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**REVIEW PAPER**

# Recent Developments on I and II Series Transition Elements Doped $SnO_2$ Nanoparticles and its Applications For Water Remediation Process: A Review

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**ABSTRACT**

The presence of various hazardous toxins such as phenols, phthalates, pesticides, dyes, heavy metals, pharmaceutical waste, etc, is continuously increasing in the water bodies from different agricultural, industrial, and domestic practices, which have brought the toxicity level to an alarming height. Often, these toxic compounds are quite stable in nature and the removal or degradation of these compounds is quite challenging, which further poses a significant threat to the environment. When it comes to enhancing the efficiency of the water purification and decontamination process, $SnO_2$ nanoparticles offer great potential owing to their low concentration and large surface area. Over the past few years, $SnO_2$ nanoparticles as a photocatalyst have garnered huge interest from the research community in the photo-degradation of toxic pollutants present in the water bodies. Among various metal oxides, particularly $SnO_2$ has emerged as the most versatile material for doping of different transition metals due to its plethora of applications such as photocatalysis, energy harnessing, sensors, solar cells, and optoelectronic devices. The pure and doped $SnO_2$ has prominent significance due to its phenomenal catalytic and physicochemical properties such as being chemically stable, inexpensive, and non-toxic. This review explores and summarizes the progress of first and second transition metal series doping in $SnO_2$ for its coherent application toward the degradation of water pollutants. We have emphasized the effect of different transition metal dopants used in the growth of $SnO_2$ nanoparticles based on their synthesis technique, source of irradiation used, nature of contaminations removed, and obtained photodegradation efficiency.

**Keywords:** *$SnO_2$ Nanoparticles, Photocatalysis, Transition Metal Doping, Wastewater Treatment*

**How to cite this article**

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## INTRODUCTION

In this materialistic world, nothing is free. The life we are enjoying today has come to us at the cost of our environment. Globally, almost every country across the world has been facing detrimental threats to the environment in the form of pollution and this burning issue has become a matter of paramount concern for environmentalists, ecologists, and scientists. Intensive use of agricultural and industrial practices, as well as excessive use of energy resources, have brought the contamination toxicity level in the environment to an alarming height. The level of water and aerial pollution continuously increases the level of harmful contaminants through the emission of toxic gases, dyes from cosmetic and textile industries as well as heavy metals from agriculture, chemical industries, pharmaceutical, and domestic waste [1-4]. The elevated level of harmful chemicals not only damages the ecosystem but also causes serious diseases in living beings [5]. To curb the growth and removal of these hazardous pollutants, various conventional and modern methods are

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available such as chemical methods, and physical and physio-chemical methods [6]. Advanced oxidation phenomena involving UV radiation, ozonation, and Fenton oxidation [7-8] are helpful in dyes synthetic dyes degradation but all the above-mentioned processes require lots of chemical substances, which again make them uneconomical. Unfortunately, all these available methods are associated with one or more practical limitations with them despite their efficacy. In recent years, to solve these nerve-wracking environmental challenges, persistent efforts are shown by the researchers to explore and develop innovative techniques by using low-cost and eco-friendly materials for environment purification. In this series of efforts, the Photocatalysis technique has emerged as a promising candidate for a "green and eco-friendly" method to eliminate toxins present in the environment as well as for clean fuel production [9-10]. It's been more than a century since the term "Photocatalysis" first came into the limelight of scientific literature. In 1911, various research communications were published incorporating the concept of Photocatalysis. The semiconducting materials which show photocatalytic activity upon conversion of irradiating light energy into chemical energy of electron-hole pairs are known as photocatalysts. Hence, while opting for a suitable photocatalyst for particular photocatalytic activity, bandgap of catalyst, level of toxicity, cost and availability are some of the important parameters which must be taken into consideration [11]. Fig. 1 shows the application of photocatalysis for the removal of different types of pollutants generally present in the water environment.

*Properties and uses of $SnO_2$*

Among various semiconducting metal oxides based photocatalysts ($TiO_2$, $Fe_2O_3$, ZnO, etc), Tin Oxide ($SnO_2$) gained tremendous attention due to its wide range of applications in different fields such as photodegradation of pollutants, electrodes for lithium-ion batteries, gas sensing, dye-based solar cells, and optoelectronic devices, etc. as shown in Fig.2. Its low-cost availability, non-toxic nature, optical transparency, long-term stability, and high thermal stability consider $SnO_2$ an excellent photocatalyst [12]. Fig. 2 shows the versatile applications of $SnO_2$ in various fields.

Tin oxide is mainly an inorganic compound with the chemical formula $SnO_2$. It usually appears as a colorless solid or powder that is insoluble in water. Stannic oxide is the other name for $SnO_2$ [13]. Tin oxide is an n-type semiconductor that shows a wide bandgap of about 3.6 eV in bulk. $SnO_2$ crystal phase structure is analogous to the rutile structure of $TiO_2$ and belongs to P42/mnm space group having lattice parameters as a=b=4.738 A˚ and c= 3.187 A˚. The different physicochemical properties of $SnO_2$ semiconductor material are represented in Table 1 [14].

Doping is considered a successful proven tool

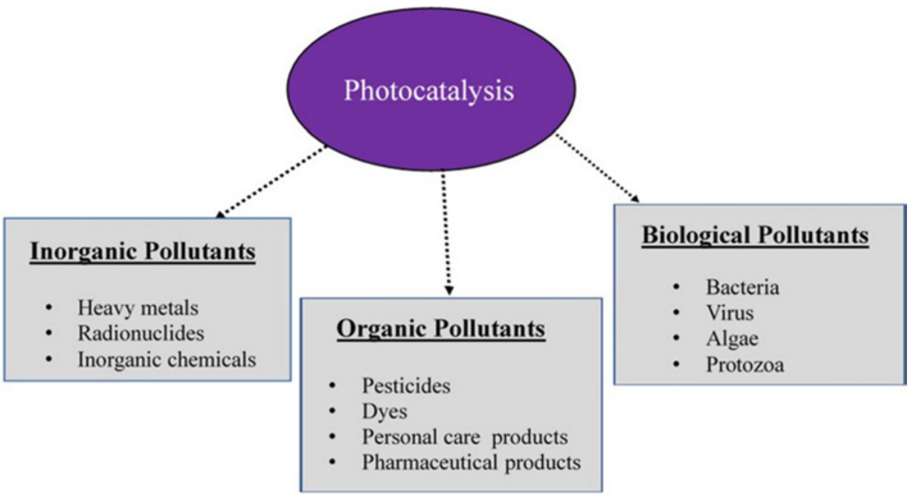


Fig. 1. Application of Photocatalysis for the removal of different types of water pollutants

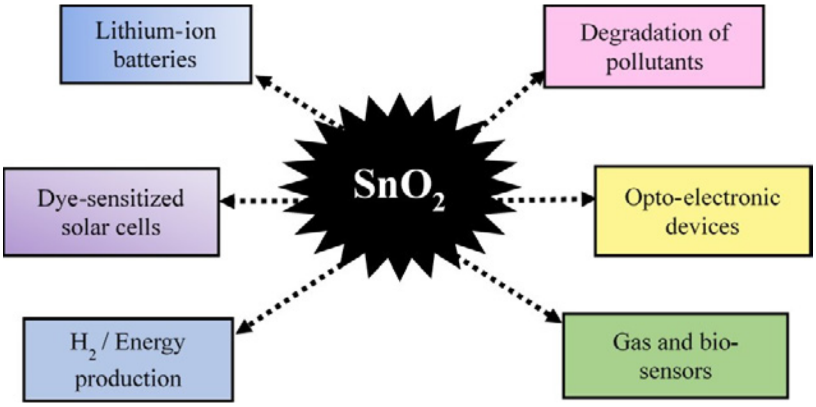


Fig 2. Versatile applications of Tin Oxide ($SnO_2$)

Table 1. Physicochemical properties of $SnO_2$ semiconductor

| Properties | Rutile |
|---|---|
| **Crystal structure** | Tetragonal |
| **Lattice parameters (A˚)** | a=b=4.738<br>c= 3.187 |
| **Space group** | P42/mnm |
| **Colour** | Transparent or white |
| **Bandgap (eV)** | 3.6 |
| **Density (g/cm3)** | 6.9 |

for tailoring the morphological, electrical, and optical properties of metal oxides. The reported literature is in agreement with the fact that oxygen vacancies offer themselves as highly occurring recombination centers in the $SnO_2$ emission process [15]. $SnO_2$ is considered a good host for doping with transition metals. The catalytic efficiency of $SnO_2$ nanoparticles significantly enhances doping with different transition metals (TMs). Transition metal-doped $SnO_2$ nanoparticles exhibit tunable bandgap and a high active surface area which further helps in improving the degradation response in the photocatalytic mechanism [16].

