Article:
Sun, H., Tillotson, M.R. orcid.org/0000-0002-3362-021X, Wang, D. et al. (1 more author) (2024) A novel Z-scheme SnS/NiAl-LDH/g-C3N4 heterojunction for piezo-photocatalytic degradation of tetracycline: Performance and mechanism. Surfaces and Interfaces, 52. 104861. ISSN: 2468-0230

https://doi.org/10.1016/j.surfin.2024.104861

Manuscript submitted to ″Surfaces and Interfaces″ as a research paper.

A novel Z-scheme SnS/NiAl-LDH/g-C_3N_4 heterojunction for piezo-photocatalytic degradation of tetracycline: Performance and mechanism

Hao Sun[a], Martin R. Tillotson[b], Dawei Wang[c], and Xu Zhao[a]*

[a]*Institute of Blue and Green Development, Shandong University, 264209 Weihai, China*

[b] *water@leeds, School of Civil Engineering, University of Leeds, Leeds LS2 9JT, United Kingdom*

[c]*Key Laboratory of Integrated Regulation and Resource Development of Shallow Lakes, Ministry of Education, College of Environment, Hohai University, Nanjing 210098, P.R. China.*

*Corresponding author.

E-mail addresses: xuzhao@sdu.edu.cn

Abstract

The construction of a heterojunction piezo-photocatalyst is one of the most effective strategies to accelerate charge transfer and improve catalytic performance. A novel ternary heterojunction was synthesized by introducing SnS nanoparticles (NPs) onto the surface of a NiAl-LDH/g-C_3N_4 (LDH/CN) nanosheets *via* a facile hydrothermal method. The separation and transfer paths of carriers was studied for the piezo-photocatalytic degradation of tetracycline (TC), a common antibiotic, under ultrasonic and visible light irradiation. The SnS/LDH/CN piezo-photocatalyst generated a built-in electric field by the piezoelectric effect, which was beneficial for the separation of electron-hole pairs. Furthermore, the Z-scheme heterojunction endowed with a larger surface area, abundant active sites, and improved light-harvesting capacity further improved piezo-photocatalytic performance for TC. In particular, a CLS-30 (30 wt% of SnS on LDH/CN) heterojunction exhibited the highest degradation efficiency with 98.5% removal of TC (20 mg/L) in 60 min, which was higher than that of ultrasonic vibration (38.2%) and visible light illumination (79.4%). TC degradation efficiency remained at almost 90% after 4 consecutive cycles. This work provides a novel viewpoint for designing high-performance and stable heterojunction piezo-photocatalysts for energy limited wastewater remediation applications.

Keywords: SnS/LDH/CN; Tetracycline; Piezo-photocatalysis; Z-scheme heterojunction

1. Introduction

In recent years the global effort towards net zero carbon emissions and environmental sustainability goals whilst remediating waterborne pollution has motivated researchers in wastewater treatment[1-3]. Antibiotics and other pharmaceutical agents, have been widely used to treat human and animal diseases [4-5], however their excessive use has resulted in serious human health and ecosystem threats which urgently require efficient governance strategies, including removal from water [6-8]. Therefore, the development of environmentally friendly advanced/nano materials, which may utilize natural energy sources such as sunlight, wind power and acoustic wave, to effectively treat waterborne pollution is one important element in this effort[9-12]. Photocatalytic technology is considered an efficient and valuable method for such pollutant degradation due to its high selectivity, low energy consumption and cyclability [13-15]. In particular, semiconductor photocatalysts have exhibited remarkable performance in the degradation of tetracycline (TC), a common class of antibiotic, through the harvesting of solar energy to convert photons into electron-hole pairs[16-17]. Indeed, a variety of photocatalysts have been reported for the treatment of waterborne pollutants, including TiO_2, g-C_3N_4, SiO_2, ZnO, and CeO_2[18-21]. Graphitic carbon nitride (g-C_3N_4; CN), with a two-dimensional layered structure, is the most extensively studied photocatalyst due to its low band gap, low toxicity, facile preparation and robust chemical stability. In addition, CN

exhibits excellent adsorption capacity, which is also regarded as an attractive property in environmental remediation[22-25]. Nevertheless, the practical applications of a single photocatalyst are restricted because of drawbacks such as low efficiency, insufficient light harvesting ability, and rapid charge-carrier recombination[26-27]. In order to enhance photocatalytic performance and efficiency, various strategies including heterojunction construction, noble metal deposition, and surface morphology modification have been proposed[28-30].

Layered double hydroxides (LDHs) are a class of layered composites with exchangeable anions. They have attracted significant attention in photocatalysis owing to their flexible and tunable chemical composition, intense adsorption capacity, and high chemical stability[31-32]. The coupling of electronegative LDHs with electropositive CN can further enhance the photocatalytic activity of these composites because of synergistic effects induced by the heterointerface under visible light illumination[33-34]. For example, Shakeel *et al*. developed a novel LDH/CN hetero-structured photocatalyst, which showed excellent Rhodamine B degradation performance compared to pure CN or LDH, and was mainly attributed to its large surface area, good conductivity and improved interfacial contact[35]. Moreover, Liu *et al*. reported ZnCr-LDH/CN composite photocatalysts that could significantly improve catalytic water dissociation activity[36].

Despite the LDH/CN heterojunction displaying improved photocatalytic efficiency, some issues such as relatively slow charge transport and poor surface redox properties remained. For the issue of rapid carriers recombination, most work has focused on material modification in the realm of photocatalysis, resulting in a single field of research[37-38]. Designing new combinations such as semiconductor heterojunction/piezoelectric materials might be expected to overcome the limitations of the photocatalytic system and accelerate the separation of photoinduced charge, thereby improving the catalytic performance.

