

SYNTHESIS OF CO-DOPED TIN OXIDE NANOPARTICLES FOR PHOTO CATALYTIC DEGRADATION OF SYNTHETIC ORGANIC DYES

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The Tin Oxide nanoparticles and Cobalt doped tin oxide nanoparticles are prepared by organic solvent assisted simple solution method calcined at 300-500⁰C. The as-prepared tin oxide nanoparticles and Co-doped nanoparticles were characterized by the analytical tools like XRD, SEM. The tetragonal structure of the SnO₂ nanoparticles and the particle size are clearly predicted from the XRD pattern; the spherical morphology showed by the SEM image. The photo catalytic activity of the nanoparticles studied in the degradation reaction of Crystal Violet, a synthetic organic dye. From the results, it is observed that the size, structure and photo catalytic activity of SnO₂ nanoparticles depend on the various calcination temperatures and dopant concentrations. The cobalt doped SnO₂ nanoparticles calcined at 500⁰ C act as a highly suitable photo catalyst for the degradation of Crystal Violet (CV).

(Received May 9, 2016; Accepted August 28, 2016)

Keywords: Crystal Violet, Nanoparticles, Organic Dye, Photo catalyst, Solution method, Tin Oxide.

1. Introduction

Most of the industries discharge hazardous pollutants, which comprise of organic chemicals and pathogens into water bodies. Pertaining of these pollutants in ground and surface water leads to intense ecological disturbance and hazardous to human health. Among all the industries, textile waste water is considered as most polluting and main concern involves adverse effect of various dyes in the environment. Since the chemicals used to produce the dyes are highly toxic to human and environment, the waste water effluents from dyeing industries creates water pollution. Water pollution is a serious problem for entire world and its leads to health dangers to humans, threats to aquatic species, disruption of food chains and destruction of ecosystems. To preserve the environment and maintain the ecological balance, the dye stuffs in industrial waste water should be removed. The dye removal in industrial waste water is a main concern in green chemistry.¹ Removal of dye from waste water has become tough issue because, most of the dyes used in textile industries are stable to light and non-biodegradable.² More over several methods have been used to removal of dye from waste water including adsorption, absorption, incineration etc., were found to be ineffective, expensive, time consuming or generates disposal problems.³ Thus most serious concerns for a better and sufficiently effective alternative which is eco-friendly, advanced oxidation process, which are currently in use. Among them, semiconductor based photo catalytic degradation has been proved as most efficient.⁴

In recent years nanostructured semiconductor materials (such as ZnO, TiO₂, SnO₂) are proved to be an excellent photo catalyst which can degrade many kind of organic persistent in textile waste water⁵⁻¹¹. Among them tin oxide, as one of the most important semiconductor material, has been used as photo catalyst for degradation of organic pollutants in waste water effluents of industries. The reports indicate that tin oxide exhibits photo activity toward

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degradation of dye and other organic pollutants.^{12,13} But the performance towards the photo activity is depends on their size and morphology. Thus its clear, method of synthesis will strongly influence the photo activity of the metal oxide. A number of techniques have been reported for the synthesis tin oxide nanomaterial including sol-gel, precipitation, spray pyrolysis, chemical vapour deposition, combustion,¹⁴⁻²⁰ such techniques are attractive because of their simple process, low cost, mild reaction conditions. Among them, simple and effective method to obtain fine and uniformed nanomaterial could be better for alternative photo catalytic activity and other applications. Furthermore, previous studies suggested that doping on tin oxide nanostructure with transition metals enhance their photo catalytic activity by change in the band structure of tin oxide. Various transition metals such as Mn, Fe, Co, Ni, Cu have been used as dopants for tin oxide nanomaterials.²¹⁻²⁵ Doping with Co is considered to be the most effective for tuning the electronic and optical properties.

In this study, much attention has been focused to optimize the simple and effective technique to synthesize very fine and uniformed particles of tin oxide nanostructure. For instance, we synthesized pure, very fine and uniformed tin oxide nanoparticle and co-doped tin oxide nanoparticles by organic solvent assisted simple solution method at various calcination temperature. The photo catalytic activity of Co-doped and undoped tin oxide particles were also evaluated by examining the degradation of Crystal violet under UV exposure. Finally an explanation for the increase in the photo catalytic activity of tin oxide is proposed based on the results obtained from XRD and SEM.

