Importance of Clean Surfaces on the Catalyst: SnS₂ Nanorings for Environmental Remediation

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Supporting Information

ABSTRACT: The focus of the work is the synthesis of SnS₂ nanomaterials with (peg-SnS₂NF) and without (sf-SnS₂NR) the involvement of the organic template and the comparative study of their catalytic activities. The synthesis of these materials was achieved in a single-step procedure aided by hexamethyldisilazane (HMDS). These nanoparticles were subjected to X-ray diffraction, transmission electron microscopy, scanning electron microscopy, Raman spectroscopy, and UV–vis spectroscopy analyses to investigate their structural, topographical, surface, and optical properties. The present work suggests that the surfactant-free SnS₂ nanoring (sf-SnS₂NR) catalyst has lower surface area compared to the poly(ethylene glycol)-stabilized SnS₂ nanoflower (peg-SnS₂NF) catalyst but shows high activity under visible light for the photoreduction of Cr(VI) and the photocatalytic degradation of organic dyes. The work exposed the importance of the clean surfaces on the catalyst and is expected to have a high impact on the photocatalytic activity of the SnS₂ nanomaterial. The study also endorses the utility of the HMDS-assisted synthetic method for the production of multifunctional semiconductor tin disulfide nanomaterials with multiple potential applications.

INTRODUCTION

The scientific community is always working for the development of an efficient and economical method for the elimination of pollutants such as organic dye molecules and heavy metal ions from aqueous solutions. Among the heavy metal ions, especially hexavalent chromium compounds Cr(VI) are highly lethal, carcinogenic, and pollutants found recurrently in wastewater from industrial processes. Metal ions, especially, hexavalent chromium compounds are more attractive for potent technological applications. Multifunctional materials possessing more than one property and safe solar energy, reusability, and low cost. The focus of the work is the synthesis of SnS₂ nanomaterials with (peg-SnS₂NF) and without (sf-SnS₂NR) the involvement of the organic template and the comparative study of their catalytic activities. The synthesis of these materials was achieved in a single-step procedure aided by hexamethyldisilazane (HMDS). These nanoparticles were subjected to X-ray diffraction, transmission electron microscopy, scanning electron microscopy, Raman spectroscopy, and UV–vis spectroscopy analyses to investigate their structural, topographical, surface, and optical properties. The present work suggests that the surfactant-free SnS₂ nanoring (sf-SnS₂NR) catalyst has lower surface area compared to the poly(ethylene glycol)-stabilized SnS₂ nanoflower (peg-SnS₂NF) catalyst but shows high activity under visible light for the photoreduction of Cr(VI) and the photocatalytic degradation of organic dyes. The work exposed the importance of the clean surfaces on the catalyst and is expected to have a high impact on the photocatalytic activity of the SnS₂ nanomaterial. The study also endorses the utility of the HMDS-assisted synthetic method for the production of multifunctional semiconductor tin disulfide nanomaterials with multiple potential applications.

RESULTS AND DISCUSSION

Synthesis, Characterization, and Morphological Analysis. For the present study, we have synthesized SnS₂ nanostructures without any organic surfactant molecules.

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covering their surfaces as well as the particles with a known amount of polymer (PEG) covering the surfaces of the particles. Simple reactants/reagents were used to synthesize these materials by single-step procedures to minimize residuals and impurities (Scheme 1). The hexamethyldisilazane (HMDS)-assisted method yielded sf-SnS2NR where there were no surfactant molecules and yielded peg-SnS2NF where PEG was used in the reaction. In these reactions, the role of HMDS was multiple since it acted as the solvent, reducing agent and also provided surroundings like the capping agent during the reaction. In the presence of metal sources and thiourea, HMDS led to the formation of a polymeric network by preventing the aggregation of the nanostructures. After completion of the reaction, by applying high vacuum, HMDS was removed, and finally, SnS2 nanostructures were obtained. In these reactions, the HMDS molecules involved in the reaction but not a part of either source materials or the product, and therefore, the reaction was termed as the HMDS-assisted synthesis.

