Enhanced photocatalytic removal of nitric oxide over Ag-decorated ZnSn(OH)$_6$ microcubes

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Abstract

Presently, most of the population has been facing a string of severe climate change problems that primarily come from the intensive emission of nitric oxide (NO), which requires a practical approach to sustain our living conditions. Herein, Ag nanoparticles-decorated ZnSn(OH)$_6$ microcubes (Ag:cZHS) photocatalysts were synthesized rapidly and used for photocatalytic NO removal under solar light activation. The properties of the newly prepared photocatalysts are comprehensively characterized by a series of routine methods. The NO removal performance over the ZnSn(OH)$_6$ microcubes (c:ZHS) photocatalysts was increased markedly upon being combined with Ag nanoparticles through the surface plasmon resonance effect. The contribution of e$^-$, h$^+$, •OH, and •O$_2$ was extensively investigated through trapping tests and electron spin resonance analysis (ESR). Also, the by-products and apparent quantum efficiency of the cZHS photocatalysts were studied.

1. Introduction

In recent years, with the rapid development of advanced industries, environmental pollution has become increasingly severe. Some notable examples include the summer heat record peaked at 55°C in the USA or the water loss by the non-typhoon in Taiwan [1, 2]. The mass emission of several toxic gases such as CO$_2$, CH$_4$, NO$_x$, VOCs [3] from manufacturing, transportation, factory, and power plant activities represents an obvious risk to the global environment and human health. Nitrogen oxide (NO$_x$) is one of the leading greenhouse gases directly causing global warming. Also, NO$_x$ represents a highly toxic gas, causing extreme weather phenomena such as acid rain, ozone layer depletion, PM$_{2.5}$ [4], or photochemical smog [5].

Nitric oxide (NO) is a primary component of NO$_x$ released during combustion processes [6], together with nitrogen dioxide (NO$_2$) which is more harmful than NO [7]. Extensive research on photocatalytic NO$_x$ removal from ambient air or flue gas has been performed using various methods, such as selective catalytic reduction, selective non–catalytic reduction, bio filtration, adsorption, absorption, and absorption photocatalytic [8–11]. Among them, photocatalytic materials have attracted much attention due to their great potential, including eco-friendly, low–cost, high efficiency, and non-toxic [12, 13]. A wide range of photocatalysts has been studied for NOx gas removals, such as Bi$_2$O$_3$ [14], ZnSn(OH)$_6$ [15], g-C$_3$N$_4$ [16], SnO$_2$ [17] and TiO$_2$ [18]. Among these materials, Zinc hydroxystannate (ZnSn(OH)$_6$) presents a highly promising photocatalyst, especially in addressing air pollution. However, its wide bandgap (~ 3.7 eV) remains the key challenge for the wide-spread use of ZnSn(OH)$_6$ in visible light [15].

Therefore, several methods have been performed to reduce the bandgap, including the combination with noble metals (Au, Ag, Cu), metal oxides (ZnO, SnO$_2$) [12, 19, 20], and non-metals (C, S) [21, 22]. The metal decoration is one of the best ways to significantly enhance the photocatalytic performance for NO$_x$ gas removal through the surface plasmon resonance (SPR) effect [23, 24]. Also, Ag is well-known as a good
combination with other semiconductors [25] to reduce their bandgap and increase photocatalytic efficiency.

In this work, silver nanoparticles (Ag NPs) were used to modify the photocatalytic ability of ZnSn(OH)$_6$ microcubes (cZHS). The photocatalytic mechanism of Ag:cZHS was determined experimentally by the photodegradation of NO under solar light. In addition, the characterizations of materials were studied by various techniques. Significantly, the presence of SPR of Ag NPs was identified by diffuse reflectance spectroscopy (DRS). The results of this work promise to provide a new and effective way to address NO pollution.

