**A Review on metal ion doped SnO2 Nanocomposites: Synthesis and Application in photocatalytic degradation and antimicrobial activities**

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**Abstract:**

Photocatalysis is the acceleration of the photoreaction in the presence of light. The most common heterogeneous photocatalysts are transition metal oxides and certain semiconductors. Among the transition metal oxides TiO2, ZnO and SnO2 are low-cost materials with good chemical and thermal stability, large surface area, high adsorption properties, less resistance to diffusion, and show faster rates of equilibrium. SnO2 is of ample interest in the field of photocatalysis due to its different morphologies, high photochemical stability, strong oxidizing power, low cost, and non-toxic nature. This paper outlines the synthesis of SnO2 by various techniques with different morphologies. Then, reviewed the design of SnO2 nanoparticles with improved performance in the areas of photodegradation and antimicrobial activities.

**Keywords**: SnO2 nanoparticles, photocatalysis, antimicrobial activities

1. **Introduction:**

Semiconductor Nps possess properties between metals and non-metals. They possess wide band gaps and showed significant alteration in their properties with band gap tuning therefore, they are very important materials in photocatalysis, photo optics, and electronic devices. Metal oxides are a widely explored and studied class of inorganic solids due to a wide variety of structures, properties, and exceptional phenomena exhibited by their Nps. Metal oxides (MO) are formed when metal ions form coordination bonds with oxides giving rise to a closely packed structure. MO plays a major role in the area of material science with extraordinary physical and chemical properties. Transition metal oxides have been used in numerous industrial applications. Metal oxides are commonly available and present in different forms possessing special shapes, compositions, structures, and chemical and physical properties[1]. Some commonly known MO include TiO2, ZnO, SnO2, VOx, MoOx, etc

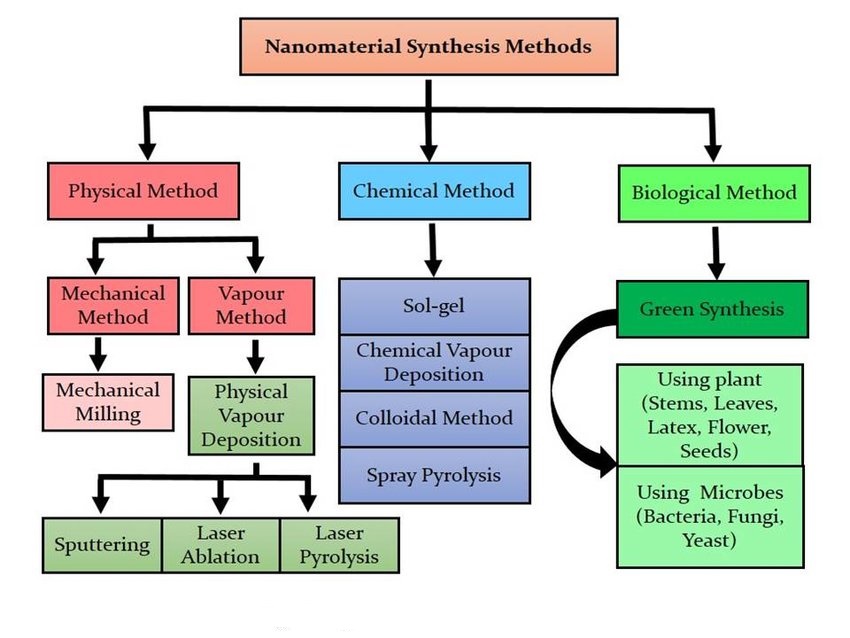
Among the metal oxides, Tin oxide (SnO2) is one of the attractive and promising material owing to its abundance, non-toxicity, low cost, relatively high chemical stability with wide energy gap (Eg = 3.6 eV at 300 K), strong thermal stability (up to 500 °C), high degree of transparency in the visible spectrum, strong chemical and physical interactions with the adsorbed species with high electron mobility (200 cm2 V-1 s-1 ), less resistivity, faster transport of photo excited electrons and holes, very high absorption capacity, more specific surface area and the presence of a huge number of active sites make SnO2 a promising candidate for a potential application in the lithium-ion batteries, sensors, catalysis, field emission displays [2], light-emitting diodes[3], dye-based solar cells[4], energy storage, glass coatings, medicine, environmental remediation[5-8], transistors, optoelectronics devices, solar cells, super capacitors, photo [9-13], catalyst supports, transparent conducting electrodes[14], antireflective coatings[15] and a proto-type material for metal oxide sensors[16]. SnO2 is used as a sensor to improve the response time and sensitivity owing to its high specific area, high chemical stability, low electrical resistance, and low density [17].

The most common heterogeneous photocatalysts are transition metal oxides and certain semiconductors. Among the transition metal oxides TiO2, ZnO and SnO2 are low-cost materials with good chemical and thermal stability, large surface area, high adsorption properties, less resistance to diffusion, and show faster rates of equilibrium [18]. SnO2 is of ample interest in the field of photocatalysis due to its different morphologies, high photochemical stability, strong oxidizing power, low-cost and non-toxic nature [19].

In this review, we outline the synthetic strategies of pure SnO2 hierarchical structures and the approaches to enhance performance. The applications of SnO2-based nanostructures in photodegradation and antimicrobial activities are also reviewed. The amendment of SnO2 with metal ions, additional semiconductors, or else noble metals could be moderately operative to accelerate the separation efficacy of photoexcited (e−/h+) and thus it enriches the photocatalytic assets to advance future research.

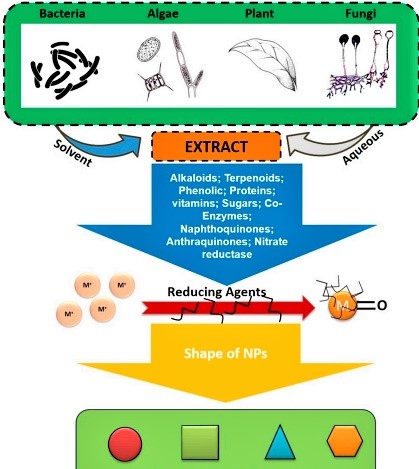
1. **SnO2 based nanomaterials**

SnO2 NPs were synthesized by various physical, chemical, and green methods (Fig.1). The chemical methods include sol–gel, hydrothermal, precipitation, mechanochemical method, microemulsion, and so forth [20]. Among the chemical methods, the most widely used technique is the sol–gel synthesis which utilizes tin precursor salt and chemical reagents that regulate the formation of the tin-containing gel. After that, the gel is exposed to heat treatment under temperatures up to 800°C to obtain SnO2 NPs. Chemical stabilizers and capping agents were added during the synthesis of SnO2 NPs to control the size and forbid agglomeration of the nanoparticles. The pH, concentration of chemicals, reaction time, and calcination temperature influence the size and morphology of nanoparticles [21]. The aforesaid methods of synthesizing SnO2 NPs utilize various perilous chemical reagents, solvents, and surfactants which create a serious threat to the environment and human health.



