Enhanced Photocatalytic Performance in Chromium(VI) Reduction and Dye Degradation using Sn3O4/SnS2 Nanocomposite and Mechanism Insight

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Research Article

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Enhanced photocatalytic performance in chromium (VI) reduction and dye degradation using Sn₃O₄/SnS₂ nanocomposite and mechanism insight

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Abstract

Detection of residual organic and inorganic species in water bodies including drinking water has led to developing strategies for their removal. Here we report a very efficient method of photoreduction of Cr (VI) and photodegradation of methylene blue dye in aqueous medium using Z-scheme heterojunction based Sn₃O₄/SnS₂ solar photocatalyst. The photocatalyst is synthesized by hydrothermal route and it is thoroughly characterized in terms of its structural, compositional, morphological and optical properties. About 100 % of Cr (VI) reduction in 60 min and 99.6 % of methylene blue degradation in 90 min is achieve under sunlight exposure at a photocatalytic rate of 0.066 min⁻¹ and 0.043 min⁻¹, respectively. The total organic carbon estimation of the post-degradation reaction medium corresponded to 85.1 % (MB) mineralization. The photocatalytic degradation is attributed to in-situ generation of reactive oxygen species (ROS) e.g., superoxide radicals, hydroxide radicals, and the role of ROS towards reduction and degradation of Cr (VI) and MB respectively, is confirmed from ROS scavenging studies. The dye degradation mechanism has been discussed by analyzing the degradation products via UPLC-Q-Tof-MS. The photocatalytic degradation of methylene blue by Sn₃O₄/SnS₂ nanocomposites is significantly enhanced as compared to SnS₂ photocatalyst, attributed to Z-scheme heterojunction and the charge carrier mobility.
Keywords
Sn$_2$O$_3$/SnS$_2$ nanocomposite, solar photocatalyst; Z-scheme heterojunction; photocatalytic reduction of Cr (VI) and photocatalytic degradation of methylene blue; degradation product analysis by UPLC-Q-Tof-MS.

Introduction
Water bodies contaminated with inorganic and organic species has a cascading impact on ecosystem and also a major cause of human health hazard (Barrera-Díaz et al. 2012; Coetzee et al. 2020; Tumolo et al. 2020). Among these, Cr (VI) and organic dyes in industrial as well as municipal wastewater are some of the most common constituents owing to their wide range of usages. For example, Cr (VI) compounds are used in electroplating, leather tanning, metal finishing, textile production, and dyeing (He et al. 2020; Karimi-Maleh et al. 2021). Consequently, large volumes of aqueous chromium wastes are generated and discharged into the environment without pretreatment (Owlad et al. 2009). Chromium compounds mostly exist in two standard oxidation states, i.e., Cr (III) and Cr (VI). Out of which, Cr (VI) is water soluble and it is highly toxic owing to its carcinogenic nature (Sedman et al. 2006; Narayani and Shetty 2013). On the other hand, Cr (III) is less toxic and can readily be precipitated out of a solution as Cr(OH)$_3$ (Mertz 1993). Similarly, organic dyes are widely used in textile industries for the colouring of fabrics such silk, cotton and wool etc (Khatri et al. 2015). These dyes are generally stable, highly water soluble, non-biodegradable and carcinogenic in nature, and hence they are hazardous to human and aquatic species (Gusain et al. 2019; Yaseen and Scholz 2019). This demands scientific attention for developing efficient technologies for removal or elimination of Cr (VI) and organic dyes from wastewater. The conventional remediation processes such coagulation, adsorption, membrane separation and precipitation are insufficient for complete removal of the
hexavalent chromium and organic dyes from water and wastewater (Hafiane et al. 2000; Katheresan et al. 2018). The efficiency of biodegradation of Cr (VI) and organic dyes is low. In view of this, advanced oxidation process (AOP) is considered to be more efficient, particularly for treating organic pollutants as it tends to mineralize the pollutants (Bethi et al. 2016). However, AOP is associated to higher operational cost and due to generation of secondary wastes. Alternately, heterogeneous semiconductor-based photocatalysis have gained major attention from the researchers for the treatment of polluted wastewater as it also has the capacity to mineralize the organic constituents (Saadati et al. 2016; Calvete et al. 2019; Di et al. 2019; Wei et al. 2020). Here light of energy greater than the band gap of the photocatalyst is needed for generating electrons and holes which are retained in thermodynamically favorable band edges, i.e., conduction band of one semiconductor materials and valence band of the other semiconducting material (Zhang et al. 2020; Wang et al. 2021). The charge carriers can diffuse to the outer surface of the photocatalyst to interact with H₂O and molecular oxygen at the outer surface of the photocatalyst to produce highly reactive oxygen species (ROS). This ROS in turn can cleave the bonds of the pollutants (e.g., dye molecules) and eventually mineralize. The major hurdles this system is associated with favourable recombination of charge carriers, loss of charge carriers due to their trapping in defect sites, poor redox property owing to band energy mismatch for ROS generation (Das and Dutta 2015; Sharma and Dutta 2018; Wang et al. 2020). In addition, most photocatalytic degradation studies are based on UV light exposure, which is a major limitation from solar harvesting technology point of view as only 6% of the sunlight constitutes UV range (Mukherjee et al. 2021). Considering all the above conditions, it may be put forward that Z-type heterojunction based photocatalyst is favourable for enhancing photocatalytic performance as demonstrated in literature (Qiang et al. 2021). The main advantage with these Z-type heterojunction is attributed to efficient inhibition of charge carrier recombination and
also decrease the defect state density (Lin et al. 2021). It is mostly found that the photocatalysts with Z-type heterojunction are made of oxides like (Li et al. 2016; Huang et al. 2019; Zhao et al. 2019; Xu et al. 2020). Contrastingly, studies based on Z-type photocatalyst made of oxides-sulphide mixed systems are much less (Di et al. 2019). One of the main concern here is the stability of the sulphide component. Considering these conditions, we present here a novel Z-type heterojunction photocatalyst comprising a low band gap SnS$_2$ as a base material in combination with Sn$_3$O$_4$ which is a large band gap materials. The photocatalyst, represented as Sn$_3$O$_4$/SnS$_2$ nanocomposites, has been thoroughly characterized and was studied sunlight mediated photoreduction of hexavalent chromium Cr (VI) and photocatalytic degradation of organic dye in aqueous medium. Hexavalent Chromium Cr (VI) and methylene blue has been chosen as a model pollutants, as it has been detected in ecosystem comprising river water, ground water, sediments and soils, and in drinking water (Fick et al. 2009; Sharma and Bhattacharya 2017; Singh et al. 2019; Khan et al. 2020). The detailed methodology for synthesis, characterization and photocatalytic degradation kinetics by Sn$_3$O$_4$/SnS$_2$ nanocomposites has been discussed. The mechanism of photocatalytic degradation of methylene blue has been discussed in the light of in-situ generated reactive oxygen species (ROS) and identification of degradation products by UPLC-Q-Tof-MS technique.