2. Experimental Section

2.1. Preparation of ZnSn(OH)$_6$ microcubes.

A pluronic@127 (F127) solution was made by adding 1.4 g of pluronic@127 (F127, CAS: 9003-11-6, Sigma-Aldrich) into 300 mL of deionized water and 200 mL of ethanol 98%. The synthesis process of cZHS is illustrated in Fig. 1. In this work, 7.5 mL of zinc acetate dihydrate 2 mM (98%, C$_4$H$_{10}$O$_6$Zn, CAS: 5970-45-6, ACROS Organics) and 7.5 mL of tin (IV) chloride pentahydrate 2 mM (SnCl$_4$.5H$_2$O, CAS: 10026-06-9, Sigma-Aldrich) were mixed and stirred for 30 min until the solution becomes transparent. Next, 15 mL of F127 and 6 mL of NaOH were added into the mixture and stirred for 30 min to achieve a homogeneous solution, and a white precipitate was formed during this step. Finally, this solution was transferred into a 50 mL teflon pot for the hydrothermal step at 100°C for 10 h. The samples were rinsed with deionized water and ethanol until the pH equals the pH of deionized water, followed by a drying step at 80°C to obtain cZHS.

2.2. Preparation of Ag nanoparticles-decorated ZnSn(OH)$_6$ microcubes.

The preparation of Ag:cZHS is shown in Fig. 1. The teflon pot for the hydrothermal process was fastly cooled down by tap water. Then, the different amounts of silver nitrate 0.01 M (AgNO$_3$, CAS: 7761-88-8, Sigma-Aldrich) were added into the hot-cZHS and stirred in 30 min. The solution turned to light-gray color after the addition of AgNO$_3$. The resulting solutions were rinsed with ethanol and deionized water several times and dried at 80°C to produce Ag:cZHS with 5 wt%, 10 wt%, 15 wt%, 20 wt%, and 30 wt% of the expected Ag donated as 5% Ag:cZHS, 10% Ag:cZHS, 15% Ag:cZHS, 20% Ag:cZHS, 30% Ag:cZHS, respectively.

2.3. The photocatalytic experiment.

For the photocatalytic test, 0.2 g of the catalysts was dispersed into a petri disk (d = 14 cm) by 10 mL of deionized water by ultrasonicator for 3 min, followed by a drying step at 80°C for 30 min to eliminate water. Then, the catalyst was placed in a photocatalytic reactor tank (volume = 3 L). The reactor tank is
made of stainless steel with a quartz-sealed top to allow light to penetrate the surface of the photocatalyst.

First, the NO 100 ppm (N₂ balanced, Ming Yang company) was diluted with zero air to reach a concentration of 500 ppb for the experimental process. The gas input was controlled by mass flow controllers (MFC); the pressure value of NO source and zero air source was 35 psi and 45 psi, respectively. The humidity and flow rate adjusted at 40% and 1.5 L min⁻¹, respectively. The concentrations of NO, NO₂, and NOₓ were recorded with a NOₓ analyzer (model 42c, Thermo-science). To eliminate the adsorption capacity of the material, we let the fabric and NO gas interact with each other in the dark environment for about 10 to 15 min until the concentration of the gases reached equilibrium. Then, a 300 W xenon lamp (λ > 300 nm) was turned on 15 min, as the solar power source of this experiment. The full spectra of the xenon lamp were shown in Fig. S1.

The recycling test attested to the durability of the catalyst. Here, the catalyst was washed with water and dried after each completion of a photocatalytic experiment, repeated five times. The trapping test determined the critical factors of NO photocatalytic degradation. The potassium iodide (KI), isopropyl alcohol (IPA), and dichromate solution (K₂Cr₂O₇) scavengers were added to trap h⁺, •OH, and e⁻. [14, 26]. The NO degradation, NO₂ conversion, and apparent quantum efficiency (AQE) were evaluated by Eqs. (S1), (S2) and (S3), respectively [27].

2.4. Characterization

Fourier transform infrared spectrophotometer (FTIR) analysis was established in the range of 400–4000 cm⁻¹ by using Jasco FT/IR-6500 to investigate molecular vibrations. X-ray diffraction (XRD) patterns were used to determine the materials' phase composition and crystal structure. This analysis was carried out using Bunaciu, Udrisioiu, and Aboul-Enein 2015 X-ray diffractometer with the Cu K radiation (λ = 0.154064 nm) and the scanning rate of 6° min⁻¹ in the 2θ range of 10° – 80°. The surface and crystal morphology of the materials were observed by scanning electron microscopy (SEM) and transmission electron microscop (TEM). The SEM images were captured using Hitachi FE-SEM S-4800N, and the TEM image was developed by the JEOL JEM 2000FXI model; samples were dispersed in ethanol and coated on a copper mesh for analysis. X-Ray photoelectron spectroscopy (XPS) analysis was also conducted for more investigation about the surface elemental composition and elemental states. Furthermore, the materials' optical property and surface area were examined using differential reflectance spectroscopy (DRS) analytic and Brunauer-Emmett-Teller (BET) analyzer, respectively. The electron spin resonance (ESR) was invested to determine the generation of radicals.