2. Experimental Methods

2.1 Materials

Tin (IV) chloride pentahydrate ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$) was purchased from Sigma- Aldrich. Sodium hydroxide, Ethanol and Crystal violet dye were purchased from Merck. As all these chemicals are Analytical Grade, they were used without further purification.

2.2. Preparation of Tin oxide nanoparticles

Tin oxide nanoparticles were synthesized by a simple solution method using ethanol as solvent. In a typical synthesis, Tin oxide nanoparticles were prepared by dissolving 1.75 g of (0.05M) Tin (IV) chloride pentahydrate in 100 ml distilled water under continuous magnetic stirring. After complete dissolution, sodium hydroxide solution was added drop wise to the above solution under constant stirring until a certain pH was attained. The solution was filtered, and the filtrate was mixed with equal amount of ethanol. The mixture was kept in sonication bath at 70° C for 3 hours. Now it was allowed to rest at room temperature for several hours. Then the clear solution was removed and the particles formed were washed and dried in an oven at 400° C for one hour. The powder obtained was used for characterization and photo catalytic studies.

2.3 Preparation of Cobalt doped Tin oxide nanoparticles

For preparing cobalt doped Tin oxide, the calculated amount of cobalt nitrate hexahydrate was added to the tin(IV) chloride solution and stirred it for one hour. Similar procedure was followed to obtain Co doped nanoparticles as in the preparation of pure tin oxide nanoparticles. Finally the obtained Co doped tin oxide particles were used for characterization and further studies.

2.4 Physical Characterization of Co doped and undoped tin oxide nanoparticles

The crystalline phase and particle size of Co doped and undoped tin oxide nanoparticles were analyzed by X-ray diffraction measurements at room temperature using X ray diffractometer with Cu K_α radiation (λ 0.1542 nm). The SEM images of doped and undoped tin oxide nanoparticles were recorded with FEI Quanta FEG 200.

2.5 Photo catalytic measurements

Photo catalytic performance of tin oxide nanoparticles and Cobalt doped tin oxide nanoparticles were evaluated by degradation of Crystal violet dye under sunlight irradiation. For the photo catalytic studies, 5 mg of as-synthesized SnO₂ and Co doped SnO₂ nanopowder were ultrasonically dispersed in 5 ml distilled water, which were used as photo reactor. A 10 μM dye solution was added to the photo reactor and thoroughly mixed and kept in the dark for 15 minutes. The reaction suspensions in photo reactor containing crystal violet dye and photo catalysts were irradiated with sunlight for different timings (15,30,45,60... minutes) with occasional shaking for uniform mixing of photo catalysts and dye solution. Then, the photo catalysts removed from suspension by centrifugation. The concentrations of crystal violet in resultant solution were monitored by UV-visible absorption spectroscopy in the wavelength range of 200-800 nm.

3. Results and Discussion

Fig 1 (a)-(c) show the XRD patterns of the as-prepared SnO₂ nanoparticles at three different calcination temperatures (300⁰C, 400⁰C and 500⁰C respectively). The XRD pattern of undoped SnO₂ shows the lines at 2 theta equal to 26.6⁰, 33.9⁰, 37.9⁰, 51.7⁰, 54.7⁰ and 61.8⁰ corresponding to the (1 1 0), (1 0 1), (1 1 1), (2 1 1), (2 2 0) and (2 2 1) planes respectively, which good agreement with reflection of tetragonal rutile phase structure of SnO₂ nanostructures (with reference to JCPDS File No.880287). No other characteristic diffraction peaks are observed, indicating high purity and crystallinity of the product. Using Scherer's equation the crystallite size of the particles are calculated as 20.7 nm. Using Williamson Hall method lattice strain acting on the nanoparticle was estimated as 0.0076. Lattice parameters and average crystallite size of synthesized samples summarized in Table 1. It is noted from the table with increase of temperature, the average crystallite size decreases. The crystallite size order lies between 18nm to 23 nm for 300⁰C – 500⁰C.