**Fig. 1**: Synthesis methods for nanoparticles [22]

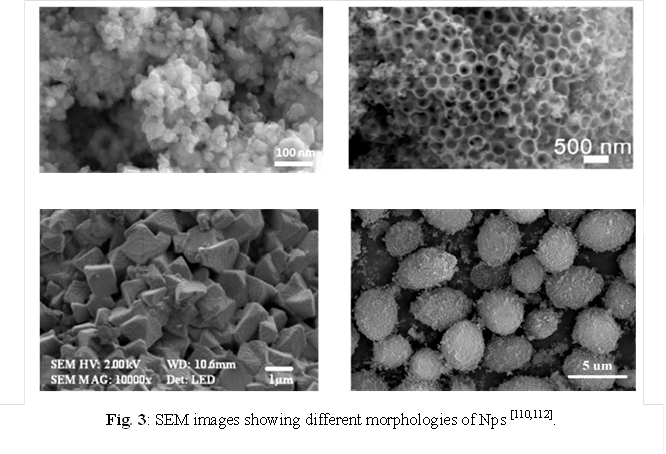
In the green synthetic strategy, biological entities like plant extract, microorganisms, or other green sources could be used as an alternative to conventional physical and chemical methods. Some of the distinct advantages that biological synthesis(Fig.2) has over physical and chemical methods are (a) clean and environmentally friendly method as nontoxic chemicals are used (b) the use of renewable sources (c) the active biological components like enzyme itself as well as phytochemicals acts as reducing and capping agent thereby minimizing the overall cost of the synthesis process (d) external experimental conditions like high pressure and temperature are not required, causing significant energy savings [22]. Considerable efforts have been devoted to synthesizing SnO2 nanostructures with different morphologies(Fig.3), such as nanorods [23], nanowires [24], nanotubes [25], nanosheets [26] and 3D nanospheres self-assembled from these low-dimensional nanostructures via interactions such as van der Waals forces, hydrogen, and covalent bonding.



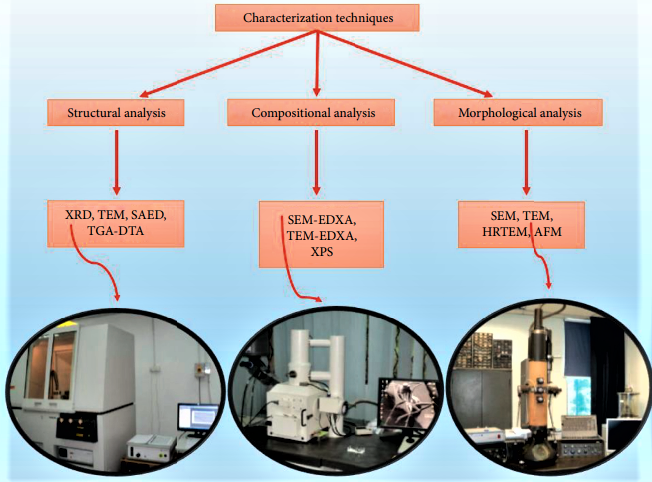
**Fig. 2: Synthesis of nanoparticles using different biological sources [29]**

several attempts have been conducted on doping SnO2 NPs with transition metals such as cobalt [26,27], nickel[28], chromium[ 30], iron[31] and vanadium[32] aiming to extend the photo response of SnO2 from the ultraviolet to the visible region. Moreover, adding amounts of these dopant species can efficiently extend the absorption edge of SnO2 NPs into the visible region which increases the photocatalytic activity. In contrast, high doping content can create electron-hole recombination sites and the wide energy band gap hinders this photo activation [33].

Different characterization techniques have been practiced for the analysis of various physicochemical properties of NPs. These techniques include X-Ray Diffraction (XRD), X-Ray Photoelectron Spectroscopy (XPS), Infrared Spectroscopy (IR), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), UV-Vis Spectroscopy, Photoluminescence Spectroscopy (PL), Brunauer–Emmett–Teller (BET) and Particle size analysis (Fig.4)[34]. Finally, the photodecomposition was studied by using pure and metal doped SnO2 nanoparticles as a catalyst under UV/visible light irradiation and antimicrobial assay was evaluated and their performances are reviewed.



**Fig 3: SEM images showing different morphologies of Nps[36,37]**

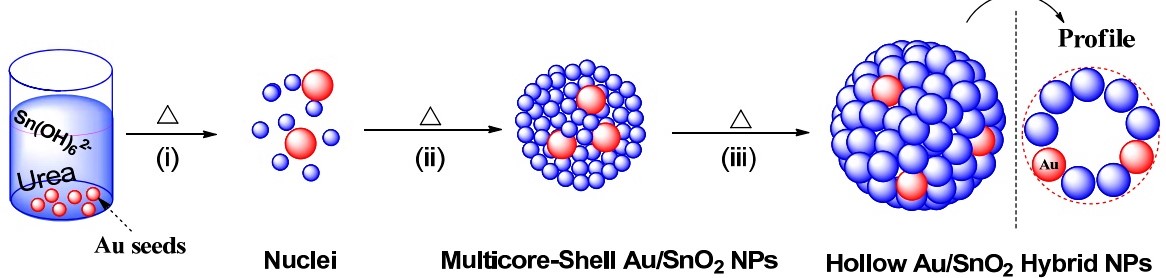


**Fig. 4:** General techniques for the characterization of nanoparticles [34]

Kumar, V et al. [38] successfully prepared Heavily F-doped SnO2 nanocrystals by sol-gel method involving low-temperature oxidation of an Sn containing fluoride complex KSnF3 as the single-source precursor with H2O2[39]. Powder X-ray diffracted peaks signified the low crystallite size which was indexed to a tetragonal unit cell with lattice constants a = 4.7106 (1) Å and c = 3.1970 (1) Å. Agglomeration of particles with an average diameter of 57 nm was observed in the TEM studies whose spot-wise EDX analysis indicated the presence of fluoride ions. The BET surface area of pure SnO2 was quite high (207.81 m2 /g) as compared to the F-doped SnO2 nanocrystals (45.16 m2 /g). The disordered nature of the rutile lattice and the enormous oxygen vacancies created due to fluoride ion doping was evident from the broad bands observed at 455, 588, and 874 cm-1 in the room-temperature Raman spectrum of SnO2:F. As a consequence of the oxygen vacancies, F-doped SnO2 was examined for its function as a photocatalyst in the degradation of aqueous Rhodamine-B (RhB) dye solution under UV irradiation. The solution turned colorless within 20 min of irradiation. Very high photocatalytic efficiency was observed for the F-doped SnO2 nanocrystals as compared to pure SnO2. The increased photocatalytic efficiency was related to the very high concentration of oxygen vacancies in SnO2 induced by F doping.