The typical X-ray diffraction patterns aided us to explore the structural properties of the as-synthesized SnS2 nanostructures (Figure 1a). The peaks were indexed according to JCPDS data card no. 23-0677, and the corresponding peaks confirmed the formation of the hexagonal structure of SnS2.18 No impurities were identified in the XRD pattern demonstrating the phase purity of nanostructures. The samples were further investigated by Raman spectra (Figure 1b) for the signature of vibrational modes of the SnS2 material. The spectra of both samples showed the strong characteristic peaks at 313.78 and 313.56 cm\(^{-1}\) for the sf-SnS2NR and peg-SnS2NF samples, respectively, which could be assigned to the A\(_{1g}\) mode of SnS2.19

Figure 2a displays optical absorption by SnS2 nanostructures within the UV and visible light spectra of wavelength ranging 250–700 nm. The absorption maximum of the materials was around 385 nm.20 The broad spectrum in the visible region suggested that both the SnS2 nanomaterials described here have the capability of harvesting visible light and hence can act as the photocatalyst while exposed to visible light. The band gap of both the SnS2 nanostructures by the Tauc method was found to be around 2.50 eV predicting its ability to work as the photocatalyst on irradiation of visible light. The band gaps
determined from DRS spectra recorded both the nanorings and nanoflowers were 2.55 and 2.45 eV, respectively.\textsuperscript{21}

The morphology of the resulting powdered sample from the reaction was analyzed by field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). The typical low-magnification FESEM image of the sf-SnS\textsubscript{2} (Figure 3a and Figure S1) revealed clearly that the sample has consisted of nanorings (sf-SnS\textsubscript{2}NR) with an average diameter of 50 nm. Further, a high-magnification FESEM image was recorded (Figure 3b), which highlighted the ring pattern of the sf-SnS\textsubscript{2}. The low- and high-magnification FESEM images of the as-synthesized peg-SnS\textsubscript{2} (Figure 3c,d, and Figure S1) showed the nanoflower (peg-SnS\textsubscript{2}NF) morphology with an average diameter of 100 nm. Even after the vigorous ultrasonic treatment, the hierarchical structures maintained their integrity showing the structural stability of the products.

Analysis by TEM also confirmed the formations of nanorings of the sf-SnS\textsubscript{2} and nanoflowers of peg-SnS\textsubscript{2} nanostructures (Figure 4 and Figure S3). A diffraction pattern (Figure 4c) consists of polycrystalline rings that can be indexed to the SnS\textsubscript{2} phase (standard diffraction file no. 23-0677). The rings were continuous and devoid of any separate bright spots indicating the crystalline nature of sf-SnS\textsubscript{2}NR. A diffraction pattern (Figure 4f) for peg-SnS\textsubscript{2}NF showed the amorphous ring pattern indicating that the PEG had indeed stabilized the SnS\textsubscript{2}NF.

The X-ray photoelectron spectroscopy (XPS) was recorded to conclude the chemical composition and bonding configuration of the as-synthesized materials. The XPS spectrum (Figure S) revealed the presence of Sn and S elements only, and no other elements like N or Si were noticed. These findings showed that as-synthesized materials were free from the surfactant on the surfaces of the catalyst. The obtained results were in consistent with the XRD and EDS results. Characteristic high-resolution XPS spectra of Sn 3d and S 2p are shown in Figure Sbc. The binding energies of Sn 3d\textsubscript{5/2} (487.66 eV), Sn 3d\textsubscript{3/2} (496.12 eV), and S 2p\textsubscript{3/2} (163.30 eV) in SnS\textsubscript{2} nanostructures were in agreement with the reported characteristic values of Sn\textsuperscript{4+} and S\textsuperscript{2−} in SnS\textsubscript{2}.

The broad band peak at 545 cm\textsuperscript{-1} in the FTIR spectrum of sf-SnS\textsubscript{2}NR was due to the vibration of Sn−S bands (Figure 6). The absence of any peak related to HMDS in the FTIR spectrum of Figure 6a confirmed the complete absence of the

![Figure 3](image3.png)

Figure 3. Morphological study of SnS\textsubscript{2} nanostructures. (a, b) FESEM micrographs of sf-SnS\textsubscript{2}NR. (c, d) FESEM micrographs of peg-SnS\textsubscript{2}NF.

![Figure 4](image4.png)

Figure 4. TEM data for the SnS\textsubscript{2} nanostructures: (a, b) sf-SnS\textsubscript{2}NR, (d, e) peg-SnS\textsubscript{2}NF, and (c, f) selected area diffraction pattern for both SnS\textsubscript{2} nanostructures.

