Tin as an Effective Doping Agent into ZnO for the Improved Photodegradation of Rhodamine B

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We have fabricated ZnO nano rods by hydrothermal method and successively doped them with tin (Sn) using different concentrations of 25, 50, 75 and 100 mg of tin chloride. XRD of the fabricated structures showed that ZnO possess hexagonal wurtzite phase. Scanning electron microscopy (SEM) was used to explore the morphology and it shows nanorod like morphology for all samples and no considerable change in the structural features were found. The dimension of nanorod is 200 to 300 nm. The doped materials were then investigated for their photo catalytic degradation of environmental pollutant Rhodamine B. The performance of doped ZnO is compared with the pristine ZnO. Scanning electron microscopy (SEM) was used to explore the morphology and it shows nanorod like morphology for all samples and no considerable change in the structural features were found. The dimension of nanorod is 200 to 300 nm. XRD of the fabricated structures showed that ZnO possess hexagonal wurtzite phase. Photo catalytic activity of rhodamine B was investigated under UV light and a maximum degradation efficiency of 85% was obtained. The optical property reveals the reduction in band gap of upto 17.14% for 100 mg Sn doped ZnO. The degradation is followed by the pseudo order kinetics. The produced results are unique in terms of facile synthesis of Sn doped ZnO and excellent photo degradation efficiency, therefore these materials can be used for other environmental applications.

Keywords: Tin Doped ZnO, Rhodamine B, Photodegradation, Aqueous Solution.

1. INTRODUCTION

Water pollution has become a serious environmental issue like rivers get contaminated and impart adverse effects to aquatic life and living beings due to its toxicity. Industrial effluents are main source of water pollution. Specifically, organic dyes and their effluents from various industries [1–3] like plastics, colorant, food and cosmetics [4–7] is major cause of water pollution. Rhodamine B ($C_{28}H_{31}ClN_2O_3$) is amongst the dyes used in textile, food, and water tracing in order to track water for the determination of its treatment capabilities, food industry and textile

industry for coloring and printing [8]. It is very harmful for living beings causing numerous diseases [9–13]. The removal of the dyes is therefore indispensable for cleaner water, environment and healthy society. Researchers have made numerous approaches for instance adsorption, flotation, chlorination, ozonation, chemical oxidation and coagulation to remove these kinds of contaminants from waste water [14–18]. But there are different issues with these approaches like some remain soluble in effluent [19–21], some are ineffective [22–24] while others leave unpleasant taste and odor [25] and they are costly [26]. Photo catalytic degradation in conjunction with nanostructured oxides materials is an environmental friendly alternative for the treatment of these dyes [27–28] and has become

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choice for the wide range of researchers [29–31] where photo catalysts are used to remove the pollutants in the presence of light source. ZnO is playing dominating role as photo catalysts [32–35] while compared to other catalysts like [36–37] due to its low cost, higher absorption efficiency than titania, easy to grow, high stability in thermal, chemical and physical environments [38–40] and is utilized in wide range of applications. Moreover, as it is a direct wide band gap material having 3.37 eV of band gap it finds applications like in LEDs, laser diodes, photovoltaic, semiconductor heterojunction, transparent conductors, and so on [41–44]. Still the lower quantum efficiency of ZnO leads to faster recombination rate of charge carriers [45] which results in poor photo degradation efficiency. Moreover, the wide band gap of ZnO restrict its absorption of ultraviolet light only leading to decrease in photocatalytic efficiency in the visible region [46]. Also, in order to get maximum juice of solar spectrum the semiconductors should have smaller band gap [47]. Besides, band gap has crucial role to improve the physical properties of semiconductors [48–50] as well as increase the efficiency of photocatalysis. To resolve this issue doping is popular way to achieve the efficiency as well as to adjust the band gap [48–50]. Among various dopants like copper, silver, Mn, Co, Eu, Ce, Gd, La, Ni, Al used by researchers [51–62]. Sn doped ZnO has gained much attention because it has good oxidation rate and can substitute into Zn lattice without any difficulty [63]. Rosaline Beura and coworkers [63], reported ZnO doped with Tin for the removal of methyl Orange and were successful to decrease the band gap upto 3.16 eV gaining a total of 1.25% reduction in band gap with good degradation efficiency of methyl orange. The same group again used Sn doping in ZnO-Graphene nano composite and got an improved reduction in band gap upto 8.97%. [64] for the degradation of four different dyes. However, the band gap study for tin doped ZnO for the removal of rhodamine B is rarely investigated and remain successful to reduce band gap by 17.14%.