**Experimental section**

**Chemicals**

Stannous chloride dihydrate (98%), stannous chloride pentahydrate (98%), thioacetamide, sodium hydroxide, trisodium citrate, diphenylcarbazide, chloroform, tert-butanol, ammonium oxalate, potassium dichromate, and ethanol (99%) were procured from HiMedia Pvt. Ltd., India. All precursors used in this study were of analytical grade and
were used without further purification. Analytical grade deionized water (Millipore) was used throughout the study.

**Synthesis Sn$_3$O$_4$/SnS$_2$ NCs**

It is a two-step process, where Sn$_3$O$_4$ nanoflakes were first prepared via hydrothermal route. In a typical process, 4 mmol of Stannous chloride dihydrate was dissolved in 12.5 mL deionized water than 12.5 mmol tri-sodium citrate dihydrate was added and stirred until a transparent solution was obtained, then 0.1 g of sodium hydroxide dissolved in 12.5 mL D.I water, was added to the above solution dropwise and stir for 1 h and finally transfer the solution into a 50 mL Teflon jar and heated at 180 °C for 12 h in a microprocessor-based temperature-controlled furnace. Finally, the autoclave was cooled to room temperature. The resulting solution of Sn$_3$O$_4$ was then precipitated with ethanol and recovered by centrifuging at 15,000 rpm for 5 min. The batch of Sn$_3$O$_4$ was washed several times with ethanol and then dried overnight in oven at 40°C.

Next 5.0 mmol SnCl$_4$.5H$_2$O was dissolved in 40 mL deionized water than 12.5 mmol of Thioacetamide was added and stir until a homogenous solution was formed. After that, a definite wt.% of Sn$_3$O$_4$ (i.e., 5 wt.%, 7 wt.% and 10 wt.%) was added to the above solution mixture under constant stirring. The whole mixture was then transferred to an autoclave and heated at 180°C for 8 h. The obtained precipitate was washed with deionised water and ethanol by centrifuging at 7000 rpm for 10 min and the final yellow product was dried at 60°C overnight. The nanocomposites will be denoted as 0.05Sn$_3$O$_4$/SnS$_2$, 0.07Sn$_3$O$_4$/SnS$_2$ and 0.10Sn$_3$O$_4$/SnS$_2$ according to the wt.% of precursor Sn$_3$O$_4$ added. Likewise, control batch of pristine SnS$_2$ was prepared following the same synthetic protocol without the addition of Sn$_3$O$_4$ nanoparticles.
Characterization’s techniques

The as-synthesized batches of Sn$_3$O$_4$/SnS$_2$ NCs with different Sn$_3$O$_4$ weight ratios, together with those of SnS$_2$ nanoparticles, Sn$_3$O$_4$ nanoparticles are characterized by powder X-ray Diffraction, X-ray photoelectron spectroscopy, field emission scanning electron microscopy, high resolution transmission electron microscopy, Brunauer-Emmett-Teller (BET) specific surface area technique, photoluminescence spectroscopy, electrochemical impedance spectroscopy and by diffused reflectance spectroscopy. The details of these techniques and sample preparation are given as Supporting Information (Section S1).

The degradation intermediates were identified by UPLC (ACQUITY I) coupled to QToF (XeVO G2-XS QToF). Mobile phase A was aqueous formic acid solution (0.1%, v/v), and mobile phase B was acetonitrile. The gradient solvent was at a flow rate of 0.3 mL/min. The MS was performed in a positive ion mode using an electrospray ionization (ESI+) source under the following conditions: capillary voltage: 2.0 kV; gas (N$_2$) flow rate: 50 L/h; gas temperature: 300 °C; nebulization pressure: 15 psi; scan time: 0.5 second.

Evaluation of Photocatalytic activity

The photocatalytic activities of the Sn$_3$O$_4$/SnS$_2$ NCs and their respective individual components (e.g., Sn$_3$O$_4$ NPs, SnS$_2$ NPs) as photocatalysts were evaluated by monitoring the photocatalytic reduction of Cr (VI) solution (50 mg L$^{-1}$) under natural sunlight irradiation. In a typical experiment, first, the pH of the initial 100 mL Cr (VI) solution was adjusted to 2.5 by adding 1M H$_2$SO$_4$ solution, then 50 mg of respective photocatalyst were dispersed in the batches of Cr (VI) solution (50 mg/L based on Cr in K$_2$Cr$_2$O$_7$ solution) taken in 250 mL beakers. This will be referred to as reaction assembly, which was subjected to slow continuous stirring (less than 100 rpm) for 60 min in dark condition to establish adsorption-desorption equilibrium. After 60 min the reaction assemblies was kept under natural sunlight
(photocatalytic experiments were carried out at IIT Roorkee (29°51'N; 77°53'E) in the month of April and May 2021. The solar irradiance was assumed to be 221 W/m² during the experiment day (Ramachandra et al. 2011). At regular intervals, 1.5 mL of the suspension was withdrawn from each reaction assembly and centrifuged at 15000 rpm for 2 min to discard any particles using Beckman Coulter Allegra TM X-22R. The concentration of Cr (VI) was monitored according to the previously reported method (Zhang et al. 2019). First, 1.0 ml of the sample was mixed with 9 ml of 0.2 M H₂SO₄ in a 10.0 ml volumetric flask. Subsequently, 0.2 ml of freshly prepared 1,5-diphenylcarbazide (250 mg/50 mL) solution was added to the above mixture. After shaking up the mixture, the solution was allowed to stand for 10-15 min to ensure full-color development. Subsequently, the solution was measured at 540 nm by UV–vis spectrophotometer (Shimadzu, UV-2400, Japan). The effect of solution pH on the photoreduction efficiency of Cr (VI) was investigated under the same condition. The chromium solution with different pH was adjusted by 0.2 M H₂SO₄ or NaOH. Organic dye methylene blue (MB) was selected as another target pollutant. The degradation of dye solution by the Sn₃O₄/SnS₂ NCs were carried out under the similar conditions as discussed above. Typically, 100 mL of MB dye solution (20 mg/L) treated with 50mg of pristine SnS₂, Sn₃O₄ and the batches of Sn₃O₄/SnS₂ as photocatalyst respectively and kept under slow continuous stirring (less than 100 rpm) for 60 min in dark conditions to establish adsorption-desorption equilibrium. The concentration variation of MB dye solution was examined by recording the absorbance of the supernatant liquid at its λ_max of 664 nm, using UV-Vis spectrophotometer (UV-1800, Shimadzu, Japan).