3. Results And Discussion

3.1. Photocatalytic activity
The photocatalytic NO removal of cZHS and Ag:cZHS materials under solar light are shown in Fig. 2a. The photocatalytic efficiency of Blank, cZHS, 1% Ag:cZHS, 5% Ag:cZHS, 10% Ag:cZHS, 20% Ag:cZHS, 30% Ag:cZHS materials are 13.01%, 52.14%, 53.86%, 61.96%, 67.6%, 87.30%, and 81.23%, respectively. The photocatalytic efficiency was significantly increased upon being combined with Ag NPs, indicating the effect of the SPR of Ag NPs. The photocatalytic efficiency of 20% Ag:cZHS reached 88.4% after only 7 min and remained unchanged until the end of the test. In contrast, the photocatalytic efficiency of cZHS increased slowly during the reaction and reached the highest efficiency of 60% at the end of the test. Thus, the 20% Ag:cZHS is the most efficient sample. Practically speaking, the reusability of materials is important, which was evaluated by a recycling test. As shown in Fig. 2b, the photocatalytic efficiency of 20% Ag:cZHS was decreased from 87.30–77.55% after 5 times recycling at the same condition. The result showed that the durability of the sample was promising. Besides, the conversion of NO to NO₂ and green products was also calculated and shown in Fig. 2c. The apparent quantum efficiency (AQE) was calculated by Eq. (S3) to understand the effect of photons on the photocatalytic ability of Ag:cZHS and cZHS (Fig. 2d). The AQE (10⁻⁴‰) value of cZHS, 1% Ag:cZHS, 5% Ag:cZHS, 10% Ag:cZHS, 20% Ag:cZHS, 30% Ag:cZHS were 3.81, 4.59, 4.60, 5.56, 7.11, and 6.51, respectively.

3.2. Materials characterizations

Figure 3a shows the FTIR spectra of 1%, 5%, 10%, 20% and 30% of Ag:cZHS and cZHS, the tracing region in the range from 400–4000 cm⁻¹. The wide peak observed in 3800 cm⁻¹ to 2750 cm⁻¹ shows OH bending and stretching vibrations [12]. Besides, the sharp peak appears at 1170 cm⁻¹, attributed to Sn – OH deformation vibration [28]. The stretching vibration of Sn-O-Sn is observed at 779 cm⁻¹ and 536 cm⁻¹ [29]. The results obtained confirm the success of the cZHS synthesis, but the signal of Zn and Ag were difficult to detect by the FTIR analysis. Therefore, the XRD diffraction was carried out to confirm the structure and crystallization of cZHS.

The XRD patterns of all samples are shown in Fig. 3b. The results show that several characteristic peaks located at 19.7°, 22.8°, 32.7°, 36.7°, 38.5°, 40.3°, 46.9°, 52.8°, 58.3°, 63° and 73° corresponding to the (111), (200), (220), (310), (311), (222), (400), (420), (422), (511), and (531) lattice planes of the cZHS, respectively [JCPDS 74-1825]. The results indicated that the cZHS has been successfully synthesized and has crystallinity with high purification in the cube phase. Furthermore, small additional peaks were overlapping at 38.2°, 44.25°, 64.5°, and 77.41° could be attributed to the (111), (200), (220), and (311) planes of the Ag NPs in the Ag:cZHS, respectively [30]. While other studies have been in the direction of peak expansion, peak intensity decreased or even peak material loss.

3.3. Morphology of materials

The SEM images in Fig. 4 show the cube shape of the sample before and after Ag NPs loading. As shown in Fig. 4a, the cZHS were synthesized with precise cube shapes, smooth surfaces. The cZHS were dispersed well in the solvent, without any conglomeration. It can be seen in Fig. 4b that the original morphology of cZHS was changed when Ag NPs were loaded onto the surface. The shape and structure of the Ag:cZHS become distinctive. However, the change is not much, which proves that this synthesis
method does not change the morphology of the substrate material. Such change in the morphology demonstrated that the Ag NPs successfully loaded onto the cZHS surface.

