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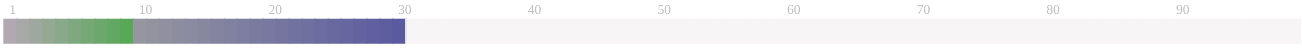

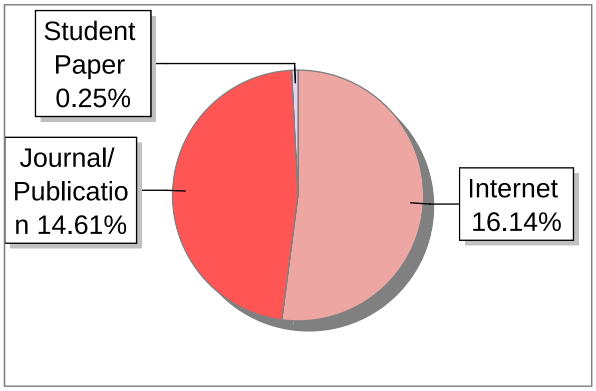

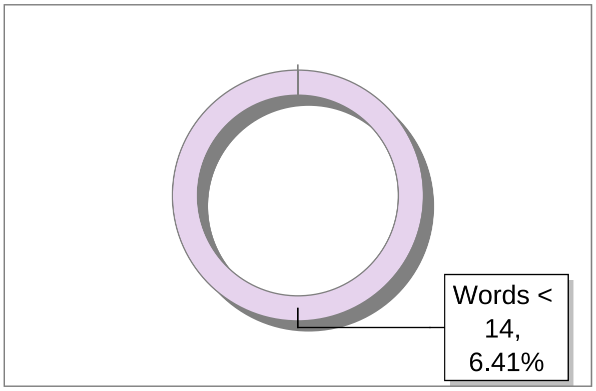

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A comprehensive review on Advancements in Metal Oxide photocatalysis: Exploring Ternary and Binary Systems

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Abstract:

Metal oxide have emerged as distinguished candidates for photocatalysis, presenting sustainable answers for harnessing solar power and environmental remediation. This evaluation delves into recent tendencies in each binary and ternary metallic oxide as photocatalysis. Binary oxides, together with titanium dioxide (TiO2) and Zinc oxide (ZnO), have been significantly studied, but their barriers have spurred investigated into ternary systems. Ternary metal oxide (TMOs), incorporating three one of a kind metallic factor, exhibit better photocatalytic properties due to synergistic consequences arising from diverse digital and optical traits. This summary gives a view of compositions of binary and ternary metallic oxides, emphasizing their roles in tactics like water splitting, pollutant degradation and hydrogen manufacturing. The challenges and future possibilities in metal oxide photocatalysis also are mentioned, highlighting the possible combination of binary and ternary metal oxides with their roles. At the same time as binary metallic oxides have laid the foundation for photocatalysis, the inherent boundaries have inspired the investigation of ternary counterparts, unveiling synergistic results that decorate performance. TMOs photocatalysts exhibit various compositions and programs, showcasing their potential in addressing global challenges. Understanding mechanisms consisting of price carriers, surface states, and doping techniques gives important insights for optimizing each binary and ternary systems. This overview underscores the significance of modern substances layout and synthesis techniques to liberate the total potential of metal oxide photocatalysts. As studies in this discipline keeps, metal oxides stand poised to contribute substantially to a sustainable and cleanser future.

Keywords: Metal oxide, Binary and ternary metal oxide, Photocatalyst.

