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# Pioneering the design of S-scheme SnS<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> nanocomposites *via* sonochemical and physical mixing methods for solar degradation of cationic rhodamine B dye

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Since the advent of photocatalysis, various research studies have been devoted to exploring novel high-performance photocatalysts for converting solar energy into chemical energy. However, the employment of natural solar radiation in the degradation of organic pollutants has not been attained until now. This novel research work recorded the employment of natural solar illumination in degrading rhodamine B [RhB] dye on the surface of S-scheme SnS<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> heterojunctions. SnS<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> heterojunctions containing different rational compositions of g-C<sub>3</sub>N<sub>4</sub> and SnS<sub>2</sub> nanoparticles were synthesized *via* sonochemical and physical mixing approaches. Sonochemistry is a novel approach with multiple applications and is of significant importance since ultrasonic waves form acoustic cavitation in solutions, enhancing chemical activity with remarkable economic value. The textural, optical and nanostructural properties of the heterojunctions were investigated through diffuse reflectance spectroscopy [DRS], high-resolution transmission electron microscopy [HRTEM], photoluminescence [PL], N<sub>2</sub>-adsorption-desorption isotherms, scanning electron microscopy [SEM], energy dispersive X-ray spectroscopy [EDX], X-ray diffraction [XRD], electrochemical impedance spectroscopy [EIS] and X-ray photoelectron spectroscopy [XPS]. The diffraction results from XRD, HRTEM and SAED analyses revealed remarkable distortion in the crystalline properties of g-C<sub>3</sub>N<sub>4</sub> upon the introduction of SnS<sub>2</sub> nanoparticles, implying a strong chemical interaction between SnS<sub>2</sub> nanoparticles and g-C<sub>3</sub>N<sub>4</sub> sheets, which manifested the construction of an effective heterojunction. Homogeneous deposition of SnS<sub>2</sub> nanoparticles on g-C<sub>3</sub>N<sub>4</sub> sheets was achieved through a sonochemical route. However, SnS<sub>2</sub> nanoparticle agglomeration was recorded on g-C<sub>3</sub>N<sub>4</sub> sheets synthesized by means of a physical mixing process. Photocatalytic experimental results revealed the degradation of 34% of RhB dye on g-C<sub>3</sub>N<sub>4</sub> sheets due to the limited absorption of natural solar radiation and the fast and uncontrolled electrostatic forces between electron-hole pairs. By incorporating 5, 10, 15 and 20 wt% SnS<sub>2</sub> nanoparticles in the ultrasonic bath on g-C<sub>3</sub>N<sub>4</sub> sheets, the amount of RhB dye discharge was raised to 51, 78, 98 and 69%, respectively, during two hours of sunlight illumination. Alternatively, only 55% of RhB dye was decomposed on the surface of CNSnS15 synthesized through the physical mixing route. Hydroxyl radicals played a crucial role in the degradation of RhB dye, as proved by the PL of terephthalic acid and scavenger trapping experiments. The charge transport mechanism followed the S-scheme mechanism, as elucidated from scavenger trapping experiments. The novel as-synthesized sonicated SnS<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> nanocomposite is considered a promising photocatalyst in degrading organic pollutants under low-cost natural solar radiation.

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## 1. Introduction

The discharge of toxic organic dyes from textile and food industries pollute water resources, posing serious threats to human health and aquatic life.<sup>1–5</sup> The complex chemical nature of antibiotics, dyes and pesticides resists their decomposition *via* traditional routes.<sup>5–10</sup> Electrochemical methods, coagulation, reverse osmosis, ion exchange and adsorption have failed

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to mitigate these toxic organic pollutants. Photocatalysis green technology has been used to degrade organic pollutants into eco-friendly species on the surface of semiconductors under solar energy.<sup>11–15</sup> MnO<sub>2</sub>, ZnS, TiO<sub>2</sub>, Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>, MoO<sub>3</sub>, CeO<sub>2</sub> and ZnO recorded strong photocatalytic reactivity in the fragmentation of organic pollutants under UV radiation.<sup>16–20</sup> However, the ultrafast Coulombic attraction force between electron–hole pairs and the poor absorbability of solar radiation reduces the efficiency of the photocatalytic process. Recently, more focus has been paid to metal-free g-C<sub>3</sub>N<sub>4</sub> sheets as a low-cost, valuable photocatalyst for solving water and energy crises. The strong chemical stability due to the conjugated system, biocompatibility, low toxicity and cost-effectiveness of g-C<sub>3</sub>N<sub>4</sub> has attracted the attention of various researchers in recent years.<sup>21–28</sup> Various investigations have been devoted to verify the photocatalytic reactivity of g-C<sub>3</sub>N<sub>4</sub> in the degradation of different organic wastes.<sup>11</sup> The experimental results revealed that g-C<sub>3</sub>N<sub>4</sub> cannot meet the practical applications in breaking down the organic pollutants due to the low tendency to capture solar radiation, low quantum efficiency, fast Coulombic recombination rate and poor oxidative efficiency of the positive holes. Several tactics were devoted to overcoming the shortcomings of g-C<sub>3</sub>N<sub>4</sub>, such as coupling with strong oxidative semiconductors to enhance the oxidative power of the heterojunction and concentrating on the production of photoinduced charge carriers. SnS<sub>2</sub> nanoparticles with narrow band gap energy, good thermal stability, non-toxicity and broad spectral response are considered novel visible light-driven photocatalysts.<sup>29–32</sup> Thi *et al.* synthesized SnS<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> by direct calcination method for photocatalytic mitigation of rhodamine B dye.<sup>33</sup> During the synthesis, g-C<sub>3</sub>N<sub>4</sub> played a buffer role in exfoliating SnS<sub>2</sub>, whereas SnS<sub>2</sub> accelerated the destruction of g-C<sub>3</sub>N<sub>4</sub> at high temperatures, resulting in an N-deficiency form with enhanced charge transport. The experimental results implied that SnS<sub>2</sub> enhanced the absorbability and the photocatalytic performance.<sup>33</sup> Liu *et al.* synthesized SnS<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> by ion exchange for the successful photocatalytic degradation of methyl orange dye.<sup>34</sup> The corresponding photocatalytic power was attributed to the role of SnS<sub>2</sub> in limiting the electron–hole recombination of g-C<sub>3</sub>N<sub>4</sub> sheets. Hydrothermal synthesis of SnS<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> was carried out by Gao *et al.* for expelling methyl orange dye under visible light. The results implied the degradation of 93% of methyl orange dye (MO), which referred to Z-scheme nanocomposite production with appropriate charge carrier separation and transportation.<sup>35</sup> The experimental results implied that SnS<sub>2</sub> increased the concentration of the charge carriers by controlling the electron–hole recombination rate. Shyagathur *et al.* recorded that only 55% of methylene blue dye was degraded on SnS<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>, prepared using the hydrothermal method, due to the weak charge transport and separation of the charge carriers.<sup>36</sup> Shyagathur *et al.* noticed that mixing RGO with SnS<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> was the main requirement for enhancing the degradation of methylene blue due to the role of RGO in enhancing the charge diffusion between SnS<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> semiconductors.<sup>36</sup> Cheng *et al.* synthesized SnS<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> by solvothermal method to degrade rhodamine B dye besides photocatalytic hydrogen production.<sup>37</sup> The experimental results implied the strong efficiency of the as-synthesized samples in the photocatalytic process,

which is attributed to the enhanced transport and separation of the photogenerated electron–hole pairs. Song *et al.* synthesized g-C<sub>3</sub>N<sub>4</sub>/SnS<sub>2</sub> van der Waals heterojunctions by embedding SnS<sub>2</sub> crystals in thin g-C<sub>3</sub>N<sub>4</sub> nanosheets to enhance the hydrogen evolution and the degradation of organic pollutants. The photocatalytic performance was evaluated, showing that the g-C<sub>3</sub>N<sub>4</sub>/SnS<sub>2</sub> heterojunctions demonstrated outstanding 2,4-dichlorophenol (2,4-DCP) photo-oxidation and Cr(vi) photoreduction capabilities simultaneously. Under visible light irradiation for 2 hours, 85% of Cr(vi) and 94% of 2,4-DCP were eliminated in the mixed solution. Furthermore, the hydrogen evolution rate increased to approximately 6.58 times that of g-C<sub>3</sub>N<sub>4</sub>.<sup>38</sup> Zhu *et al.* successfully synthesized ultrafine SnS<sub>2</sub> supported on a porous g-C<sub>3</sub>N<sub>4</sub> sheet (SnS<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>) 0D/2D heterojunction adopting a solvothermal process to degrade rhodamine B (RhB) under visible light. The photodegradation efficiency reached 96.8% after 105 minutes of irradiation, with a reaction rate constant (*k*) of 3.3% min<sup>-1</sup>, showing 8.25 and 8.05 times enhancement compared to pure g-C<sub>3</sub>N<sub>4</sub> and SnS<sub>2</sub>, respectively. Furthermore, trapping experiments confirmed that the superoxide radicals and holes (h<sup>+</sup>) are the primary active species in this photocatalytic system.<sup>39</sup> Tamilarasu *et al.* developed MoS<sub>2</sub>–SnS<sub>2</sub>@g-C<sub>3</sub>N<sub>4</sub> catalysis *via* the conventional hydrothermal method. The degradation efficiency of the synthesized samples was assessed using methylene blue dye. The photodegradation efficiency reached 86.6% after 90 minutes of irradiation.<sup>40</sup> Alnahdi *et al.* prepared 3DF-SnS<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> photocatalysts using a simple solvothermal method. The photocatalytic performance was evaluated by following the decomposition of rhodamine B [RhB] dye. Compared to other nanohybrids in the study, the optimized 3DF-SnS<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> structure showed excellent efficiency in degrading 90.15% RhB dye.<sup>41</sup> Thanh *et al.* successfully fabricated SnS<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> composites with SnS<sub>2</sub> nanosheets on a porous g-C<sub>3</sub>N<sub>4</sub> substrate. The composites exhibited superior rhodamine B [RhB] photodegradation compared to pure SnS<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub>, achieving a maximum removal efficiency of 92.22% after 6 hours of light irradiation.<sup>42</sup> Fan *et al.* successfully synthesized g-C<sub>3</sub>N<sub>4</sub>/Ag<sub>2</sub>S/SnS<sub>2</sub> with Ag<sub>2</sub>S quantum dots as electron mediators through the ion exchange process and self-peeling of sheets of g-C<sub>3</sub>N<sub>4</sub>. Compared with the pristine materials, the photocatalyst g-C<sub>3</sub>N<sub>4</sub>/Ag<sub>2</sub>S/SnS<sub>2</sub> demonstrated significantly enhanced photocatalytic performance under visible light exposure.<sup>43</sup> Liu *et al.* synthesized g-C<sub>3</sub>N<sub>4</sub>/SnS<sub>2</sub> nanocomposites to eliminate hexavalent uranium (U(vi)). Two-dimensional (2D) hexagonal SnS<sub>2</sub> nanosheets were incorporated to enhance the absorbability of the nanocomposites. Notably, during the photocatalytic test under sunlight, the U(vi) removal rate using 0.08-SnCN reached 90% within 2 hours. The findings of the experimental results suggested that U(vi) was reduced by superoxide radicals.<sup>44</sup> All the previous research studies were concentrated on the synthesis of SnS<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> nanocomposite through hydrothermal, solvothermal, ion exchange and co-precipitation routes that consumed huge amounts of energy and accompanied by poor distribution of SnS<sub>2</sub> on g-C<sub>3</sub>N<sub>4</sub> sheets.<sup>33–38</sup> A drawback of the traditional synthesis method is the long duration of synthesis, which is due to the time taken to attain homogeneity in temperature using autoclaves and conventional



heating systems. Therefore, there is a great need to fabricate novel photocatalysts by applying ultrasonic waves generated in the ultrasonic bath to act as an energy supplier for depositing nanoparticles on  $g\text{-C}_3\text{N}_4$  sheets. The sonochemical process is a clean and efficient synthesis route that prohibits the reaction with a huge amount of energy for accelerating the reactant molecules to hybridize with each other and produce effective heterojunctions. Sonochemistry is responsible for the production of hotspots that generate extraordinary materials with manipulated morphologies and structures. Ultrasound is a longitudinal wave type with a high frequency of 20 kHz, surpassing the upper human auditory perception limit.<sup>45</sup> Air cavities, shock waves and air bubbles are produced in the sonochemical bath to prevent the transfer of excessive energy

to the reaction medium. The reaction occurs inside the bubble among the chemical precursors. The emerged bubbles undergo rapid and excessive expansion, causing their size to increase dramatically compared to the equilibrium radius, followed by eventual collapse. Upon collapse, the stored concentrated energy within the bubble is rapidly released in a short time, resulting in around 5000 K extremely localized and transient temperatures and nearly 1000 bar pressures, according to the thermal "hot spot" theory.<sup>45</sup> These features usually generate the heterojunction by homogeneous dispersion of the guest materials on the sheets of  $g\text{-C}_3\text{N}_4$ . Compared with conventional methods, ultrasound-assisted methods are valuable in accelerating chemical reactions, generating a new phase and influencing the structure and surface of the synthesized particles