The leached concentrations of respective constituents in the photocatalysts, viz. Sn from the batch of Cr (VI) solution treated with 0.07Sn₃O₄/SnS₂ NCs were determined by ICP-OES. The details of sample preparation are given as supporting information (Section S2). The photostability and re-usability of the best performing photocatalyst, i.e.,
0.07Sn$_3$O$_4$/SnS$_2$ NCs was assessed by monitoring photocatalytic reduction of Cr (VI) for five successive cycles. At the end of each cycle, the used photocatalyst was recovered, dried, and reused for the next cycle. After completing five cycles of photocatalytic reduction, the stability of the photocatalyst was studied by XRD and FESEM.

**Results and Discussion**

The powder X-ray diffraction (XRD) method was used to investigate the crystalline structure and phase composition of the as-synthesized batches of Sn$_3$O$_4$, SnS$_2$ and the Sn$_3$O$_4$/SnS$_2$ NCs. The characteristic Bragg reflection peaks for pristine SnS$_2$ were detected at 2\(\theta\)=14.8°, 28.1°, 32.0°, 33.5°, 46.0°, 49.9° and 52.4° (Fig. 1), which can be indexed to the (0 0 1), (1 0 0), (0 0 2), (1 0 1), (0 0 3), (1 1 0) and (1 1 1) crystal planes of SnS$_2$ hexagonal phase. (JCPDS Card no.89-2358). Similarly, the characteristic Bragg diffraction peaks for pristine Sn$_3$O$_4$ NPs were detected at 2\(\theta\) = 26.9°, 32.1°, 37.0°, and 51.7° (Fig.1), which were indexed to the (1 1 1), (1 2 2), (1 3 0), and (1 3 2) planes of triclinic Sn$_3$O$_4$, respectively (JCPDS Card No.- 16-0737). The XRD pattern of 0.05Sn$_3$O$_4$/SnS$_2$ displayed characteristic peaks of pristine SnS$_2$ along with few smaller intensity peaks corresponding to Sn$_3$O$_4$ (Table-S1). The intensity of the diffraction peaks of Sn$_3$O$_4$ increased for the batches of 0.07Sn$_3$O$_4$/SnS$_2$ and 0.10Sn$_3$O$_4$/SnS$_2$, indicating gradual coverage of Sn$_3$O$_4$ nanoparticles on SnS$_2$ surface. The detail information about crystallite sizes of the batches of Sn$_3$O$_4$/SnS$_2$ NCs and SnS$_2$ were discuss in the supporting information (Section S3).

The morphology of Sn$_3$O$_4$/SnS$_2$ NCs, along with their respective components e.g., SnS$_2$ nanoparticles and Sn$_3$O$_4$ nanoflakes were analysed by electron microscopy (given as Supporting Information, Fig. S1). The FE-SEM image of pure SnS$_2$ completely composed of clusters of nanoparticles with diameters in the range of 80–100 nm (Fig S1a). Sn$_3$O$_4$ was composed of relatively smooth irregular nanoflakes of size ranging in between 100–400 nm long and thickness about 10 nm (Fig S1b). The FE-SEM image of 0.07Sn$_3$O$_4$/SnS$_2$ NCs
mostly revealed nanoclusters of SnS$_2$, which is the major component in the nanocomposites, along with distribution of irregular shaped nanoflakes of Sn$_3$O$_4$ (Fig S1c-d). The energy dispersive X-ray (EDX) spectrum of 0.07Sn$_3$O$_4$/SnS$_2$ NCs revealed the characteristic X-rays of Sn, S, and O. (Fig S1e), which indicated about formation of heterostructures of Sn$_3$O$_4$/SnS$_2$. The morphology of the batch of 0.07Sn$_3$O$_4$/SnS$_2$ NCs was better revealed from the transmission electron microscopy (TEM) images. Here both nanoclusters of SnS$_2$ and irregular shaped Sn$_3$O$_4$ nanoflakes could be observed corresponding to formation of Sn$_3$O$_4$/SnS$_2$ nanocomposites (Fig. 2a). The SnS$_2$ nanoclusters were 80-100 nm long and the sizes of Sn$_3$O$_4$ were in the range of 50-70 nm long and about 10 to 15 nm in width. The formation of heterostructures of Sn$_3$O$_4$/SnS$_2$ is evident from the higher resolution TEM image which revealed heterojunction of SnS$_2$ nanoclusters and the irregular shaped Sn$_3$O$_4$ nanoflakes (Fig. 2b). The crystalline nature of Sn$_3$O$_4$/SnS$_2$ NCs is revealed from the lattice fringes with corresponded to binary materials with interatomic layer spacing of 0.314 nm and 0.330 nm (Fig. 2c). They correspond to the (1 0 0) lattice plane of hexagonal SnS$_2$ and (1 1 1) plane of triclinic Sn$_3$O$_4$, respectively. The selected area electron diffraction (SAED) pattern confirmed the strong interference patterns due to polycrystalline nature of Sn$_3$O$_4$/SnS$_2$ NCs (Fig. 2d). The results of XRD, FESEM and TEM confirmed formation of Sn$_3$O$_4$/SnS$_2$ heterostructure.

The proposed structure of 0.07Sn$_3$O$_4$/SnS$_2$ was further corroborated by compositional analysis of tin (Sn), oxygen (O) and sulphur elements by XPS measurement (Fig. 3a). The binding energy peaks of Sn 3d shows two peaks at 486.88 eV and 495.29 eV, which are assigned to Sn 3d$_{5/2}$ and Sn 3d$_{3/2}$, respectively, suggesting the presence of Sn$^{4+}$ in 0.07Sn$_3$O$_4$/SnS$_2$ (Fig. 3b). The binding energy peaks of S 2p displays a two strong peak at 161.72 eV and 162.85 eV corresponding to S 2p$_{3/2}$ and S 2p$_{1/2}$, respectively, which was attributed to the S$^{2-}$ state (Fig. 3c). The O1s binding energy peak is deconvoluted into two
peaks at 532.03 eV and 531.13 eV (Fig. 3d). The peaks corresponded to O-Sn$^{4+}$ bond and O-Sn$^{2+}$, respectively, which are relevant to the proposed structural constituent of 0.07Sn$_3$O$_4$/SnS$_2$ NCs. Therefore, the XPS results are consistent with the XRD and HRTEM findings shown above. This further provides more evidence that the obtained 0.07Sn$_3$O$_4$/SnS$_2$ composite consists of SnS$_2$ and Sn$_3$O$_4$.