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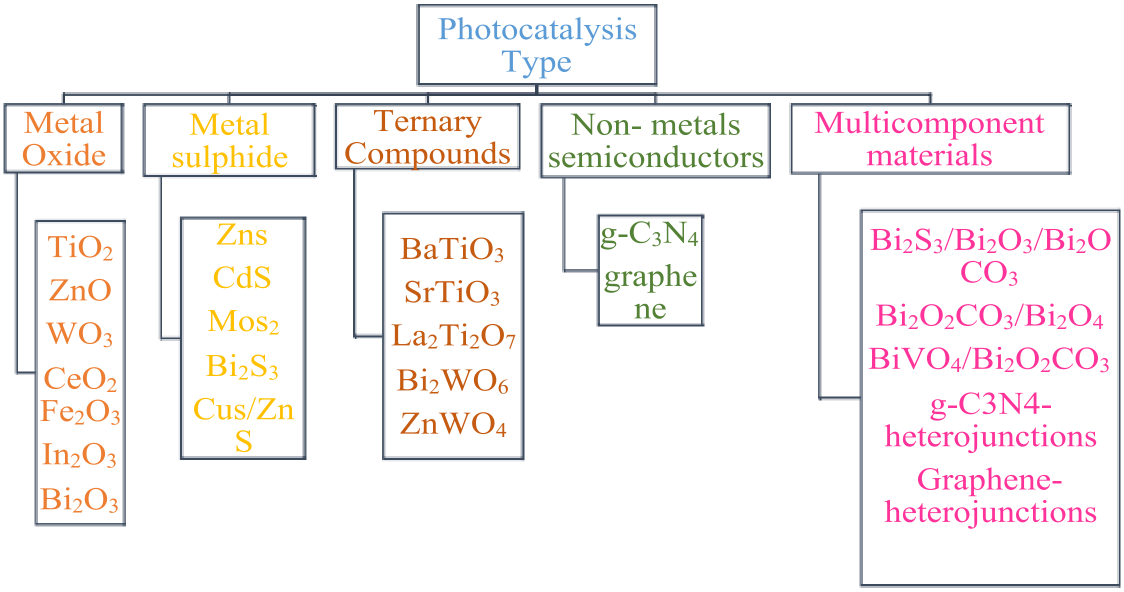
Introduction:

Water covers across the earth is about (70%) of planet's surface. Water which is smooth and secure is essential to all residing beings [1]. It plays a vital role in biological process including hydration, digestion and cellular functions. Human activities, industrial process, and agriculture have significant impacts on water quality and availability. Issues such as water pollution, over extraction of ground water, and climate change can affect the balance of water resources. Sustainable management of water is crucial for maintaining ecosystem and ensuring the well- being of human societies. Due to fast increasing industrialization and world population is mainly responsible for water pollution, because hazardous waste is directly mixed into the water and it is not only effect on human but also aquatic life which present in water [2]. During each year about 1.8 million children are dying due to drinking polluted water, [3-4] also lot of diseases causes due to polluted water and thus purification of water is paramount importance. However, availability of surface water mostly invariable and also qualities of water is always being declined due to continuous release of chemicals direct to environment, mainly due to aggravation of agricultural, industrial, domestic, pharmaceutical, etc. production [5-6]. There are a lot of techniques used for water purification. Now a days purification of water is carried out usually form physical and chemical techniques like UV treatment, chlorination, ozonation, etc. Purification techniques are depending on the region, available sources and also pollutants present in water [7-11].

Photocatalysis plays crucial role in the development of sustainable technologies, particularly in the context environmental protection clean energy production. Photocatalysis is a process that uses light to activate a substance (catalyst) to speed up a chemical reaction. The catalyst involved in photocatalysis is typically a semiconductor material that absorbs photons of light and uses that energy to drive a chemical reaction. This process is widely studied and applied in various fields, including environmental remediation, water purification, and energy conversion. In this process it utilizes solar energy or UV- Visible light for degradation of organic pollutants into inorganic particle [12-18]. Since there are a variety of metallic semiconductor which used as a photocatalytic material such as (TiO_2, CaO, ZnO, Wo_3, $ZnWO_4$, ZrO_2, $BiTiO_3$, $SrTiO_3$, Fe_2O_3, Ag_2CO_3, BiOBr, BiOCl, $CaFe_2O_4$, BiOCl, $ZnFe_2O_4$) and metal sulphide such as (ZnS, CdS, $CuInS_2$, $AgIn_5S_8$ etc.) Metal oxide have gained significant attention in the field of photocatalysis due to their unique properties and potential applications in various environmental and energy- related process. It's important to note that the effectiveness of a photocatalyst depends on various factors, along with specific application, light source, and target molecules. Researchers continue to explore and develop new material oxide photocatalysts for improved performance and expanded applications. Depending upon the properties of metal oxide there are a various type of photocatalysis found in nanoscience which are used for water purification. Some of them are listed below [19-33].