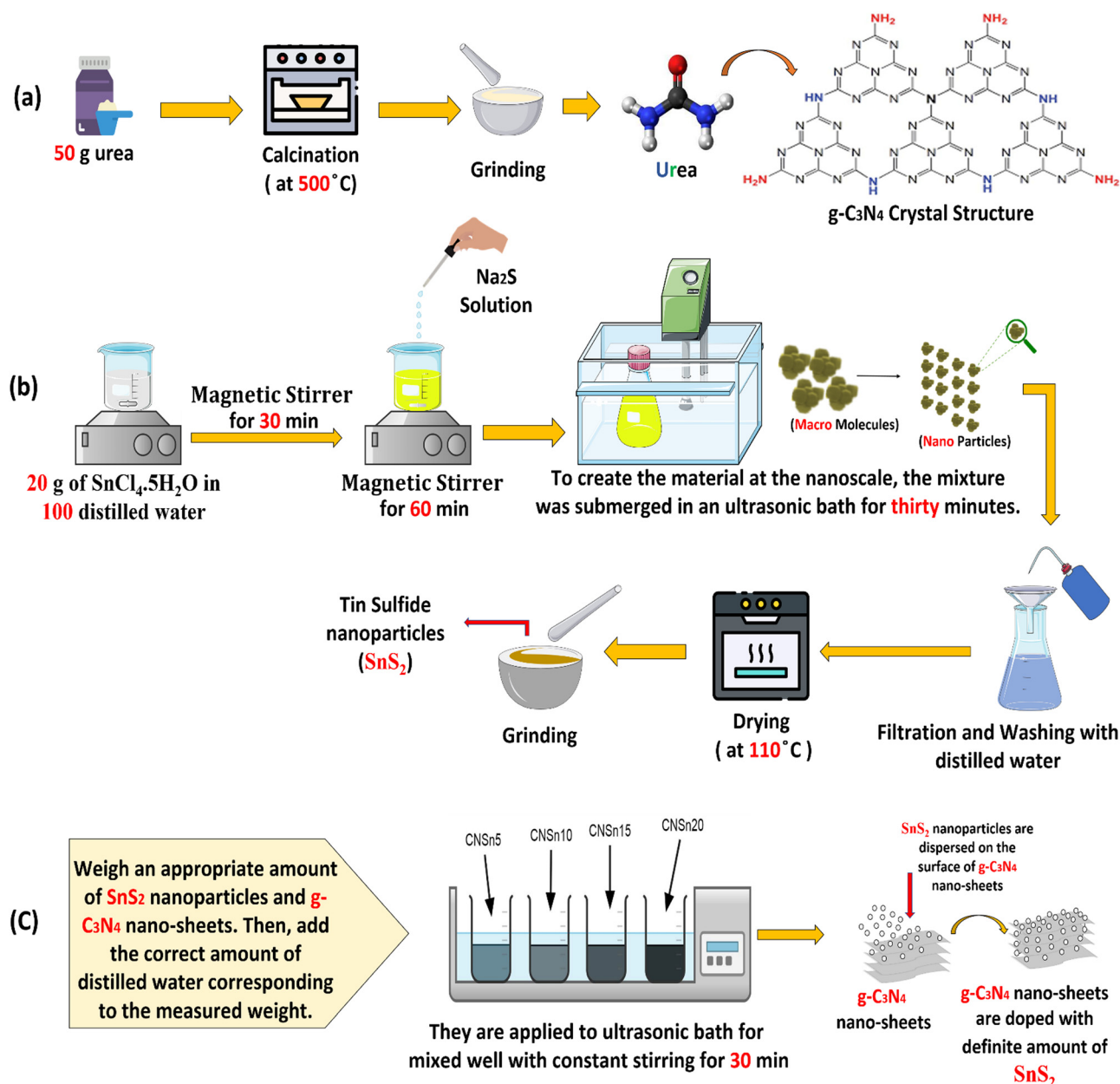


Fig. 1 Scheme for the synthesis of (a)  $g\text{-C}_3\text{N}_4$ , (b)  $\text{SnS}_2$  and (c)  $\text{SnS}_2/g\text{-C}_3\text{N}_4$  nanocomposites.



through acoustic cavitation. Moreover, the photocatalytic performance of  $\text{SnS}_2/\text{g-C}_3\text{N}_4$  nanocomposites in expelling organic dyes was investigated by previous researchers under UV and visible light radiations, which constitute only 50% of the natural sunlight radiation. However, the employment of natural solar radiation with strong power [600–1200] W to expel various organic pollutants on  $\text{SnS}_2/\text{g-C}_3\text{N}_4$  nanocomposite containing various proportions of photothermal  $\text{SnS}_2$  photocatalyst has not been studied until now. In this novel research, a successful manipulation of S-scheme  $\text{SnS}_2/\text{g-C}_3\text{N}_4$  heterojunctions embedded in various concentrations of  $\text{SnS}_2$  and  $\text{g-C}_3\text{N}_4$  was carried out. The surface investigation and the morphological changes are investigated by EDX, XRD, XPS, SEM, Mapping, DRS, HRTEM, PL and  $\text{N}_2$ -adsorption-desorption developed techniques. The photocatalytic power of hybrid  $\text{SnS}_2/\text{g-C}_3\text{N}_4$  heterojunctions was detected by following the fragmentation of RhB dye under natural solar radiation of 1000 W power. The experimental results for photocatalytic degradation of rhodamine B dye on the optimum sample CNSn15 heterojunction synthesized by the sonochemical and physical mixing processes were compared to give a clear clue on the effect of preparation mode on the efficiency of the photocatalyst. S-scheme charge diffusion was suggested to record the electron-hole transfer mechanism based on the results of trapping experiments and terephthalic PL analysis. The novel  $\text{SnS}_2/\text{g-C}_3\text{N}_4$  heterojunction could be considered a successful photocatalyst for utilizing natural solar radiation in the degradation of various organic pollutants dispersed in wastewater.

## 2. Experimental research work

### 2.1. Material

The reagents and solvents utilized in this study are all of analytical grade, and they were all used exactly as supplied. We obtained pure ammonia solution ( $\text{NH}_4\text{OH}$ ) ( $M_{\text{wt}} = 17.031 \text{ g mol}^{-1}$ ,  $\geq 25\%$ ), ammonium oxalate ( $(\text{NH}_4)_2\text{C}_2\text{O}_4$ ) ( $M_{\text{wt}} = 124.01 \text{ g mol}^{-1}$ ,  $\geq 99\%$ ), urea ( $M_{\text{wt}} = 60.06 \text{ g mol}^{-1}$ ,  $\geq 99\%$ ), sodium sulfide ( $\text{Na}_2\text{S}$ ), benzoquinone ( $\text{C}_6\text{H}_4\text{O}_2$ ) ( $M_{\text{wt}} = 108.09 \text{ g mol}^{-1}$ ,  $\geq 99\%$ ), tin(IV) chloride ( $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ ), terephthalic acid ( $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$ ) ( $M_{\text{wt}} = 166.13 \text{ g mol}^{-1}$ ,  $\geq 99\%$ ), and isopropanol ( $\text{C}_3\text{H}_8\text{O}$ ) ( $M_{\text{wt}} = 60.096 \text{ g mol}^{-1}$ ,  $\geq 99\%$ ) from Fluka Company.

### 2.2. Preparation of pristine materials and heterojunctions

**2.2.1 Preparation of  $\text{g-C}_3\text{N}_4$  sheets.** Microcrystalline highly purified urea (100 g) was exposed to heating in a porcelain reactor under air flow from room temperature to  $540^\circ\text{C}$  by fixed and low rate process [Fig. 1a]. The reactor was calcined at  $540^\circ\text{C}$  for five hours for complete condensation of urea and evolution of ammonia gas. The reactor was left under ambient conditions for 24 hours in the closed muffle for slow cooling. Spongy  $\text{g-C}_3\text{N}_4$  sheets were generated with muff color in the porcelain mortar. Finally, a mild grinding of the resultant solid specimen was carefully carried out to prevent the deterioration of the sample.

**2.2.2. Preparation of  $\text{SnS}_2$  semiconductor.**  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  (27 g) was dissolved in freshly prepared bi-distilled water with

constant stirring for 50 minutes. A solution of sodium sulfide dissolved in bi-distilled water was added to the stannic chloride solution drop by drop till the formation of a black precipitate of  $\text{SnS}_2$  [Fig. 1b]. The black precipitate was irradiated sonochemically for 40 minutes in a 200 W ultrasonic bath. Then, the sonicated  $\text{SnS}_2$  was collected by filtration, followed by washing with bi-distilled water to remove any foreign materials. Finally, the solid specimen was dried at  $115^\circ\text{C}$  for eight hours.

**2.2.3. Preparation of  $\text{SnS}_2/\text{g-C}_3\text{N}_4$  by sonochemical route.** A stoichiometric amount of pristine  $\text{SnS}_2$  and  $\text{g-C}_3\text{N}_4$  sheets distributed in bi-distilled water were coupled in an ultrasonic bath of 200 W power for 50 min for obtaining 5, 10 and 15 wt% of  $\text{SnS}_2/\text{g-C}_3\text{N}_4$  [Fig. 1c]. Then, each of the sonicated mixtures was filtered and purified extensively with distilled water. The above mixtures were dried at  $110^\circ\text{C}$  for 24 hours. The photocatalysts were denoted as  $\text{g-C}_3\text{N}_4$ ,  $\text{SnS}_2$ , CNSn5, CNSn10, CNSn15 and CNSn20 for pristine  $\text{g-C}_3\text{N}_4$ ,  $\text{SnS}_2$  and the solid samples embedded 5, 10, 15 and 20 wt%  $\text{SnS}_2$ , respectively.

**2.2.4. Preparation of  $\text{SnS}_2/\text{g-C}_3\text{N}_4$  by physical mixing method.**  $\text{SnS}_2$  nanoparticles (0.15 g) and 0.85 g of  $\text{g-C}_3\text{N}_4$  were mixed together in porcelain mortar and ground. After a while, the mixture is subjected to a vortex shaker for 30 min to ensure the homogeneity of the as-synthesized heterojunction. Finally, the solid specimens were subjected to drying at  $100^\circ\text{C}$  overnight to obtain 15 wt%  $\text{SnS}_2$  deposited on  $\text{g-C}_3\text{N}_4$  by the physical mixing process.

