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Development of SnO_2: Ag Nanoparticle as an Affordable Catalyst for the Degradation of Gentian Violet Dye

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***Abstract:** An effective visible catalyst (SnO_2:Ag) was successfully synthesized using co-precipitation method for the decomposition of the dye Gentian Violet (GV). In addition to XRD, SEM and UV – Visible analysis, a variety of other physicochemical measurements were used to validate the as-prepared SnO_2:Ag nanoparticles. The phase identification of prepared sample is characterized by X – ray powder diffraction (XRD), which confirms the tetragonal rutile structure. The surface morphology is examined using a scanning electron microscope (SEM) and the optical absorption and the band gap value are calculated using the UV-visible spectrum. These results confirm the synthesis of nanoparticles by successive steps. A nanoparticles was demonstrated to be a superior catalyst for the degradation of GV dye when exposed to UV light. The photocatalytic activity studies are discussed using SnO_2:Ag nanoparticles. The degradation efficiency of the nanoparticle is 96 % towards the degradation of the GV dye.*

***Keywords:** Co-precipitation method, XRD, UV-Visible Spectroscopy, SEM and Gentian Violet dye.*

I. INTRODUCTION

Now a day, the increase of industrial activities has intensified problems in environmental pollution and the deterioration of several ecosystems with the accumulation of pollutants, especially dyes. Effluents containing various dyes are discharged from various industrial processes. According to World Health Organization (WHO) the metals of the most immediate concern are effluents from various textile industries (cationic, anionic and neutral dyes), organic acids, heavy metals. Dyes may be found in wastewater discharges from the manufacture of pigments dyes and textile operations. The waste generated by the textile industry not only poses a threat to human health, but also poses a threat to the environment, so appropriate remedial technologies are needed [1–3]. In particular, organic dyes are highly stable and easily identifiable compounds in water, which can cause life-threatening problems. Therefore, various technologies such as adsorption, membrane filtration, chemical oxidation, biological digestion, electrochemical oxidation and advanced oxidation process (AOP) are widely used to remove organic pollutants in water. Compared with other methods, the AOP-based semiconductor photocatalytic decomposition process has been proven to be efficient and environmentally friendly. Among the most promising approaches, semiconductor-based photocatalysts have been recognized for their economic, environmentally friendly, and well-organized nature. In addition, semiconductor based photodegradation processes have attracted curiosity due to their harmlessness, effectiveness, and stability [[4, 5]. There are numerous metal oxide semiconductor materials in various shapes and structures that have proven effective in the degradation of organic dyes, including ZnO, TiO_2, CuO, and MgO. Compared to TiO_2, ZnO has a broad direct band gap (3.37 eV), high binding energy for excitation (60 meV), and excellent electrical, mechanical, and optical and photocatalytic properties. Ag doped with metal oxides can significantly improve the photocatalytic activity.

According to experimental calculations, SnO_2 is significant n-type semiconductors with a broad energy band gap (3.6 eV) among the metal oxides (ZnO, TiO_2, WO_3, CeO_3 and so on). It has a wide range of uses in gas sensors, optoelectronic devices, dye base solar cells, secondary lithium batteries, and catalysts due to its optical transparency in the visible area. The Sol-gel and microwave procedures, evaporative breakdown of solution [6], template-assisted growth [7], wet chemical synthesis [8], and gas-phase reaction [9, 10] are only a few of the many techniques used to create silver doped SnO_2 nanoparticles. For the synthesis of silver doped SnO_2 nanoparticles, we chose the chemical co-precipitation approach over the others because it allows us to easily regulate the structural and surface characteristics of the nanoparticles.

Transparent conducting oxides such as SnO_2 have a great technological potential related to the ideal combination of electrical and optical properties. Since they have found many applications in technology, the SnO_2-based systems are extensively studied. Particularly, for gas sensing materials the sensitivity is strongly dependent upon the crystallite size and shape, inasmuch as this property is influenced by the surface to volume ratio in SnO_2:Ag systems [11].