Table 1. The Crystallite size and Structural Parameters of SnO₂ in different Calcination temperature

Temp.(⁰ C)	D ₁₀₁ (nm)	a (Å ⁰)	c (Å ⁰)	Δa (Å ⁰)	Δc (Å ⁰)
300 ⁰ C	22.50	4.6265	3.1105	0.1105	0.0755
400 ⁰ C	21.69	4.6562	3.1014	0.0808	0.0846
500 ⁰ C	19.15	4.6259	3.1170	0.1111	0.0690

Table 2. The Crystallite size and Structural Parameters of SnO₂ in different Co concentration

Sample	D ₁₀₁ (nm)	a (Å ⁰)	c (Å ⁰)	Δa (Å ⁰)	Δc (Å ⁰)
SnO ₂	19.15	4.6259	3.1170	0.1111	0.0690
Sn _{0.98} Co _{0.02} O ₂	18.81	4.8991	3.1014	0.0808	0.0846
Sn _{0.96} Co _{0.04} O ₂	18.23	4.8924	3.1170	0.1111	0.0690

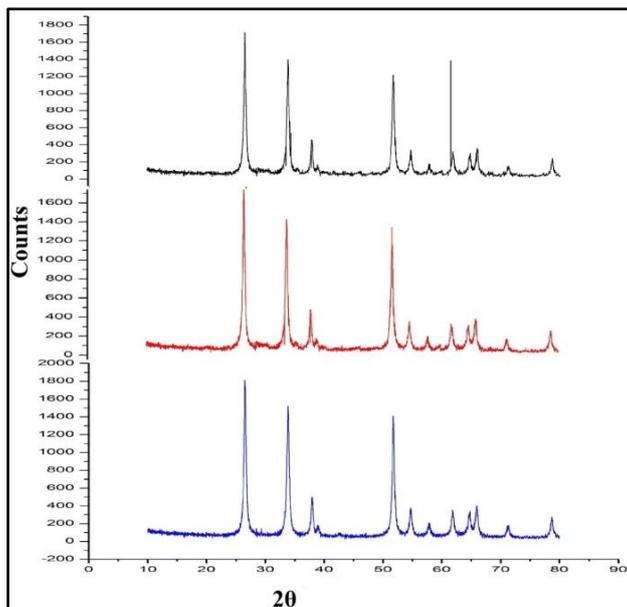


Fig.1 XRD Pattern of SnO_2 nanoparticles Calcined at a) 300°C b) 400°C c) 500°C

Fig. 2 (a)- (c) show the XRD pattern of the SnO_2 and Co-doped SnO_2 samples (at various concentration levels) calcined at 500°C . It is clearly evident that the diffraction peaks corresponding to the rutile type tin oxide detected for undoped as well as Co doped SnO_2 . It is also indicating that, Co doping does not affect the structural unit cell of tin oxide. No additional peaks in cobalt doped particles indicating the absence of impurities such as cobalt oxide and hence the cobalt highly incorporated into the tin oxide lattice structure. Comparing the intensities of the series of XRD peaks, we noted that the diffraction peak intensities became stronger with decreasing dopant concentration and hence increasing the dopant concentration increases the size.

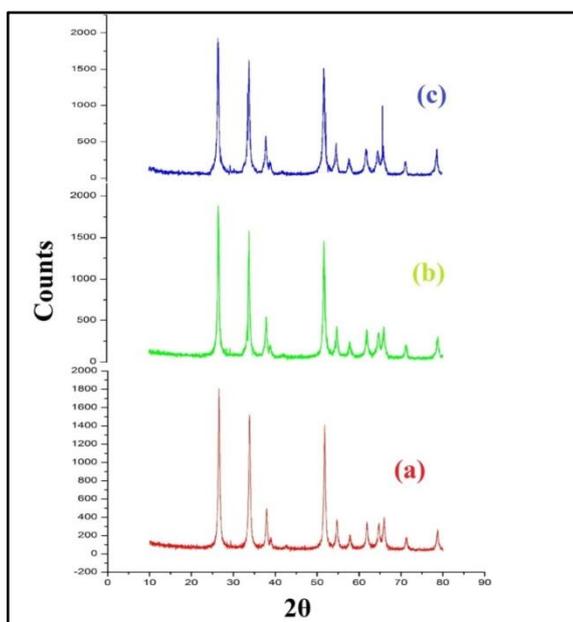


Fig.2 XRD pattern of a) undoped SnO_2 b) 2 % Co doped SnO_2 c) 4% Co doped SnO_2

The surface morphology of undoped and Co doped SnO_2 were studied using SEM techniques. Fig.3 (a-d) show the SEM images of undoped SnO_2 , Co doped SnO_2 at 2% and 4%