Although ample work on $SnO_2$ nanoparticles has been reported by the research community, still $SnO_2$ nanoparticles are hot area of research. A large number of research publications including some comprehensive review articles covering various aspects of $SnO_2$ have already been published. For instance, Al Hamdi et al. [17] published a comprehensive review of $SnO_2$ as a photocatalyst for the water remediation process. R.Rajput .et.al reviewed the development of Hydro/solvothermal synthesized visible light-responsive modified $SnO_2$ nanoparticles for water treatment [14]. Y.Tadesse and co-workers reviewed green synthesis methodologies, mechanisms, and applications of Tin oxide nanoparticles [18].

A very limited number of reviews have been published within the last five years on the use of tin oxide as the photocatalyst for water remediation applications by the increasing interest of the scientific community in tin oxide as the potential photocatalyst. However, most of the review papers reported only selective transition metals doped $SnO_2$-based photocatalytic materials. To the best of our knowledge, this is the first review report that encompassed the doping of complete first and second transition series elements with $SnO_2$ towards its applications for the removal of various water pollutants. This review focuses primarily on the purification of synthetic dyes wastewater by spotlighting the role of first and second-series transition metal doping in $SnO_2$ nanoparticles.

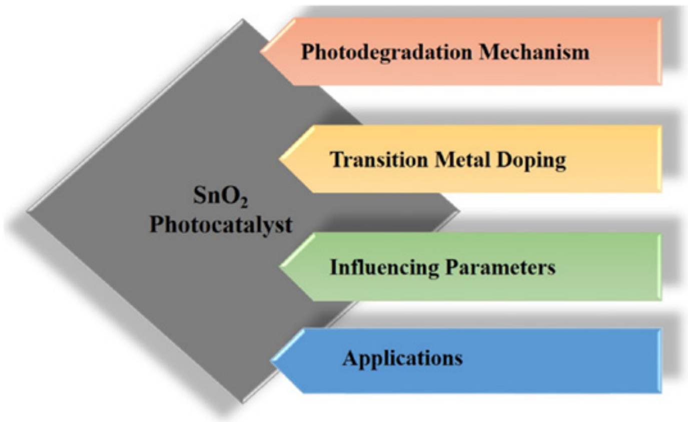


Fig. 3. Review paper roadmap focusing on photodegradation mechanism, synthesis strategies, transition metal doping, influencing parameters, and applications of $SnO_2$ Photocatalyst

Hence, the present review intends to assess a detailed analysis of the first and second series of transition metals doped $SnO_2$ nanoparticles photocatalyst covering the most commonly used synthesis methods, doping effects, different parameters affecting the photocatalytic activity, and also review the progress of removal of water-based toxic contaminations through $SnO_2$ nanoparticles. Fig. 3 shows the roadmap of this review paper focusing on photodegradation mechanism, synthesis strategies, transition metal doping, influencing parameters, and applications of $SnO_2$ Photocatalyst.

*$SnO_2$ semiconductor as a photocatalyst*

Among different metal oxide semiconductors, $SnO_2$ has gained the widespread attention of researchers due to its multifaceted applications. As stated above, $SnO_2$ is an n-type semiconductor material with a bandgap, i.e. 3.6 eV, which corresponds to activation with photons of the wavelength of about 350 nm (UV-A range). R. Saravanan and co-workers [19] reported that in the photocatalytic process, a redox reaction i.e. successive photo-oxidation and reduction of catalyst takes place upon irradiation of light energy. The photocatalysis mechanism initiates when light energy of suitable wavelength ($E \geq E_g$), where $E_g$ stands for bandgap energy, falls on the surface of semiconducting material in terms of photons. The valence shell electrons absorb energy from photons and jump to the conduction band of material which results in the formation of e−/h+ pairs. The h+ in the valence band oxidized and react with the $H_2O$ molecules to generate hydroxyl radicals (OH•). The e− present in the conduction band reacts with dissolved oxygen and triggers the formation of superoxide-free radical ($O_2^{-\bullet}$) anion or hydroperoxyl ($\bullet O_2H$) radicals. After that these radicals react with the intermediate and convert the toxic pollutants into $CO_2$ and $H_2O$. The overall reaction steps are shown below [20]. Fig. 4 shows the schematic photodegradation mechanism of $SnO_2$ nanoparticles as a photocatalyst.

$$SnO_2 + h\nu \rightarrow SnO_2\,(e^- + h^+)$$
$$SnO_2\,(h^+_{VB}) + H_2O \rightarrow SnO_2 + H^+ + OH\bullet$$
$$SnO_2\,(h^+_{VB}) + OH^- \rightarrow SnO_2 + OH^\bullet$$
$$SnO_2\,(e^-_{CB}) + O_2 \rightarrow SnO_2 + O_2^{-\bullet}$$
$$O_2^{-\bullet} + H^+ \rightarrow HO_2\bullet$$
$$O_2^{-\bullet} \text{ or } \bullet OH + \text{pollutants} \rightarrow CO_2 + H_2O$$

Due to the wide bandgap energy value, $SnO_2$ can only be activated in the UV range of the electromagnetic spectrum [21]. However, doping or semiconductor coupling can modify the catalytic activity of $SnO_2$ by tailoring the absorption spectrum from the UV range to the visible range. As compared to pure $SnO_2$, doped $SnO_2$ has shown magnificent photocatalytic activity attributed to the high surface area with effective separation of photogenerated EHP and centralized electric field enhancement effect [22-23].

*Synthesis techniques for $SnO_2$ nanoparticles*

For the synthesis of $SnO_2$ nanoparticles, various strategies such as sol-gel, hydrothermal, co-precipitation, solvothermal, and solution-

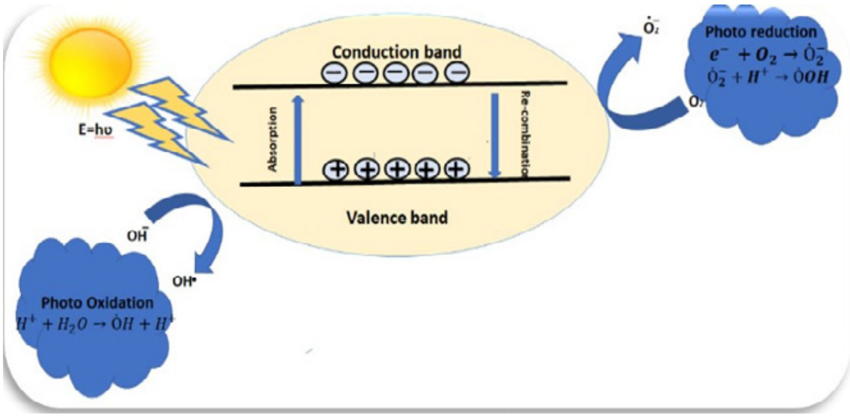


Fig.4. Schematic photodegradation mechanism of $SnO_2$ as a photocatalyst

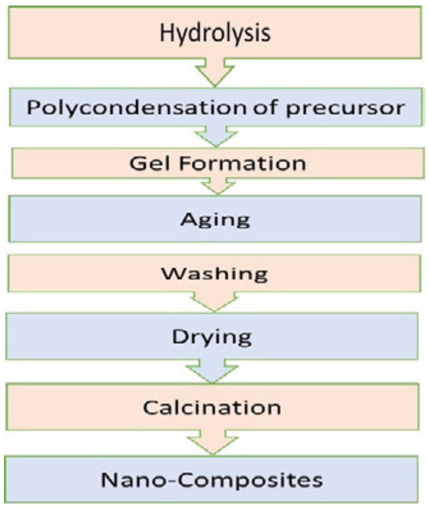


Fig. 5. A schematic flowchart of the sol-gel technique

based methods, etc have been adopted. Some most commonly used techniques for the synthesis of $SnO_2$ are discussed as follows:

*Sol-Gel Method*

The Sol-Gel process has been considered a key technology that has gained widespread popularity in recent years, due to its simplicity and flexible nature. It allows using different materials to synthesize metal oxide and their nanocomposites at an affordable price. The choice of drying conditions also plays a crucial role in the formation of aerogels and xerogels [24]. Fig. 5 shows a schematic flowchart of the Sol-Gel method.

Azam. et. al prepared Mn-doped $SnO_2$, $SnCl_4{\cdot}5H_2O$, and $MnCl_2{\cdot}4H_2O$ as the precursors via a sol-gel approach. They studied the effect of Mn doping on the structural and optical properties of $SnO_2$ NPs. It was observed that with the increase in Mn concentration, the crystallite size tends to reduce as the incorporation of Mn ions into the host lattice prevents the growth of crystal grains [25].

Kumar et.al [26] synthesized $SnO_2$ spherical nanoparticles by using Psidium Guajava Leave Extract and degraded reactive yellow 186 dye under direct sunlight. The biosynthesized $SnO_2$ nanoparticles photodegraded 90% of the dye with in 3hrs. This shows that the green synthesis method is an emerging technique that can be explored further to obtain promising results for solar-driven water remediation.