![Figure 5](image5.png)

Figure 5. XPS spectrum of the as synthesized sf-SnS\textsubscript{2}NR for the elements: (a) survey spectrum, (b) Sn 3d, and (c) S 2p.

![Figure 6](image6.png)

Figure 6. FTIR spectra of the as synthesized SnS\textsubscript{2} nanostructures: (a) sf-SnS\textsubscript{2}NR and (b) peg-SnS\textsubscript{2}NF.
capping agent on the surfaces of SnS$_2$ nanorings. The presence of the signature of PEG (Figure 6b) in the FTIR spectrum confirmed that PEG has effectively worked as a surfactant to stabilize SnS$_2$NF.

The photocatalytic application is mainly dependent on surface contact, and hence, the surface area of the materials is an essential factor. We have determined the surface area by the nitrogen adsorption−desorption isotherm for both the SnS$_2$ nanostructures (Figure 7). It was observed clearly that both the materials were mesoporous, and the BET surface areas for sf-SnS$_2$NR and peg-SnS$_2$NF were 26.33 and 33.60 m$^2$/g, respectively. The surface area of the flower-like nanostructures was found to be higher than that of the ring-like nanostructure. This observation was quite the opposite of the catalytic activity performance (vide infra).

**Photoreduction of Cr(VI) to Cr(III).** The results displayed in Figure 8 elucidate the photocatalytic reduction of aqueous Cr(VI) (at pH 3) using sf-SnS$_2$ NR and peg-SnS$_2$ NF as catalysts under visible light irradiation. Few controlled reactions wherein (Figure S7) the direct photolysis (in the absence of catalyst) or catalysis (in the absence of light) alone could not drive the reduction of Cr(VI). Therefore, the reduction of aqueous Cr(VI) was the photocatalytically driven reaction completely rather than simple physical adsorption of Cr(VI). The formation of photoreduced product Cr(III) from the toxic Cr(VI) in all these reactions was confirmed by coordinating it with PDCA (Figure S8).

In the presence of the sf-SnS$_2$NR catalyst, the toxic Cr(VI) reduction happened swiftly with a reaction rate of 0.244 min$^{-1}$, approached 99% reduction, and reached the equilibrium in 10 min. While in the case of peg-SnS$_2$NF, a reaction rate of 0.0982 min$^{-1}$ was observed and approached only 84% reduction in 18 min. Hence, the sf-SnS$_2$NR acts as a more active photocatalyst for the reduction of Cr(VI) compared to photocatalysts in earlier reports (Table 1). Interestingly, in the case of catalytic decomposition of hydrogen peroxide, Zboril and co-workers also noticed high catalytic activity of iron(III) oxide nanoparticles having relatively lesser surface area. All these results supported our assumption clearly on the
importance of clean surfaces on catalysts rather than the larger surface area.

**Effect of Amount of Catalyst and Pollutant Cr(VI).** It was necessary to understand the catalyst loading parameters after the results above of stable and rapid photocatalytic activity of the sf-SnS$_2$NR toward the reduction of toxic Cr(VI). Therefore, the effect of the concentration of Cr(VI) and the amount of catalyst on the rate of the reaction were studied while keeping the other parameters constant. Figure 9 shows the reduction of Cr(VI) when the catalyst (sf-SnS$_2$NR) quantities were varied. The irradiation time required for the complete reduction of Cr(VI) decreased with increasing initial amount of SnS$_2$ photocatalyst. It was observed that $k_{app}$ depends on the concentration of the Cr(VI) solution and the amount of catalyst added. When the amount (between 0.15 and 0.60 g L$^{-1}$) of sf-SnS$_2$NR catalyst was varied, there was an incremental change in the photocatalytic performance. The rate constant of the reduction reaction had the linear relationship (from 0.01507 to 0.81122 min$^{-1}$) with the amount of catalyst dosage. The increase of the efficiencies of Cr(VI) reduction with the increase of the initial amount of SnS$_2$ can be ascribed to the increase in both absorbed light and the numbers of surface active sites. These results suggested that the photocatalytic activity of sf-SnS$_2$NR could be improved by increasing the amount of catalyst.

