Research Article

Abimbola E. Oluwalana and Peter A. Ajibade*

Preparation and morphological studies of tin sulfide nanoparticles and use as efficient photocatalysts for the degradation of rhodamine B and phenol

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Abstract: Tin sulfide nanoparticles were prepared from tin (II) dithiocarbamate complexes: bis(benzylmethyl dithiocarbamate)tin(II) (SnS1), bis(dibenzyl dithiocarbamate)tin(II) (SnS2), and bis(imidazolyl dithiocarbamate)tin(II) (SnS3) single-source precursors. Powder X-ray diffraction patterns of the as-prepared tin sulfide nanoparticles confirmed orthorhombic crystalline phase irrespective of the tin(II) dithiocarbamate precursors used to prepare the tin sulfide nanoparticles. Transmission electron microscopic images showed SnS nanoparticles with average particle size of 1.35 ± 0.04 nm for SnS1, 2.63 ± 0.65 nm for SnS2, and 1.55 ± 0.15 nm for SnS3. The energy bandgap of the SnS nanoparticles obtained from Tauc plots are in the range 3.80–4.37 eV. The as-prepared SnS nanoparticles were used as photocatalysts for the degradation of rhodamine B with efficiency of 90.97, 61.53, and 80.26% for SnS1, SnS2, and SnS3, respectively, while for phenol degradation efficiency was 96.45, 75.13, and 90.69% after 180 min. The results indicate that the as-prepared SnS nanoparticle are efficient photocatalyst for rhodamine B and phenol degradation. The photocatalytic degradation of rhodamine B and phenol follows pseudo-first-order reaction kinetics model from which the photodegradation rate could be obtained. Scavenger studies show that electrons (e^-), hydroxy radicals ($^{\bullet}\text{OH}$), and holes (h^+) play significant role in the photodegradation of rhodamine B and phenol by the SnS nanoparticles. Recyclability studies

show the SnS photocatalyst could be reused for four cycles without losing its photodegradation ability.

Keywords: tin(II) dithiocarbamate, single-source precursor, tin sulfide, nanoparticles, photocatalysis, recyclability

1 Introduction

In recent years, coordination chemistry of dithiocarbamate has received considerable attention because of its ability to coordinate metal ions in different oxidation states to give complexes in different structural motifs [1]. Interest in tin(II) dithiocarbamate is due to its structural diversity [2], wide range of applications in agriculture, catalysis, biology, and as single-source precursors for the preparation of metal sulfide nanoparticles [1,3,4]. Over the years, IV–VI semiconductors' nanoparticles are being studied due to their optical properties and small bandgap which make them useful for various applications in optoelectronic devices. Among this class of compound, SnS nanoparticles are of particular interest because of its high absorption coefficient, and photoelectric conversion efficiency [5–7]. In addition, it is being used as supercapacitor [8], solar cell [9,10], sensor [11], photodetector [12], and photocatalyst [13].

The divalent and tetravalent oxidation states of tin are common in most of its compound. Thus, SnS nanoparticles exist in different crystalline phases, which include SnS (divalent), SnS₂ (tetravalent) Sn₂S₃, and Sn₃S₄ (mixed valency) [7]. SnS is one of the promising semiconductor nanoparticles that are being explored as potential photocatalyst for dye degradation to address problems associated with environmental pollution due to its high stability, tunable optical properties, nontoxic, and low bandgap (1.3–1.5 eV) [13,14]. Due to interest in the potential applications of SnS and SnS₂ nanoparticles, several methods such as coprecipitation [15], aerosol-assisted chemical

* **Corresponding author: Peter A. Ajibade**, School of Chemistry and Physics, University of KwaZulu-Natal, Private Bag X01, Scottsville, Pietermaritzburg 3209, South Africa, e-mail: ajibadep@ukzn.ac.za
Abimbola E. Oluwalana: School of Chemistry and Physics, University of KwaZulu-Natal, Private Bag X01, Scottsville, Pietermaritzburg 3209, South Africa

vapor deposition [16], chemical spray pyrolysis [17], thermal evaporation [18], sputtering [19], microwave-assisted radiation [20], atomic layer deposition [21], and single-source precursors [22–24] have been used to prepare tin sulfur nanoparticles. Among these synthetic approaches, the use of single-source precursor in which the tin sulfur bond is already formed in the complexes could result in clean high-quality SnS nanoparticles [22]. The use of different single-source precursors could lead to tin sulfur nanoparticles with different size, shape, and optical properties. Hence, the use of three tin(II) dithiocarbamate complexes as single-source precursors in this paper to prepare tin sulfur nanoparticles and study the effect of the different precursors on the morphology and photocatalytic properties of the as-prepared tin sulfur nanoparticles.

