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Fabrication of TiO₂@SnS₂ core—shell nanocomposites *via* a thermal decomposition approach for sunlight-driven photodegradation of crystal violet

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In the current study, $TiO_2@SnS_2$ core-shell nanocomposites were prepared via a facile thermal decomposition method. The synthesis consists of thermal decomposition of tin chloride pentahydrate and thiourea in the presence of NaOH-modified TiO_2 microspheres in diphenyl ether (DPE) at \sim 200 °C in air. The synthesized $TiO_2@SnS_2$ core-shell nanocomposites were characterized by XRD, FT-IR, TGA, FESEM, TEM, EDXA, UV-DRS, PL and XPS. The XRD results indicate the presence of both TiO_2 and SnS_2 phases in the core-shell nanocomposites. FESEM, TEM and EDX analyses results confirm uniform coating of SnS_2 nanoparticles on the surface modified TiO_2 microspheres. XPS analysis results confirm the presence of Sn^{4+} , Ti^{4+} , O^{2-} and S^{2-} in the $TiO_2@SnS_2$ nanocomposites. After their characterization, the $TiO_2@SnS_2$ core-shell nanocomposites were explored for their catalytic activity towards the photodegradation of a toxic dye (crystal violet (CV)) in an aqueous solution under sunlight. The photodegradation efficiency of $TiO_2@SnS_2$ core-shell nanocomposites is better than that of TiO_2 microspheres, SnS_2 nanoparticles and other metal sulfide nanoparticles/nanocomposites reported in the literature.

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1 Introduction

Water pollution from dyes threatens ecosystems across the globe. As human population and economies expand, water pollution has become one of the major issues. The unavailability of sufficient freshwater not only affects human life but it also affects biodiversity and other ecosystems.¹ Textile industries produce organic contaminants such as synthetic dyes in high amounts. The dyes do not bind tightly to the fabric and about 20% of them are discharged without any prior treatment into water systems and cause pollution.² The toxic dyes are often stable, carcinogenic and poisonous.³ In the past few decades, scientists have been working on different methods for the treatment of contaminated water. Photocatalysis is widely explored for the degradation of toxic dyes. It has advantages such as use of sunlight, low cost and being an environment friendly process.⁴

Photocatalysts based on metal oxide nanoparticles such as TiO₂,⁵ MoO_{3-x},⁶ Cu₂O,⁷ WO₃,⁸ and NiCo₂O₄,⁹ and metal sulfide nanoparticles such as NiS,¹⁰ MoS₂,¹¹ CuS,¹² and SnS₂,¹³ have been explored as catalysts for the degradation of toxic dyes. Several core–shell nanocomposites such as CuS/ZnO,¹⁴ ZnO@ZnS,¹⁵ CoFe₂O₄@CoWO₄,¹⁶ MoO₃@MoS₂,¹⁷ CdS@ZnO,¹⁸

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 TiO_2 @ $CoFe_3O_4$, ¹⁹ WO_3 @ TiO_2 , ²⁰ $ZnIn_2S_4$ @ CeO_2 , ²¹ ZnO@ SnS_2 , ²² and α - Fe_2O_3 @ SnO_2 / Ti_3C_2 ²³ have been explored for the photodegradation of dyes such as methylene blue, congo red, rhodamine B, methyl orange, malachite green, *etc.* and they show better activity than pure metal sulfide and metal oxide nanoparticles.

Different SnS₂ based nanocomposites are reported in the literature such as SnS₂/chitosan, synthesized via the precipitation method, for photodegradation of crystal violet,24 SnS₂/biochar nanocomposite, synthesized via the hydrothermal route, for photodegradation of amoxycillin and congo red,25 SnS2/ BiVO₄ nanocomposite, synthesized via the hydrothermal route, for photocatalytic degradation of ciprofloxacin,26 SnS2/CdO nanocomposite, synthesized via the precipitation method, for photodegradation of RhB and congo red, 27 SnS₂/Ag₃VO₄ nanocomposite, synthesized via the hydrothermal method, for phoblue,28 todegradation methylene SnS₂/NiCo-LDH nanocomposite, synthesized via the co-precipitation method, for photodegradation of thiamethoxam, 29 polyaniline/SnS₂ nanocomposite, synthesized by the hydrothermal method, for hydrogen evolution,30 PVDF/SnS2 nanocomposite, synthesized via the hydrothermal method, for piezoelectric energy harvesting,31 CeO2/SnS2/polyaniline nanocomposite, synthesized via the hydrothermal method, for photocatalytic reduction of $Cr(v_1)^{32}$ PbS: SnS₂ nanocomposite, synthesized *via* the precipitation method, for ethanol sensing,³³ Pd/SnS₂/SnO₂

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nanocomposite, synthesized via the hydrothermal method, for detection of H2,34 Au/SnS2 nanocomposite, synthesized via chemical reduction method, as a NO2 gas sensor, 35 MoS2/SnS2 nanocomposite, synthesized via the hydrothermal method, as an anode in sodium ion batteries, 36 SnS₂/CuO nanocomposite, synthesized by the precipitation method, in broadband photodetectors, 37 BiOI@SnS2 core-shell nanocomposite, synthesized via the co-precipitation method, for photodegradation of RhB,³⁸ and MnFe₂O₄@SnS₂ core-shell nanocomposite, synthesized via the hydrothermal method, for photodegradation of methylene blue.39

 TiO_2 is a semiconductor with a wide band gap $(E_g \text{ (bulk)})$ 3.2 eV).40 It is a well-known semiconductor for environmental remediation and it exhibits high recombination of photogenerated electrons and holes leading to its low photocatalytic activity. SnS2 is economical and non-toxic with good thermal stability.41,42 It has a narrow band gap of about 1.9 eV 43 and is known to exhibit good photocatalytic activity. 42,44 To improve the photocatalytic activity of TiO2 further, formation of a nanocomposite of TiO₂ with SnS₂ has been proposed. Both the valence band (VB) and conduction band (CB) of SnS2 lie below those of TiO2. Due to this, during light irradiation, the photogenerated electrons from the CB of SnS2 are easily transferred to that of TiO2. This enhances the separation of electrons and holes and improves the photocatalytic efficiency. 45 TiO₂-SnS₂ nanocomposites are useful for various applications such as photodegradation of dyes such as methyl orange, methylene blue and RhB,46-48 photodegradation of antibiotics such as tetracycline, 49 NO2 gas sensors, 50,51 humidity sensors, 52,53 protection of stainless steel,54 photodetectors,55 H2 gas production,56,57 biosensors,58 photoreduction of Cr(vI),45 photocatalytic H₂ evolution,⁵⁹ anode material in lithium-ion batteries,60 photodegradation of diclofenac,61 selfdecontaminating textiles,62 photoelectrochemical water splitting,63 photodegradation of diethyl sulfide,64 electrocatalytic oxygen evolution,65 and photocatalytic reduction of CO2.66

In the current study, TiO₂@SnS₂ core-shell nanocomposites have been synthesized. The novelty of this work is as follows. In the literature, TiO2-SnS2 nanocomposites have been reported (e.g., yolk-shell SnS2-TiO2 microsphere composite67 and SnS₂@TiO₂ double shell nanocomposite⁴⁷) but the core-shell structure of the nanocomposite (TiO₂@SnS₂) has not been previously reported. The thermal decomposition method has been used for the synthesis of different metal sulfide nanoparticles and their nanocomposites. However, the synthesis of a TiO₂@SnS₂ nanocomposite has not been previously reported using this approach. The reported methods used for the synthesis of TiO₂-SnS₂ nanocomposites in the literature (solvothermal,50 hydrothermal,52 chemical bath deposition,55 and sol-gel method61) have disadvantages such as use of high pressure (50 bar to 2 kbar) and prolonged reaction time (12 h to 16 h). For example, the sol-gel method requires a reaction time of up to 7 days, and the chemical bath deposition method is a two-step process and often requires an inert environment. The current study reports the synthesis of TiO2@SnS2 core-shell nanocomposites using a thermal decomposition method with a shorter synthesis time (60 min) without the need of an inert

environment. The TiO2@SnS2 core-shell nanocomposites were first characterized using various techniques and then they were explored for their photocatalytic activity towards the photodegradation of CV.

Experimental 2

2.1 **Materials**

Titanium isopropoxide (TIP) (97%, Sigma-Aldrich), SnCl₄·5H₂O (98%, Sigma-Aldrich), thiourea (98%, SRL Chemicals), methanol (MeOH) (99%, Rankem), acetonitrile (99.5%, Rankem), dodecylamine (DDA) (99%, Rankem), sodium hydroxide (99%, Rankem), diphenyl ether (DPE, 99%, Sigma-Aldrich) and crystal violet (CV, 97%, Sigma-Aldrich) were used.

