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Review Article

Hybrid ZnO–MnO_2 Nanomaterials for Glucose Detection: A Review of Recent Progress

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Abstract: *Accurate and timely glucose detection is critical in biomedical diagnostics, particularly for effective management of diabetes mellitus. Traditional glucose sensors often face challenges in sensitivity, selectivity, and stability, necessitating the development of novel materials.* ***Objective:*** *This review aims to critically analyze the recent advances in the development of zinc oxide (ZnO) and manganese dioxide (MnO_2) nanocomposite-based glucose sensors, emphasizing their potential in improving sensor performance.* ***Methods:*** *A comprehensive literature review was conducted focusing on studies published over the past decade. Sources were selected from peer-reviewed journals indexed in databases such as PubMed, Scopus, and Web of Science. Key aspects reviewed include synthesis strategies (e.g., hydrothermal, sol-gel, chemical bath deposition), structural and morphological analysis via techniques such as SEM, TEM, and XRD, and electrochemical evaluation through methods including cyclic voltammetry and chronoamperometry. Comparative performance metrics like sensitivity ($\mu A \cdot mM^{-1} \cdot cm^{-2}$), detection limit ($\mu M$), linear response range, and response time (s) were extracted and analyzed.* ***Results:*** *ZnO-MnO_2 nanocomposites demonstrated notable improvements in glucose sensor performance, offering enhanced electron transfer kinetics, greater surface area for enzyme immobilization, and improved biocompatibility. Sensitivities ranged up to 3670 $\mu A \cdot mM^{-1} \cdot cm^{-2}$, with detection limits as low as 0.3 μM and response times below 5 seconds. Composite formation methods significantly influenced morphology and, consequently, the electrochemical behavior of sensors.* ***Conclusion:*** *ZnO-MnO_2 nanocomposites hold considerable promise as materials for high-performance glucose sensing. Their synergistic electrochemical properties enable superior analytical characteristics. However, challenges remain in terms of long-term stability, reproducibility, and cost-effective scale-up. Future research should focus on integration into wearable platforms, real-time monitoring, and non-enzymatic detection approaches.*

Keywords: Nanostructure, Diabetes Mellitus, Glucose, Sensors, Sensitivity

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Introduction

In today's world, the benefits of scientific and technological advancements are evident in nearly every aspect of daily life. We rely extensively on a wide array of electronic devices—including computers, printers, smartphones, microwave ovens, refrigerators, air conditioners, remote controls, smoke detectors, and infrared thermometers—not only for convenience but also to enhance our ability to interact with and manage our environment. A central component in the functionality of these devices is the sensor. Sensors are critical elements capable of detecting fluctuations in physical parameters—such as temperature, pressure, humidity, force, motion, or electric current—and converting these variations into readable signals for interpretation, control, and analysis (1,2). Meanwhile, transducers serve as devices that convert one form of energy into another, bridging the gap between physical phenomena and measurable output. In any measurement system, the sensor forms the core, and an ideal sensor is expected to possess certain essential characteristics: a broad measurement range, minimal drift over time, straightforward calibration, high sensitivity, sharp selectivity, linear signal output, fine resolution, consistent repeatability, strong reproducibility, and a rapid response time (3,4). The proliferation of sensor technologies and their increasing relevance are driven by their extensive deployment across diverse fields, such as environmental surveillance, food safety analysis, healthcare diagnostics, automotive systems, industrial automation, national defense, space exploration, and homeland security.

Novelty of Work

This review uniquely focuses on recent advances in ZnO–MnO_2 nanocomposites for glucose sensing, a topic not yet thoroughly covered. It highlights the impact of morphology, synthesis methods, and composite synergy on sensor performance. Both enzymatic and non-enzymatic platforms are critically compared for the first time in a single review. The article also outlines current challenges and future prospects for real-world biosensor applications.

Sensor

The sensor can be defined as the device that measures and identifies the properties and records it, show the changes, and reacts to it in different method (9). It can be stated as the device which has the ability to detect the physical quantity of a system and shows it as a product. In various systems, these reactions take place at an electrode and this working is called sensors (8).

Sensor Categorization

Sensors can be systematically classified according to the nature of the quantities they detect or the manner in which they operate (Figure 1). These classifications include: (a) based on power dependency—active versus passive sensors; (b) based on interaction method—contact versus non-contact sensors; (c) based on comparison framework—absolute versus relative sensors; (d) based on signal format—analog versus digital sensors; and (e) based on detection mechanism—physical, chemical, thermal, and biological sensors (5,6). Each category encompasses the following distinctions:

Active sensors necessitate an external power supply to function. Examples include thermistors and strain gauges, which operate by modifying electrical parameters such as resistance in response to stimuli. These are often termed parametric sensors.

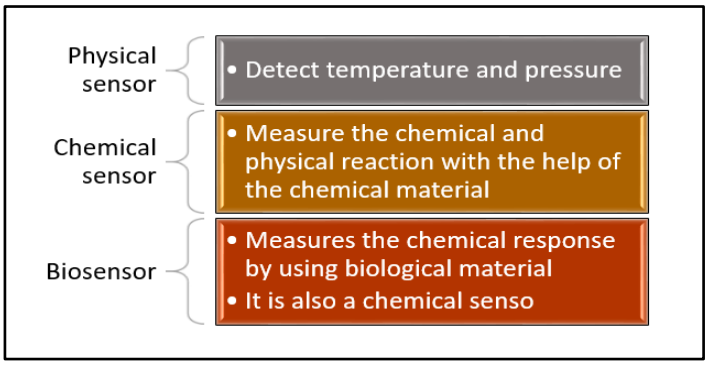
Passive sensors, by contrast, do not require any external energy input. Instead, they generate their own signal in response to environmental changes. Notable examples include thermocouples, which generate voltage due to temperature differences, and piezoelectric sensors, which convert mechanical stress into electrical signals. These are classified as self-generating sensors.