respectively. It can be seen that spherical morphology observed for all the samples and uniformly distributed over the surface. The crystallite size of the samples is in good agreement with the size calculated from Scherer's formula. It can also indicate that the particles size decreases for increasing dopant concentration and the dopant concentration had no major effect on surface morphology.

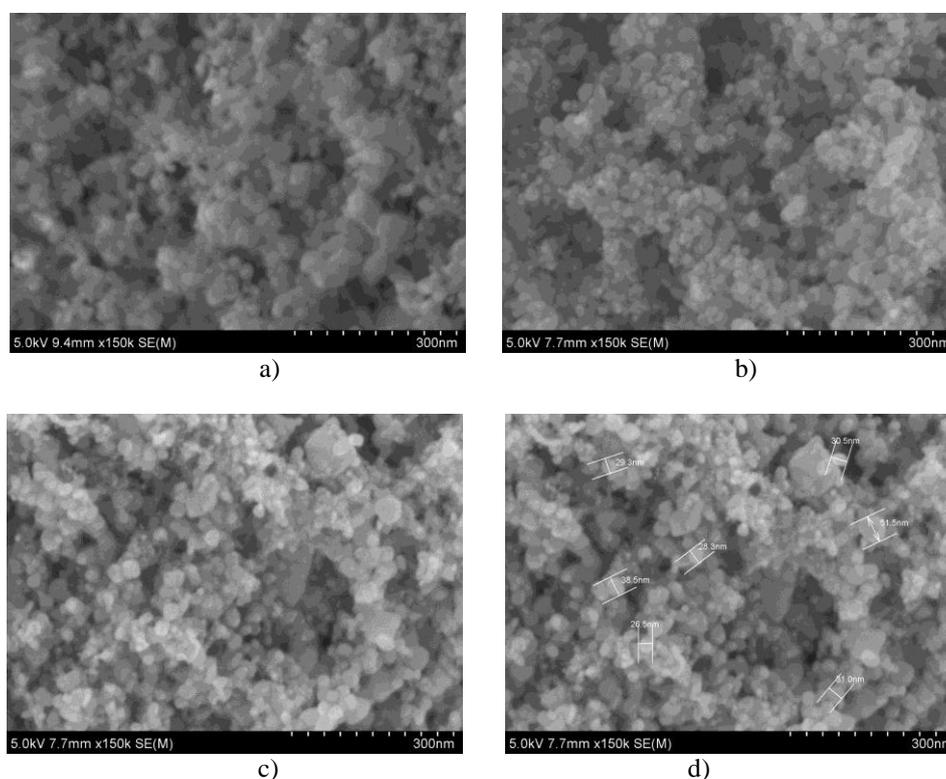


Fig.3 SEM images of SnO_2 synthesized a) at 400°C b) at 500°C c) 2% Co doped SnO_2 d) 4% Co doped SnO_2

Photo catalytic degradation of Crystal Violet

Photo Catalytic Performance of as synthesized three kinds of catalysts under different exposure conditions namely UV light, Sun light and dark conditions were examined by observing the change in optical absorption band of the dye solution at 580 nm during photo catalytic degradation of the dye. The same experiment also performed without catalyst. But in this case, no remarkable degradation of dye is observed and hence catalyst is only responsible for degradation of dye.