2.2 Preparation of materials

2.2.1 Synthesis of TiO₂ microspheres. TiO₂ microspheres were prepared using a reported wet chemical method.68 Typically, 0.18 mL of H₂O and 0.345 mL of dodecyl amine (DDA) were taken in a mixture of solvents (100 mL of methanol and 50 mL of acetonitrile) and the contents were stirred for 10 min. After this, 1 mL of titanium isopropoxide was added and the reaction mixture was further stirred for about 6 h at room temperature. The contents were centrifuged, and the collected product was washed with MeOH and dried in an oven at 60 °C for 12 h to obtain as-prepared TiO2 microspheres. Dodecylamine acts as a surfactant during the synthesis of TiO2 microspheres. Its hydrophilic amine group interacts with polar solvent molecules (methanol), while the hydrophobic tail interacts with non-polar titanium isopropoxide. During the hydrolysis and condensation of TIP, it forms TiO2 nuclei. The hydrophobic tail of DDA binds to TiO₂ particles via van der Waals forces preventing agglomeration. This stabilizes the dispersion, lowers surface energy, and leads to controlled nucleation and growth, resulting in uniform TiO2 microspheres. 69,70 The as-prepared TiO2 microspheres were calcined at 500 °C for 3 h (heating rate = 2° min⁻¹) to obtain calcined TiO2 microspheres. The calcined TiO2 microspheres were surface-modified using NaOH.71 For this, 100 mg of calcined TiO₂ microspheres were added to 10 mL of 5 M NaOH aqueous solution and left at room temperature for about 24 h. The contents were centrifuged, washed with de-ionised water and with 0.1 N HCl solution. The sample was dried in an oven at 60 $^{\circ}$ C for 12 h to obtain NaOH-modified TiO2 microspheres (TiO2-NaOH).

Zeta potential measurements were done for calcined TiO₂ and NaOH-modified TiO2. The surface charge as measured from the zeta potential analyzer was +10.1 mV and -11.8 mV for TiO_2 calc. and TiO2-NaOH, respectively. The change in surface charge from positive to negative indicates successful surface modification of TiO2 microspheres with NaOH.

2.2.2 Synthesis of TiO₂@SnS₂ core-shell nanocomposites. To synthesize TiO2@SnS2 core-shell nanocomposites, 100 mg of TiO2-NaOH microspheres were taken in 10 mL of DPE in a 50 mL RB flask. The contents were sonicated for one min followed by addition of x mmol of $SnCl_4 \cdot 5H_2O$ and 2x mmol of

Table 1 Synthetic details of TiO₂@SnS₂ core-shell nanocomposites and their sample codes

Sample code	TiO ₂ –NaOH (mg)	SnCl ₄ ·5H ₂ O (mmol)	Thiourea (mmol)	Solvent	Reaction temperature (°C)	Reaction time (min)
SnS_2	_	0.50	1.0	Diphenyl ether	200 ± 2	60 ± 5
TiO_2 - SnS_2 -0.05	100	0.05	0.1	Diphenyl ether	200 ± 2	60 ± 5
TiO_2 -SnS ₂ -0.1	100	0.10	0.2	Diphenyl ether	200 ± 2	60 ± 5
TiO_2 - SnS_2 -0.15	100	0.15	0.3	Diphenyl ether	200 ± 2	60 ± 5

thiourea (Table 1). After refluxing the reaction mixture for about 60 min in air at about 200 °C, the contents were allowed to cool to RT, followed by the addition of about 20 mL of MeOH. The obtained brown precipitate was centrifuged and washed (2–3 times) with methanol. The precipitate was dried in a vacuum desiccator overnight to obtain the $TiO_2@SnS_2$ core–shell nanocomposite. Pure SnS_2 nanoparticles were also synthesized using a similar synthetic approach in the absence of TiO_2 –NaOH microspheres.

2.3 Photocatalytic studies

Crystal violet is toxic and carcinogenic with a complex structure and is widely used in textiles, microbiological staining, printing, *etc.*, and leads to water pollution. CV is a cationic triphenylmethane dye which is highly resistant to natural degradation.

All the photodegradation experiments were done under sunlight irradiation between 1 PM and 2 PM at Indian Institute of Technology Roorkee, Roorkee, India between March 2024 and May 2024. The solar irradiance data were obtained using the average solar data sourced from ProfileSolar.72 The average intensity of the sun during spring (March-May) is about 6.62 kWh per m² per day, i.e., 276 W m⁻² h⁻¹. The photocatalytic experiments were done by taking 5 mg each of TiO2@SnS2 coreshell nanocomposites in 5 mL of CV aqueous solution (2×10^{-5}) M) in a test tube followed by sonication for one minute. The adsorption-desorption equilibrium was achieved by keeping the mixture in the dark for about 30 min. After that, the contents were exposed to sunlight for 60 min. The contents were centrifuged to remove the photocatalyst and the supernatant solutions were analysed using UV-Vis spectroscopy. A blank experiment (i.e., no catalyst) was also carried out to understand the self-degradation of crystal violet under sunlight. The % degradation of crystal violet was estimated using the following formula:

Degradation\% =
$$(1 - C_t/C_0) \times 100$$

where C_0 and C_t denote the concentration of crystal violet at adsorption equilibrium and at any irradiation time 't', respectively.

2.4 Characterization

Powder X-ray diffraction (XRD) measurements were carried out for phase identification using a Rigaku Miniflex 600 powder X-ray diffractometer (Cu-K $_{\alpha}$, $\lambda=1.5406$ Å). A Thermo Nicolet FT-IR spectrophotometer was used for recording FT-IR spectra of the

samples in the range of 4000-400 cm⁻¹ using KBr pellets. For thermogravimetric analysis (TGA), a PerkinElmer Pyris Diamond instrument was employed in the temperature range of 30-1000 °C (heating rate = 10 °C min⁻¹) in air. The morphological and EDX analyses of the samples were done using a Thermofisher Apreo field emission SEM (operating voltage = 20 kV). TEM measurements were done using a Thermofisher TALOS F200X transmission electron microscope (operating voltage = 200 kV). For the TEM analysis, 1 mg of each sample was taken in a test tube to which 5 mL of ethanol was added. The mixture was sonicated for about 45 min and then drop-cast over a copper grid followed by drying overnight at room temperature. HRTEM images and SAED patterns of the nanocomposites were recorded using the same instrument. EDS line scan and elemental mapping of the nanocomposites were recorded using a JEOL JEM-3200FS transmission electron microscope (operating voltage = 300 kV; energy resolution = 127 eV). The measurements were performed by carefully optimizing the acquisition parameters, such as beam current and dwell time, to minimize beam effects and no significant beaminduced sample damage was observed during the EDS measurements. The oxidation states of the elements present in the TiO2@SnS2 core-shell nanocomposites were determined using a Physical Electronics PHI 5000 Versa Probe III XPS spectrometer using Al-K α radiation ($\lambda = 1486.6$ eV). The optical studies on the core-shell nanocomposites were done using a Cary 5000 UV-Vis-NIR spectrophotometer in the reflectance mode in the wavelength range 300 nm to 800 nm. A diffuse reflectance accessory was used for this purpose. About 10 mg of each sample powder was used to measure the reflectance spectra. The specific surface area of the samples was measured via N₂ physisorption at 77 K on a Nova 2200e Quantachrome instrument using the BET method. A Shimadzu UV-2600 UV-Vis spectrophotometer was used for recording absorption spectra during the photodegradation studies. Photoluminescence (PL) spectral measurements were made using a Fluoromax-4 spectrofluorometer at room temperature. 1 mg of sample powder was dispersed in about 3 mL of deionized water by sonication and PL spectra were recorded for the dispersion with an excitation wavelength of 450 nm.