The specific surface area of pristine SnS$_2$ and 0.07Sn$_3$O$_4$/SnS$_2$ NCs were analysed by N$_2$ adsorption-desorption isotherms and information about its porous nature was obtained from the BJH pore size distribution plot (Table S2). The BET plot of pure SnS$_2$ and 0.07Sn$_3$O$_4$/SnS$_2$ NCs revealed type-IV isotherm (Fig. 4) and the corresponding BET surface area was determined as 55.06 m$^2$ g$^{-1}$ and 60.44 m$^2$ g$^{-1}$, respectively. The growth of Sn$_3$O$_4$ nanoflakes on the surface of the SnS$_2$ surface increased the surface areas and the pore volume of the 0.07Sn$_3$O$_4$/SnS$_2$ composites (Table S2). A narrow pore size distribution between 2-4 nm is obtained (inset of Fig. 4), which suggested mesoporous nature of the 0.07Sn$_3$O$_4$/SnS$_2$ NCs. The mesoporous nature is also corroborated from the Type-IV isotherm plot (Peng et al. 2015). The high surface area and mesoporous structures of the 0.07Sn$_3$O$_4$/SnS$_2$ composites, which is favourable for better interaction with pollutant molecules for adsorption and photocatalytic degradation.

The band gap of the as-synthesized batches of Sn$_3$O$_4$/SnS$_2$ NCs and its constituents, e.g., pristine batches of SnS$_2$ NPs and Sn$_3$O$_4$ NPs were determined from diffused reflectance spectroscopy studies. The pristine Sn$_3$O$_4$ nanoflakes and Sn$_3$O$_4$/SnS$_2$ NCs strongly absorbance in the UV and visible light region (Fig. S2), whereas the SnS$_2$ nanoclusters absorb only in the visible region (Fig. S2). The diffused reflectance spectra were converted to absorption spectra using conventional Kubelka-Munk function (Kortüm 1969), and the optical band gap was determined from Tauc plot given as, (Tauc et al. 1966)

$$(ahv)^{1/n} = A(hv - E_g).$$
In this equation $\alpha$, $h$, $\nu$ and $A$ refers to the absorption coefficient, Planck’s constant, incident light frequency and proportionality constant, respectively. The value of ‘n’ is considered according to the nature of electronic transition, i.e. $n= \frac{1}{2}$ for direct transition and $n= 2$ for indirect transition. The Tauc’s plots of $0.05\text{Sn}_3\text{O}_4/\text{SnS}_2$ NCs, $0.07\text{Sn}_3\text{O}_4/\text{SnS}_2$ NCs, $0.10\text{Sn}_3\text{O}_4/\text{SnS}_2$ NCs and $\text{SnS}_2$ nanoclusters are given in Fig. 5. The band gap of these materials were estimated by extrapolating the linear part of the respective Tauc plots to $(\alpha h \nu)^2 = 0$, as shown in Fig. 5 and by assuming the phenomenon of direct transition. The band gap of $0.05\text{Sn}_3\text{O}_4/\text{SnS}_2$ NCs, $0.07\text{Sn}_3\text{O}_4/\text{SnS}_2$ NCs, and $0.10\text{Sn}_3\text{O}_4/\text{SnS}_2$ NCs were determined to be $2.23$ eV, $2.24$ eV and $2.25$ eV, respectively, which were similar to that of $\text{SnS}_2$ nanoclusters ($E_g= 2.20$ eV).

**Photocatalytic performance**

The photocatalytic reduction of Cr (VI) (50 mg/L) by the batches of $\text{Sn}_3\text{O}_4/\text{SnS}_2$ nanocomposites (e.g., $0.05\text{Sn}_3\text{O}_4/\text{SnS}_2$ NCs, $0.07\text{Sn}_3\text{O}_4/\text{SnS}_2$ NCs, and $0.10\text{Sn}_3\text{O}_4/\text{SnS}_2$ NCs) and those by the individual components, e.g., $\text{SnS}_2$ nanoclusters and $\text{Sn}_3\text{O}_4$ nanoflakes are given as a plot of $C_t/C_0$ versus time (Fig. 6a). Here $C_0$ and $C_t$ are the initial concentration and concentration of Cr (VI) after a definite time of sunlight exposure. The decrease in the concentration of Cr (VI) due to adsorption on the respective photocatalysts was first determined from the dark experiment. About $40\%$ of Cr (VI) was adsorbed on the batches of nanocomposites (i.e., $0.05\text{Sn}_3\text{O}_4/\text{SnS}_2$ NCs, $0.07\text{Sn}_3\text{O}_4/\text{SnS}_2$ NCs, and $0.10\text{Sn}_3\text{O}_4/\text{SnS}_2$ NCs) while about $14\%$ of Cr (VI) was adsorbed on $\text{SnS}_2$ nanoclusters and $\text{Sn}_3\text{O}_4$ nanoflakes (Fig. 6a). The higher adsorption of Cr (VI) is primarily attributable to larger surface area and more favourable pore volume in $\text{Sn}_3\text{O}_4/\text{SnS}_2$ NCs (i.e., $60.44$ m$^2$ g$^{-1}$) as compared to $55.06$ m$^2$ g$^{-1}$ for pristine $\text{SnS}_2$ nanoclusters. As $\text{Sn}_3\text{O}_4$ fraction was very less in the nanocomposites so its comparison was not done. The control experiment indicates that the self-decomposition of Cr (VI) is almost negligible whereas $\text{Sn}_3\text{O}_4$ shows poor photocatalytic reduction activity after 60
min sunlight irradiation. All the batches of SnO$_3$/SnS$_2$ nanocomposites clearly displayed significantly higher photocatalytic reduction activity than that of pure SnS$_2$ after the 60 min sunlight exposure, which indicates that SnO$_3$ plays an important role in the enhancement of Cr (VI) reduction. The 0.07SnO$_3$/SnS$_2$ NCs manifested the highest photocatalytic activity (about 100 % removal efficiency of Cr (VI) after 60 min sunlight irradiations), while only 66 % of Cr (VI) was reduced under same condition using SnS$_2$ as photocatalyst. Furthermore, it may be remarked here that the photocatalytic reduction of Cr (VI) by SnO$_3$/SnS$_2$ NCs are depend on the content of SnO$_3$ in SnO$_3$/SnS$_2$ NCs. The photocatalytic reduction activity of 0.07SnO$_3$/SnS$_2$ NCs reached the highest. However, 0.10SnO$_3$/SnS$_2$ NCs displayed a decrease in photocatalytic reduction activity, when the SnO$_3$ content was further increased.

The most possible reason for the decrease in photocatalytic reduction activity of 0.10SnO$_3$/SnS$_2$ NCs was that the excess of SnO$_3$ covering the active site of SnO$_3$/SnS$_2$ NCs, so the number of active sites were reduced. The increase in photocatalytic reduction activity of 0.07SnO$_3$/SnS$_2$ can be substantiated with the increase in surface area and pore volume (as observed in BET results, Table-S2), help in better absorptivity of the Cr (VI) molecules on the photocatalyst surface as well as formation of heterojunctions in the SnO$_3$/SnS$_2$ NCs significantly assist in interfacial charge separation of the photoexcited excitons during the course of photocatalytic reduction process.

