2D SnS2 Nanostructure-Derived Photocatalytic Degradation of Organic Pollutants Under Visible Light

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Wastewater produced by the textile industry contains various dyes and organic compounds that directly or indirectly affect surface water or groundwater pollution. Visible-light-driven semiconductor photocatalysis is the leading pathway for the degradation of environmental pollutants. Herein we report the bottom-up hydrothermal growth of 2D tin disulfide nanostructures (SnS2 NSs) for the efficient photodegradation of organic pollutants such as Rhodamine B (Rh.B) and Methyl Violet (M.V) in an aqueous medium under visible light (λ > 400 nm) irradiation. The as-synthesized SnS2 NSs were characterized by various structural, morphological, and optical techniques such as XRD, RAMAN, TEM, UV–Vis, Brunauer–Emmett–Teller, etc. Furthermore, the low bandgap (~1.6 eV), the high surface area (56 m²/g), and the anionic nature of SnS2 NSs attribute to it as an efficient photocatalyst for photocatalytic applications. The photocatalytic properties of SnS2 NSs showed good degradation efficiency of 94 and 99.6% for Rh.B and M.V, respectively, in 25 min. The kinetic rate constant of these dyes was estimated by using the Langmuir–Hinshelwood model. Here we also performed the recyclability test of the photocatalyst and discussed the plausible mechanism for the photocatalytic degradation of organic pollutants. The XPS spectra of SnS2 NSs were studied before and after the photodegradation of Rh.B and M.V, indicating the high stability of the photocatalyst. Moreover, in vitro cytotoxicity was also evaluated against human cervical cancer cell lines (HeLa cells) with different concentrations (0–1,000 μg/ml) of as-synthesized SnS2 NSs. This intended work provides a possible treatment for the degradation of organic pollutants under visible light to balance the aquatic ecosystems.

Keywords: semiconductor photocatalyst, 2D SnS2 NSs, hydrothermal growth, photocatalytic degradation, organic dyes

INTRODUCTION

The efficient disposal of environmental pollutants is one of the major problems, of which water pollution is the prime concern. Due to the rapid growth of industrial activity, chemical fertilizers and raw sewage have a direct or indirect impact on surface water or groundwater pollution (Schwarzenbach et al., 2010; Li et al., 2020a; Li et al., 2021). Commercially, over 100,000 dyes are available, and 700,000 tonnes are produced each year (Robinson et al., 2001). Among other pollutants, organic pollutants are becoming a major source of environmental contamination.
Organic dyes are widely used in various industrial fields such as the leather industry, food, plastics, cosmetics, coloring agent in textile, and many more (Xie et al., 2000; Brillas and Martínez-Huitle, 2015). Approximately 10–20% of organic dyes that originate as wastewater from industries affect the balance of aquatic ecosystems. Organic dyes are toxic, mutagenic, carcinogenic, have disobedient molecules, and have low biodegradability (Xie et al.). To reduce the organic contaminants from wastewater, various methods have been adopted, such as ozonization, carbon adsorption, flocculation, and activated sludge process which is very tedious, unable to remove organic pollutants, requires expansive tools, and can also lead to secondary pollution (Patll and Shinde, 1988; Stock et al., 2000; Kim et al., 2016). However, to overcome these limitations, the photocatalytic degradation process is an effective and authentic technique that can be used to remove organic pollutants in the aqueous medium. In this process, the photocatalyst converts toxic organic dyes into nontoxic intermediates under ultraviolet or visible light irradiation (Zhong et al., 2009; Li et al., 2019).