Fig.No.1: Types of Photocatalysis used to remove pollutants from water.



There are a various deposition techniques are used to deposit above metal oxide in nanoscale range like a thin layer on glass/conducting plate or as an electrode [34]

Table No.1: Thin film deposition Techniques with materials and application.

Sr.No.	Deposition Method	Thin film material	Application
1.	Ultrasonic Spray Pyrolysis	ZnO, SnO_2-Fe_2O_3, TiO_2, Gd-CeO_2	Solar cell, sensors, Metal oxide coating, solid oxide fuel Cell, Photocatalysis [35]
2.	Chemical Bath Deposition Method	ZnS, PbS, ZnO	Solar cell, Optoelectronics, Photocatalysis [36-38]
3.	Successive Ionic Layer Adsorption and reaction (SILAR)	CdO, ZnO, CuO	Gas Sensing, Photocatalysis, Supercapacitor [39-41]
4.	Sol-gel Method	TiO_2, TiO_2-SiO_2, CZTS	Solar cell, Photocatalysis, Gas Sensing Self-Cleaning [42-45]
5.	Electrodeposition	Cu_2O, Ga:CdS, $Co(OH)_2$, WO_3	Optoelectronics, Solar cell, Supercapacitor, Photocatalysis [46-49]
6.	Chemical Vapour Deposition (CVD)	B: ZnO, F: Mn_3O_4	Solar cell, Optoelectronics, Photocatalysis, Gas sensing [50-51]
7.	Plasma enhanced-Chemical Vapour deposition	TiO_2, SiO_2	Antireflecting coating, dielectric and biomedical applications, Photocatalysis [52-55]
8.	Magnetron Sputtering	TiO_2-SiO_2, CdTe,	Photocatalysis, Solar cell [56-57]
9.	Triode Sputtering	AlN, In_2O_3	Surface acoustic wave application, photovoltaic and optoelectronic application [58-59]
10.	DC sputtering	TiO_2, ITO, Mn_3N_2	Photocatalysis, Photovoltaic, Supercapacitor [60-62]
11.	Flash evaporation	A-$FAPbI_3$, CdTe	Solar cells [63-64]
12.	Laser Evaporation	$NiMoS_2$, TiO_2/Au/TiO_2	Dye- sensitized solar cells, Photocatalysis [65-66]

Photocatalysis:

Photocatalysis refers to the acceleration of a chemical reaction through the absorption of light by a substance known as a photocatalyst. Photocatalysis is a process that involves the use of a catalyst to accelerate a photoreaction, typically driven by light. Efficiency of photocatalysts depends on various factors such as bandgap, charge carrier mobility, surface area, ability to suppress recombination Photocatalysis. In this process light is used to activate catalyst to speed up chemical reaction. Fujishima et al. use TiO$_2$ as a photocatalyst for the production O$_2$ and H$_2$ from water and discovered water photolysis [67]. For expansion in other potential application and to improve the photocatalytic efficiency the simple binary metal oxide or metal free semiconductor, such as ZnO, TiO2, WO3, etc have been widely studied as a photocatalyst [68-73]. The efficiency of photocatalytic method depends on properties of photocatalyst such as a) surface area material which includes adsorption phenomenon b) morphology of a material on which electron-hole recombination depends [74].

