of about 200 °C–450 °C. In the gas sensor, especially in ZnO-based sensors, the morphology of the sensing materials has an important role on their gas sensing properties.

3b.3. Nickel oxides

NiO nanostructures are model semiconductors of p-type conductivity. They are used extensively in many applications, such as catalysis, battery electrodes, and gas sensors. The flower-like morphology of NiO could enhance electrochemical activity of the electrode and provide larger contact area between active material and electrolyte. They have better electrochemical properties than conventional materials.

3c. Carbon based nanomaterials

Carbon based nano materials have excellent properties such as good conductivity, high stability, low cost, wide potential windows and easy surface functionalization [19]. Carbon nanotubes (CNTs), graphene and nano/ mesoporous carbon were used for various electroanalytical applications. Their nanostructures provide efficient exposure of surface groups for the binding between analyte molecules and transduction material, leading to high detection performance for environmental pollutants.

3c.1. Carbon nanotubes

CNT-based sensors can be used to detect changes in their electronic properties resulting from the sorption of molecules on their surface. The electronic properties of CNTs encourage their use as electrodes to mediate electron–transfer reactions with electroactive species in solution Carbon nanotubes (CNTs) are one of the most important materials because of their unique electronic, chemical,

and mechanical properties since they were discovered by Sumio Iijima in 1991. CNTs is a 2D nanomaterial possessed sp^2 carbon units with several nanometers in diameter and many microns in length. There are two types of CNTs, multi-walled (MW) and single-walled (SW). There are many production techniques for CNT such as electrical arc discharge, laser ablation, and chemical vapor deposition CVD methods. CNTs can be either the conductivity properties of metals or semiconductors, depending on the diameter and the degree of chirality. They have high electronic conductivity for the electron transfer reactions and better electrochemical and chemical stabilities in both aqueous and non-aqueous solutions.[20]. The sensing mechanism of CNT-based gas sensors is based on their p-type CNT semiconducting property. Generally, CNT electrical conductance is modified through the electron transfer between the CNTs and the oxidizing or reducing gas molecules adsorbed on the CNT surface. The electric resistance of p-type CNTs decreases with increasing the number of the adsorbed oxidizing gas molecules[21]. Many CNTs based environmental nanosensors have been synthesized, including composite, pastes, film, and functionalised CNT sensors. This is due to the unique properties of large surface area, fast charge transfers as well as the compatibility and synergistic effect with the other electrode materials. Maduraiveeran et al.[22] have synthesized single-walled carbon nanotube nanosensors for the detection of the toxic phenolic compounds (catechol, p-cresol and p-nitrophenol), widely presented in aqueous and biological systems. This type of sensors exhibited high sensitivity, good reproducibility and stability. Gooding et al.[23] have discovered that the electroanalytical performance of SWNTs is more efficient than the corresponding MWNTs. For the SWNT based nanosensors, the oxygen-functionalized carbon nanotube is in direct contact with the solution, resulting in a fast electron transfer and excellent electrochemical detection. However, the reactions with MWNTs have been performed mainly with nanotubes in the non-oriented style and the sidewalls were mainly in contact with the solution, inhibiting the charge transport and thus reducing detection performance. According to Shetti et al.[24] the inclusion of $RuTiO_2$ nanoparticles and MWCNTs into the carbon matrix is launched as a best challenging composite material, and the tailored sensor stood proficient for the electrochemical study of clozapine drug 'CLZ'. Zhao et al.[25] developed MWNTs modified with polyamido sulfonic acid (PASA) film for the detection of hydroquinone and catechol. The response current using PASA/MWNTs/GC electrode was almost two times higher than the sum of peak currents at the PASA/GC and MWNTs/GC electrodes. This can be explained by the presence of the electron-rich N atoms and high SO_3^- electron density in the polymer film. Carbon nanotubes (CNTs) can serve as scaffolds for immobilization of biomolecules at their surface, and combine several exceptional physical, chemical, electrical, and optical characteristics. This makes them one of the best materials for the transduction of signals associated with the recognition of analytes, metabolites, or disease biomarkers [26]. Chen et al.[27] reported aligned CNT biosensor as a uniform sensing platform that could be extended to real-time detections of various biomarkers.

3c.2. Graphene

Graphene is a unique two-dimensional nanostructure that allows fast electron transport. It has a theoretical surface area of $2630 \text{ m}^2 \text{ g}^{-1}$, which is approximately 260 times greater than graphite and twice that of carbon nanotubes. Besides, it is a semiconductor with a zero band-gap, exhibiting ambipolar electric field effect with high charge carrier mobility ($15,000\text{--}20,000 \text{ cm}^2 / \text{Vs}$). Graphene also possesses superior mechanical and thermal characteristics. Thus, graphene increases the electrochemical catalytic activity of the materials by greatly enlarging the surface area. There are many economic and high-yield processes for the production of graphene, such as the Hummers method rGO, electrochemical reduction, and chemical vapor deposition (CVD). The morphology and electrochemical properties of graphene makes it ideal for environmental sensing. Goh et al.[28] have concluded the high performance of graphene nanoribbons-based electrodes toward electrochemical detection of explosive 2, 4, 6- trinitrotoluene (TNT). Functionalization of graphene with various metal oxide nanoparticles can further improve the sensitivity of graphene toward glucose detection. Metal oxide nanoparticles are excellent catalysts, due to their high ratio of surface atoms with free valences to the cluster of total atoms. They may even provide electrochemical reversibility for redox reactions [29][30]. It is worth mentioning that graphene is also playing an important role in the biosensor field due to its remarkable physical, optical, electrochemical and magnetic properties. Xu et al.[31] discussed the commonly used prostate cancer (PC) protein biomarkers for biosensor, the unique properties of graphene and the roles of graphene-based materials for biosensing.