The photocatalytic reduction mechanism was studied by fitting the time dependent Cr (VI) reduction data with pseudo first-order kinetics model. The first order kinetics model is given as:

$$\ln(C_0/C_t) = k_1t$$

(1)

where, $C_0$ and $C_t$ are already defined, $k_1$ (min$^{-1}$) is the first order photocatalytic reduction rate constant for Cr (VI). (Table-1) The corresponding photocatalytic reduction rate of 0.07SnO$_3$/SnS$_2$ ($k_1= 0.066$ min$^{-1}$) is 5.5 times than pristine SnS$_2$ ($k= 0.012$ min$^{-1}$) and 66
times with respect to Sn$_3$O$_4$ (k=0.0010 min$^{-1}$, Fig.6b). The corresponding UV-vis absorption spectra recorded during the photocatalytic reduction of Cr (VI) solution by the optimized 0.07Sn$_3$O$_4$/SnS$_2$ photocatalyst under sunlight irradiation is given as Supporting Information (Fig.S3a). It can be seen that the intensity of the characteristic absorption peak of Cr (VI) at about 540 nm decreased gradually and it nearly disappeared after 60 min. Additionally, the solution after the photocatalytic reduction of Cr (VI) over 0.07Sn$_3$O$_4$/SnS$_2$ sample was detected using ICP-OES with Cr (VI) standard curve to confirm the content of Cr ions in solution (Fig.S4). The results show that the contents of Cr ions are 0.037 mg/L for sunlight light-driven photocatalytic reduction of Cr (VI).

**Effects of pH on photocatalytic reduction of Cr (VI)**

The Cr (VI) removal efficiency continuously decreased with the increasing pH of the initial solution. When the pH was increased to 10.50, the total removal rate of Cr (VI) was considerably reduced to 14.91%. These results are also presented in the corresponding UV–vis absorption spectra (Fig.S5). The higher reduction potential at acidic conditions indicates that the reaction is more feasible under acidic conditions. The reasons for the above results are as follows. First, Cr (VI) exists mainly as dichromate anion (Cr$_2$O$_7^{2-}$) and hydrogen chromate ion (HCrO$_4^-$) under acidic conditions and as chromate ion (CrO$_4^{2-}$) under alkaline conditions. Secondly, under acidic condition, the reduction potential (E Cr$_2$O$_7^{2-}$/Cr$^{3+}$) is 1.23 V vs NHE and (E HCrO$_4^-$/Cr$^{3+}$) is 1.35 V vs NHE which is much more positive then the reduction potential under alkaline condition i.e. (E CrO$_4^{2-}$/Cr$^{3+}$ = -0.13V vs NHE), so tendency to reduce from Cr$^{6+}$ to Cr$^{3+}$ under acidic condition is much more easier then alkaline condition (Equation 2-4). The reactions that occur in acidic and alkaline solutions are:

**Cr reduction under acidic medium**

\[
\begin{align*}
\text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+ + 6\text{e}^- & \rightarrow 2 \text{Cr}^{3+} + 7 \text{H}_2\text{O} \\
\text{HCrO}_4^- + 7\text{H}^+ + 3\text{e}^- & \rightarrow 2 \text{Cr}^{3+} + 7 \text{H}_2\text{O}
\end{align*}
\]
Cr reduction under alkaline medium

\[
\text{CrO}_4^{2-} + 4\text{H}_2\text{O} + 3\text{e}^- \rightarrow \text{Cr(OH)}_3 + 5\text{OH} \quad (4)
\]

Overall, the photocatalytic reduction of Cr (VI) consumes H\(^+\) and acidic conditions are more favorable for Cr (VI) reduction than basic one.

Photocatalytic degradation of methylene blue (MB) dye

The photocatalytic degradation of another class of pollutants with different molecular structure, i.e., methylene blue (MB, 20 mg/L) was investigated by all the batches of 0.07Sn\(_3\)O\(_4\)/SnS\(_2\) NCs and those by Sn\(_3\)O\(_4\) and SnS\(_2\) NCs. The photocatalytic degradation profile including the initial dark experiments for MB by all the batches of photocatalysts under study are given in Fig. 6c. The 0.07Sn\(_3\)O\(_4\)/SnS\(_2\) nanocomposite shows 36% adsorption of MB dye in the dark condition, whereas Sn\(_3\)O\(_4\) and SnS\(_2\) shows 11% and 13% adsorption respectively, indicating that high adsorption capacity favors in the photocatalytic process. As expected, the sunlight mediated MB degradation was significantly higher for the batches of Sn\(_3\)O\(_4\)/SnS\(_2\) NCs as compared to those by Sn\(_3\)O\(_4\) and SnS\(_2\). The best result, i.e., 99.6% degradation of MB was recorded for the batch treated with 0.07Sn\(_3\)O\(_4\)/SnS\(_2\) NCs. The degradation followed pseudo-first order kinetic model (Fig. 6d). The corresponding photocatalytic degradation rate for 0.07Sn\(_3\)O\(_4\)/SnS\(_2\) (\(k_2 = 0.043\ \text{min}^{-1}\)), which is 5.37 times higher than the pristine SnS\(_2\) (\(k = 0.008\ \text{min}^{-1}\)) and 10.75 times higher than Sn\(_3\)O\(_4\) (\(k = 0.004\ \text{min}^{-1}\)). The corresponding UV-vis absorption spectra recorded during the photocatalytic degradation of MB dye solution by the optimized 0.07Sn\(_3\)O\(_4\)/SnS\(_2\) photocatalyst under sunlight irradiation is given as Supporting Information (Fig.S3b). It can be seen that the
intensity of the characteristic absorption peak of MB at about 665 nm decreased gradually and it nearly disappeared after 90 min.

The degree of mineralization of MB dye was estimated from total organic content (TOC) in the respective residual solutions treated with 0.07Sn₃O₄/SnS₂ NCs after photocatalytic degradation for 90 minutes sunlight exposure. Expectedly, these values were high then the TOC removal by pristine SnS₂ and Sn₃O₄ (supporting information Fig. S6). The TOC values were 85.1 % for MB dye, which corresponded to 99.6 % degradation respectively. Similar trend on incomplete degradation from TOC results are also found in literature (Du et al. 2021). It may be assumed that longer sunlight exposure could lead to complete mineralization of MB dye into CO₂ and H₂O by treating with the photocatalyst (Liu et al. 2020).

The pathways for photocatalytic degradation of MB were addressed by identifying the tentative intermediates (represented as P) corresponding to the mass fragments analyzed by UPLC-Q-ToF-MS (Scheme 1).