Photocatalytic process is based on the generation of electron–hole pair in the semiconductor on absorption of light energy. The generated electron–hole reacts with oxygen from the surrounding and the aqueous solution to give highly reactive oxygen species such as superoxide and hydroxide radicals [25]. These radicals are responsible for the degradation of organic contaminants through photocatalytic process. Das and Dutta [25] reported the use of SnS nanorods for the degradation of trypan blue in the presence of sunlight which was favorable due to the inhibition of electron–hole recombination on the surface of the nanorods. Kabouche *et al.* [13] reported the elimination of rhodamine B using SnS nanoparticles under sunlight at 88.46% after 4 h. Chen *et al.* [26] report the degradation of rhodamine B and phenol at 64.8 and 51.5% for pristine SnS₂ nanosheets after 4 h. SnS negatively charged nature was reported to be responsible for its superior visible light photocatalytic performance of cationic dyes [27]. The degradation of organic dyes have been reported to be influenced by the shape, size, and recombination properties of SnS nanoparticles [28]. To the best of our knowledge, the photocatalytic activity of SnS on phenol is minimal compared to SnS₂. In view of this, there is a need to investigate photocatalytic efficiency and reusability of tin sulfide nanoparticles for the degradation of colored and colorless organic contaminants as related to particle size and recombination effect of as-synthesized SnS nanoparticles. In this study, we report the synthesis and characterization of three tin(II) dithiocarbamate complexes and their use as molecular precursor to prepare SnS nanoparticles *via* hot injection method. The as-prepared SnS nanoparticles were used as photocatalyst for the degradation of rhodamine B and phenol under

visible light irradiation, the photodegradation kinetics, mechanism, and recyclability were also evaluated.

2 Experimental

2.1 Materials

Tin(II) chloride dihydrate, tri-*n*-octyl phosphine (TOP), hexadecylamine (HDA), methanol, rhodamine B, phenol, silver nitrate (SN), isopropanol (IPA), ammonium oxalate (AO), and acrylamide (AC) were purchased from Sigma-Aldrich and used without further purification. Potassium salt of benzyl methyl dithiocarbamate (L¹), dibenzyl dithiocarbamate (L²), and imidazolyl dithiocarbamate (L³) were prepared using modified literature methods [29–31].

2.2 Characterization techniques

Infrared spectra data were obtained from Agilent Technologies Cary 630 FTIR spectrometer in the frequency region of 4,000–650 cm^{−1}. The ¹H and ¹³C NMR spectra of the complexes were measured using Bruker Avance III 400 MHz NMR spectrometer. Elemental analysis was carried out using ThermoScientific Flash 2000. The crystalline phases of the synthesized nanoparticles were identified using a powder X-ray diffraction (XRD) pattern obtained from Philips PW1830 diffraction spectrometer operated at 40 kV and 40 mA equipped with Co anode of K α = 1.79290 Å. The size, shape, lattice fringes, and selected area electron diffraction (SAED) patterns of the nanoparticles were investigated using a JEOL JEM-2100 high-resolution transmission electron microscope (HRTEM). Image J analysis software was used to measure the particle size distribution based on 150–250 nanoparticles. Perkin Elmer 25 UV-Vis spectrophotometer and LS 45 fluorescence were used for optical absorption and emission measurement, respectively.

2.3 Synthesis of tin(II) dithiocarbamate complexes

Tin chloride dihydrate (2.5 mmol, 0.5641 g) was dissolved in 20 mL ethanol and added dropwise to 5 mmol ethanolic solution of ligands (benzyl methyl dithiocarbamate (L¹), dibenzyl dithiocarbamate (L²), and imidazolyl dithiocarbamate (L³) (0.9800 g, 0.9225 g and 1.0965 g)). The reaction was stirred at room temperature for 3 h (Scheme 1). The

Scheme 1: Preparation of the tin(II) dithiocarbamate complexes.

resulting precipitate was washed severally with ethanol and dried under vacuum.