### 2.3. Characterization techniques

PAnalytical X'PERT MPD diffractometer analyzed the remarked features of the as-synthesized pristine materials and the nanocomposites with  $2\theta$  values varied from  $10$ – $70^\circ$ . The experimental adsorption isotherms were evaluated to investigate the textural properties and detect the surface area. The particle configuration was evaluated with HRTEM [JOEL]. The electronic structure and the elemental composition were verified by

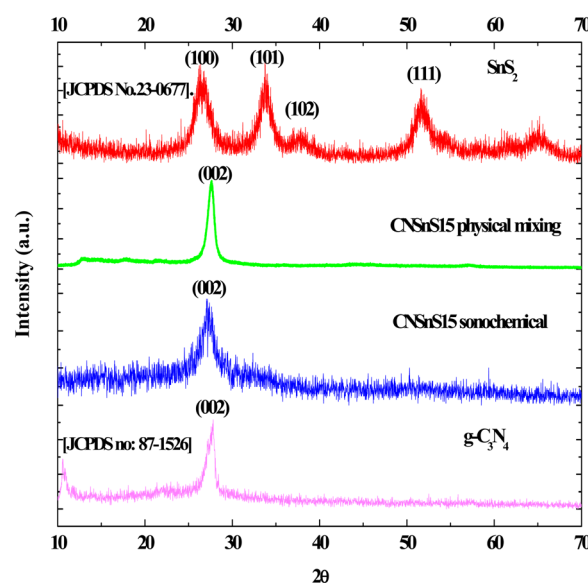


Fig. 2 XRD of  $\text{g-C}_3\text{N}_4$ ,  $\text{SnS}_2$  and CNSn15 prepared via the sonochemical method and CNSn15 prepared via physical mixing.



Thermo Fisher Scientific XPS. DRS curves were constructed by a JASCO spectrometer (V-570) for band energy structure estimation. The photoluminescence of the solid sample was estimated using a Thermo Fischer technique for predicting the charge carrier separation efficiency. The photocatalytic degradation of RhB dye under natural sunlight radiation was carried out to record the heterojunction photocatalytic performance for the nanocomposite-embedded definite compositions of SnS<sub>2</sub>. The extent of adsorption of the solid samples was determined under dark conditions by directing 100 ml of  $2 \times 10^{-5}$  M RhB dye to 0.05 g of the photocatalyst under dark conditions for 60 minutes. Then, the mixture of the solid-dye solution was irradiated with natural solar radiation of 1000 W power for 120 minutes. Stoichiometric proportions of the dye-photocatalyst mixture were taken off at definite interval times to analyze the remainder

concentration of the RhB dye solution using spectrophotometer progress. Isopropanol, benzoquinone and ammonium oxalate are three types of scavengers of concentration  $1 \times 10^{-3}$  M, which were added separately to the mixture of dye solution and photocatalyst under the same reaction parameters to monitor the nature of reactive species responsible for the redox reaction. PL spectrum of alkaline terephthalic acid solution was recorded to identify the nature and concentration of the hydroxyl radicals.

### 3. The experimental results

#### 3.1. Physical properties

The crystalline properties of the pristine g-C<sub>3</sub>N<sub>4</sub>, SnS<sub>2</sub> and CNSnS15 heterojunction prepared by sonochemical and

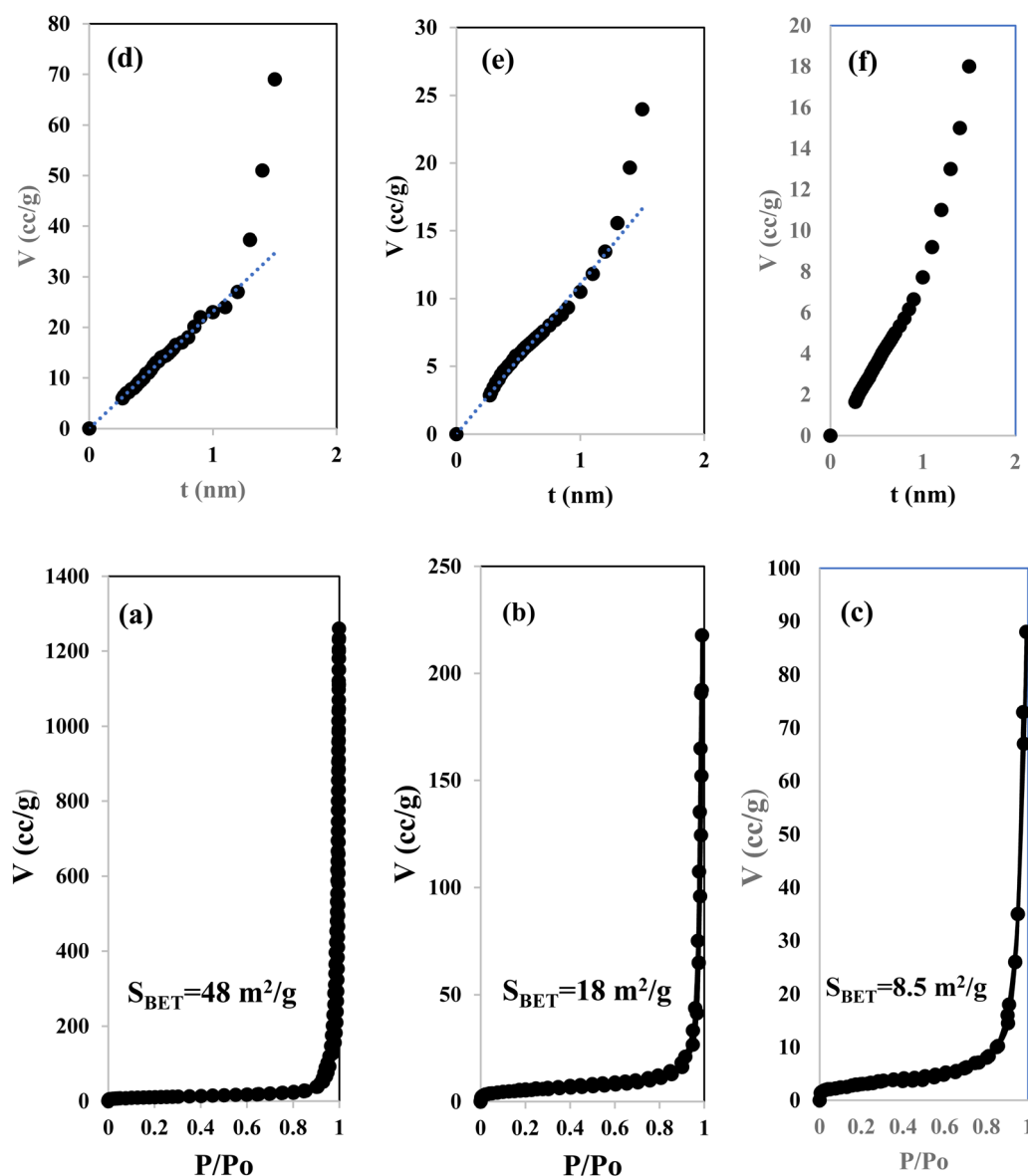


Fig. 3  $N_2$ -adsorption isotherms of (a) g-C<sub>3</sub>N<sub>4</sub> and (b) CNSnS15 synthesized via the sonochemical route and (c) CNSnS15 synthesized via physical mixing.  $V_a$ - $t$  plot for (d) g-C<sub>3</sub>N<sub>4</sub> and (e) CNSnS15 synthesized via the sonochemical route and (f) CNSnS15 synthesized via physical mixing.



physical mixing methods were determined by XRD [Fig. 2]. XRD pattern of  $g\text{-C}_3\text{N}_4$  showed diffraction peaks at  $2\theta = 27.18$  and  $13.08$ , which ascribed to (002) and (100) planes of orthorhombic phase [JCPDS no: 87-1526]. On the other hand, the XRD pattern of  $\text{SnS}_2$  showed diffraction peaks at  $2\theta = 28.2$ ,  $32.4$  and  $52^\circ$  referred to (100), (101) and (102) planes of the hexagonal structure with the  $P\bar{3}m1$  space group [JCPDS No. 23-0677]. XRD pattern of CNSnS15 prepared by sonochemical and physical mixing methods showed the main diffraction pattern of the (002) plane of  $g\text{-C}_3\text{N}_4$  sheets and (011) plane of  $\text{SnS}_2$ , implying the successful heterojunction generation. The peak intensity of the (002) plane of orthorhombic  $g\text{-C}_3\text{N}_4$  reduced with deposition of 15 wt% of  $\text{SnS}_2$  on the  $g\text{-C}_3\text{N}_4$  surface. However, the (001) plane of orthorhombic  $g\text{-C}_3\text{N}_4$  completely disappeared. The remarkable shift in the diffraction peak positions of  $g\text{-C}_3\text{N}_4$  to a low diffraction angle was recorded, revealing the damage in the crystalline structure of  $g\text{-C}_3\text{N}_4$  sheets by introducing  $\text{SnS}_2$  nanoparticles as a result of the simultaneous coupling between  $\text{SnS}_2$  nanoparticles and  $g\text{-C}_3\text{N}_4$  sheets for constructing an effective  $\text{SnS}_2/g\text{-C}_3\text{N}_4$  heterojunction [Fig. 2]. The crystalline size estimated by the Debye Scherrer equation from the most intense peak is 27, 9.1, 11.4 and 22.8 for  $g\text{-C}_3\text{N}_4$ ,  $\text{SnS}_2$ , and CNSnS15 prepared by sonochemical and physical mixing processes, respectively. The peak intensity of  $g\text{-C}_3\text{N}_4$  sheets and  $\text{SnS}_2$  are strongly decremented in the heterojunction with the incorporation of 15 wt%  $\text{SnS}_2$ , which was ascribed to coupling  $g\text{-C}_3\text{N}_4$  and  $\text{SnS}_2$  under the sonochemical condition. It is well known that the waves, air bubbles, shocks and air cavities generated in the ultrasonic bath with high frequency break down large agglomerates into particles in nanodimensions. Recent experimental studies revealed that the incorporation of  $\text{SnS}_2$  on  $g\text{-C}_3\text{N}_4$  shifted the peak position to a small angle, implying the strong chemical interaction between  $\text{SnS}_2$  and  $g\text{-C}_3\text{N}_4$  sheets<sup>32–34</sup>