You, H et al. [40] synthesized Hollow Au–SnO2 super symmetric nanostructures with high surface area by a solution reaction with N, N-dimethylformamide (DMF) as a solvent in the presence of PVP and PEG as capping agents and demonstrated that the initially formed ultrafine SnO2 nanoclusters assembled to form hollow hexapods and then further in situ self-assembly induced the formation of higher-ordered hollow structures[40].

Wu, W et al. [41] synthesized hollow hybrid nanostructures using a seed-mediated hydrothermal method by XRD patterns indicated strong rutile tin oxide phase peaks and weak gold peaks with lattice constant a =4.738 Å and c = 3.187 Å (JCPDS No. 41-1445) [41]. The average crystallite sizes calculated by the Deby-Scherrer formula were about 10.8 nm which was in agreement with the diameter of 40 small grains and the HRTEM result. The presence of Au, as well as Sn and O, was confirmed by the EDX spectrum. The formation and shape evolution of hollow SnO2-Au hybrid nanostructures were studied (Fig.5).



**Fig. 5**: Schematic illustration of the formation and shape evolution of hollow SnO2-Au hybrid nanostructures[41]

Davis, M et al. [42] utilized a facile, sol–gel method for synthesizing highly crystalline, Fe-doped SnO2 nano architectures with efficient photocatalytic degradation of RhB under ultraviolet irradiation[42]. The photocatalytic activity of these materials was studied by examining the degradation of RhB with pure SnO2 and each Fe-modified sample (3 and 5 %), all annealed at 3500C. EDS confirmed the presence of Fe in the most active Fe-modified SnO2 sample. It was found that the 5 % Fe-modified SnO2 degraded RhB by more than half after 2 h.

Ansari, S et al. [43] synthesized Ag–SnO2 nanocomposites with different concentrations of silver precursor (1 mM and 3 mM) by using an EAB without toxic chemicals, surfactants, and organic solvents at room temperature using an electrochemically active biofilm. Ag–SnO2 nanocomposites showed a broad absorption peak from 400–550nm, which was attributed to the surface plasmon resonance absorption of AgNPs. Nanocomposites exhibited enhanced photocatalytic activity under visible light irradiation for the degradation of methyl orange, methylene blue, 4-nitrophenol, and 2-chlorophenol compared with pure SnO2 nanostructures. It is seen that, after visible light irradiation on Methyl orange (MO) and Methylene Blue (MB) for 6 h and 5 h, respectively, almost complete degradation occurred.

Toloman, D et al. [44] synthesized a series of Co-doped SnO2 nanoparticles by chemical precipitation method using tin chloride dihydrate, cobalt chloride hexahydrate, sodium hydroxide, and ethanol. The crystallinity of the samples increased with the increase of doping degree. The photocatalytic activity of the sample was evaluated against RhB synthetic solution, under visible light irradiation. All the samples showed photocatalytic activity, the best performance was obtained using 1.0% Co–SnO2.

Ran, L et al. [45] developed a facile infiltration route for synthesizing hollow-structured SnO2  with an adjustable Ti doping content using SiO2 microspheres as hard templates via an improved Stober method[45]. The crystal structure and morphology of samples were not affected by Ti doping and they retained a highly crystalline state and hollow spherical nanostructure with a particle diameter of about 300 nm. Ti is uniformly incorporated into the lattice of SiO2 materials in the form of Ti4+. In comparison with pure SiO2 hollow spherical sample, Ti-doped SiO2 with a doping content of 20 mol% displayed the highest photocatalytic activity with 92% MB photo catalytically decomposed under UV light irradiation with 54% MB photo catalytically decomposed under visible light irradiation within a degradation time of 135 min.

Zhao, Q et al. [46] prepared Zn-doped SnO2 hierarchical architectures (ZSHAs) with controllable size using a facile hydrothermal method which was composed of two-dimensional (2D) nanosheets with a thickness of about 40 nm. The XRD pattern indexed the crystal to the tetragonal rutile structure of SnO2. TEM studies indicated the nanosheets structures and confirmed its single crystalline feature with the lattice spacing of 0.34nm. EDX analysis demonstrated that the nanosheet structures were composed of Zn, Sn and O elements. Photocatalytic activities of ZSHAs had been evaluated by the degradation measurement of methylene blue (MB), methylene orange (MO), and rhodamine B (RhB) respectively.

Khan, M. M et al. [47] synthesized Au–SnO2 nanocomposite using an electrochemically active biofilm. XRD findings were confirmed further using a Reitfield refinement. The spectrum of the Au–SnO2 nanocomposite showed a broad absorption peak from 500 to 600 nm in the visible region which was assigned to the surface plasmon resonance absorption of the Au NPs. The size of the SnO2 nanoparticles was in the range of 25–30 nm. XPS was used to examine the chemical states and surface composition of the Au–SnO2 nanocomposite and P–SnO2 nanoparticles. Au–SnO2 nanocomposite was also tested for the visible-light-induced photocatalytic degradation of Congo red and Methylene blue and showed approximately 10 and 6-fold higher photocatalytic degradation activity respectively compared to P–SnO2. These results showed that the Au–SnO2 nanocomposite exhibited excellent and higher visible-light-induced photocatalytic activities than the P–SnO2 nanoparticle.

Chandran, D et al. [48] successfully prepared the Pure and Co-doped SnO2 nanoparticles by sol–gel method with different concentrations of cobalt (0.75, 3, and 4 at%). As compared to pure SnO2, the broadening of diffraction peaks and degradation of crystallinity was observed with an increase in cobalt content which implied a reduction in crystallite size. Compared to pure SnO2 the doped samples exhibited an extra peak between 375 and 505 nm. The photocatalytic efficiency of pure and doped samples was determined by the degradation of MB solution under daylight illumination.

Sivakarthik, P et al. [49] successfully synthesized SnO2 and Co-doped SnO2 nanoparticles by organic solvent-assisted simple solution method calcined at 300-5000C. Photocatalytic degradation of synthetic organic dye namely Crystal violet in the presence of the doped and Co-doped SnO2 at different concentrations had been investigated. The result indicated that 4% Co doping calcined at 5000C exhibited the highest photocatalytic activity towards degradation of Crystal violet dye.