A. Experimental Details

Synthesis of Ag doped SnO_2

Nanoparticle samples of SnO_2: Ag were prepared by Co-precipitation method. The starting materials are Tin Chloride $SnCl_2/AgCl_2$ and Sodium hydroxide (NaOH). We dissolved 1M of $SnCl_2$in 100 ml H_2O under heating and continuous stirring of 30 minutes. Then, various concentrations (x=1 and 3%) of silver nitrate [$AgNO_3$] were used for preparing the doped samples. Then sodium hydroxide (0.5 mol) was dissolved in 100 ml of distilled water and added drop wise to the stirring solution of Tin chloride and the mixture was stirred using magnetic Stirrer for 2 hours. The precipitate was filtered and annealed at 80° C. The dried sample was also calcined at 550° C.

II. RESULT AND DISCUSSSIONS

A. Structural Properties

Pure and Ag doped SnO_2 nanoparticles

Figure 1 revealed the crystal structure and phase of the SnO_2 and SnO_2:Ag were recorded by XRD analysis. The peaks at 2θ values at 26.1º, 33.2º, 37.4º and 51.2º can be associated with (110), (101), (200) and (211) respectively. Peaks can be ascribed to tetragonal rutile structure.

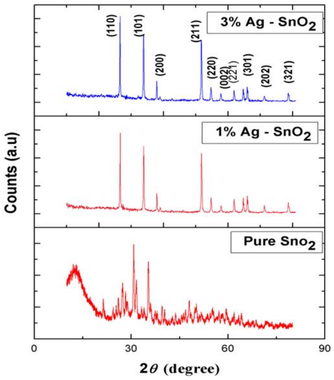

Figure 1 XRD for undoped and Ag doped SnO_2 for various concentrations (1% and 3%)

The lattice constant 'a' and 'c' of tetragonal rutile structure of SnO_2 can be calculated using the relation given below.

$$\frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2}$$

The peaks in the XRD spectrum correspond to those of the SnO_2 pattern [**12**] from the JCPDS data (powder diffraction file card no: 88-0287) having tetragonal rutile structure with lattice constants a=4.737Å, C=3.1864Å and a/c=1.4866. The a and c values obtained for Ag doped SnO_2 nanoparticles prepared in this work are a=4.6111,c=3.1864 and a/c= 1.2171.

Table 1 Peak position, crystallite size, the lattice parameter a, c and its ratio

Sample	Ag doping wt%	2θ values along (110) plane deg	Crystallite size D in (nm)	A (Å)	B (Å)	a/c
Pure SnO_2	0	26.9	45.2	4.6111	3.7884	1.2171
	1	26.6	41.3	4.7391	3.1886	1.4862
	3	26.5	38.1	4.7460	3.1907	1.4874

From XRD studies the crystallite size were in the range 38 to 45 nm and the crystallite size decrease with increasing Ag doping concentration it may be due to the small ionic radii of Ag^+ (0.115nm) when compared to Sn^{2+} ion (0.118 nm) [13].

B. Optical Properties

UV-Visible Spectra for Ag doped SnO_2 nanoparticles

The UV-Vis absorption spectroscopy has been carried out to understand the optical properties and electronic interaction of doped nanoparticles. In order to confirm the substitution of Sn^{2+} by Ag^+ ions, the optical absorption spectra for SnO_2:Ag nanoparticles were measured at room temperature as shown in Figure 2.

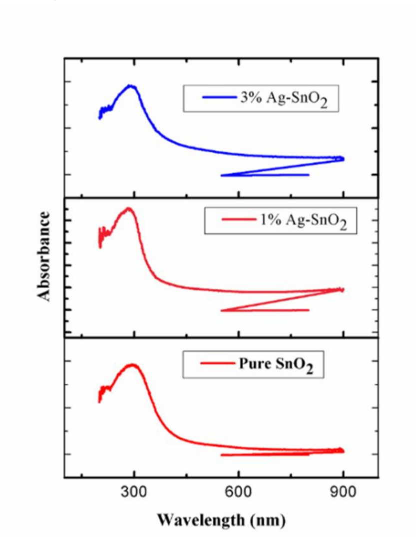

Fig. 2 UV absorbance spectra for undoped and Ag doped SnO_2 for various concentration (1 and 3%)

The absorption spectrum of pure SnO_2 shows the sharp absorption peak at 299 nm (3.27ev). The increase in band gap is mainly due to the incorporation of Ag atoms in SnO_2.The band gap spectra of Ag doped SnO_2 in various concentrations of 1 wt % and 3 wt % Ag doped SnO_2 samples were shown in Figure 2.1, 2.2 and 2.3.