Some important Points about Photocatalysis:

1. **Semiconductor Catalysts:** Photocatalysis often involves semiconductor materials, such as titanium dioxide (TiO$_2$) or Zinc Oxide (ZnO). These materials can absorb light energy and generate electron- hole pairs, initiating chemical reactions.
2. **Absorption of Photons:** When photocatalyst is exposed to light, it absorbs photons. The energy from these photons is sufficient to excite electrons in the semiconductor material from the valence band to the conduction band and form electron-hole pairs.
3. **Generation of Electron-Hole Pairs:** The absorbed energy promotes electron from the valence band to conduction band and leave behind a positively charged hole in the valence band. The formation of these electron-hole pairs is a key step in the photocatalytic process.
4. **Redox Reactions:** Separated electrons and holes in the semiconductor can participate in the redox reactions.
5. **Reaction with target Molecules:** The excited electrons and holes migrate to the surface of the semiconductor and react with adsorbed molecules or contaminants.
6. **Regeneration of Catalyst:** Catalyst provide a pathway for electron-hole pairs. After the completion of reaction catalyst can return to its original state and cycle repeated as long as light is available. It does not take part in a chemical reaction; it only increases the rate or speed of chemical reaction.
7. **Applications:**
    - **Environmental Remediation:** To remove the pollutants from air and photocatalysis method is used. The reactive species generated by the catalyst can break down organic pollutants, toxins and pathogens.
    - **Water Purification:** It can be employed to disinfect water by killing bacteria and other microorganisms.
    - **Self-Cleaning surfaces:** Photocatalytic materials are used to create self-cleaning surfaces, as they can break down and remove organic contaminants when exposed to light.
    - **Hydrogen Production:** Photocatalysis is also investigated for its potential in generating hydrogen through water splitting, which is a clean and sustainable energy source.
8. **Challenges:** While photocatalysis holds promise for various applications, challenges include the need for efficient catalysts, optimization of reaction condition, and addressing issues related to catalyst stability and reusability.
9. **Research and Development:** Ongoing research aims to develop aims to develop new photocatalytic materials, improve the efficiency of existing catalysts, and explore novel

applications for this technology.

Fig No. 2 Basic Mechanism

Water pollution due to industrialization has grown to be a continuously growing trouble, which is affecting human lifestyles and the aquatic ecosystem international in all factors [75]. It is expected that over one thousand million humans dwelling in the arid areas could have a primary shortage of water via 2025 [76]. It’s far, consequently, essential to treat waste water, in any other case they can pose both acute and persistent effect on human lifestyles and within the environment. Presently, there are four maximum popular strategies comprising physical adsorption, flocculation, chemical oxidation and photo-catalytic degradation, that have been followed to grid of natural contaminants from water [77-78]. The major drawback of those strategies is that they go way an expansion of chemical reagents and polymer electrolytes in water, which led to the era of unmanageable sludge and deposits. Photocatalysis then again, depends on in-situ image generated hydroxyl radicals (OH), superoxide radicals and positively charged (H^+) which completely decompose natural contaminants. For this reason, photocatalysis is an efficient, environmentally-friendly, low price and an easy operation for the elimination of contaminants [79]. To begin with, traditional porous cloth and nano based totally substances have been being used as adsorbents. The maximum usually used adsorbents for waste water treatment are activated carbon, zeolites, carbon nanotubes, mesoporous silica and chitosan beads [80]. However, they confronted technical obstacles including inefficiency, operational problems, excessive energy necessities, and lower financial gain. A perfect adsorbent ought to have high porosity and a big floor location with precise adsorbent web sites. Therefore, alternative photocatalytic materials have been extraordinarily suitable [81].

