



METAL OXIDE NANOMATERIALS BASED BIOSENSORS: A REVIEW

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ABSTRACT

Biosensor is a typical device that reacts with the substances whose chemical nature are analyzed and gives readable information. Nanomaterials with excellent physical, chemical and optical properties have created much attention in the design and fabrication of efficient biosensors. In recent years, the metal oxide nanoparticles play a main role in diagnosis and detection diseases. In this paper, the nature of metal oxide nanoparticles and their applications in biosensors are briefly summarized. The applications of metal oxide biosensors such as zinc oxide, copper oxide, iron oxide, manganese oxide are also reviewed.

Keywords: Zinc Oxide; Copper Oxide; Iron Oxide; Manganese Oxide; Biosensors

INTRODUCTION

Biosensor is an analytical device which consists of receptor, transducer and amplifier. The first person who invented the biosensor is L.L Clark in 1956. With the help of oxygen electrode, he detected the oxygen in the blood (Heineman *et al.*, 2006). The history of biosensors crossed five generations: In first generation, the

biosensors measure the composition of analyte and product of bio receptor. In second generation biosensors, the efficiency of biosensors are enriched with the co-reactants (Singh *et al.*, 2021). Second generation sensors are called as amperometric biosensors. In third to fifth generation, the bio-receptors are considered

as an essential sensing element and the direct interface between the bioreceptor and electrode are created without any intermediate. Low cost and high sensitive biosensors are able to achieve in this generation (Li *et al.*, 2017).

The increasing global population brings forth considerable challenges to the health care sector for the diagnostics, testing and medical care. In the developing countries, such situations lead to increased cost related with the diagnostic procedure. The easily assessed portable diagnostic device has to be developed that integrate the technology to produce rapid results (Thakur *et al.*, 2022). Nanotechnology has the wider advancement with the aid of metal oxide nanomaterials particularly harnessing for the diagnostic applications. Nano biosensing initially is carried out for the glucose detection (Banigoet *al.*, 2020), afterwards several changes have made and brought it into the market.

In this decade nanotechnology shows much advancement in the development of biosensors and its applications and numerous nanoparticles have been designed and used with improved performance and selectivity (Khan 2020). Nowadays biosensors are mainly used to detect the disease and harmful chemicals. There is a

heavy demand of biosensors in the field of science and technology. Researchers in the field developed materials in the nanoscale and achieved more in sensor technology. Recent research with the integration of nanostructure materials in biosensors offers a potentials role in detection and identification (Zhao *et al.*, 2020: Zhang *et al.*, 2020: Zhang and Wang, 2020). Nano materials in the biosensors are considered to be important because it increases the level needed to stabilize the biomaterials thus sensitivity increases, catalysis the reaction process, reacting at low potentials and rapid electron transfer (Zhu *et al.*, 2020: Alam *et al.*, 2020a,b : Liet *al.*, 2020). The usage of nano biosensors makes the reduction of devices there by removes the chemical intermediates, which plays a major role in the development of third generation (Zhang *et al.*, 2019: Xu *et al.*, 2014: Wang *et al.*, 2013). This review finely investigates the nanomaterials in biosensing applications.

BIOSENSORS

Sensor is a tool directly measures the compound in a test sample and the device is capable to produce continuous and reversible response without the damage of the sample. Nano biosensor is a tool that detects gases, chemicals, biological agents, electric fields, light, heat, etc by combining

electronic component with nanomaterials that produces signal with respect to the analyte's concentration. The mechanism involved in the metal oxide based biosensor utilizes its electrical properties of metal oxides. When the test sample or analyte's interact with the metal oxide nanostructure its electrical conductivity changes by varying its charge distribution and the electrical signal which was detected to the analyte's concentration.

The conventional biosensors consist of the elements such as analyte, bioreceptor, transducer, electronic circuit and display elements. The biosensor detection of the required substance is known as analyte, whereas glucose and lactate are much reported in the literature. A bioreceptor is a molecule that identifies analyte. The process of signal development from the combination of bioreceptor and an analyte is known as biorecognition. Few examples are conversion of heat, pH, light etc. Transducer is energy transfer devices that transform one form to another and quantifies the signal by biorecognition activity and the process is called signalization. The main classes of transducers are thermometric, magnetometric, electrochemical, optical and piezo electric. Transducer mechanism categorizes as electrochemical biosensors

transform biosensing technology into portable one. Transducer output is connected to the electrical circuit that converts analog to digital signal. The display unit generates the biosensor results in image, numerical and graphical forms.

In nano-biosensors, when the nanostructure materials interact with the analyte, the transducer converts the information due to the interaction into a measurable effect (Cui *et al.*, 2021: Xu *et al.*, 2020). The mechanical transducer converts the interaction to a resonant frequency, electrochemical transducer converts the information into change in potential or current and optical transducer converts this into the change in intensity or frequency (Zhou *et al.*, 2019: Shen *et al.*, 2020: Jiang *et al.*, 2017). The variations in the respective parameters are measured using a proper reading system (Xiaoping Huang *et al.*, 2021).

