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Functional Metal Oxide Nanoparticles properties, Synthesis, and band gap engineering to advanced applications: A review

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Abstract

Metal oxide nanoparticles (MONPs) have attracted considerable interest due to their distinct characteristics and wide-ranging applications in areas like Photocatalysis, sensing, and biomedical technologies. This review offers an in-depth examination of the synthesis techniques, properties, and uses of MONPs, concentrating on their electronic structure, band gap engineering, and the factors that affect their performance. Various synthesis methods, such as sol-gel, co-precipitation, hydrothermal, and green synthesis, are discussed, with an emphasis on their benefits and drawbacks. The electronic properties of MONPs, including their band gap, are analyzed thoroughly, highlighting the significance of understanding the link between electronic structure and material performance. Factors influencing the band gap, such as particle size, oxidation state, temperature, and doping, are investigated, providing insights into strategies for adjusting the properties of MONPs. The review also explores the applications of MONPs, especially in photocatalysis, gas sensing, and biomedicine. The potential of MONPs as photocatalysts for environmental cleanup and energy generation is discussed, along with the challenges and future opportunities in this field. The use of MONPs in gas sensing applications, focusing on their sensitivity, selectivity, and stability, is also examined. Finally, the biomedical applications of MONPs, including drug delivery and wound healing, are highlighted, addressing concerns about their toxicity and biocompatibility. This comprehensive review aims to serve as a valuable resource for researchers and practitioners working with metal oxide nanoparticles, offering insights into their synthesis, properties, and varied applications.

Keywords: Metal oxide, nanoparticles, synthesis, applications, photocatalysis

Introduction

Metal oxides (MOs) are significant because of their adjustable electrical, magnetic, and optical properties. These have numerous applications. Metal oxides (MOs) exhibit stability and durability, leading to their extensive application across various industries, including environmental, security, medicinal, petrochemical, and agricultural sectors. The surface morphology and crystalline structure of metal oxides can be modified through alterations in synthesis methods and conditions [1]. Metal oxide nanoparticles (MONPs) constitute a significant class of nanomaterials with extensive applications in science and technology due to their unique properties, including a high surface-to-volume ratio, extensive surface area, and natural abundance [2]. Metal oxides are significant in various domains of chemistry, physics, and materials science. Metal elements can generate a wide variety of oxide compounds. These elements can assume various structural geometries, with an electronic structure that may display metallic, semiconductor, or insulator characteristics. Oxides are utilized in technological applications for the fabrication of microelectronic circuits, sensors, piezoelectric devices, fuel cells, surface passivation coatings against corrosion, and as catalysts [3, 4]. Oxide nanoparticles demonstrate distinctive physical and chemical characteristics attributable to their small dimensions and the abundance of corner or edge surface sites. The size of particles is anticipated to affect three significant categories of properties within any material. The initial component includes the structural characteristics, specifically the lattice symmetry and cell parameters [5-7]. Oxides that are frequently examined as catalytic materials are categorized into the structural classes of corundum, perovskite, rutile, and layered structure. The locations of the ions might not align with the optimal positions of maximum symmetry. Distortions are observed in FeO, NiO, MnO, and CoO when compared to the cubic lattice, as well as in VO_2, NbO_2, MoO_2, and WO_2 in relation to the ideal rutile structure [8-10]. The rocksalt structure consists of a three-dimensional arrangement of alternating cations and anions. Each ion occupies the center of an octahedron, with the vertices comprised of ions of the opposing type. Eight cations and anions. Each ion occupies the center of an octahedron, with the vertices comprised of ions of the opposing type. The structure consists of corner-sharing octahedra. A wurtzite structure is characterized by a hexagonal crystal system, commonly observed in certain semiconductor materials. Corundum, rutile, and spinel structures consist of layers of closely packed oxygen ions [11-13].