In the last few years, semiconductor-based photocatalysts have attracted much attention among researchers due to their tremendous properties, such as light-absorbing ability in visible and near-field regions, high surface area, and abundant active surface sites (Guo et al., 2010; Xie et al., 2010; Zhang et al., 2011; Tian et al., 2017). Recently, in the IV–VI group semiconductors, tin disulfides (SnS₂) have engrossed much consideration due to their strong anisotropic optical property in various potential applications, such as in electrical switching, solar cell, and catalytic reactions (Zhang et al., 2011a; Du et al., 2013; Song et al., 2013). SnS₂ is an n-type semiconducting material with the general formula MX₂ (where M stands for metal atom Sn, Mo, and W, and X stands for chalcogen atom S, Se, and Te) which belongs to the two-dimensional-layered metal dichalcogenides family. Structurally, SnS₂ has a hexagonal CdI₂-type crystal structure in which one layer of Sn atom has been sandwiched between two layers of S atom via in-plane covalent

| Dyes         | Chemical formula | Molar mass | Chemical structure |
|--------------|------------------|------------|--------------------|
| Rhodamine B  | C₂₈H₃₁ClN₂O₃    | 479.02 g/mol | ![Chemical structure of Rhodamine B](image1) |
| Methyl violet| C₂₄H₂₈N₃Cl      | 393.959 g/mol| ![Chemical structure of Methyl violet](image2) |
bonding and has weak van der Waals force between the adjacent layers. SnS₂ has been widely used in various technological applications, such as sensors, energy storage, photodetectors, solar cell, and many more (Tan et al., 2011; Umar et al., 2013; Su et al., 2015; Srivastava et al., 2019). Moreover, tin disulfide is earth-abundant, cost-effective, has high carrier mobility, has a large surface active site, less toxic, and chemically stable in both acidic and neutral conditions, which make them a promising material for the degradation of organic pollutants (Li et al., 2012a; Umar et al., 2013; Lorenz et al., 2014). To date, various 2D SnS₂-based nanostructures have been reported for photocatalytic application (Li et al., 2012b; Umar et al., 2013; Balu et al., 2018). However, all these methods have low degradation efficiency and were covered with inorganic materials or any organic surfactant molecules which restrict any interaction on their material surface and corresponds to a reduced catalytic activity. Therefore, it is of utmost importance to develop a novel photocatalyst which has abundant active sites, is biocompatible, has lower toxicity, and has a wider spectral response for the degradation of organic pollutants.

Therefore, in the present investigation, we report the synthesis of SnS₂ NSs using a facile one-pot bottom-up ecofriendly hydrothermal method without a subsequent surface treatment. The as-synthesized SnS₂ NSs show a low bandgap, a high surface area, and an anionic character. Furthermore, it has been observed that the degradation efficiency of organic dyes such as Rh.B and M.V is ~94 and ~99.6%, respectively, using SnS₂ NSs as a photocatalyst under visible light in 25 min. The recyclability test and underneath detailed degradation mechanism were also discussed in the present work. Here we also estimated the in vitro cytotoxicity against human cervical cancer cell line (HeLa cells) with various concentrations of as-synthesized SnS₂ NSs.

**EXPERIMENTAL TECHNIQUES**

**Materials**

Tin (IV) chloride pentahydrate (SnCl₄·5H₂O) and methyl violet were purchased from Molychem, India. Thioacetamide (C₂H₅NS) was purchased from OTTO Chemical, India. Rhodamine B and methyl violet were purchased from HIMEDIA, India. The human cervical cancer cell line (HeLa cells) was procured from the National Centre for Cell Sciences, Pune, India. The culture medium (RPMI-1640), fetal bovine serum, antibiotics, trypsin, and EDTA solutions were procured from Sigma Aldrich. The dimethyl sulphoxide (DMSO) was purchased from SRL Chemicals. Distilled water was used in the present work. All chemicals were used without any decontamination and were of analytical grade.

The molecular weight and chemical structure of organic dyes (such as Rhodamine B and Methyl Violet) used in the present work is shown above.

