



Transformative Potential of Nonmetal doped Transition Metal Oxide Nanoparticles for Multifaceted Applications

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Abstract

Nonmetal doped transition metal oxide nanoparticles (TMONPs) have attracted much attention from researchers due to their novel magnetic, optical, and electrochemical properties. Due to such distinct features of TMONPs, these are deemed suitable in applications such as super-capacitors, lithium-ion batteries, non-volatile memory circuits, energy management devices, energy storage, and conversion applications such as solar cells, and infrared detectors. From these discoveries outlined, the identification of specific developments such as catalysis, energy storage, environmental remediation, and biomedical applications can be outdone. This chapter represents a critical evaluation of the synthesis methods, doping techniques, characterization, and recent applications of non-metal doped TMONPs.



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Abbreviations

TMONPs - Transition Metal Oxide Nanoparticles

TMOs - Transition Metal Oxides

TiO₂ - Titanium Dioxide

ZnO - Zinc Oxide

Fe₂O₃ - Iron Oxide

OER - Oxygen Evolution Reaction

HER - Hydrogen Evolution Reaction

SEM - Scanning Electron Microscopy

TEM - Transmission Electron Microscopy

XRD - X-Ray Diffraction

EDX - Energy Dispersive X-Ray Spectroscopy

FTIR - Fourier-Transform Infrared Spectroscopy

BET - Brunauer-Emmett-Teller (Analysis)

TGA - Thermogravimetric Analysis

DTA - Differential Thermal Analysis

MRI - Magnetic Resonance Imaging

CNTs - Carbon Nanotubes

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ALD - Atomic Layer Deposition

GO - Graphene Oxide

GR-TiO₂ - Graphene-Titanium Dioxide Composite

CNDs - Carbon Nanodots

Introduction

Overview of Transition Metal Oxides

Transition metal oxides (TMOs) are compounds formed by oxygen atoms bonded to transition metals, elements found in groups 3-12 of the modern periodic table. These oxides tend to have diverse characteristics in terms of physical properties like high melting point, conductivity, variable oxidation states, etc., and chemical properties due to the diverse electronic configurations. Of the TMOs identified in Table 1, both the dopant and host materials exhibit a diverse range of applications,

including catalytic, electronic, optical, and magnetic applications specific to primarily titanium dioxide (TiO₂), zinc oxide (ZnO), and iron oxide (Fe₂O₃)¹. Figure 1 showcases the latest advancements in Transition Metal Oxides.

The chemical behaviour of TMOs is a result of the d-electrons being responsible for different oxidation states of the transition metals² and thus forming different bonds. It also allows TMOs to display low dielectric constants, flexibility in the band gap, and magnetic structures. For this reason, they are employed in various applications ranging from photo-catalysis for environmental remediation, energy storage in lithium-ion batteries,³ and optically transparent conductive oxides for optoelectronics devices.⁴

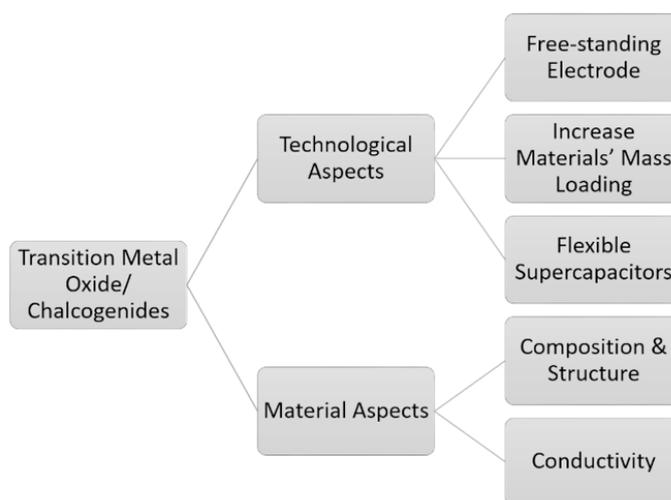


Fig. 1: Recent advances in Transition Metal Oxides

Advantages and Potential Applications of Nonmetals-Doped TMO nanoparticles (TMONPs)

Doping involves the introduction of impurities into a metal or semiconductor to deliberately alter its electrical, thermal, or structural properties. Further, doping can enhance conductivity, modify band structure, and improve the overall performance of the material for specific applications. Doping with nonmetal anions or molecules also shows a significant effect on the TMONPs by affecting the electronic structure. The chemical state and location of the dopant are crucial to the effectiveness of the doping process. The purpose of doping transition metal oxides with nonmetals is to enhance their

intrinsic properties like optical properties, thermal stability, electrical conductivity, magnetic properties, etc., and expand their applications. This chapter focuses on the recent progress in the nonmetal doping of TMONPs.⁵

Nonmetal dopants, such as nitrogen, sulphur, and carbon, lead to new energy levels within the band structure of the TMOs, thereby changing their electrical, optical, and catalytic properties.⁶ For instance, doping of nitrogen into TiO₂ can considerably decrease the band gap,⁷ which enables the material to be more effective in photocatalytic applications. Besides, doping enhances the

electrochemical properties of supercapacitors by providing higher energy density. Likewise, when sulphur is doped into ZnO, it can also show improved photocatalytic and photoelectrochemical behaviour because the presence of defective anions facilitates charge separation, thereby reducing the rate of recombination⁸. Also, sulphur-doped TiO₂ can improve lithium-ion diffusion,⁹ leading to higher battery capacity and faster charging.