Fig. 3 illustrates the physisorption isotherms of nitrogen gas at 77 K on pristine  $g\text{-C}_3\text{N}_4$  and CNSnS15 heterojunction synthesized by sonochemical and physical mixing processes. The adsorption isotherms of the as-synthesized samples are classified as type II isotherms, which refer to the non-porous solid structure [Fig. 3a–c]. The surface area of  $g\text{-C}_3\text{N}_4$  and CNSnS15 prepared by sonochemical and physical mixing methods evaluated from the BET equation was 48, 18 and  $8.4 \text{ m}^2 \text{ g}^{-1}$ , respectively. The surface area measurements revealed a depression in 60%  $g\text{-C}_3\text{N}_4$  surface area of the solid sample prepared by the sonochemical route, which implied that the strong adhesion of  $\text{SnS}_2$  nanoparticles on  $g\text{-C}_3\text{N}_4$  sheets decremented the surface area available to adsorb  $\text{N}_2$  gas that was further proved by HRTEM analysis. However, a drastic depression in the surface area of  $g\text{-C}_3\text{N}_4$  by 80% for the sample prepared by the physical mixing method revealed the agglomeration of  $\text{SnS}_2$  nanoparticles on  $g\text{-C}_3\text{N}_4$  sheets. Although the adsorption-desorption isotherm is completely reversible, the corresponding  $V_a-t$  plot indicated that the solid specimens are porous where an upward deviation is taking place in the three cases [Fig. 3d–f]. The absence of a hysteresis loop from these isotherms showed that no capillary condensation was taking place, a characteristic related to

macro- or non-porous solids; however, the upward deviation in the  $V_a-t$  plots indicated the presence of pores that fall in the mesoporous range. This phenomenon is interpreted as reversible capillary condensation controlled by the size (wide micro and narrow mesopores) and the shape (cones and wedges) of the pores. This reversible capillary condensation in the  $\text{N}_2$  adsorption process followed the same mechanism on desorption, making the adsorption isotherm free of any hysteresis. SEM defined the morphology of the heterojunction, which clarifies the dispersion of  $\text{SnS}_2$  nanoparticles with large amounts on the surface of  $g\text{-C}_3\text{N}_4$  sheets [Fig. 4a]. These results reflected the strong chemical affinity of  $\text{SnS}_2$  nanoparticles to adhere strongly on  $g\text{-C}_3\text{N}_4$  sheets. Mapping and EDX analysis were carried out to analyze the compositions of the sonicated CNSnS15 heterojunction and to verify the dispersion of  $\text{SnS}_2$  and  $g\text{-C}_3\text{N}_4$  with respect to each other. The experimental results extracted from mapping and EDX analysis revealed that C, N, Sn and S are the main constituents of the  $\text{SnS}_2/g\text{-C}_3\text{N}_4$  heterojunction without any other impurities [Fig. 4b–g]. Mapping analysis revealed the homogeneous chemical dispersion of  $\text{SnS}_2$  on  $g\text{-C}_3\text{N}_4$  sheets. HRTEM analysis investigated the crystalline size and the nanostructure of the CNSnS15 heterojunction synthesized by sonochemical and physical mixing processes [Fig. 5]. The  $g\text{-C}_3\text{N}_4$  recorded a laminar sheet structure with

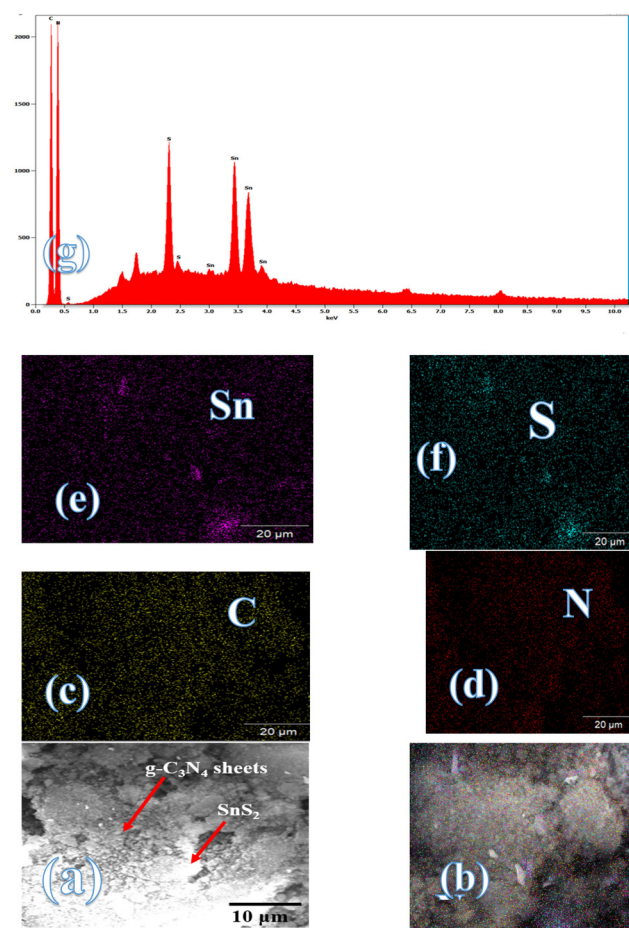


Fig. 4 (a) SEM of CNSnS15 and mapping of (b) CNSnS15, (c) C, (d) N, (e) Sn, (f) S and (g) EDX of CNSnS15 prepared using the sonochemical method.



wrinkle points and a spongy texture [Fig. 5a]. SnS<sub>2</sub> nanoparticles induced porous layers that prohibited the sheets with super positions for enhancing the mass diffusion reactions for pollutant molecules. Fig. 5b displays the TEM analysis of CNSnS15 synthesized by the physical mixing process that revealed the agglomeration of SnS<sub>2</sub> on g-C<sub>3</sub>N<sub>4</sub>, which hinders light penetration. The intimate contact between g-C<sub>3</sub>N<sub>4</sub> sheets and SnS<sub>2</sub> favored the successful building of the S-scheme heterojunction for the solid sample synthesized by the sonochemical process. HRTEM recorded the interplanar distance of 0.315 and 0.267 nm, which referred to the (002) and (101) planes of g-C<sub>3</sub>N<sub>4</sub> and SnS<sub>2</sub>, respectively [Fig. 5c and d]. The SAED image of CNSnS15 [Fig. 5e and f] recorded the existence of two diffraction rings belonging to (002) and (101) planes of g-C<sub>3</sub>N<sub>4</sub> and SnS<sub>2</sub>, respectively. The experimental data extracted from Mapping, EDX, HRTEM, and SEM analyses implied the successful construction of the SnS<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> heterojunction. XPS measurement analyzed the chemical compositions and the oxidation state of the constituents of pristine g-C<sub>3</sub>N<sub>4</sub>, SnS<sub>2</sub> and CNSnS15 nanocomposite with high precision [Fig. 6]. The C 1s spectrum in the pristine g-C<sub>3</sub>N<sub>4</sub> was resolved into four deconvoluted peaks at 284.6, 285.9, 288.1 and 289.0 eV, which referred to the C–C, N–C=N and C–OH bonding, respectively [Fig. 6a]. The N 1s spectrum in the pristine g-C<sub>3</sub>N<sub>4</sub> was resolved into three deconvoluted peaks at 399.1, 400.2 and 404.6 eV that ascribed to C–N=C bonding,

N–(C)<sub>3</sub> bonding and CN–H bonding, respectively [Fig. 6b]. The spectrum of Sn 3d in the pristine SnS<sub>2</sub> nanoparticles was resolved into two peaks of Sn 3d<sub>3/2</sub> and Sn 3d<sub>5/2</sub> observed at 495.6 and 487.1 eV, respectively [Fig. 6c]. The S (2p) spectrum was resolved into two deconvoluted peaks at 167.8 and 169.1 eV, which ascribed to S 2p<sub>3/2</sub> and 2p<sub>1/2</sub> [Fig. 6d]. XPS spectrum of the CNSnS15 heterojunction showed the same characteristic peaks of C, N, Sn and S recorded in the pristine materials. The C 1s spectrum in the CNSnS15 heterojunction was resolved into four deconvoluted peaks at 284.6, 286.1, 288.3 and 289.5 eV, which referred to C–C, N–C=N and C–OH bonding, respectively [Fig. 6e]. The N 1s spectrum in the CNSnS15 heterojunction was resolved into three deconvoluted peaks at 399.1, 400.4 and 404.8 eV that ascribed to C–N=C bonding, N–(C)<sub>3</sub> bonding and CN–H bonding, respectively [Fig. 6f]. The spectrum of Sn 3d was resolved into two peaks of Sn 3d<sub>3/2</sub> and Sn 3d<sub>5/2</sub> observed at 495.6 and 487.3 eV [Fig. 6g]. The S (2p) spectrum was resolved into two deconvoluted peaks at 168.4 and 169.1 eV, which is ascribed to S 2p<sub>3/2</sub> and 2p<sub>1/2</sub> [Fig. 6h]. It is interesting to notice a little shift in the peak spectrum of C (1s), Sn (3d) and S (2p) to higher binding energy values, revealing the electron density coupling between g-C<sub>3</sub>N<sub>4</sub> and SnS<sub>2</sub> nanoparticles, implying the successful construction of the SnS<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> heterojunction.

Diffuse reflectance spectrum [DRS] and photoluminescence analysis [PL] investigated the optical properties of the

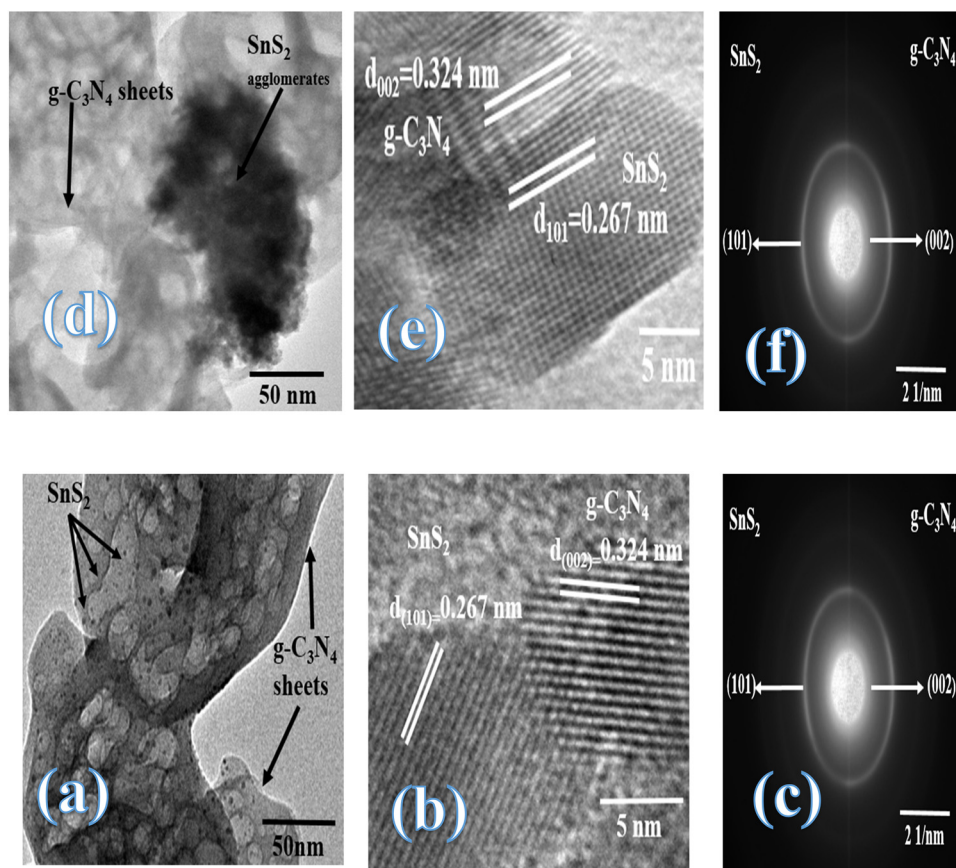


Fig. 5 (a) TEM, (b) HRTEM, (c) SAED of the CNSnS15 heterojunction prepared by employing the sonochemical process. (d) TEM, (e) HRTEM, and (f) SAED of the CNSnS15 heterojunction prepared using the physical mixing process.