2.3.1 $[\text{Sn}(\text{L}^1)_2]$

Yield: 69%, 1.0399 g; melting point: 132.3–134.3°C. ESI- MS^+ (m/z) [$\text{M} + \text{DMSO}$] 591, anal. calcd for $\text{C}_{18}\text{H}_{22}\text{N}_2\text{SnS}_4$ (%), C: 42.28, H: 3.94, N: 5.48; found. C: 41.97, H: 4.01, N: 5.56. ^1H -NMR: ($\text{DMSO}-d_6$): δ 2.55 (s, 6H $-\text{CH}_3$), 5.32 (s, 4H $-\text{CH}_2$), 7.31–7.50 (m, 10H $-\text{C}_6\text{H}_5$), ^{13}C -NMR: (CDCl_3) δ 39.4 (CH_3), 56.3 (CH_2), 127.9–129.1 (C_6H_5), 190.3 (CS_2). Selected FTIR bands (cm^{-1}): 1,250 $\nu(\text{C}-\text{N})$, 1,498 $\nu(\text{N}-\text{CS}_2)$, 960 $\nu(\text{C}-\text{S})$.

2.3.2 $[\text{Sn}(\text{L}^2)_2]$

Yield: 73%, 1.4314 g; melting point: 102.4–103.6°C. ESI- MS^+ (m/z) [$\text{M} + \text{DMSO}$] 745, anal. calcd for $\text{C}_{30}\text{H}_{30}\text{N}_2\text{SnS}_4$ (%), C: 54.31, H: 4.25, N: 4.22; found. C: 54.34, H: 4.25, N: 4.22. ^1H -NMR: ($\text{DMSO}-d_6$) δ 5.07 (s, 8H CH_2), 7.31–7.48 (m, 20H C_6H_5), ^{13}C -NMR: ($\text{DMSO}-d_6$) δ 59.7 ($\text{N}-\text{CH}_2$), 127.9–129.9 (C_6H_5), 190.4 (CS_2). Selected FTIR bands (cm^{-1}): 1,214 ($\text{C}-\text{N}$), 970 ($\text{C}-\text{S}$), 1,490 ($\text{N}-\text{CS}_2$).

2.3.3 $[\text{Sn}(\text{L}^3)_2]$

Yield: 52%, 0.6205 g; melting point: decomposes at 250°C. Selected FTIR bands (cm^{-1}): 1,276 $\nu(\text{C}-\text{N})$, 1,447 $\nu(\text{N}-\text{CS}_2)$, 997 $\nu(\text{C}-\text{S})$.

2.4 Preparation of HDA-capped SnS nanoparticles

Around 0.4 g of each tin(II) dithiocarbamate complex was dissolved in 5 mL of TOP before introducing into 4 g of hot HDA at 120°C under nitrogen and stirred for 1 h. Afterward, the mixture was cooled to 70°C, followed by the addition of cold methanol. The product was separated by centrifugation. Tin sulfide synthesized from $[\text{Sn}(\text{L}^1)_2]$, $[\text{Sn}(\text{L}^2)_2]$, and $[\text{Sn}(\text{L}^3)_2]$ was labeled SnS1, SnS2, and SnS3, respectively.

2.5 Evaluation of the photocatalytic degradation of rhodamine B by the HDA-capped SnS nanoparticles

The photocatalytic activity of the synthesized SnS nanoparticles was evaluated by measuring the degradation of aqueous rhodamine B and phenol solution ($3 \times 10^{-5} \text{ M}$). Typically, 40 mg of the catalyst (SnS) was dispersed into 40 mL of the organic pollutants. The reaction solution was stirred for 30 min in the dark to attain adsorption and desorption equilibrium between the pollutant and the catalyst (SnS) prior to visible-light irradiation. The solution was placed 10 cm away from 80 W high-pressure mercury lamp. Around 4 mL of solution was taken at regular intervals (30 min) for 180 min. The degradation

process was monitored using UV-Vis spectrophotometer at 553 and 270 nm wavelength for rhodamine B and phenol, respectively.

3 Results and discussion

3.1 Spectroscopic studies

The mode of coordination of the dithiocarbamate ligands to the tin(II) ion is determined by the $\nu_{(C-S)}$ vibrational mode (Figures S1–S3). A single band in the range $960\text{--}997\text{ cm}^{-1}$ appeared in the complexes for $\nu_{(C-S)}$ vibration, which indicate the dithiocarbamate anions coordinate to the tin(II) ion in bidentate chelating mode [32,33] through the two sulfur atoms. Also, an intermediate band between single and double bond C–N appeared in the range $1,447\text{--}1,498\text{ cm}^{-1}$, which can be attributed to the delocalization of the electron density within the N–CS₂ bonds of the dithiocarbamate to the tin(II) center [34].