Contact sensors necessitate direct physical interaction with the target medium, whereas non-contact sensors, such as optical and magnetic sensors, function through indirect means and can operate at a distance.

Absolute sensors provide outputs that are directly proportional to a measurable physical phenomenon on a fixed reference scale, whereas relative sensors output measurements as a deviation or comparison against a known standard or baseline.

Analog sensors produce continuous output signals that reflect variations in the measured parameter, while digital sensors generate discrete, quantized signals—usually in the form of electrical pulses.

Based on their signal detection mechanisms, sensors may be categorized as physical (e.g., detecting pressure, force, displacement), chemical (e.g., sensing gas concentrations or pH levels), thermal (e.g., responding to



temperature changes), or biological (e.g., recognizing biomolecular interactions).

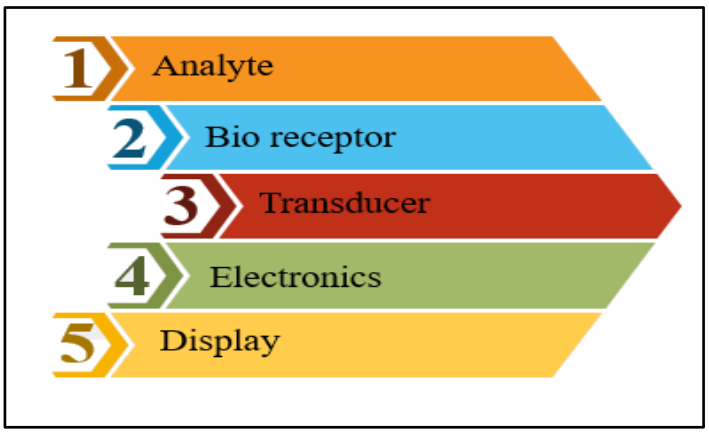
Fig.1

Biosensor

Biosensor measures the chemical response by using biological material. It is also a chemical sensor. It detects components like DNA and biomolecules. According to research conducted in 1962, the biosensor was created to immobilize the enzyme at the electrochemical indicator to form the enzymatic detonators which can be used as for sensing (7).

In the Oxford Dictionary of biochemistry, the biosensor is defined as the device that utilizes some chemical reactions that are facilitated by isolated enzymes, tissues, various organelles, and detect the full cell, with the help of electronic and visual signals (11). According to research, the biosensor is a device that is used to convert the biomatrix properties like enzyme, antibody, and microorganism into other electric signals whose amplitude is determined by the describe analyte used in the solution (12). Theses sensors were also becoming essential in multi-disciplinary fields like medicine, health care, biological examination, and environmental analysis and used by food industries.

Biosensor is a logical device which is used to convert the physical and chemical properties of a biomatrix into electrical signals. Its amplitude mainly depends on the concentration of the mention analyte in solution



(13). It is considered as important in the health, food, environmental and chemical industries.

Figure:2 Components of biosensor

Analyte

An analyte is a kind of material that is used for detection purposes. For example, glucose is an analyte in a biosensor that is used to identify glucose.

Bio receptor

A particle that only recognized the analyte is called a bio receptor. For example, enzymes, DNA, cells, and different antibodies. In this process signal is generated in the form of heat, light, and pH to transform the analyte and with bio, the receptor is called biorecognition.

Transducer

According to research, it is the device that transforms the chemical and physical variations into a measurable signal (9), the transducer is the word which is derived from the Latin word which is called as “traduce” in which energy is converted the bio receptor into another quantifiable form or signal. It is a component that converts one energy into another form. This kind of conversion in the biosensor is known as signalization. Many transducers produced different signals like electrical and optical. This process is done by interacting with the analyte directly and with the help mediator (10). The analyte surface can be liquid, gas, substance, and bioactive material. The analyte is a major key to produce the detecting and regulate the system in a biosensor.

Electronics

This is the element of the biosensor in which the signals transfer and prepare it to show on screen.in this part complex electronic system is operated such as amplification and changes of signal form source to another form. Likewise, when the system operates then it is displayed on the screen of the biosensor.

Display

In this part, the system shows the direct interpretation of the liquid crystal display of a machine that allows us to form signals which are understandable by the user. It also has soft and hardware that generate the ending point on the screen. The result obtained in a different form depending on the user requirement. The schematic representation of the biosensor is given below.

Overview of Biosensors

Structure and Working Mechanism

A biosensor is a sophisticated analytical device that combines a biologically sensitive element with a physicochemical transducer to detect and quantify the presence of specific substances, usually in minute concentrations. The key functional units of a biosensor include: (a) the analyte, (b) the bioreceptor, (c) the transducer, (d) electronic components, and (e) the output display (Figure 2) (7).

The analyte is the target substance to be detected, which could be a biomolecule such as glucose, urea, cholesterol, ammonia, or a pathogen.

The bioreceptor is the biologically derived entity—such as an enzyme, antibody, DNA sequence, cell receptor, or microorganism—that specifically recognizes and interacts with the analyte.

The transducer acts as the conversion unit that translates the biorecognition event into a quantifiable physical signal, such as an electrical current, optical signal, or thermal change.

The electronics module amplifies, filters, and processes the raw signal, preparing it for display.

The display unit visually presents the interpreted data, often in a user-friendly and easily readable format such as a digital readout.

The detection process in biosensors often involves highly selective binding interactions or catalytic reactions, which lead to physical changes measurable by the transducer. This integration of biological specificity with physical detection forms the foundation of biosensor functionality.

Historical Development

The progression of biosensor technologies has undergone significant transformation over the decades, marked by three primary generational advancements:

First-generation biosensors were designed to directly measure the product of the analyte's biochemical reaction, typically involving an enzyme that generates a signal in the absence of intermediate molecules.