In case of MB, two possible degradation pathways were proposed. On the one pathway, after a series of demethylation, the structure of MB dye (m/z=284) were destroyed and the intermediates P1 (m/z = 255) were appeared. This can be explained that hydroxyl radicals (·OH) facilitates demethylation of the organic compounds. The intermediate P1 is further demethylated and deaminated to form intermediate P2 (m/z= 198), which was further oxidised to form intermediate P3 with (m/z= 214). The intermediates P3 finally oxidized to smaller molecule like H₂O, CO₂. In the second pathway the sulphur-nitrogen conjugated system in the MB molecule is attacked by hydroxyl radical and degraded into intermediate P4 (m/z= 166). The intermediate P4 undergoes a series of demethylation to form intermediate P5 (m/z= 151) and P6 (m/z= 138), which was further oxidised to form intermediate P7 with (m/z= 126) and P8 (m/z= 109). Now the intermediate P8 undergoes further oxidation and
form a smaller molecule i.e., P9 with (m/z 97). In the end, small molecules P9 were further oxidized into carbon dioxide and water.

**Re-usability of photocatalyst**

The robustness of the as-synthesized batch of 0.07Sn₃O₄/SnS₂ NCs as photocatalyst was assessed from its chemical and photo-stability. The chemical stability was determined from metal ion leaching during the photocatalytic degradation process. The concentrations of leached metal ions of Sn at the end of five photocatalytic cycle, determined by calibration method using ICP-OES analysis, suggested minimal leaching (less than 7 %), as given in Supporting information Table S3). The concentrations of the leached metal ions in the reaction medium were determined from the respective calibration plots (Fig. S7). These results suggested excellent chemical stability of 0.07Sn₃O₄/SnS₂ NCs as photocatalyst.

The photo-stability of 0.07Sn₃O₄/SnS₂ NCs as photocatalyst for Cr (VI) photoreduction is reflected from the re-usability of the photocatalyst for at least five successive cycles of photocatalytic reduction under optimized conditions. The photoreduction patterns are similar and the rate of photocatalytic reduction for all the five cycles are nearly similar (Fig. 7a). The stability of 0.07Sn₃O₄/SnS₂ NCs in the reaction medium was further confirmed from the XRD pattern of the used photocatalyst recovered after the 5th cycle (Fig. 7b). The lattice parameters of the used photocatalyst are expectedly similar (Table S4, given as Supporting information). Furthermore, the morphology of the used 0.07Sn₃O₄/SnS₂ NCs recorded by FE-SEM also did not show any significant changes with respect to the pristine batch of photocatalyst (Fig. 7c).

**Photocatalytic reaction mechanism**

Broadly, photocatalytic reduction or degradation is initiated by absorption of photons of energy greater than the band gap of the photocatalyst followed by inhibition of charge carrier recombination (Sharma and Dutta 2018). Various factors are responsible for inhibition
of charge carrier recombination, out of which the two significant ones are presence of defect
states of energy lesser than that of the conduction band and mobility of charge carriers to the
surface of the photocatalyst for ROS generation.

The photoluminescence spectra of pristine Sn$_3$O$_4$ nanoflakes SnS$_2$ nanoparticles,
0.05Sn$_3$O$_4$/SnS$_2$ NCs, 0.07Sn$_3$O$_4$/SnS$_2$ NCs, and 0.10Sn$_3$O$_4$/SnS$_2$ NCs revealed one radiative
transitions, which corresponding to inter-band transition (~ 460 nm) (Fig. 8a) (Sharma and
Dutta 2018). Notably, the PL emission intensities for inter-band transition were significantly
decreased for the batch of Sn$_3$O$_4$/SnS$_2$ NCs as compared to that of Sn$_3$O$_4$ and SnS$_2$. The
decrease in the PL intensity is consistent with increase in the rate of photocatalytic reduction
and degradation. These results indicated that the charge carrier recombination is inhibited in
Sn$_3$O$_4$/SnS$_2$ and favoured interfacial charge transfer due to formation of heterojunction. These
separated charge carriers have to move to the surface of the photocatalyst for generating
reactive oxygen species (ROS) reacting with molecular oxygen and water. The mobility of
the charge carriers in SnS$_2$ and Sn$_3$O$_4$/SnS$_2$ NCs along with was studied from electrochemical
impedance spectroscopy (EIS) measurements. The radius of the arc in the Nyquist plot for the
electrode made of 0.07Sn$_3$O$_4$/SnS$_2$ was smaller than the one made of SnS$_2$ (Fig. 8b). Arc with
smaller radius, i.e., 0.07Sn$_3$O$_4$/SnS$_2$ NC, is attributed to lower the impedance or higher charge
carrier transport (Li et al. 2018b; Yi et al. 2019). Furthermore, the slope in the mid-frequency
region corresponding to the Warburg region is more for 0.07Sn$_3$O$_4$/SnS$_2$, which implied
higher diffusion current than in pristine SnS$_2$. These results are consistent with more
favourable charge carrier transport in 0.07Sn$_3$O$_4$/SnS$_2$ as compared to the pristine SnS$_2$ and
complemented with the higher photocatalytic activity exhibited by observed in
0.07Sn$_3$O$_4$/SnS$_2$.

The interfacial charge transfer in a heterogeneous photocatalyst would depend on
favourable configuration of conduction band and valence band energies in the photocatalyst.
Empirically, the minimum energy of conduction band ($E_{CB}$) and the maximum energy of the valence band ($E_{VB}$) were calculated by using the following expressions: (Reddy et al. 1998)