Figure 5 shows the morphology and structure of cZHS and 20% Ag:cZHS. As shown in Fig. 5a, b, the TEM images of the pristine cZHS with the precise edges and a length range from 300 nm – 600 nm match well with SEM images. It is observed in Fig. 5c, d that the presence of Ag NPs covered on the surface of cZHS cubes with a diameter less than 10 nm. Furthermore, the dots appearing in Fig. 5d are predicted to be Ag NPs. In contrast, in Fig. 5b, the dots of Ag NPs do not appear; instead, the nanopores were created by the F127. These nanopores were filled with Ag NPs in 20% Ag: cZHS.

3.4. Specific surface area of the materials

The N\textsubscript{2} adsorption isotherms of cZHS and 20% Ag:cZHS are shown in Fig. 6. The quantity adsorbed of cZHS is higher than that of the 20% Ag:cZHS. In addition, as shown in Table 1, the BET surface area of cZHS and 20% Ag:cZHS is 20.24 m\textsuperscript{2} g\textsuperscript{-1} and 34.93 m\textsuperscript{2} g\textsuperscript{-1}, respectively. The total pore volume and average pore width of cZHS and 20% Ag:cZHS are 0.034 cm\textsuperscript{3} g\textsuperscript{-1}, 6.702 nm, and 0.0267 cm\textsuperscript{3} g\textsuperscript{-1}, 3.967 nm, respectively. These results confirm that the higher total pore volume and average pore width of cZHS are due to the presence of F127, which increases the porosity of the sample [31]. The hypothesis that Ag NPs filled the nanopores of cZHS has been determined by the lower total pore volume and average pore width of 20% Ag:cZHS.

| Samples       | BET surface area (m\textsuperscript{2} g\textsuperscript{-1}) | Total pore volume (cm\textsuperscript{3} g\textsuperscript{-1}) | Average pore width (nm) |
|---------------|-------------------------------------------------------------|---------------------------------------------------------------|------------------------|
| cZHS          | 20.24                                                        | 0.034                                                         | 6.702                  |
| 20% Ag:cZHS   | 34.93                                                        | 0.027                                                         | 3.067                  |

3.5. Optical properties of materials

The optical absorption properties of cZHS and 20% Ag:cZHS are shown in Fig. 7. In Fig. 7 (a), the 20% Ag:cZHS could reflect photons with a wavelength in the range of UV light (300 nm > \lambda > 400 nm). At the wavelength from 300 nm to 400 nm, an SPR peak appears, which was generated by Ag NPs. Besides, the formation of a peak of SPR in the range of UV (200 nm < \lambda < 300 nm) and the DRS tail of the 20% Ag:cZHS does not coincide with the Ox axis in the range of IR. In contrast, in the cZHS, there is a peak present at around 360 nm. The morphology of this peak is bizarre and attributed to the manipulation of the DRS operator. However, after repeated measurements of DRS, we concluded that the appearance of this peak of the cZHS sample was due to the influence of F127 on the surface of the material. As shown in Fig. 7b, Kubelka-Munk plots of DRS reveals the band structure of cZHS is an indirect transition with the bandgap of 5.34 eV. The 20% Ag:cZHS has a smaller bandgap (5.1 eV), which is expected to have better photocatalytic activity.
The surface chemistry of materials is shown in Fig. 8. Figure 8a shows that the peaks around are assigned to Sn 3d, O 1s, and Zn 2p of cZHS. Furthermore, the peak around 370 eV of 20% Ag:cZHS corresponds to the Ag 3d. The HR-XPS of Sn 3d5, O 1s, and Zn 2p3 are shown in Fig. 8a, b and c, respectively. The peak at 485.3 eV, 493.8 eV, 531.8 eV, and 1020 eV corresponds to Sn 3d5/2, Sn 3d3/2, O 1s, and Zn 2p3/2, respectively. The HR-XPS of Ag 3d is shown in Fig. 8e; there are two peaks of Ag 3d at 367.7 and 373.6, corresponding to Ag 3d5/2 and Ag 3d3/2, respectively. In addition, XPS is a directly used tool to measure the valence-band maximum (VBM) of the materials. In Fig. 8f, the VBM of cZHS is 2.55 eV, and 20% Ag:cZHS is 4.08. The VBM of 20% Ag:cZHS is higher than the cZHS is 1.53 eV, electrons provided by Ag enhance electron transport.