Polarized electric fields generated by piezoelectric materials under mechanical energy can promote the separation and transfer of charge carriers. Moreover, charge separation can enable participation in redox reactions which enhance catalytic activity and degrade pollutants in water[39-40]. The combination of piezocatalysis and photocatalysis is regarded as a novel approach for gathering and utilizing abundant natural energy sources[41-42]. For the past few years, tin sulfide (SnS) has been known to possess excellent piezoelectric properties and has been application in the piezoelectric catalysis field. For example, Tian *et al*. reported that SnS nanobelt piezocatalysts converted CO_2 into acetate with 100% selectivity under the vibration energy[43]. Cao *et al*. prepared a SnS_2/SnS heterojunction with improved output efficiency by the

piezoelectric effect[44]. Here, the synergistic effect of the SnS piezocatalyst and the LDH/CN heterojunction provided a stable charge supply and accelerated interfacial charge transfer through a built-in electric field. In addition, the redox ability of SnS/LDH/CN composites were further enhanced, which made it one of the most promising piezo-photocatalysts for antibiotic degradation. Although research in environmental remediation has focused on LDH/CN-based photocatalysts there are, to the best of our knowledge, no reports of the Z-scheme SnS/LDH/CN ternary heterojunction as piezo-photocatalysts for degradation of antibiotics.

In this study, we wish to report a novel Z-scheme SnS/LDH/CN heterojunction piezo-photocatalyst prepared via a simple hydrothermal method, and used for high-efficiency degradation of antibiotics. The integration of LDH/CN nanosheets and SnS piezoelectric material combines the advantages of piezoelectric and heterojunction systems which makes it one of the most promising available piezo-photocatalysts for antibiotic degradation. The morphology, surface chemical composition, and piezo-photocatalytic performance of the synthesized SnS/LDH/CN composite were analyzed through a series of characterization and degradation experiments. Furthermore, the mechanism of antibiotic degradation was explored using the results of active species trapping and electron spin resonance (ESR) tests. The work therefore offers a new insight

into the synthesis of ternary heterojunction materials as high-performance piezo-photocatalyts for the degradation of antibiotics.

2. Experimental section

2.1 Materials

Analytical grade chemicals, including melamine, nickel (II) nitrate hexahydrate ($Ni(NO_3)_2·6H_2O$), aluminum nitrate nonahydrate ($Al(NO_3)_3·9H_2O$), sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), polyvinylpyrrolidone (PVP), tin (II) chloride ($SnCl_2$), thioacetamide, ethanol, and tetracycline (TC) were obtained from Sigma-Aldrich. TC, 1,4-benzoquinone (BQ), tert-butyl alcohol (t-BuOH), ethylenediaminetetraacetic acid (EDTA) and dimethyl sulfoxide (C_2H_6OS, DMSO) were purchased from the Shanghai Aladdin Biochemical Technology Co., LTD. Deionized (DI) water was used throughout.

2.2. Preparation of materials

2.2.1 Preparation of the LDH/CN heterojunction

The LDH/CN composites were fabricated via a simple hydrothermal route. An amount of CN nanosheets were formed by heating melamine in a tube furnace, as reported in previous work[45]. The prepared CN powder was dispersed into 250 mL of deionized water. Following addition of 0.12 M $Ni(NO_3)_2·6H_2O$ and 0.04 M $Al(NO_3)_3·9H_2O$, the

resulting mixture was stirred using a magnetic stirrer bar for 10 min. Subsequently, 0.5 M NaOH and 2.0 M Na_2CO_3 were dissolved into the above suspension. The pH value of the mixture remained at 9.0, with continuous stirring for 30 min. The resulting homogeneous solution was transferred to a Teflon-lined autoclave which was maintained at 160 °C for 5 h. Finally, the resulting precipitate was recovered and washed, before air-drying at 80 °C overnight. LDH was synthesized without the addition of CN using a similar procedure.

2.2.2 Preparation of SnS/LDH/CN

In this process, a calculated amount of LDH/CN was placed in 200 mL of deionized water. $SnCl_2$ (5 mmol) and thioacetamide (5 mmol) were dispersed into the above-mentioned suspension and stirred for 10 min. Then, 200 mg of PVP was added under vigorous stirring. The final suspension was transferred to an autoclave and maintained at 120 ^{o}C for 12 h. Deionized water and ethanol were used to wash the product several times. A series of SnS/LDH/CN samples with varying SnS content were prepared, and denoted CLS-10, CLS-20, CLS-30 and CLS-40. SnS was prepared in the absence of LDH/CN using the same method.

2.3 Catalyst characterization

X-ray diffraction patterns (XRD, D2 PHASER, Bruker) was employed to analyze

crystal structure with Cu Kα as radiation source (30 kV, λ = 1.542 Å) in the 2θ range of 10–70°. Fourier transform infrared (FTIR) spectra was measured on a Bruker infrared spectrometer (VERTEX 80V, Germany). The surface morphology of the samples were observed using scanning electron microscopy (SEM; S-4300SE, 15 kV) and transmission electron microscopy (TEM; JEM-2100F, JEOL Ltd). X-ray photoelectron spectroscopy (XPS) was carried out on an ESCA LAB MK-II spectrometer with monochromatized Al Kα radiation using an ion source energy for charge compensation. The light absorbing potential and band structure were obtained by ultraviolet-visible diffuse reflectance spectra (UV–vis DRS; Hitachi S-3100 spectrophotometer). The specific surface areas (SBET) were measured using a BEL BELSORP device using samples prepared by degassing in vacuum for 12 h. Photoluminescence (PL) spectra were recorded on a RAM Boss analytical instrument to assess charge carrier separation of samples. Electrochemical impedance spectroscopy (EIS) of as-prepared samples was measured by an Ivium electrochemical workstation in a conventional three-electrode system with 0.5 M Na_2SO_4 solution as the supporting electrolyte. A platinum wire, modified Ni foam, and the Ag/AgCl electrode were employed as the counter, working, and reference electrodes, respectively. The frequency range of measurement was between 0.1 and 10 kHz with a 5 mV amplitude sine-wave potential. The active species in the degradation process were

detected by trapping experiments; 1,4-benzoquinone (BQ), isopropanol (IPA) and ethylenediaminetetraacetic acid (EDTA) were used as scavenging agents for superoxide radical ($\cdot O^{2-}$), hydroxyl radical ($\cdot OH$) and hole (h^+) species, respectively. Furthermore, electron spin resonance (ESR) measurements were performed on a Bruker EMX PLUS spectrometer using 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as scavenger.