3 Results and discussion

3.1 X-ray diffraction

The powder XRD patterns of calcined TiO₂ (before NaOH modification) and TiO₂ (after modification with NaOH) are displayed in Fig. S1. The XRD patterns of both the samples show

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peaks at similar 2θ values and match with that of anatase TiO₂ (ICPDS file no. 84-1286) indicating that there is no change in the TiO₂ phase after modification with NaOH. The XRD patterns of TiO2-NaOH, SnS2 nanoparticles and TiO2@SnS2 core-shell nanocomposites are displayed in Fig. 1. The XRD pattern of TiO_2 -NaOH microspheres shows peaks at $2\theta = 25.39^{\circ}$, 36.96° , 37.93°, 38.76°, 48.02°, 53.94°, 55.19°, 62.74°, 68.93°, 70.39°, 75.14° and 76.2° which correspond to (101), (103), (004), (112), (200), (105), (211), (204), (116), (220), (215) and (301) planes, respectively, of the anatase phase of TiO2. The XRD pattern of SnS_2 nanoparticles shows peaks at $2\theta = 28.32^{\circ}$, 32.16° , 41.83° , 45.94°, 50.04°, 52.51°, 58.48°, 60.76°, 63.05°, 67.30° and 70.48° indexed to (100), (011), (012), (003), (110), (111), (200), (201), (004), (202) and (113) planes, respectively, of the Berndtite-2T phase of hexagonal SnS₂ (JCPDS file no. 83-1705). The powder XRD patterns of TiO₂@SnS₂ core-shell nanocomposites (TiO₂-SnS₂-0.05, TiO₂-SnS₂-0.1 and TiO₂-SnS₂-0.15) show peaks due to the anatase phase of TiO_2 and also show peaks at $2\theta = 28.59^{\circ}$ and 50.35° due to (100) and (110) planes of the Berndtite-2T phase of hexagonal SnS2. It is known that the crystallite coherence and stacking faults of nanoparticles may influence the activity.73 The crystallite size of SnS2 nanoparticles was estimated from the XRD patterns of SnS2, TiO2-SnS2-0.05, TiO2-SnS₂-0.1 and TiO₂-SnS₂-0.15 and the values are 11.6 nm, 10.2 nm, 8.8 nm and 8.4 nm, respectively. The crystallite size of TiO₂ was estimated from the XRD patterns of TiO₂-NaOH, TiO₂-SnS₂-0.05, TiO₂-SnS₂-0.1, and TiO₂-SnS₂-0.15 and the values are 16.2 nm, 15.9 nm, 15.1 nm, and 14.4 nm, respectively.

The dislocation density and crystallite strain for TiO_2 and SnS_2 were estimated for the $TiO_2@SnS_2$ core–shell nanocomposites. Dislocation density (ρ) is defined as the number of dislocation lines per unit volume and is estimated using eqn. (1).⁷⁴

$$\rho = (1/D^2) \tag{1}$$

where D is the crystallite size.

The dislocation density values for SnS_2 in SnS_2 , TiO_2 – SnS_2 -0.05, TiO_2 – SnS_2 -0.1 and TiO_2 – SnS_2 -0.15 are 0.0074 nm⁻², 0.0096

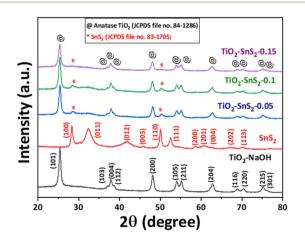


Fig. 1 XRD patterns of TiO_2 -NaOH, SnS_2 nanoparticles and $TiO_2@-SnS_2$ core-shell nanocomposites.

nm⁻², 0.0129 nm⁻², and 0.014 nm⁻², respectively. The dislocation density values for TiO₂ in TiO₂–NaOH, TiO₂–SnS₂-0.05, TiO₂–SnS₂-0.1 and TiO₂–SnS₂-0.15 are 0.0038 nm⁻², 0.0039 nm⁻², 0.0043 nm⁻², and 0.0048 nm⁻², respectively. The dislocation density of both TiO₂ and SnS₂ lattices is small. This suggests a high degree of crystallinity of TiO₂–NaOH, SnS₂, and TiO₂@SnS₂ core–shell nanocomposites. Also, the dislocation density increases as the thickness of the shell in the core–shell nanocomposites increases. Crystallite strain is defined as the small distortion in the crystal lattice due to defects or dislocations, causing a slight variation in atomic positions. Due to this, broadening of XRD peaks is observed without change in peak positions. The crystallite strain was estimated using eqn. (2).⁷⁵

$$\beta \cos \theta = K \lambda / D + 4\varepsilon \sin \theta \tag{2}$$

where ε is the crystallite strain (or microstrain) and is determined from the slope of linear fit of the plot between β cos θ and $4\sin\theta$, commonly known as the Williamson–Hall plot. Fig. S2 provides the Williamson–Hall plots for TiO₂–NaOH and TiO₂@SnS₂ core–shell nanocomposites. The crystallite strain (ε) values for TiO₂–NaOH, TiO₂–SnS₂-0.05, TiO₂–SnS₂-0.1 and TiO₂–SnS₂-0.15 are 0.00378, 0.00395, 0.00432, and 0.00468, respectively. There is an increase in crystallite strain as shell (SnS₂) thickness increases. The presence of more number of dislocation lines/defects (dislocation density) leads to higher microstrain in the lattice.^{76,77} The crystallite strain for SnS₂ could not be estimated as there are only two peaks due to SnS₂ in the XRD patterns of TiO₂@SnS₂ core–shell nanocomposites.

The TiO_2 microspheres (as prepared) were calcined at 750 °C and XRD analysis of the sample was performed to confirm the phase of TiO_2 . The XRD pattern of TiO_2 calcined at 500 °C matches with the anatase phase of TiO_2 (JCPDS file no. 84-1286) whereas the XRD pattern of TiO_2 calcined at 750 °C matches with the rutile phase of TiO_2 (JCPDS file no. 04-0551) (Fig. S3). This indicates that phase transformation of TiO_2 from anatase into rutile takes place between 650 °C and 800 °C.

3.2 Functional group analysis

The FT-IR spectra of unmodified calcined TiO₂ microspheres and TiO2-NaOH are given in Fig. S4. The intensities of IR bands due to OH stretching and bending are more intense in the case of TiO2-NaOH microspheres compared to unmodified TiO2 indicating the successful modification of calcined TiO2 microspheres with NaOH. The FT-IR spectra of TiO2-NaOH, SnS2 nanoparticles, and TiO₂@SnS₂ core-shell nanocomposites are displayed in Fig. S5. The IR band positions and their assignments for all the samples are given in Table S1. The IR spectrum of TiO₂-NaOH microspheres shows bands at 3428 cm⁻¹ and 1637 cm⁻¹ due to the stretching and bending vibration of physisorbed water molecules.78 The characteristic band due to Ti-O vibration is observed at about 624 cm⁻¹.79 The IR spectra of SnS₂ nanoparticles and TiO₂@SnS₂ core-shell nanocomposites show vibrational bands at about 3397 cm⁻¹ and 1638 cm⁻¹ assigned to OH stretching and bending of physisorbed water molecules.80 The IR bands observed at about 2925 cm⁻¹, 2852 cm⁻¹ and 1384 cm⁻¹ are attributed to asymmetric

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stretching, symmetric stretching and bending vibration of C-H bond, respectively.81 The IR band at about 1178 cm⁻¹ corresponds to C-N stretching.82 The IR spectrum of SnS2 nanoparticles shows an additional band at 862 cm⁻¹ assigned to C-H bending.83 The band at about 611 cm⁻¹ is assigned to Sn-S stretching.84

3.3 Thermogravimetric analysis

The TGA curves of TiO2-NaOH, SnS2 nanoparticles, and TiO2@ SnS₂ core-shell nanocomposites are given in Fig. S6. The DTG plot for TiO2-NaOH is given in Fig. S7. The TiO2-NaOH microspheres show a two-step weight loss of about 3% in the temperature range of 30–1000 °C. The first weight loss of \sim 1.3% below 350 °C is due to the loss of physisorbed water molecules.85 The second weight loss of about 1.7% between 650 °C and 800 °C is due to the loss of chemically bonded OH groups from the surface of TiO₂ (dehydroxylation) and conversion of anatase TiO₂ to rutile phase.68 The TGA curve of SnS2 nanoparticles shows a three-step weight loss pattern. The first weight loss of about 3% below 230 $^{\circ}$ C is due to the loss of surface-adsorbed water molecules. The second weight loss of about 48.5% between 230 °C and 440 °C is attributed to the removal of organic moieties. The third weight loss of about 15.5% is due to oxidation of SnS₂ into SnO₂.86 The TiO₂@SnS₂ core-shell nanocomposites (TiO₂-SnS₂-0.05, TiO₂-SnS₂-0.1 and TiO₂-SnS₂-0.15) show two-step weight loss patterns. The first weight loss of $\sim 3.0\%$, 3.1% and 3.8%, respectively, observed below 440 °C is due to the loss of physisorbed water molecules and removal of organic moieties. The second weight loss of about 1.9%, 3.4%, and 3.6%, respectively, between 440 °C and 530 °C is attributed to oxidation of SnS2 into SnO2.87 The TGA studies indicate a total weight loss of about 4.9%, 6.5% and 7.4% in TiO₂-SnS₂-0.05, TiO₂-SnS₂-0.1, and TiO₂-SnS₂-0.15. In the core-shell nanocomposites, the % weight loss due to TiO2 is negligible and it is primarily due to the presence of SnS₂ in the TiO₂@SnS₂ core-shell nanocomposites. In the TiO₂@SnS₂ coreshell nanocomposites, an increase in weight loss is observed with increase in the concentration of SnS2 nanoparticles (shell) on the TiO2 core.