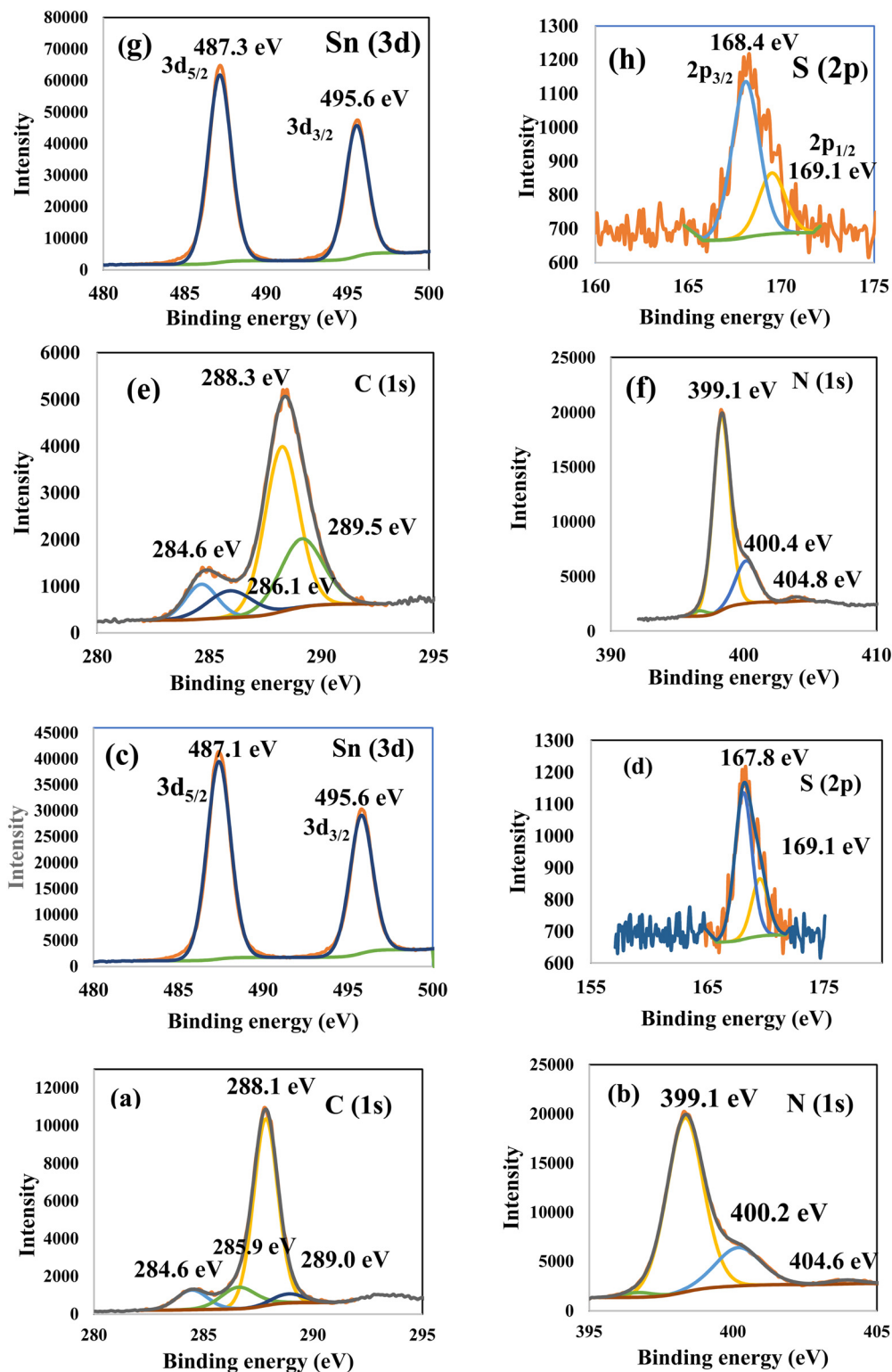


Fig. 6 XPS of (a) C and (b) N in  $g\text{-C}_3\text{N}_4$ ; (c) Sn and (d) S in  $\text{SnS}_2$ ; and (e) C, (f) N, and (g) Sn (h) S in  $\text{CNSn15}$  heterojunction prepared using the sonochemical process.

as-synthesized samples. The DRS displayed an absorption edge at 439 and 784 nm, which referred to the absorbability of  $g\text{-C}_3\text{N}_4$  and  $\text{SnS}_2$ , respectively, implying the absorbability of  $g\text{-C}_3\text{N}_4$  in the initial stage of the visible region; however,  $\text{SnS}_2$

strongly absorbs the full broad spectrum of the sunlight radiation due to its narrow band gap energy [Fig. 7a]. It is interesting to notice that incorporating 15 and 20 wt%  $\text{SnS}_2$  on the  $g\text{-C}_3\text{N}_4$  surface enhanced the absorbability of the nanocomposite to



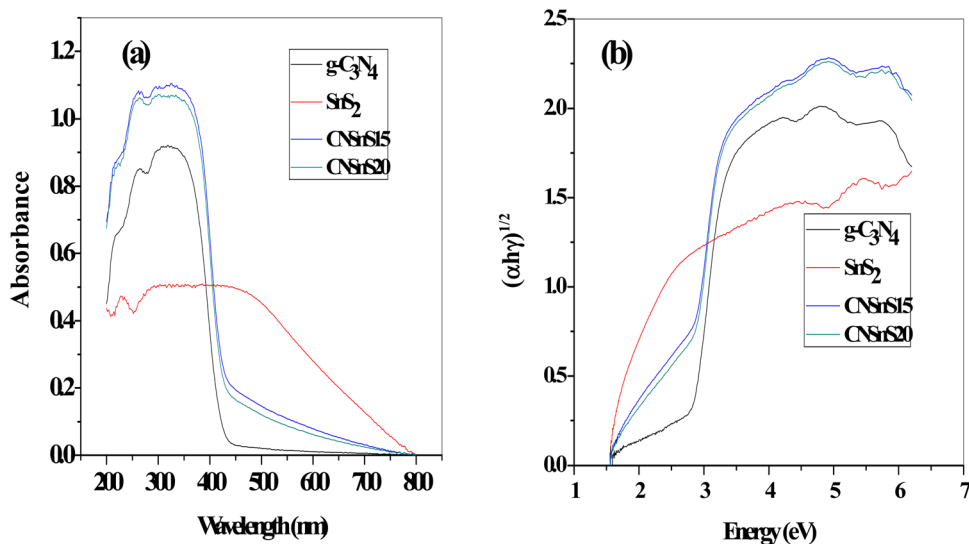


Fig. 7 (a) DRS of g-C<sub>3</sub>N<sub>4</sub>, SnS<sub>2</sub>, CNSnS15 and CNSnS20 prepared through the sonochemical process, (b) Tauc plots of g-C<sub>3</sub>N<sub>4</sub>, SnS<sub>2</sub>, CNSnS15 and CNSnS20 prepared through the sonochemical process.

utilize the full broad spectrum of the natural sunlight. Tauc plots represented the band gap energy from the tangent of the linear section, and the estimated band gap energy is 2.8, 1.7, 2.4 and 2.3 for g-C<sub>3</sub>N<sub>4</sub>, SnS<sub>2</sub>, CNSnS15 and SnS20, respectively [Fig. 7b]. The band gap energy results revealed that the electron density hybridization between g-C<sub>3</sub>N<sub>4</sub> and SnS<sub>2</sub> decremented the band gap energy and improved the fraction of light absorbability.

The band structure, including the potential of valence and conduction band, was estimated according to the following formula to follow up the direction of electron-hole pair transport between g-C<sub>3</sub>N<sub>4</sub> and SnS<sub>2</sub> nanoparticles:

$$E_{VB} = X_{\text{semiconductor}} - E_e + 0.5E_g \quad (1)$$

$$E_{CB} = E_{VB} - E_g \quad (2)$$

4.7 and 5.8 eV are the reported values for electronegativity [ $X$ ] of g-C<sub>3</sub>N<sub>4</sub> and SnS<sub>2</sub>, respectively and  $E_g$  is the band gap energy calculated from the tangent straight line of the Tauc plot. According to the above equation, the valence and conduction band potentials are +1.6 and -1.2 V for g-C<sub>3</sub>N<sub>4</sub> and +2.15 and +0.35 V for SnS<sub>2</sub> nanoparticles, respectively. The primary role of SnS<sub>2</sub> nanoparticles in improving the charge carrier separation and transportation efficiency was determined by constructing the PL spectrum of the solid specimens [Fig. 8]. The PL spectrum displayed a broad signal at 450 nm, implying the strong Coulombic electron-hole attraction force between electron-hole pairs in g-C<sub>3</sub>N<sub>4</sub> sheets. Hybridizing g-C<sub>3</sub>N<sub>4</sub> with 5, 10 and 15 wt% SnS<sub>2</sub> reduced and controlled the recombination rate of the charge carriers by 26, 30 and 40% [Fig. 8a].

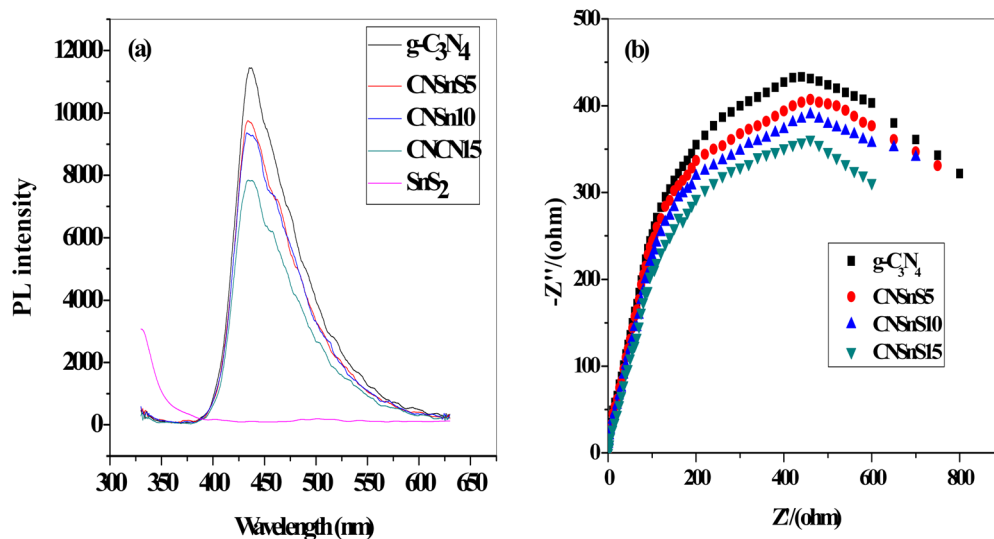


Fig. 8 (a) PL of g-C<sub>3</sub>N<sub>4</sub>, SnS<sub>2</sub>, CNSnS5, CNSnS10 and CNSnS15. (b) EIS plots of g-C<sub>3</sub>N<sub>4</sub>, CNSnS5, CNSnS10 and CNSnS15 prepared via the sonochemical method.



The experimental results from PL analysis revealed that the separation and transportation efficiency of the electron-hole pairs of  $g\text{-C}_3\text{N}_4$  was enhanced with the incorporation of various compositions of  $\text{SnS}_2$  nanoparticles. The excitonic electron-hole pairs were generated at the conduction [CB] and valence bands [VB] due to the falling of sunlight radiations on the semiconductor surface with energy higher than the band gap energy. These generated charge carriers are responsible for redox processes at the heterojunction-solution interface. Under sunlight illumination with 1000 W power, the electrons produced and accumulated in the CB of  $g\text{-C}_3\text{N}_4$  will diffuse to the CB of  $\text{SnS}_2$  and then recombine with the photogenerated holes that exist in the VB of  $g\text{-C}_3\text{N}_4$  since the VB of  $g\text{-C}_3\text{N}_4$  is just below the CB  $\text{SnS}_2$ . However, the electron conduction band of  $g\text{-C}_3\text{N}_4$  and positive holes of  $\text{SnS}_2$  are preserved for a series of successful oxidation-reduction reactions for degrading organic pollutant molecules. Fig. 8b displays the electrochemical impedance spectrum [EIS] of the pristine and heterojunction samples. The Nyquist plot of the heterojunction samples has the smallest arc compared with the pristine  $g\text{-C}_3\text{N}_4$  sheets.

These experimental results implied the lowest interface resistance of electron transport in heterojunction samples, which promotes charge carrier separation. The experimental results revealed that CNSnS15 heterojunction has the lowest arc, revealing that the incorporation of 15 wt%  $\text{SnS}_2$  improved the separation efficiency of the charge carriers, which is consistent with the results extracted from PL analysis.