Second-generation biosensors introduced mediators—such as redox-active molecules or nanomaterials—to enhance electron transfer between the bioreceptor and the transducer, thereby improving sensitivity and stability.

Third-generation biosensors represent a more integrated approach, enabling direct electron transfer between the bioreceptor and the transducer, effectively removing the need for external mediators. These devices often utilize advanced nanomaterials or conductive polymers to facilitate this direct interaction, offering faster response times and greater miniaturization potential (8-16).

Biosensor Features

For a biosensor to be deemed effective, it must exhibit a combination of essential features that ensure performance reliability and analytical precision: (a) Selectivity: The capacity to distinguish the target analyte from other coexisting substances, ensuring high specificity even in complex biological matrices. (b) Sensitivity: The ability to detect minute concentrations of the analyte with a strong signal-to-noise ratio, often down to nanomolar or picomolar levels. (c) Linearity: A consistent and proportional response over a defined range of analyte concentrations, which is crucial for accurate quantification. (d) Response Time: The duration required for the biosensor to reach a stable signal after exposure to the analyte; faster response times are preferred for real-time monitoring. (e) Reproducibility: The capability of the biosensor to deliver consistent results across multiple tests and under similar conditions. (f) Stability: The long-term reliability and performance consistency of the biosensor under various environmental or storage conditions, including resistance to degradation or fouling (3,4,17).

Types of Biosensors

Biosensors may be categorized using various classification systems, depending on the component or technology used. The most common classifications are:

Based on bioreceptor: Enzymatic, immunological, nucleic acid-based, cell-based, and biomimetic sensors.

Based on transduction principle: Electrochemical (amperometric, potentiometric, conductometric), optical (fluorescence, absorbance, surface plasmon resonance), piezoelectric, and thermal (calorimetric) sensors.

Based on application or detection platform: Wearable biosensors, point-of-care (POC) diagnostics, lab-on-chip systems, and smart biosensing devices.

Based on detection system: Use of photonic crystals, SPR (surface plasmon resonance), FETs (field-effect transistors), or microfluidic systems for signal detection and amplification (18).

Bioreceptor-Based Classifications

Biosensors can be broadly divided into two main groups based on their biorecognition mechanism:

Catalytic biosensors: These operate by catalyzing the conversion of the analyte into a product, which is then detected by the transducer. Common bioreceptors include enzymes, microorganisms, and organelles.

Affinity biosensors: These rely on specific binding interactions between the analyte and a recognition element, such as antibodies or nucleic acids, without any chemical transformation. The strength and specificity of these binding interactions are central to detection accuracy (19).

Enzyme Biosensors

Enzyme-based biosensors employ specific enzymes to recognize and catalyze reactions with the target analyte. These enzymes act as biocatalysts, significantly increasing the reaction rate, thereby facilitating rapid detection. The resulting biochemical reaction often produces by-products—such as hydrogen peroxide or protons—that can be quantitatively measured by the transducer. Electrochemical detection methods, including amperometric and potentiometric techniques, are commonly employed in these biosensors. Examples include glucose biosensors using glucose oxidase and urea biosensors utilizing urease (20-27). Despite their widespread usage, enzyme biosensors can suffer from limited stability due to the enzyme's sensitivity to pH, temperature, and humidity, which can elevate production costs and reduce shelf life.

Antibody Biosensors

Antibody-based biosensors, or immunosensors, are designed to leverage the high specificity of antigen-antibody interactions for analyte detection. These biosensors can operate in two formats: label-free, where the physical change (e.g., mass or refractive index) caused by antigen binding is directly measured, and labeled, where the detection is enhanced using fluorescent or electrochemical tags. Immunosensors offer exceptional selectivity and are widely applied in clinical diagnostics, environmental analysis, and food safety testing. Challenges remain in terms of antibody stability and potential cross-reactivity, but ongoing advances in monoclonal antibody production and nanomaterial-assisted platforms continue to improve performance (27-31).

Classification Based on Transducers

According to their operating principle, transducers are broadly categorized as electrochemical, optical, thermal, electronic, and nano-material based sensor

Electrochemical Biosensors

Electrochemical biosensors are extensively employed for analyzing DNA hybridization, interaction with DNA-binding drugs, and monitoring glucose levels. These biosensors operate on the principle that various chemical reactions lead to the generation or consumption of electrons or ions. Such activities result in alterations in the solution's electrical properties, which can be detected and quantified for analytical purposes.

Electrochemical biosensors are typically categorized based on the type of electrical signal they measure:

- Conductimetric
- Amperometric
- Potentiometric

Conductimetric Biosensors

In this approach, the sensor tracks changes in the electrical conductivity or resistance of a solution. The presence of electrochemical reactions introduces ions or electrons into the medium, modifying its conductivity. This variation is then calibrated for analytical measurement. Though this technique is less sensitive compared to others, applying an alternating current (AC) signal helps suppress unwanted phenomena such as Faradaic currents, double-layer capacitance, and concentration gradients.

Amperometric Biosensors

Amperometric biosensors offer high sensitivity and are designed to detect electroactive compounds in biological samples. Since not all biological analytes are naturally electroactive, enzymes are often used to catalyze specific reactions, making detection possible through the resulting electrochemical changes.

Potentiometric Biosensors

These sensors measure the potential difference related to oxidation-reduction reactions. Their function is based on applying a varying voltage to an electrode in a solution, inducing current flow due to electrochemical interactions. The voltage level at which these reactions occur corresponds to specific species, enabling their identification (28-35).

Optical Biosensors

Optical biosensors are analytical instruments that integrate a biological recognition component with an optical signal transduction mechanism. These devices function by generating optical signals directly related to the concentration of the target analyte, enabling real-time and label-free detection of multiple analytes simultaneously.