Furthermore, Figure 10 depicts the effect of initial concentration of Cr(VI) aqueous solution on the photocatalytic reduction of Cr(VI) while keeping the catalyst dosage (sf-SnS$_2$NR) constant. It was clear that the efficiencies of reduction of Cr(VI) in photocatalytic systems consisting of 100 and 200 mg L$^{-1}$ Cr(VI) were observed to be 99 and 81%, respectively. (Rate constants were 0.244 and 0.088 min$^{-1}$.) The decrease in the efficiencies of the reduction reaction with the increase of initial Cr(VI) concentration can be attributed to the following two aspects. First, since the reaction occurs on the surface of the photocatalyst, the limited surface active sites of the photocatalyst are not sufficient at higher Cr(VI) concentration. Second, Cr(VI) in a high concentration can absorb the visible light (420–480 nm), thus decreasing the proportion of light received by the SnS$_2$ photocatalyst.

**Effect of pH on Cr(VI) Reduction.** The effect of pH on the photocatalytic reduction of Cr(VI) in the presence of sf-SnS$_2$NR was examined by keeping the photocatalyst dosage constant and varying the initial pH from 3 to 5. It was noticed that the photocatalytic reduction of Cr(VI) was retarded with increased pH (Figure S4). There was a gradual decrease in the rate constant: 0.24475 min$^{-1}$ at pH 3 and 0.09406 min$^{-1}$ at pH 5. It was witnessed that the Cr(VI) reduction at low pH was much higher than that in a high pH condition. It was assumed that the increased dissolution of sf-SnS$_2$NR and along with lower concentration of H$^+$ in high pH was responsible for the decreased photocatalytic activity.

**Stability and Reusability.** The stability and reusability of any photocatalyst during the photocatalytic reaction are critical factors for its industrial usage. Therefore, it is necessary to study the stability of the as-synthesized sf-SnS$_2$NR in the photocatalytic reduction reactions involving aqueous Cr(VI). The recyclability of the catalyst for photocatalytic reduction of Cr(VI) is illustrated in Figure 8c. The performance of the sf-SnS$_2$NR photocatalyst did not show any significant loss up to 10 cycles. This revealed the durability of sf-SnS$_2$NR as the photocatalyst in the reduction of aqueous Cr(VI). While checking the reusability of both the SnS$_2$ nanostructures for 10 cycles, it was observed that there was only 5% efficiency loss for sf-SnS$_2$NR, whereas, in the case of peg-SnS$_2$NF, the efficiency loss was 5–10% (Figure 8c,d).

We have analyzed the catalyst after completion of the 10th cycle using SEM and EDX to identify the accumulation of Cr on the catalyst surface. There are no adsorbed chromium ions found over the catalyst surface (Figures S2 and S6). The XRD pattern of the materials was recorded after photocatalytic reduction, and no change in the XRD pattern occurs after the reduction process (Figure S5). It implies that the sf-SnS$_2$NR had high stability and did not corrode during the photocatalytic reduction of Cr(VI), which showed its potential applications for the treatment of polluted water.

**Morphology Effect and the Importance of Clean Surface on the Catalyst.** In the photocatalytic reduction of Cr(VI), the ring-like nanostructure was more efficient than nanoflower-like morphology (Figure 8). The rates of photocatalytic reduction of Cr(VI) by sf-SnS$_2$NR and peg-SnS$_2$NF were compared by varying the quantity of the catalysts (Figure 8).
9). In every case, the sf-SnS2NR showed superior photocatalytic activity than the peg-SnS2NF. The variance in the photocatalytic activity of both the SnS2 nanomaterials may be explained by the collective action of several factors. Except the specific surface area, almost all the factors were the same as revealed by the various characterization techniques, and it can be said that the difference in photocatalytic activity of SnS2 nanomaterials was influenced exclusively by a single parameter, that is, clean surfaces and morphology.

It is known that the adsorption and desorption of molecules on the surface of catalysts directly affect the photocatalytic process. Thus, the clean surfaces on the catalyst and relatively higher surface area of the porous sf-SnS2NR allowed more number of surface coordination sites exposed to the solution than the peg-SnS2NF. Moreover, the presence of clean surfaces on the catalyst surface helped more efficient transportation of the reactant molecules to the active sites and, thus, enhances the efficiency of photocatalysis. The low surface area and surfactant-free surfaces of the sf-SnS2NR make nanorings a better material for the photocatalytic reduction of Cr(VI) compared to the PEG-coated nanoflower, that is, peg-SnS2NF.