We report a significant decrease in the band gap of ZnO from 3.5 to 2.9 eV which is 17.14% with addition of 100 mg of tin in ZnO. Moreover, the addition of tin reduced band gap from 3.5 eV of pristine ZnO to 3.39, 3.23, 3.06 and 2.90 eV for the 25, 50, 75 and 100 mg of tin dopant respectively. This study shows that the doping has remarkable effect upon the ZnO band gap. The efficiency of degradation of rhodamine B was found to be increasing up to 85% with reduction of band gap and increase in doping concentration.

2. MATERIALS AND METHODS

2.1. Materials

Tin (II) chloride (SnCl_2 , $M = 189.6$), zinc acetate dihydrate ($\text{ZnC}_4\text{H}_6\text{O}_4$), solution of ammonia (25%) were obtained from Merck. Rhodamine B, and ethanol

Figure 1. XRD results of pristine ZnO versus doped ZnO with 25, 50, 75 and 100 mg of tin doping concentration.

were obtained from Sigma–Aldrich and were used as received condition. The deionized water was used in all experiments.

2.2. Synthesis of Sn Doped ZnO Nanostructures

We used precipitation process for the synthesis of ZnO nanostructures and doping with Sn. We used a zinc acetate di-hydrate and 25% ammonia as precursors. At first different contents of tin ranging from 25, 50, 75 and 100 mg were dispersed in ethanol (5 mL) and then sonicated for 30 minutes. Zinc acetate di-hydrate (2.22 g) was dissolved into 100 mL of the deionized water then 25% ammonia (5 mL) was added to zinc precursor. We took five beakers having zinc acetate di-hydrate as well as ammonia. Four of them with individual concentration of SnCl_2 ranging from 25, 50, 75 and 100 mg of SnCl_2 were added in 5 mL

Figure 2. SEM images of 25 mg doped ZnO nano rods (a) and 50 mg doped ZnO nano rods (b), 75 mg doped ZnO (c) 100 mg doped ZnO (d).

Figure 3. Elemental mapping for 25 mg doped ZnO nano rods (a) and 50 mg doped ZnO nano rods (b), 75 mg doped ZnO (c) 100 mg doped ZnO (d).

of ethanol and thereby were labeled as e 1, 2, 3, and 4 samples respectively. Fifth beaker with concentration of zinc acetate di-hydrate as well as ammonia was labeled as pristine sample. Aluminum foil was applied to cover the beakers to restrict the evaporation of growth solution. The oven temperature was set and heated at 90 °C followed

by placement of beakers into the oven for holding time of 5 hours. After holding time passed the beakers were removed from oven. A white product was seemed in each beaker. The white product, which was separated by filtering, drying and was ready for characterization.

The morphological analysis of tin doped nanostructures were done by scanning Electron microscope at an accelerating voltage of 3 kV, composition was estimated by energy dispersive spectroscopy (EDS), crystal structure was studied by X-ray diffraction at applied conditions of CuK α radiation ($\lambda = 1.5418 \text{ \AA}$) at a generator voltage of 45 kV and a current of 45 mA., while the optical properties were obtained by Perkins UV-vis spectrophotometer.

Rhodamine B was considered to degrade owing to its importance using ZnO samples in aqueous solution. A Rhodamine B concentration of 0.0001 M was made in the deionized water followed by the addition of 10 mg of each material in separate flasks. Then solutions were stirred in ultrasonic bath for 30 to 40 mins in order to achieve equilibrium for adsorption and desorption conditions. Then dye containing photocatalysts was illuminated with UV light of wavelength 365 nm with a power of 10 Watt for activation of catalysts and used for different time intervals. The dye concentration before to the photocatalytic process was estimated from UV-visible

Figure 4. UV-visible spectra of pristine ZnO (a), (b) reaction kinetics (c) kinetics of photo degradation of Rhodamine B i.e., $\ln(C_0/C_t)$ versus time (d) photo degradation efficiency of pure ZnO.

absorption spectrum. The degradation performance of tin doped ZnO was demonstrated via % percent degradation of Rhodamine and was estimated from the below Eq. (1).

$$\%CR = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

The C_0 and C_t are corresponded to the initial concentrations of Rhodamine (mg/L) and after a time interval of (t) during UV light illumination.