Zhang *et al.*¹⁰ proposed that Carbon-doping into ZnO nanoparticles resulted in the reduced bandgap of ZnO, enhanced the separation efficiency of electron-hole pairs, and significantly boosted the photocatalytic performance under visible light.

Doping can also improve the charge carrier mobility, which is essential for applications in electronics and photovoltaics. Kim *et al.*¹¹ reported that Nitrogen-doped TiO₂ has been keen on exhibiting higher

electron mobility, resulting in better performance in dye-sensitized solar cells.

Nonmetal doping also participates in the regulation of the surface chemistry of TMONPs, which is crucial for catalytic processes.¹² Through the alteration of surface properties, nonmetal doped TMONPs serve more active sites for the reaction to happen and hence improve the catalytic activity. This mainly benefits photocatalytic water splitting, CO₂ reduction, and pollutant degradation reactions.

Further, doping in TMONPs provides biomedical advantages such as biocompatibility, targeted drug delivery, and good contrast for imaging. For instance, carbon-doped ZnO nanoparticles can serve as potential photodynamic agents for therapeutic applications and bioimaging.¹³ Figure 2 shows the potential applications of nonmetal doped TMONPs.



Fig. 2: Potential applications of nonmetal doped TMONPs

Furthermore, doping with nonmetals can develop the thermal and chemical stability of TMONPs, making them stronger for industrial applications. Incorporating nonmetals can also facilitate the

synthesis of nanostructured TMOs with controlled morphology and size, further enhancing their application potential [Refer to Table 1].

Table 1: Some examples of TMONPs with nonmetal dopant and their applications

Non-Metal Dopant	Tmonps	Synthesis Procedure	Applications	References
Nitrogen (N)	TiO ₂	conventional precipitation route	photocatalytic hydrogen generation	[69-91]
		Sol-gel method	Photocatalysis	
		Solvothermal synthesis	Degradation of benzene	
		Hydrothermal Synthesis	dye-sensitization of solar cells	
	ZnO	Hydrothermal Synthesis	Photocatalysis	
		Sol-gel method	Visible photocatalytic degradation	
Sulfur (S)	TiO ₂	Scaffold template technique	photocatalytic dye degradation	
		Ball Milling Process	Dielectric Properties	
		Hydrothermal synthesis	Degradation of methyl orange	
	ZnO	Sol-gel Method	Antibacterial activities	
		hydrothermal method	Optical properties study	
	α - Fe ₂ O ₃	Microwave synthesis	Photodegradation of methyl orange	
Carbon (C)	TiO ₂	Sol-gel	Visible-light photocatalysis	
		Hydrothermal synthesis	Use in optical devices	
	ZnO	Hydrothermal synthesis	Photocatalytic performance	
		Sol-gel	Magnetic properties	
Phosphorous (P)	Co ₃ O ₄	Hydrothermal Method	Hydrogen evolution	
	TiO ₂	Sol-gel Method	Photocatalytic properties under the solar light irradiation	
	ZnO	Sol-gel Method	Structural and Optical Properties study	
Iodine (I)	TiO ₂	Sol-gel Method	Photocatalytic and antibacterial activities	
		Hydrothermal synthesis	Improved dye degradation.	

Purpose and Scope of the Chapter

The present chapter aims to provide a comprehensive overview to disseminate the current understanding of the TMONPs doped with nonmetals.

- It aims at providing the methods used in doping and the changes that have occurred in the structural, optical, electrical, and magnetic properties, due to nonmetal doping.
- The areas highlighted for focus include the identification of several synthesis techniques.
- It also discusses various characterization methods used to describe the structural efficiency and functionality of doped TMONPs.
- In addition, the chapter focuses on their versatile applications in the field the energy and environment.

Materials and Methods

Synthesis of Transition Metal Oxide Nanoparticles Sol-gel Method

TMONPs can be synthesized using the sol-gel method, which entails transitioning a liquid "sol" (mostly colloidal) into a solid "gel" phase. For instance, titanium dioxide (TiO₂) nanoparticles can be synthesized from titanium alkoxides precursor, which on hydrolysis and poly-condensation produces a gel that on further drying and calcination, yields nanoparticles.¹⁴ MAM Khan *et al.*¹⁵ studied the synthesis of ZnO nanoparticles with different Mn doping concentrations by sol-gel wet chemical route. The sol-gel technique provides good control over the composition and structure of the nanoparticles, making it suitable for applications like catalysis and photo-catalysis.¹⁶

This method involves converting a liquid solution ("sol") into a solid ("gel") phase. For example, titanium dioxide (TiO₂) nanoparticles can be made using titanium alkoxides. The process includes following steps

- **Hydrolysis:** Titanium alkoxides react with water.
- **Condensation:** The products of hydrolysis react to form a gel.
- **Gel Formation:** A three-dimensional network forms, creating a gel.
- **Drying and Calcination:** The gel is dried and heated to produce nanoparticles.