SnS2 having a central metal ion with the d10 configuration favors the separation of photogenerated charges due to the highly dispersive conduction band. Afterward, the capture photoexcited electron at the conduction band takes place. In this process, the separated electron involves in the reduction of Cr(VI) to generate Cr(III).34 As an evidence of the photoinduced interfacial charge transfer process, the photoluminescence (PL) and time-resolved photoluminescence (TRPL) of sf-SnS2NR were recorded and compared with those of peg-SnS2NF (Figure 11).

The sf-SnS2 NR showed a less intense PL peak compared to the peg-SnS2 NF (Figure 11a). This observation suggested that the interfacial charge transfer on sf-SnS2 NR inhibited the recombination of photoinduced charge carriers.35 Afterward, the time-resolved transient photoluminescence decay (TRPL) spectrum was recorded to understand this process (Figure 11b). The average lifetime (⟨τ⟩) of sf-SnS2 NR (1.30 ns) was found to be less than that of peg-SnS2NF (2.49 ns). This drop in the lifetime points to the effective carrier separation in clean surfaces of sf-SnS2NR. When the transient photocurrent responses are studied, the sf-SnS2NR showed a good response compared to the response of peg-SnS2NF (Figure S9). This phenomenon occurs because of the smooth transfer of generated electrons from the conduction band (CB) to the valence band (VB) of sf-SnS2NR, and this assumption was validated with the quenching of emission.

The clean surfaces remarkably enhanced the separation efficacy of photoinduced charge carriers on sf-SnS2 NR through the photoinduced interfacial charge transfer Figure 9. In the photocatalysis progression, the photogenerated holes were trapped by the hydroxyl groups (or H2O) on the surface to yield OH radicals. Meanwhile, the dissolved oxygen molecules react with electrons and yield superoxide radical anions, O2−, which on protonation generate the hydroperoxy, HO2 radicals. This radical forms the hydroxyl radical OH, which involves the decomposition of the organic dye. Altogether, the efficient charge separation on the clean surfaces affords the enhanced photocatalytic activities. Therefore, all
these findings undoubtedly express the importance of clean surfaces on catalysts to achieve high catalytic performance.36

**Photocatalytic Degradation of Dyes.** Apart from toxic Cr(VI) reduction reactions, the photocatalytic activity of the synthesized sf-SnS2NR was found to have practical application in the degradation of some water pollutants like organic dyes (RhB and MO). Figure 12 reveals the results of the degradation of RhB by visible light irradiation (sunlight) in the presence of the sf-SnS2NR. In the controlled reactions, no reaction happened in the absence of light and SnS2 catalyst samples, indicating the importance of the photocatalyst for the degradation of the dye (Figure S7). After addition of the photocatalyst, a rapid decrease in peak intensity was observed. The complete degradation of 60 mL of 5 mg L\(^{-1}\) RhB with 30 mg of sf-SnS2NR was observed in only 12 min. The apparent rate constant (\(k_{\text{app}}\)) calculated from the linear plot of \(\ln[A_t]/[A_0]\) versus time was found to be 0.1744 min\(^{-1}\). While in the case of peg-SnS2NF, it took nearly 36 min to degrade the dye,
and the rate constant \( (k_{\text{app}}) \) was calculated as 0.04695 min\(^{-1}\) (Figure 12a,b). The decrease in absorption intensity of RhB at \( \lambda_{\text{max}} \) with progression of the reaction time without any shift of the absorption wavelength suggested complete cleavage of the RhB chromophores.

The efficiency of the sf-SnS\(_2\)NR photocatalyst for the degradation of the MO dye was also tested (Figure 13). Exceptional efficiency was observed in the case of MO with a rate constant (calculated from the linear plot of \( \ln[A]/[A_0] \) vs time) of 0.06752 min\(^{-1}\) and dye degradation time of 30 min for 60 mL of 5 mg L\(^{-1}\) MO dye with 30 mg of sf-SnS\(_2\)NR (Figure 13a,b). While in the case of peg-SnS\(_2\)NF, it took nearly 48 min to degrade the dye, and the apparent rate constant \( (k_{\text{app}}) \) was calculated as 0.03313 min\(^{-1}\). In these cases, no noticeable degradation and no shift in peak positions were observed in the absence of the SnS\(_2\) catalyst under the same experimental conditions. Hence, we found that the sf-SnS\(_2\)NR is the best photocatalyst for the photocatalytic reactions.