METAL OXIDE BASED BIOSENSORS

Different methods are available for the preparation of nanomaterials, includes top down and bottom up methodology (Barabadi *et al.*, 2019). That is the macroscopic scale to nanoscale with top down methodology or individual to larger one with bottom methodology. The bottom up techniques includes sol-gel, chemical

vapour deposition, hydrothermal etc. Bottom up methodology includes ball milling, thermal decomposition, sputtering and more. The metal oxide nanomaterials in the form of nanowires, nanorods, quantum dots, carbon nanotubes have been considered as a potential one in the sensor technology. Designing these nanomaterials layer by layer into a new dimension it is possibly improving the sensing capacity of the sensors. Specifically the metal oxide based nanomaterials are easy to customize into a desired structure and properties by tuning the preparation condition which matches the conditions of bio sensing applications. The customization of materials enhances the biosensors to attain high sensitivity but also controls its performance and efficiency.

Metal oxide nanoparticles are integrated for the nano biosensor fabrication because of its bioanalytical activities in the fields of diagnostics, treatment and bio imaging (Tran and Le 2015). To assess enzyme-based reactions amperometric equipment are used. The fluorescent quantum dot device, utilizes nanoparticles for measuring the binding efficacy and immune labeling applications. Electrochemical tests and biological field – effect transistor test makes use of carbon-based nanostructures including reduced

graphene oxide. Fluorescent tests are detected through the quenching characteristics of graphene (Singh *et al.*, 2016). Based on their size that defines the fluorescence qualities, quantum dots provide a wide range of applications in the areas of sensors and imaging. Quantum dots have several advantages over conventional dyes, including a higher yield of molar extinction and quantum coefficient, a wider range of absorption and smaller spectra of emission, photo bleach resistance (Kargozar *et al.*, 2020). They are widely utilized in FET as well as in sandwich assays. Nano-biosensors are indeed a useful tool in tissue engineering for either diagnosis or therapy (Sheervalilou *et al.*, 2020).

Metal oxide nanomaterials have been identified with their outstanding physicochemical properties such as mechanical, thermal and electrical properties which enhances the responsiveness, sensitivity and functionality of biosensors. One dimensional structured material like nanowires and nanorods can make easy charge and signal transfer. Quantum dots are a special class thereby the optical properties are tuned in such a way that make the signal multiplexing and amplification. Metal oxides such as copper oxide, zinc oxide, iron oxide, nickel oxide, cobalt oxide etc. have

been used widely in which zinc oxide and copper oxide show higher electron mobility rate (Shi *et al.*, 2014). By tailoring these nanostructured materials, researchers are interested in investing the biosensor technology extending from diagnostics to environmental monitoring.

ZINC OXIDE (ZnO) BASED BIOSENSORS

ZnO has an excellent property such as higher isoelectric point, exciton binding energy and electron mobility makes the material promising for biosensor fabrication (Arshi *et al.*, 2022). The wide band gap semiconductor in the visible region helps the materials to remain large electric field and attains higher breakdown voltage (Li *et al.*, 2022). Zero dimensional zinc oxide nanomaterials have a large surface area implies that make good interaction between the target and elements. The elongated one dimensional zinc oxide nanostructures are stable in efficient charge transfer that in turn leads to improved signal transduction, accuracy and response. Two dimensional zinc oxide nanostructures makes the multiple detection of biosensing. Moreover these nanostructures are well suitable for sensing applications that improve the sensors ability to target in a multiple analysis. Recent developments of sensitive

and portable biosensors are used for the detection of pesticides in agriculture.

Zinc oxide is a widely used biosensor to detect the ascorbic acid, cholesterol, cancer cells and glucose and moreover. Silver-ZnO with graphene oxide coated polymer nanocomposites are used for the detection of E.Coli bacteria (Roy *et al.*, 2017). The electrochemical sensor zinc oxide and multiwalled carbon nanotubes modify carbon paste electrode which sense the naproxen (Tashkhourian *et al.*, 2014). Zinc oxide coated with carbon electrode has been reported for the detection of para-nitrophenol (Bashami *et al.*, 2015). The porous surface of zinc oxide nanoparticles are reported for the detection of pesticides (Fallatah *et al.*, 2022).

ZINC OXIDE NANORODS BIOSENSORS

Nanorods are rod shaped nanostructures with dimensions 1 -100 nm have been identified as an excellent biosensors for the detection of metal ions, carbohydrate etc (Cao *et al.*, 2014). Zinc oxide nanorods designed as a field effect transistor are used as a biosensors for the detection of phosphate and glucose (Ahmad *et al.*, 2017). Zinc oxide nanorods on a chitosan films are reported for the biosensor detection (Bagyalakshmi *et al.*, 2020). The

biosensor configuration of coreless silica fiber incorporated with zinc oxide nanorod prepared by hydrothermal, the optical sensor for the detection of isopropanal vapour thereby potentially used to monitor diabetes. An innovative approach of fiber sensors embedded with zinc oxide coating are selective biosensor detects the volatile organic compounds (Swargiary *et al.*, 2022). Zinc oxide nanowires are nanometer diameter wire like structure which exhibit excellent thermal, mechanical and optoelectronic properties; are widely used for the fabrication of biosensors (Ramanathan *et al.*, 2005).