The biorecognition elements employed in optical biosensors include enzymes, antibodies, aptamers, whole cells, and tissue samples. The optical transducer responds to the physical or chemical changes triggered by these biological components, resulting in variations in light absorption, transmission, reflection, refraction, phase, amplitude, frequency, or polarization.

Optical biosensors are broadly categorized into two types based on their detection strategy:

Label-free biosensors, in which the optical signal arises directly from the interaction between the analyte and the transducer surface.

Label-based biosensors, where the signal is produced using colorimetric, fluorescent, or luminescent markers.

Various optical phenomena can be utilized in the design of these sensors, including:

- Surface Plasmon Resonance (SPR)
- Evanescent Wave (EW) fluorescence
- Optical waveguide interferometry
- Chemiluminescence
- Fluorescence
- Refractive index-based sensing
- Surface-Enhanced Raman Scattering (SERS)

Among these, the most widely adopted optical biosensors include:

- Fluorescence-based optical biosensors
- Chemiluminescence-based optical biosensors
- SPR-based optical biosensors
- Optical fiber-based biosensors (36-49)

Nanomaterial-Based Biosensors (Nanobiosensors)

The emergence of nanotechnology has significantly transformed biosensor development, fostering interdisciplinary research and innovation. Nanomaterials (NMs), including nanoparticles (NPs)—both metallic and oxide-based—nanowires (NWs), nanorods (NRs), carbon nanotubes (CNTs), quantum dots (QDs), and dendrimer-based nanocomposites, offer a unique set of properties that enhance biosensor performance by enabling precise control over size and morphology.

Although nanobiosensors operate on principles similar to traditional macro- and micro-scale biosensors, their use of nanoscale components allows for superior signal conversion and data interpretation (50). These devices offer several advantages over their conventional counterparts due to their nanoscale dimensionality and multifunctional capabilities. Nanobiosensors play crucial roles in (a) monitoring physicochemical phenomena in inaccessible regions, (b) detecting biomolecules within organelles and for medical diagnostics, (c) quantifying nanoscale particles in industrial and environmental settings, and (d) identifying trace levels of hazardous substances (51).

The classification of nanomaterials has facilitated targeted improvements in biosensing mechanisms. For instance, sensors incorporating metallic nanoparticles serve as signal amplifiers. CNT-based biosensors improve reaction specificity and kinetics, while NWs enhance charge mobility. QDs function as contrast agents to boost optical detection responses.

Nanoparticle-Based Biosensors

Nanoparticles are extensively employed in biomedical domains such as diagnostics, bioimaging, therapeutic delivery, and sensor fabrication. Their nanoscale dimensions and morphologies significantly influence their interaction with biological targets, making them ideal candidates for bioanalytical applications (52). NPs are particularly effective in electrode surface modifications, enhancing electrochemical sensitivity and specificity (53). Additionally, catalytically active NMs, including transition metal oxides, serve as nanoenzymes facilitating biochemical reactions on biosensors.

Commonly used nanoparticles include metals (Au, Ag, Pt, Pd, Co, Fe, Cu) and metal oxides (ZnO, TiO_2, SnO_2, MnO_2), each exhibiting remarkable optical, electronic, magnetic, chemical, mechanical, and catalytic attributes. Their biosensing performance can be tailored by coating with diverse matrices like metal oxides, silica, polymers, graphene, fibers, and dendrimers (55).

Gold Nanoparticles (AuNPs): Due to their outstanding optical and electronic characteristics, AuNPs are widely studied in biomedicine. Their benefits include facile synthesis, stability, biocompatibility, broad electrochemical potential, and high catalytic activity (56,57). For example, Wu et al. developed an AuNP-based electrochemical sensor for detecting uranyl in natural waters with a detection range of 2.4–480 µg/L and a limit of 0.3 µg/L via anodic stripping voltammetry (58). Luo et al. designed a graphene quantum dot (GQD) and AuNP-based fluorescent "turn-on" sensor for Pb^{2+}, achieving detection limits of 16.7 nM across a range of 50 nM to 4 µM (59). Ghasemi et al. introduced a bimetallic Au-Ni NP doped sensor using an agro-waste-derived aluminosilicate framework, showing a detection limit of 0.063 µM for glucose (60).

Silver Nanoparticles (AgNPs): Noted for SERS activity, biocompatibility, and high conductivity, AgNPs are popular in biosensing (61–63). Rivero et al. demonstrated a dual-mode LSPR and LMR optical fiber sensor with a sensitivity of 0.943 nm per %RH and a quick response time, applicable to respiratory monitoring (64). Mehdinia et al. created a multifunctional colorimetric probe using biosynthesized AgNPs for Fe^{2+}, H_2O_2, and glucose with detection limits of 0.54, 0.032, and 0.29 µM respectively (65).

Platinum Nanoparticles (PtNPs): These are preferred for their electrochemical properties and enhanced electron transfer, influenced by surface reactivity and crystallography (133). Liu et al. produced a PtNP/a-IGZO ammonia sensor with a response of 1467 at 1000 ppm NH_3 (66). Dharuman et al. combined Pt and ZnO with graphitic carbon nitride for non-enzymatic glucose sensing, with reusability in blood samples and a broad linear detection range (67).

Palladium Nanoparticles (PdNPs): Recognized for their high catalytic efficiency and economic advantage over noble metals, PdNPs are highly versatile (68). Ye et al. synthesized Pd/Co-NCNTs showing high sensitivity (343.909 µA mM^{-1}) and a detection limit of 0.007 µM for hydrazine (69). Swihart et al. created Pd-decorated graphene oxide nanoballs for H_2 detection with a response of 14.8% at 2% H_2 (70). Afzali et al. built a Pd-modified sensor for detecting pemetrexed with a limit of 0.33 nM using square-wave voltammetry (71).