Metal oxide and Metal sulphide as a photocatalyst:

Metal oxide and metal sulphide skinny film photocatalysts can decompose an expansion of organic pollution into less dangerous response merchandise and the most common pollutant used for degradation exams are MB, RhB and MO dye. The development in thin film technology offers a wide commercial utility of steel oxide skinny movie photocatalysts. Even though TiO2 and ZnO are most studied and commercially a success material because of sure obstacles consisting of extensive band hole, lower efficiency, and so on, there’s scope for different metallic oxides and metal sulphides. The surface morphology, electronic shape, crystalline length, thickness and deposition method of skinny film particularly influences its photocatalytic performance. In case of steel oxide, doing of steel or non-metal not handiest reduce the band hole electricity however additionally decreases the recombination of electrons and holes. Similarly, the photo electrocatalysis phenomenon determined to be efficient to make use electron mob present at the conduction band after irradiation. The degradation mechanism is related to the digital shape of the photocatalyst and bonding among pollutant species and catalyst. The addition of small amount of surfactant can be one of the methods to growth the surface vicinity of thin films. Further, utilization of a spread of substrate and modification in electronic shape can effectively decorate photocatalytic performance [82].

Here is a list of some metal oxides and metal sulphides which are commonly used as photocatalysts, along with their roles, efficiencies and band gap values are given in table. Depending upon the crystal structure, doping, and specific synthesis methods efficiency and band gap values are varied.

Table No.2: List of metal oxide and metal sulphides with role, efficiency and band gap.

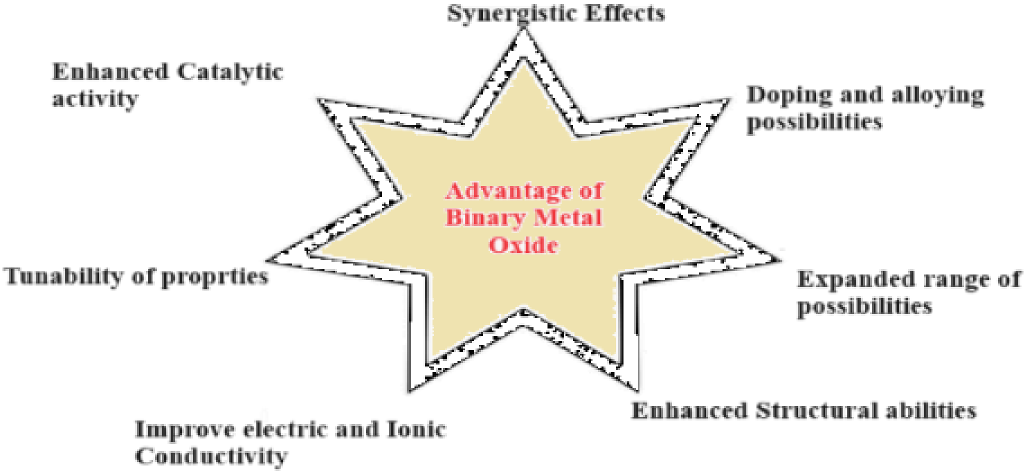
Sr. No.	Name of Metal Oxide	Role	Efficiency	Band Gap
1.	Titanium Dioxide (TiO_2)	Water purification, air Purification, and self-cleaning surfaces	High efficiency in UV light and limited Efficiency in visible light	3.0-3.2eV
2.	Zinc Oxide (ZnO)	Water treatment and UV Filter in sunscreens	Moderate efficiency in UV and Visible light	3.3 eV
3.	Iron Oxide (Fe_2O_3)	Water oxidation and Pollutant degradation	Moderate efficiency in visible light	2.0-2.2eV
4.	Tungsten Oxide (WO_3)	Water splitting and Environmental Remediation	Variable efficiency in Visible light range	2.4-2.8eV

Sr. No.	Name of Metal Sulphide	Role	Efficiency	Band Gap
1	Cadmium sulphide (CdS)	Hydrogen production and Pollutant degradation	High efficiency in Visible light range	2.4-2.5eV
2	Copper sulphide (Cu_2S)	Solar energy conversion And environmental Applications	Variable efficiency In Visible light range	variable
3	Zinc sulphide (ZnS)	Hydrogen production And photocatalytic Degradation	Moderate efficiency In visible light range	3.5-3.8eV
4	Nickel sulphide (NiS)	Hydrogen evolution Reactions	Variable efficiency In Visible light range	Variable