The sol-gel method is a simple and cost-effective technique that provides good control over the size

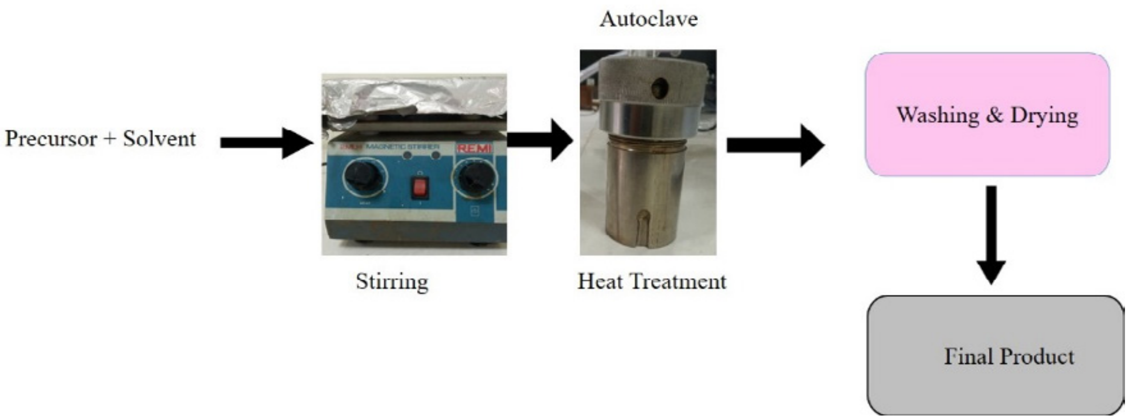


Fig. 6. Pictorial representation of the hydrothermal synthesis

and shape of the nanoparticles and also produces better homogeneity results [27].

*Hydrothermal Method*

Hydrothermal synthesis has been considered a solution reaction-based approach. The process of formation of nanomaterials can occur in a wide range of temperatures i.e. from room temperature to very high temperature. The synthesis process takes place in a closed Teflon-coated stainless-steel autoclave. This method is widely used to synthesize different types of nanomaterials [28]. Fig. 6 shows a pictorial diagram of the hydrothermal technique.

Huang et al [29] reported the fabrication of 3D $SnO_2$ hierarchical superstructures (SOHS) using template-free hydrothermal synthesis. They selected methylene blue dye to examine the photodegradation activity of the sample and observed that the sample SOHS-1 has achieved the highest degradation efficiency among all the other samples. The enhanced degradation performance is ascribed due to the high surface-to-volume ratio and abundant catalytic activity sites.

K. Bhuvaneswari and her group utilized the hydrothermal technique for the preparation of $SnO_2$ nanoparticles and a plate-like structure using cetyl trimethyl ammonium bromide (CTAB) surfactant. It was reported that the pure $SnO_2$ samples were poor absorbers as compared to CTAB synthesized samples. Under UV-vis light irradiation, they analyzed the prepared sample for the degradation of RhB, MB, and MO dye and found that the CTAB- $SnO_2$-24 h sample shows higher photocatalytic efficiency as the refined morphology provides a more active surface for the reaction and hence enhanced the efficiency [30].

*Co-precipitation Method*

Co-precipitation is a simple, fast, and cost-effective process to synthesize pure and doped nanoparticles. It involves the atomic mixing of particles which further yields the products with ideal stoichiometry at a low-temperature range. Due to its simplicity, it is widely used for industrial applications and also provides good morphological controls. Ahmad and his group [31] prepared pure and Cd-doped $SnO_2$ using $SnCl_2.2H_2O$ and anhydrous $CdCl_2$ as precursor materials. They found that the particle size decreased initially on 1% of doping and further increased with increasing dopant concentration due to the expansion of the lattice attributed to the swapping of cations of different radii.

L. Nejati-Moghadam et al [32] successfully synthesized $SnO_2$ nanoparticles using bis (acetylacetone) ethylenediamine as a capping agent and ammonia as a precipitation agent. They opted for Methyl orange and Eriochromschwarz-T as model pollutants to check the photodegradation performance of the prepared material and observed the complete degradation of dyes within 120 min. With the increasing irradiation time, the concentration of dyes tends to decrease as more dye is absorbed on the catalyst surface.

*Solvothermal Method*

Solvothermal synthesis is a facile technique that can produce a variety of organized structures relatively at high temperatures. The characteristics of the material can be tailored by altering some parameters such as reaction time, temperature, solvent type, precursor type, etc.

Tikkun Jia et al [33] used this methodology for the synthesis of Zn doped $SnO_2$ hierarchical architectures of different morphologies and the degradation of RhB dye was evaluated under UV lamp exposure. The alkaline quantity (NaOH) of the solution had a noticeable effect on the morphology and formed nanoflowers and nanourchin structures. The samples with urchin morphology reflected better photocatalytic activity due to the intrinsic oxygen vacancies created by the $Zn^{2+}$ ions into the host lattice.

Bhuvaneswari et al [34] successfully synthesized EDA (ethylenediamine) assisted $SnO_2$ nanorods and they reported that the addition of EDA significantly altered the morphology and optical absorption spectra. The degradation of methylene blue dye was monitored and the EDA-$SnO_2$ nanorods have shown excellent degradation of dye in 90 min. The enhanced performance was attributed due to the more intrinsic oxygen vacancies which provide high surface activity.

*Transition metal doping in $SnO_2$*

Doping is the modification of photocatalyst by introducing impurities in it, which helps in reducing the bandgap. Doping is a part of bandgap engineering, which helps in avoiding the recombination process by enhancing the trapping of electrons [35].

Doping not only alters the morphology and surface area but also helps in improving photocatalytic activity. The introduction of dopants in the photocatalyst exhibits excellent performance due to the following reasons-

- It helps in avoiding the electron-hole recombination process
- Providing enhanced surface area
- Helps in increasing the pore size of the sample [16]

Though, control doping with different materials provides novel possibilities to optimize the properties of semiconducting nanomaterials and is a beneficial method to achieve enhanced efficiency and photoluminescence in the visible range. However, as compared to bare systems the longer emission lifetime of doped semiconductor nanomaterial is still facing challenges in their utilization for many practical devices. Hence, whether "To dope or not to dope" is still debatable [36].

According to IUPAC, a transition metal is defined as an element whose atom has an incomplete d subshell. Various researchers have doped $SnO_2$ with different transition metals such as Zn, Ni, Co, and Mn. Doping of $SnO_2$ with transition elements not only optimizes the electronic structure and conductivity but also increases the catalytic activity of the material [37].

This section incorporates the doping of $SnO_2$ semiconductors with the first and second series of transition metals for their photocatalytic applications toward water purification.

*First transition series elements doped $SnO_2$ nanoparticles:*

*Scandium (Sc)-doped $SnO_2$*

Scandium (Sc) is classified as a 3d transition metal and also a rare earth element rather than an earth-abundant element. Due to poor availability (rare earth metal) and wide bandgap energy of about 6.0 eV, which remains only active in the UV region hence Scandium as a photocatalyst or as a dopant for photocatalytic applications is still quite challenging. The effect of Sc doping on photocatalytic properties has not been much reported but still, this material has the potential to be explored further yet [38].

*Titanium (Ti)-doped $SnO_2$*

Titanium is considered a transition element that belongs to the d block and group 4 of the periodic table. It has high reactivity with oxygen and doping of Ti into $SnO_2$ lattice results in a decrease in lattice constants. Lei Ran et al [39] synthesized the hollow structured Ti-doped $SnO_2$ via an improved Stober method. The doping of Ti into $SnO_2$ prevents the recombination process and results in enhancing photocatalytic activity. The photocatalytic activity of the obtained sample was investigated by the decomposition of methylene blue (MB) under UV and visible-light illumination.

Hanen Letif et al. [40] successfully prepared the Ti-doped $SnO_2$ by facile and low-cost co-precipitation route at different concentrations. The pure and doped nanoparticles were crystallized in the tetragonal structure. Precisely, the highest concentration of Ti improved the photocatalytic performance. The improvement in efficiency was due to the extended absorption edge from the UV light to the visible light region.

*Vanadium (V)-doped $SnO_2$*

Vanadium is the 20$^{th}$ most abundant element which lies left of chromium and right of titanium in the first series of transition metals. The incorporation of vanadium into the $SnO_2$ lattice reduced the cell volume due to the small radii of vanadium ions.

J. Mazloom et al [41] synthesized V-doped $SnO_2$ using the sol-gel route. As compared to the pure sample the quenching in green luminescence intensity was observed in the doped sample. V doping decreased the intensity and possesses high photocatalytic performance as a result of the reduced bandgap. To degrade the methylene blue and rhodamine B, the obtained sample exhibited excellent photocatalytic activity.