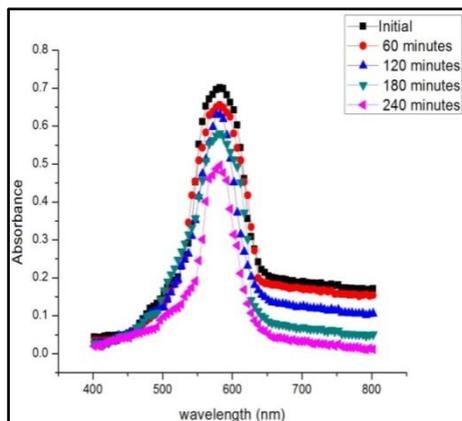


Fig 4 Photocatalytic degradation of CV under UV irradiation by SnO_2 photocatalyst

Fig 4 Shows the UV-Visible spectra of CV irradiated with UV light with as prepared catalytic materials under different time interval. It can be observed that the maximum degradation occurred only after 180 mins for the absorption band of 580 nm. At the same time, even after 180 minutes there is no significant change absorption band at 580 nm in the UV-Visible spectra of CV under dark conditions. The Photo catalytic degradation of CV was carried out using as prepared photo catalyst of undoped and Co doped samples under sunlight and its results of UV-Visible spectra depicted in Fig 5(a),(b)&(c). It can exhibits CV shows strong absorption band at 580 nm and addition of photo catalyst tends to decreasing absorption band. It can also be seen that, maximum absorption band of CV at 580 nm steadily decreases with increasing the irradiation times. Fig. 6 shows the degradation percentage calculated as follows:

% of Degradation = $(C_0 - C)/C_0 \times 100$ where C_0 and C are initial dye concentration and actual dye concentration at particular time respectively. The 4 % and 2 % Co doped SnO_2 photo catalyst degrade most of the CV dye solution in 150 min. In contrast, the pure SnO_2 photo catalyst degrades less amount of CV than Co doped photo catalysts. It is clearly indicating that the presence of Cobalt in tin oxide matrix accelerates the photo catalytic process. Both 2 % and 4 % Co doped tin oxide nanoparticles are highly efficient photo catalytic activity for degradation of CV. However, 4% Co doping tends to intensify the photo catalytic activity of SnO_2 nano catalysts. To examine the advantage and applicability of 4 % Co doped photo catalyst, reusability of the catalyst were tested for photo degradation of CV and the results are depicted in fig.7. The reusability test clearly expose that Co doped photo catalyst quit stable during the heterogeneous photo catalysis since there is no decrease in activity of catalyst up to 4 runs. However, it lost its activity to below 90 % only after 6 runs. Additionally, the photo catalytic activity of SnO_2 synthesized at different calcination temperatures i.e. 300°C , 400°C , 500°C were also performed. It can clearly indicates that the photo catalytic activity of SnO_2 is follow the order $500^\circ\text{C} > 400^\circ\text{C} > 300^\circ\text{C}$. The Photo catalytic activity of SnO_2 synthesized at 500°C shows highest activity for degradation of CV.