The ¹H-NMR spectrum of [Sn(L¹)₂] in Figure S4 displayed a singlet peak of six protons at 2.55 ppm which is assigned to the methyl protons, the methylene protons resonated as a singlet at 5.32 ppm with four protons, while the dithiocarbamate aromatic ring protons appeared as a multiplet in the region of 7.31–7.80 ppm. In [Sn(L²)₂] the methylene proton has a singlet peak at 5.02 ppm with eight protons, while the aromatic ring resonated as multiplet in the range 7.31–7.48 ppm with 20 protons (Figure S5). The –CH₂ proton peaks appeared at the same region in [Sn(L¹)₂] and [Sn(L²)₂] due to the alkyl derivative attached to the nitrogen atom [25].

¹³C-NMR of [Sn(L¹)₂] and [Sn(L²)₂] showed a signal at 190.3 and 190.4 ppm, respectively, due to CS₂, the peak shifted downfield due to significant contribution from the N–C π -electrons of the dithiocarbamate moiety. The nitrogen atom experiences a δ^+ surplus charge localization while –CS₂M metallochelate a δ^- delocalization. The aromatic carbon resonated around 127.9–129.9 ppm, the methylene proton resonated at 56.3 and 59.7 ppm for [Sn(L¹)₂] and [Sn(L²)₂], respectively, while in [Sn(L¹)₂] methyl carbon resonated at 39.4 ppm.

3.2 Morphological studies of the SnS nanoparticles

3.2.1 XRD analysis

The XRD patterns of the SnS nanoparticles are presented in Figure 1. The 2θ peaks at 22.8° , 24.5° , 27.6° , 39.2° , 42.8° , 44.1° , 47.0° , 48.1° , 49.9° , 52.0° , 53.4° , 56.6° , 58.1° , 60.8° ,

Figure 1: Powder X-ray diffraction pattern of SnS1 (a) SnS2 (b) and SnS3 (c) nanoparticles.

and 69.5° are indexed to (110), (120), (021), (131), (141), (102), (002), (211), (112), (511), (122), (061), (420), (103), and (081) planes of SnS orthorhombic (*o*-SnS) phase (JCPDS 39-0354; herzenbergite) [1]. The calculated lattice parameter $a = 0.4328\text{ nm}$, $b = 0.1119\text{ nm}$, and $c = 0.3978\text{ nm}$ are consistent with standard values. In the XRD patterns,

SnS_2 , Sn_2S_3 , and Sn_3S_4 characteristic peaks were not observed indicating the formation of pure SnS phase irrespective of the tin(II) dithiocarbamate precursor used to prepare the nanoparticles.

3.2.2 HRTEM and SEM analysis of the SnS nanoparticles

The HRTEM images, lattice fringes, SAED patterns, and the particle size distribution graph of the as-synthesized SnS nanoparticles are presented in Figure 2. SnS1 obtained from $[\text{Sn}(\text{L}^1)_2]$ is spherically shaped and well dispersed with average particle size of 1.35 ± 0.04 nm. Monodispersed nanoparticles were obtained for SnS2 prepared from $[\text{Sn}(\text{L}^2)_2]$ with average particle size of 2.63 ± 0.65 nm while SnS3 obtained from $[\text{Sn}(\text{L}^3)_2]$ is monodispersed with a size distribution of 1.55 ± 0.15 nm. The results indicate that the as-synthesized SnS nanoparticles are quantum dots due to their size being less than 10 nm. The results indicate that the precursors have an effect on the size of the nanoparticles obtained, as a result of the different binding strength of the dithiocarbamate moiety to the tin(II) metal center, which leads to different rate of decomposition of the precursor during thermolysis [35,36]. An interplanar lattice fringe d -spacing of 0.34 nm that is visible in the HRTEM images for SnS1 and SnS3 corresponds to the d -spacing of (222) plane of α -SnS [37], while 0.27 and 0.32 nm was obtained in SnS2 that corresponds to (011) and (200) planes, respectively, of α -SnS [38]. The SAED patterns of SnS1 and SnS2 show bright spots in the diffraction rings, which indicates that the as-synthesized SnS nanoparticles are crystalline in nature [39]. In addition, the clear spots indicate that the as-synthesized SnS composed of a single crystalline structure [40] as confirmed by XRD. SnS3 is amorphous in nature as evidence by the SAED patterns as there is no diffraction ring or spot [41].