Mani, R et al. [50] also synthesized pure and Co-doped SnO2 nanoparticles by simple chemical precipitation method. Powder XRD results revealed that both pure and Co-doped SnO2 nanoparticles were indexed to a tetragonal rutile type structure (Fig6a). The photocatalytic degradation of phenol and benzoic acid was systematically investigated using Co–SnO2 catalyst under UV irradiation. The result showed that Co-doped SnO2 possessed the highest photo-catalytic property as compared to pure SnO2.

Ben Haj Othman et al. [51] successfully prepared highly iron-doped tin dioxide nanoparticles (Sn1-xFexO2 NPs), with x varying from 0 to 0.2 by simple hydrothermal method. The results showed that the SnO2 NPs are about 10 nm in diameter with a fairly narrow particle size distribution. The obtained size is similar to that obtained from XRD results and showed that the structure of SnO2 is kept the same even for a relatively high Fe doping level. UV-Vis results indicated that the band gap of SnO2NPs could be controlled by using Fe addition. The enhancement of RhB degradation under visible light irradiation by the introduction of the Fe into the SnO2 NPs is not due only to the reduction of the gap value but to the stimulation of electron exchanges with Fe doping.

Soltan, W. B et al. [52] successfully synthesized Nanocrystalline mesoporous pure and vanadium-doped (0–10 at%) SnO2 nanopowders by the polyol route at atmospheric pressure from ammonium metavanadate and tin (IV) tetrachloride from a combination of tin and vanadium precursors. XRD patterns of undoped and V-doped SnO2 materials exhibited the typical rutile-type tetragonal structure of SnO2 with average crystallite sizes ranging from 8.8 to 5.4 nm when the vanadium content was increased up to 10 at%. From UV– visible Diffuse Reflectance Spectroscopy, particle size was decreased by a decrease of the band gap energy value from 3.36 eV for pure SnO2 down to 2.2 eV for 10 at% V-doped SnO2. The increase in vanadium amount led to a slight rise of the specific area and a concomitant diminution of the average pore size which was related to the decrease of the mean crystallite size upon V doping. This trend opened the route to promising potential applications of these V-doped nanopowders in the field of photocatalysis under visible light since the variation of the vanadium concentration allowed for tuning the optical absorption of these materials.

Sinha, T et al. [53] successfully synthesized Ag-SnO2 nanocomposites by simple precipitation method. TEM pattern clearly depicted the formation of sphere-shaped Ag-SnO2 nanocomposite having an average particle diameter of 8−10 nm. The X-ray and EDAX results provided evidence that the SnO2 surface was successfully decorated by Ag and confirmed the formation of Ag-SnO2 nanocomposite The Ag-SnO2 nanocomposite thus synthesized was exploited for the abatement of four industrially emerging pollutants (MB, RB, MV6B, and 4-NP) from the aqueous phase and was also used as an antibacterial and antioxidant agent.

Nasir, Z et al. [54] successfully prepared Co-doped SnO2 NPs of average size ~30-40 nm by co-precipitation method using SnCl2.2H2O and CoCl2.2H2O as Sn and Co precursors. XRD and SEM confirmed the formation of the nanoparticles. The enhanced photocatalytic activities of the NPs with increased doping concentration were reported through a degradation process in the presence of MB dye under UV light irradiation.

Qamar, M. A et al. [55] successfully synthesized Co-doped SnO2 nanoparticles by using a simple and cheap co-precipitation method.  When these SnO2 were doped with Co, the band gap energy is further decreased*.* UV-Vis-spectrophotometer measurement found a band gap of 3.36 eV for un-doped SnO2 nanoparticles and it decreased to 1.48 eV for 5eV. The antibacterial activity of Co-doped SnO2 nanoparticles against the chosen bacteria was given on the basis of inhibition zone (mm). Co-doped SnO2nanoparticles with a concentration of 500 μL exhibited significant and maximum antibacterial activity against both bacterial strains i.e. *Escherichia coli* and *Bacillus subtilis* with zone of inhibition of (16 ± 0.8 mm) and (22 ± 1.6 mm) respectively.

Karpuraranjith, M et al. [56] successfully synthesized a biotemplate-zinc-tin oxide hybrid structure by a chemical precipitation method and annealed at 500°C. The X-ray diffraction peaks indicated a distinctive rutile structure of SnO2 with average crystalline sizes of 1.54–9.01 nm. The optical band gap energy was found to be 3.19 eV for the hybrid structure. The surface area and pore volume estimated by the CS-Zn0.25Sn0.75O hybrid structures material was found to have a higher value. Thus, the bio template-based zinc-tin oxide hybrid structure proved to be a promising material for improving photocatalytic activity.

Mala, N et al. [57] successfully synthesized Pristine and (Mg+Co) doped tin oxide nanoparticles by a cost-effective wet chemical method. The XRD pattern of (Mg+Co) doped SnO2 nanoparticles was similar to that of pristine SnO2 nanoparticles indicating that the doped nanoparticles also had a rutile hexagonal structure. The presence of hydroxyl groups was mainly responsible for the antibacterial and photocatalytic response of the material.

Sakwises, L et al. [58] successfully prepared SnO2 and Mn-doped SnO2 nanoparticles by wet chemical synthetic route using SnCl2, MnCl2, and triethanolamine. FTIR and XRD revealed 40% wt of Mn completely substituted. The efficiency of SnO2 and Mn-doped SnO2 was investigated on the photocatalytic activity on methylene blue degradation for 4 hours. No significant alteration in photocatalytic efficiency was observed if the Mn atom was partially substituted.

Bhuvaneswari, K et al. [59] successfully synthesized the pure SnO2, Cd / Zn-doped SnO2 nanopowders by microwave irradiation method attached on the surface of Silk fibroin (SF). After linking SF the Photo catalytic activity was increased due to the decreasing crystallite size, larger active surface area, and smaller particle distribution. The SF-linked Zn-doped SnO2 photocatalyst had higher MB degradation.

Babu, B et al. [60] successfully synthesized Mn-doped SnO2 quantum dots (QDs) with different Mn concentrations by solution combustion synthesis. The structural properties of the undoped and Mn-doped SnO2 QDs were investigated by X-ray diffraction patterns showing the tetragonal rutile structure of SnO2. The photocatalytic degradation of MO dye was measured under visible light irradiation using the Mn-doped SnO2 QDs as catalysts. 3 mol% Mn doped SnO2 QDs showed the 17 times higher photocatalytic performance than SnO2 QDs within 240 min.