Ch. Venkata Reddy et al [42] prepared V doped $SnO_2$ at different concentrations of vanadium via combustion synthesis technique. X-ray photoelectron spectroscopy confirmed the existence of $V^{4+}$ species in the $SnO_2$ lattice. With increasing dopant concentration bandgap energies decreases and also enhance the photocatalytic activity, as doping in $SnO_2$ shift the absorption edge to the visible region.

R. Shyamala et al [43] synthesized V doped $SnO_2$ using ammonium metavanadate and stannous chloride by sol-gel approach. They concluded that with an increase in the dopant amount the absorption edge shows a redshift and hence the value of bandgap energies decreases from 3.77 to 2.9 eV. They studied the photodegradation of MO and concluded that the V/$SnO_2$ sample exhibited higher photocatalytic performance due to a lower bandgap value.

H. Letif et al [44] incorporated the co-precipitation method to prepare the V-doped $SnO_2$ NPs and their results displayed the photocatalytic degradation of rhodamine B under UV light illumination. The absorption edge of the doped sample exhibited a red shift due to increasing dopant concentration hence, the doped samples achieved higher photocatalytic activity as compared to the bare sample.

*Chromium (Cr)-doped $SnO_2$*

Chromium with atomic number 24 belongs to group 6 of the periodic table. The highly polished chromium can reflect about 70% of visible and 90% of visible light. As the ionic radius of $Cr^{3+}$ (63 °A) is close to that of $Sn^{4+}$ (74 °A), which means that $Cr^{3+}$ ions can easily incorporate into the $SnO_2$ lattice or substitute the position of $Sn^{4+}$ in the crystal without altering its rutile structure [45].

Ch. Venkata Reddy and group [46] successfully prepared the Chromium (Cr)-doped $SnO_2$ quantum dots (QDs) with different doping concentrations via a simple combustion technique. The XPS spectra confirm the existence of $Sn^{4+}$, $Cr^{3+}$, and O ions respectively in the host lattice and the Cr-doped $SnO_2$ QDs exhibit higher photocatalytic activity as the introduction of Cr ions into the lattice decreased the intensity and hence reduces the recombination rate of photogenerated electron and hole.

Taybeh Karimi et al [47] reported the preparation of pure and doped (Cr)-doped tin dioxide ($SnO_2$) nanoparticles via a chemical precipitation route. Their studies reveal that the particle size decreases due to the incorporation of Cr ions into the host lattice as dopants affect the growth mechanism of the particles. Also, the small size of the particles offers the remarkable photocatalytic degradation of methylene blue dye.

*Manganese (Mn)-doped $SnO_2$*

Mn is classified as the third most abundant transition element. The substitution of $Mn^{+4}$ (0.53° A) ion in place of $Sn^{+4}$ (0.69°A) ions into the host lattice results in the contraction of the cell parameters. K. Anandan et al [48] described the synthesis of bare and doped Mn-doped $SnO_2$ nanoparticles by precipitation method. Their optical studies revealed that the bandgap of the Mn-doped $SnO_2$ nanoparticles increased on increasing the Mn concentration due to the small particle size.

L. Sakwises and co-workers [49] investigated $SnO_2$ and Mn-doped $SnO_2$ particles prepared via chemical synthetic technique. The group used this material in the photocatalytic degradation of methylene blue. They have reported that the pure $SnO_2$ exhibits higher efficiency rather than the doped sample due to the same oxidation state of Mn and Sn, hence no difference was notified on partial substitution of Mn ions into $SnO_2$ lattice.

M. Ramamoorthy et al [50] used a chemical precipitation route and synthesized Mn-doped $SnO_2$ loaded with (0.5 g) corn cob activated carbon. The photocatalytic activity of obtained samples was studied by photodegradation of methylene blue dye under sunlight illumination. The doped samples loaded with corn cob exhibited higher degradation efficiency as the loading of corn cob could be the carrier for generated electrons, hence improving the efficiency.

Pritam Borker et al [51] used the co-precipitation technique to synthesize Mn-doped $SnO_2$ nanowires and the photocatalytic activity of nanocomposites was studied by the degradation of naphthol blue-black dye under UV light. They reported that the dye was not able to degrade in the dark, therefore the dye solution was bubbled with $O_2$ to enhance the photocatalytic performance. Aeration provides better results as it prevents the recombination process and hence enhanced the photocatalytic efficiency of Mn-doped $SnO_2$ nanowires.

*Iron (Fe)-doped $SnO_2$*

Iron is a metal that belongs to group 8 and the first transition series of the periodic table. Fe atoms are incorporated into $SnO_2$ lattice at substitutional or at interstitial sites. The cell volume and lattice parameters gradually decrease with increasing dopant amount [52]. Marauo Davis et al. [53] successfully synthesized Fe-doped $SnO_2$ nano architectures via a sol-gel route using inorganic salts as starting materials. They concluded that only 5% of dopant concentration degrades about 55% of dye under and this can be only achieved due to the small crystallite size, high-internal surface area, and porous aerogel network.

Zhang et al. [54] successfully used a simple solvothermal technique to fabricate Fe-doped $SnO_2$ echinus-like particles. They investigated the synthesized material for degradation of RhB and Cr (VI) under UV light illumination and Fe-doped $SnO_2$ samples displayed better degradation performance due to the high active surface area and high porosity.

Othmen et al. [55] prepared Fe-doped tin dioxide nanoparticles using a hydrothermal process with different concentrations of Fe and the presence of $Fe^{4+}$ ions in the host lattice was detected by Mössbauer spectroscopy. Under UV exposure the addition of iron diminishes the photocatalytic efficiency but is only enhanced under visible light due to the wide bandgap values of $SnO_2$ samples.

R. Mani et al [56] utilized a chemical precipitation technique to synthesize (Fe) doped $SnO_2$ nanoparticles. TEM revealed that the samples are spherical in shape and the average size was about 24-42nm. Further, the photocatalytic degradation of phenol and benzoic acid was studied and doped samples have a high-efficiency rate due to narrow bandgap value and high active sites.

Amna Afzaal et al [57] incorporated sol-gel and hydrothermal routes to synthesized $SnO_2$-$SiO_2$ and Fe doped $SnO_2$-$SiO_2$ nanocomposites respectively, using a zwitterionic surfactant. The incorporation of iron into nanocomposite observed the redshift due to the small bandgap and transfer of electrons thus refining the optical properties hence, the doped nanocomposite exhibits enhanced degradation efficiency of methylene blue.

Othmen et al [58] used three steps elaboration method and successfully reported the synthesis of Fe-doped $SnO_2$ NPs, which were further loaded on rGO sheets. They studied the photodegradation of rhodamine B dye under visible light irradiation and due to the presence of oxygen functional groups in graphene oxide, the electrons were entrapped by dissolved oxygen on the surface of the semiconductor, hence increasing the photocatalytic performance of the doped sample.

Qing Wang et al [59] synthesized Fe doped $SnO_2$ at different concentrations with decorated layer g-$C_3N_4$ via chemical precipitation technique. The photocatalytic performance of prepared samples was evaluated under visible light illumination by degradation of Rhodamine B (RhB) and Methylene blue (MB). The dopant helps in reducing the bandgap value and improved the photocatalytic activity.

*Cobalt (Co)-doped $SnO_2$*

Cobalt with atomic number 27 belongs to group VIII of the periodic table. The presence of Co ions in the $SnO_2$ lattice results in decreasing the grain size and increasing oxygen deficiency of the $SnO_2$ lattice. These properties can influence the photocatalytic performance of pure $SnO_2$. Entradas et al [60] reported the Co-doped $SnO_2$ nanopowders via a chemical route and their optical study demonstrated a redshift due to band-to-tail and tail-to-tail transitions. They also studied the photocatalytic behavior of prepared nanocomposites in the degradation of 4-hydroxybenzoic acid (4-HBA) under UV light and complete photodegradation of dye was achieved within 60 min.

R. Mani et al [61] successfully synthesized pure and Co-doped $SnO_2$ nanoparticles via chemical precipitation. The effect of doping on the structural, optical, and photocatalytic activity was studied by using different characterization techniques. The doped material showed highly promising photodegradation properties when checked for the degradation of phenol and benzoic acid and was found superior to bare $SnO_2$ nanoparticles. The enhanced catalytic performance was attributed due to small bandgap values and high specific surface area.

Z. Nasir et al [62] utilized the co-precipitation method to prepare Co-doped tin oxide nanoparticles and further their photocatalytic and antimicrobial properties were investigated. The photocatalytic performance of Co-doped $SnO_2$ NPs was examined against MB and the increasing level of dopant concentration results in enhancing the photocatalytic activity due to the formation of more trapping sites and lower recombination rate.

D. Toloman et al [63] prepared Co-doped $SnO_2$ nanoparticles via chemical precipitation. The structure of the samples was in the tetragonal rutile phase and the presence of Co ions in the host lattice results in declining the oxygen valencies. The obtained doped samples showed high photocatalytic efficiency against RhB solution under visible light illumination due to small recombination rates, visible light absorption, and high amounts of •OH and •O− $^2$ radicals.