Hydrothermal Synthesis

Hydrothermal synthesis involves the process of forming nanoparticles under high temperature and high-pressure conditions using water as a solvent, which is crucial for a well-crystallized and homogeneous structure of nanoparticles. Mohan *et al.* employed a hydrothermal method for the synthesis of zinc oxide (ZnO) nanoparticles using zinc nitrate and sodium hydroxide.¹⁷ The hydrothermal method is preferable when it concerns synthesizing nanoparticles of high purity that are perfect for use in sensors, electronics, and photocatalytic applications.^{18,19,20}

This method uses high temperature and pressure with water to form well-crystallized nanoparticles.

- **Dissolution:** Metal precursors dissolve in water.
- **Nucleation:** High temperature and pressure cause nanoparticles to form.
- **Crystal Growth:** Temperature and time control the size of particles.
- **Post-Treatment:** The product is washed and dried.

Co-precipitation Method

Co-precipitation synthesis method involves the instantaneous precipitation of multiple components from a homogeneous solution. For example, Bolivar *et al.* prepared iron oxide (Fe₃O₄) nanoparticles with a mixture of ferric and ferrous ions that are precipitated with a base such as ammonia, followed by magnetic field precipitation.²¹ Vijayaprasath *et al.* synthesized Ni/Mn co-doped ZnO nanoparticles to study their structural and magnetic behavior.²² Gandhi *et al.* synthesized cobalt doped ZnO nanoparticles by co-precipitation method and studied their magnetic properties.²³ This method is particularly useful for the mass production of nanoparticles bearing uniform size and composition, suitable for magnetic storage and bioimaging.²⁴

Here, multiple components precipitate from a solution at the same time.

- **Ionic Mixing:** Metal ions mix in a solution.
- **Precipitation:** A base is added to form insoluble hydroxides.

- **Aging and Transformation:** The hydroxides change into metal oxides.
- **Separation and Drying:** The product is filtered, washed, and dried.

Other Relevant Methods

Other synthesis processes comprise combustion synthesis,²⁵ microwave-assisted synthesis,²⁶ and electrochemical deposition.²⁷

Combustion Synthesis

- **Precursor Preparation:** Mix metal precursors with a fuel.
- **Ignition:** Trigger an exothermic reaction to generate heat.
- **Particle Formation:** Particles form during combustion.
- **Cooling and Collection:** Collect particles after cooling.

Microwave-Assisted Synthesis

- **Precursor Solution:** Dissolve metal salts in a solvent.
- **Microwave Heating:** Apply uniform heating to promote rapid particle formation.
- **Particle Growth:** Control reaction conditions to shape and size particles.
- **Cooling and Collection:** Collect and purify the nanoparticles.

Electrochemical Deposition

- **Electrolysis:** Reduce metal ions at the cathode.
- **Deposition:** Regulate voltage to control film thickness.
- **Crystallization:** Improve nanoparticle quality through heating.

Michalow *et al.*²⁸ employed the combustion method to synthesize Niobium-doped titanium dioxide nanoparticles by burning a pre-formed paste made of a titanium precursor and a niobium salt.

Falk *et al.*²⁹ synthesized anatase TiO₂ nanoparticles by microwave-assisted synthesis to induce high photocatalytic activity with increased crystallinity and phase transformation. Electrochemical deposition offers the opportunity to fine-tune both the size and composition of the deposited nanoparticles using the electrochemical parameters. Altogether, these synthesis methods offer flexible routes to synthesize high-performance TMONPs.

Summary of Benefits, Challenges, and Efficiency

- **Combustion Synthesis:** Rapid, high-yield process with a simple setup but prone to particle agglomeration. Efficient for large-scale production but offers limited control over particle size and morphology.
- **Microwave-Assisted Synthesis:** Fast, energy-efficient method with uniform heating but requires specialized equipment. Highly efficient but limited to materials that absorb microwave radiation.
- **Electrochemical Deposition:** Provides precise control over film thickness and composition but has a complex setup. Efficient for thin films but restricted to conductive substrates.

Figure 3 shows a few other methods to synthesize nonmetal doped TMONPs.