### 3.2. The experimental photocatalytic results concerned with the degradation of RhB dye

Rhodamine B is employed in the cosmetics, food and cloth industry due to its vibrant red color and stable conjugated aromatic structure. The degradation of RhB dye was extensively investigated through traditional processes, such as coagulation, adsorption, ion exchange, reverse osmosis and microbiological methods. However, these methods are energy consumers, have high costs and may transport the primary pollutant into secondary ones, which require further treatment and analysis. Photocatalysis is an efficient low-cost process for the degradation of RhB dye molecules into non-toxic species under natural solar

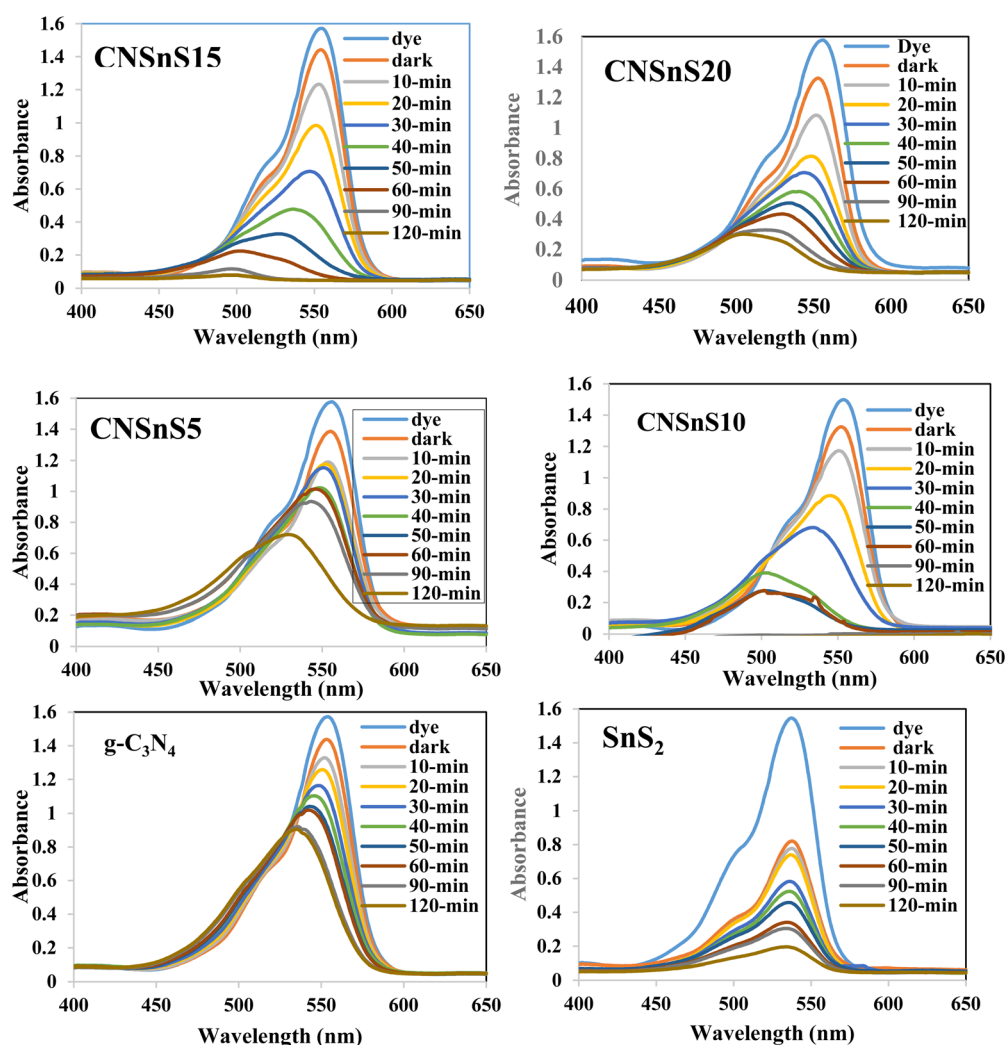


Fig. 9 Photocatalytic degradation of rhodamine B dye over the surface of the as-synthesized samples prepared using the sonochemical process.



radiation. Under sunlight illumination of 1000 W power, the photocatalytic performance of  $g\text{-C}_3\text{N}_4$ ,  $\text{SnS}_2$  and  $\text{SnS}_2/g\text{-C}_3\text{N}_4$  heterojunctions was investigated and recorded under mild operating conditions and displayed in Fig. 9. The experimental results implied that 4% of RhB dye molecules were degraded under sunlight illumination in the absence of photocatalyst revealing the strong chemical stability of the aromatic structure of the organic dye molecules. Before exposure to natural solar radiation, the photocatalyst was mixed and stirred with the RhB dye solution for one hour to calculate the extent of the solid specimens to remove RhB dye through adsorption. The adsorption process is usually accompanied by strong deposition of dye molecules on the solid surface, which may block the active sites of the solid and hinder the recyclability of the solid specimens in various industrial applications. The experimental adsorption results revealed that the amount of RhB dye removed *via* the adsorption process did not exceed 10% over the heterojunction surface. With sunlight irradiation on the dye–solid mixture, a huge amount of radicals migrated to the semiconductor surface to mineralize RhB dye molecules. The photocatalytic profile illustrated in Fig. 9 recorded the depression in the concentration of RhB with prolonged time of solar light illumination. On examining the photocatalytic spectrum, one can notice the remarkable shift in the peak position, which is ascribed to the dissociation of RhB dye into intermediates of organic molecules. The  $g\text{-C}_3\text{N}_4$  sheets decomposed 34% of RhB during two hours of sunlight exposure. On the contrary,  $\text{SnS}_2$  nanoparticles degraded 78% of RhB dye by the adsorption-coupled photocatalytic process. About 50% of RhB was removed from the aqueous medium through the adsorption process on the surface of pristine  $\text{SnS}_2$  due to the attractive force between the negatively charged surface and the cationic dye molecules. Incorporating 5 and 10 wt% of  $\text{SnS}_2$  on  $g\text{-C}_3\text{N}_4$  sheets enhanced the decomposition of RhB dye to 50 and 71%. Further, loading  $g\text{-C}_3\text{N}_4$  sheets with 15 wt%  $\text{SnS}_2$  enhanced the decomposition of RhB dye to 98%. However, a pronounced depression in the removal of RhB dye to 81% was recorded for the nanocomposite containing 20 wt%  $\text{SnS}_2$  [Fig. 10a]. The shift in the absorption peak position of RhB dye to a lower wavelength compared with the initial dye concentration was recorded in the photocatalytic spectrum profile of RhB dye degradation on the semiconductor surface [Fig. 9]. These experimental results displayed in the spectrum of photocatalytic removal of RhB dye accounted for the generation of various chemical intermediate through a de-ethylation mechanism. In fact, the degradation of RhB proceeded through fragmentation stages that generated a series of intermediate components through the removal of ethyl groups one by one, as observed by the gradual shift in the peak position toward the lower wavelength. De-ethylation of the fully  $N,N,N,N$ -tetra-ethylated rhodamine molecule generated  $N,N,N$ -tri-ethylated rhodamine at 548 nm,  $N,N$ -di-ethylated rhodamine at 539 nm,  $N$ -ethylated rhodamine at 518 nm and rhodamine at 499 nm. The pseudo first-order rate constant was determined from the graphical plot between the time of light illumination and  $\ln(a-x)$  was 0.0039, 0.0121, 0.0047, 0.013, 0.027 and 0.017  $\text{min}^{-1}$  for  $g\text{-C}_3\text{N}_4$ ,  $\text{SnS}_2$ , CNSnS5, CNSnS10, CNSnS15 and CNSnS20 [Fig. 10b]. The precise analysis of the charge transport mechanism and type of

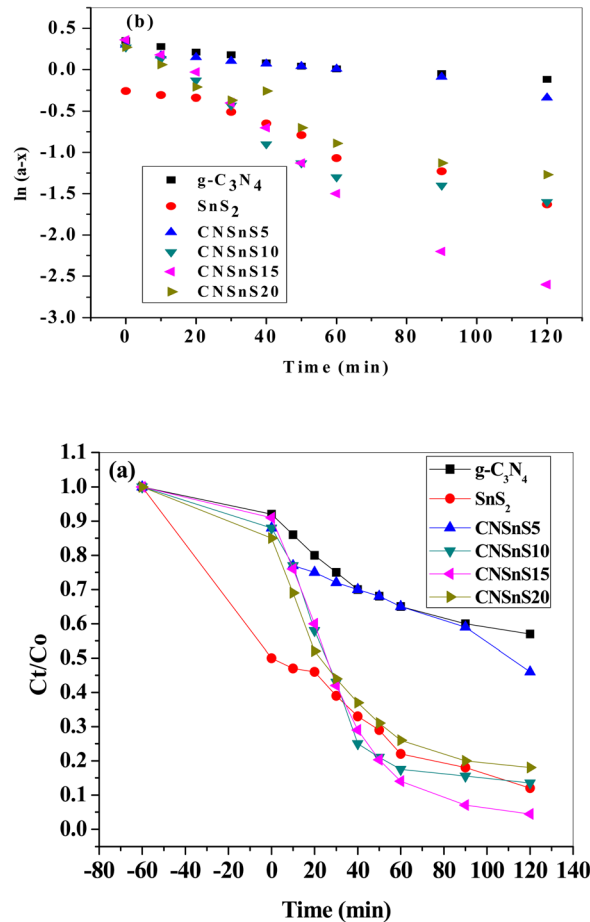


Fig. 10 (a) The variation of the photocatalytic degradation of RhB dye with time of irradiation on the surface of the as-synthesized samples. (b) Pseudo-first order plot of the photocatalytic degradation of rhodamine B dye over the surface of the as-synthesized samples.

the reactive species playing a crucial role in the photocatalytic degradation of RhB dye was investigated by scavenger trapping reagents, such as benzoquinone, isopropanol and ammonium oxalate to trap superoxide, hydroxyl radicals and positive holes, respectively. Benzoquinone, isopropanol and ammonium oxalate reduced the photocatalytic degradation of RhB dye from 98% to 53%, 34% and 82%, respectively, implying that the reactive oxygen species are the crucial species involved in the photodegradation process [Fig. 11a]. The generation of hydroxyl radicals was estimated through the hydroxylation of terephthalic acid in a basic medium under natural solar illumination. The brilliant emission peak recorded at 426 nm revealed the enhancement in the production of hydroxyl radicals [ $E_{\text{OH}\cdot/\text{H}_2\text{O}} = +1.88 \text{ eV}$ ] on the surface of the CNSnS15 heterojunction [Fig. 11b]. These results revealed that hydroxyl radicals were produced by water oxidation with positive holes of  $\text{SnS}_2$  nanoparticles. These results were in agreement with scavenger trapping experiments that proved that hydroxyl radicals are the most effective species for dye degradation. The reusability was carried out on the optimum solid specimens under natural solar irradiation, as shown in Fig. 11c. In each cycle, the photocatalyst was washed with bi-distilled water