*Nickel (Ni)-doped $SnO_2$*

Nickel is the first-row transition element in the periodic table and belongs to a group (VIIIb) of the periodic table. It is a naturally occurring metallic element with a shiny appearance. H. Chen et al [64] used the hydrothermal process to synthesize Nickel-doped tin dioxide microspheres with various doping amounts and further characterized by using different techniques. The prepared samples show excellent photocatalytic efficiency as compared to pure $SnO_2$ under visible light irradiation. The dopant plays a vital role in reducing bandgap and recombination rate, further boosting the activity and stability of the catalyst.

M. Kandasamy et al [65] prepared Ni-doped $SnO_2$ nanoparticles (NPs) via a co-precipitation route and then investigated the properties for sensing and photocatalytic applications. The photocatalytic degradation of Rhodamine B (RhB), Congo red (CR), and Direct red (DR) dyes were monitored under Visible light irradiation. The doped NPs showed enhanced degradation efficiency due to the termination of the recombination process at higher doping concentrations.

Ateeq Ahmed et al [66] synthesized Ni-doped $SnO_2$ NPs via sol-gel technique with different amounts of dopant. The degradation rate of RhB was studied under UV light irradiation and reported that $SnO_2$ with 6% of Ni doping exhibited higher photocatalytic activity due to better adsorption of dye on the surface.

Chen and group [67] used a hydrothermal technique to synthesize Ni-doped $SnO_2$ quantum dots and $SnCl_4.5H_2O$, $NiCl_2.6H_2O$ is the main precursor, vitamin C as a stabilizer, and $Na_2CO_3$ as a precipitator. The effect of the doping concentration on the degradation efficiency was investigated and revealed that the doping reduces the bandgap and recombination rate. Hence, enhanced the photocatalytic activity of the doped catalyst.

S. Asaithambi et al [68] prepared rutile structured Ni-doped tin oxide NPs using a simple co-precipitation technique. It was observed that on increasing the level of doping, the average size of particles decreased from about 27 nm to 22 nm as a result of defects produced by the Ni doping. The photodegradation of methylene blue was examined for the pure and doped sample under a visible light source and the doped sample exhibited higher photodegradation efficiency due to its smaller size and high active surface area.

*Copper (Cu)-doped $SnO_2$*

Copper with atomic no. 29 classified as a transition element belongs to group 11 of the periodic table having a face-centered cubic structure. S. Vadivel et al [69] reported the synthesis of bare and copper (Cu) doped $SnO_2$ nanocrystalline thin films via the chemical bath deposition method. The redshift in spectrum displayed the decrease in band gap value due to charge-transfer transitions, hence promoting the photocatalytic behavior of Cu doped samples.

M. Sathishkumar et al [70] demonstrated the photocatalytic and antibacterial activity of pure and Cu-doped $SnO_2$ NPs synthesized by a microwave-assisted method. They studied the degradation properties of dyes were examined under UV light illumination and higher efficiency was obtained at about 9% of Cu doping. Due to the smaller size of particles and small surface roughness, the highest wavelength value was only observed for 9% of Cu doping.

*Zinc (Zn)-doped $SnO_2$*

Zinc with atomic no. 30 belongs to group 12 of the periodic table. It is the 24$^{th}$ most abundant element in the earth's crust. X. Jia et al [71] fabricated Zn doped $SnO_2$ nanoparticles through the precipitation technique. The photocatalytic activities of samples were evaluated using rhodamine B dye and the obtained decomposition rate of RhB for doped $SnO_2$ nanoparticles was about 99% due to smaller bandgap value and high surface activity.

In another study, the photodegradation of brilliant green (organic dye) under UV light was studied by N. Shanmugam et al [72]. The obtained results revealed that 0.75 M of Zn-doped $SnO_2$ decolorized brilliant green faster than other doping concentrations due to the narrow bandgap value which promotes the production of exciton and thus favors the photodegradation rate.

W. Soltan et al [73] prepared nanocrystalline and nanoporous Zn-doped $SnO_2$ materials via a simple polyol method. Fine-tuning of textural and optical properties was done by varying the zinc concentration. They revealed that the higher dosage of a catalyst lowers the degradation rate due to the turbidity of the solution and agglomeration of NPs. Hence, the optimum dosage of catalyst improves the performance and the complete discoloration of MB solution was achieved after 120 min.

M. Yurddaskal and group [74] compared the catalytic performance of pure and Zn-doped $SnO_2$ nanoparticles at different concentrations. The photocatalytic activity of prepared samples was evaluated by studying the decomposition of MB dye solution under a UV light source. The 1% doped sample exhibited higher efficiency but further doping reduced the degradation performance due to the increasing recombination process.

Chu et al [75] fabricated the Zn-doped $SnO_2$ flower-like nanostructures via hydrothermal technique and further, the photodegradation of RhB dye was studied under visible light illumination. The prepared Zn-doped $SnO_2$ nanostructures achieved higher photocatalytic activity in the decomposition of rhodamine B dye than pure $SnO_2$ as doping results in higher charge separation and lower electron-hole recombination.

Lu et al [76] synthesized Zn-doped $SnO_2$ pompon-like hierarchical structure using the hydro-thermal route and zinc nitrate, sodium oxalate and zinc nitrate hexahydrate are the major precursors. Further, MB, MO, RhB, and CR dyes were selected as model pollutants to examine the degradation efficiency of synthesized materials. Among them, the Zn-doped $SnO_2$ catalyst showed excellent photodegradation behavior due to the oxygen vacancies and more doping sites.

Suthakaran et al [77] introduced the surfactant-assisted hydrothermal method to synthesize undoped and Zn doped $SnO_2$ NPs using sodium hexametaphosphate (SHMP) as a surfactant. Further, they examine the synthesized NPs for the photodegradation of methyl violet dye. The incorporation of surfactant reduces the intensity of the strong absorption band with increasing time which indicates the decolorization of MV and hence enhances the photocatalytic activity. Table 2. shows a summary of the Photocatalytic behavior of the first series of Transition metals doped $SnO_2$ semiconductors.

*Second transition series elements doped $SnO_2$ nanoparticles:*

*Yttrium (Y) doped $SnO_2$*

Yttrium with atomic no. 39 is considered the rare-earth element which belongs to group 3 of the periodic table. The surface separation of $Y^{3+}$ ions creates oxygen vacancies that possess great optical conductivity. The effect of yttrium ($Y^{3+}$) doping obstructs the recombination process and enhances photocatalytic performance. A. Baig et al [97] reported the photodegradation of Y-doped $SnO_2$ NPs, which were prepared by a hydrothermal process with various doping amounts. They examined the structural, optical, and photocatalytic properties of the obtained sample. The doping results in decreasing the band gap values and thus provides more active surface sites. Hence, doping enhances the photodegradation of methylene blue dye in the visible region.

*Zirconium (Zr) doped $SnO_2$*

Zr with atomic no. 40 is a strong transition metal that lies in group 4 of the periodic table. Suthakaran et al [98] used the surfactant-assisted hydrothermal method to synthesize pure and Zr doped $SnO_2$ NPs. Tin (IV) chloride pentahydrate and zirconyl chloride octahydrates are the main precursors and sodium hexametaphosphate is used as a surfactant. An increment in the doping amount results in lower recombination rates thus promoting the efficiency rate. Further, the synthesized NPs for the photodecomposition of methyl violet (MV) dye was investigated under sunlight illumination for 120 min.

Similarly, A. Baig et al [99] synthesized the Zr doped $SnO_2$ nanostructures via a low-cost co-precipitation technique. The obtained nanoparticles were spherical and consisted of agglomerated particles and 4% Zr doping showed enhanced photodegradation of methyl orange dye which occurs due to the defects produced by the NPs.