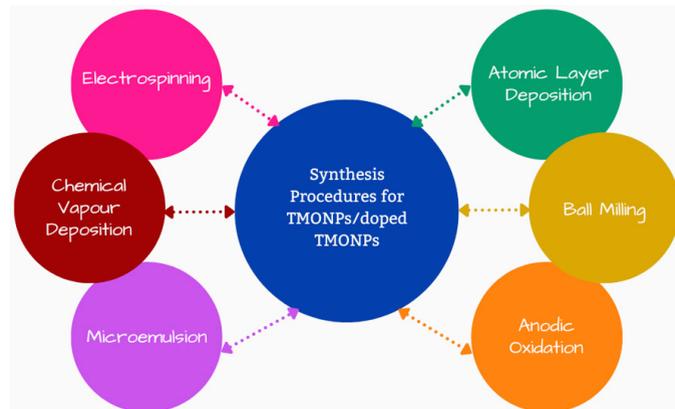


Fig. 3: Methods to synthesize nonmetal doped TMONPs

Doping Techniques

Chemical Doping

Chemical doping involves introducing dopant atoms into the host material during synthesis by evenly distributing dopants within the host material. For instance, Darzi *et al.* synthesized nitrogen-doped titanium dioxide (TiO₂) nanoparticles using a sol-gel method with an acid catalysis process, resulting in the desired narrowing of the band gap and an enhancement in the photocatalytic activity.³⁰ Than *et al.* synthesized N-doped TiO₂ nanoparticles, where the nitrogen atoms replace oxygen atoms in the TiO₂ lattice, resulting in a reduced band gap and enhanced visible-light-driven photocatalytic activity.³¹

Physical Doping

Physical doping refers to techniques where dopant atoms are physically introduced into the host nanoparticles, often after the initial synthesis. This can be done through ball milling, thermal diffusion, or sputtering.³² Cho *et al.* successfully synthesized sulfur-doped ZnO nanostars using a chemical vapor

deposition method³³ and studied the significant influence of sulfur doping on the morphology of ZnO nanostructures, paving the way for photocatalysis, sensing, and other fields.

Ion Implantation

Ion implantation is the process where the dopant ions are purposely directed and embedded in the host material with the help of an ion beam.³⁴ As reported by Shieh *et al.*, cobalt ions can indeed affect the optical properties of TiO₂ thin films leading to enhanced visible light response and different photoluminescence characteristics.³⁵

The doping techniques mentioned above and many other methods such as Spin-coating,³⁶ In-situ doping,³⁷ Photolithography,³⁸ and Diffusion doping are some of the most efficient ways of increasing the properties of transition metal oxide nanoparticles, enabling their use in a broad range of applications. Table 2 shows the TMONPs with nonmetal doping and their key properties.

Table 2: Nonmetal doped TMONPs with their key properties

TMONPs	Doping Element	Synthesis Method	Key Properties	References
TiO ₂	N	Precipitation Method	Reduced band gap, enhanced visible light absorption	65-69
Fe ₂ O ₃	C	Sol-gel method	Enhanced magnetic properties, Increased surface area	
ZnO	S	Combustion method	Improved electrical conductivity, Additional active sites	
NiO	B	Pyrolysis method	Improved thermal stability, Enhanced electrochemical performance	
Co ₃ O ₄	N	Hydothermal Method	Enhanced catalytic activity, reduced activation energy	

Characterization Techniques

X-ray Diffraction (XRD)

X-ray diffraction (XRD) is extensively used to identify phases, assess the crystalline quality, and determine the crystallite size in transition metal oxide-based nanoparticles. Doping affects the crystal structure by disrupting the crystalline symmetry of the material, altering the lattice constants, inhibiting structural distortions, and reducing crystallinity.³⁹ So, crystallographic analysis can also reveal how doping affects the crystal structure to enhance material properties.⁴⁰

Scanning Electron Microscopy (SEM)

SEM provides surface images of nanoparticles illustrating their morphology and size. Nair *et al.* explained that the SEM images of undoped ZnO have a slightly smaller grain size than Co-doped ZnO.⁴¹ Vu *et al.* illustrated the morphology of nonmetal doped TiO₂ nanotubes with a diameter ranging from 20 to 30 nm and a length of 150 to 200 nm.⁴²

Table 3: Showing Characterization techniques and its significance

Sl.No.	Characterization Method	Description	Purpose	Key Parameter Analyzed	Significance	Alternate Techniques
1	UV-Vis Spectroscopy	Measures absorbance across UV-visible wavelengths.	Analyze optical properties of nano-particles	Band gap energy, absorbance spectrum	Provides size and electronic structure information.	Photoluminescence Spectroscopy (PL), Raman Spectroscopy
2	FTIR (Fourier Transform Infrared Spectroscopy)	Measures infrared absorption to analyze functional groups.	Identify chemical bonds and functional groups	Vibrational frequencies of functional groups	Identifies chemical bonds and surface functionalization.	Raman Spectroscopy, XPS (X-ray Photoelectron Spectroscopy)
3	XRD (X-ray Diffraction)	Analyzes crystal structure and phase purity.	Determine crystalline structure	Crystal structure, phase identification	Provides crystallinity and phase identification.	SAED (Selected Area Electron Diffraction), TEM
4	FESEM (Field Emission Scanning Electron Microscopy)	Captures high-resolution images for surface morphology.	Visualize surface morphology	Particle size, surface topography	Determines nanoparticle morphology and size distribution.	TEM, AFM (Atomic Force Microscopy)
5	EDX (Energy Dispersive X-ray Spectroscopy)	Performs elemental analysis by detecting X-ray emissions.	Identify elemental composition	Elemental composition, impurity detection	Provides elemental composition and distribution.	ICP-MS (Inductively Coupled Plasma Mass Spectrometry), XPS
6	Zeta Potential	Measures surface charge and stability in colloidal suspensions.	Measure colloidal stability	Surface charge, stability	Provides insight into colloidal stability and aggregation.	DLS (Dynamic Light Scattering), Electrophoretic Mobility
7	Impedance Spectroscopy	Measures electrical impedance across frequencies.	Analyze electrical properties	Conductivity, resistivity, dielectric constant	Provides electrical and dielectric properties.	Electrochemical Impedance Spectroscopy (EIS), Conductivity