**Hydrothermal Synthesis of SnS₂ Nanostructures**

Scheme 1 shows the schematic of the one-pot bottom-up hydrothermal synthesis of SnS₂ NSs. SnCl₄·5H₂O and C₂H₅NS were used as the starting precursor of Tin (Sn⁴⁺) and sulfur (S²⁻) sources, respectively, for the growth of SnS₂ NSs. In the typical reaction process, SnCl₄·5H₂O (~1.8 g) and C₂H₅NS (~1.6 g) were completely dissolved in 60 ml of distilled water and vigorously stirred for 120 min at room temperature. Afterward, the complete solution was transferred in a Teflon-lined autoclave at 180°C for 12 h. After the proposed reaction time, the autoclave is allowed to cool down at room temperature. A yellowish color solution was obtained, which was further washed several times with distilled water, and the sample was finally dried in vacuum at 80°C for 6 h.

**Synthesis Reaction**

During the hydrothermal synthesis, the hydrolysis of thioacetamide produced ammonium acetate (CH₃CO₂NH₄) and hydrogen sulfide (H₂S) as products. The reaction between Sn⁴⁺ and H₂S produced a yellow color perception which is responsible for SnS₂ NSs. The possible reactions for the formation of SnS₂ NSs are shown by Eqs. 1, 2 as follows (Zhang et al., 2011a):

\[
\text{C}_2\text{H}_2\text{NS} + 2\text{H}_2\text{O} \rightarrow \text{CH}_3\text{CO}^- + \text{NH}_4^+ + \text{H}_2\text{S} \quad (1)
\]

\[
\text{Sn}^{4+} + \text{H}_2\text{S} \rightarrow \text{SnS}_2 + 4\text{H}^+ \quad (2)
\]

The obtained powder was then further characterized in detail and used as an efficient photocatalyst for the photocatalytic degradation of Rh.B and M.V.

**Instruments Used for Characterization**

The morphology and the structure of as-synthesized SnS₂ NSs were examined using a transmission electron microscope (TEM,
FEI-Technai G² F20, United States) with an accelerating voltage of 200 kV. The crystal phase and the crystallinity were examined by an X-ray diffractometer (PANalytical, United Kingdom) using Cu–Kα radiation (λ = 1.54178 Å) at a scanning rate of 1°/s, ranging from 10° to 80°. Raman spectrophotometer (Renishaw, United Kingdom) was used to analyze the structural and the phase purities of as-synthesized SnS₂ NSs. Fourier transform infrared (FTIR) spectrometer (Frontier, Perkin Elmer, United States) was used to determine the functional group. Total organic carbon (TOC) was measured using Lotix TOC Analyzer. The specific surface area was measured by Gemini VII 2390 surface area analyzer (Micromeritics, United States). All the photocatalytic activity of dyes was performed by using a UV–Vis spectrometer (UV-1800 SHIMADZU, Japan). X-ray photoelectron spectroscopy (XPS) was analyzed using PHI Versa Probe III.

Cell Culture and Cell Viability

Human cervical cancer cell line (HeLa cells) was cultured and maintained under a controlled atmospheric temperature at 37°C under 5% CO₂ in RPMI-1640 medium, supplemented with 10% fetal bovine serum, penicillin (100 U ml⁻¹), and streptomycin (100 mg ml⁻¹). The 3-dimethylthiazol-2,5-diphenyltetrazolium bromide (MTT) assay was performed to evaluate cell viability after 24 h of cell seeding in the presence or absence of SnS₂ NSs. In
brief, HeLa cells were seeded in a 96-well polystyrene plate (TCP), with a density of $1 \times 10^4$ cells per well, and incubated under controlled conditions (5% CO$_2$, 37°C) for 24 h. After that, the cells were treated with different concentrations (1.562, 3.125, 6.255, 12.5, 25, 50, 100, 200, 400, 800, and 1,000 μg/ml) of SnS$_2$ NSs and incubated for 24 h at 37°C. After that, the cells were incubated with MTT solution (0.5 mg/ml in culture medium) at 37°C for 4 h and allowed formazan crystal formation. After incubation, the supernatant was removed, and 200 μl of DMSO was added and incubated for 30 min at 37°C. After the complete dissolution of formazan crystals, the optical density of the solution was measured at 540 nm by a microplate reader (PerkinElmer Victor 4 microplate reader). The wells without SnS$_2$ NSs were used as controls. The values were expressed as mean ± standard deviation ($n$ = 3). Cell viability was calculated using the following equation:

$$\text{Cell viability (\%) } = \frac{[\text{Abs}]_{\text{test}}}{[\text{Abs}]_{\text{control}}} \times 100$$