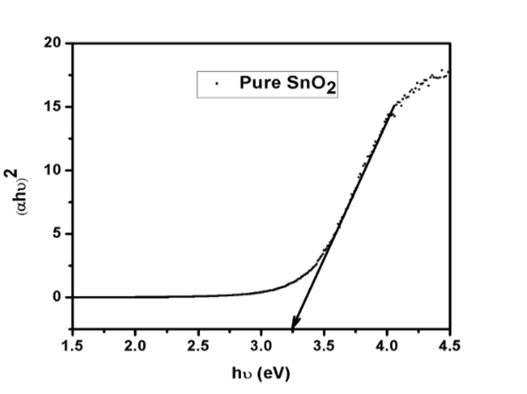

Fig. 2.1 Band gap diagram for undoped SnO_2

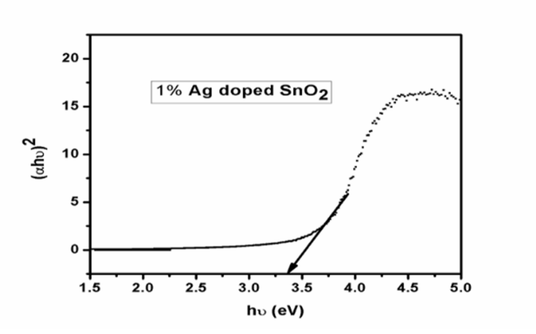

Fig. 2.2 Band gap diagram for 1% Ag doped SnO_2

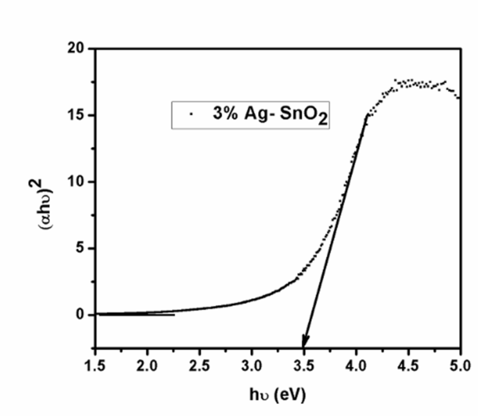

Fig. 2.3 Band gap diagram for 3% Ag doped SnO_2

The above plot exhibited a fundamental absorption edges at 286 nm and 283 nm corresponds to 3.39 ev and 3.49 ev respectively. The resultant values confirm that the well blue shift was occurred by increasing the dopant concentration due to the high incorporation of Ag within SnO_2, which makes the material as a vastly doped SnO_2:Ag nanoparticle [**14**].

Table 2 UV Visible absorption data for the SnO_2 and SnO_2:Ag nanoparticles

Sample	Ag doping (wt %)	λ (nm)	Band gap (eV)
Pure SnO_2	0	299	3.27
	1	286	3.39
	3	283	3.49

C. Morphological Properties

SEM for pure SnO_2 and Ag doped SnO_2

The surface morphology of as-prepared pure SnO_2 and SnO_2:Ag was analyzed by SEM spectroscopic analysis was shown in Figure 3.1, 3.2, and 3.3.