Asaithambi, S et al. [61] successfully synthesized Pure and cobalt (Co)-doped SnO2 nanoparticles by using a simple co-precipitation method. The presence of tin, oxygen, and Co species was found in energy-dispersive X-ray spectra. The photo-catalytic activities of pure and Co-doped SnO2 nanoparticles were investigated by studying the photodecomposition of brilliant green dye an organic pollutant

Sujatha, K et al. [62] synthesized and characterized pure, zinc-doped, and surfactant-assisted Zn-doped SnO2 NPs using the co-precipitation method. The surfactants-assisted Zn-doped SnO2 nanoparticles revealed a great shift from 3.292 eV to 3.695 eV in the band gap values estimated from Tauc’s plot. Triton-assisted Zn-doped SnO2 nanoparticles were found to have high photocatalytic activity (80%) and better optical properties among the synthesized NPs. The rate of recombination of photogenerated electron–hole pair (e−, h+) was very fast in pure, CTAB and SDS-assisted Zn doped SnO2 NPs which prevents the formation of hydroxyl radical compared to TRITON-assisted Zn dopedSnO2NPs.

Letifi, H et al. [63] reported a novel photo-catalytic study of vanadium-doped SnO2 nanoparticles (SnO2: V NPs) in Rhodamine-B degradation. These NPs had been prepared with vanadium concentrations varying from 0% to 4% via the co-precipitation method. Optical studies showed that the absorption edge of SnO2:V NPs showed a redshift with the increasing vanadium concentration. This red shift led to a decrease in the optical band gap from 3.25 eV to 2.55 eV. Rhodamine B dye (RhB) has been used to study the photo-catalytic degradation of all synthesized NPs. As compared to undoped SnO2 NPs, the photocatalytic activity of SnO2:V NPs had been improved.

Sathish Kumar, M et al. [64] successfully studied the enhanced antibacterial and photocatalytic activity of pure and Copper (Cu) doped SnO2 nanoparticles via the microwave-assisted method. Tin chloride dihydrate (SnCl2̇.2H2O) and Copper chloride hexahydrate (CuCl2̇.6H2O) were used as tin and copper sources respectively for the preparation of NPs. Optical properties were investigated by UV visible and Photoluminescence spectroscopy and the bandgap energy value had been found to be 3.54 eV for pure SnO2 nanoparticles and it was decreased to 3.20 eV for Cu-doped SnO2 nanoparticles. The antibacterial activities evaluated by the disc diffusion method against *P. aeruginosa* and *S. aureus* microorganisms showed Cu-doped SnO2 nanoparticles had an excellent zone of inhibition against both microorganisms. Pure SnO2 had less inhibition zone compared with Cu-doped SnO2 due to the large particle size and low releasing of Sn4+ ions which generate low ROS. When Cu doping concentration was increased, a higher inhibition zone was formed against both bacteria due to an increase in the rate of release of Cu2+ ions and Sn4+ ions and large surface area of crystal which enhanced the generation of ROS. Also, the photocatalytic gradation properties of prepared samples were evaluated for Methylene blue and Rhodamine B aqueous solution dye under ultraviolet light.

Sujatha, K et al. [65] successfully synthesized, Fe-doped, and surfactant-assisted (CTAB, SDS, and Triton) Fe-doped SnO2 NPs by a simple co-precipitation method with water as a distinctive solvent using tin chloride dihydrate, ferric chloride as precursors with ethanol and ammonia. An increase in the band gap was observed due to the addition of Fe and surfactants. The photocatalytic study confirmed that pure SnO2 NPs exhibited a significant photo-degradation of methylene blue dye under sunlight. Maximum dye (MB) degradation was observed above 120min in pure SnO2 NPs; whereas the degradation was decreased in Fe-doped and surfactant-assisted Fe-doped SnO2 NPs. The photocatalytic property depends on the morphology, energy gap, and particle size of NPs.

Ali Baig et al. [66] prepared Pristine and Fe-doped tin SnO2 nanoparticles by microwave-aided co-precipitation method using Tin chloride (SnCl2.5H2O; 98%), ethanol (C2H5OH) Iron Chloride (FeCl2.5H2O; 98%) and Sodium hydroxide (NaOH; 99%).. The intensity will be decreased by the nominal defect due to the Fe dopant. The 4 % of Fe-doped SnO2 NPs had higher photocatalytic action associated with the pristine and 2 % of Fe-SnO2, and maximum MO dye degradation efficiency of 87.2 % has been attained 200 min under visible light. The antibacterial activity of pristine and Fe-doped SnO2 nanoparticles was determined against gram-negative (*E. coli*) and gram-positive (*S.aureus*) bacteria. The studies proved that the antibacterial activities of produced Fe-doped SnO2 NPs have a momentous performance against various gram-positive(G+) and gram-negative (G-) bacteria.

Wang, Q et al. [67] synthesized Novel material Fe (1, 2 and 3 wt%) doped SnO2 decorated layered g-C3N4 through a simple chemical precipitation method using SnCl2.2H2O, FeCl3.6H2O, aqua ammonia, urea as raw materials [67]. The as-prepared hybrid material 1wt% Fe–SnO2/g-C3N4 (1 wt% Fe–SCN) exhibited enhanced activity or both photodegradation of Rhodamine B and Methylene blue under simulated solar light irradiation. It was found that Fe doping reduced the band gap of Fe–SnO2 and formed a Z-scheme heterojunction between Fe-doped SnO2 and g-C3N4, which effectively promoted the separation of photo-generated electrons and holes.

Ramamoorthy, M et al. [68] synthesized Mn-doped SnO2 loaded with a (0.5 g) corn cob activated carbon (Mn: SnO2/CCAC) by chemical precipitation method using Tin (II) chloride dehydrate (SnCl2.H2O), oxalic acid dehydrate(C2H2O4.2H2O), and manganese (II) acetate tetrahydrate (CH3COO)2Mn.4H2O) and its photocatalytic performance was estimated by photodegradation of methylene blue under sunlight irradiation. The band gap value (Mn: SnO2/CCAC) was decreased (3.49 eV) compared to pure SnO2 and Mn-doped SnO2 samples. It was confirmed that the particle size, band gap, emission, hydroxyl group, and surface area were enhanced for the Mn (0.10 M) SnO2/CCAC photocatalyst compared to the pure SnO2 and Mn-doped (0.10 M) SnO2.