Sample Preparation for the Photocatalytic Activity of Dyes Using SnS$_2$ NSs

The photocatalytic activities of the synthesized SnS$_2$ NSs were evaluated by investigating the photodegradation of Rh.B and M.V under visible light radiation. The stock solution of 100 ml, with the concentration of 10 mg/L (10 ppm) of Rh.B and M.V, was prepared and stored in a dark room. A fluorescent lamp of 40 W ($\lambda >420$ nm), with a radiation intensity of 0.79 W/m$^2$, was used for the light source. The volume of the initial solution (10 ml) of Rh.B and M.V was taken out for further photocatalytic activity. For the photocatalytic experiments, 5 mg of SnS$_2$ NSs was added to 10 ppm solution of M.V and Rh.B and stirred for 5 min from the initial phase of the solution. The decomposed dyes of the different solutions were measured by using a UV spectrometer after regular time intervals. The concentration of aqueous M.V and Rh.B was determined by measuring its absorbance value, ranging from 400 to 800 nm, using a UV spectrophotometer. Furthermore, the detailed photodegradation study of M.V and Rh.B is also discussed in the present work.

RESULT AND DISCUSSIONS

Structural and Morphological Characterizations of SnS$_2$ NSs

The as-synthesized SnS$_2$ NSs are well characterized in terms of their structural, morphological, and optical properties. Powder X-Ray diffraction has been performed to determine the crystallinity and the crystal phase of as-synthesized SnS$_2$ NSs, as shown in Figure 1A. The characteristic diffraction peaks observed at 15.0°, 28.1°, 32.1°, 46.1°, 50.1°, 52.4°, and 70.3°...
correspond to planes (001), (100), (101), (003), (110), (111), and (113), respectively.

The observed XRD pattern of SnS$_2$ NSs is well suited with JCPDS card no. 22-0677, which suggests the hexagonal phase of SnS$_2$ with lattice constant $a = 3.649$ Å and $c = 5.899$ Å and having space group: P-3m1 (164). The average crystallite size of as-synthesized materials was calculated by the Debye–Scherer formula which is given below:

$$D = \frac{K \lambda}{\beta \cos \theta}$$

where $K$ represents the shape factor, $\beta$ represents the broadening of the diffraction line at half-maximum intensity (radians), and $\theta$ represents Bragg’s angle. The average crystallite size of SnS$_2$ NSs was estimated to be $\sim 30$ nm from the Scherer formula.

RAMAN is a versatile and non-destructive technique to evaluate the structural and vibrational properties of nanomaterials. The RAMAN spectra of as-synthesized SnS$_2$ NSs were recorded with a laser excitation source of 532 nm, as shown in Figure 1B. There are two characteristic peaks located at 224 and 310 cm$^{-1}$, which correspond to $E_g$ (in-plane vibrational mode) and $A_{1g}$ (out-of-plane vibrational mode) modes, respectively (Deepika Bharatula et al., 2016).

The size and the morphology of as-synthesized SnS$_2$ NSs were determined by TEM, as shown in Figures 1C–F. A typical high-resolution transmission electron microscope image of SnS$_2$ is shown in Figure 1F. The morphology of as-synthesized SnS$_2$ was found to be nanostructures in nature. The interlayer spacing of as-synthesized SnS$_2$ NSs is 0.32 nm, which corresponds to the (100) crystalline plane, as shown in the inset of Figure 1F (Umar et al.).