$$E_{CB} = \chi(A_aB_b) - \frac{1}{2}E_g + E_o$$

$$E_{VB} = E_{CB} + E_g$$

where, $E_g$ is the band gap of 0.07Sn$_3$O$_4$/SnS$_2$ NCs, $E_{CB}$ is the potential of the conduction band, $E_{VB}$ is the valence band potential, $E_o$ is the scale factor taken as $-4.50$ eV, i.e., the energy of free electrons on the normal hydrogen electrode (NHE scale). The parameter $\chi(A_aB_b)$ corresponds to the absolute electronegativity of a semiconductor material type $A_aB_b$, which is calculated as the geometric mean of the electronegativity of the constituent atoms. The electronegativity value for Sn$_3$O$_4$ and SnS$_2$ are calculated to be $5.91$ eV and $5.37$ eV, respectively, which are consistent with literature (Gao et al. 2016; Li et al. 2018a). The $E_{CB}$ and $E_{VB}$ of Sn$_3$O$_4$ are deduced as $0.01$ eV and $2.81$ eV, respectively. Similarly, the $E_{CB}$ and the $E_{VB}$ of SnS$_2$ are $-0.11$ eV and $2.09$ eV, respectively. Since the conduction band potential of SnS$_2$ is more negative than that of Sn$_3$O$_4$, the photogenerated electrons in the conduction band of SnS$_2$ will migrate to the conduction band of Sn$_3$O$_4$, according to the traditional separation process of electron-hole pairs (Luo et al. 2019). By this charge transfer mode, the accumulated electrons in the conduction band of Sn$_3$O$_4$ cannot reduce O$_2$ into O$_2^{-*}$ radicals because the conduction band potential of Sn$_3$O$_4$ is more positive than that of the O$_2^{-*}$ radical ($-0.046$ eV vs N.H.E) (Li et al. 2018a). Thus, it is not favourable for producing the main reactive species O$_2^{-*}$ if transfer of photogenerated charge occurs by the traditional electron-hole transfer process. However, the results of this trapping experiments revealed that O$_2^{-*}$ play an important role in the organic pollutant degradation process. On the basis of the above results, a possible Z-scheme mechanism for Cr (VI) reduction and MB degradation using the Sn$_3$O$_4$/SnS$_2$ heterojunction photocatalyst was proposed, as illustrated in scheme-2a and 2b. Unlike the traditional model, the Z-scheme
mechanism photocatalysts retain the stronger oxidation and reduction ability, which deeply contributed to the improvement of photocatalytic performance (Liu et al. 2018; Lin et al. 2021; Qiang et al. 2021). Under visible-light irradiation, both SnS$_2$ and Sn$_3$O$_4$ can absorb visible light photons to produce photogenerated electrons and holes. In case Cr (VI) photoreduction (scheme-2a), the photogenerated electrons in conduction band of Sn$_3$O$_4$ ($e_{CB}^-$) would transfer to valence band of SnS$_2$ to recombine instantly with the photogenerated holes ($h_{VB}^+$), while the valence band holes of Sn$_3$O$_4$ incite the decomposition of water with the photo-oxidation reaction. On the other hand, the conduction band electrons of SnS$_2$ could easily utilize for the reduction of Cr (VI) to Cr (III), as the potential of conduction band of SnS$_2$ (-0.11 eV) is more negative than the potential required for Cr (VI) photoreduction ($E(\text{Cr}^{6+/\text{Cr}^{3+}}) = 0.55$ eV vs. NHE). The pathways of Cr (VI) reduction are depicted in Eqs. (7-9).

\begin{align}
\text{SnS}_2 + \text{hv} & \rightarrow e_{CB}^- + h_{VB}^+ \tag{7} \\
\text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+ + 6e^- & \rightarrow 2 \text{Cr}^{3+} + 7 \text{H}_2\text{O} \tag{8} \\
2\text{H}_2\text{O} + 4h^+ & \rightarrow \text{O}_2 + 4\text{H}^+ \tag{9}
\end{align}

The possible photocatalytic degradation mechanism of MB by Sn$_3$O$_4$/SnS$_2$ NCs is shown in (Scheme 2b). By analyzing the relative band gap positions of $E_{CB}$ and the $E_{VB}$ of SnS$_2$ and Sn$_3$O$_4$, it can be found that the thermodynamic driving force of $e^-$ in conduction band of SnS$_2$ is enough to reduce the adsorbed oxygen to generate $\text{O}_2^{-}$ ($E(\text{O}_2/\text{O}_2^{-}) = -0.046$ eV vs. NHE). Meanwhile, the lower valence band potentials of Sn$_3$O$_4$ (2.81 eV) instead of SnS$_2$ (2.09 eV) can oxidize OH$^-$ to OH$^-$ owing to the standard redox potential of OH$^-$/OH$^-$ with 2.3 eV. Therefore, it is clear that in this heterojunction system, $\text{O}_2^{-}$ and $\cdot$OH are the mainstream active sites who truly matter in this photocatalytic degradation reaction.

This is well supported by the radical trapping studies (Fig. 9c), and the photogenerated charge carrier transfer process can be described as follows:
SnS₂ + hv $\rightarrow e_{CB}^- + h_{VB}^+$  \hspace{1cm} (10)
Sn₃O₄ + hv $\rightarrow e_{CB}^- + h_{VB}^+$  \hspace{1cm} (11)
SnS₂ ($e_{CB}^- + h_{VB}^+$) + Sn₃O₄ ($e_{CB}^- + h_{VB}^+$) $\rightarrow$ SnS₂ ($e_{CB}^-$) + Sn₃O₄ ($h_{VB}^+$)  \hspace{1cm} (12)
SnS₂ ($h_{VB}^+$) + Sn₃O₄ ($e_{CB}^-$) $\rightarrow$ Recombination  \hspace{1cm} (13)
Sn₃O₄ ($h_{VB}^+$) + OH⁻ $\rightarrow$ OH⁻ + H₂O  \hspace{1cm} (14)
SnS₂ ($e_{CB}^-$) + O₂ $\rightarrow$ SnS₂ + O₂⁻  \hspace{1cm} (15)
O₂⁻ + dye (aq) $\rightarrow$ CO₂ + H₂O  \hspace{1cm} (16)
OH⁻ + dye (aq) $\rightarrow$ CO₂ + H₂O  \hspace{1cm} (17)

Consequently conclusion can be drawn that the photo-degradation by Sn₃O₄/SnS₂ heterojunctions followed a direct Z-scheme mechanism, which not only promotes the separation efficiency of photogenerated electrons and holes but also shows a strong redox ability for antibiotic degradation.

Reactive oxygen species (ROS) scavenging studies

The influence of in-situ generated ROS in the reaction medium towards degradation of MB has been explored from some of the specific ROS scavenging action. The discussion in the previous section strongly indicated the role of superoxide radicals (O₂⁻) towards photocatalytic degradation of MB by the optimum performing batch of 0.07Sn₃O₄/SnS₂. In this pursuit, the hydroxide radicals (OH⁻) are expected to play important role. Apart from this, generation of superoxide radicals (O₂⁻) is relevant when photoexcited electrons are involved during photocatalytic process. In view of this photocatalytic degradation of MB by 0.07Sn₃O₄/SnS₂ NCs was monitored under optimized conditions in the presence of specific ROS scavengers, e.g. isopropyl alcohol (IPA, 1 mM) for scavenging OH⁻ radicals (Sharma et al. 2017); ammonium oxalate (AO, 1 mM) for scavenging h⁺ (Sharma and Dutta 2015); and chloroform (1 mM) for scavenging O₂⁻ (Mukherjee et al. 2021) radical, respectively. The ROS scavenging action was evident from the decrease in the rate of photocatalytic
degradation of MB (Fig. 8c). The most significant decrease in the rate of photocatalytic
degradation of MB was observed for the batch treated with chloroform, i.e., super oxide
radical scavenger (Table S5). This strongly suggested that the super oxide radical played very
important role in the photocatalytic degradation of MB by 0.07Sn₃O₄/SnS₂ photocatalyst.
Besides, the decrease in the rate of photocatalytic degradation of MB by 0.07Sn₃O₄/SnS₂ in
the presence of isopropyl alcohol (OH⁻ radicals scavenger) suggested that the photoexcited
holes were also involved in generating ROS in the reaction medium. The ROS scavenging
studies complimented the PL results of 0.07Sn₃O₄/SnS₂ regarding predominant generation of
super oxide radicals due to inhibition photoexcited charge carriers for the batch of
0.07Sn₃O₄/SnS₂ NC and consequential enhanced photocatalytic degradation of MB.