Suthakaran, S et al. [69] had successfully prepared Zr-doped SnO2 NPs by surfactant-assisted hydrothermal method using Tin (IV) chloride pentahydrate (SnCl4.5H2O), Zirconyl chloride octahydrate (ZrOCl2.8H2O), sodium hydroxide (NaOH), and sodium hexametaphosphate as starting materials. The results of XRD confirmed that the bare, SHMP-assisted, and Zr-doped SnO2 NPs were polycrystalline in nature with a tetragonal structure and remained stable even after higher concentrations of Zr doping. Photocatalytic measurements showed that doped NPs improved the photodegradation percentage of the MV dye, which could open up a new way to address water contamination and environmental pollution.

Baig, A et al. [70] successfully synthesized Zr-doped SnO2 (Zr: SnO2) nanostructures (NSs) with altered concentrations of Zr (2 and 4%) were organized by facile hydrothermal co-precipitation mode, that nanocrystalline pristine and Zr-doped SnO2 NPs by tetragonal rutile-type construction and the crystallite size was about ~ 41 to 36 nm. The photocatalytic performances of 4% of Zr-doped SnO2 nanoparticles (NPs) were thoroughly explored in the photodegradation of methyl orange (MO) dye, thus revealing higher photocatalytic activity in the degradation of MO than pristine and 2% of Zr-doped SnO2 under via visible-light exposure. Related to pristine SnO2, the 4% Zr doped SnO2NPs were accessible to greater photocatalytic capability, and antibacterial action was attained against *E. coli* and *S. aureus* bacteria through the agar well diffusion system.

Baig, A et al. [71] successfully synthesized SnO2 NPs via a simple hydrothermal chemical route with different doping concentrations (0, 2, and 4 at%) of Y. X-ray diffraction (XRD) studies showed that the undoped and Y: SnO2 NPs had a fine crystalline texture with a tetragonal structure and particle size range of 27–15 nm, although the size decreased with Y3+doping. HRSEM revealed agglomeration morphologies and identical crystallite spreading. Optical absorption was investigated by UV-visible diffuse reflectance spectroscopy and showed a red shift in bandgap energy for Y3+ doped SnO2 NPs, enhanced photocatalytic activity was observed for the doped samples and the 4% Y: SnO2 NPs exhibited excellent photodegradation of methylene blue aqueous dye in visible light, demonstrating 92.34% degradation in 180 min. The other photocatalysts also demonstrated greater than 85% photodegradation efficiency and high stability, with no significant reduction in activity observed after five cycles. The antibacterial analysis showed the 4% Y: SnO2 NPs (100 µL) exhibited a larger ZOI than the undoped and 2% Y: SnO2 samples. The undoped/pristine SnO2 NPs showed the smallest antibacterial activity, due to the small concentration of the as-prepared NPs evident in the *E. coli* and *S. aureus* bacterial strains. However, with the highest doping concentration (4%) of Y in SnO2 NPs, the ZOI was clearly observed.

Carolin, L et al. [72] prepared In–SnO2 nanomaterial using the precipitation method and sonication technique. The band gap energy of the prepared SnO2 and In-doped SnO2 nanocomposites was calculated to be 3.7 and 3.1 eV. In–SnO2photo catalyst showed that the catalyst has great reusability properties Photo catalytic efficiency of the photocatalyst was performed under UV light using RR 120 dye at pH 7 and 0.150 g as the optimum pH and catalytic concentration. photocatalytic activity of In–SnO2 nanocomposite is directly related to the formation of OH Radical. The antibacterial activity of In-doped SnO2 is higher than that of undoped SnO2.

Chu, L et al. [73] successfully synthesized Bi-doped SnO2 quantum dots via a one-step hydrothermal method. Photo catalysts were evaluated under simulated sunlight irradiation by photocatalytic degradation of Rhodamine B (RhB) and Ciprofloxacin hydrochloride (CIP) solution. The outstanding photodegradation efficiency of the obtained composites was due to enhanced absorbance of light as well as the effective separation and migration of photo-generated carriers. The antibacterial activity of CIP toward *Escherichia coli* DH5a had been largely eliminated after 5Bi-SnO2 treatment. Bi-doped SnO2 quantum dots had good practical application prospects for their high efficiency and excellent stability.

Prabhu et al. [74] synthesized Pure SnO2 and Zn: SnO2 nanoparticles by flame synthesis method using the high-temperature oxy-acetylene flame. irregular, agglomerated, nanoflowers and nano clustered SnO2 nanoparticles change to nano cubical and nanoflake Zn: SnO2 nanoparticles with an enhanced crystalline structure. MB degradation analysis shows the high performance of SnO2 and Zn: SnO2 nanoparticles as photocatalysts under UV light due to the formation of highly reactive (OH- ) hydroxyl radicals and superoxide(O2-) radicals.

Salah Ud Din et al. [75] synthesized SnO2 nanoparticles by utilizing leaf extract of Populus ciliate. XRD, EDAX, and antioxidant studies were carried out. The antibacterial effects of prepared SnO2 nanoparticles were studied using the agar well diffusion method against Gram-positive bacteria (S. pyogene and S. aureus) and Gram-negative bacteria (K. pneumoniae and E. coli).