3.6. Photocatalytic mechanism over the materials.

The trapping test considered the critical factors of photocatalytic degradation of NO, as shown in Fig. 9. In the trapping test, the h+, e−, and •OH were trapped by adding the KI, K2Cr2O7, and IPA scavengers, respectively. The trapping results indicate that e− and •OH contributed equally to the photocatalytic activity of 20% Ag:cZHS. The photocatalytic efficiency of the 20% Ag:cZHS was decreased dramatically by adding KI. The ESR was invested in determining the generation of radicals of 20% Ag:cZHS. Figure 9b shows that the 20% Ag:cZHS generate more •O2 radicals than •OH. These results explained that in the 20% Ag:cZHS, the e− react with O2 before forming •OH radicals.

A proposed mechanism on the photocatalytic NO removal of the Ag:cZHS under solar light is presented in Fig. 10. Under light activation, the electrons and holes are generated in the valence band of the cZHS. The photo-generated electrons spontaneously move to the conduction band of the cZHS and are isolated by the interface between the cZHS and the Ag NPs [32]. These electrons can reduce adsorbed O2 on the surface to produce •O2, as evidenced from the ERS results. These •O2 radicals could get more electrons to produce •OH species. In the meantime, the photo-generated holes in the VB oxidized adsorbed water on the surface of cZHS to •OH radicals. The •O2 and •OH radicals assist in the removal of NO [33]. Thus, the introduction of Ag NPs drastically enhances photocatalytic NO removal of the cZHS through the surface plasmonic effect, resulting in a better photoresponse and excellent electron-hole pairs separation.

4. Conclusions

In this work, the Ag:cZHS nanocomposite photocatalysts are prepared by a rapid and straightforward physical mixing process. The as-prepared Ag:cZHS nanocomposite photocatalysts show a remarkable improvement of NO removal under solar light through the surface plasmonic effect from Ag NPs. With 20% of Ag loading, a photocatalytic performance of 87.3% is achieved, much higher than that of the bare cZHS (52.14%). The green product yield produced from the 20% Ag:cZHS is also the highest (87.26%). This sample also has an excellent photostability and recycling ability with a photocatalytic performance of approximately 77% even after five repetitive runs. This study presents the promise of Ag:cZHS nanocomposite photocatalysts for addressing air pollution.
Declarations

Availability of supporting data

All data generated or analyzed during this study are included in this published article (and its supplementary information files).

Competing interests

We declare there are no competing financial interests.

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Authors' contributions

Minh-Thuan Pham: methodology (recycle test, trapping test), visualization, writing-original draft, editing, data curation. Van-Thi Nguyen: methodology (photocatalytic test, synthesis materials). Truc-Mai Thi Nguyen: data curation, investigation, editing. Hong-Huy Tran: data curation, investigation, editing. Hieu Trung Nguyen: editing. Jheng-Jie Jiang: investigation, visualization. Sheng-Jie You: formal analysis (FTIR, XRD, SEM, NO analysis), project administration. Ya-Fen Wang: formal analysis (XPS, ESR, NO analysis, TEM), chemical conceptualization, supervision, funding acquisition.

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References

1. Chao YC, Hsieh TC, Chen CW, Cheng CT, Li HC, Yeh KC, et al. Impact assessment of reservoir desiltation measures for downstream riverbed migration in climate change: A case study in northern Taiwan. J Hydro-Environ Res. 2021;37:67–81.

2. Marazziti D, Cianconci P, Mucci F, Foresi L, Chiarantini I, Della Vecchia A. Climate change, environment pollution, COVID-19 pandemic and mental health. Sci Total Environ. 2021;773:145182.

3. Saini J, Dutta M, Marques G. A comprehensive review on indoor air quality monitoring systems for enhanced public health. Sustain Environ Res. 2020;30(1):6.
4. Bungadaeng S, Prueksasit T, Siriwong W. Inhalation exposure to respirable particulate matter among workers in relation to their e-waste open burning activities in Buriram Province, Thailand. Sustain Environ Res. 2019;29(1):26.

5. Erme K, Jõgi I. Metal Oxides as Catalysts and Adsorbents in Ozone Oxidation of NOx. Environ Sci Technol. 2019;53(9):5266–71.

6. Li XH, Chen XM, Hu GX, Li LX, Su HN, Wang YY, et al. Response to the Svingen Comments on Li et al. Effects of in Utero Exposure to Dicyclohexyl Phthalate on Rat Fetal Leydig Cells. Int. J. Environ. Res. Public Health, 2016, 13, 246. Int J Environ Res Public Health. 2016;13(6):533.