3.4 FESEM and EDX analyses

The coating of SnS₂ nanoparticles over the TiO₂ microspheres was first done using unmodified as-prepared TiO2 (i.e., before calcination) and unmodified calcined TiO2 microspheres. Fig. S8 shows the FESEM images of TiO2@SnS2 nanocomposites synthesized using unmodified as-prepared TiO2 and unmodified calcined TiO2 microspheres. The EDX results (Table S2) give distribution of different elements (Ti, O, Sn and S) in the thus prepared TiO2@SnS2 nanocomposites. Both FESEM and EDX results of TiO2@SnS2 nanocomposites, synthesized using asprepared TiO2 and unmodified calcined TiO2 microspheres, indicate non-uniform coating of SnS₂ nanoparticles on the TiO₂ microspheres. Hence, the synthesis of TiO₂@SnS₂ core-shell nanocomposites was attempted using NaOH-modified TiO2 microspheres. The SEM images of TiO2-NaOH, SnS2 nanoparticles, and TiO2@SnS2 core-shell nanocomposites, synthesized using TiO2-NaOH microspheres as the core, are given in

Fig. S9. The FESEM image of TiO₂-NaOH microspheres displays spherical particles with a diameter of about 471 \pm 17 nm. The FESEM image of SnS2 nanoparticles shows flake-like morphology. The FESEM images of TiO2@SnS2 core-shell nanocomposites (TiO₂-SnS₂-0.05, TiO₂-SnS₂-0.1 and TiO₂-SnS₂-0.15) show that SnS₂ nanoparticles are uniformly coated over the TiO₂-NaOH microspheres. The EDX results (Table S3) indicate uniform distribution of different elements (Ti, O, Sn, and S) in all the core-shell nanocomposites. In the TiO₂@SnS₂ core-shell nanocomposites, an increase in weight% of Sn and S is observed with an increase in [Sn⁴⁺]:[S²⁻] ratio used during their synthesis.

3.5 TEM analysis

The TEM micrographs of TiO2-NaOH, SnS2 nanoparticles, and TiO₂@SnS₂ core-shell nanocomposites are displayed in Fig. 2. The TiO₂-NaOH microspheres show spherical morphology with a diameter of about 488 nm. The SnS₂ nanoparticles show flakelike morphology. The flake thickness was estimated using the TEM image. The particle size histogram is shown in Fig. S10, and the mean thickness is about 52 \pm 12 nm. The TEM micrographs of TiO2@SnS2 core-shell nanocomposites (TiO2-SnS₂-0.05, TiO₂-SnS₂-0.1 and TiO₂-SnS₂-0.15) show uniform coating of SnS₂ nanoparticles on the TiO₂ microspheres. Table 2 summarizes the particle diameter, core size and shell thickness observed from the TEM micrographs of TiO2@SnS2 core-shell nanocomposites. The overall diameter of TiO₂@SnS₂ core-shell nanocomposites varies from 457 nm to 503 nm. The core diameter in the TiO2@SnS2 core-shell nanocomposites varies from 434 nm to 489 nm. The thickness of the shell (SnS₂ nanoparticles) over the TiO₂ microspheres varies from 14 nm to 26 nm. This variation of thickness of the shell is due to the synthetic conditions. Use of different amounts of SnCl₄·5H₂O and thiourea during the synthesis of TiO2@SnS2 core-shell nanocomposites leads to variation in shell thickness. The EDS spectrum and elemental analysis data (from TEM measurements) for TiO₂-SnS₂-0.15 are given in Fig. S11 and Table S4, respectively. The TEM EDS analysis was performed at three different spots and the results confirm the uniform presence of Ti, Sn, S, and O in the core-shell nanocomposites (TiO₂-SnS₂-0.15). The EDS line scanning data and elemental mapping images (from SEM) of TiO2@SnS2 core-shell nanocomposites (TiO₂-SnS₂-0.15) are shown in Fig. 3. The EDS line scan (Fig. 3(a)) indicates that the concentration of titanium and oxygen at the edge is less and that of tin and sulfur is high. On moving from the edge to the centre of the particle, the concentration of Ti and O increases and that of Sn and S decreases. The elemental mapping results (Fig. 3(b)) also indicate that Sn and S are predominantly located at the edges of TiO₂ microspheres. On the other hand, Ti and O are present more at the centre. This indicates the successful formation of TiO₂@SnS₂ core-shell nanocomposites.

The SAED patterns of TiO2-NaOH microspheres, SnS2 nanoparticles, and TiO2@SnS2 core-shell nanocomposites are displayed in Fig. S12. The SAED pattern of TiO2-NaOH microspheres shows rings that correspond to the planes of anatase

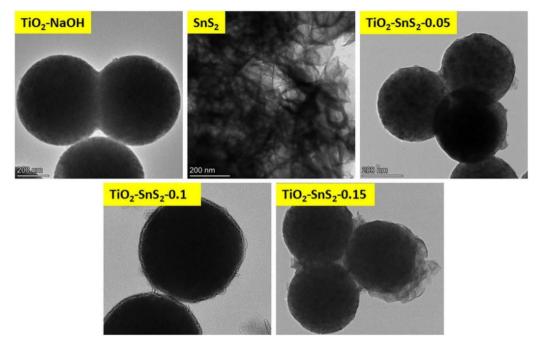


Fig. 2 TEM images of TiO₂-NaOH, SnS₂ nanoparticles and TiO₂@SnS₂ core-shell nanocomposites.

Table 2 Summary of results from TEM studies of TiO₂@SnS₂ core-shell nanocomposites

Sample code	Particle diameter (nm)	Flake thickness (nm)	Core size (nm)	Shell thickness (nm)
TiO ₂ -NaOH	488	_	_	_
SnS_2	_	52 ± 12	_	_
TiO_2 - SnS_2 -0.05	457	_	434	14
TiO_2 - SnS_2 -0.1	478	_	456	21
TiO_2 - SnS_2 - 0.15	503	- -	489	26

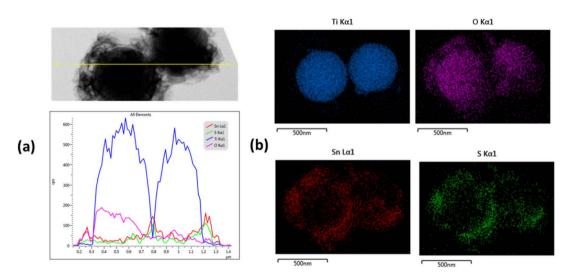


Fig. 3 (a) EDS line scan and (b) elemental mapping data of $TiO_2-SnS_2-0.15$ core-shell nanocomposite.

TiO₂ (JCPDS file no. 84-1286). The rings, observed in the SAED pattern of SnS₂ nanoparticles, correspond to the planes of SnS₂ (JCPDS file no. 83-1705). The SAED patterns of TiO₂@SnS₂ coreshell nanocomposites (TiO₂-SnS₂-0.05, TiO₂-SnS₂-0.1 and TiO₂-SnS₂-0.15) show rings attributed to reflections due to both TiO₂ and SnS₂.

The HRTEM images of TiO2-NaOH microspheres, SnS2 nanoparticles, and TiO₂@SnS₂ core-shell nanocomposites are given in Fig. S13. The observed lattice fringes in the HRTEM image of TiO₂-NaOH with a d spacing of 3.49 Å are attributed to the (101) plane of TiO₂ (JCPDS file no. 84-1286). The lattice fringes in the HRTEM image of SnS₂ nanoparticles with a d spacing of 3.15 Å is attributed to the (100) plane of SnS₂ (JCPDS file no. 83-1705). The d spacing values (estimated from the lattice fringes) of TiO2@SnS2 core-shell nanocomposites (TiO₂-SnS₂-0.05, TiO₂-SnS₂-0.1 and TiO₂-SnS₂-0.15) are 3.49 Å and 3.15 Å attributed to the (101) plane of TiO₂ and (100) plane of SnS2, respectively. The specific surface area of TiO2-NaOH microspheres, SnS₂ nanoparticles, and TiO₂@SnS₂ core-shell nanocomposites (TiO2-SnS2-0.05, TiO2-SnS2-0.1 and TiO2-SnS2-0.15), as measured by the BET method, are 9 m² g⁻¹, 17 m² g⁻¹, 10 m 2 g $^{-1}$, 13 m 2 g $^{-1}$, and 19 m 2 g $^{-1}$, respectively.