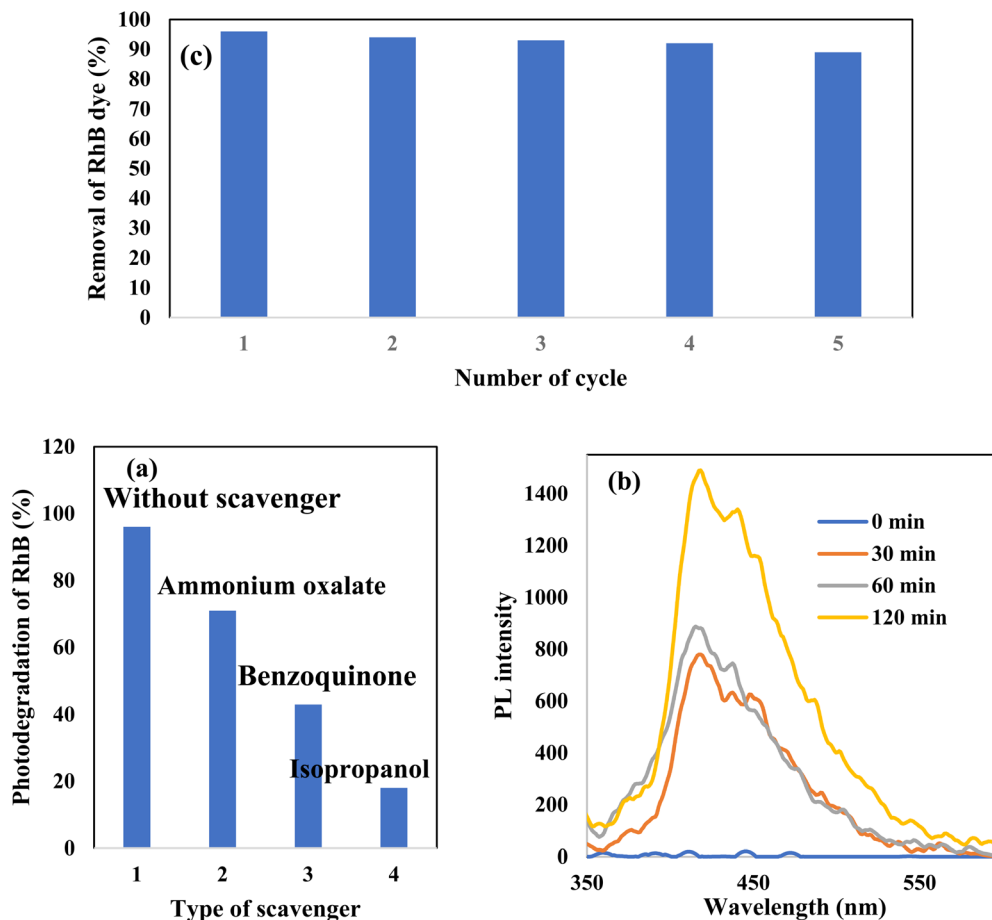


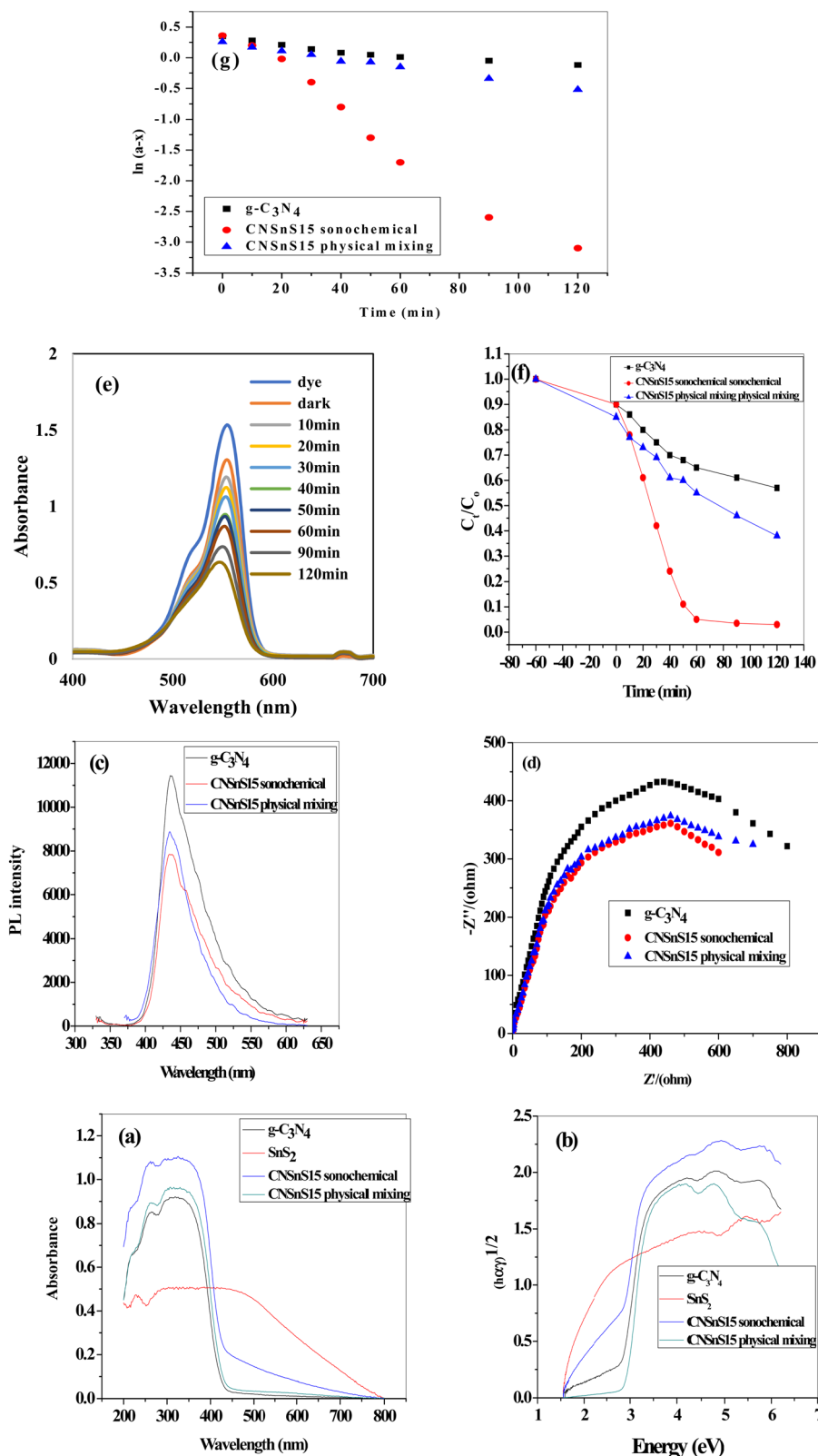
Fig. 11 (a) Effect of various scavengers on the photocatalytic degradation of RhB dye over the surface of the CNSnS15 heterojunction, (b) PL spectrum of terephthalic acid at 325 nm excitation wavelength over the CNSnS15 heterojunction and (c) recycling of CNSnS15 in the photocatalytic degradation of rhodamine B for five consecutive cycles.

repeatedly before the subsequent cycle. The overall removal (%) of RhB dye did not noticeably change even after the five consecutive cycles were completed, implying the strong chemical stability of the photocatalyst in degrading the dye pollutants several times. The complete degradation of rhodamine B dye into eco-friendly species was evaluated by carrying out the total organic carbon [TOC] analysis. TOC contents fall from  $71.3 \text{ mg L}^{-1}$  to  $7.5 \text{ mg mL}^{-1}$ , accounting for the fragmentation of 90% of RhB dye, similar to the values extracted from the photocatalytic spectrum analysis.

To investigate the effect of the mode of preparation of the photocatalyst on the optical properties and the photocatalytic efficiency, the optimum sample CNSnS15 was prepared by the physical mixing process and the experimental results were compared with those recorded on the sample prepared by the sonochemical route. DRS analysis and Tauc plot represented in Fig. 12a and b revealed that the CNSnS15 photocatalyst prepared by the sonochemical route exhibited strong absorbability of visible light radiations rather than the sample synthesized by the physical mixing process. The band gap energy calculated from the Tauc plot is 2.8, 2.4 and 2.6 eV for  $g\text{-C}_3\text{N}_4$  and CNSnS15 prepared by sonochemical and physical mixing

methods, respectively. PL analysis results implied that the sample prepared by physical mixing showed a high electron-hole recombination rate, which limited the photocatalytic reactivity compared with the sample prepared by the sonochemical route [Fig. 12c]. Fig. 12d displays the electrochemical impedance spectrum [EIS] of the pristine  $g\text{-C}_3\text{N}_4$  and CNSnS15 heterojunction prepared by sonochemical and physical mixing routes. The Nyquist plot of the CNSnS15 heterojunction has a small arc radius compared with  $g\text{-C}_3\text{N}_4$  sheets. These experimental results implied the lowest interface resistance of electron transport in CNSnS15 heterojunctions prepared by different methods. However, CNSnS15 heterojunction prepared *via* the sonochemical route has a lower arc compared with the solid specimen prepared *via* the physical mixing method, revealing that the incorporation of 15 wt%  $\text{SnS}_2$  under the sonochemical process enhanced the separation efficiency of charge carriers, which is consistent with the results extracted from PL analysis. The photocatalytic degradation of the RhB dye on the sample prepared by physical mixing revealed the decomposition of 55% of RhB dye compared with 96% decomposition on the sample prepared by the sonochemical route [Fig. 12e and f]. The pseudo first-order rate for the





**Fig. 12** (a) DRS spectrum of g-C<sub>3</sub>N<sub>4</sub>, CNSnS15 synthesized *via* sonochemical and physical mixing methods, (b) Tauc plot spectrum of g-C<sub>3</sub>N<sub>4</sub> and CNSnS15 synthesized *via* sonochemical and physical mixing methods, (c) PL spectrum of g-C<sub>3</sub>N<sub>4</sub> and CNSnS15 synthesized *via* sonochemical and physical mixing methods, (d) EIS plot of g-C<sub>3</sub>N<sub>4</sub> and CNSnS15 prepared *via* sonochemical and physical mixing methods, (e) absorption spectrum for the photocatalytic degradation of rhodamine B dye over SnSnS15 prepared *via* the physical mixing method, (f) photocatalytic removal of RhB dye over g-C<sub>3</sub>N<sub>4</sub> and CNSnS15 prepared *via* sonochemical and physical mixing methods, and (g) pseudo-first order plot for the photocatalytic removal of RhB dye over g-C<sub>3</sub>N<sub>4</sub> and CNSnS15 prepared *via* sonochemical and physical mixing methods.



photocatalytic degradation of RhB dye on the surface of the sample prepared by physical mixing is  $0.00165 \text{ min}^{-1}$ , which is nearly half the rate of dye decomposition on the surface of the solid prepared by the sonochemical route [Fig. 12g]. All the above experimental results implied that the photocatalyst synthesized by the sonochemical route exhibited better electron-hole separation and transport and strong photocatalytic efficiency in degrading the RhB dye compared with the sample synthesized by the physical mixing route. The exceptional photocatalytic reactivity of the sonicated CNSn15 was attributed to the proper dispersion of  $\text{SnS}_2$  on  $g\text{-C}_3\text{N}_4$  sheets as

recorded in the TEM analysis, which facilitates the construction of the  $\text{SnS}_2/g\text{-C}_3\text{N}_4$  heterojunction with remarkable high absorbability of visible light radiation and efficient electron-hole transport and separation. On the other hand, the agglomeration of  $\text{SnS}_2$  nanoparticles on  $g\text{-C}_3\text{N}_4$  sheets for the solid prepared by the physical mixing route reduced the light absorbability and increased the probability of the electron-hole recombination rate. These experimental results implied that the sonochemical process is an efficient route for the successful production of  $\text{SnS}_2/g\text{-C}_3\text{N}_4$  heterojunctions with exceptional photocatalytic reactivity compared with the physical mixing process.