7. Kampa M, Castanas E. Human health effects of air pollution. Environ Pollut. 2008;151(2):362–7.

8. Gao L, Mi XH, Zhou Y, Li W. A pilot study on the regeneration of ferrous chelate complex in NOx scrubber solution by a biofilm electrode reactor. Bioresour Technol. 2011;102(3):2605–9.

9. Hu JD, Chen DY, Li NJ, Xu QF, Li H, He JH, et al. In situ fabrication of Bi2O2CO3/MoS2 on carbon nanofibers for efficient photocatalytic removal of NO under visible-light irradiation. Appl Catal B-Environ. 2017;217:224–31.

10. Boubnov A, Carvalho HWP, Doronkin DE, Günter T, Gallo E, Atkins AJ, et al. Selective Catalytic Reduction of NO Over Fe-ZSM-5: Mechanistic Insights by Operando HERFD-XANES and Valence-to-Core X-ray Emission Spectroscopy. J Am Chem Soc. 2014;136(37):13006–15.

11. Miditana SR, Tirukkovalluri SR, Raju IM, Alim SA, Jaishree G, Chippada MLVP. Gemini surfactant assisted synthesis of mesoporous Mn/Mg bimetal doped TiO2 nanomaterial: characterization and photocatalytic activity studies under visible light irradiation. Sustain Environ Res. 2021;31(1):6.

12. Pham MT, Bui DP, Lin IF, Phuong NH, Huang Y, Cao J, et al. Enhanced near-visible-light photocatalytic removal of formaldehyde over Au-assisted ZnSn(OH)6 microcubes. Environ Technol Innov. 2020;20:101112.

13. Li X, Yu JG, Jaroniec M. Hierarchical photocatalysts. Chem Soc Rev. 2016;45(9):2603–36.

14. Pham MT, Hussain A, Bui DP, Nguyen TMT, You SJ, Wang YF. Surface plasmon resonance enhanced photocatalysis of Ag nanoparticles-decorated Bi2S3 nanorods for NO degradation. Environ Technol Innov. 2021;23:101755.

15. Pham MT, Tran HH, Nguyen TMT, Bui DP, Huang Y, Cao J, et al. Revealing DeNOx and DeVOC Reactions via the Study of the Surface and Bandstructure of ZnSn(OH)6 Photocatalysts. Acta Mater. 2021;215:117068.

16. Li X, Dong GH, Guo FJ, Zhu PF, Huang Y, Wang CY. Enhancement of photocatalytic NO removal activity of g-C3N4 by modification with illite particles. Environ Sci Nano. 2020;7(7):1990–8.

17. Huy TH, Phat BD, Thi CM, Viet PV. High photocatalytic removal of NO gas over SnO2 nanoparticles under solar light. Environ Chem Lett. 2018;17(1):527–31.

18. Duan YY, Zhang M, Wang L, Wang F, Yang LP, Li XY, et al. Plasmonic Ag-TiO2 – x nanocomposites for the photocatalytic removal of NO under visible light with high selectivity: The role of oxygen vacancies. Appl Catal B-Environ. 2017;204:67–77.
19. Lu YF, Huang Y, Cao JJ, Li HW, Ho WK, Lee SC. Constructing Z-scheme SnO2/N-doped carbon quantum dots/ZnSn(OH)6 nanohybrids with high redox ability for NOx removal under VIS-NIR light. J Mater Chem A. 2019;7(26):15782–93.

20. Yu XJ, Lu HX, Li Q, Zhao YL, Zhang LW, Fan BB, et al. Hydrothermal synthesis and characterization of micro/nanostructured ZnSn(OH)6/ZnO composite architectures. Cryst Res Technol. 2011;46(11):1175–80.

21. Zhang YY, Wang LL, Yang ML, Wang J, Shi JS. Carbon quantum dots sensitized ZnSn(OH)6 for visible light-driven photocatalytic water purification. Appl Surf Sci. 2019;466:515–24.

22. Lian XY, Chen Z, Yu X, Fan TT, Dong YY, Zhai HS, et al. Enhancing the photocatalytic activity of ZnSn(OH)6 achieved by gradual sulfur doping tactics. Nanoscale. 2019;11(19):9444–56.

23. Hou W, Cronin SB. A Review of Surface Plasmon Resonance-Enhanced Photocatalysis. Adv Funct Mater. 2013;23(13):1612–9.