3.6 Optical properties

The optical properties of TiO2-NaOH microspheres, SnS2 nanoparticles, and TiO2@SnS2 core-shell nanocomposites were studied using UV-Vis DRS spectroscopy (Fig. 4) and the Tauc plots (Fig. S14) were used to estimate the band gap. The UV-Vis DRS measurements were done three times for each sample. Table S5 includes error bars for the band gap.88 The band gap of TiO2-NaOH microspheres and SnS2 nanoparticles are 3.1 eV and 2.03 eV, respectively. The TiO2@SnS2 core-shell nanocomposites (TiO₂-SnS₂-0.05, TiO₂-SnS₂-0.1 and TiO₂-SnS₂-0.15) have band gaps of 2.23 eV, 2.18 eV and 2.15 eV, respectively. The TiO2@SnS2 core-shell nanocomposites exhibit band gap only due to SnS2 suggesting that the TiO2 microspheres are coated with a thick shell of SnS₂ nanoparticles. The band gap values were also estimated using K-M plots89 (Fig. S15) and the values are summarized in Table S5. Although the band gap of a semiconductor can be estimated using both Tauc plots and K-M plots, the band gap values estimated using K-M plots can often be misleading. This is because the K-M function is proportional to the ratio of the absorption and scattering coefficients (a) and considered as an approximate. Furthermore, the K-M

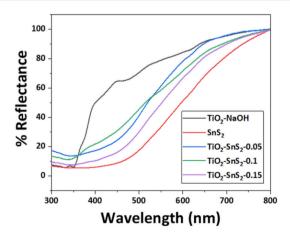


Fig. 4 UV-Vis DRS spectra of TiO_2 -NaOH, SnS_2 nanoparticles and TiO_2 @ SnS_2 core-shell nanocomposites.

function does not consider the nature of the electronic transition (direct or indirect in a semiconductor).⁹⁰

3.7 PL spectroscopy

The PL spectra of $TiO_2@SnS_2$ core–shell nanocomposites (λ_{exc} = 450 nm) are shown in Fig. 5. The PL spectra of TiO_2 –NaOH microspheres, SnS_2 nanoparticles, and $TiO_2@SnS_2$ core–shell nanocomposites exhibit an emission peak at \sim 590 nm. This emission peak is due to the recombination of electrons with holes that are trapped above the valence state. 91–93 The emission peak at about 590 nm in SnS_2 nanoparticles is due to the near band edge emission of the SnS_2 phase. 94 The order of PL intensity in the samples is: TiO_2 –NaOH > SnS_2 > TiO_2 – SnS_2 -0.05 > TiO_2 – SnS_2 -0.1 > TiO_2 – SnS_2 -0.15. The PL intensity is the least for TiO_2 – SnS_2 -0.15 and it is expected to show the highest photocatalytic activity among all the samples.

3.8 XPS analysis

The oxidation states of different elements present in TiO2-NaOH microspheres, SnS₂ nanoparticles and TiO₂@SnS₂ coreshell nanocomposite (TiO2-SnS2-0.15) were determined by XPS analysis, and the results are given in Fig. 6. Table S6 summarizes binding energies of all the elements (Ti, O, Sn and S) present in the samples. As shown in the Ti 2p spectrum of TiO2-NaOH (Fig. 6(a)), the peaks at 456.2 eV and 462.3 eV correspond to Ti 2p_{3/2} and Ti 2p_{1/2} of Ti⁴⁺, respectively. The O 1s spectrum of TiO2-NaOH shows peaks at 530.9 eV and 532.1 eV due to lattice oxygen (O²⁻) and surface hydroxyl (OH) oxygen, respectively. 95,96 The Sn 3d spectrum of SnS₂ nanoparticles (Fig. 6(b)) shows peaks at 486.0 eV and 494.4 eV due to Sn 3d_{5/2} and Sn 3d_{3/2} of Sn⁴⁺, respectively. The S 2p spectrum of SnS₂ nanoparticles shows peaks at 165.0 eV and 166.2 eV corresponding to S 2p_{3/2} and S 2p_{1/2}, respectively.97 The XPS spectrum of the TiO₂@SnS₂ core-shell nanocomposite (TiO2-SnS2-0.15) is shown in Fig. 6(c). The Ti 2p spectrum of TiO₂-SnS₂-0.15 shows peaks at 458.0 eV and 463.7 eV attributed to Ti $2p_{3/2}$ and Ti $2p_{1/2}$ of Ti⁴⁺, respectively. The O 1s spectrum of TiO2-SnS2-0.15 shows peaks at 531.0 eV and 532.3 eV assigned to lattice oxygen and surface hydroxyl oxygen, respectively. 95,96 The Sn 3d spectrum of TiO2-

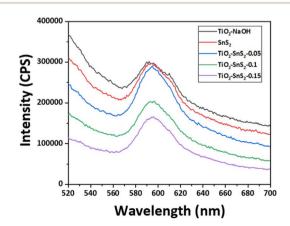
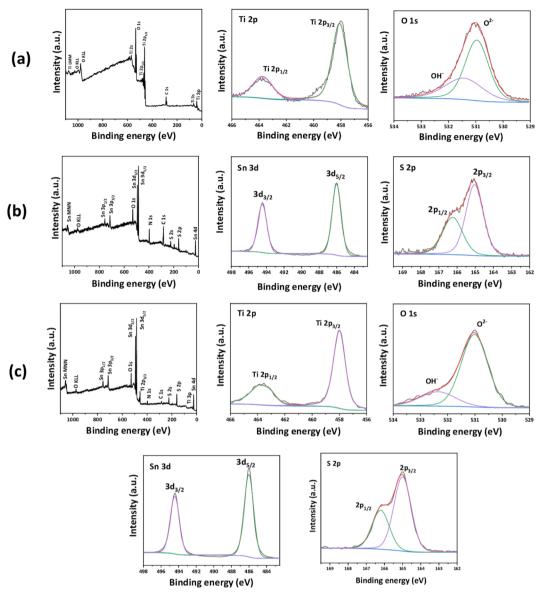


Fig. 5 PL spectra of TiO_2 -NaOH, SnS_2 nanoparticles and TiO_2 @ SnS_2 core-shell nanocomposites.

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XPS spectra of (a) TiO_2 -NaOH microspheres, (b) SnS_2 nanoparticles and (c) TiO_2 @ SnS_2 core-shell nanocomposite (TiO_2 - SnS_2 -0.15).

 SnS_2 -0.15 shows peaks at 485.9 eV and 494.3 eV due to $Sn 3d_{5/2}$ and Sn 3d_{3/2} of Sn⁴⁺, respectively. The S 2p spectrum of TiO₂-SnS₂-0.15 shows peaks at 164.9 eV and 166.2 eV due to S 2p_{3/2} and S 2p_{1/2}, respectively.⁹⁷

There is a minor decrease in Sn 3d and S 2p binding energy values on going from pure SnS2 nanoparticles to the TiO2@SnS2 core-shell nanocomposites. Also, a minor increase in Ti 2p and O 1s binding energies is observed on going from pure TiO₂ microspheres (TiO₂-NaOH) to the core-shell nanocomposites. The shifts in binding energies in the XPS spectrum of the TiO₂@SnS₂ core-shell nanocomposite could be due to electron transfer from the core (TiO₂) to the shell (SnS₂) during the formation of the core-shell nanocomposite. The electron transfer leads to a partial positive charge on TiO2, leading to an increase in binding energies of Ti 2p and O 1s and a partial negative charge on SnS2, leading to a decrease in binding energies of Sn 3d and S 2p.98-100

To investigate the charge transfer and band (VB and CB) positions in TiO2@SnS2 core-shell nanocomposites, XPS-VB (UPS spectra) measurements were performed. Fig. S16 provides the XPS-VB spectra of TiO2-NaOH microspheres, SnS2 nanoparticles and TiO₂-SnS₂-0.15. The valence band positions estimated from the XPS-VB spectra for TiO2-NaOH microspheres, SnS₂ nanoparticles and TiO₂-SnS₂-0.15 are 2.83 eV, 1.35 eV and 1.78 eV, respectively. In the TiO₂@SnS₂ core-shell nanocomposites, electron transfer occurs from the core (TiO₂) to the shell (SnS₂). The intermediate valence band position of TiO₂-SnS₂-0.15 suggests successful heterostructure formation and interfacial charge transfer between TiO2 and SnS2.101,102 From the optical studies (DRS spectra), the band gaps for TiO₂-NaOH and SnS_2 are 3.1 eV and 2.02 eV, respectively. On applying

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the equation, $E_{CB} = E_{VB} - E_{g}$, the conduction band positions of TiO_2 -NaOH and SnS_2 nanoparticles are -0.27 eV and -0.67 eV, respectively. To further confirm the charge transfer in TiO2@-SnS₂ core-shell nanocomposites, EIS measurements were also performed (see Section 3.15 for more details).