3c.3.Porous carbon

Porous carbon is characterized by a high surface area, accessible surface chemistry, and short pathway for mass and electron transfer. It has attracted considerable attention in the field of electrochemical sensors. Niu et al.[32] have synthesized a bismuth porous carbon nanocomposite based screen-printed electrodes (SPEs) for heavy metal detection. The nano-composite was synthesized via a combined onestep sol-gel and pyrolysis process, followed by the milling down to a specific particle size distribution for the screen printing ink. The resulting electrodes showed high sensitivity toward the detection of Pb^{2+} and Cd^{2+} ions at concentration levels below 4 ppb in tap drinking water and wastewater systems. Wang et al.[33] have integrated cobalt nanoparticles/3D-KSCs nanocomposite electrode with a 3D honeycomb porous structure. This nanostructure exhibited good electrocatalytic performances toward the oxidation and detection of amino acid.

3d. Polymer and bio-nanomaterials

The nanostructures electrochemical sensors and biosensors based on polymeric and biomaterials showed high performance with rapid response and selectivity. This is attributed to their radiant, electrical, catalytic, mechanical, thermal and physical properties. Using polymeric and bio-nanomaterials, the fabrication of electrochemical sensors can be achieved through the combination of novel analytical and scientific methods, including of combinatorial and high-throughput materials screening with micro- and nanofabrication and microfluidics.

3d.1. Polymer nanomaterials

Many effort on the technology of polymeric nanomaterials have been established for the detection of food and environmental pollutants. Polymeric nanomaterials provide many analytical strategies for the detection and determination of the chemically and biological toxic contaminations in gases and liquids for numerous health and environmental applications. The fabrication of the nanocomposites with many combinations such as; metal nanoparticles, metal oxide nanoparticles, (carbon nanotube) CNT and graphene further improve the electrochemical sensing properties of polymeric nanomaterials. The combination of the matrix and nanofiller contributions are important in enhancing the biocompatibility, excellent sensitivity and selectivity. The polyaniline (PANI) nanofibers modified with bentonite nanohybrid were developed for gas sensor applications used for analysis of toxic gases such as acetone, benzene, ethanol and toluene [34]. Navale et al. [35] have investigated the gas sensing properties of polypyrrole (PPy)/a-Fe₂O₃ nanocomposites toward various oxidizing (NO₂) and the reducing (CH₃OH, C₂H₅OH, H₂S and NH₃) gases at room temperature. Recently, Lee et al. [36] have fabricated poly(dopamine) (pDA)-modified indium tin oxide (ITO) electrodes for the detection of hydrazine (N₂H₄). In another work conducted by Liu et al. [37] single-walled carbon nanohorns (SWCNHs)-hollow Pt nanospheres/dendrimer sensors were prepared. The combination of high specific surface area of SWCNHs and the catalytically active Pt nano-particles were comprised in the biosensor.

3d.2. Bio-nanomaterials:

Union of the catalytic ability of biomolecules with unique nanoscale materials furnish a variety of collections for nanosensors. A well-defined nanostructure with biomaterials can be prepared by the self-organization of biological molecules. Sabela and co-workers [37] have developed MWNTs nanobiocomposite of L-phenylalanine ammonia-lyase enzyme for electrochemical biosensing of capsaicin. The developed biosensor showed a low detection limit of 0.18 mg mL⁻¹. Li et al. [38] have developed a self-assembled monolayers (SAMs) approach sensors for the detection of Escherichia coli O157:H7. This may lead to a portable biosensor method for routine monitoring of food borne pathogens. The signal of the impedance can be altered by the immobilization of the biomaterials onto the surface of the printed interdigitated micro-electrodes (SPIMs). This developed immunosensor showed a low detection limit of 10¹ cfu ml⁻¹ and a linear range from 10² to 10⁷ cfu ml⁻¹.

4. Conclusions

A number of nanosensors have been reviewed, classified and weighed according to energy source, structure, and materials. Mainly, optical nanosensors are effective for chemical monitoring within a cell. Electromagnetic nanosensors are effective for amplification of sensitivity of existing sensors. Mechanical nanosensors are utilized for measuring the physical and mechanical properties and motion related measurements. A no. of nano structured materials used for nanosensors were put forwarded like: metals and metal oxides, grapheme, carbon nanotubes, polymers and biomaterials. As nanosensors are not so much old, the advancement in this field has been extraordinary. Today a lot of research is going on nanotechnology and its tools so one may be optimistic for further advancement in the field of nanosensors. This can be attained through the increased performance of existing nanosensors and newer nanosensors based on novel mechanisms and new nanomaterials.

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