COPPER OXIDE BASED BIOSENSOR

Copper oxide nanomaterials experiences in two forms namely CuO and Cu₂O, they are quite easily fabricated by low costs with highly crystalline nature. Tailoring the required size and shape, copper oxide nanoparticles are utilized as a biosensors which is used to detect hydrogen, hydrogen peroxide etc. Copper oxide nanoparticles decorated with carbon ionic electrode has been reported for the detection of hydrogen (Ping *et al.*, 2010). Biosensor made up of reduced graphene with copper oxide nanoparticles and copper oxide nanoparticles decorated carbon spheres detects glucose effectively (Khoshhesab

2015 and Zhang *et al.*, 2015). Cheng *et al.*, (2021) introduces colorimetric sensor fabricated by porous about 5.8 nm copper oxide spheres for hydrogen peroxide detection. These porous CuO spheres are efficient detection of hydrogen peroxide when subjecting to a simple low cost filter paper test.

IRON OXIDE BASED BIOSENSOR

Iron oxide nanoparticles in Fe₂O₃ and Fe₃O₄ phase have extensively utilizing in designing biosensors for detecting heavy organic and metal ions etc. It's a transition metal oxide with renowned properties such as biocompatibility, electrochemical attributes and its abundance in which α -Fe₂O₃ act as a modifying agent. Iron oxide undergoes electrochemical reduction and oxidation showing variable valence state. Meta ion mediated hydrothermal synthesis of iron oxide nanoparticles experiencing cubic, rhombic and discal configurations have identified with electrocatalytic activity which in turn detects dopamine and uric acid.

Indium tin oxide coated with glass plate deposited iron oxide/chitosen thin films successfully detect urea (Kaushik *et al.*, 2009). Iron oxide–graphene oxide matrix biosensors detect dopamine and uric acid (Caiet *et al.*, 2019). The nanocomposites made

with ferrite oxide and graphene are used for the detection of zinc, cadmium and metal ions (Li *et al.*, 2015 and Lee *et al.*, 2016) reported silver/ iron oxide/ graphene oxide nanocomposites which detect the nitrate. Ran *et al.*, (2017) designed electrochemical sensor, made up of bromocresol green and iron oxide incorporated in chitosan for detecting serotonin.

MANGANESE OXIDE BASED BIOSENSOR

Manganese oxide nanoparticles in the three different phases namely MnO, MnO₂ and Mn₃O₄ are extensively opted as an electrode materials and used in the fabrication of different biosensors. These oxides are highly eco-friendly, easily fabricate with low cost and notable property of higher energy density (Battilocchio *et al.*, 2014). It is a transition metal oxide able to interface widely with the biological systems and possess variable oxidation states and catalytic effect allows the material to electron transfer which is utilized in bio sensing mechanisms. It mediates the electron transfer between the molecules and electrode surfaces leads to the more efficient biosensing platform.

The tunable electrocatalytic behaviour of manganese oxide, coupled with its compatibility with various biomolecules,

holds promise for the detection of a wide array of analytes. Furthermore, manganese oxide nanostructures, including nanoparticles, nanowires, and nanosheets, offer high surface area-to-volume ratios, enhancing the immobilization of biomolecules and enabling signal amplification. In enzyme biosensors, the magnesium oxide nanoparticles have the ability to possess electron transfer in between the electrodes and enzymes that allow reliable biosensing. Magnesium oxide based biosensors have been reported for the detection of glucose, metals, pollutants and hydrogen peroxide (Ramesh *et al.*, 2022).

QUANTUM DOT BASED BIOSENSORS

Quantum dots are semiconducting nanomaterials with 2 to 10 nm in diameter. Based on the diameter size it experiences different colours; quantum dots of 5 to 6 nm diameter shows orange or red colour while smaller diameter of 2 to 3 nm shows blue or green colours. The properties of the quantum dots can be tuned by confining its size and shape. The feasible approach for the synthesis of quantum dots is top down method in which one can fabricate graphene oxide carbon dots. This type of metal oxide quantum dots are the optical biosensors used to sense the organic compounds (Ma *et al.*, 2018).

CONCLUSIONS

Biosensors are considered as a versatile tool for detecting different analytes such as metal ions, amino acid, glucose, different gases and disease related too. This review highlights the metal oxide nanoparticles on designing biosensor applications. The utilization of nano biosensors liberates good sensitivity, selectivity and stability due to its charge mobility, surface area and electrochemical properties. The main challenge involved in this technology concerns about the safety and ethical consideration. In future perspectives the integration of artificial intelligence, cyber physical system, cloud computing makes a better way for commercial marketing. To conclude, the metal oxide based biosensors stands as a massive achievement of diagnostics and transformative advancements in the sensor technology.

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