2.4 Evaluation of degradation efficiency

The performance of the as-synthesized catalysts was measured by the degradation of TC. Typically, 20 mg catalyst samples were mixed with 100 mL aqueous TC solution (20 mg/L) and stirred continuously for 30 min in the dark to achieve an adsorption/desorption equilibrium. The degradation experiment was then performed under ultrasonic vibration (120 W, 40 kHz) and/or light (200 W Xenon lamp, $\lambda > 420$ nm, 100 mW/cm^2). At a given time interval, 5.0 mL of reaction solution was extracted and centrifuged to remove the photocatalyst. The characteristic absorption peak of TC at 357 nm was analyzed using a UV-vis spectrophotometer.

3. Results and discussion

3.1. Structure, morphology, and elemental state

XRD patterns for all as-prepared catalysts are shown in **Fig. 1**(a). The XRD spectra of the prepared CN nanosheets showed two distinct emission peaks at 27.3° and 13.1°,

188 corresponding to the (002) and (100) planes and exhibiting the characteristic structure of
189 aromatic systems and typical interlayer packing[46]. The LDH samples displayed the
190 characteristic peaks of hydrotalcite- type compounds, which were well assigned to a
191 typical hexagonal MgAl-LDH (JCPDF 22-0452). Compared with CN, the (002) peak of
192 LDH/CN was weaker and slightly shifted, and was mainly attributed to the formation of
193 heterojunctions. The diffraction peaks at 26.1°, 27.5°, 30.6°, 31.4° and 39.1° accord with
194 the (120), (021), (101), (111), and (131) planes, respectively, demonstrating that SnS
195 nanoparticles were synthesized. The XRD spectra of the SnS/LDH/CN samples showed
196 distinctive diffraction peaks for SnS, LDH, and CN; increasing the SnS content of the
197 samples resulted in the LDH and CN diffraction peaks becoming weaker, reflecting the
198 successful combination of SnS and LDH/CN.

199 The FT-IR spectra were analyzed to further determine the structure of the as-
200 prepared SnS/LDH/CN catalyst (**Fig. 1**(b)). The signals at 3445 cm^{-1} and 1350 cm^{-1} were
201 assigned to O-H and CO_3^{2-} of LDH stretching vibrations, respectively[47]. In addition,
202 the peak at 790 cm^{-1} could correspond to the stretching and bending vibrations of metal-
203 oxygen (Al-O, Mg-O) bonds. For the bare SnS sample, the absorption peak at 570 cm^{-1}
204 was attributed to the Sn-S bond. The bending vibrations of water molecules may account
205 for another peak at 1637 cm^{-1}. The SnS/LDH/CN composites with different SnS content

showed similar peaks corresponding to the main peaks of SnS, LDH and CN. The FTIR spectra results further demonstrated the successful combination of SnS and LDH/CN, in agreement with XRD data.

The morphologies and microstructures of the as-synthesized samples were analyzed by SEM and TEM, and the resulting images are shown in **Fig. 2**. The pristine CN (**Fig. 2** (a)) revealed an ultrathin lamellar stacked structure. The SEM image of LDH in Fig. 2 (b) exhibited a layered structure consisting of several thin sheets. The SEM and TEM images (**Fig. 2** (c) and (e)) showed that SnS are spherical nanometer microspheres with particle size. From the SEM and TEM images of the CSL-30 composite (**Fig. 2** (d) and (f)), it may be observed that the SnS NPs and LDH/CN nanosheets were integrated. In agreement with the EDX spectra (**Fig. 2** (k)), the corresponding elemental mappings of SLC-15 (**Fig. 2** (g-l)) clearly demonstrate the presence of C, N, Sn, S, Mg, Al, and Sn, further demonstrating the combination of SnS and LDH in the composites.

Fig. 3 shows the N_2 adsorption-desorption isotherms and pore size distribution curves for the LDH, LDH/CN, and CLS-30 samples. As displayed in **Fig. 3** (a), the isotherms with type H3 hysteresis loops belong to type IV, which demonstrated the mesoporous structure of the samples. As shown in **Table S1**, the S_{BET} of the LDH sample was calculated as 28.27 m^2/g, providing abundant active sites and high specific surface.

The surface area of LDH/CN and CLS-30 increased significantly with CN and SnS loading, which may be ascribed to the formation of new hybridization. The higher specific surface areas of the heterojunctions are capable of improving the catalytic performance by speeding up charge transfer[48]. The results of pore size distribution are shown in **Fig. 3** (b). According to the IUPAC definition, pore sizes in the range 2 nm to 40 nm range for all samples revealed that the pores were mesoporous. Therefore, the prepared samples can effectively adsorb pollutants in the degradation process and enhance catalytic properties.