Copper Nanoparticles (CuNPs): CuNPs offer a cost-effective alternative with good conductivity and electrocatalytic behavior. Huang et al. developed CuNP-based glucose sensors on graphite, yielding sensitivities of 7254.1 and 3804.5 µA mM^{-1} cm^{-2} across two concentration ranges (72). Roushani et al. integrated CuNPs into a composite for H_2O_2 sensing, achieving a detection limit of 0.11 µM (73). Zhao et al. designed a Cu/rGO buckypaper electrode for glucose with a limit of 11 µM (74).

Metal Oxide-Based Nanoparticles

Metal oxide nanoparticles are widely used in sensing applications due to their diverse electrical, magnetic, and catalytic behaviors. These oxides act as cost-effective electrocatalysts for detecting biological and chemical targets.

Commonly explored metal oxides include CuO, NiO, Fe_2O_3, Co_3O_4, MnO_2, ZnO, TiO_2, SnO_2, CdO, MoO_3, and CeO_2 (75).

Nickel Oxide (NiO) NPs: These p-type semiconductors have a direct bandgap (3.56 eV) and exhibit remarkable magnetic and catalytic traits (76). Duan et al. created FET glucose biosensors based on Ni/Cu-MOFs with a 0.51 µM detection limit (77). Kamyabi et al. employed NiO-modified nickel foam for glucose sensing, achieving a limit of 5.0×10^{-10} M (78,79).

Cobalt Oxide (Co_3O_4) NPs: These exhibit high optical and electrochemical activity. Chu et al. fabricated a glutamate biosensor with a sensitivity of 20.12 µA mM^{-1} cm^{-2} (79), and Wazir et al. produced a potentiometric urea biosensor on Co_3O_4-chitosan with a slope of 45 mV/decade (80). Ge et al. developed a Co_3O_4-Au PEC biosensor for miRNA-141 with a 0.2 pM detection limit (81).

Iron Oxide and Manganese Oxide NPs: These are magnetic and enable fast electron transfer. Phan et al. explored magnetic ribbons with nanoholes for drug detection (85), and Zhang et al. reported a fast LF-NMR biosensor for Salmonella with a detection limit of 2.6×10^4 CFU/mL (86). Stankovic et al. built MnO_2-decorated graphene nanoribbon sensors for glucose with a 0.05 mM limit and 56.32 µA $mmol^{-1}$ cm^{-2} sensitivity (87).

Other Metal Oxides:

TiO_2: Used in medical and optical sensors. Tereshchenko et al. fabricated a TiO_2-based immunosensor for Salmonella with sensitivity in the 10^3–10^5 cL/mL range (92,93).

SnO_2: Applied in gas and pesticide detection (91).

MoO_3: Ravikumar et al. developed MoO_3-based sensors for rapid H_2O_2 detection (94).

ZnO as a Promising Material for Biosensing Applications

Zinc oxide (ZnO) has garnered significant scientific attention over the past decade due to its distinctive nanostructural features and multifunctional physical properties. Classified as an inorganic II–VI group binary semiconductor, ZnO possesses a direct wide bandgap of 3.37 eV located in the near-ultraviolet range and boasts a relatively high exciton binding energy of 60 meV at ambient temperature (88-90). These unique traits have positioned ZnO as a vital material in the realm of electronics and optoelectronics, particularly in high-performance and robust device applications. Thanks to its wide bandgap, ZnO can tolerate elevated temperatures, high electric fields, and large breakdown voltages, making it suitable for high-power operations (95). Furthermore, its optical transparency and semiconducting nature have led to its widespread use as a transparent conducting oxide (TCO) in electronic components.

ZnO exhibits intrinsic n-type conductivity, primarily due to the presence of native defects such as oxygen vacancies and zinc interstitials within its crystal lattice. Although ZnO can crystallize into three different forms—namely zinc blende, wurtzite, and rocksalt—the hexagonal wurtzite configuration is the most thermodynamically stable under standard temperature and pressure conditions (95). In this structure, illustrated in Figure 2, Zn^{2+} and O^{2-} ions alternate along the crystallographic c-axis, forming layers that lack inversion symmetry. This tetrahedral coordination results in spontaneous polarization effects, thereby endowing ZnO with inherent piezoelectric properties (96).

The stacking of oppositely charged ions along the c-axis gives rise to polar surfaces: the positively charged Zn-(0001) and the negatively charged O-(0001). These surface terminations significantly influence the material's physical and chemical interactions. The coexistence of polar and nonpolar planes enables ZnO to exhibit tunable electrical properties, which are particularly advantageous for developing high-performance biosensors.

In addition to inducing spontaneous polarity, the tetrahedral bonding structure of ZnO also indicates sp^3 hybridization with a substantial ionic contribution to the Zn–O bond, attributable to the large electronegativity gap between zinc and oxygen atoms. On the Phillips scale, ZnO is categorized with an ionicity factor of fi = 0.616, positioning it near the boundary between ionic and covalent bonding characteristics (97). The differential surface relaxation energies of the polar planes further encourage anisotropic growth of ZnO nanostructures, which often display properties distinct from their bulk counterparts (98,99). These anisotropic structures are particularly suitable as transducer materials in biosensors, as they promote improved electron transfer and increased sensitivity in biomolecular detection.

ZnO's Role in Biosensing Technology

In recent years, ZnO thin films and nanostructures have demonstrated significant promise for the immobilization of biomolecules, enhancing their role in biosensor development. Technologically, ZnO offers multiple advantages: ease of surface modification, a high isoelectric point (IEP), compatibility with low-temperature fabrication methods, high biocompatibility, and excellent electron mobility (100,101). The unique electrical and chemical features of ZnO at the nanoscale, such as large surface area and enhanced charge transport at interfaces, contribute to improved detection sensitivity in biosensing platforms.