**Table 1: Summary of various methods for metal ion doped SnO2-based nanostructure synthesis**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Authors and year** | **Sample** | **Synthesis route** | **Structural characterization** | **Applications & results** | **Ref.** |
| Kumar, V et al. (2011) | F- SnO2 | sol-gel method | PXRD (a = 4.7106 Å & c = 3.1970 Å), TEM (Agglomeration with an average diameter of 57 nm ), BET (45.16 m2 /g), Raman spectrum (455, 588, and 874 cm-1 ), EDX, Pore size analysis (13.97 nm) | Increased photocatalytic efficiency in the degradation of aqueous Rhodamine-B (RhB) dye solution under UV irradiation. | 39 |
| You, H  et al. (2013) | Au–SnO2 | solution reaction | XRD( rutile-type ), SEM(dendrites with staggered form and perpendicular form), TEM (nanotubes, diameter 50 nm & shell thickness of about 25 nm), SAED, BET (300.2 m2 g-1). | Enhanced photocatalytic performance in the photodegradation of R6G molecules. | 40 |
| Wu, W  et al. (2013) | Au–SnO2 | hydrothermal method | XRD (crystallite sizes 10.8 nm ), HRTEM, BET ( 93.2 m2g-1), EDX, BET(93.2 m2g-1 ) pore size(16.8 nm), UV-DRS(Eg= 3.32eV) | The improved photocatalytic degradation of RhB under UV and visible light irradiation. | 41 |
| Davis, M  et al. (2013) | Fe-SnO2 | sol–gel method | XRD(3nm), Gas sorption analyses (330 m2 g-1), Electron microscopy studies, Pore size analysis, EDX | Efficient photocatalytic degradation of RhB under ultraviolet irradiation, 5 % Fe-modified SnO2 degraded RhB by more than half after 2 h | 42 |
| Ansari, S  et al. (2014) | Ag–SnO2 | EAB  (electrochemically active biofilm). | XRD(Crystallite sizes of 11.00 nm, 14.20 nm and 14.57 nm)., surface plasmon resonance absorption(400–550nm) | Enhanced photocatalytic activity under visible light irradiation for the degradation of methyl orange, methylene blue. | 43 |
| Toloman, D et al. (2014) | Co -SnO2 | chemical precipitation method | XRD (tetragonal rutile, crystallite size 8.8 nm for 5% Co doped SnO2), EPR. | The photo catalytic activity of the sample was evaluated against RhB synthetic solution, under visible light irradiation. | 44 |
| Ran, L  et al. (2015) | Ti-SnO2 | facile infiltration route(stober method) | XRD(crystalline state with a particle diameter of about 300 nm). BET (from 26.2 ± 0.5 m2 g−1 in SiO2 to 35.6 ± 0.5 m2 g−1 in SiO2 (20% Ti)). | Highest photocatalytic activity with 92% MB & 54% MB photo catalytically decomposed under UV light irradiation in 135 min. | 45 |
| Zhao, Q  et al. (2015) | Zn-SnO2 | hydrothermal method | XRD (tetragonal rutile structure), SEM(2D nanosheets), TEM (single crystalline feature with the lattice spacing of 0.34nm), EDX. | Photocatalytic degradation of methylene blue (MB-91%), methylene orange (MO-40%), and rhodamine B (RhB-60%) in 60min. | 46 |
| Khan, M. M  et al. (2015) | Au–SnO2 | electrochemically active biofilm. | XRD(crystallite size is of 25–30 nm). UV-Vis(500-600nm), XPS. | 10 and 6-fold higher photocatalytic degradation of Congo red and Methylene blue. | 47 |
| Chandran, D et al. (2015) | Co- SnO2 | sol–gel method | XRD (tetragonal rutile-type), HRTEM (interplanar spacing of 0.34 nm), UV spectra(375-505nm) | The photocatalytic efficiency was determined by the degradation of the MB solution under daylight illumination. | 48 |
| Sivakarthik, P et al. (2016) | Co -SnO2 | simple solution method | XRD (tetragonal structure & particle size of 18 nm to 22 nm)., SEM (spherical morphology) | exhibited high photocatalytic activity towards the degradation of Crystal violet dye. | 49 |
| Mani, R  et al. (2017) | Co -SnO2 | chemical precipitation method | XRD (tetragonal rutile, average crystalline size 48, 41, and 32 nm), TEM, FTIR, UV-Vis(Eg=3.58, 3.32, 3.12ev) | The photocatalytic degradation of phenol & benzoic acid was investigated under UV irradiation. | 50 |
| Ben Haj Othmen  et al. (2016) | Fe-doped SnO2 NPs | hydrothermal method. | XRD (tetragonal rutile structure), HRTEM, BET, UV-Vis. | Enhanced photocatalytic degradation of RhB under visible light irradiation. | 51 |
| Soltan, W. B et al. (2016) | V- SnO2 | polyol route | XRD(rutile-type tetragonal structure with average crystallite sizes 8.8 to 5.4 nm), UV-DRS(2.2eV) | photocatalysis under visible light by variation of vanadium allowed for tuning the optical absorption. | 52 |
| Sinha, T et al.(2016) | Ag-SnO2 | Simple precipitation method | XRD, TEM (average particle diameter of 8−10 nm), EDAX, SAED | Exploited for the abatement of 4 industrially emerging pollutants (MB,RB, MV6B, and 4-NP) & also used as antibacterial(Pseudomonas aeruginosa, Escherichia coli, and Bacillus subtilis) | 53 |
| Nasir, Z  et al. (2017) | Co -SnO2 | co-precipitation method | XRD (tetragonal-rutile type structures ), SEM, TEM, SAED | Enhanced photocatalytic degradation of MB dye under UV light irradiation & also antimicrobial effect. | 16 |
| Qamar, M. A et al. (2017) | Co-SnO2 | co-precipitation method. | XRD (tetragonal structure having average crystallite size 24.86 nm), SEM(spherical shape), EDX, UV-Vis(Eg=1.48eV) | Antibacterial activity against both bacterial strains i.e. Escherichia coli(16 ± 0.8 mm) & Bacillus subtilis(22 ± 1.6 mm) | 17 |
| Karpuraranjith, M et al. (2017) | Zn-SnO2 | Chemical precipitation method | XRD(distinctive rutile structure with average crystalline sizes of 1.54–9.01 nm), SEM(cluster), EDAX, TEM(agglomerated), UV-Vis(3.19eV) | bio template-based Zn-SnO2 proved to be a promising material for improving photocatalytic activity. | 18 |
| Mala, N  et al. (2017) | (Mg+Co) doped SnO2 | wet chemical method | XRD (rutile hexagonal structure with an average crystallite size of 24 and 25 nm), FTIR. | The degradation efficiency of pristine SnO2 was 82% for MB and 86% for Malachite Green (MG). | 19 |
| Sakwises, L et al. (2017) | Mn-SnO2 | wet chemical synthetic route | FTIR and XRD revealed 40% wt of Mn completely substituted, EDX. | The degradation of organic pollutants (MB) under UV irradiation. | 20 |
| Bhuvaneswari, K et al. (2018) | Cd / Zn-doped SnO2 | Microwave irradiation method | XRD (rutile-tetragonal system with an average crystallite size 43.4, 22.8, and 24.3 nm), FTIR, UV-Vis spectra. | Photocatalytic activity of Zn-doped SnO2 nanoparticles showed high MB degradation efficiency of 99.6 %. | 21 |
| Babu, B  et al. (2018) | Mn-SnO2 | solution combustion | XRD(tetragonal rutile structure with an crystallite size ranged from 5 to 4.4 nm), SAED, FTIR, UV-Vis(Eg=3.07ev) | The photocatalytic degradation of MO dye was measured under visible light irradiation. | 22 |
| Asaithambi,S et al. (2019) | Co- SnO2 | co-precipitation method | XRD (cassiterite tetragonal SnO2 structure with average crystalline between 26.4 nm and 23.1 nm), FTIR, UV-Vis(Eg=3.47eV), HRTEM, SAED. | Co-doped SnO2 had higher photocatalytic activity & maximum degradation efficiency of 91% under visible light irradiation. | 23 |
| Sujatha, K et al. (2019) | Zn -SnO2 | co-precipitation method | XRD(rutile tetragonal with crystallite size 9.34 nm), SEM(Spherical), EDX, UV-Vis(Eg=3.69eV) | High photocatalytic activity (80%) and better optical properties. | 24 |
| Letifi, H  et al. (2019) | V-SnO2 | co-precipitation method | XRD(tetragonal structure & the average crystal size is 10nm), UV-Vis(Eg=2.55eV) | Rhodamine B dye (RhB) has been used to study the photocatalytic degradation (95% in 150min) | 25 |
| Sathishkumar, M  et al. (2020) | Cu- SnO2 | microwave assisted method | XRD(tetragonal rutile phase and average crystal size was found to be 29 nm ), TEM(Spherical), UV-Vis(3.20eV). | Enhanced antibacterial (P. aeruginosa & S. aureus ) and photocatalytic activity(MB, RhB) | 26 |
| Sujatha, K et al. (2020) | Fe-SnO2 | co-precipitation method | XRD (tetragonal rutile structure with a crystallite sizes 6.347 nm), SEM, TEM, EDAX, UV-Vis. | Enhanced degradation of dye (MB) was found to be 49% respectively. | 27 |
| Ali Baig  et al. (2020) | Fe- SnO2 | co-precipitation method | XRD (tetragonal structure with crystalline size was found to be between 28 nm), HRTEM(agglomerated), UVDRS(Eg=2.65eV) | Higher photocatalytic MO dye degradation efficiency of 87.2 % under visible light & antibacterial activity was determined against E.coli and S.aureus bacteria. | 28 |
| Wang, Q  et al. (2020) | Fe -SnO2 | simple chemical precipitation method | XRD, HRTEM, EDS, XPS, UVDRS | Enhanced photocatalytic activity & photodegradation of Rhodamine B and Methylene blue under simulated solar light irradiation. | 29 |
| Ramamoorthy, M  et al. (2020) | Mn-SnO2 | chemical precipitation method | XRD (rutile tetragonal structure, crystallite size 13.79nm), UV-Vis(Eg=3.49eV) | photocatalytic performance was estimated by photodegradation of methylene blue under sunlight irradiation. | 30 |
| Suthakaran, S  et al. (2020) | Zr -SnO2 | hydrothermal method | XRD ( polycrystalline in nature with tetragonal structure),  TEM(hexagonal morphology with an average particle size of 4.1 nm), PL. | Photocatalytic measurements showed that doped NPs improved the photodegradation percentage of the MV dye. | 31 |
| Baig, A  et al. (2020) | Zr-SnO2 | facile hydrothermal co-precipitation | XRD(tetragonal rutile-type construction and the crystallite size was about ~ 41 to 36 nm), SEM, EDX, UVDRS(2.87eV) | photodegradation of methyl orange (MO) dye revealed higher photocatalytic activity. antibacterial action was attained against E. coli and S. aureus bacteria. | 32 |
| Baig, A  et al. (2020) | Y-SnO2 | hydrothermal chemical route | XRD ( tetragonal structure and particle size range of 27–15 nm), SEM(agglomeration), UVDRS | Enhanced photodegradation of methylene blue dye in visible light (92.34% in 180min), antibacterial activity against E. coli and S. aureus | 33 |
| Carolin, L et al. (2020) | In–SnO2 | precipitation method and sonication technique | XRD (cassiterite structure and average size of 40–50 nm & 60–80 nm)  HRTEM (showed Particle size of 8–10 nm for In–SnO2 & 20–30 nm for bare SnO2), EDX, UVDRS(Eg=3.1ev) | The photocatalytic efficiency of the photocatalyst was performed under UV light using RR 120 dye and enhanced antibacterial activity against B. Subtilis and V. cholera (22 mm and 14 mm) | 34 |
| Chu, L  et al. (2020) | Bi-SnO2 | hydrothermal method | XRD (revealed that Bi has entered into the SnO2 crystal lattice to substitute Sn during the synthesis process) XPS, BET, Pore volume analysis. | photocatalytic degradation of Rhodamine B (RhB) and Ciprofloxacin hydrochloride (CIP) solution under simulated sunlight irradiation. The antibacterial activity of CIP toward Escherichia coli DH5a. | 35 |
| Sivarama Prabhu P  (2021) | Zn:SnO2 | Flame oxidation process | XRD showed average crystalline size 20 to 30nm and a band gap found to be 3.5 to 3.6V | Photocatalytic degradation of methylene blue dye was found to be 88% | 74 |
| Salah Ud Din etal [2022] | SnO2 | biosynthesis | The FTIR and TGA results confirm the presence of a hydroxyl group in the sample. Band gap was found to be <1v | Antibacterial studies were carried out | 75 |