XPS analysis was used to measure surface chemical compositions and states of the as-prepared catalysts. **Fig. 4** (a) shows full-scan survey spectra of SnS, LDH, CN and CLS-30. The XPS spectrum for the CLS-30 nanohybrids displays the presence of Sn, S, C, N, Mg, and Al elements. As shown in **Fig. 4** (b), the C 1s peak of CN is located at 283.9 eV, and the peak at 287.3 eV may be attributed to graphitic carbon (C-C), and sp^2-hybridized carbon atoms bonded to N in aromatic rings (N-C=N), respectively. The peak signals of C 1s shifted to a higher binding energy after introducing of SnS and LDH. For LDH nanosheets (**Fig. 4** (c)), the Ni $2p_{3/2}$ (855.8 eV) and Ni $2p_{1/2}$ (873.4 eV) peaks, along with two satellite peaks, demonstrate the presence of Ni^{2+} species. The binding energies of Ni 2p show no obvious change compared with the SnS/LDH/CN heterojunction. As

242 shown in **Fig. 4** (d), the Al 2p peaks located at 67.9 and 73.2 eV were observed,
243 corresponding to Al $2p_{3/2}$ and Al $2p_{1/2}$, respectively. For the Sn 3d XPS spectrum (**Fig. 4**
244 (e)), the binding energies at 485.3 eV and 493.8 eV were consistent with the Sn $3d_{5/2}$ and
245 Sn $3d_{3/2}$ states, respectively. The peak intensities of the CLS-30 samples were slightly
246 higher after integrating with LDH/CN. Similarly, the binding energy of S2p (**Fig. 4** (f)) at
247 161.1 and 162.8 eV may be assigned to S $2p_{3/2}$ and S $2p_{1/2}$, respectively. The signal peaks
248 of the CLS-15 sample shifted to higher binding energies compared to the bare SnS catalyst,
249 which indicated the decrease of S electron density. Generally, electron density could be
250 changed in binding energies *via* electron screening effects. These findings show that
251 coupling SnS NPs with LDH/CN nanosheets could speed up charge transfer and change
252 the binding energies.

253 *3.2. Optical and electronic characteristics*

254 The UV–vis DRS of all the prepared samples are shown in **Fig. 5** (a). The bare SnS
255 exhibited a high absorption edge over the entire visible light region, reflecting its
256 remarkable capability. The LDH sample showed an obvious absorption range from 220
257 to 300 nm, which was ascribed to the presence of metal cations in the LDH layer.
258 Compared with bare CN and LDH, an improved absorbency and significant red shift in
259 the visible light region was obtained through the generation of LDH/CN composites,

which could be ascribed to rapid charge separation of the heterojunction. The SnS/LDH/CN composites showed significantly enhanced optical adsorption properties with the increased SnS content, indicating interactions between SnS and LDH/CN in the hybrids. Overall the outcomes indicate that adding SnS nanoparticles to LDH/CN nanosheets could increase the number of photoinduced charge carriers and boost photocatalytic performance. The band gap energies **Fig. 5** (b) for CN, LDH, SnS and SnS/LDH/CN were 2.71, 2.41, 1.67 and 2.48 eV, which were obtained from the extrapolated intercept on the abscissa.

The transfer and separation efficiency of the charge carriers were analyzed using PL measurements. As displayed in **Fig. 6** (a), a strong absorption peak was observed for CN around 460 nm. The emission peak for LDH/CN was lower than that of CN, which was in agreement with the enhanced charge transfer efficiency. The SnS/LDH/CN heterojunctions showed a weaker PL peak compared with the binary catalysts, which was mainly attributed to greater availability of electrons and holes for catalytic reactions. The PL signal peak for SnS/LDH/CN also exhibited an obvious blue shift, indicating that the recombination of photogenerated carriers was inhibited. The lowest PL intensity was obtained for the CLS-30 composites in accord with the photocatalytic activity results. The EIS were further employed to measure the transfer process of photoinduced charge

carriers (**Fig. 6** (b)). The arc radius of an EIS plot reflects the resistance and efficiency of charge transfer[49]. As expected, the results showed that the arc radius for the CLS-30 heterojunction was smaller than that of the single and binary catalysts, corresponding to its faster carrier migration ability.

3.3. Piezo-photocatalytic degradation of TC

The catalytic degradation activity of the as-synthesized samples was evaluated through TC degradation under visible light irradiation, ultrasonic vibration, and both visible light irradiation & ultrasonic vibration (**Fig. 7**). As displayed in **Fig. 7**(a), all as-prepared catalysts exhibited low piezocatalytic ability for degradation of TC, with SnS disoplaying the highest TC degradation rate (38.2 %). TC was hardly degraded by CN, LDH, or LDH/CN with vibration alone. Meanwhile, the degradation efficiency of SnS/LDH/CN composites gradually improved with increasing SnS content. These results showed that SnS possesses some piezoelectric performance. The photocatalytic results in **Fig. 7**(b) showed the degradation rates followed the order: SnS/LDH/CN > LDH/CN > SnS > LDH > CN. It was clear that the SnS NPs loading on the surface of the LDH/CN could significantly enhance photocatalytic performance, which was ascribed to the formation of a ternary heterojunction. The CLS-30 heterojunctions showed the highest photocatalytic efficiency for TC degradation after 60 min under illumination. Similarly,

296 CLS-30 achieved the best degradation rate (98.5%) compared with CN, LDH, SnS and
297 LDH/CN under simultaneous ultrasonic vibration and visible light conditions (**Fig. 7**(e)),
298 indicating the synergistic effect of the heterojunction and piezoelectric properties. The
299 pseudo-first-order reaction kinetics for TC degradation is displayed in **Fig. 7** (b, d, f). The
300 high reaction rate constant (K) of SnS/LDH/CN reflected the outstanding degradation rate
301 under piezocatalysis, photocatalysis and piezo-photocatalysis. The results further
302 demonstrated that improved degradation efficiency was due to the combination of the
303 LDH/CN heterojunction and piezoelectric effect of SnS. In addition, the stability and
304 durability of the CLS-30 samples was evaluated by recycling experiments (**Fig. 8** (a)).
305 The piezo-photocatalytic performance of CLS-30 retained high stability (89.3%) after
306 four consecutive cycles. The XRD and XPS patterns (**Figs. S1** and **S2**) of the CLS-30
307 composites showed no significant changes before and after use, indicating structural
308 stability and reusable properties.