The IEP of ZnO is approximately 9.5, significantly higher than that of most biomolecules. This disparity results in strong electrostatic attraction at physiological pH, where biomolecules are generally negatively charged. The resulting strong interaction allows for stable biomolecule immobilization on the positively charged ZnO surface—an essential factor for designing effective biosensors.

ZnO's dual ionic and semiconducting properties enable high-sensitivity detection of biomarkers at extremely low concentrations. Moreover, ZnO nanostructures can be synthesized using cost-effective and scalable fabrication processes, which is ideal for developing portable, miniaturized, and affordable point-of-care (POC) diagnostic devices (102,103). By fine-tuning parameters such as nanostructure width, length, and surface density, it is possible to confine biomolecules more efficiently and enhance target detection. Precise engineering of ZnO's surface polarity further allows for improved selectivity in sensing applications.

Numerous studies have demonstrated that combining ZnO with other organic or inorganic materials—either through doping or by forming hybrid nanocomposites—can improve its sensing capabilities for specific biomarkers (104,105). The comparable size of ZnO nanostructures to biological targets also allows for effective interaction with minimal sample volumes, making them ideal for real-time, label-free biosensing.

Different morphologies of ZnO nanostructures offer flexibility in device architecture, enabling their integration into various biosensor configurations. These devices operate based on measurable changes in electrical conductivity upon the interaction of the ZnO surface with biological fluids, where binding events perturb the local charge distribution. Such variations in conductivity can be used to detect target analytes with high sensitivity and specificity.

These advantageous characteristics have led to the development of a wide range of ZnO-based biosensing platforms for detecting important biomarkers such as glucose, urea, lactic acid, and cardiac troponins. The following sections will delve into the various synthesis methods for ZnO nanostructures, techniques for surface functionalization, and detailed mechanisms underlying biosensing through charge perturbation at the nanostructured ZnO–sample interface.

Morphological Versatility and Functional Role of ZnO Nanostructures in Biosensing Applications

Zinc oxide (ZnO) is widely acknowledged as a multifunctional semiconductor nanomaterial, exhibiting diverse physicochemical properties that make it highly suitable for use in various analytical detection platforms. These include mass-sensitive biosensors (106), electrochemical sensors (107), and optical detection systems (108). The morphology and dimensionality of ZnO nanostructures significantly influence their physicochemical properties, thereby playing a critical role in the enhancement of biosensor performance.

ZnO nanostructures can be broadly categorized into four morphological dimensions based on their geometry and aspect ratio: zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) structures (109). Each category offers distinct surface characteristics, electronic behavior, and biomolecular interaction capabilities.

0D nanostructures, such as nanoparticles (110) and quantum dots (11), exhibit a high surface-to-volume ratio, enhancing the adsorption and immobilization of biomolecules.

1D nanostructures, including nanorods (112), nanotubes (113), nanowires (114), and nanofibers (115), provide a direct pathway for charge carriers, promoting rapid electron transport while maintaining excellent surface reactivity.

2D morphologies, such as nanodisks (116), nanoflakes (117), nanosheets (118), and nanowalls (119), offer large lateral dimensions that support higher biomolecule loading and improved signal response.

3D architectures, often assembled from 0D, 1D, or 2D building blocks, present hierarchically structured materials with enhanced porosity and surface area, beneficial for signal amplification and target analyte capture (120).

Among these, 0D ZnO nanostructures have received considerable attention due to their remarkable surface reactivity and enhanced biomolecule interaction capabilities (121). The increase in specific surface area with decreasing particle size promotes more effective adsorption of enzymes and other bio-receptors, leading to improved sensitivity and selectivity in biosensing applications (122). However, this advantage is often offset by limitations in charge carrier mobility. A smaller grain size typically introduces more grain boundaries, which act as scattering centers and hinder electron transport (123).

Research has shown that the application of nanoparticles—including ZnO—in diverse fields such as drug delivery, food packaging, and agriculture has revolutionized conventional technologies (124). These

nanoparticles are synthesized via various chemical methods, including emulsion solvent diffusion, solvent displacement, and precipitation techniques. However, the broader industrial adoption of nanomaterials necessitates innovations to mitigate environmental and biochemical contamination (125). The development of eco-friendly and scalable synthesis routes is therefore crucial for both sensor performance and environmental sustainability.

In addition, 1D ZnO nanostructures, particularly nanorods and nanowires with diameters typically below 40 nm, are widely employed due to their high aspect ratios and efficient charge transport characteristics (126, 127). These structures provide stable and conductive pathways for electrons, essential for improving sensor response times and reducing background noise (127,128).

Several synthesis techniques have been employed for the fabrication of ZnO nanostructures, each offering advantages in terms of crystal quality, scalability, and cost-effectiveness. Common methods include spray pyrolysis, hydrothermal synthesis, chemical vapor deposition (CVD), radio frequency (RF) sputtering, pulsed laser deposition, contact printing, microwave irradiation, and inkjet printing (129-142). The choice of synthesis method significantly impacts the resultant nanostructure morphology, surface chemistry, and ultimately, the biosensor's functional performance.

Industrial and Biomedical Significance of Zinc Oxide Nanostructures

Zinc oxide (ZnO) nanoparticles hold significant industrial and biomedical value due to their versatile functional properties. One of their key applications is in the formulation of sunscreens and skincare products. ZnO nanoparticles, particularly those with diameters below 200 nm, exhibit high efficiency in scattering ultraviolet (UV) radiation, including X-rays emitted by solar exposure, thereby protecting skin cells from oxidative stress and radical-induced damage (143–148). These nanoparticles are widely incorporated into dermatological formulations such as creams, lotions, and foot care products due to their excellent light-blocking ability and skin compatibility. Moreover, ZnO enhances the sensory texture and stability of cosmetic products while contributing a notable sun protection factor (SPF), making it a valuable additive in personal care industries (149).