### Photophysical Characterization and Specific Surface Area Measurements of SnS$_2$ NSs

The photophysical property of as-synthesized SnS$_2$ NSs was estimated by UV–Vis diffuse reflectance spectra and FTIR. The absorption spectrum of SnS$_2$ NSs was recorded in the wavelength range of 200–800 nm, as shown in Figure 2A. The broad absorption spectrum in the visible region indicates that
the as-synthesized SnS$_2$ NSs are capable of harvesting visible light and act as an efficient photocatalyst for photocatalytic reactions under a visible regime. The optical energy bandgap of as-synthesized SnS$_2$ NSs was determined by the band edge absorption relation as follows:

\[(\alpha h\vartheta)^{1/n} = B(h\vartheta - E_g)\]

where $E_g$ is the optical energy bandgap, $B$ is the optical-transition-dependent constant, $n$ characterizes the transition ($n = 2$ for allowed transition and $n = 3$ for forbidden transition), and $h$ is the Planck’s constant. Here the absorption coefficient ($\alpha$) was determined by the Kubelka–Munk function for estimating the absorption edge energy. So, the curves of [F(R$_\infty$)h$\nu$]$^{1/2}$ vs. (h$\nu$) for SnS$_2$ NSs are plotted in the inset of Figure 2A (Zhang et al., 2011b). The bandgap of as-synthesized SnS$_2$ NSs was calculated to be 1.6 eV. The lower bandgap indicates the visible-light-driven photocatalytic activity.

FTIR was performed to determine the function group over the surface of as-synthesized SnS$_2$ NSs. In Figure 2B, the FTIR spectrum of SnS$_2$ NSs was recorded, ranging from 400 to 4,000 cm$^{-1}$. The peaks located at 3,226, 2,907, 1,610, 1,414, 1,194, 934, 612, and 545 cm$^{-1}$ correspond to $-\text{OH}$, $-\text{CH}$, C=O, $-\text{S}$=O, $-\text{C}$=OH, N–H, C–H, and Sn–S, respectively. The presence of functional groups such as $-\text{OH}$, $-\text{COOH}$, and S=O may be responsible for making the SnS$_2$ NSs anionic or negatively charged. This could lead to SnS$_2$ as a promising material for the removal of cationic organic contaminants in an aqueous solution. Furthermore, electrostatic adsorption might be the prime factor for the interaction of selectively positive charged dyes such as Rh.B and M.V with negatively charged SnS$_2$ (Han et al., 2017). Hence, SnS$_2$ could be the superior adsorbent for industrial dyes, especially cationic dyes such as Rh.B and M.V, as shown in Scheme 2.

For photocatalytic applications, the designing of materials with a high surface area plays a crucial role in providing abundant active sites. This leads to the diffusion of dye molecules and enhancing the adsorption capability during the dye degradation process (Zhu et al., 2013; Han et al., 2017). In the present work, N$_2$ adsorption–desorption isotherms and the corresponding Barratt–Joyner–Halenda (BJH) adsorption curve have been performed over SnS$_2$ NSs, as shown in Figure 2C. The pore size of as-synthesized SnS$_2$ NSs has been estimated by using the BJH method. This suggests that the pore size of SnS$_2$ NSs varies from 5.5 to 16 nm, as shown in the inset of Figure 2C. The Brunauer–Emmett–Teller analysis suggests that the surface area of as-synthesized SnS$_2$ NSs is 56.6 m$^2$/g, with pore volume of 0.184 cc/g and average pore width of 10 nm. This measurement reveals that the as-synthesized SnS$_2$ NSs possess a high surface area
which provides an ample amount of surface adsorption sites, and a relatively large pore size might suggest the diffusion of organic dyes.