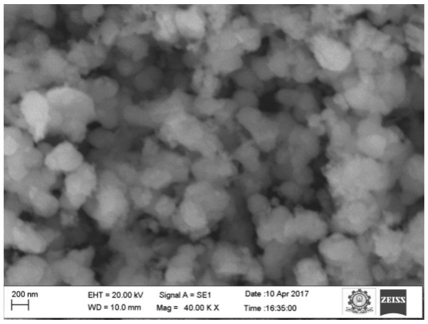

Fig. 3.1 SEM image for pure SnO_2

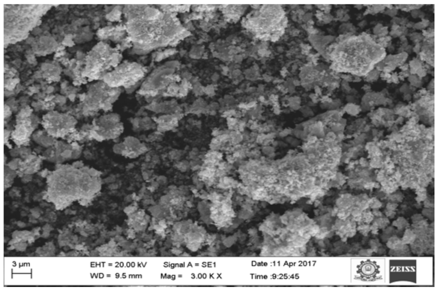

Fig. 3.2 SEM image for 1% Ag-SnO_2

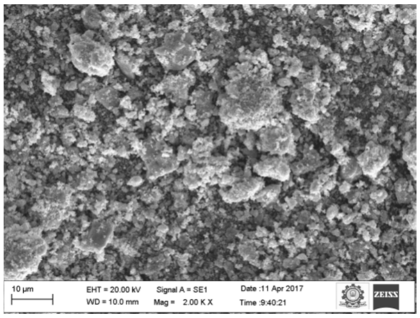

Fig. 3.3 SEM images for 3% Ag-SnO_2

The above figures shows the SEM images of Ag doped SnO_2 with different concentration of 1wt% and 3wt% respectively. The Pure SnO_2 shows the tetragonal shape. This tetragonal shape is changed to spherical for various doping concentration of Ag (1 wt% and 3 wt%). This indicates that the Ag doping into SnO_2 can change the surface character of the primary nanoparticles, which was deduced to be from the effects of the diffusion of Ag^+ into the SnO_2 lattice, and the formation of Ag-O-Sn bond on the surface of the doped samples were confirmed **[15, 16].**

D. Applications of Nanomaterials

Photocatalytic activity

It is important from mechanistic and application point of view to study the dependence of substrate concentration on the photocatalytic degradation rate**.** Photocatalytic activity studies confirmed that when increase the dose of the catalyst with increase the percentage of removal (%R) and Ag-doped nanoparticles enhanced the rate of degradation of Gentian Violet (GV) dyes. In the absence of catalyst, pure SnO_2 which has the lower efficiency (0.1g in 58% and 0.5g in 65% removal of dye). In the presence of catalyst, Percentage removal of dyes increased with the increased with increase in contact time and dose of catalyst. Amount of dyes adsorbed increases with the decrease in particle size of catalyst. This results shows that the efficiency of catalyst increases upto 96.00 % for the removal of GV dye **[17-21].**

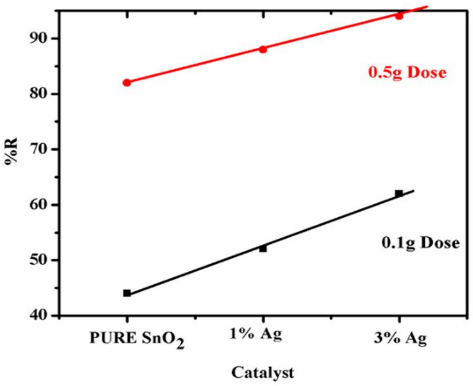

Fig 5. Photodegradation of GV dye on pure SnO_2 and Ag doped SnO_2.

III. CONCLUSION

A novel SnO_2 nanomaterial are well dispersed on Ag nanoparticle was demonstrated by a fruitful coprecipitation method. As prepared nanoparticle was characterized thoroughly by adopting various analytical techniques. This nanoparticle could be used as economically very feasible catalyst alternative to other commercially available catalyst for the cost effective treatment of effluents, especially for the removal of industrial dyes in general and Gentian Violet in particular using co-precipitation method. The XRD pattern of the Ag doped SnO_2 nanoparticles were indexed to the tetragonal structure with average crystallite sizes in the range 45 -38 nm. The UV- Visible spectral studies concluded that the optical band gap of the Ag doped SnO_2 were found to be 3.27 eV, 3.39 eV and 3.49eV. The SEM images revealed that the Pure SnO_2 shows the tetragonal shape. This tetragonal shape is changed to spherical for various doping concentration of Ag. Photocatalytic activity studies confirmed that when increase the dose of the catalyst with increase the percentage of removal (%R) and Ag-doped nanoparticles enhanced the rate of degradation of dyes.