The present review deals with recent development in metal oxide nanoparticles. The study highlights the synthesis methods of metal oxide nanoparticles, types of metal oxide nanoparticles, factors affecting the band gap of metal oxide nanoparticles and applications of metal oxide nanoparticles in the different field

Literature Review

Types of Metal Oxide

Metal oxides consist of ionic compounds formed by positively charged metal ions paired with negatively charged oxygen ions. The significant electrostatic attraction present between these oppositely charged ions results in the creation of solid and durable ionic bonds can display metallic, semiconductor, or insulator qualities, with the potential to tailor their electrical characteristics by altering their morphology, stoichiometry, and by doping [14]. Semiconductors exhibit distinctive electronic characteristics that set them apart from other materials. Semiconductors can be classified into two categories: elemental semiconductors and compound semiconductors. The first category includes elements from group IV of the periodic table, like silicon (Si) and germanium (Ge). In contrast, the second category arises from the combinations of materials from groups III and V (known as III-V semiconductors) or II and VI (referred to as II-VI semiconductors) of the periodic table [15]. Solid semiconductors may exist as amorphous, polycrystalline, or single-crystal materials. An amorphous material lacks organization, with atoms positioned randomly, and is characterized by relatively complicated atomic or molecule structures. Polycrystalline materials are solids composed of numerous small crystals, known as micro-crystals, which range in size from nanometers to millimeters. These micro-crystals are separated by boundaries and typically exhibit random crystallographic orientations. The atoms are loosely arranged at the boundaries of micro-crystals, resulting in mechanical and chemical instability. Consequently, the occurrence of cracks and corrosion is more prevalent at grain boundaries [16]. Single crystal materials have a uniform three-dimensional arrangement of atoms, ions, or molecules throughout their structure. Elemental semiconductors possess an electronic configuration characterized by 4 valence electrons, necessitating the addition of 4 additional electrons to achieve a stable electronic configuration. The electrons form covalent bonds with adjacent atoms, and their spatial configuration resembles one electron positioned at the center of a tetrahedron, with the other atoms located at its vertices [17].Basic crystalline structures include the simple cubic, which contains 1 atom per cell; the body-centered cubic, with 2 atoms per cell; the face-centered cubic, which has 4 atoms per cell; and the simple hexagonal, comprising 3 atoms per cell..Based on the number of different elements they are made up of, compound semiconductors might be binary, ternary, or quaternary. Ternary semiconductors are made up of two different binary semiconductors that have one element in common. The other two elements are in the same group on the periodic table [18].

The energy bandgap of a compound semiconductor is contingent upon the band type of each constituent binary semiconductor. Semiconductor metal oxides are classified into two categories: n-type and p-type. N-type semiconductor metal oxides contain oxygen-vacancy donors that facilitate n-type conductivity, with electrons serving as the predominant charge carriers. P-type semiconductors exhibit a deficiency of metal ions, with holes serving as the predominant charge carriers [19]. Nonetheless, the electronic structure spectrum of these materials is broad, categorized primarily into two groups: transition and non-transition-metal oxides, with the latter encompassing both pre- and post-transition-metal oxides. In transition-metal oxides, the s-orbitals of cationic metal ions are consistently fully occupied by electrons, although their d-orbitals may be partially unoccupied. In transition-metal oxides, the energy difference between a cation dn configuration and either a d^{n+1} or d^{n-1} configuration is frequently minimal, facilitating rapid transformations among the various forms, albeit with unstable structures. This characteristic renders them more responsive to environmental factors compared to pre-transition-metal oxides [20].

Materials with d^0 and d^{10} electronic configurations, specifically pre- and post-transition-metal oxides, are noted for their stable properties. Pre-transition-metal oxides are typically anticipated to exhibit significant inertness because of their substantial band gaps, which hinder the formation of electrons and holes.

According to their electrical properties, materials can be divided into three categories: conductors, semiconductors, and insulators. Semiconductors are a broad family of crystalline solids that exhibit electrical conductivity and resistance similar to conductors and nonconductors (insulators). Because its structure contains very few free electrons (from additional impurities), it behaves at ambient temperature as an insulator [21].

Classification of Semiconductors

Semiconductor materials can be categorized into two main types according to their energy gap: intrinsic and extrinsic semiconductors.

1. Intrinsic semiconductors

This semiconductor is composed of a pure material devoid of impurities. In intrinsic semiconductors, the quantity of holes is equivalent to the quantity of electrons present in the conduction band. In an intrinsic semiconductor, the energy available at room temperature is adequate for valence electrons to transition to the conduction band.".