309 *3.4. Mechanistic study*

310 Trapping tests were carried out using the CLS-30 samples in the presence of various
311 scavengers under identical conditions in order to explore the piezo-photocatalytic
312 degradation mechanism. As shown in **Fig. 8** (b) EDTA, IPA, and BQ were used as
313 scavenging agents for H^+, $\cdot OH$, and $\cdot O_2^-$ species, respectively. The TC degradation

efficiency on the addition of the BQ and EDTA scavengers was suppressed, which demonstrated $\cdot O_2^-$ and H^+ dominated the reaction process. Simultaneously, the introduction of IPA as an·OH scavenger showed it played a subordinate role in TC degradation. To further validate the catalytic mechanism, ESR measurements were performed using DMPO as the ·OH and $\cdot O_2^-$ radical scavengers trapping agent. As DMPO-·OH spectra show (**Fig. 8** (c)), four characteristic signals (peak intensity = 1:2:2:1) were observed for LDH, LDH/CN and CLS-30, indicating that ·OH radicals were produced in the three reactions. It is obvious that the ·OH peak intensity for CLS-30 was stronger than that of pure LDH and binary LDH/CN, which revealed that more ·OH radicals were generated during the catalytic process. From **Fig. 8** (d), six characteristic signals related to $\cdot O_2^-$ were exhibited for LDH/CN and CLS-30. However, no obvious characteristic peaks were obtained for LDH, corresponding with the position of its conduction band (CB). Furthermore, CLS-30 showed the strongest DMPO-$\cdot O_2^-$ signals than those of the other samples, proving that it significantly promoted the formation of $\cdot O_2^-$ radicals from molecular oxygen. The results demonstrated that the SnS/LDH/CN heterojunction could effectively enhance the separation efficiency of photogenerated carriers and catalytic performance through the combination of SnS, LDH and CN.

A reasonable mechanism for the SnS/LDH/CN composite in TC degradation was

proposed on the basis of these experimental results (**Fig. 9**). Under light irradiation, the CN, SnS and LDH were excited to produce electron-hole pairs under visible-light irradiation. The photogenerated electrons on the CB of SnS and LDH rapidly migrate and recombine with the holes in the valence band (VB) of CN. Therefore, electrons accumulate in the CB of CN, and the highly positive holes remain in the VB of SnS and LDH, respectively. Here, the Z-scheme heterojunction structure favours the broadening of the carrier transport channel to accelerate charge transfer[50-51]. In the degradation process, the accumulated surface electrons in the CB of CN react with O_2 to generate $\cdot O_2^-$, and the photogenerated holes on the VB of SnS and LDH possess sufficient energy to oxidize H_2O into ·OH radicals. Meanwhile, SnS can generate a built-in electric field under stir, which provids a powerful driving force for the migration and separation of photogenerated carriers. The built-in electric fields can significantly improve degradation efficiency by producing more free radicals and inhibiting recombination of electrons and holes. Therefore, the SnS/LDH/CN composites achieve greater radical density through combination of heterojunction and piezoelectric properties to participate in the degradation of TC, hence showing enhanced piezo-photocatalytic performance. Degradation of TC over the SnS/LDH/CN piezo-photocatalytic system can thus be described:

$$SnS/LDH/CN + h\nu \longrightarrow h^+ + e^- \quad (1)$$

$$e^- + O_2 \longrightarrow \cdot O_2^- \quad (2)$$

$$\cdot O_2^- + e^- + 2H^+ \longrightarrow H_2O_2 \quad (3)$$

$$H_2O_2 + e^- \longrightarrow \cdot OH + OH^- \quad (4)$$

$$(\cdot O_2^- + h^+ + \cdot OH) + TC \longrightarrow \text{Degradation products} \quad (5)$$

4. Conclusions

We have developed a novel ternary SnS/LDH/CN heterojunction synthesized by a simple hydrothermal method and which exhibits excellent piezo-photocatalytic performance. Notably, the CLS-30 composition catalyst exhibited significantly improved piezo-photocatalytic activity over that of other variants. The improved piezo-photocatalytic performance is attributed mainly to the synergistic effect of both Z-scheme heterojunction and piezoelectric effects for accelerating the transfer of photo-generated carriers. Moreover, the unique nanosheet intercalation structure offers ample active sites and enhances ionic transport electrical conductivity for TC degradation. The prepared SnS/LDH/CN heterojunctions reveal high stability with little activity loss over four continuous cycles. This study therefore offers an innovative method for the synthesis of

highly efficient and Z-scheme heterojunction piezo-photocatalysts for the degradation of TC, which is of significance for environmental remediation.

Author contribution statement

Hao Sun: Writing-original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Writing-review & editing, Data curation, Conceptualization. **Martin R. Tillotson**：Writing-review & editing, Visualization, Investigation. **Dawei, Wang**：Visualization, Investigation. **Xu Zhao**: Writing-review & editing, Visualization, Resources, Funding acquisition.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 72074136, 72033005). And the Taishan Scholar Youth Expert Program of Shandong Province (NO. tsqn202103020).

References

[1] S. Khandaker, M.M. Bashar, A. Islam, M.T. Hossain, S.H. Teo, M.R. Awual, Sustainable energy generation from textile biowaste and its challenges: A comprehensive review, Renew. Sust. Energ. Rev. 157 (2022) 112051.

[2] R. Niu, J. Ren, J.J. Koh, L. Chen, J. Gong, J. Qu, X. Xu, J. Azadmanjiri, J. Min, Bio-Inspired Sandwich-Structured All-Day-Round Solar Evaporator for Synergistic Clean

Water and Electricity Generation, Adv. Energy Mater. 13 (2023) 2302451.