These materials are actively researched, advancements in synthesis techniques and modifications continue to improve their efficiency and broaden their applicability in various photocatalytic process, but alone metal oxide and metal sulphide has some limitations, after 2009 maximum awareness is carried out to improve the possessions of nanomaterials such as chemical reactivity, optical, electrical and magnetic properties for better result [83], thus to increase the efficiency we need binary and ternary metal oxide as a photocatalyst.

Binary Metal Oxide as Photocatalysis:

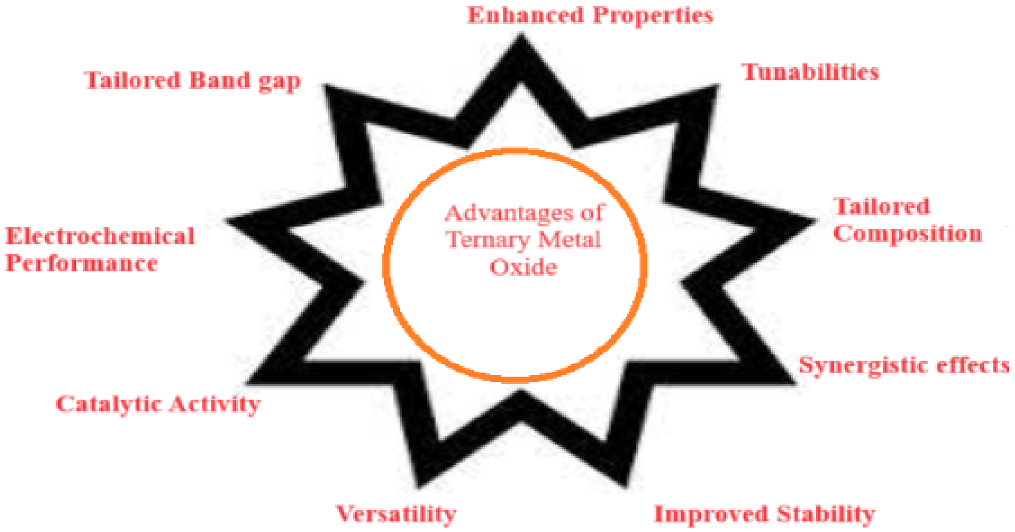
Binary metal oxides, which are compounds composed of two different metal elements and oxygen, can offer several advantages over single metal oxides. It's important that the specific benefits depend on the choice of metal elements, their ratios, and the intended application. Researchers often explore different combinations to discover new materials with optimized properties for specific technological needs.