The unadulterated state of the semiconductor is referred to as the intrinsic semiconductor. An intrinsic semiconductor refers to a semiconductor material that has not been doped with any impurities.

Holes in the valence band represent vacancies resulting from electrons that have been thermally excited to the conduction band. An intrinsic semiconductor is capable to conduct a little current even at room temperature, but it is not useful for the preparation of various electronic devices [22].

2. Extrinsic semiconductors

The pure state of an extrinsic semiconductor material is altered through the introduction of impurities in very small amounts. The additional impurities are referred to as "dopant(s) or doping agent(s)." Based on the valence of doping materials, extrinsic semiconductors can be categorized into two distinct types: n-type and p-type

The semiconductor in which intentional impurities are added to enhance its conductivity is referred to as extrinsic semiconductors. Conductive materials are recognized as extrinsic semiconductors. The semiconductors that have been doped involve the introduction of holes or electrons through the incorporation of an impurity, which is a foreign atom. A semiconductor that has an impurity added at a controlled rate to enhance its conductivity is referred to as an extrinsic semiconductor.

Doping involves the incorporation of impurity atoms into the semiconductor lattice, therefore disturbing the crystal structure and forming either electron-deficient (P-type) or electron-rich (N-type) areas inside the material [23].

3. n-type semiconductor

The n-type semiconductor is formed when semiconductor materials like silicon and germanium are doped with pentavalent elements

4. p-type semiconductor

The term "P-type" refers to the "positive charge" caused by the addition of trivalent impurity atoms to silicon. In this example, the trivalent atom binds with four surrounding silicon atoms, creating a hole (with a positive charge) for each trivalent doping atom [24].

5. The p-n junction

In a single semiconductor crystal, the formation of a p-n junction occurs when p-type and n-type regions are present. In this junction, the "majority carriers" are found in the "holes" on the p-side and in the "electrons" on the n-side [25].

6. Band gap

The band gap, a fundamental feature of a semiconductor, dictates its electrical and optical capabilities. The capacity of materials to absorb light is intricately linked to their classification and characteristics, as characterized by their band gap energy (Eg). The band gap value in semiconducting materials significantly influences their potential applications across various scientific domains, such as photovoltaics, solar cells, photoelectrochemical cells, photoluminescence, lasers, and diodes [26].

The band gap is a defining characteristic of semiconductor materials, impacting various physicochemical properties and delineating the operational capabilities and constraints of contemporary semiconductor devices

Over the past few decades, band gap engineering has become a significant technique in the practical investigation of metal oxide nanoparticles.

Impurities may be introduced into semiconductors to establish energy levels within the band gap. Doping in semiconductors has been extensively studied both experimentally and theoretically due to its various applications, including enhanced luminescence, photocatalytic activity, band gap tuning, and improved electron transport. In solid-state physics, for insulators and semiconductors, band gap energy denotes the energy difference between the valence band maximum and the conduction band minimum. This is closely associated with the HOMO/LUMO gap in chemistry [27].

In an insulator or semiconductor, the energy band gap, Eg, exists between the occupied valence band, Ev, and the unoccupied conduction band at absolute zero (0 K). The band gap, or energy gap, refers to the difference in energy levels within a solid material that allows for the existence of electron states.

The band gap significantly influences the electrical conductivity of solids. Substances with large band gaps typically function as insulators, whereas those with smaller band gaps are classified as semiconductors. Conductors possess either very small band gaps or none at all, resulting from the overlap between the valence and conduction bands. The excitation of valence electrons into the conduction band results in an increase in the conductivity of a semiconductor. The energy gap in most semiconductors ranges from 0.1 to 6.2 eV [28].

Factors affecting Band Gap of Metal Oxide nanoparticles

1. **Synthesis Methods:** Various synthesis methods can result in different oxidation states of metal cations within the oxide structure, which in turn exhibit distinct contributions to the band gap based on their oxidation state. Manipulating the synthesis method allows for the customisation of the band gap in metal oxide nanoparticles for targeted applications.