The mechanism of photoreduction of Cr(VI) and degradation of pollutants like RhB and MO is illustrated in Figure 14. Due to the narrow band gap, the sf-SnS\(_2\)NR can be excited by sunlight efficiently to produce electron–hole pairs. Due to the availability of free and clean surfaces on the catalyst, the generated charges will quickly be promoted to the excited state. Simultaneously, the recombination of electron–hole pairs was suppressed owing to the direct oxidation of pollutants.

The catalysts were reused in the water purification to determine the durability of the photocatalyst. For this purpose, the reaction mixture was centrifuged after each run of the reactions to separate the catalyst. Then, the regenerated catalyst was reused with the fresh reactants in the subsequent cycle of the photocatalytic reaction under the same experimental conditions. The results showed that the sf-SnS\(_2\)NR could be used repeatedly for at least 10 times without significant deactivation. However, the peg-SnS\(_2\)NF displayed a gradual decrease in dye degradation after five cycles. The peg-SnS\(_2\)NF was not robust since it contained big-sized SnS\(_2\) nanoflowers that may perhaps be leached easily in the liquid phase reaction.

### CONCLUSIONS

By the simple wet chemical approach, surfactant-free SnS\(_2\) nanorings (sf-SnS\(_2\)NR) and PEG-stabilized SnS\(_2\) nanoflowers (peg-SnS\(_2\)NF) were prepared at gram scale. The developed semiconductor tin disulfide nanomaterials showed multiple potential applications, especially in photoreduction and photodegradation. It was emphasized that as-synthesized SnS\(_2\) nanostructures exhibited great photocatalytic activity in the reduction of carcinogenic Cr(VI) to nontoxic Cr(III) under ambient conditions. The SnS\(_2\) nanostructures efficiently degraded mutagenic dyes (MO and RhB) to nontoxic products in a shorter period. The improved photoactivities are ascribed to the effective charge transfer across the clean surfaces of the catalyst, as evidenced by the electron microscopic analyses and steady-state and time-resolved transient photoluminescence decay studies. In all cases, the reusability of the sf-SnS\(_2\)NR photocatalyst was excellent over many cycles.

The excellent photocatalytic behavior of SnS\(_2\) can be credited to the following factors. (i) The clean surfaces on the catalyst enhanced electron mobility in the nanorings. (ii) The specific 2D morphology of the ring structure also contributed to the efficient charge carrier separation in the material. Therefore, the present work provides new insight into developing photocatalysts with clean surfaces for the effective charge separation and photocatalytic remediation of pollutants from wastewater.

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**Figure 14.** Schematic representation of mechanism of the SnS\(_2\) photocatalyst.
and refluxed for 3 h to complete the reaction. After cooling, the obtained yellow particles were collected by centrifugation and washed with abundant deionized water and methanol to remove unreacted starting materials. Finally, the product was dried under vacuum at 120 °C for 3 h before further analysis.

**Synthesis of PEG-SnS$_2$ Nanoflowers (peg-SnS$_2$ NF).** To prepare peg-SnS$_2$NF, we followed the same experimental procedure as mentioned above. Additionally, poly(ethylene glycol) (PEG-400) (10 mL) was added to the reaction flask containing other reactants: tin and sulfur sources, (Table 2) and HMDS. After completion of the reaction, the resultant yellow powder was isolated and washed many times with deionized water (3 $\times$ 20 mL) followed by methanol (3 $\times$ 20 mL) repeatedly, separated by centrifugation, and dried at 120 °C for 3 h for analysis.

**Photocatalytic Activity. General Description of Photocatalytic Activity Test.** The photocatalytic activities of both sf-SnS$_2$NR and peg-SnS$_2$NF were assessed from the experiment of degradation/reduction of different pollutants. All of the photocatalytic tests were performed under standard conditions at room temperature with exposure to natural sunlight, which covered the entire wavelength distribution of the light in the visible region.