[3] A. Aghahosseini, A.A. Solomon, C. Breyer, T. Pregger, S. Simon, P. Strachan, A. Jäger-Waldau, Energy system transition pathways to meet the global electricity demand for ambitious climate targets and cost competitiveness, Appl. energy 331 (2023) 120401.

[4] J.R. Rohr, C.B. Barrett, D.J. Civitello, M.E. Craft, B. Delius, G.A. DeLeo, P.J. Hudson, N. Jouanard, K.H. Nguyen, R.S. Ostfeld, J.V. Remais, G. Riveau, S.H. Sokolow, D. Tilman, Emerging human infectious diseases and the links to global food production, Nat. Sustain. 2 (2019) 445-456.

[5] G. Dantas, M.O. Sommer, R.D. Oluwasegun, G.M. Church, Bacteria subsisting on antibiotics, Science. 320 (2008) 100-103.

[6] M. Diamant, S. Baruch, E. Kassem, K. Muhsen, D. Samet, M. Leshno, U. Obolski, A game theoretic approach reveals that discretizing clinical information can reduce antibiotic misuse, Nat. Commun. 12 (2021) 1148.

[7] X. Shi, Y. Xa, W. Wei, B.J. Ni, Accelerated spread of antibiotic resistance genes (ARGs) induced by non-antibiotic conditions: roles and mechanisms, Water Res. 224 (2022) 119060.

[8] M.L. Nadimpalli, S.J. Marks, M.C. Montealegre, R.H. Gilman, M.J. Pajuelo, M. Saito, P. Tsukayama, S.M. Njenga, J. Kiiru, J. Swarthout, M.A. Islam, T.R. Julian, A.J. Pickering,

Urban informal settlements as hotspots of antimicrobial resistance and the need to curb environmental transmission, Nat. Microbiol. 5 (2020) 787-795.

[9] S. Vyas, P. Prajapati, A.V. Shah, S. Varjani, Municipal solid waste management: Dynamics, risk assessment, ecological influence, advancements, constraints and perspectives, Sci. Total Environ. 814 (2022) 152802.

[10] N. Mariotti, M. Bonomo, L. Fagiolari, N. Barbero, C. Gerbaldi, F. Bella, C. Barolo, Recent advances in eco-friendly and cost-effective materials towards sustainable dye-sensitized solar cells, Green chem. 22 (2020) 7168-7218.

[11] Y. Lan, Y. Liu, J. Li, D. Chen, G. He, I.P. Parkin, Natural clay-based materials for energy storage and conversion applications, Adv. Sci. 8 (2021) 2004036.

[12] K. Yuan, J. Shi, W. Aftab, M. Qin, A. Usman, F. Zhou, Y. Lv, S. Gao, R. Zou, Engineering the thermal conductivity of functional phase-change materials for heat energy conversion, storage, and utilization, Adv. Funct. Mater. 30 (2020) 1904228.

[13] T. Xu, R. Zou, X. Lei, X. Qi, Q. Wu, W. Yao, Q. Xu, New and stable g-C_3N_4/HAp composites as highly efficient photocatalysts for tetracycline fast degradation, Appl. Catal. B. 245 (2019) 662-671.

[14] Z. Liang, C.F. Yan, S. Rtimi, J. Bandara, Piezoelectric materials for catalytic/photocatalytic removal of pollutants: Recent advances and outlook, Appl. Catal.

438 B. 241 (2019) 256-269.

439 [15] Y. Lu, Y. Cai, S. Zhang, L. Zhuang, B. Hu, S. Wang, J. Chen, X. Wang, Application
440 of biochar-based photocatalysts for adsorption-(photo) degradation/reduction of
441 environmental contaminants: mechanism, challenges and perspective, Biochar, 4 (2022)
442 45.

443 [16] W. Shi, M. Li, X. Huang, H. Ren, F. Guo, Y. Tang, C. Lu, Construction of
444 $CuBi_2O_4/Bi_2MoO_6$ p-n heterojunction with nanosheets-on-microrods structure for
445 improved photocatalytic activity towards broad-spectrum antibiotics degradation, Chem.
446 Eng. J. 394 (2020) 125009.

447 [17] X. Yu, J. Huang, J. Zhao, S. Liu, D. Xiang, Y. Tang, J. Li, Q. Guo, X. Ma, J. Zhao,
448 (Efficient visible light photocatalytic antibiotic elimination performance induced by
449 nanostructured Ag/AgCl@Ti^{3+}-TiO_2 mesocrystals, Chem. Eng. J. 403 (2021) 126359.

450 [18] D. Chen, Y. Cheng, N. Zhou, P. Chen, Y. Wang, K. Li, S. Huo, P. Cheng, P. Peng, R.
451 Zhang, L. Wang, H. Liu, Y. Liu, R. Ruan, Photocatalytic degradation of organic pollutants
452 using TiO_2-based photocatalysts: A review, J. Clean. Prod. 268 (2020) 121725.

453 [19] H. Qiu, R. Zhang, Y. Yu, R. Shen, H. Gao, BiOI-on-SiO_2 microspheres: A floating
454 photocatalyst for degradation of diesel oil and dye wastewater, Sci. Total Environ. 706
455 (2020) 136043.