As a promising compound, titania (TiO2) has been widely used in the photocatalytic degradation of natural pollution of water and air. Pure TiO2 has electricity hole of 3.2eV, hence UV mild is necessary to excite electrons on the TiO2 floor. To spark off the photocatalyst with better performance and longer wavelength, some of strategies have been added [84]. One strategy is put together TiO2/metallic oxide nanocomposites which include SiO2/TiO2 [85], CdS/TiO2 [86], ZnO/TiO2 [87], SnO2/TiO2 [88]. Lifetime of photo-brought about price consists of is a prime factor for improving photocatalytic interest. As for ZnO-TiO2 [89], the electron transfers from the conduction band of ZnO to that of TiO2 below illumination, and conversely, the holes switch from the valence band of TiO2 to that of ZnO. Accordingly, the life of photoinduced pairs increases because their recombination charge decreases. So that it will expand the range of excitation energies of TiO2 into the visible vicinity, materials of the slender band gap, such as ZnO, had been coupled with TiO2 [90]. The band gap of ZnO and TiO2 is quite massive so they are not capable of absorb the essential part of the sun spectrum i.e. the seen location efficaciously and may simply absorb a small range of the UV area this is why the highest quality and powerful utilization of sun radiations in this subject is still considered as a assignment. Numerous attempts have been made so that the absorption range of TiO2 and ZnO can be extended to the visible light region, which consist of deposition of noble metals, doping of transition metals and coupling of various semiconductor systems, etc [91]. Out of a majority of these available metal oxides, ZnO has demonstrated to be an fantastic and promising photocatalyst, because of its first rate characteristics find it irresistible less expensive price, precise oxidation potential, large free excitation binding strength, flexibility in fabrication, and many others. Moreover, every other critical issue is the rapid recombination charge of photo generated electron hole pairs inside TiO2 NPs. So, plenty of tries had been made to discover techniques facilitating the photoactivation of TiO2 below seen-mild. TiO2 doping with numerous materials could be taken into consideration as an easy approach to improve its photocatalytic overall performance [92]. substrate and the ratio TiO2/RhB were also investigated in the photocatalytic degradation of RhB. There may be a hinderance that limits using ZnO as a photoelectrode due to its n-kind behaviour, that doesn’t permit ZnO to manipulate its electric conductivity [93]. Whilst transition metals like Ag, Mn, Fe, Co, Cr, Al and so forth are doped in ZnO there may be a alternate inside the electric, optical and magnetic residences with the changing of doping concentration [94]. surface defects create energetic sites and this is why analysing the effect of doped ZnO on its photocatalytic hobby turns into vital [95]. In current years, graphene oxide is referred to as a promising cloth to improve the structural stability and photocatalytic pastime of TiO2 NPs [96]. Alternatively, adheration of TiO2 NPs to head layers now not simplest prompted electrons for photovoltaic reactions but also prevented recombination with photo- generated holes [97]. In a single record, a simple solvothermal approach changed into used to graft TiO2 NPs on go (TiO2- pass as binary nanocomposite). Photograph- degradation interest of TiO2- pass nanocomposite became investigated on the degradation of MB and MO beneath UV-mild irradiation and in comparison, with pristine TiO2 NPs [98].

Ternary Metal Oxide as a photocatalysis:

Compared with the easy binary metal oxides, the TMOs possess a more complicated composition, chemical bonding among distinctive cations and oxygen atoms and bendy crystal structure [99]. Ternary metal oxides, which consist of three different elements, offer several advantages over binary metal oxides. It's important that the advantages of ternary metal oxides depend on the specific elements chosen and their proportions. The selection of elements and their ratios plays a critical role in determining the material's properties and performance in various applications.



The complex shape gives vast benefits for TMOs as photocatalysts. First, the band aspects potentials for TMOs are appropriate for diverse photoinduced reactions. In addition, the presence of various metallic ions in the lattice of TMOs lets in for extra flexibility in designing and enhancing the band structure as well as other photophysical residences. Through band shape engineering, the capacity of sun harvesting and photon-excitation energy conversion may be optimized, inclusive of the fabrication of heterojunctions and the introduction of illness states [100]. Given that water photocatalysis changed into observed with the aid of Fijishima et al. with TiO2 as a photocatalyst for the manufacturing of O2 and H2 from water, many kinds of semiconductors have been fabricated and implemented as photocatalyst, especially for the broadly studied oxide materials. It's far usual that the homes of substances significantly modified in keeping with their synthesis process, chemical additives, morphologies, floor amendment, elements doping and the formation of composites and so on [101-106]. The simple binary steel oxides or metal loose semiconductors, consisting of TiO2, ZnO, WO3 and C3N4, and so on., had been broadly studied as photocatalyst to understand the essential precept. The development of photocatalytic efficiency and the enlargement in different potential applications [107-112]. The ternary metal oxides (AxByOz) with extra flexible band structures own splendid capability to be carried out as photocatalysts. An extensive range of ternary metal oxides (TMOs) had been fabricated, and their photocatalytic pastime related to morphology, electronic, optical houses should be in addition investigated. The one-of-a-kind constituent factors within the AxByOz composition offer more than one alternative to alter the materials with tunning physical and chemical residence for an enhancement of photocatalytic performance [113].