In biomedical imaging, ZnO demonstrates strong green luminescence, making it a promising agent for bioimaging applications. Furthermore, ZnO nanoparticles have shown considerable potential in gene delivery systems, a breakthrough in therapeutic strategies for genetic disorders such as adenosine deaminase severe combined immunodeficiency (ADA-SCID), diabetes, and other metabolic or hereditary diseases. The capability of ZnO to facilitate cellular uptake and transfection highlights its role as an emerging vector in non-viral gene therapy.

Structurally engineered ZnO nanomaterials—such as quantum dots and tetrapod-shaped architectures—have found extensive use in the development of sensors (150–152). These nanostructures offer enhanced surface area, quantum confinement effects, and tunable electronic properties, making them highly effective in detecting environmental pollutants and biomedical analytes. ZnO-based biosensors have been employed for the detection of biologically relevant molecules including cholesterol, enzymes, and disease biomarkers, owing to their superior sensitivity, fast response times, and chemical stability (153, 154).

Additionally, ZnO nanostructures synthesized via sol-gel and hydrothermal methods have been tailored for temperature and gas sensing applications, particularly in ethanol detection. The sensing mechanism involves the adsorption of oxygen species on the ZnO surface, which withdraw electrons from the conduction band and form a depletion layer. This modulates the electrical conductivity of ZnO, thereby enhancing its sensing response in the presence of target analytes (155).

Significance of Manganese Oxide (MnO_2)

Nanocomposites composed of metals and metal oxides have emerged as essential components in the fabrication of high-performance electrochemical sensors. Among various metal oxides such as SiO_2, CuO, ZnO, and ZrO_2 manganese dioxide (MnO_2) has garnered substantial research interest due to its unique physicochemical properties, cost-effectiveness, and environmental abundance (156–158). These materials are widely favored for their high surface area, chemical stability, tunable morphology, and compatibility with various fabrication techniques.

MnO_2, a transition metal oxide, is particularly notable for its exceptional structural versatility and electrochemical performance, including a high theoretical specific capacitance (~1370 F g^{-1}) and pseudocapacitive behavior even at low mass loadings (close to mg cm^{-2}) on current collectors (159–162). However, MnO_2 also exhibits relatively low intrinsic electrical conductivity (~10^{-5} to 10^{-6} S cm^{-1}), which can limit its performance in some applications unless modified or combined with conductive materials.

MnO_2 has found extensive use in ion-exchange processes, molecular adsorption, catalysis, and energy storage systems, including batteries and supercapacitors. Its catalytic activity extends to both oxidation and reduction reactions, making it valuable for environmental and biomedical sensing platforms. The nanostructured form of MnO_2 facilitates efficient charge transfer at the electrolyte/cation interface, thereby enhancing pseudocapacitive behavior, rate capability, and electrochemical reversibility (163, 164).

One of MnO_2's key advantages is its ability to exist in multiple crystallographic polymorphs, such as α-, β-, γ-, and δ-MnO_2, each associated with distinct electrochemical characteristics (165, 166). These polymorphs exhibit diverse tunnel or layered structures that influence ionic transport and surface reactivity. MnO_2 nanostructures have been synthesized in various morphologies—including nanoflowers (167, 168), nanosheets (169–171), nanotubes (172), and nanowires (173–175)—to exploit these unique properties for enhanced sensor performance.

The dimensionality and morphology of MnO_2 nanostructures have proven to be crucial in determining their functional behavior. As one-dimensional (1D) and two-dimensional (2D) nanostructures gained prominence, researchers observed enhanced anisotropic electrical and surface properties, which led to improved interaction with analytes and better sensing performance. The synthesis of these nanostructures is commonly achieved through techniques such as thermal decomposition, hydrothermal processing, reflux methods, and sol-gel reactions, often involving redox reactions between permanganate (MnO_4^-) and Mn^{2+} or MnO_2 intermediates (175).

In summary, MnO_2-based nanomaterials offer a combination of structural diversity, electrochemical activity, and synthetic versatility that make them ideal candidates for biosensor development. Ongoing research continues to explore novel MnO_2 morphologies and hybrid composites

Morphological Versatility and Functional Role of MnO_2 Nanostructures in Glucose Sensing Applications

Manganese dioxide (MnO_2) nanostructures have emerged as promising materials in the development of glucose sensors due to their diverse morphologies, redox activity, and catalytic properties. The ability to synthesize MnO_2 in various nanostructured forms—such as nanorods, nanowires, nanosheets, nanotubes, and hierarchical architectures—significantly influences its electrochemical behavior and biosensing performance.

The morphology of MnO_2 plays a critical role in determining its surface area, porosity, and electron transport capability. For example, MnO_2 nanosheets provide a high surface area for enzyme (e.g., glucose oxidase) immobilization, thereby increasing the catalytic efficiency and sensitivity of enzymatic glucose sensors. In contrast, MnO_2 nanorods and nanowires facilitate fast electron transfer between the enzyme and the electrode, enhancing the electrochemical response.

Furthermore, MnO_2 exhibits intrinsic enzyme-mimetic activity, acting as a peroxidase-like catalyst in non-enzymatic glucose sensors. This enables the oxidation of glucose without the need for biological recognition elements, offering improved stability and resistance to harsh conditions such as high temperature or pH variations. The catalytic efficiency of MnO_2 in such systems is heavily influenced by its morphology, with 3D hierarchical structures often demonstrating superior performance due to their larger active surface areas and better mass transport.

Moreover, MnO_2 is frequently incorporated into composite nanomaterials with other metal oxides (like ZnO), conductive polymers, or carbon-based materials (like graphene), which further enhances its sensing capabilities. These composites leverage the unique properties of each component to achieve high sensitivity, low detection limits, and rapid response times.