Table 2. Photocatalytic behaviour of first series Transition metals doped $SnO_2$ semiconductor material. [MB: Methylene blue, MO: Methylene Orange]

| Photocatalyst | Preparation Method | Light Source | Contaminations | Photodegradation behavior | Ref. |
|---|---|---|---|---|---|
| **Ti- $SnO_2$** | • Stober Method | • UV-Vis | • Methylene blue | • 92% under UV; 54% under visible light | **[39]** |
| | • Co-precipitation | • UV-Vis | • Rhodamine B | • 95% and 52% within 120 min under UV and visible light | **[40]** |
| **V- $SnO_2$** | • Co-precipitation | • UV | • Rhodamine B | • 95% dye degraded within 150 min | **[44]** |
| | • Sol-gel | • UV | • MO | • Higher photocatalytic performance | **[78]** |
| **Cr- $SnO_2$** | • Combustion technique | • UV | • MO | • 98.9% efficiency in 100 min | **[46]** |
| | • Chemical precipitation | • UV | • MB | • Enhanced degradation rate | **[47]** |
| **Mn- $SnO_2$** | • Solution combustion | • Visible | • MO | • 92% dye degraded after 240 min | **[79]** |
| | • Sol-gel dip coating | • Sunlight | • Methyl red | • Moderate photocatalytic performance | **[80]** |
| **Fe- $SnO_2$** | • Microwave-assisted co-precipitation | • Visible | • Methyl orange | • 87.2% dye degraded | **[81]** |
| | • Sol-gel | • UV | • Methylene blue | • 80% degradation efficiency | **[82]** |
| **Co- $SnO_2$** | • Co-precipitation | • Visible | • Brilliant green dye | • 91% degradation rate | **[83]** |
| | • Sol-gel & Sonochemical | • Xenon lamp | • Coomassie Brilliant Blue dye | • 85% degradation efficiency | **[84]** |
| | • Solution method | • Sunlight | • Crystal Violet dye | • 4% doping show the highest efficiency | **[85]** |
| | • Co-precipitation | | • Pathogenic bacteria | • 99% of bacteria destroyed | **[86]** |
| **Co- $SnO_2$** | | | | | |
| **Ni- $SnO_2$** | • Wet chemical synthesis | • Sunlight | • Congo Red | • 83% dye degraded in 2 hrs | **[87]** |
| | • Sol-gel | • Visible | • Methylene Blue | • 3% doping show 94.33% efficiency | **[88]** |
| | • Chemical synthesis | • UV | • Phenol; Benzoic acid & MO | • 65%; 89%; 95% respectively | **[89]** |
| **Cu- $SnO_2$** | • Co-precipitation | • UV-visible | • RhB | • 3% doped sample show better results | **[90]** |
| | • Combustion synthesis | • Visible | • Methyl orange | • 99% degraded in 120 min | **[91]** |
| | • Precipitation | • Sunlight | • Azo dyes | • 97% for CR & 91% for RhB | **[92]** |
| **Zn- $SnO_2$** | • Microwave irradiation | • Mercury lamp | • Methylene Blue | • 99.6% degradation rate | **[93]** |
| | • Spray pyrolysis | • UV-visible | • Organic dyes | • 90% for MB & 87% for MG | **[94]** |
| | • Co-precipitation | • UV | • MO | • 80% within 120 min | **[95]** |
| | • Hydrothermal | • 500 W Hglamp | • Acidfuchsine | • 96% in 80 min | **[96]** |

*Niobium (Nb) doped $SnO_2$*

Niobium is a light grey transition metal with atomic no. 41 and belongs to group 5 of the periodic table. A. Sadeghzadeh-Attar [100] fabricated the Nb-doped $SnO_2/V_2O_5$ hetero- structured nanocomposites by using hydrothermal and liquid-phase deposition-based processes. $SnO_2$ nanotubes were doped with different concentrations and the synthesized nanocomposite exhibited higher degradation due to the efficient charge separation.

*Molybdenum (Mo) doped $SnO_2$*

Molybdenum is a chemical element in group 6 of the periodic table with atomic no. 42. It exists in two different oxidation states such as $Mo^{6+}$ and $Mo^{4+}$ having ionic radii. Therefore, it is expected that more Mo ions could be incorporated into the $SnO_2$ lattice by replacing more $Sn^{4+}$ ions. N. Manjula et al [101] successfully investigated the photocatalytic behavior of Mo-doped $SnO_2$ ($SnO_2$: Mo) nanopowders synthesized by a cost-effective chemical method. Doping shifts the absorption edge towards the visible region therefore, the doped sample exhibit a higher degradation rate as compared to the bare sample.

*Palladium (Pd) doped $SnO_2$*

Palladium with atomic no. 46 belongs to group 10 in the periodic table. It is considered the most precious and rarest earth metal. R. Janmanee et al [102] utilized the thermal decomposition method to synthesize Palladium doped $SnO_2$ NPs using Vent Pulp as the dispersant and tin tetrachloride pentahydrate and ammonium hydroxide as a precursor. The photocatalytic activity of the obtained samples for the degradation of sucrose and glucose under UVA-light irradiation was examined and it was concluded that due to their smaller size, the Pd doped $SnO_2$ NPs demonstrated a good efficiency rate.

*Silver (Ag) doped $SnO_2$*

Silver with chemical symbol Ag and atomic no. 47 is a white lustrous metal located in period 5 and group 11 of the periodic table. It is classified as a soft, white, and lustrous transition element. K. Vignesh et al [103] reported the photocatalytic behavior of Ag-doped $SnO_2$ modified with curcumin. The NPs were synthesized via combined precipitation and chemical impregnation techniques. The modified photocatalysts revealed a redshift in the visible region and the enhanced activity of the Cu-Ag-$SnO_2$ sample was ascribed due to the existence of more reactive oxygen species.

S. Ansari et al [104] used silver in the synthesis of enhanced $SnO_2$ nanocomposites using an electrochemically active biofilm. The prepared material was then analyzed in the degradation of various organic dyes and toxins, such as methyl orange, methylene blue, 4-nitrophenol, and 2-chlorophenol. They showed higher photocatalytic activity as compared to pure $SnO_2$ nanostructures upon exposure to light in the visible region due to a lower recombination process.

M. Ahmed et al [105] successfully prepared mesoporous Ag- $SnO_2$ NPs via sol-gel process using PVP as the pore and structure-directing agent. Due to the deposition of Ag ions on the wall of pores, super micropores were created and the hydroxyl radicals and holes are responsible for the degradation of methylene blue dye.

B. Babu et al [106] successfully synthesized Ag doped $SnO_2$ QDS via one-pot synthesis using hydrazine. The photocatalytic activity of prepared material was synthesized at different amounts of Ag. Doping of Ag ions results in increasing the high active surface area thus the doped sample degrades about 98% of Rhodamine B (RhB) dye. Table 3. shows a summary of the Photocatalytic behavior of Second series Transition metals doped $SnO_2$ semiconductors.

Some second series transition elements such as Technetium (Tc), Ruthenium (Ru), Rhodium (Rh), and Cadmium (Cd) are not widely reported in the literature as a dopant with $SnO_2$ for photocatalytic applications. Technetium-99 (Tc) is a problematic fission product and due to its long half-life, it complicates the long-term disposal of nuclear waste [120]. K. R. Arangayagam et al [121] reported the synthesis Ru doped ZnO as photocatalyst but no literature reported for Ru doped $SnO_2$ for photocatalytic applications. Rh and Cd doped semiconductors are reported in the literature for different applications such as in the field of hydrogen production, dye-sensitized solar cells, and sensors with other metal oxide semiconductors [112-124].

*Parameters altering the photocatalytic activity of $SnO_2$ Nanoparticles*

Different operating parameters can affect the photocatalytic degradation of various pollutants present in the wastewater such as catalyst concentration, pH value, light intensity,

Table 3. Photocatalytic behaviour of Second series Transition metals doped $SnO_2$ semiconductor material

| Photocatalyst | Preparation Method | Light Source | Contaminations | Photodegradation behavior | Ref. |
|---|---|---|---|---|---|
| **$Y$- $SnO_2$** | • Biosynthesis | | • Bacillus subtilis | • Doped sample shows better activity | **[107]** |
| **$ZrO_2$-$SnO_2$** | • Hydrothermal | • UV light | • Azo dye | • 96% degradation after 30 min | **[108]** |
| **Nb-sno2** | • Co-precipitation | • Sunlight | • Organic dye | • Less efficiency than the co-doped sample | **[109]** |
| **Mo- $SnO_2$** | • Chemical method | • Visible light | • Methyl Orange & Rhodamine B | • 90.23% degradation against MO and 81.14% degradation against RhB | **[101]** |
| **Pd- $SnO_2$** | • Sol-gel dip coating | | • E. coli, S. aereus, & S. cerevisiae | • Improved catalytic performance | **[110]** |
| | • Template method with Sol-gel | • UV | • Methylene Blue | • 85.3% degradation rate | **[111]** |
| **Ag-$SnO_2$** | • Precipitation | • Visible | • Carbamazepine | • 86.5% degrade in 120 min | **[112]** |
| | • Hydrothermal | • Visible | • Phenol | • 91% degradation after 50 min | **[113]** |
| | • Microwave Hydrothermal | • UV | • Organic dye | • 3% doped sample show better efficiency | **[114]** |
| | • Co-precipitate | | • Pathogens | • Higher efficiency as compared to bare sample | **[115]** |
| | • Biosynthesis | | • Xanthomonas oryzae(bacterial leaf) | • Doped samples exhibit higher efficiency | **[116]** |
| | • Two-step hydrothermal | • UV-Vis | • Rhodamine B | • 93% degraded within 35 min | **[117]** |
| **Cds- $SnO_2$** | • Microwave irradiation | • UV & natural sunlight | • Methylene blue | • 95% degradation rate | **[118]** |
| | • Chemical synthesis | • UV | • Acid violet 7 | • 99% dye degraded | **[119]** |

temperature, surface area, and crystallinity. This section concisely reviews some of the following parameters [125].