						Measurements
8	BET Surface Area Analysis	Measures surface area via gas adsorption.	Measure surface area and porosity	Surface area, pore volume	Provides surface area, pore volume, and distribution, crucial for catalysis.	BJH (Barrett-Joyner-Halenda) Method, Mercury Porosimetry
9	TGA/DTA (Thermogravimetric Analysis / Differential Thermal Analysis)	Measures weight loss and heat flow with temperature variation.	Analyze thermal stability	Weight loss, decomposition temperature	Provides thermal stability and decomposition information.	DSC (Differential Scanning Calorimetry)
10	NMR (Nuclear Magnetic Resonance)	C13 and proton NMR analyze molecular structure and dynamics.	Determine molecular structure	Chemical environment, bonding	Provides chemical environment and structure information.	Mass Spectrometry (MS), EPR (Electron Paramagnetic Resonance)
11	Cyclic Voltammetry	Studies redox behavior via cyclic voltage sweeps.	Analyze redox properties	Redox activity, electron transfer	Provides electrochemical properties and reaction kinetics.	Potentiostatic Methods, Chronoamperometry

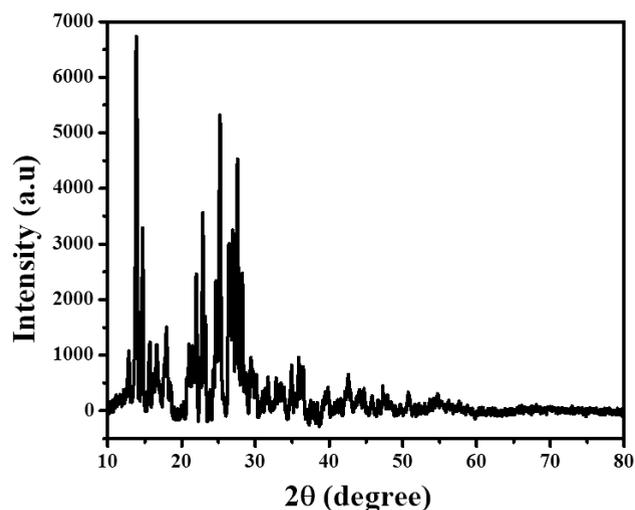


Fig. 4: Showing XRD of Materials

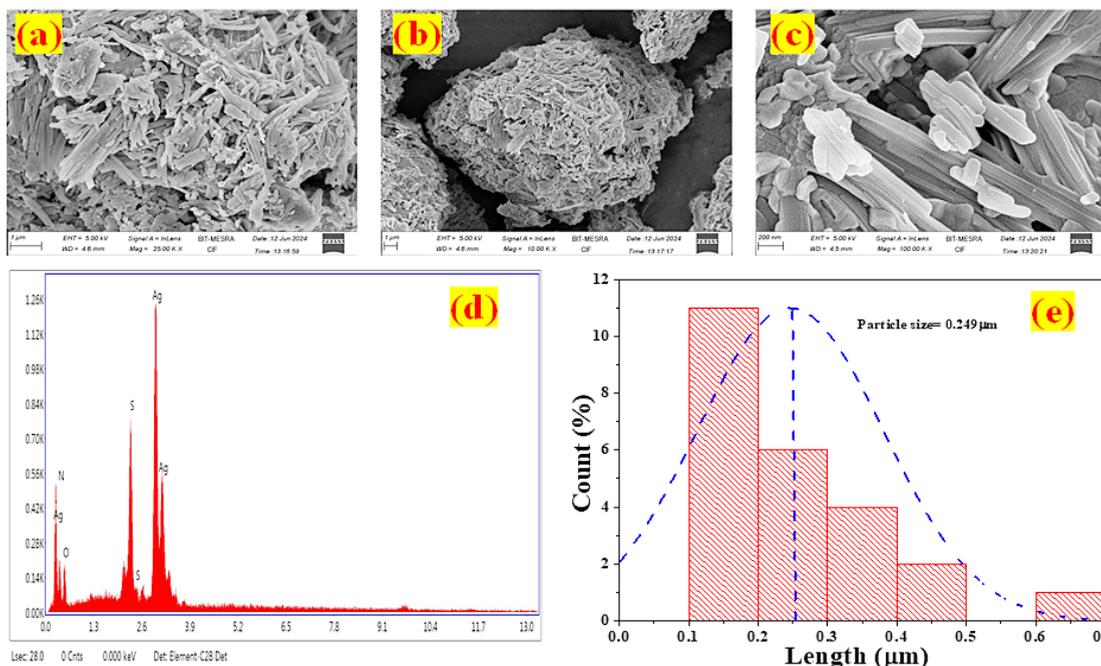


Fig. 5: Showing: FESEM EDX analysis of materials

Transmission Electron Microscopy (TEM)