**Cell Viability Performance**

The biocompatibility of the SnS$_2$ NSs was evaluated using MTT assay. In this assay, the metabolic activity of the cells was measured and correlated with the number of viable cells. The results of cell viability are shown in Figure 3, which suggests that SnS$_2$ NSs do not exert obvious toxicity even at a very high concentration of 400 $\mu$g/ml (cell viability ~90%), but at higher concentrations (800 and 1,000 $\mu$g/ml (46.22 and 26.45%)) significant toxicity was observed. Wang et al. (2020) reported that a hydrothermally synthesized SnS$_2$ nanostructures shows good biocompatibility and use for photothermal therapy. Another study conducted by Feng et al. (2020) has developed a Ce-doped SnO$_2$/SnS$_2$-based photoelectrochemical cytosensor for recognition of tumor-associated macrophages. These studies significantly confirmed that SnS$_2$-based materials have low toxicity and excellent biocompatibility for aquatic ecosystems.

**Photocatalytic Activity**

The photocatalytic activity of as-synthesized SnS$_2$ NSs showed remarkable properties, such as adsorption of targeted organic pollutants, photoabsorption within a given light energy region, and the separation and transporting rate of the photogenerated electrons and holes in the photocatalyst.

The absorbance spectra of M.V and Rh.B are shown in Figure 4. The sequential change of the UV–Vis absorption spectra of M.V and Rh.B under visible light irradiation in regular time intervals are shown in Figures 4A,B. The photocatalytic degradation was recorded at wavelengths of 584 and 554 nm for M.V and Rh.B, respectively. Remarkably, it was found that, with increasing visible light time exposure, the absorption intensity continuously decreased in the presence of as-synthesized SnS$_2$ NSs. The degradation efficiency or removal efficiency of organic dyes was estimated by the following equation:

\[
\text{Degradation efficiency (\%)} = \frac{C - C_0}{C_0} \times 100
\]

where $C$ and $C_0$ are dye concentrations after and before exposure to visible light irradiation, respectively.

The relative concentration of organic dyes such as M.V and Rh.B has been analyzed in the absence and presence of visible light irradiation using SnS$_2$ NSs, as shown in Figure 4C. The degradation histogram, as shown in Figure 4D, reveals that the organic dyes such as M.V and Rh.B are degraded up to 99.6 and 94.0%, respectively, in 25 min under visible light irradiation. However, in the absence of visible light irradiation, the degradation rate of Rh.B and M.V was almost negligible.
The behavior of photocatalytic activity is a tedious process that is driven by many parameters such as temperature, light intensity, catalyst loading, and concentration of organic pollutants. The photocatalytic kinetic behavior of SnS₂ NSs has been obtained from the Langmuir–Henshelwood model. The catalytic decomposition was estimated by using a pseudo-first-order reaction kinetics equation which is given by:

\[
\ln \left( \frac{C_0}{C} \right) = kt
\]

where \( C_0 \), \( C \), \( k \), and \( t \) are initial concentration, varying concentration, kinetic constant, and time, respectively. Figure 5A shows the kinetic rate constant \( k \) for the initial concentrations of M.V and Rh.B. The first-order reaction kinetic constant is 0.2236 and 0.0845 min\(^{-1}\) for M.V and Rh.B, respectively.

Stability and reusability play a vital role in the valuation of photocatalyst life cycle because photoanodic corrosion restricts their stability. To identify the stability and the reusability property of SnS₂ NSs, the degradation process has been performed up to
five times. In every cycle, SnS$_2$ NSs were reused for their photocatalytic activity by using the separation and centrifuge method. A histogram graph has been plotted between the degradation efficiency of dye removal and the number of cycles, as shown in **Figure 5B**. In the first cycle, it has been observed that the photodegradation of aqueous solution of M.V and Rh.B has been degraded up to $\sim$99.6 and $\sim$94.0%, respectively. After performing this experiment, it has been found that the degradation efficiency is $\sim$91 and $\sim$97%, respectively, for Rh.B and M.V at the fifth cycle, which reveals the excellent stability and recyclability properties of SnS$_2$ NSs.

The mineralization capability of photocatalysts is also an important criterion to evaluate their photocatalytic efficiency. Thus, the TOC removal efficiency of Rh.B and M.V by SnS$_2$ NSs was investigated using a TOC analyzer. In **Figure 5C**, the TOC removal ratio of Rh.B and M.V reached $\sim$60 and $\sim$70% using SnS$_2$ NSs under visible light irradiation in 25 min, respectively. These findings demonstrate that SnS$_2$ NSs can easily mineralize Rh.B and M.V during the photocatalytic process and could be effectively mineralized into residual organic molecules, indicating their high potential for practical applications.