The SEM images of the SnS nanoparticles in Figure S6 have powdery morphology due to high surface energy and the small particle size [42]. The elemental mapping of the samples was done and the EDX spectrum (Figure S7) confirms the formation of SnS nanoparticles through the detection of Sn and S peaks in the atomic ratio of 1:1 in agreement with the expected value. The carbon (C) and oxygen peaks could be ascribed to the capping agents while gold (Au) peak detected is attributed to coating of samples using gold.

3.3 Optical studies of the SnS nanoparticles

The UV-Vis absorption spectra and Tauc plot of the as-synthesized SnS nanoparticles are presented in Figure 3a

and b. The nanoparticle absorption band edges were observed at 320, 285, and 307 nm for SnS1, SnS2, and SnS3, respectively. On extrapolation of $(ah\nu)^2$ vs $h\nu$ plots straight-line portion to the x -axis using direct allowed transition, the bandgap energy values were found to be 3.80 eV for SnS1, 4.37 for SnS2, and 4.07 eV for SnS3, which are blue-shifted in comparison to the bulk SnS (1.51 eV) which can be ascribed to quantum confinement effect enhancement due to the size of the nanoparticles, defects, and grain boundary disorder [43,44]. It has been shown that the bandgap energy values are beneficial for photocatalytic activity; hence the decreased bandgap of SnS1 toward the visible region shows that high energy is needed for the recombination of electron-hole pair occurrence [45]. The emission spectra (Figure 3c) were used to study electron-hole pair separation and recombination effect of HDA-capped SnS nanoparticles via the emission intensity. The emission peaks were observed at 394, 400, and 403 nm for SnS1, SnS2, and SnS3, respectively, which could be attributed to excitons of SnS radiative recombination [44,46]. However, the intensity was noticed to follow the order SnS2 > SnS3 > SnS1, which suggests that SnS1 has the longest separation time for the electron-hole pair generated while SnS2 has fast separation efficiency of photoinduced charge carriers [47]. The lower recombination rate of the electron-hole pair observed in SnS1 and SnS3 will make these nanoparticles show higher photocatalytic efficiency (Figures 4a and 5a). Overall, the result shows that the dithiocarbamate moiety bonded to tin(II) metal center played a significant role in the decomposition which affected the optical properties of the as-synthesized SnS nanoparticles.

3.4 Photocatalytic activity and stability of SnS nanoparticles

The degradation of rhodamine B and phenol by SnS nanoparticles under mercury light irradiation is observed by absorption spectra. Rhodamine B and phenol absorption maxima at 553 and 270 nm was observed to decrease with time, which indicates the degradation of the organic contaminants (Figures S7 and S8). The photodegradation of rhodamine B was 90.97, 61.53, and 80.26% by SnS1, SnS2, and SnS3, respectively, while against phenol it was 96.45, 75.13, and 90.69% after 180 min as shown in Figures 4a and 5a. The low degradation efficiency observed by SnS2 for the degradation of rhodamine B and phenol could be attributed to the fast recombination of photogenerated electron-hole pair as detected in the photoluminescence

Figure 2: HRTEM images: (a) SAED patterns; (b) lattice fringes; (c) corresponding size distribution graph (insert) of SnS nanoparticles.

Figure 3: (a) SnS nanoparticles absorption spectra; (b) Tauc plots; and (c) emission spectra.

spectra (Figure 3c). In addition, the particle size of the as-prepared SnS nanoparticles influences the photocatalytic properties as the large particle size resulted in lower degradation efficiency [48]. The as-prepared SnS nanoparticles showed better degradation of rhodamine B and phenol compared to previous studies in the literature as presented in Table 1.