In summary, the morphological versatility of MnO_2 nanostructures directly contributes to its functional role in glucose sensing by tuning its surface chemistry, conductivity, and catalytic behavior. This makes MnO_2-based nanomaterials highly adaptable for both enzymatic and non-enzymatic glucose sensors, addressing key challenges such as sensitivity, selectivity, and stability in real-time biosensing applications.

ZnO–MnO_2 Nanocomposites for Glucose Biosensing

The development of highly sensitive and selective glucose biosensors remains a major focus in the field of biomedical diagnostics and point-of-care testing. In recent years, zinc oxide (ZnO) and manganese dioxide (MnO_2) nanocomposites have emerged as promising hybrid materials for electrochemical glucose sensors due to their synergistic physicochemical and electrochemical properties.

ZnO, a II–VI semiconductor with a wide bandgap (3.37 eV), offers high isoelectric point (~9.5), chemical stability, biocompatibility, and excellent electron mobility, making it ideal for enzyme immobilization and charge transport in biosensors (177-179). On the other hand, MnO_2 contributes high catalytic activity, pseudocapacitive behavior, and a large specific surface area, enabling enhanced electron transfer kinetics and redox reaction facilitation (180).

When integrated into a composite, ZnO–MnO_2 nanostructures combine the advantages of both materials, resulting in improved electrochemical performance, higher sensitivity, and better stability compared to individual components. ZnO acts as a conductive support matrix for the dispersion of MnO_2 nanoparticles or nanoflakes, which can facilitate the catalytic oxidation of glucose either directly or in the presence of immobilized glucose oxidase (GOx).

Studies have shown that ZnO–MnO_2 composites can be synthesized using methods such as hydrothermal growth, sol-gel processing, or co-precipitation, followed by thermal treatment. These composites often exhibit hierarchical morphologies such as nanorods decorated with MnO_2 nanosheets, flower-like architectures, or core–shell structures. These configurations provide a high surface area, enhanced enzyme loading, and effective mass transport, all of which contribute to better sensor performance.

For instance, ZnO nanorods/MnO_2 nanosheets composites have demonstrated remarkable glucose sensing characteristics, including low detection limits (as low as 0.5 µM), wide linear ranges (up to 10 mM), and fast response times (within a few seconds). Additionally, the presence of MnO_2 enhances the redox reaction by acting as a mediator for electron transfer from glucose oxidation products to the electrode surface, which improves both sensitivity and signal stability.

Furthermore, ZnO–MnO_2 nanocomposites have been successfully employed in both enzymatic and non-enzymatic glucose sensors. In enzymatic platforms, GOx is immobilized on the surface of the composite, where the ZnO provides a stable immobilization matrix and the MnO_2 promotes catalytic activity. In non-enzymatic sensors, MnO_2 plays a more direct role in catalyzing glucose oxidation, while ZnO ensures good conductivity and structural support. (176,181-182)

These results affirm the potential of ZnO–MnO_2 composites as efficient glucose-sensing platforms. Their low cost, ease of synthesis, and tunable surface properties make them highly attractive for developing next-generation biosensors.

Conclusion

This review has presented a comprehensive overview of biosensors, emphasizing their fundamental structure, working principles, and classifications. A typical biosensor consists of three core components: a biorecognition element, a transducer, and a signal processor. Based on the type of transduction mechanism, biosensors are broadly categorized into electrochemical, optical, thermal, and piezoelectric types. The selection of appropriate materials for each component significantly influences the sensitivity, selectivity, and stability of the biosensor.

Metal oxide nanoparticles (MONPs) have garnered significant interest in biosensing due to their unique physicochemical properties, including high surface area-to-volume ratios, excellent chemical stability, catalytic activity, and tunable electronic structures. Among these, nanocomposites—hybrid materials composed of two or more distinct nanomaterials—offer enhanced functionalities through synergistic effects. The integration of different metal oxides into composite structures enables improved charge transport, enhanced catalytic efficiency, and superior biomolecule immobilization, all of which are critical for high-performance biosensor applications.

Focusing specifically on ZnO–MnO_2-based nanocomposites, these materials combine the advantages of both constituents: ZnO contributes excellent electron mobility, high isoelectric point, and structural versatility, while MnO_2 provides outstanding redox behavior and catalytic activity. The engineered nanostructures, such as ZnO nanorods decorated with MnO_2 nanosheets, flower-like morphologies, or core–shell architectures, result in high surface areas and efficient enzyme loading, enabling improved electron transfer and analyte accessibility.

Numerous studies have demonstrated the superior performance of ZnO–MnO_2 nanocomposites in glucose biosensing, both in enzymatic and non-enzymatic configurations. These platforms exhibit low detection limits, wide linear response ranges, fast response times, and good long-term stability. In enzymatic systems, ZnO offers a favorable environment for enzyme immobilization, while MnO_2 acts as a mediator to enhance redox reactions. In non-enzymatic systems, MnO_2 plays a more direct role in catalyzing glucose oxidation, with ZnO supporting structural integrity and electron conductivity.

In conclusion, ZnO–MnO_2-based biosensors hold significant promise for the next generation of sensing technologies due to their cost-effectiveness, ease of fabrication, and enhanced performance metrics. Ongoing research should aim to optimize synthesis parameters, explore multifunctionality for detecting various analytes, and integrate these materials into flexible, portable, and real-time sensing devices for clinical, environmental, and industrial applications.

Declarations

Data Availability statement

All data generated or analysed during the study are included in the manuscript.

Ethics approval and consent to participate

Approved by the department concerned. (

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The authors declared the absence of a conflict of interest.

Author Contribution

SS (Assistant professor)

Review of Literature, Manuscript drafting, Study Design, manuscript review, critical input. Conception of Study, Development of Research Methodology Design

All authors reviewed the results and approved the final version of the manuscript. They are also accountable for the integrity of the study.

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