XPS was performed to determine the distribution of elements and compositional states on the surface of the sample. The XPS spectra of as-synthesized SnS$_2$ NSs were investigated before and after the photocatalytic degradation of Rhodamine B and methyl violet after five successive cycles, as shown in **Figure 6**. The XPS survey spectrum (0–1,000 eV) evidences the presence of C, O, Sn, and S elements, as shown in **Figure 6A**. In **Figures 6B,C**, the XPS pattern of Sn 3d in pristine SnS$_2$ NSs shows two prominent peaks at 486.4 and 494.8 eV, which correspond to Sn 3d$_{5/2}$ and Sn 3d$_{3/2}$, respectively. The XPS spectra of S 2p in bare SnS$_2$ NSs reveal two peaks at 161.4 and 162.4 eV, which correspond to S 2p$_{3/2}$ and S 2p$_{1/2}$, respectively (Hu et al., 2013). After the photodegradation of Rhodamine B and methyl violet, the Sn 3d and S 2p peaks of SnS$_2$ NSs are slightly shifted to a lower binding energy ($\sim$0.2 eV) compared to the pristine SnS$_2$ NSs. This might be attributed to the photoreduction of SnS$_2$ NSs that occurred on the surface throughout the photodegradation process, confirming the high stability and sustainability of the photocatalyst (Shi et al., 2010; Zhai et al., 2017).

Among various 2D SnS$_2$-based nanostructured materials, the as-synthesized SnS$_2$ NSs revealed a highly efficient photocatalytic activity for organic pollutants such as Rh.B and M.V under visible-light-driven irradiation, as shown in **Table 1**.

### Photocatalytic Mechanism

The main advantages of the photocatalytic activity of semiconductor catalysts are the photoabsorption ability within the given light regime and the separation and transfer of photogenerated electrons and holes in themselves. Under visible light irradiation, the degradation of organic dyes such as Rh.B and M.V over the surface of as-synthesized semiconducting SnS$_2$ NSs has been demonstrated by a schematic, as shown in **Scheme 3**.

A narrow bandgap semiconductor catalyst allows more photons to get absorbed, resulting in excellent catalytic activity under visible light irradiation. In the photocatalytic mechanism, a photocatalyst directly attacks the chromophore of organic pollutants due to the weak interaction between the photocatalyst and the dye (Saison et al., 2011). Due to the highly reactive free radicals in the photocatalytic degradation process, all contaminants break into inorganic substances or small molecules through the addition reaction, substitution reaction, and the electron transfer between free radicals and organic pollutants.

The generation of electron–hole pairs and the excitation of valence band electron will take place under visible light irradiation. The excited electron from the valence band will further transfer the electron to the conduction band, which results in the generation of $e^-/h^+$ pairs. The holes from the valence band of as-synthesized SnS$_2$ NSs react with hydroxyl groups by breaking the water molecules and form highly reactive hydroxyl radicals ($^\cdot$OH), which react with other organic compounds to break down into smaller, non-toxic molecules.
and the electron from the conduction band react with the oxygen molecules attached over the surface of SnS2 NSs and forms superoxide anion radicals (\(\cdot\)O\(_2\)). Furthermore, these \(\cdot\)O\(_2\) react with H\(^+\) and produce H\(_2\)O\(_2\), and finally this H\(_2\)O\(_2\) deteriorates into hydroxyl radicals (\(\cdot\)OH) (Cao et al., 2017).