**3. Conclusions**

In this review, the synthesis of SnO2 hierarchical structures, their modifications by doping and compositing with other materials, and the synthesis of stannate nanomaterials with different morphologies including nanoparticles, nanorods, nanosheets, nanosphere, and porous and hollow structures were discussed. Tin oxide nanomaterials have been expected to be powerful photocatalysts for the degradation of organic pollutants in aqueous solution due to their excellent properties such as transparency, low cost, environmental friendliness, good chemical and biological inertness, nontoxicity, easy production and high photosensitivity, photostability, and thermodynamic stability. Tin oxide is also known for its antimicrobial activity especially antibacterial properties against many gram-positive and gram-negative bacteria.

Despite the great potential of SnO2 semiconductors for photo-catalytic applications and the antioxidant capacity of nanoparticles against free radicals, its experimental applicability as a pure material is incomplete because of the high activation energy of the metal oxide. This activation energy is equivalent to irradiation with UV light and the direct (swift) recombination rate of the photo-generated conduction electron (e‾ CB) in the Sn 4d(5S) band and with a hole in the O 2p valence band. To improve the industrial application of SnO2 and enhance the photo-catalytic activity, the recombination rate of the electron-hole pairs needs to be inhibited. One option is to dope other semiconductors of different electron energy band gap to the metal oxide. Possibly the photo-catalytic activity of the new combination material would then be improved because it would decrease the recombination rate of electron-hole pairs and lower the activation energy.

After the introduction of components with different chemical compositions, SnO2-based nanomaterial got wide applications. However, it is still a challenge in the large-scale synthesis of SnO2 nanocrystals with more specific facets exposed. Looking into the future, with extensive research in nanostructures synthesis to accurately control dimension and composition, a critical understanding of the modified properties of materials at the nanoscale, and the hierarchical assembly of nanostructures with exquisite spatial control, progress will be made and new and interesting nanosystems will create the technologies of the future.

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