24. Menon S, Agarwal H, Shanmugam VK. Catalytical degradation of industrial dyes using biosynthesized selenium nanoparticles and evaluating its antimicrobial activities. Sustain Environ Res. 2021;31(1):2.

25. Gangadharan P, Nambi IM. The performance of Cu2+ as dissolved cathodic electron-shuttle mediator for Cr6+ reduction in the microbial fuel cell. Sustain Environ Res. 2020;30(1):19.

26. Xu X, Sun YF, Fan ZH, Zhao DQ, Xiong SM, Zhang BY, et al. Mechanisms for ·O2- and ·OH Production on Flowerlike BiVO4 Photocatalysis Based on Electron Spin Resonance. Front Chem. 2018;6(64).

27. Ohtani B. Photocatalysis by inorganic solid materials: Revisiting its definition, concepts, and experimental procedures. Adv Inorg Chem. 2011;63:395–430.

28. Odeh AO. Qualitative and quantitative ATR-FTIR analysis and its application to coal char of different ranks. J Fuel Chem Technol. 2015;43(2):129–37.

29. Wan WJ, Li YH, Ren XP, Zhao YP, Gao F, Zhao HY. 2D SnO2 Nanosheets: Synthesis, Characterization, Structures, and Excellent Sensing Performance to Ethylene Glycol. Nanomaterials. 2018;8(2):112.

30. Mansor Bin A, Kamyar S, Majid D, Wan Md Zin Wan Y, Nor Azowa I. Synthesis and Characterization of Silver/Clay Nanocomposites by Chemical Reduction Method. Am J Appl Sci. 2009;6(11):1909–14.

31. Samsudin EM, Hamid SBA, Juan JC, Basirun WJ. Influence of triblock copolymer (pluronic F127) on enhancing the physico-chemical properties and photocatalytic response of mesoporous TiO2. Appl Surf Sci. 2015;355:959–68.

32. Bui DP, Nguyen MT, Tran HH, You SJ, Wang YF, Pham VV. Green synthesis of Ag@SnO2 nanocomposites for enhancing photocatalysis of nitrogen monoxide removal under solar light irradiation. Catal Commun. 2020;136:105902.

33. Huy TH, Bui DP, Kang F, Wang YF, Liu SH, Thi CM, et al. SnO2/TiO2 nanotube heterojunction: The first investigation of NO degradation by visible light-driven photocatalysis. Chemosphere. 2019;215:323–32.
Figure 1

The synthesis process of cZHS and Ag:cZHS.
Figure 2

The photocatalytic activity (a), the recycling test (b), NO conversion (c), apparent quantum efficiency (d) of the materials.
Figure 3

FTIR spectrum and XRD patterns of cZHS (a), and Ag:cZHS (b).

Figure 4

SEM images of ZHS (a) and 20% Ag:cZHS (b).
Figure 5

TEM images of ZHS (a, b) and 20% Ag: cZHS (c, d).
Figure 6

N2 adsorption-desorption isotherms of cZHS and 20% Ag:cZHS.

Figure 7

(a) Reflectance (%) vs. Wavelength (nm)

(b) (Fhv)^2 vs. Energy (eV)

SPR
DRS spectra (a), and Kubelka-Munk function (b) of cZHS and 20% Ag: cZHS.

Figure 8

XPS survey (a), high-resolution Sn 3d XPS (b), high-resolution O 1s XPS (c), high-resolution Zn 2p XPS (d), high-resolution Ag 3d XPS (e), and valence band edge spectra (f) of cZHS and 20% Ag:cZHS.
Figure 9

Trapping results (a) and ESR signals of •OH radicals and •O2 radicals of cZHS (b) of the 20% Ag:cZHS.

\[
\begin{align*}
\text{Trap } h^+ & \quad 21.1 \\
\text{Trap } e^- & \quad 57.26 \\
\text{Trap } \cdot \text{OH} & \quad 61.68 \\
\text{Untrap} & \quad 87.31
\end{align*}
\]

\[
\begin{align*}
\text{Intensity (a.u.)} & \\
\text{Magnetic energy (Gauss)} & \\
\text{•OH (UV-Light)} & \\
\text{•OH (Dark)} & \\
\text{•O2 (UV-Light)} & \\
\text{•O2 (Dark)} & \\
\end{align*}
\]
Figure 10

Schematic of photocatalytic reactions of the Ag:cZHS to treat NO gas.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- SupplementarydataR1.docx