The plausible photocatalytic degradation mechanism for the catalytic behavior of as-synthesized semiconductor SnS\(_2\) NSs was suggested by the given equations as follows:

\[
\begin{align*}
\text{SnS}_2 + \text{hv} &\rightarrow \text{h}^+ (\text{VB}) + e^- (\text{CB}) \\
\text{H}_2\text{O} &\rightarrow \text{H}^+ + \text{OH}^- \\
\text{O}_2 + e^- &\rightarrow \text{O}_2^- \\
\text{O}_2^- + \text{H}^+ &\rightarrow \text{H}_2\text{O}_2 \\
\text{H}_2\text{O}_2 &\rightarrow \text{OH}^- \\
\text{OH}^- + \text{h}^+ &\rightarrow \text{OH} \\
\text{Dye} + \text{OH} &\rightarrow \text{dye} \rightarrow \text{degradation products (CO}_2/\text{H}_2\text{O)}
\end{align*}
\]

In general, highly reactive oxyradicals such as hydroxyl (\(\cdot\)OH\(^+\)) and superoxide anion (\(\cdot\)O\(_2\)) are responsible for the degradation of organic dyes such as Rh.B and M.V in the presence of visible light irradiation. However, at room temperature, the hydroxyl group (\(\cdot\)OH\(^+\)) plays a vital role in the degradation of organic dyes with a simple magnetic stirring process. These highly reactive oxyradicals are formed over the surface of an as-synthesized SnS\(_2\) catalyst by the separation of electron–hole (\(e^-/h^+\)) pairs (Umar et al.). Organic dyes react with the hydroxyl groups (\(\cdot\)OH\(^+\)) and superoxide anion (\(\cdot\)O\(_2\)) break into smaller molecules, and generate intermediates, such as CO\(_2\), H\(_2\)O, etc. Finally, under visible light irradiation, the transformation or oxidation of harmful organic dyes into less harmful chemicals takes place.

**CONCLUSION**

In summary, SnS\(_2\) NSs have been synthesized successfully using the facile single-step bottom-up hydrothermal method. The obtained SnS\(_2\) NSs have a low bandgap (~1.6 eV), a high surface area (56 m\(^2\)/g), and an anionic nature, resulting in an efficient photocatalyst for the degradation of organic dyes. The as-synthesized SnS\(_2\) NSs have been used for the removal of organic dyes such as Rh.B and M.V. SnS\(_2\) NSs exhibited good degradation efficiency for Rh.B (94%) and M.V (99.6%) in 25 min. The kinetic rate constant for Rh.B and M.V was calculated by using the first-order Langmuir–Hinshelwood model. The recyclability test suggests the excellent stability of the photocatalyst for up to five cycles. The XPS spectrum of SnS\(_2\) NSs was investigated before and after the photodegradation of Rhodamine B and Methyl Violet, suggesting the high stability of the photocatalyst. Herein we have also discussed the detailed degradation mechanism for the removal of dyes, which suggests the formation of a large number of oxyxaradicals and enhanced photocatalytic performance of as-synthesized SnS\(_2\) NSs. Moreover, in vitro cytotoxicity was also evaluated against human cervical cancer cell lines (HeLa cells) with different concentrations (0–1,000 \(\mu\)g/ml) of as-synthesized SnS\(_2\) NSs. In the present investigations, we believed that this highly responsive photocatalyst opened a new avenue for the degradation of environmental pollutants by the modification of the energy bandgap and charge nature on the photocatalyst surface.

**DATA AVAILABILITY STATEMENT**

The raw data supporting the conclusion of this article will be made available by the authors, without undue reservation.

**AUTHOR CONTRIBUTIONS**

RS and AS conceived the idea of 2D SnS\(_2\) nanostructure-based photocatalytic degradation. RS carried out the whole experiments, analyzed the data, and wrote the draft of the manuscript. PK and SR helped to do photocatalytic experiments. SU discussed all experiment results. UY and PS also contributed to testing in-vitro cytotoxicity of 2D SnS\(_2\) nanostructures and to preparing a robotic model. SU given scientific suggestions and comments on the manuscript. AS supervised the research at all stages and led all groups. All the authors discussed the results and commented on the manuscript.

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