2. **Particle Size:** The band gap energy increases as the particle size of semiconductor nanoparticles diminishes. The impact of size on band gap was investigated, revealing that for semiconductors with narrow to moderate band gaps, the band gap increases as size diminishes. As the particle size diminishes, the intervals between the bands expand due to the increase in lattice parameters corresponding to the reduction in diameter. Nanoparticles and nanostructures exhibit a similar trend in the variation of band gap energy; however, the band gap energy in nanostructures is lower than that in nanoparticles of equivalent size due to augmented lattice strain and a larger surface-to-volume ratio in nanoparticles compared to nanostructures of the same dimensions [29].

3. **Oxidation State:** The oxidation state of the metal cation in the oxide can affect the band gap. The various oxidation states of the metal cation can result in changes to the electronic structure and, consequently, the band gap.

4. **Temperature:** As temperature rises, the lattice structure of nanoparticles expands, influencing atomic spacing and electron energy levels. This may result in a reduction of the band gap. Elevated temperatures enhance electron mobility and lattice distortions, leading to a reduction in the bandgap width. Elevated temperatures decrease the bandgap of a semiconductor, consequently influencing various semiconductor material parameters. The reduction in the band gap of a semiconductor with rising temperature can be interpreted as an increase in the energy of the electrons within the material. The band gap of the nanoparticles decreases as the annealing temperature increases [30].

5. **Doping:** Doping metal oxides with rare earth metals offers the advantage of facilitating interactions with functional groups, attributed to the presence of 4f vacant orbitals. Doping rare earth metals induces an absorbance shift to the visible region of the electromagnetic spectrum, thereby enhancing photocatalytic activity in this range [31].

Synthesis of MOS Nanoparticles

Nanoparticle synthesis can be accomplished through either a "top-down" or "bottom-up" methodology. The top-down approach involves the size reduction of bulk materials to produce nanoparticles. The bottom-up approach involves the synthesis of nanoparticles through chemical, physical, and biological methods. Chemical and physical synthesis routes, specifically bottom-up approaches, are commonly utilized in the synthesis of MONPs, resulting in an efficient yield of nanoparticles [32].

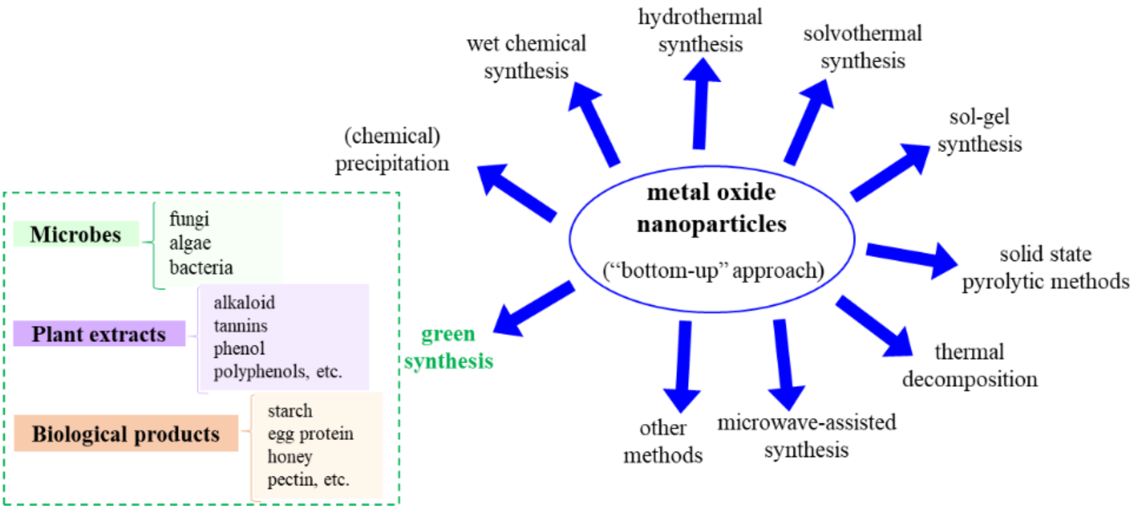

Figure 1. Possible metal oxide nanoparticle synthesis methods ("bottom-up" approach).