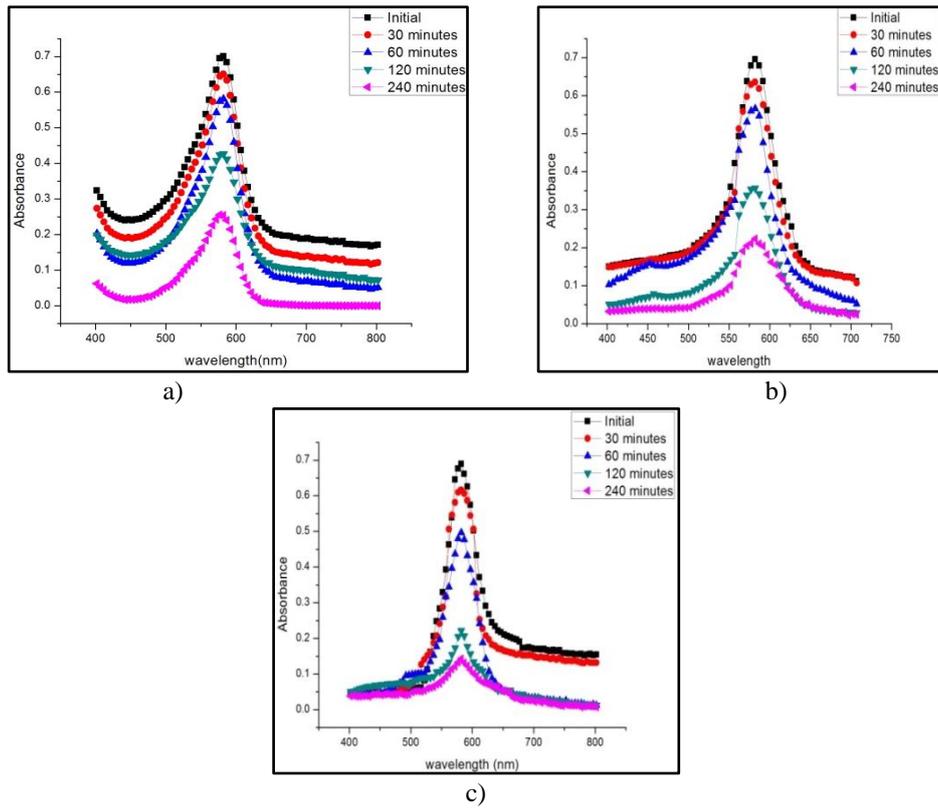


Fig 5. Photocatalytic degradation of CV under sun light by a) SnO_2 b) 2 % Co doped and c) 4 % Co doped SnO_2 particles

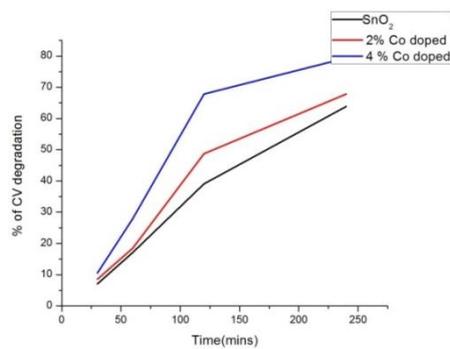


Fig 6 Degradation percentage of CV at various time interval by undoped, 2 % Co doped and 4 % Co doped SnO_2 nanoparticles

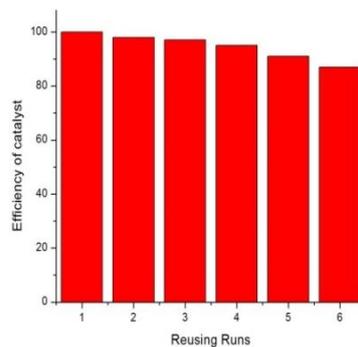
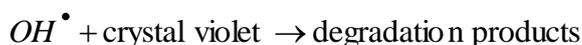
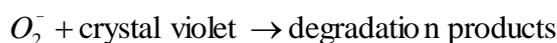
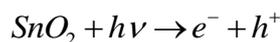


Fig. 7 Repeated cycles upto 7 times of photodegradation of CV over 4% Co doped photo catalyst

At Last, we study the mechanism photo catalytic degradation of CV, which follows the selective photo oxidation by electron transfer. Initially, the dye molecules adsorbed on the surface of SnO₂ nano particles followed by irradiation of sunlight leads to generation of electron hole pair in SnO₂ nanostructures. Interaction of photo generated electrons and holes with adsorbed oxygen molecule and hydroxyl group leads to the formation of superoxide anion radical (O₂⁻) and hydroxyl radical (OH[•]) respectively. Finally, the most reactive hydroxyl radical and superoxide anion radical react with CV dye adsorbed on SnO₂ nanostructure leads to the degradation of dye molecules. The mechanism of photo catalytic degradation of CV can be summarized as follows.



In general, Co doped SnO₂ are stable, excellent photo catalyst for degradation of Crystal Violet dye and can be reused with slight loss in their activity.

4. Conclusion

SnO₂ and Co doped SnO₂ nanoparticles have been successfully synthesized by organic solvent assisted simple solution method. XRD results show that the particle size is in the range from 18 nm to 22 nm and it is shown that the crystallite size decreases with increasing the dopant concentration; and the nanoparticle has rutile structure. SEM images depicts the spherical morphology of nanoparticles and doping does not affect the shape of the nanoparticles. Photo catalytic degradation a synthetic organic dye, namely, Crystal violet in the presence of the doped and Co doped SnO₂ at different concentration have been investigated. Both doped and Co doped SnO₂ nanoparticles are found to be excellent photo catalyst for the degradation of Crystal Violet. The result indicated that 4% Co doping exhibits highest photo catalytic activity towards degradation of Crystal violet dye. The reusability test of the photo catalyst proves the stability of the catalyst.

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