3.9 Mechanism of formation of TiO₂@SnS₂ core-shell nanocomposites

Scheme 1 illustrates the proposed mechanism of formation of TiO2@SnS2 core-shell nanocomposites. At first, on surface modification with NaOH, hydroxyl groups are attached on the surface of TiO2 microspheres. This can be evidenced from the IR spectral studies (Fig. S4). Due to the presence of hydroxyl groups on the surface of TiO₂ microspheres, Sn⁴⁺ ions are attached on the surface of TiO2 via electrostatic interaction. This is followed by the thermal decomposition of thiourea to form H2S and the formation of TiO2@SnS2 core-shell nanocomposites. The reactions involved in the formation of SnS₂ nanoparticles over TiO2-NaOH microspheres are given in eqn (3) and (4).103-105

$$SC(NH_2)_2 \xrightarrow{150^{\circ}C} NH_2CN + H_2S \tag{3}$$

$$Sn^{4+} + S^{2-} \to SnS_2$$
 (4)

SnS₂ nanoflakes are formed by the thermal decomposition of SnCl₄·5H₂O and thiourea in DPE. The formation of nanoflakes is a two-step process, i.e., nucleation followed by growth. 106 At first, tin chloride reacts with thiourea leading to the formation of a small cluster of SnS₂ (nuclei). The presence of chloride ions leads to oriented growth of particles. The chloride ions adsorbed on the transverse planes of SnS₂ particles inhibit growth in those directions. As a result, the growth occurs in the longitudinal axis leading to the formation of SnS2 nanoflakes.82

3.10 Photocatalytic activity

The photocatalytic activity of TiO2@SnS2 core-shell nanocomposites was studied using crystal violet as the dye pollutant (see Section 2.3 for more details). As indicated by the UV-Vis spectral results (Fig. 7) on the photodegradation experiments, TiO₂-SnS₂-0.15 achieved about 99% degradation of crystal violet within 60 minutes under sunlight. TiO2-NaOH microspheres, SnS₂ nanoparticles, TiO₂-SnS₂-0.05, and TiO₂-SnS₂-0.1 degrade about 53.1%, 60.2%, 61.5%, and 78.2% of crystal violet, respectively. This indicates that TiO₂-SnS₂-0.15 is a better photocatalyst for the degradation of crystal violet compared to

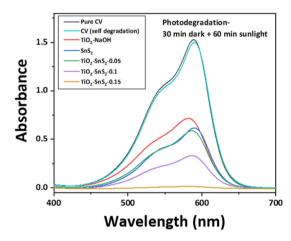
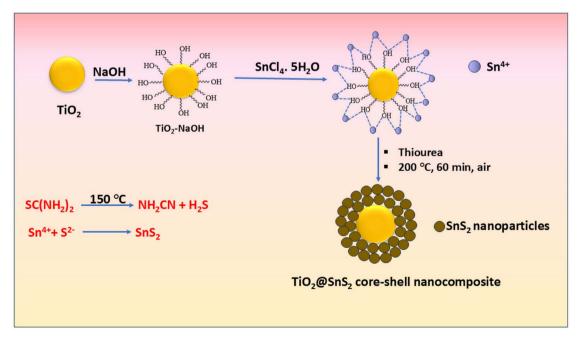


Fig. 7 UV-Vis spectral results indicating the photodegradation of CV using TiO2@SnS2 core-shell nanocomposites.



Scheme 1 Mechanism of formation of TiO₂@SnS₂ core-shell nanocomposites.

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TiO₂-NaOH microspheres, SnS₂ nanoparticles and other core-

shell nanocomposites. The self-degradation of crystal violet under sunlight, tested in the absence of any catalyst, was about 1.9%.

Furthermore, dark experiments were carried out in the absence of sunlight to understand adsorption of CV on the TiO2@SnS2 core-shell nanocomposites. In this experiment, 5 mg of each catalyst was taken in a test tube to which 5 mL of CV aqueous solution $(2 \times 10^{-5} \text{ M})$ was added. The test tubes were sonicated for one min followed by keeping them in the dark for 30 min/90 min. The UV-Vis absorbance spectra recorded for the supernatant solutions obtained after centrifugation of each mixture are shown in Fig. S17. The % adsorption by TiO2-NaOH microspheres, SnS2 nanoparticles and TiO2@SnS2 core-shell nanocomposites (TiO₂-SnS₂-0.05, TiO₂-SnS₂-0.1 and TiO₂-SnS₂-0.15) are 15%, 28.1%, 31.3%, 37.9% and 49%, respectively in 30 min and 26%, 47.9%, 34.8%, 39.9% and 53.8%, respectively in 90 min. The adsorption and photodegradation studies indicate that the TiO2@SnS2 core-shell nanocomposites act as a good photocatalyst for the degradation of CV and not as an adsorbent.

Furthermore, kinetic experiments were carried out by taking 6 test tubes each containing 5 mg of catalyst (TiO2-NaOH microspheres, SnS2 nanoparticles, and TiO2@SnS2 core-shell nanocomposites (TiO2-SnS2-0.05, TiO2-SnS2-0.1 and TiO2-SnS2-0.15)) and 5 mL of CV aqueous solution (2 \times 10⁻⁵ M). The mixtures were kept in the dark for 30 min which was followed by irradiation with sunlight for different time periods (10-60 min). UV-Vis spectra were recorded for the supernatant solutions obtained after centrifuging the mixture in each test tube.

The kinetics results are shown in Fig. 8(a) and TiO₂-SnS₂-0.15 shows maximum degradation in 60 min. The kinetics of photodegradation of CV by TiO₂-SnS₂-0.15 follows pseudo 1st order kinetics as indicated by $-\ln(C_t/C_0)$ against irradiation time plots shown in Fig. 8(b). The rate constant values were determined using the kinetic curves. Table 3 summarizes the % adsorption (30 min/90 min), % total degradation (90 min), % photodegradation only, rate constant and R² values for TiO₂-

NaOH microspheres, SnS₂ nanoparticles and TiO₂@SnS₂ coreshell nanocomposites (TiO₂-SnS₂-0.05, TiO₂-SnS₂-0.1 and TiO₂-SnS₂-0.15). The rate constant values are in the order: TiO₂-SnS₂- $0.15 > TiO_2 - SnS_2 - 0.1 > TiO_2 - SnS_2 - 0.05 > SnS_2 > TiO_2 - NaOH$ indicating that TiO₂-SnS₂-0.15 is the best photocatalyst among all the samples. The better photocatalytic activity of TiO₂-SnS₂-0.15 is attributed to a lower rate of recombination of electron and hole pairs in TiO₂-SnS₂-0.15 as indicated by the PL spectral studies (Fig. 5). The photocatalytic degradation results were compared with those reported in the literature (Table S7). 24,107-128 In the literature, more time (70-390 min) is required for the photodegradation of CV. Wherever lesser time is reported (30-45 min), 116,117 either the amount of catalyst used is high (250 mg/100 mL) or the % photodegradation is less (83-93%). The TiO₂@SnS₂ core-shell nanocomposites (e.g., TiO₂-SnS₂-0.15), reported in the current work, achieved 99% degradation of CV within 60 minutes under sunlight.

3.11 Effect of pH

The photocatalytic degradation efficiency of a catalyst is affected by the pH of the solution. The effect of pH on the photodegradation efficiency of TiO2-SnS2-0.15 was studied by varying the pH of the solution between 2 and 10. The pH of the solutions was varied using 0.1 M HCl and 0.1 M NaOH. The experiment was performed by taking 5 mg of catalyst (TiO2- SnS_2 -0.15) in 5 mL of CV aqueous solution (2 \times 10⁻⁵ M) at different pH values (2-10) in different test tubes. The contents were kept in the dark (for 30 min) followed by irradiation with sunlight for 60 min and UV-Vis absorbance spectra were measured for the supernatant solutions obtained after centrifugation. The variation of the photodegradation efficiency of TiO₂-SnS₂-0.15 with pH is shown in Fig. S18(a). The results indicate that maximum photocatalytic efficiency is observed at pH = 7.

At lower pH, there are more H⁺ ions in the solution that make the surface of the catalyst positively charged (zeta potential = +19.0 mV at pH = 4). Crystal violet is a cationic dye, and it will experience electrostatic repulsion towards the surface

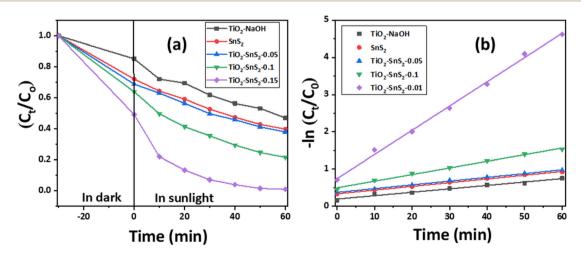


Fig. 8 (a) (C_t/C_0) plots and (b) $-\ln(C_t/C_0)$ vs. time plots for TiO_2 -NaOH microspheres, SnS_2 nanoparticles and TiO_2 @ SnS_2 core-shell nanocomposites as the catalyst for the photodegradation of CV.