The synthesis methods of MONPs are categorised into two primary groups: (i) physical methods, including ball milling, sputtering, laser ablation, electrospraying, and electron beam evaporation; and (ii) chemical methods, comprising the sol–gel method, polyol method, hydrothermal method, co-precipitation method, microemulsion technique, and chemical vapor deposition. The primary advantage of chemical methods lies in their ability to produce particles with specific size, dimension, composition, and structure, which can be beneficial for applications in catalysis, sensing, and electronic devices [33].

1. Sol–gel method

The sol–gel method is a recognized synthetic approach for the preparation of high-quality metal oxide nanoparticles (MONPs) and mixed oxide composites. This method demonstrates superior control over the texture and surface characteristics of the materials. The sol–gel method comprises five essential steps: hydrolysis, polycondensation, aging, drying, and thermal decomposition

The sol-gel method has multiple advantages for the synthesis of materials, especially ceramics and thin films. These advantages include low-temperature synthesis, effective composition control, high purity, and the capability to produce fine powders. This method enables the customization of materials at the molecular level, resulting in improved properties. The sol-gel process enables the production of materials in diverse forms, such as fine powders and thin films, thereby facilitating their application in contexts requiring these specific forms [34].

The sol-gel method is versatile for producing materials with unique properties; however, it presents several drawbacks. These include high raw material costs, potential shrinkage and cracking during drying, challenges in achieving precise control over nanoparticle size and shape, and limitations in large-scale industrial production [35].

2. Coprecipitation method

Coprecipitation is a commonly employed method for synthesizing metal oxide nanoparticles and metal/ceramic nanocomposite. The concentration of starting reagents, pH, and heating effects significantly influence the size and shape of nanoparticles

Coprecipitation is the process of achieving a uniform conformation in a homogeneous solution with multiple cations through a precipitation reaction. This technique is a crucial method for synthesizing spinel nanoferrites that incorporate two or more types of metal elements. The coprecipitation method facilitates the rapid formation of homogeneous nanomaterials exhibiting diverse size distributions through various chemical reactions in solution [36].

The co-precipitation synthesis method has two significant disadvantages: the potential for impurities arising from secondary reactions and the challenge of regulating the nucleation and particle growth rates, which leads to a broad distribution of particle sizes

3. Hydrothermal method

The hydrothermal synthesis method is a highly effective technique for modifying the morphology of a prepared sample through adjustments in the synthesis conditions. Hydrothermal synthesis (HS) involves a process in which aqueous precursors undergo high-pressure and high-temperature conditions within a vessel and an autoclave reactor

Hydrothermal synthesis is a chemical process that takes place in an aqueous solution of mixed precursors at temperatures exceeding the boiling point of water. Hydrothermal synthesis allows for the omission of the calcination step. In hydrothermal synthesis, elevated temperatures enhance particle diffusion, resulting in rapid crystal growth. Hydrothermal synthesis is generally conducted in a closed system known as an autoclave, presenting fewer environmental concerns compared to various other powder production methods. Hydrothermal synthesis is an efficient, environmentally friendly, and cost-effective method for producing powders characterized by high uniformity and purity. Water temperature is a critical parameter in the hydrothermal synthesis process, as it influences the reaction rate, ionisation degree, particle size, and crystalline structure of powders [37, 38].

1. Advantages of Hydrothermal Method

The hydrothermal method offers the advantage of producing crystalline phases that remain stable at temperatures exceeding their melting points. The method effectively facilitates the growth of large, high-quality crystals while ensuring compositional control

2. Disadvantages of Hydrothermal Method

High cost of equipment such as autoclave, Safety issues during the reaction process, High reaction temperature. The reaction takes long time [39].