3. RESULTS AND DISCUSSION

3.1. XRD

Pristine ZnO and doped ZnO with various concentrations of tin were investigated by XRD (see Fig. 1). The set of peaks at positions of 31.737° , 34.420° , 36.225° , 47.515° , 56.536° , 62.836° , 66.304° , 67.893° , 69.015° , 72.561° and 76.891° was observed with respective planes of ZnO corresponding to (010), (002), (011), (012), (110), (013), (020), (112), (021), (004) and (022) crystal planes respectively. For the determination of crystal structure and phase analysis the obtained XRD results are in good similarity to the

standard JCPDS card no. 96-900-4182. It was observed that the diffraction patterns showed no remarkable variations in the intensity while compared to pristine ZnO.

3.2. SEM and EDS

The morphological analysis of the samples was investigated by scanning electron microscope. It was clearly seen that the nano rods were successively formed and there were no big changes observed even after by the addition of tin doping concentrations. As shown in Figure 2. The doped samples of ZnO with tin with low concentration are bigger in size as can be visualized from the Figures 2(a), (b). The size of nanorods is few microns in length with an average diameter of 200–300 nm. It can also be observed that at higher concentration of tin chloride the nanorods started to become thinner as seen in Figures 2(c), (d).

The elemental mapping spectra are illustrated in Figures 3(a)–(d) for tin doped ZnO which ensures the presence of Sn, oxygen and Zn as main elements. Whereas Cr and Ag were also seen as impurity from the substrate.

Figure 5. UV-visible spectra for different tin concentrations such as 25, 50, 75, and 100 mg in ZnO nanorods for removal of Rhodamine B at eight-time variations from 30–240 minutes at each 30 minutes intervals.

3.3. UV-Visible Spectra

3.3.1. Pristine ZnO

The nanostructures including pure ZnO and doped ZnO were used to treat Rhodamine B to check its photo degradation in aqueous solution under UV light at different time intervals. The results for the pristine ZnO are depicted in Figure 4 whereby Figure 4(a) shows UV-visible absorption spectra. C_t/C_0 curve corresponds to the undoped ZnO for degradation of Rhodamine under exposure of UV light Figure 4(b). Figure 4(c) shows kinetics of degradation of rhodamine and efficiency of degradation is depicted in Figure 4(d) for pristine ZnO the maximum degradation efficiency was observed to be 22%. The poor performance of pristine ZnO can be added to the fast charge recombination rate and large energy band gap. Further photo degradation kinetics was found to be pseudo order kinetically as can be seen in the Figures 4(b), (c).

3.3.2. Sn-Doped ZnO

UV-vis absorption results for the tin doping in ZnO nano-rods with varying concentrations are shown in Figure 5. At first 10 mg of each of the 25, 50, 75 and 100 mg tin doped

ZnO samples were added to Rhodamine dye solution under UV exposure for the time irradiation of 30 to 240 minutes with 30 minutes of time interval each for getting photo degradation of Rhodamine B Figures 5(a)–(d).

With addition of dopant impurity of tin (25, 50, 75 and 100 mg) the degradation efficiency was seemed to be increasing. In comparison the maximum degradation of 22% for undoped ZnO was observed and with increase in doping concentration and increase in the efficiency of upto 85% was achieved for doping concentration of 100 mg of tin, that shows that there is a remarkable improvement in photo degradation of Rhodamine by doping ZnO with tin.

Figure 6(a) shows C_t/C_0 curve for Sn-doped ZnO for Rhodamine dye under UV light exposure. Degradation kinetics follows pseudo-first-order rate Figure 6(b). The photo degradation efficiency for doped ZnO is given in Figure 6(c) that clearly shows that by increasing doping concentration of Sn results in increasing the degradation efficiency. Doping of 25, 50, 75 and 100 mg of Sn in ZnO resulted in increase in degradation efficiency of 43, 62, 70 and 85% respectively. It was observed that a maximum

Figure 6. UV-Vis results for tin doped ZnO nano rods for Rhodamine B degradation (a) reaction kinetics Plot C_t/C_0 versus time (b) degradation kinetics curve for $\ln(C_0/C_t)$ versus time (c) photo degradation efficiency.

of 85% efficiency for degradation of Rhodamine B was achieved by 100 mg doping of tin. The favorable photodegradation efficiency can be attributed to the decrease in recombination rate and increase in the charge separation of charge carriers which are further supported by the decrease in the optical band gap of tin doped ZnO samples.