TEM offers high-resolution imaging and can identify the lattice structure of the nanoparticles. Anandan *et al.* showed the particle diameter estimation via TEM, which revealed an average diameter of approximately 29 nm for pure TiO₂ and 21 nm for 1 wt% IO₃⁻ doped TiO₂.⁴³ Ahmmad *et al.*⁴⁴ analyzed the TEM images and explained that each sub-microsphere comprises aggregated TiO₂ nanoparticles ranging in size from 20 to 40 nm, exhibiting rough surfaces, confirming the polycrystalline nature of the anatase and rutile phases within the TiO₂ sub-microspheres.

Fourier-Transform Infrared (FTIR) and Raman Spectroscopy

FTIR and Raman spectroscopy can identify chemical bonds and molecular structures, essential for analyzing dopant effects on the nanoparticle. Khalid *et al.* studied the FTIR spectra for GO, TiO₂, and GR-TiO₂ composite samples, revealing the disappearance of the C=O peak at 1720 cm⁻¹ in the GR-TiO₂ sample, which signifies the reduction of GO to graphene during the hydrothermal process.⁴⁵ Caratto *et al.*⁴⁶ prepared Nitrogen-doped TiO₂ nanoparticles on glass substrates to verify homogeneity. Raman spectroscopy analysis reveals

a peak at 146 cm⁻¹, related to O–Ti–O bending vibrations, shifted towards lower wavenumbers (up to 140 cm⁻¹ for 15% ammonia), indicating the presence of N³⁻ ions in interstitial sites.

Other Techniques

Several other techniques are also gaining popularity for characterizing transition metal oxide nanomaterials. These techniques include UV-visible spectroscopy,⁴⁷ Atomic Force Microscopy (AFM),⁴⁸ Brunauer-Emmett-Teller (BET) analysis,⁴⁹ Thermogravimetric Analysis (TGA),⁵⁰ and Differential Thermal Analysis (DTA). Researchers also utilize TGA/DTA to study the thermal performance of samples. Energy-dispersive X-ray (EDX),⁵¹ often coupled with SEM or TEM, provides elemental analysis and mapping, confirming the presence and distribution of dopants.

Zeta Potentials

The zeta potential is a measure of the surface effective electric charge of nanoparticles, which is determined by their charge stability. The zeta potential indicates the particle's ability to move when an electric field is applied. The stability of particles improves with increasing magnitude, with particles

agglomerating in the 0-5 mV range, remaining highly stable at 40 mV and above. The zeta potential somewhat stable in the 20-40 mV range, and being was determined using the Zetasizer Nano ZS.

Table 4: Showing Zeta potential value and its significance

Application	Description	Zeta Potential Range (mV)	Significance of Material (26.2 mV)
Water Treatment	Positive zeta potential attracts and absorbs negatively charged contaminants (e.g., anionic dyes, organic pollutants, heavy metal anions). Suitable for coagulation and flocculation processes in water purification.	+20 to +40 (moderate stability)	The material's zeta potential (+26.2 mV) ensures sufficient stability for coagulation and adsorption in water purification.
Catalysis	Positive surface charge enhances interactions with negatively charged reactants, facilitating specific oxidation or reduction reactions.	+20 to +30	The material's charge allows it to interact effectively with anionic reactants, benefiting catalytic applications.
Drug Delivery	Positive zeta potential aids in interacting with negatively charged cell membranes for targeted drug delivery. Moderate stability ensures dispersion in biological fluids while allowing aggregation under specific conditions for controlled drug release.	+20 to +30 (stable dispersion)	The material's moderate stability ensures good dispersion in biological fluids while retaining its charge for drug delivery.
Agriculture	Positively charged particles interact with negatively charged soil components or plant roots, aiding in the delivery of nutrients or agrochemicals.	+20 to +40 (suitable stability)	The material's stability and positive charge make it effective for delivering nutrients or agrochemicals in soils.
Energy Storage	Materials with moderate stability and uniform charge distribution are suitable for supercapacitors or batteries. Positive zeta potential suggests potential use as an electrode material due to good dispersion in liquid electrolytes.	+20 to +40	The material's zeta potential ensures uniform dispersion in liquid electrolytes, enhancing its potential as an electrode.

Nanomaterials Monodispersity and positive charge in Coatings or Inks ensure even distribution, making the material ideal for uniform film formation in coatings.	+20 to +40	The material's positive charge and stability enhance its application in coatings, ensuring uniform distribution.
It can be used in stable ink or paint formulations.		