*Catalyst Concentration*

Various studies reveal that the photocatalytic efficiency first increases along with the catalyst loading and then reduces at a high dosage. An extreme concentration of catalyst particles would block the path of light, which further results in the scattering of light and hence decrease the photocatalytic activity [126-127].

S. Chakraborty et al [128] studied the effect of $SnO_2$ NPs loading on photocatalytic degradation of 4-aminopyridine under solar light exposure for 120 min. They reported the effect of two parameters such as catalyst concentration and pH of the solution on photocatalytic activity of $SnO_2$ nanoparticles and the catalyst with various concentrations were added to the 4-AP solution. On increasing the catalyst dosage, the absorption of photons also increases followed by the increment in active sites on the surface of the catalyst. Hence, the photocatalytic efficiency increase with increasing catalyst loading. Barkha Rani et al [129] successfully explained the significant influence of catalyst amount on the photocatalytic degradation of methylene blue dye. The synthesized samples revealed that the increase in catalyst amount provides higher active sites for the adsorption of dye. Hence, the degradation rate was found to increase with an increased dosage amount.

*Effect of pH*

pH is one of the most significant factors which not only affects the oxidation potential but also influences the charge of the potential [130]. A slightly acidic pH range enhances the attraction of the pollutant to the photocatalyst surface, which results in increasing the degradation efficiency. Also, the degradation rate declines if the range of pH drops below a certain value. Hence it is an important factor that can modify the photocatalytic activity of the particles [131]. Z. Fzhu [132] et al analyzed the efficacy of pH on the photocatalytic activity of $SnO_2$ microspheres, synthesized via microwave solvothermal technique. The RhB dye degradation efficiency was studied at different pH ranges. They found that at pH 2.91 and 6.18, the absorbance of dye molecules was 2-3 times higher due to the availability of large binding sites for dye molecules.

Similarly, M. Najjar et al [133] studied the effect of pH on the photocatalytic activity and reported that the photodegradation of EBT dye is enhanced when the pH of the reaction mixture is higher due to the attraction between cationic dye molecules and $OH^-$ ions.

*Light intensity*

When the incident energy is equal to or more than the bandgap energy then only the semiconductor catalyst absorbs it. On increasing the intensity of incident light, the feasibility of catalyst excitation was also raised. Light of lower intensity reduces the generation of free radicals, hence reducing the degradation rate. Therefore, photocatalytic activity increases with increasing light intensity [134]. M. Dhanlakshmii et al [135] fabricated the visible-light-driven Ir doped $SnO_2$ NPs. They concluded that the enhancement in the degradation efficiency rate results in an increment of light intensity as the light of higher intensity is capable of generating more reactive radicals hence improving the photodegradation rate.

*Temperature*

The photodegradation rate also depends on the temperature of the reaction. The photocatalytic activity increases at elevated temperature range due to improvement in the mobility of charge carriers. However, further, an increase in temperature beyond a certain range results in increasing the recombination process and hence reducing the degradation rate [136]. K. Prakash et al [137] reported the formation of $SnO_2$ photocatalyst for mineralization of methylene blue dye solution at different temperature ranges. They found that increase in the annealing temperature range produces remarkable enhancement in the degradation efficiency of dye as the movement of photoelectron-hole pairs generates more OH radicals. But the further increase in the temperature results in increasing the recombination rate thus better results is acquired when the temperature range is retained between 20 °C and 70 °C.

Similarly, Hao Yuon [138] et al analyzed the impact of calcination temperature on the methyl orange dye degradation and the results revealed that the sample prepared at a higher temperature reported enhanced degradation efficiency and then decreases due to variation in particle size and phase composition of the particles.

*Surface area and Crystallinity*

Size and surface area play a very crucial role in the photocatalytic efficiency of photocatalysts. Small size and high active surface area offer enhanced degradation qualities towards the removal of pollutants from the existing environment. Therefore, modification by doping not only reduces the bandgap value but also enlarges the surface of the catalyst [139]. Soumia Haya and co-workers [140] compared the photocatalytic efficiency of pure and Sr doped $SnO_2$ NPs for the degradation of methylene blue dye under UV light exposure. The effect of doping was examined by investigating the crystal morphology. The average size was calculated by the Debye Scherer equation which revealed the decrement in crystal size hence providing a large surface area that further offers the more active sites thus promoting the photocatalytic efficiency.

Ameer Azam et al [25] studied the efficacy of Mn ions doping on the structural and optical properties of $SnO_2$ NPs prepared by the sol-gel approach. The crystal structure and morphological studies were carried out and it was observed that the crystal size reduced from 16.2 nm to 7.1 nm as the doping of Mn ions prevents the growth of the crystal. The effect of various influencing factors on the particle size and crystallinity of $SnO_2$ nanoparticles is summarized in Table 4.

*Applications of Bare/Doped $SnO_2$ Photocatalyst for Degradation of wastewater pollutants*

Globally, the uncontrolled increasing level of water pollution has turned into a major threat. The major pollutants are broadly classified into organic, inorganic, and biological contaminants. Among them, organic pollutants are of major concern due to their mutagenic effects even after exposure to a little amount [141]. The majority of organic pollutants are emitted with large-scale industrial and agricultural practices i.e. reckless use of chemicals and fertilizers [142]. Fig. 7 shows the various applications of $SnO_2$ toward water decontamination.

Various researchers reported the mineralization

Table 4. Effect of influencing parameters on the particle size and crystallinity of $SnO_2$ nanoparticles.

| (SnO2)Catalyst Conc.(gm/L) | Light source | pH | Calcination Temp(C°) | Particle size (nm) | crystallinity | Preparation method | Ref. |
|---|---|---|---|---|---|---|---|
| 0.5- 2.0 | UV lAMP | 3.0 | 700 | 25-50 | Tetragonal rutile | Precipitation method | [128] |
| 10 | UV | 2-8 | 200 | 2.0-3.5 | pristine rutile | hydrothermal | [129] |
| 50 | UV | 2.9 - 9.05 | 140-180 | 6.0-7.8 | microspheres | Solvothermal | [132] |
| 0.08 -0.43 | UV lAMP | 5.0-9.0 | 600-800 | 4.5-19.5 | Tetragonal rutile | Sol-Gel method | [133] |
| 10-75 | UV | 2.0-12 | 550-600 | 41.36-65.8 | microspheres | hydrothermal | [137] |
| 100 | Hg lamp | 3.0-9.0 | 700-900 | 30-40 | Cubic | precipitation | [138] |

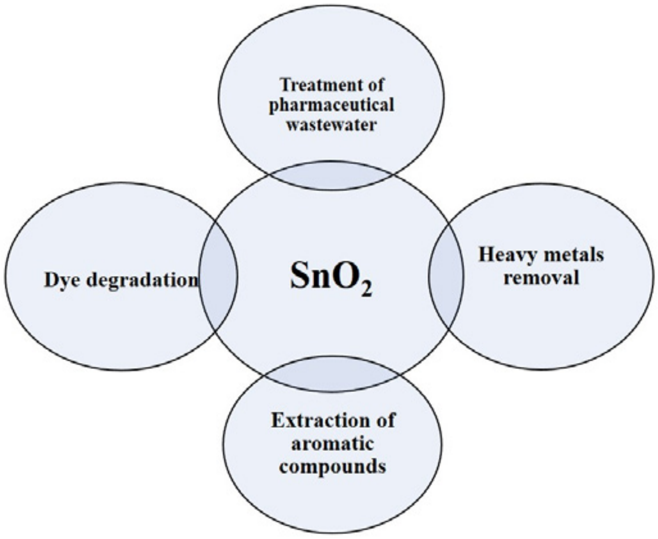


Fig. 7. Applications of $SnO_2$ toward water decontamination

of wastewater pollutants using $SnO_2$ has been summarized below:

*Degradation of pharmaceutical pollutants*

Pharmaceuticals products (PP) like sulfamonomethoxine (SMM), naproxen (NPX), ciprofloxacin (CIP), amoxicillin (AMX), tetracycline, and many more are significantly used for healthcare systems. These products are difficult to degrade as they produce secondary pollution [143]. Hojamberdiev et al [144] examined the degradation process for different pharmaceuticals and personal care products (PPCPs): metoprolol, carbamazepine, acetaminophen, and triclosan. Under visible light exposure, the obtained sample degraded about 70% of acetaminophen, 67% of metoprolol, 40% of carbamazepine, and 40% of triclosan within 120 min. The difference in the removal efficiency of PPCPs is due to the variation in physicochemical properties of the composite, chemical structures of PPCPs, and the interactions between PPCP molecules and the photo-catalyst surface.

Begum and group [145] utilized a chemical precipitation technique to synthesize $SnO_2$ nanoparticles using anhydrous aspartic acid and surfactants at different annealing temperatures. They evaluated the photocatalytic activity of the synthesized sample for detoxification of carbamazepine (CBZ), an antiseptic drug. The obtained SC1 and SS1 NPs samples can degrade about 97% and 92% respectively, beneath UV-C light within 1 h.