456 [20] F.H. Abdullah, N.A. Bakar, M.A. Bakar, Current advancements on the fabrication,
457 modification, and industrial application of zinc oxide as photocatalyst in the removal of
458 organic and inorganic contaminants in aquatic systems, J. Hazard. Mater. 424 (2022)
459 127416.
460 [21] F. Dalanta, T.D. Kusworo, Synergistic adsorption and photocatalytic properties of
461 AC/TiO_2/CeO_2 composite for phenol and ammonia–nitrogen compound degradations
462 from petroleum refinery wastewater, Chem. Eng. J. 434, (2022).134687.
463 [22] M. Aggarwal, S. Basu, N.P. Shetti, M.N. Nadagouda, E.E. Kwon, Y.K. Park, T.M.
464 Aminabhavi, Photocatalytic carbon dioxide reduction: Exploring the role of ultrathin 2D
465 graphitic carbon nitride (g-C_3N_4), Chem. Eng. J. 425 (2021) 131402.
466 [23] G. Mamba, A.K. Mishra, Graphitic carbon nitride (g-C_3N_4) nanocomposites: a new
467 and exciting generation of visible light driven photocatalysts for environmental pollution
468 remediation, Appl. Catal. B. 198 (2016) 347-377.
469 [24] X. Zhou, P. Wang, M. Li, M. Wu, B. Jin, J. Luo, M. Chen, X. Zhou, Y. Zhang, Zhou,
470 X. Synergistic effect of phosphorus doping and MoS_2 co-catalysts on g-C_3N_4
471 photocatalysts for enhanced solar water splitting, J. Mater Sci Technol. 158 (2023) 171-
472 179.
473 [25] X. Zhou, X. Yu, L. Peng, J. Luo, X. Ning, X. Fan, X. Zhou, X. Zhou. Pd (II)

474 coordination molecule modified g-C_3N_4 for boosting photocatalytic hydrogen production,
475 J. Colloid Interface Sci. 671 (2024) 134-144.
476 [26] J. Niu, J. Albero, P. Atienzar, H. García, Porous Single-Crystal-Based Inorganic
477 Semiconductor Photocatalysts for Energy Production and Environmental Remediation:
478 Preparation, Modification, and Applications, Adv Funct Mater. 30 (2020) 1908984.
479 [27] J.A. Nasir, A. Munir, N. Ahmad, T.U. Haq, Z. Khan, Z. Rehman, Photocatalytic Z-
480 Scheme Overall Water Splitting: Recent Advances in Theory and Experiments, Adv Mater.
481 33 (2021) 2105195.
482 [28] J. Feng, J. Bian, L. Bai, S. Xi, Y. Wang, C. Chen, L. Jing, Efficient wide-spectrum
483 photocatalytic overall water splitting over ultrathin molecular nickel
484 phthalocyanine/$BiVO_4$ Z-scheme heterojunctions without noble metals, Appl. Catal. B.
485 295 (2021) 120260.
486 [29] Y. Chen, Y. Wang, W. Li, Q. Yang, Q. Hou, L. Wei, L. Liu, F. Huang, M. Ju,
487 Enhancement of photocatalytic performance with the use of noble-metal-decorated TiO_2
488 nanocrystals as highly active catalysts for aerobic oxidation under visible-light irradiation,
489 Appl. Catal. B. 210 (2017) 352-367.
490 [30] M. Farbod, M. Kajbafvala, Surface modification of TiO_2 nanoparticles by magnetic
491 ions: Synthesis and application in enhancement of photocatalytic performance, Appl.

492 Catal. B. 219 (2017) 344-352.

493 [31] G. Zhao, J. Zou, X. Chen, J. Yu, F. Jiao, Layered double hydroxides materials for

494 photo (electro-) catalytic applications, Chem. Eng. J. 397 (2020) 125407.

495 [32] S. Mallakpour, M. Hatami, C.M. Hussain, Recent innovations in functionalized

496 layered double hydroxides: Fabrication, characterization, and industrial applications, Adv

497 Colloid Interfac. 283 (2020) 102216.

498 [33] B. Song, Z. Zeng, G. Zeng, J. Gong, R. Xiao, S. Ye, M. Chen, C. Lai, P. Xu, X. Tang,

499 Powerful combination of g-C_3N_4 and LDHs for enhanced photocatalytic performance: a

500 review of strategy, synthesis, and applications, Adv Colloid Interfac. 272 (2019) 101999.

501 [34] Y. Yu, D. Chen, W. Xu, J. Fang, J. Sun, Z. Liu, Y. Chen, Y. Liang, Z. Fang,

502 Synergistic adsorption-photocatalytic degradation of different antibiotics in seawater by

503 a porous g-C_3N_4/calcined-LDH and its application in synthetic mariculture wastewater, J

504 Hazard Mater. 416 (2021) 126183.

505 [35] M. Shakeel, M. Arif, G. Yasin, B. Li, H.D. Khan, Layered by layered Ni-Mn-LDH/g-

506 C_3N_4 nanohybrid for multi-purpose photo/electrocatalysis: morphology controlled

507 strategy for effective charge carriers separation, Appl. Catal. B. 242 (2019) 485-498.

508 [36] X. Liu, J. Liang, X. Song, H. Yang, X. Li, H. Dai, Y. Song, Y. Liu, J. Hu, X. Pan, X.

509 OuYang, Z. Liang, Enhanced water dissociation performance of graphitic-C_3N_4

510 assembled with ZnCr-layered double hydroxide, Chem. Eng. J. 337 (2018) 560-566.

511 [37] C. Feng, Z.P. Wu, K.W. Ye, J. Huang, H. Zhang, Surface modification of 2D

512 photocatalysts for solar energy conversion, Adv Mater. 34 (2022) 2200180.

513 [38] L. Xong, J. Tang, Strategies and challenges on selectivity of photocatalytic oxidation

514 of organic substances, Adv. Energy Mater. 11 (2021) 2003216.

515 [39] X. Yan, G. Li, Z. Wang, Z. Yu, K. Wang, Y. Wu, Recent progress on piezoelectric

516 materials for renewable energy conversion, Nano Energy. 77 (2020) 105180.

517 [40] Y. Zhang, W. Jie, P. Chen, W. Liu, J. Hao, Ferroelectric and piezoelectric effects on

518 the optical process in advanced materials and devices, Adv Mater. 30 (2018) 1707007.

519 [41] L. Zhou, S. Dai, S. Xu, Y. She, Y. Li, S. Leveneur, Y. Qin, Piezoelectric effect

520 synergistically enhances the performance of Ti_{32}-oxo-cluster/$BaTiO_3$/CuS pn

521 heterojunction photocatalytic degradation of pollutants, Appl. Catal. B. 291 (2021)

522 120019.