The concentration curves of rhodamine B and phenol residual in the presence of the as-prepared SnS nanoparticles are presented in Figures 4b and 5b. A blank test of the

rhodamine B and phenol without catalyst shows that the organic contaminants are stable under visible light irradiation. The absence of degradation by the organic contaminants indicates that the degradation process is not by photolysis but by the presence of the catalyst [27]. The photocatalytic degradation kinetics of rhodamine B and phenol evaluated was using the *pseudo-first-order* model [26].

$$\ln \frac{C_t}{C_0} = -kt,$$

where k is the rate constant (min^{-1}), C_t and C_0 are the concentration at time t and initial concentration of rhodamine B, respectively. The photodegradation rate constant was calculated to be 0.3926, 0.1517, and 0.2642 min^{-1} for SnS1, SnS2, and SnS3, respectively, from the slope of the fitted line in Figure 4c for rhodamine B, with a correlation coefficient >0.98 . Phenol rate constant of degradation was calculated to be 0.51, 0.2295, and 0.3777 min^{-1} for SnS1, SnS2, and SnS3, respectively, with correlation coefficient >0.99 from the fitted line shown in Figure 5c.

The stability and recyclability of catalyst are an important factor in practical application. Hence, the stability of the as-synthesized SnS nanoparticles was investigated for stability by performing the photodegradation of rhodamine B and phenol using the same catalyst four times. The results (Figure 4d–f) clearly show that as-synthesized SnS nanophotocatalyst showed slight degradation efficiency after four cycles and this indicates that the catalysts are stable and can be reused for the photodegradation of rhodamine B. In phenol, the same process was followed and about 6.01, 8.23, and 7.56% degradation efficiency reduction were observed for SnS1, SnS2, and SnS3, respectively, as shown in Figure 5d–f. The reduction in efficiency observed could be attributed to reaction of byproducts on the catalyst active site, or deposition of the organic contaminants on the catalyst surface or loss of catalyst during the process of washing and collection [57].

3.4.1 Effect of scavengers on the photocatalytic degradation of rhodamine B

Photodegradation process is controlled by the migration of electron–hole pair photogenerated to the surface of the catalyst [58,59]. Consequently, it is important to know the effect of superoxide radical (O_2^-), holes (h^+), electrons (e^-), and hydroxyl radical ($\text{OH}^\bullet$) on the photodegradation of rhodamine B by HDA-capped SnS nanoparticles. Hence, scavengers such as SN were used for e^- , AC for O_2^- , AO for h^+ , and IPA for $\text{OH}^\bullet$ were introduced to the photocatalytic system [60,61].

Figure 4: (a) Degradation bar chart; (b) plot of C_t/C_0 versus time; (c) kinetic studies; (d–f) recycling runs using SnS as photocatalyst for rhodamine B degradation.

Photodegradation efficiency of rhodamine B decreases significantly after the addition of SN, AO, and IPA from 90.97% to 4.19, 18.86 and 11.71%, respectively (Figure 6a), while the

addition of AC reduced the efficiency to 47.15%. This shows that e^- , h^+ , and $\cdot OH$ are the main active species in the degradation of rhodamine B using SnS1 nanoparticles with O_2^- serving

Figure 5: (a) Degradation bar chart; (b) plot of C_t/C_0 versus time; (c) kinetic studies; (d–f) recycling runs using SnS as photocatalyst for phenol degradation.

as a secondary oxidant species [62]. The use of SnS2 as photocatalyst, SN, AO, and IPA inhibited the photodegradation of rhodamine B significantly indicating that e^- , h^+ , and $\cdot OH$ are the main active species involve, while $\cdot O_2^-$ plays minor role in

the degradation process. Also, SnS3 followed the same trend as observed in SnS1 and SnS2. The addition of SN, IPA, and AO (e^- , $\cdot OH$, and h^+ scavengers) leads to a decrease in the degradation efficiency, which indicate that the photogenerated

Table 1: Rhodamine B and phenol photodegradation by SnS nanoparticles

Irradiation time (min)	Light source	Organic pollutant	Degradation (%)	Ref.
210	350 W xenon arc lamp	Rhodamine B	67.21	[49]
240	Solar light (90 mW cm ⁻²)	Rhodamine B	38	[50]
90	500 W xenon lamp	Rhodamine B	11	[51]
180	100 W incandescent lamp	Rhodamine B	58.3	[52]
90	Xenon lamp (XQ350W)	Rhodamine B	20	[53]
120	300 W xenon arc lamp	Rhodamine B	61	[54]
120	500 W xenon arc lamp	Rhodamine B	64.8	[26]
120	Solar-simulator	Rhodamine B	77	[55]
240	500 W xenon lamp	Phenol	63.1	[56]
60	300 W xenon lamp	Phenol	1.7	[27]
60	300 W Xe lamp	Phenol	15.6	[57]
240	500 W xenon arc lamp	Phenol	51.5	[26]
180	80 W mercury lamp	Rhodamine B	90.97	This work
180	80 W mercury lamp	Phenol	96.45	This work

electron-hole pairs are important in the photodegradation process which is confirmed by the degradation process involving the $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ radicals. From the results obtained, the order of reactive oxidative species responsible for photocatalytic degradation by the SnS nanoparticles is $e^- > \cdot\text{OH} > h^+ > \cdot\text{O}_2^-$.