Results

The study examined the effects of nonmetal doping on the properties of transition metal oxide nanoparticles (TMONPs). Results showed that XRD analysis confirmed changes in lattice parameters, with nitrogen-doped TiO₂ showing reduced crystallite size, promoting better surface reactivity. SEM and TEM revealed uniform, smaller particles with increased surface roughness, crucial for catalytic and electrochemical applications. UV-Vis spectroscopy showed a bandgap reduction in nitrogen and carbon-doped ZnO, enhancing visible light absorption. FTIR spectra confirmed dopant-induced vibrational shifts, highlighting modifications in chemical bonds. Impedance spectroscopy showed increased conductivity in sulfur and nitrogen-doped ZnO, attributed to improved charge carrier mobility and reduced recombination rates. Cyclic voltammetry revealed enhanced redox activity, particularly in sulfur-doped NiCoOx nanorods. Nonmetal-doped TMONPs demonstrated higher photocatalytic degradation rates of organic pollutants, while carbon-doped ZnO showed superior phenol degradation under visible light.

Discussions

Nonmetal-doped TMONPs exhibit enhanced performance due to synergistic effects between the host lattice and dopants. Dopants create lattice distortions, forming oxygen vacancies and mid-gap states, which reduce crystallite size and increase active surface area. Carbon and sulfur doping introduce mid-gap states near the conduction band, enabling visible light absorption and broadening the material's applicability in photocatalysis and solar cells. Sulfur doping introduces defective anions, facilitating charge separation, leading to increased photocatalytic efficiency and electrochemical performance. Nitrogen doping enhances electron mobility, benefiting supercapacitors and dye-sensitized solar cells. Surface chemistry changes

due to nonmetal doping create more reactive sites, making these materials suitable for pollutant degradation, hydrogen evolution reactions, and CO₂ reduction. Carbon-doped ZnO's photodynamic properties and stability support targeted drug delivery and bioimaging, while Ag-Fe₂O₃ nanoparticles show potential as antibacterial agents. Nonmetal doping enhances thermal and chemical stability, crucial for industrial scalability, and maintains structural integrity under high-temperature applications, supporting their use in supercapacitors and energy devices.

Applications of Nonmetal Doped TMONPs Photocatalysis

Nonmetal doped TMONPs exhibit enhanced photocatalytic properties due to their unique electrical properties, high surface area, suitable band gap, and presence of active sites.⁵² Due to these properties, they are widely used in various photocatalytic applications, such as photocatalytic water splitting including both oxygen evolution reaction (OER) and hydrogen evolution reaction (HER). Ansari *et al.*⁵³ reported that N-doped TiO₂ enhances photocatalytic efficiency enabling broad solar spectrum absorption for water splitting reactions. The nitrogen doping subsequently reduces the band gap enabling it to absorb visible light and generate more charge carriers to facilitate the splitting of water molecules to produce oxygen and hydrogen, contributing to sustainable hydrogen production for fuel cells. Zhang *et al.*⁵⁴ studied that Sulfur doped ZnO facilitated oxidation of CO and reduction of NOx, contributing to air purification and emission control. Qu *et al.*⁵⁴ demonstrated the potential of phosphorus-doped cobalt sulfides as efficient and stable electro-catalysts for hydrogen evolution, highlighting the importance of rational design in developing advanced catalytic materials. Figure 4 shows the advantages of nonmetal doped TMONPs for photocatalytic applications.

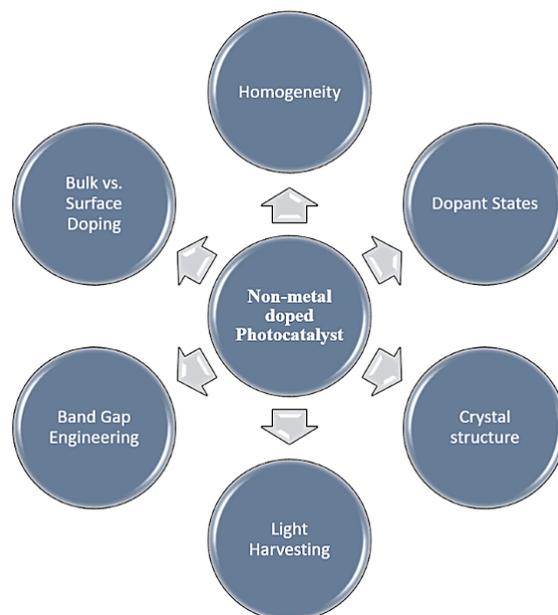


Fig. 6: Advantages of nonmetal doped TMONPs as photocatalysts

Electrocatalysis

Nonmetal doped TMONPs serve as efficient electrocatalysts to accelerate electrochemical reactions essential for energy conversion and storage technologies. Li *et al.*⁵⁶ stated that S-doped NiCoOx nanorods exhibit efficient OER catalysis with increased active surface area and enhanced electronic states due to sulfur incorporation, further improving water-splitting performance, and highlighting a promising system for practical hydrogen production.