Table 3	Photocatalytic	degradation results	of crystal violet	using TiO2@SnS2	core-shell nanocomposites
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Sample code	% Adsorption (30 min)	% Adsorption (90 min)	Total degradation% (30 min dark + 60 min sunlight)	Photodegradation % only (60 min)	Rate constant for photodegradation (min ⁻¹)	R^2
TiO ₂ -NaOH	15.0	26.0	53.1	38.1	9.1×10^{-3}	0.98
SnS_2	28.1	47.9	60.2	32.1	9.5×10^{-3}	0.98
TiO_2 -SnS ₂ -0.05	31.3	34.8	61.5	30.2	1.0×10^{-2}	0.99
TiO_2 - SnS_2 -0.1	37.9	39.9	78.2	38.3	1.7×10^{-2}	0.99
$\mathrm{TiO_{2}SnS_{2}0.15}$	49.0	53.8	99.0	50.0	6.4×10^{-2}	0.99

of the catalyst in an acidic medium leading to a decrease in the photocatalytic efficiency. On the other hand, in basic medium, the presence of more OH^- ions in the solution will lead to a negatively charged catalyst surface (zeta potential = $-21.4~\rm mV$ at pH = 10). This results in an electrostatic attraction towards crystal violet leading to higher photodegradation efficiency by the catalyst. ¹²⁹

3.12 Effect of catalyst dosage

To determine the optimum amount of catalyst required to degrade CV using $TiO_2@SnS_2$ core–shell nanocomposites, the effect of catalyst dosage on the photodegradation efficiency was studied. The catalyst (TiO_2 – SnS_2 -0.15) was taken in different amounts (1–8 mg) in 5 mL of aqueous CV solution (2 × 10⁻⁵ M) in test tubes. The mixtures were kept in the dark (for 30 min) followed by sunlight irradiation for 60 min and the UV-Vis absorbance spectra were measured for the supernatant solutions obtained after centrifugation. The UV-Vis spectral results shown in Fig. S18(b) indicate that 5 mg of TiO_2 – SnS_2 -0.15 in 5 mL of CV is the optimum catalyst dosage for the photodegradation of CV.¹³⁰

3.13 Scavenger tests

To understand the mechanism of photodegradation of CV by TiO_2 – SnS_2 -0.15, scavenger tests were performed. Different scavengers (isopropyl alcohol (IPA), ammonium oxalate (AO) and p-benzoquinone (PBQ)) were used to trap OH', O_2 ' and h^+ , respectively. 127,131 In a typical experiment, 10 mM of scavenger was added to 5 mL aqueous solution of CV (2 \times 10 $^{-5}$ M) followed by the addition of 5 mg of catalyst (TiO_2 – SnS_2 -0.15). The contents were kept in the dark (for 30 min) followed by irradiation with sunlight for 60 min and UV-Vis absorbance spectra were measured for the supernatant solutions obtained after centrifugation. The scavenger test results (Fig. S19) show a decrease of about 15.2%, 39.4% and 53.4% in the presence of IPA, PBQ, and AO, respectively. This indicates that O_2 ' and h^+ are the major species responsible for the photodegradation of CV using TiO_2 @ SnS_2 core–shell nanocomposites as the catalyst.

3.14 Mechanism of photodegradation of crystal violet

Crystal violet degrades *via* two different pathways, *i.e.*, *N*-demethylation and oxidative degradation. ^{106,132} In the first case, reactive oxygen species (ROS) attack the *N*,*N*-dimethyl groups of the CV molecules leading to the formation of *N*-de-methylated CV species. In the second case, the ROS species attack the

central carbon of CV facilitated by its conjugated aminotriphenylmethane structure leading to disruption in the conjugation and decolourisation of CV. This step leads to the formation of intermediates such as 4-(N,N-dimethylamino)-4'-(N',N-dimethylamino)benzophenone and 4-(N,N-dimethylamino)phenol. Both these steps can occur simultaneously or one-by-one. The formed intermediates undergo further oxidation leading to ring opening and complete mineralisation of CV leading to formation of CO₂ and H₂O. The formation of CO₂ and H₂O. The formation of CO₂ and H₂O. The formation of CO₃ and H₂O. The formation of CO₄ and H₄O.

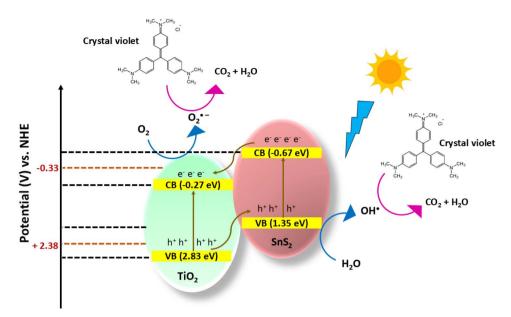
Scheme 2 gives the proposed mechanism of photodegradation of crystal violet in the presence of TiO₂@SnS₂ coreshell nanocomposites as the catalyst. The valence band (VB) and conduction band (CB) positions of TiO₂ are located at 2.83 eV and -0.27 eV, respectively.¹³⁴ The VB and CB of SnS₂ are located at 1.35 eV and -0.67 eV, respectively,⁴⁶ indicating a more negative band potential than that of TiO₂ (see Section 3.8, XPS-VB results).

Upon irradiation with sunlight, electrons in the VB of SnS_2 are excited to its CB, leaving behind photogenerated holes. Due to the favourable band alignment, the excited electrons in the CB of SnS_2 migrate to the CB of TiO_2 , while the holes in the VB of TiO_2 migrate to that of SnS_2 . This charge transfer effectively suppresses electron–hole recombination, enhancing the photocatalytic activity. The electrons in the CB of TiO_2 interact with dissolved O_2 molecules to generate superoxide radicals $(O_2$. while the holes in the VB of SnS_2 oxidize water molecules to produce OH. These highly reactive species then attack and degrade crystal violet molecules into harmless end products $(CO_2$ and $H_2O)$. 129,135,136

The standard potential for O_2/O_2 . is -0.33 V and that for OH^-/OH^+ is 2.38 V. The VB of TiO_2 (2.83 V) is more positive than that of OH^-/OH^+ (2.38 V) indicating that OH^+ could be generated. Similarly, the conduction band of SnS_2 (-0.67 V) is more negative than that of O_2/O_2 . (-0.33 V) indicating that O_2 . could also be generated. The generation of both OH^+ and O_2 . by $TiO_2@SnS_2$ core–shell nanocomposites on solar irradiation leads to the degradation of crystal violet into CO_2 and OH_2 0 as shown in Scheme 2.

3.15 EIS studies

Electrochemical Impedance Spectroscopy (EIS) measurements were performed for TiO₂–NaOH, SnS₂ nanoparticles and TiO₂@SnS₂ core–shell nanocomposites (TiO₂–SnS₂-0.05, TiO₂–SnS₂-0.1 and TiO₂–SnS₂-0.15) to understand the charge separation. The samples were deposited onto FTO (fluorine-doped tin oxide) glass substrates (dimensions: 1 cm \times 2 cm). For each



Scheme 2 Mechanism of photodegradation of crystal violet using TiO₂@SnS₂ core-shell nanocomposites as the catalyst.

sample, 30 mg of the sample (TiO2-NaOH, SnS2 nanoparticles and TiO₂@SnS₂ core-shell nanocomposites) was dispersed in 3 mL of ethanol to form a homogeneous slurry. The mixture was subjected to sonication for 45 minutes to ensure uniform dispersion. Subsequently, the slurry was drop-cast onto the FTO substrates and dried in an oven (at ~ 50 °C).

The electrochemical measurements were conducted using a conventional three-electrode system. The modified FTO glass slides (coated with TiO2-NaOH, SnS2 and TiO2@SnS2 core-shell nanocomposites) served as the working electrode. Ag/AgCl electrode was employed as the reference electrode. A platinum wire was employed as the counter electrode. The EIS measurements were performed in 0.1 M KOH aqueous solution as the electrolyte, over a frequency range of 0.1 Hz to 100 kHz (Multi Autolab/M204 electrochemical workstation (Metrohm Autolab B·V., Netherlands)).

Fig. S20 provides the Nyquist plots for all the samples. The order of arc radius is as follows: TiO2-NaOH > SnS2 > TiO2-SnS2- $0.05 > TiO_2-SnS_2-0.1 > TiO_2-SnS_2-0.15$. The arc radius in the Nyquist plot corresponds to charge transfer resistance (R_{ct}) at the interface of the electrode and electrolyte. 137 A smaller arc radius indicates lower charge-transfer resistance (R_{ct}), which suggests faster interfacial charge transfer. The smaller arc radius observed in TiO2-SnS2-0.15 among all the samples suggests faster interfacial charge transfer and thus its better photocatalytic efficiency towards degradation of crystal violet compared to the other samples.