On UV light irradiating of SnO₂-doped ZnO nanocomposites, the electrons and holes were produced in CB and VB of SnO₂ and ZnO. Subsequently the CB of ZnO lies above the CB of SnO₂, therefore, the photogenerated electrons produced get shifted from the CB of ZnO to that of SnO₂. On opposing, the holes get shifted from the VB of SnO₂ to VB of ZnO. In addition, on adsorption of O₂ on the surface of photocatalyst, an active oxygen species (O₂^{•-}, a radical anion) formed due to the electrons present in the CB of SnO₂ which on protonation formed OOH radical. At the end, [•]OH radicals generated which are accountable for the degradation of complex dye molecules into smaller compounds. On the other hand, h⁺ also react with ⁻OH and gives to the formation of [•]OH present in the VB of ZnO. On the surface of the photocatalyst, the general reactions can be described as below [65]:

Therefore, (O₂^{•-}, [•]OOH and [•]OH) active species of oxygen were engendered when the reactant molecule get

adsorbed on the surface of SnO₂ doped ZnO nanoparticles. The degradation of dye is mainly due to these active species.

The photocatalysis mechanism can correlated to the optical band gap as it absorbs the photogenerated charge carriers via superficial crystal defects. Photocatalytic effect is attributed to the presence of ZnO itself and tin induction into it. The superior performance of tin doped ZnO is connected to the varying conduction and valence band inside the semiconducting ZnO. The decreases in optical band gap offers the change in the energy states which uplift the charge separation using tin doped ZnO nanostructures. This further reduces the recombination of charge carriers and consequently superfast photodegradation efficiency is observed. During the illumination of UV light, the photo produced charge carriers are stimulating to Sn within ZnO which are playing a critical participation for the absorption of photo generated electrons with the provision of superoxide radicals. The high intensity of produced superoxide radicals further fosters the degradation process; thus, we have found an excellent 85% photodegradation efficiency.

3.3.3. Effect of Tin Doping on Optical Band Gap of ZnO

We also studied band gap effect as given Figures 7(a), (b). Figure 7(a), shows the normal UV-visible spectra for the different samples and Figure 7(b), shows Tauc plot for the calculation of band gap. Tauc, s plot gives the information about the direct and indirect band gap for a semiconducting material, we see a direct band for the doped and pure ZnO samples. Here band gap for the pristine ZnO was 3.5 eV which was decreased with increase in tin content. We have achieved a total reduction in band gap of 17.14% that shows that doping enhances the reduction in band gap. The reduction of band gap with respect to increasing of tin concentration is shown in Table I. Therefore, increasing doping concentration of tin not only reduces band gap but it also increases degradation efficiency leading to that fact

Figure 7. (a.) UV-visible absorption spectra for various Sn doped ZnO samples, (b) the estimation of optical band gap of various ZnO samples.

Table I. Band gap for undoped versus Sn-doped ZnO.

Sample	Cut off wavelength	Band gap (eV)
Pristine ZnO	334.0	3.5
25 mg tin doped	345.11	3.39
50 mg tin doped	362.16	3.23
75 mg tin doped	382.53	3.06
100 mg tin doped	403.32	2.90

that band gap has linear relationship with the degradation efficiency.

4. CONCLUSION

We successively obtained Sn-doped ZnO nanorods by hydrothermal method. The SEM and XRD results confirmed that there were no significant changes in the morphology of doped structures. The photodegradation efficiency was increased with increased in doping concentration. The maximum degradation efficiency of 85% was achieved for degradation of Rhodamine B. The optical study showed significant decrease in band gap with respect to increase in doping content of tin and maximum reduction of up to 17.14% was achieved which shows that tin plays remarkable role on ZnO band gap and the structures are suitable to be applied for waste water treatment. The used strategy for Rhodamine B degradation is simple, low cost, environment friendly and uses earth abundant and nonprecious materials, therefore scale up production of materials for energy and other environmental applications.

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