Green Synthesis of Metal Oxide Nanoparticles

The synthesis of metal/metal oxide nanoparticles has extensively utilized plant biodiversity, leveraging the presence of effective phytochemicals found in various plant extracts. Notably, leaves contain compounds such as ketones, aldehydes, flavones, amides, terpenoids, carboxylic acids, phenols, and ascorbic acids. The components possess the ability to reduce metal salts into metal nanoparticles. Given the constraints of current methods in nanomaterial synthesis, there is a necessity to develop environmentally sustainable approaches that are clean, non-toxic, and ecologically sound. This has initiated the development of "green nanotechnology" as a distinct field of study [80]. The application of green methods, including plant extracts, microorganism biomolecules, and industrial and agricultural wastes, represents effective techniques for synthesizing nanoparticles with reduced or negligible toxicity relative to conventional methods [40, 41]

In the synthesis of nanoparticles using plant leaf extract, the extract is combined with metal precursor solutions under varying reaction conditions.The parameters influencing the conditions of plant leaf extract are acknowledged to regulate the rate of nanoparticle formation, along with their yield and stability[83].Plant leaf extracts contain phytochemicals that exhibit significant potential for the rapid reduction of metal ions, in contrast to fungi and bacteria, which require extended incubation periods. Consequently, plant leaf extracts are regarded as a superior and non-toxic source for the synthesis of metal and metal oxide nanoparticles. Plants contain several key phytochemicals, including flavones, terpenoids, sugars, ketones, aldehydes, carboxylic acids, and amides, which play a crucial role in the bioreduction of nanoparticles [42, 43].

1. Advantages of Plants Extracts

A straightforward and cost-effective approach the temperature within the extraction system can be regulated

2. Limitations

Plants distributions, Raw material Values, Long reaction time, Uneven and irregular shape and size, low yield, low removal efficiency

Applications of Metal Oxide Nanoparticles

Metal oxide nanoparticles are recognized as one of the most promising nanomaterials across various fields, attributed to their distinctive physical and chemical properties, including thermal conductivity and heat transfer capabilities Metal oxide nanoparticles possess numerous applications, including microelectronics, energy storage, environmental decontamination, gas sensing, ceramic fabrication, biomedicine, and catalysis [44].

1. Gas Sensors

Semiconductor metal oxide gas sensors represent the most extensively studied category of gas sensors. Recently, size-modulated metal oxides (SMOs) ranging from 1 nm to 100 nm are increasingly utilized for gas sensing, attributed to their size-dependent properties.The research demonstrates that dopants or impurities improve the gas sensing characteristics of SMOs through various mechanisms, including alterations in microstructure or morphology, the formation of stoichiometric solid solutions, modifications to activation energy, the generation of oxygen vacancies, or changes in electronic structure and band gap [45].

Gas sensors have seen a rise in application within industrial production and everyday life in recent years. Metal oxide semiconductor gas sensing materials are preferred due to their excellent physical and chemical properties, cost-effectiveness, and simple preparation techniques [46]

Currently, gas sensors are extensively utilized in flammable detection, explosive detection, and environmental monitoring. Gas sensors have the potential for widespread application in the detection and warning of toxic and harmful gases. Nanostructured materials have garnered significant scientific interest due to their size-dependent physical properties and elevated surface-to-volume ratio [47].

2. Photocatalyst

Metal oxides hold significant technological relevance in environmental remediation and electronics due to their ability to generate charge carriers upon receiving the necessary energy input. The advantageous configuration of electronic structure, light absorption properties, and charge transport characteristics in many metal oxides facilitates their application as Photocatalysis. Among the various wastewater treatment technologies, photocatalysis has attracted significant attention because of its remarkable efficiency, cleanliness, and sustainability [48].

Various approaches to modifying photo catalysts have been explored, including doping with noble or non-noble metals, crystal facet engineering, physical deposition, dye sensitization, and the implementation of the Z-scheme photo catalyst system. The purpose of these modifications is to improve the catalytic properties of photo catalysts [49]

Photocatalysis is an efficient method for the degradation of various organic pollutants, dyes, and pathogenic viruses and fungi, utilizing UV or visible light from the solar spectrum. Metal oxides are regarded as promising photocatalysts due to their cost-effectiveness, efficiency, straightforward fabrication methods, ample availability, and environmental sustainability for photocatalytic applications [50]

Summary and Prospects

The present review work discusses the metal oxide nanoparticles and their synthesis routes. The applications of metal oxide nanoparticles in different field are also discussed.

We have provided compressive summary of band gap of metal oxide nanoparticles and the factors affecting the band gap of metal oxide nanoparticles. This review article includes all the important applications of metal oxide nanoparticles that will help further research.

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