In the presence of a mercury lamp (visible light), irradiation of the SnS nanoparticles causes the excitation of the valence band electrons to the conduction band. Electron-hole pairs are generated, which migrate to the SnS surface, where they undergo redox reaction with rhodamine B on the SnS surface. The electrons generated react with oxygen to give superoxide and hydroxyl radicals through reduction, which degrades rhodamine B into CO_2 , H_2O , NH_4^+ , NO_3^- , and Cl^- [61].

3.4.2 Effect of scavengers on the photocatalytic degradation of phenol

To investigate the mechanism of phenol photodegradation over the as-synthesized SnS catalyst, scavengers such as SN, AC, AO, and IPA were used as trapping agents for e^- , $\cdot\text{O}_2^-$, h^+ , and $\cdot\text{OH}$ radicals [60,61]. h^+ , $\cdot\text{O}_2^-$, and $\cdot\text{OH}$ directly oxidize phenol to CO_2 and H_2O , while e^- reduces the benzene ring structure followed by oxidation [63]. Hence it is important to investigate the radicals responsible for the degradation process of phenol over the as-synthesized SnS quantum dots. In Figure 6b, the addition of AO inhibited degradation efficiency from 96.45 to 10.87% (SnS1), 75.13 to 9.41% (SnS2), and 90.69 to 8.53% (SnS3). The reduction in efficiency is an indication that photogenerated holes (h^+) are reactive species during the photodegradation process. Similarly, the addition of IPA reduced the performance of SnS1 (96.45–21.02%), SnS2

(75.13–12.87%), and SnS3 (90.69–11.88%), suggesting that $\cdot\text{OH}$ also played an important role in the degradation of phenol in the catalyst. Phenol degradation was inhibited by e^- trapping, which indicates that some phenols were degraded *via* reduction mechanism through the SnS catalyst [64]. Moreover, Figure 6b demonstrates that the presence of AC reduces the photodegradation efficiency to 39.57, 32.83, and 42.53% for SnS1, SnS2, and SnS3, respectively. These results suggest that although e^- was involved in the photodegradation process, $\cdot\text{O}_2^-$ also played an active role [65]. This trend confirms that the reactive species follows the sequence of $h^+ > \cdot\text{OH} > e^- > \cdot\text{O}_2^-$ which corresponds to what is in the literature [46,48,66].

4 Conclusion

In summary, we have synthesized tin(II) complexes of benzyl methyl dithiocarbamate, dibenzyl dithiocarbamate, and imidazolyl dithiocarbamate and used them as molecular precursors to prepare SnS1, SnS2, and SnS3 nanoparticles, respectively, *via* solvothermal method at low temperature (120°C). Monodispersed spherical nanoparticles were obtained for SnS1 and SnS2 with average particle size of 1.35 ± 0.04 and 2.63 ± 0.65 nm, respectively, while SnS3 was agglomerated with average size of 1.55 ± 0.15 nm. Different bandgap energy was obtained for the as-prepared SnS nanoparticles 3.80 eV (SnS1), 4.37 eV (SnS2), and 4.07 eV (SnS3). The results indicate that the bandgap energy can be tuned using different dithiocarbamate complexes due to variation in the obtained nanoparticle size. The synthesized SnS nanoparticles were used as photocatalyst for rhodamine B degradation under visible light

Figure 6: (a) Effect of scavengers on the photodegradation of rhodamine B and (b) phenol, by SnS nanoparticles.

irradiation, degradation efficiency of 90.97, 61.55, and 80.26% was achieved for SnS1, SnS2, and SnS3, respectively, and their corresponding degradation in phenol was 96.45, 75.13, and 90.69%. The result obtained shows that the nanoparticle size has an influence on the photodegradation efficiency. Electrons (e^-), holes (h^+), and radicals (O_2^- and $OH^\cdot$) were found to be active in rhodamine B and phenol degradation using SnS nanoparticles. Also, the nanoparticles were highly stable and reusable.

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