It may be concluded that Sn₃O₄/SnS₂ nanocomposites are excellent solar photocatalyst
which can be used for photoreduction of Cr (VI) and degradation of MB without any
exogenous oxidant, e.g., ozone or hydrogen peroxide. It also does not require any electricity
for operation. Further studies needs to be done to check its efficiency in real time tertiary
treatment in water treatment plants.

**Conclusion**

A novel photocatalyst, viz. Sn₃O₄/SnS₂ nanocomposite has been synthesized by a
simple two-step hydrothermal synthetic route, which exhibited enhanced photocatalytic
activity than its constituents towards photoreduction of hexavalent chromium Cr (VI) and
degradation of methylene blue (MB) under natural sunlight. The rate constant for
photocatalytic reduction and degradation of Cr (VI) and MB, respectively, by
0.07Sn₃O₄/SnS₂ were about five times higher than that of SnS₂ photocatalyst. The improved
rate constant has been discussed in the light of separation of the photogenerated charge
carriers owing to formation of a Z-scheme heterojunction and sustained release of reactive
oxygen species in the reaction medium. The photocatalytic degradation mechanism has been
addressed by analyzing the degradation product by UPLC-Q-ToF-MS and from total carbon content. The excellent chemical and photostability and re-usability of SnO$_2$/SnS$_2$ nanocomposite, makes it an efficient photocatalyst choice for the potential degradation of organic compounds in wastewater.

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**Authors contributions** Gandharve Kumar contributed to the study conception and design and experiments. R.K. Dutta supervised the work and prepared the manuscript.

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Table captions

Table 1. Summary of the photocatalytic reduction of Cr (VI) and photocatalytic degradation of methylene blue experiments carried out under optimized condition, i.e. photocatalyst and sunlight.

Figure Captions.

Fig. 1 XRD patterns of the as-synthesized batches of SnS$_2$ nanoparticles, Sn$_3$O$_4$ nanoflakes, 0.05Sn$_3$O$_4$/SnS$_2$ nanocomposite, 0.07Sn$_3$O$_4$/SnS$_2$ nanocomposite, and 0.10Sn$_3$O$_4$/SnS$_2$ nanocomposite.

Fig. 2 Low resolution transmission electron microscopy images of 0.07Sn$_3$O$_4$/SnS$_2$ (a-b); higher resolution transmission electron microscopy images of 0.07Sn$_3$O$_4$/SnS$_2$ (c); (d) selected area electron diffraction pattern of 0.07Sn$_3$O$_4$/SnS$_2$
**Fig. 3** Binding energy spectra of 0.07Sn\textsubscript{3}O\textsubscript{4}/SnS\textsubscript{2} nanocomposite obtained from X-ray photoelectron spectroscopy measurements of (a) survey spectrum; (b) Sn 3d; (c) S 2p; and (d) O 1s.

**Fig. 4** N\textsubscript{2} adsorption-desorption isotherms of pristine SnS\textsubscript{2} and 0.07Sn\textsubscript{3}O\textsubscript{4}/SnS\textsubscript{2} NCs (Inset represents the respective pore size distribution curves of pristine SnS\textsubscript{2} and 0.07Sn\textsubscript{3}O\textsubscript{4}/SnS\textsubscript{2} NCs).

**Fig. 5** Tauc’s plot of pristine Sn\textsubscript{3}O\textsubscript{4}, pristine SnS\textsubscript{2}, and Sn\textsubscript{3}O\textsubscript{4}/SnS\textsubscript{2} composites.

**Fig. 6** a) Dynamic curves of photocatalytic reduction of Cr( VI) by different photocatalysts under sunlight irradiation, b) pseudo first-order kinetic fitting of Cr (VI) reduction over different photocatalyst under sunlight irradiation, c) Dynamic curves of photocatalytic degradation of MB by different photocatalysts under sunlight irradiation, and d) pseudo first-order kinetic fitting of MB degradation over different photocatalyst under sunlight irradiation, under sunlight.

**Fig. 7** (a) Recyclability of the 0.07Sn\textsubscript{3}O\textsubscript{4}/SnS\textsubscript{2} NCs up to five photocatalytic reduction cycles; (b) X-ray diffraction pattern and (c) scanning electron microscopy image of the recycled photocatalyst.

**Fig. 8** a) Steady state room-temperature photoluminescence (PL) spectra, (b) electrochemical impedance spectra of SnS\textsubscript{2} and 0.07Sn\textsubscript{3}O\textsubscript{4}/SnS\textsubscript{2}, and, (c) Effect of reactive oxygen species scavengers on photocatalytic reduction of Cr (VI) by 0.07Sn\textsubscript{3}O\textsubscript{4}/SnS\textsubscript{2} nanocomposites under sunlight.

**Scheme 1** Schematic diagram of proposed MB degradation pathway by 0.07Sn\textsubscript{3}O\textsubscript{4}/SnS\textsubscript{2} NCS along with MS spectra of possible intermediate of MB photodegradation by 0.07Sn\textsubscript{3}O\textsubscript{4}/SnS\textsubscript{2}.

**Scheme 2.** Possible photocatalytic mechanism of Cr (VI) (a) and MB (b) on 0.07Sn\textsubscript{3}O\textsubscript{4}/SnS\textsubscript{2} nanocomposites
| Sample name   | % adsorption | % Reduction | 1st order kinetics Sunlight (Cr(VI)) | % adsorption | % Degradation | 1st order kinetics Sunlight (MB) |
|--------------|--------------|-------------|-------------------------------------|--------------|---------------|----------------------------------|
|              |              |             | Rate constant (min⁻¹) | R²           | Rate constant (min⁻¹) | R²     |
| 0.10Sn₃O₄/SnS₂ | 21%          | 89%         | 0.032                              | 0.994        | 33%           | 0.020                           | 0.989 |
| 0.07Sn₃O₄/SnS₂ | 17%          | 100%        | 0.066                              | 0.991        | 36%           | 0.043                           | 0.996 |
| 0.05Sn₃O₄/SnS₂ | 20%          | 90%         | 0.034                              | 0.993        | 30%           | 0.015                           | 0.990 |
| SnS₂          | 14%          | 66%         | 0.012                              | 0.995        | 13%           | 0.008                           | 0.991 |
| Sn₃O₄         | 15%          | 18%         | 0.0010                             | 0.974        | 11%           | 0.004                           | 0.970 |
| Blank         | NA           | 10%         | 0.002                              | 0.983        | NA            | 0.001                           | 0.975 |
Figures

Fig. 1.
Fig. 2.
Fig. 3.
Fig. 4.

[Graph showing adsorption quantity vs. relative pressure]

Fig. 5.

[Graph showing absorption coefficient squared vs. energy]

35
Fig. 6.
Fig. 7.
Fig. 8.
Scheme 1.
Scheme 2.
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