The photocatalyst (SnS$_2$ or peg-SnS$_2$; 30 mg) was added to 60 mL of either Rh-B (5 mg/L), MO (5 mg/L), or Cr(VI) (100 mg/L of pH 3) aqueous solution separately. Then, the reaction mixtures were stirred under dark for 1 h under the open environment at room temperature to ensure the formation of the adsorption–desorption equilibrium between the catalyst and reactants. Then, from the stock solution, 60 mL of suspension was positioned inside a beaker and irradiated with the sunlight. After regular intervals of time, 3 mL of a sample was taken and centrifuged at 3000 rpm to remove the catalyst. The concentrations of the reaction mixture in the supernatant solution were determined by recording absorption spectra. A gradual decrease in the characteristic absorption peak at 550 nm (Rh B), 450 nm (MO), and 350 nm (Cr(VI)) was noted, and each experiment was repeated twice. The reaction and degradation efficiency was calculated by using the following eq 1:

$$
\eta = \left( \frac{C_0 - C}{C_0} \right) \times 100\%
$$

(1)

The photocatalytic degradation rate of Cr(VI) and organic dyes followed the Langmuir–Hinshelwood eq 2

$$
\ln \left( \frac{C_0}{C} \right) = k_{\text{app}} t
$$

(2)

where $k_{\text{app}}$ is the apparent rate constant of the pseudo-first order, $t$ is the irradiation time, and $C_0$ and $C$ are the initial and instant residual concentrations of the Cr(VI), Rh B, and MO solution. Reduction and degradation experiments were carried out on a recycled SnS$_2$ sample to study the stability of the SnS$_2$ photocatalyst.

**Cr(VI) Reduction Test.** The photocatalytic reaction was performed at room temperature. In a beaker, 30 mg of photocatalyst and 60 mL of 100 mg L$^{-1}$ $K_2CrO_4$ aqueous solution (pH = 3) were stirred for a sufficient amount of time to reach the adsorption–desorption equilibrium. Then, it was exposed to sunlight to initiate the reaction.

To confirm the photocatalytic reduction of Cr(VI), we have performed few controlled reactions by following our previous article. The reduced product Cr(III) was confirmed by forming a metal complex with 2,6-pyridine dicarboxylic acid (PDCA). The controlled reactions were monitored by UV–vis spectra, and the results are displayed in Figure S8.

**Degradation of Organic Dyes.** The photocatalytic dye degradation experiments were performed by measuring the optical absorption of the organic pollutants. By determining the peak intensity of the dye against time in the presence of catalyst under visible light irradiation, the photocatalytic activity was studied. Thirty milligrams of sf-SnS$_2$NF or peg-SnS$_2$NF was utilized for the degradation of 60 mL of 5 mg L$^{-1}$ solutions of RhB and MO, respectively.

**Catalyst Reproducibility and Stability.** Initially, the stability of synthesized SnS$_2$ nanostructures was checked by execution of XRD studies on the samples stored up to 1 month. All the photocatalytic experiments were repeated several times by varying the amounts of catalyst and concentrations of the substrates. The reduction of Cr(VI) and dye degradation were carried out up to 10 times with the recycled SnS$_2$ catalyst to check the stability of the catalyst and reproducibility of the obtained results. After completion of each cycle, the photocatalyst was recovered by centrifugation, washed with 1 M nitric acid solution and deionized water to diminish the amount of Cr(III) deposited on the surface of the catalyst, and dried under vacuum at 60 °C for 4 h.

### Table 2. Reaction Conditions for the Synthesis of SnS$_2$ Diverse Nanoarchitectures

| SL no. | amount of tin source (g) | amount of sulfur source (g) | amount of HMDS (mL) | amount of PEG (mL) | morphology |
|--------|--------------------------|-----------------------------|---------------------|-------------------|------------|
| 1      | 0.2                      | 0.08                        | 5                   | 0                 | rings      |
| 2      | 0.2                      | 0.08                        | 5                   | 10                | flowers    |
| 3      | 0.2                      | 0.08                        | 0                   | 0                 | no reaction |

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01766.

- XRD pattern, FESEM and TEM images, pH effect on dichromate reduction, photoreduction of dichromate, degradation of organic dyes in the absence of catalyst, and proof of Cr(III) formation (PDF)

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**Notes**

The authors declare no competing financial interest.

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