IV. ACKNOWLEDGEMENTS

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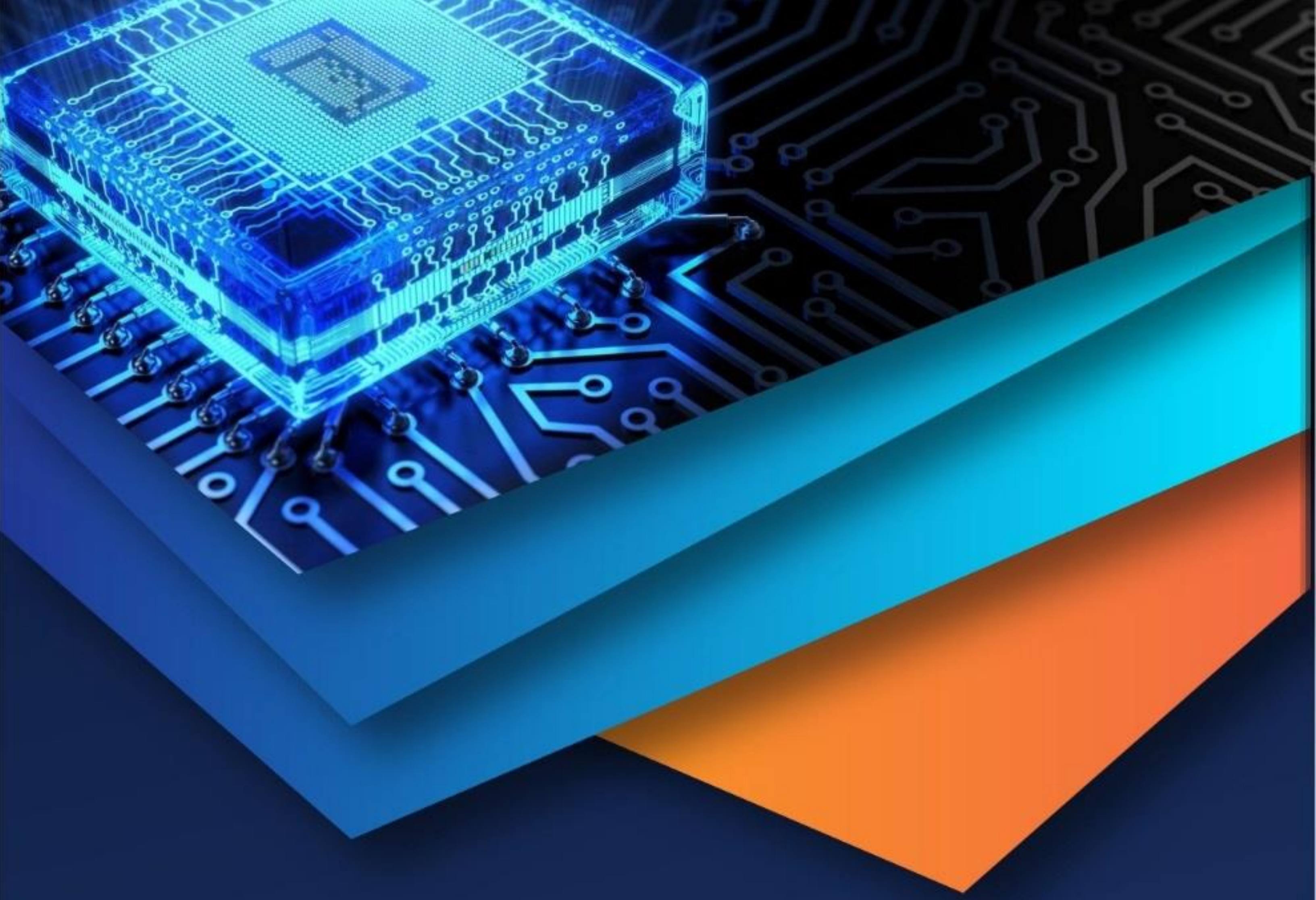

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