Here is some ternary heterostructure metal oxide are listed with their role and band gap value,

Sr. No.	Ternary Oxide	Role	Band Gap
1.	TiO2/SnO2/ZnO [114]	Photocatalysis-Degradation of Water pollutants, Water splitting	TiO2-3.2eV SnO2-3.6eV ZnO-3.3eV
2.	MoS2/WS2/Graphene [115]	Catalysis, Electronic device Hydrogen Evolution reaction Pollutant Degradation	MoS2-1.8eV WS2-1.6eV
3.	Cu2O/ZnO/CuO [116]	Photocatalysis, Gas sensing Degradation of Organic pollutants, Hydrogen production	Cu2O-2.0eV ZnO-3.3eV CuO-1.2eV
4.	Bi2wO6/BiVO4/TiO2 [117]	Photocatalysis- Water oxidation, Pollutant degradation	Bi2WO6-2.8ev BiVO4-2.4eV TiO2-3.2eV
5.	CdS/ZnS/Ag2S [118]	Photocatalysis- Hydrogen Production, Degradation of Pollutants, Optoelectronics	Cds-2.4eV ZnS-3.7eV Ag2S-1.0eV
6.	Fe2o3/TiO2/Graphene [119]	Photocatalysis, Energy storage	Fe2o3-2.2eV TiO2-3.2eV
7.	CuIns2/CdS/ZnS [120]	Photocatalysis, Photovoltaics	CuInS2-1.5eV CdS-2.4eV ZnS-3.7eV
8.	ZnO/SnO2/In2O3 [121]	Gas sensing, Photocatalysis	ZnO-3.3eV SnO2-3.6eV In2O3-3.75eV
9.	Bi2MoO6/BiVO4/WO3 [122]	Photocatalysis, Water Treatment	Bi2MoO6-1.89eV BiVO4-2.4eV WO3-2.8eV
10.	TiO2/Fe2O3/SnO2 [123]	Photocatalysis, Solar cells	TiO2-3.2eV Fe2O3-2.2eV SnO2-3.6eV
11.	NiO/CdS/ZnO [124]	Photocatalysis, Optoelectronics	NiO-3.5eV CdS-2.4eV ZnO-3.3eV
12.	CuFeO2/Fe2O3/ZnO [125]	Photocatalysis, Energy Storage	CuFeO21.15eV Fe2O3-2.2eV ZnO-3.3eV
13.	Cu2O/ZnO/In2O3 [126]	Photocatalysis, Gas sensing	Cu2O-2.2eV ZnO-3.3eV In2O3-3.75eV

14.	MoS2/WS2/BN [127]	Electronic devices, Catalysis	MoS2-1.8eV WS2-1.6eV BN-2.44eV
15.	ZnO/CdS/Graphene [128]	Photocatalysis, Energy Storage	ZnO-3.3eV CdS-2.4eV

Efficiency and performance of these ternary heterostructures can be influenced by several factors, including synthesis methods, morphologies, and specific experimental conditions.

Conclusion:

In Conclusion, metal oxide represents key area of research for harnessing solar energy and mitigating environmental challenges. Binary metal oxide has been extensively studied, but their limitations have led to explore ternary metal oxide systems the diverse composition of ternary metal oxide photocatalysts have shown promising results in various applications, including water splitting, pollutant degradation, and hydrogen production. The understanding of underlying mechanisms, such as charge carriers, surface sates, and doping strategies, provides insights into optimizing the photocatalytic activity of both binary and ternary systems.

ACKNOWLEDGEMENT:

One of the author Jayashri Vitthal Waghmode would like to acknowledge to Mahatma Jyotiba Phule Research and Training Institute for providing financial support.

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