523 [42] K. Das, D. Majhi, Y.P. Bhoi, B.G. Mishra, Combustion synthesis, characterization

524 and photocatalytic application of CuS/$Bi_4Ti_3O_{12}$ pn heterojunction materials towards

525 efficient degradation of 2-methyl-4-chlorophenoxyacetic acid herbicide under visible

526 light, Chem. Eng. J. 362 (2019) 588-599.

527 [43] W. Tian, N. Li, D. Chen, Q. Xu, H. Li, C. Yan, J. Lu, Vibration-driven Reduction of

528 CO_2 to Acetate with 100% Selectivity by SnS Nanobelt Piezocatalysts, Angew Chem. 135
529 (2023) e202306964.
530 [44] V.A. Cao, M. Kim, W. Hu, S. Lee, S. Youn, J. Chang, H.S. Chang, J. Nah, Enhanced
531 piezoelectric output performance of the SnS_2/SnS heterostructure thin-film piezoelectric
532 nanogenerator realized by atomic layer deposition, ACS nano. 15 (2021) 10428-10436.
533 [45] L. Li, J. Zhang, Q. Zhang, X. Wang, W.L. Dai, Superior sponge-like carbon self-
534 doping graphitic carbon nitride nanosheets derived from supramolecular pre-assembly of
535 a melamine-cyanuric acid complex for photocatalytic H_2 evolution, Nanotechnology, 32
536 (2021) 155604.
537 [46] J. Cheng, Z. Hu, K. Lv, X. Wu, Q. Li, Y. Li, X. Li, J. Sun, Drastic promoting the
538 visible photoreactivity of layered carbon nitride by polymerization of dicyandiamide at
539 high pressure, Appl. Catal. B. 232 (2018) 330-339.
540 [47] K.S. Abou-El-Sherbini, I.M. Kenawy, M.A. Hafez, H.R. Lotfy, Z.M. AbdElbary,
541 Synthesis of novel CO32−/Cl−-bearing 3(Mg+Zn)/(Al+Fe) layered double hydroxides
542 for the removal of anionic hazards, J Environ Chem Eng. 3 (2015) 2707-2721.
543 [48] L. Li, D. Ma, Q. Xu, S. Huang, Constructing hierarchical $ZnIn_2S_4$/g-C_3N_4 S-scheme
544 heterojunction for boosted CO_2 photoreduction performance, Chem. Eng. J. 437 (2022)
545 135153.

546 [49] J. Li, Y. Ma, Z. Ye, M. Zhou, H. Wang, C. Ma, D.Wang, P. Huo, Y. Yan, Fast electron
547 transfer and enhanced visible light photocatalytic activity using multi-dimensional
548 components of carbon quantum dots@3D daisy-like In_2S_3/single-wall carbon nanotubes,
549 Appl. Catal. B. 204 (2017) 224-238.
550 [50] J. Luo, X. Ning, L. Zhan, X. Zhou, Facile construction of a fascinating Z-scheme
551 AgI/$Zn_3V_2O_8$ photocatalyst for the photocatalytic degradation of tetracycline under
552 visible light irradiation, Sep. Purif. Technol. 255 (2021) 117691.
553 [51] Y. Lin, Q. Zhang, Y. Li, Y. Liu, K. Xu, J. Huang, X. Zhou, Peng, F. The evolution
554 from a typical type-I CdS/ZnS to type-II and Z-scheme hybrid structure for efficient and
555 stable hydrogen production under visible light, ACS Sustainable Chem. Eng. 8 (2020)
556 4537-4546.
557
558
559
560
561
562
563

564

565

566

567

568

569

570

571

572

573 **Fig. 1.** (a) XRD patterns for CN, LDH, SnS, LDH/CN and SnS/LDH/CN hybrids with

574 different weight ratios; (b) FT-IR spectra for CN, LDH, SnS, LDH/CN and

575 SnS/LDH/CN hybrids with different weight ratios.

576 **Fig. 2.** (a) FE-SEM of CN nanosheets; (b) FE-SEM of LDH nanosheets; (c) FE-SEM of

577 SnS nanoparticles; (d) FE-SEM of CLS-30 hybrid; (e) FE-TEM of SnS nanoparticles; (f)

578 FE-TEM of CLS-30 hybrid; (g)-(l) elemental mappings of CLS-30; and (m) EDX

579 spectrum of CLS-30.

580 **Fig. 3.** (a) N_2 adsorption-desorption isotherms of the as-prepared samples; and (b) pore

581 size distributions of the samples.

582 **Fig. 4.** XPS spectra of CN, SnS, LDH and CLS-30 (a) Survey spectra; (b) C 1s; (c) Ni

583 2p; (d) Al 2p; (e) Sn 3d; and (f) S 2p.

584 **Fig. 5. (a)** UV-vis DRS spectrum of as-prepared samples; (b) band gap energies of as-

585 prepared samples.

586 **Fig. 6.** (a) PL spectra of as-prepared samples; and (b) EIS of pure LDH, SnS, LDH/CN,

587 and CLS-30 composites.

588 **Fig 7.** TC degradation experiments for CN, LDH, SnS, LDH/CN and CLS catalysts for

589 (a) Piezocatalytic, (c) photocatalytic, and (e) piezo-photocatalytic performance; and (b),

590 (d) and (f) show the corresponding first-order kinetics plots of the different catalysts.

591 **Fig. 8.** (a) Cycling runs of CLS-30; (b) free radical trapping tests of TC degradation by

592 CLS-30; and (c-d) ESR spectra of LDH, LDH/CN, and CLS-30.

593 **Fig. 9.** Piezo-photocatalytic mechanism of TC degradation by CLS-30.