Chu et al [146] successfully prepared bismuth-doped $SnO_2$ quantum dots using a one-step hydrothermal process. The photocatalytic behavior of the prepared sample was analyzed for the mineralization of ciprofloxacin hydrochloride (CIP) and RhB dye solution under-stimulated sunlight illumination and the degradation efficiencies were 1.75 and 1.53 times higher than that of the pure sample. The outstanding performance of the composites was due to the enhanced absorbance of

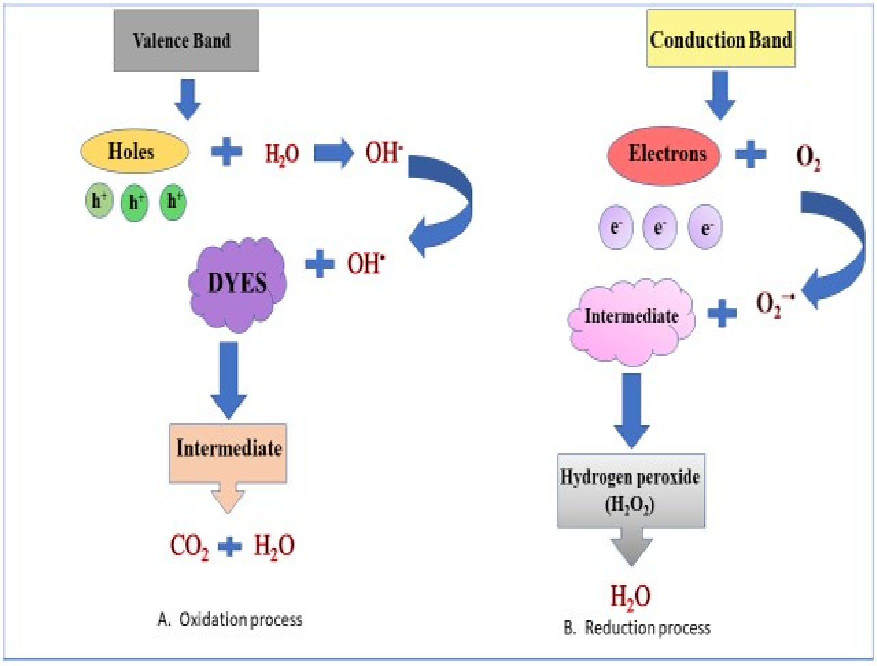


Fig. 8. Pictorial representation of degradation mechanism of dyes

light and lower recombination rate.

Begum et al [147] introduced the hydrothermal synthesis process to produce $SnO_2$/activated carbon nanocomposites tin chloride pentahydrate, sugarcane juice, and activated carbon. The prepared sample was used further for the mineralization of naproxen beneath sunlight irradiation and showed that the obtained nanocomposite degraded 94% of the naproxen due to the availability of larger active sites available on the surface.

*Photocatalytic Degradation of Dyes*

Nowadays, synthetic dyes are the major abundant pollutant detected in water bodies. These highly pigmented dyes cause eutrophication and agitations in marine life [148]. The degradation mechanism of dyes is shown below in Fig. 8.

Jyoti Bala Kaundal et al [149] synthesized $SnO_2$ decorated Polystyrene ($SnO_2$-PS) polymer nanocomposites using thermocol packing waste via a sol-gel chemical route and their photocatalytic studies revealed that 99% of indigo dye was degraded within 30 minutes due to the smaller size of NPs hence, makes it a preferable photocatalyst.

Morvarid Najjar et al [133] synthesized $SnO_2$ nanoparticles with the help of the sol-gel synthesis route and the gel obtained was calcined at different temperatures. They concluded that the increase in irradiation time results in decreasing the absorbance of dye solution and the obtained degradation rate of Eriochrome Black T (EBT) dye was about 35.9%

Taehee Kim et al [150] synthesized $SnO_2$ aerogel/reduced graphene oxide (rGO) nanocomposites via the sol-gel technique. The obtained nanocomposites exhibit enhanced photocatalytic activity for the degradation of methyl orange due to the high surface area of graphene flakes. Hence, the prepared nanocomposites are termed a suitable candidate for the photodegradation of pollutants in industrial wastewater.

Vijay Kumar et al [151] utilized a two-step sol-gel approach to synthesize $SnO_2$/CdS heterostructures and they concluded that prepared $SnO_2$/CdS heterostructures exhibit improved photocatalytic performance due to the excessive separation of photogenerated electrons and holes in the photocatalytic region.

Al-Hamdi et al [139] prepared Iodine doped tin oxide ($SnO_2$:I) nanoparticles using the sol-gel approach. In this work, the photocatalytic activities of synthesized NPs for phenol degradation were studied and the iodine doped $SnO_2$ under UV irradiation degrades phenol very quickly within 30 minutes due to the high optical absorption of doped particles.

*Photocatalytic degradation of other organic pollutants*

Aromatic compounds are considered another organic pollutant that is mainly discharged into water bodies by different industries[152-153]. These are colorless or pale yellow solids with one or more hydroxyl groups attached to the ring. The discharge of these pollutants into the environment causes a significant threat to the ecosystem [154].

Al-Hamdi et al [155] reported the mineralization of phenol with rare earth metals doped $SnO_2$ NPs. Lanthanum, cerium, and neodymium were used as dopants and they showed that the lanthanum doped $SnO_2$ was tremendously effective for the degradation of phenol as they are most photoactive. Under UV- light exposure more than 95% of phenol mineralized from the sample. The results revealed that the obtained doped sample was much better than the bare sample.

K. Saravanakumar et al [113] introduced a simple and fast one-step hydrothermal route to produce spheres like $Ag/SnO_2$ nanocomposite. Different spectroscopic and microscopic techniques were used to evaluate their light absorption and morphological properties. The incorporation of Ag into the $SnO_2$ lattice improved the photocatalytic performance due to the reduced recombination mechanism, which was examined by the PL spectrum. Further, beneath visible light illumination, 91% of phenol was degraded within 50 min.

Liu et al [156] successfully fabricated the core–shell structural CdS@SnO2 nanorods. The integration of Cds having a small bang value i.e. 204 eV with $SnO_2$ having a wide bandgap of about 3.6 eV was found to be favorable. Under visible light exposure, the photocatalytic performance for the oxidation of benzyl alcohol to benzaldehyde was higher than that of neet semiconductors as a result of an extended lifetime and improved e−–h+ pairs separation.

J.Ebrahimian et al [157] reported the production of $SnO_2$ nanoparticles via the green synthesis route using the extract of chaste tree (Vitex agnus-castus) with casticin, quercetin, and kaempferol as reducing and stabilizing agents. 91.7% of dye degraded within 190 min due to a higher adsorption rate of $Co^{2+}$ ions on the surface.

## CONCLUSION

This review paper significantly highlights the modification of $SnO_2$ by doping of first and second transition series metals. The key issues that are addressed in this review are as follows:

1. $SnO_2$ is considered the most preferable and attractive photocatalyst for the removal of pollutants present in wastewater. Also, the addition of transition metal dopants further improves photocatalytic performance.

2. Different synthesis methodologies such as sol-gel, hydrothermal, and co-precipitation are the most approachable routes for preparing doped $SnO_2$ nanoparticles, owing to their simplicity. The sol-gel method is considered the most preferable method due to its better homogeneity results.

3. Various studies reveal that TM doping helps in reducing the recombination process which further improves the photocatalytic behavior of nanoparticles. Hence, it is possible to acquire the visible light active photocatalyst by altering the different operating parameters such as pH, dopant concentration, time, and temperature which significantly affect the photocatalytic performance.

4. TM doping is found to increase the photodegradation behavior of $SnO_2$ based photocatalysts. The above-summarized results exhibited the excellent photodegradation of dyes, pharmaceutical waste, and other toxic organic pollutants. Various researchers have successfully synthesized transition metal-doped $SnO_2$ nanoparticles, but the first and second series transition metal-doped $SnO_2$ for their photocatalytic applications have yet not been fully explored.

5. With a thorough analysis, it has been observed that the majority of the work with $SnO_2$ nanoparticles as photocatalysts for water purification is reported under UV and Visible light radiation only. But recent developments in the field show that it is possible to use solar-driven $SnO_2$ nanoparticles for the removal of synthetic dyes/ toxins.

6. We have compared the effect of different transition metal dopants used in tin oxide nanoparticles based on their synthesis technique, source of irradiation used, types of contaminations removed, and obtained photodegradation efficiency.

The ability of $SnO_2$ nanoparticles to completely deal with different toxic pollutants in water bodies without producing harmful by-products has unrolled the novel research approach to be pursued. $SnO_2$ is still a hot topic for new research findings across the world. Various researchers are working on it by varying the different doping elements and concentrations to get desired outcomes. As it is a well-known fact that transition elements are quite popular elements for doping, we hope that this review will help the researcher community.


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## DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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