3.16 Time resolved PL decay experiments

PL decay experiments were performed using an FLS-1000-xs-t (Edinburgh Instruments) system for TiO2-NaOH microspheres, SnS₂ nanoparticles, and TiO₂@SnS₂ core-shell nanocomposites (TiO₂-SnS₂-0.05, TiO₂-SnS₂-0.1 and TiO₂-SnS₂-0.15) and the data are presented in Fig. S21. The excitation and

emission wavelengths were 450 nm and 590 nm, respectively. The PL decay curves were well fitted according to the biexponential function in the form of $R(t) = A + B_1 \exp(-t/\tau_1) + B_2$ $\exp(-t/\tau_2)$.

Where, A is a constant background offset, B_1 and B_2 are amplitude coefficients of the two decay components, τ_1 is the lifetime of the faster decay component and τ_2 is the lifetime of the slower decay component.

The average lifetime τ_{avg} was calculated using the formula $\tau_{\text{avg}} = (B_1 \tau_1^2 + B_2 \tau_2^2)/(B_1 \tau_1 + B_2 \tau_2)$. Table S8 summarizes the fluorescence decay components for all the samples. The average lifetime (τ_{avo}) values estimated for TiO₂-NaOH microspheres, SnS₂ nanoparticles, TiO₂-SnS₂-0.05, TiO₂-SnS₂-0.1, and TiO₂-SnS₂-0.15 are 8.37 ns, 10.82 ns, 10.91 ns, 12.44 ns, and 14.39 ns, respectively. The observed trend in lifetime follows the order: $TiO_2 - SnS_2 - 0.15 > TiO_2 - SnS_2 - 0.1 > TiO_2 - SnS_2 - 0.05 > SnS_2 > TiO_2$. TiO₂-SnS₂-0.15 exhibits a higher average PL decay lifetime indicating a slower recombination rate of photogenerated excitons, indicating more effective charge separation and better photocatalytic efficiency towards the degradation of crystal violet.

3.17 Detection of hydroxyl radicals

To prove the formation of hydroxyl radicals during the photodegradation of CV by TiO2-SnS2-0.15, PL spectral studies were performed using terephthalic acid. Terephthalic acid is nonfluorescent but on reaction with hydroxyl radicals, it produces 2-hydroxyl terephthalic acid, which is fluorescent. About 40 mg of catalyst (TiO2-SnS2-0.15) was taken in a beaker containing an aqueous solution of terephthalic acid $(5 \times 10^{-4} \text{ M})$ and NaOH (2 \times 10⁻³ M). After sunlight irradiation, PL spectra were recorded at periodic time intervals for the supernatant solutions obtained after centrifugation ($\lambda_{exc} = 315$ nm). An emission band at 425 nm (Fig. S22) is observed with an increase in PL intensity as a function of time indicating the generation of hydroxyl radicals with time.

3.18 Recyclability and scalability

Photodegradation experiments were performed repeatedly to understand the stability and reusability of TiO2@SnS2 coreshell nanocomposites. In this experiment, an aqueous solution containing 70 mg of catalyst (TiO2-SnS2-0.15) and 70 mL of CV aqueous solution $(2 \times 10^{-5} \text{ M})$ was kept in the dark (for 30 min) followed by irradiation with sunlight for 60 min. The UV-Vis absorbance spectrum was measured for the supernatant solution obtained after centrifugation. The catalyst was recovered by centrifugation and washed with methanol several times and finally dried in an oven at 60 °C for 12 h. Five cycles of photocatalytic degradation experiments were carried out using the catalyst recovered after each cycle. The recyclability test results (Fig. S23) show a decrease of about 12.5% in photodegradation efficiency of TiO2-SnS2-0.15 after 5 cycles indicating that TiO2-SnS₂-0.15 is a photocatalyst with good recyclability. Furthermore, to determine the stability of the catalyst (TiO₂-SnS₂-0.15), characterization of the recovered catalyst was performed. Fig. S24 provides the XRD pattern, FT-IR spectrum and FESEM image of the catalyst recovered after the recyclability test. The post-recyclability EDX analysis results are provided in Table S9. The results indicate no change in the phase or morphology of the catalyst after repeated use indicating its high stability.

Nanomaterials have been explored as catalysts for photo-degradation of toxic dyes by easy design using different synthetic approaches. Their size, chemical composition and morphology can be easily controlled using optimized synthetic conditions but due to various environmental concerns and economic viability, their large-scale use for environmental remediation is still limited. In the current work, TiO₂@SnS₂ core-shell nanocomposites demonstrate promising photocatalytic activity under laboratory conditions. The synthetic method and photodegradation results in the current study are reproducible, but large-scale production and long-term stability are unexplored.¹⁴⁰

3.19 Potential application of TiO₂@SnS₂ core-shell nanocomposites as C-2 catalysts

Chemical reactions in which two carbon containing products (e.g., ethanol, ethylene or acetic acid) are formed through C–C coupling reactions are called C-2 reactions. This is particularly relevant for electrocatalytic and photocatalytic $\rm CO_2$ reduction and syngas conversion. For a material to be used as a catalyst in a C-2 reaction, the following properties are important: (a) the presence of active sites that can stabilise key intermediates such as *CO, *CH₂ and *CHO, (b) efficient separation of charge carriers (in photocatalysis), and (c) a favourable and stable surface that can promote C–C coupling under the reaction conditions.

Metal sulfide nanoparticles and their nanocomposites have been employed as catalysts for C-2 reactions. For example, $ZnIn_2S_4$ nanosheets activated by nitrogen-doped carbon have been used for electrocatalytic CO_2 reduction to ethanol. ¹⁴¹ SnO_2 /

SnS₂/Cu₂SnS₃ heterojunction has been used for photocatalytic reduction of CO2 to ethanol.142 The TiO2@SnS2 core-shell nanocomposites are potential materials as catalysts for C-2 reactions. They can catalyze C-C coupling reactions in the following ways. The formation of TiO2@SnS2 core-shell nanocomposites builds a type-II heterojunction between TiO₂ and SnS₂. On solar irradiation, SnS₂ absorbs photons and generates an electron-hole pair (see Section 3.14), reducing the recombination of photogenerated excitons and promoting long-lived charge carriers for surface reactions. In the second step, the photogenerated electrons in the CB of TiO₂ can be used for the formation of intermediate species such as *CO, *CHO or *CH3 from CO₂/CO. SnS₂ is well known to stabilize intermediates such as *CO. Furthermore, the C-C coupling can occur in the third step via reductive dimerization of surface-bound *CO or *CH₃ on the catalyst's surface. This leads to the formation of C-2 species such as acetaldehyde. In the final step, the photogenerated electrons and protons (typically from water oxidation) can hydrogenate acetaldehyde to produce ethanol.

From XPS results (Section 3.8), it was found that charge transfer takes place from core TiO₂ to shell SnS₂, indicating interfacial charge redistribution.⁴⁶ An increase in binding energy is observed for Ti 2p and O 1s, whereas a decrease in binding energy is observed for Sn 3d and S 2p in the TiO₂@SnS₂ core–shell nanocomposites. This suggests that there is more electron density on the surface of SnS₂ after the formation of TiO₂@SnS₂ core–shell nanocomposites. The electron-rich SnS₂ surface is beneficial in stabilizing electrophilic species (C-1) such as CHO and provides them sufficient residence time for C–C coupling reactions and can enhance catalytic activity compared to the individual components.

4 Conclusions

In the present study, TiO₂@SnS₂ core-shell nanocomposites were synthesized using the thermal decomposition method using different [Sn4+]:[S2-] ratios. The core-shell nanocomposites were characterized using several analytical techniques. The XRD results confirmed the presence of both TiO2 and SnS₂ phases in the core-shell nanocomposites. FESEM and TEM analyses confirmed uniform coating of SnS2 nanoparticles on the TiO₂ microspheres indicating their core-shell structure. The TiO₂@SnS₂ core-shell nanocomposites demonstrate good catalytic activity towards the photodegradation of CV in aqueous solutions under sunlight. The photocatalytic efficiency of TiO₂@SnS₂ core-shell nanocomposites is better than that of the individual constituents and other metal-sulfide based nanocomposites that are reported in the literature. The TiO₂@SnS₂ core-shell nanocomposites, reported in the present study, have other potential applications, e.g., sodium-ion batteries, gas sensors, water splitting, etc.

Author contributions

Nainy Khera: Methodology, data collection and interpretation, writing – original draft. Pethaiyan Jeevanandam: Conceptualization, project administrat

Paper

Conflicts of interest

There are no conflicts to declare.

Data availability

All the data supporting this study have been included in the main manuscript and the SI.

Some additional data supporting this article have been included as part of SI. See DOI: https://doi.org/10.1039/d5na00533g.

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