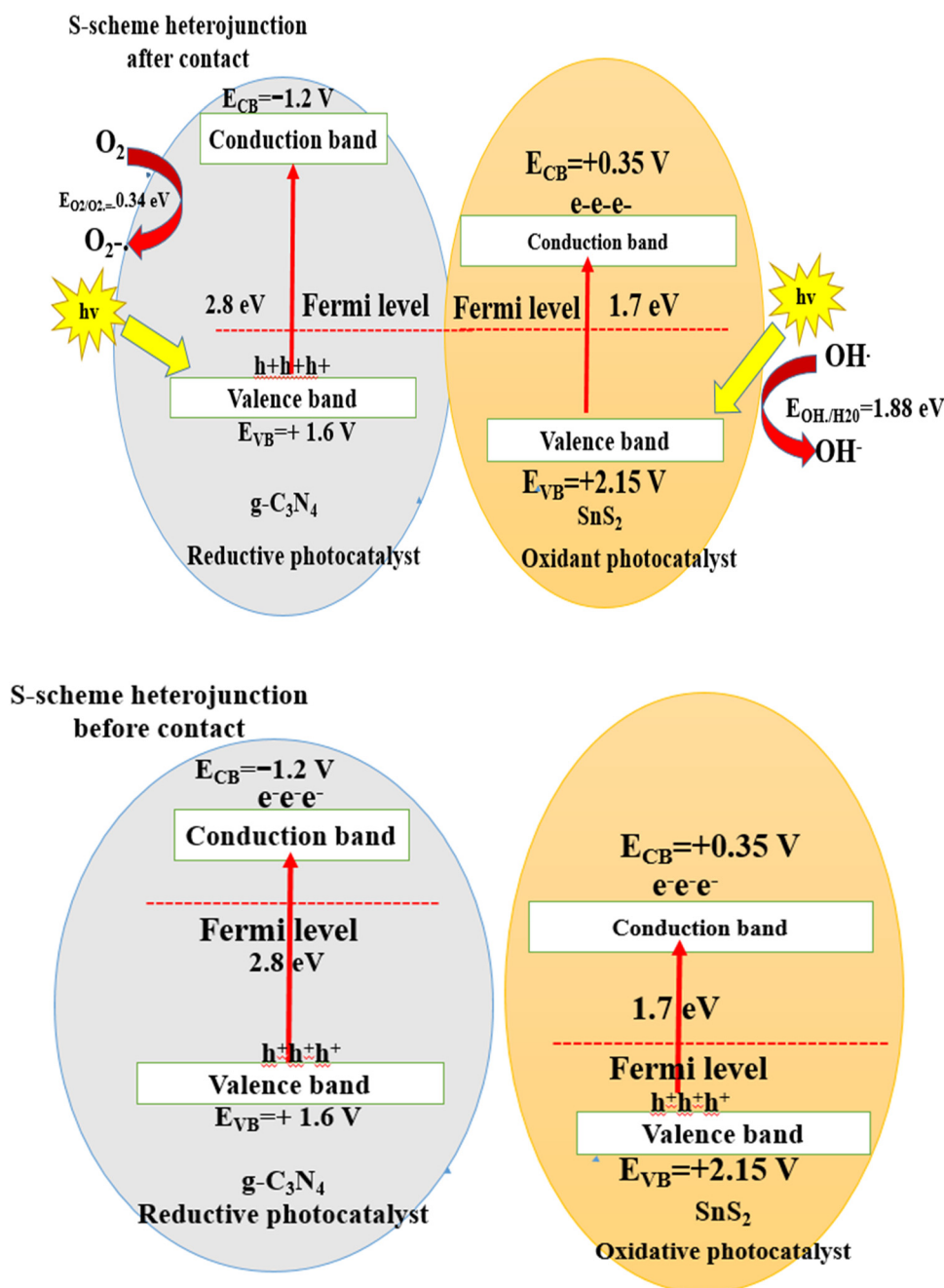


Fig. 13 S-scheme for charge transport before and after the contact of  $g\text{-C}_3\text{N}_4$  and  $\text{SnS}_2$  semiconductors.



Table 1 Comparative investigation of the degradation of toxic organic dyes using the SnS<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> system

Photocatalyst	Mode of preparation	organic dye	Light source	Degradation efficiency (%)	Ref.
SnS <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	Sonochemical	Rhodamine B	Natural sunlight	97	Our research
SnS <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	Direct calcination	Rhodamine B	60 W–220 V lamp	95	33
SnS <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	Ion exchange	Methyl orange	350 W xenon lamp	93	34
SnS <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	Hydrothermal	Methyl orange	350 W visible lamp	97	35
SnS <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	Hydrothermal	Methylene blue	300 W visible light	56	36
SnS <sub>2</sub> /RGO/g-C <sub>3</sub> N <sub>4</sub>	SnS <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	Methylene blue	300 W visible lamp	86	36
SnS <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	Solvothermal	Rhodamine B	300 W xenon lamp	91	37
SnS <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	Solvothermal	2,4-dichlorophenol	300 W xenon lamp	94	38
SnS <sub>2</sub> dot/g-C <sub>3</sub> N <sub>4</sub>	Solvothermal	Rhodamine B	300 W xenon lamp	96.8	39
MoS <sub>2</sub> -SnS <sub>2</sub> @g-C <sub>3</sub> N <sub>4</sub>	Hydrothermal	Methylene blue	300 W xenon lamp	86.6	40
3DF-SnS <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	Solvothermal	Rhodamine B	400 W xenon lamp	90.15	41
SnS <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	Calcination	Rhodamine B	60 W–220 V lamp	92.2	42
g-C <sub>3</sub> N <sub>4</sub> /Ag <sub>2</sub> S/SnS <sub>2</sub>	Sonochemical	Methyl orange	500 W xenon lamp	96.8	43
SnS <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	Calcination	Hexavalent uranium	Sunlight	90	44

The mechanism of fragmentation of the RhB dye on the surface of the SnS<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> heterojunction interface under sunlight illumination can be elucidated through scavenger trapping analysis and the band structure of the heterojunction. The famous type II heterojunction and the recent S-scheme mechanism can account for the diffusion of electron-hole pairs between the selected semiconductors.<sup>46–62</sup> Through a type-II charge transfer mode, both SnS<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> semiconductors absorbed a definite amount of energy and were excited to generate photoinduced negative electrons and positive holes under natural light illumination. The excited electrons in the conduction band of g-C<sub>3</sub>N<sub>4</sub> were simultaneously diffused to the conduction band of SnS<sub>2</sub> with a lower negative potential. On the contrary, the photogenerated holes were transported from the valence band of SnS<sub>2</sub> to that of g-C<sub>3</sub>N<sub>4</sub> of a lower positive potential. Based on this charge transport, the photoinduced electrons were accumulated in the conduction band of SnS<sub>2</sub> with a small reduction potential, whereas photoinduced holes were accumulated on the valence band of g-C<sub>3</sub>N<sub>4</sub> with a low oxidation potential. This electron transport was rejected from the thermodynamic and kinetic aspects due to the loss of charge carriers of high redox potential. Moreover, the electrons in the conduction band in SnS<sub>2</sub> fail to generate the superoxide radicals ( $E_{O_2/O_2^{\bullet-}} = -0.34\text{ eV}$ ) and the positive holes in the valence band of g-C<sub>3</sub>N<sub>4</sub> fail to oxidize water and generate hydroxyl radicals ( $E_{H_2O/OH^{\bullet}} = +1.88\text{ eV}$ ). The experimental results of the PL spectrum of terephthalic acid and the scavenger trapping experiments implied the production of hydroxyl and superoxide radicals, which reject the aspects of charge transport through the type (II) mechanism. The S-scheme charge migration is a more precise mechanism in elucidating the proper direction of the electron-hole diffusion route [Fig. 13]. On direct irradiation of sunlight on the heterojunction interface, electrons were diffused from g-C<sub>3</sub>N<sub>4</sub> to SnS<sub>2</sub>, generating the depletion and accumulation layers at the interface boundary of g-C<sub>3</sub>N<sub>4</sub> and SnS<sub>2</sub>, respectively. This electron migration marked a negative and positive charge on SnS<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> regions, respectively. Due to simultaneous charge diffusion, an internal electric field traversed from the g-C<sub>3</sub>N<sub>4</sub> to the SnS<sub>2</sub> side. The Fermi levels of g-C<sub>3</sub>N<sub>4</sub> and SnS<sub>2</sub> move upwards and

downwards to reach an equalization position at the interface region between SnS<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> sheets. At this neutralized region, the weak charge carriers of g-C<sub>3</sub>N<sub>4</sub> ( $E_{VB} = +1.6\text{ V}$ ) and SnS<sub>2</sub> ( $E_{CB} = +0.1\text{ V}$ ) are removed by the electrostatic attraction force. However, the positive hole of SnS<sub>2</sub> ( $E_{VB} = +2.28\text{ eV}$ ) and electrons of g-C<sub>3</sub>N<sub>4</sub> ( $E_{CB} = -1.2\text{ V}$ ) were maintained for playing a crucial role in the redox process. The photocatalytic experimental results of SnS<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> in this research were compared with the recent studies [Table 1]. The results recorded in Table 1 revealed that the sonicated SnS<sub>2</sub>/C<sub>3</sub>N<sub>4</sub> synthesized by the sonochemical route displayed an excellent photocatalytic performance in the removal of various organic pollutants compared with the nanocomposites synthesized by the hydrothermal, solvothermal and ion exchange processes.<sup>33–42</sup> Moreover, various recent research studies revealed that the addition of RGO,<sup>36</sup> MoS<sub>2</sub><sup>40</sup> and Ag<sub>2</sub>S<sup>43</sup> was required to facilitate the charge diffusion between SnS<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub>. All the previous photocatalytic processes on the mineralization of organic pollutants under UV and visible light sources are expensive and exhibit limited power to employ on an industrial scale. However, the degradation of RhB dye as a cationic pollutant model was carried out in our research under natural sunlight radiation, considering the low cost and the available illumination source in our country.

## Conclusions

Herein, the adjusted S-scheme SnS<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> heterojunction with an aligned band structure and a narrow mesoporous texture were synthesized by sonochemical and physical mixing processes for solar degradation of rhodamine B dye under natural sunlight radiation of 1000 W power. SnS<sub>2</sub> nanoparticles with 1.7 eV band gap energy were dispersed sonochemically on the wrapped g-C<sub>3</sub>N<sub>4</sub> sheets in localized positions, generating a porous sheet structure that facilitates the transport of organic dye molecules. However, the agglomeration of SnS<sub>2</sub> nanoparticles on g-C<sub>3</sub>N<sub>4</sub> sheets was recorded for the heterojunction synthesized by the physical mixing process, which restricts the light transport to the photocatalyst surface and reduces the photocatalytic efficiency. DRS, PL, HRTEM, N<sub>2</sub>-adsorption-desorption isotherms,



SEM, EIS and SAED analyses verified the engineering of the SnS<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> heterojunction with excellent absorbability of sunlight radiation and better transport and separation of electron-hole pairs. PL analysis of an alkaline solution of terephthalic acid detected the solar production of hydroxyl radicals. However, the experimental trapping agents elucidated the direction of the charge carrier transport by adopting the concept of the S-scheme heterojunction. Thoroughly, in the S-scheme process, the undesirable holes and electrons of g-C<sub>3</sub>N<sub>4</sub> and SnS<sub>2</sub> with weak redox potentials were removed by the electrostatic attraction force at the interface boundary of the semiconductors surface. On the contrary, SnS<sub>2</sub> positive holes and g-C<sub>3</sub>N<sub>4</sub> electrons degraded RhB dye molecules under sunlight illumination. The photocatalytic optimized experiments recorded that the sonicated nanocomposite CNSnS15 with 15 wt% SnS<sub>2</sub> degraded 96% of RhB dye and exhibited strong stability in the mineralization of the toxic organic dye for five consecutive cycles. The novel SnS<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> heterojunction with extra-ordinary redox efficiency under natural sunlight radiation is considered a promising photocatalyst for the degradation of various toxic organic pollutants.

## Data availability

Data will be made available on request.

## Conflicts of interest

There are no conflicts to declare.

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