Pollutant Degradation

Nonmetal doped TMONPs play an active role in the degradation of pollutants in both water and air purification processes. Yu *et al.* demonstrated that C-TiO₂ nanoparticles exhibit superior visible light photocatalytic activity for phenol degradation due to effective charge transfer and prolonged lifetime of photogenerated charges.⁵⁷ Similarly, N-doped TiO₂ nanoparticles have demonstrated effective degradation of airborne pollutants under visible light by facilitating the breakdown of various air pollutants as studied by Wang *et al.*⁵⁸

Supercapacitors

Supercapacitors bridge the gap between batteries and dielectric capacitors by offering both higher power density and higher energy density. The

electrode materials used in supercapacitors need to be conductive and possess a high surface area.⁵⁹ Consequently, TMONPs, are favored because of their superior specific capacitance and extended cycle life.⁶⁰ Lin *et al.* showed that nitrogen-doped carbon nanotubes (CNTs) combined with transition metal oxides like MnO₂ NPs result in supercapacitors with high specific capacitance with excellent cyclic stability.⁶¹ Vinothkumar *et al.*⁶² synthesized calcium-doped copper oxide nanoparticles to be used as an efficient bifunctional electrocatalyst for various supercapacitor applications.

Drug Delivery and Bioimaging

Nonmetal doping increases the surface area and active sites of TMONPs, allowing for higher drug loading capacity. It can improve the responsiveness of TMONPs to external stimuli (e.g., pH, temperature), enabling controlled and sustained release of therapeutic agents.

El-Bassuony *et al.*⁶⁴ reported Ag-Fe₂O₃ nanoparticles as potential antibacterial agents in drug delivery systems and for magnetic resonance imaging (MRI) contrast enhancement.⁶³ Bajpai *et al.* investigated the synthesis and multifunctional applications of nitrogen and phosphorus-doped carbon nanodots (N, P-doped CNDs). The research

highlights the utility of N, P-doped CNDs in cellular bio-imaging. Their strong fluorescence properties enable effective imaging of cells, making them suitable for diagnostic and research purposes .

Table 5: A comparative analysis of non-metal doped and undoped transition metal oxide nanoparticles

Property	Undoped Transition Metal Oxide Nanoparticles	Non-Metal Doped Transition Metal Oxide Nanoparticles
Band Gap Energy	Typically wide band gaps, limiting visible light absorption.	Reduced band gaps, enhancing visible light absorption. For instance, sulfur-doped ZnO exhibits a band gap of 2.81 eV, compared to 3.2 eV for undoped ZnO.
Photocatalytic Activity	Limited activity under visible light due to larger band gaps.	Enhanced activity under visible light. Sulfur-doped ZnO showed an 81.4% degradation efficiency for organic dyes under solar irradiation.
Structural Properties	Retain intrinsic crystal structures with minimal defects.	Introduction of dopants can induce defects or oxygen vacancies, influencing properties. For example, nitrogen-doped ZnO nanoparticles exhibit a reduced crystallite size of 12 nm.
Mechanism of Property Enhancement	Properties are intrinsic to the material's composition.	Dopants introduce mid-gap states or modify electronic structures, facilitating visible light absorption and improved charge separation. Nitrogen doping in ZnO creates localized states above the valence band, reducing the band gap.

Conclusion

The doping of nonmetal into transition metal oxides showcases highly improved structural, optical, electrical, and magnetic properties of the TMONPs. It is feasible to use sol-gel, hydrothermal, or co-precipitation synthesis methods to produce doped TMONPs. The characterization techniques which include XRD, SEM, TEM, and EDX, can assist in determining the structural and morphological parameters. Nonmetal doping of TMONPs finds applications in catalysis, energy storage, environmental, and biomedical sectors, which reveals their multifunctional and versatile applications. Nonmetal doped TMONPs hold significance in advancing both environmental remediation and energy applications. Their potential to degrade industrial pollutants in ambient conditions will lead to advancements in photocatalytic environmental remediation. Further, nonmetal doped TMONPs play an important role in sustainable energy through their

superior electrical and optical properties, thereby increasing the efficiency of solar cells, fuel cells, and supercapacitors.

Ongoing research is also concentrating on innovative doping technologies, including plasma-assisted doping and atomic layer deposition, to gain precise oversight on dopant distribution and concentration for improved performance. Interdisciplinary techniques combining materials science, chemistry, and engineering are being applied to fully realize the potential of nonmetal doped TMONPs to resolve some global issues related to environment and energy contributing to a cleaner and sustainable world.

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This research did not involve human participants, animal subjects, or any material that requires ethical approval.

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This study did not involve human participants, and therefore, informed consent was not required.

Permission to Reproduce Material from other Sources

Not applicable.

Author Contributions

- **Rajesh Kumar:** Conceptualization, writing original draft and data interpretation.
- **Shruti Jaiswal:** Designed the chapter content and data analysis.
- **Rudhima Raj:** Draft and data analysis.
- **Dr. Anil Kumar Delta:** supervision, writing original draft and data interpretation.
- **Dr. Smriti Singh:** Conceptualization, visualization, supervision, writing original draft and data interpretation

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