Photoredox-Catalyzed Decomposition of Nitric Oxide over Au-Enhanced Surface Plasmon Resonance ZnSn(OH)₆ Microcubes

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ABSTRACT

Air pollution is one of the most concerning issues today because of its adverse effects on living organisms and the environment. Therein, nitric oxide (NO) is the leading cause of the greenhouse effect, acid rain, and respiratory diseases. Therefore, discovering a low-cost, environmentally friendly, highly efficient photocatalysis technique to remove NO is necessary and urgent. In this work, the ZnSn(OH)₆ microcubes (cZHS) catalyst was decorated with golden nanoparticles (Au:cZHS) to enhance the photoredox-catalyzed degradation of NO under solar light by surface plasmon resonance (SPR). This work demonstrated the contribution of SPR to the photoredox performance of the ZHS. Herein, the photoredox efficiency of the cZHS increased dramatically under the effecting of SPR from the golden nanoparticles, the photoredox efficiency of the Au:cZHS reached 75%, about four times higher than that of cZHS. In addition, the generation of other nitrogen species, nitrogen dioxide (NO₂) conversion, and the reusability of the materials are calculated and discussed carefully by theory and experiment. On the other hand, the contribution and lifespan of radicals are also investigated clearly with trapping experiments and time-dependent electron spin resonance (ESR). This study provided the reader with a clear understanding of the SPR effect on the photocatalytic performance of cZHS, which may be necessary for future related studies.

Keywords: Photocatalysis, Nitric oxide, ZnSn(OH)₆, Au nanoparticles, Surface Plasmon Resonance

1 INTRODUCTION

Nitrogen oxides (NOₓ) are becoming a concern in affecting air quality because they have affected organisms and play a significant role in global warming (Lammel and Graßl, 1995; Wild et al., 2001; Manullang et al., 2022). NOₓ includes nitric oxide (NO) and nitrogen dioxide (NO₂) (Li et al., 2018; Muñoz et al., 2019). Therein, NO accounts for the majority of NOₓ (Anthonysamy et al., 2018; Wu et al., 2022). It pollutes the air and directly affects humans, animals, and plants (Harikrishnan et al., 2005; Hu et al., 2019; Wang et al., 2022). Therefore, the discovery and development of NO treatment technologies are of great interest to scientists and engineers (Chou et al., 2022). The photoredox-catalytic technology is the most promising method because of the advantages of low cost, high durability, high reusability, and simple operation (Maggos et al., 2007; Lasek et al., 2013; Wood et al., 2020; Li et al., 2023).

Recent reports show that the ZnSn(OH)₆ microcube (cZHS) has attracted the attention of researchers because of its photoredox-catalytic applicabilities in alternative energies, sensors,
and environments (Fu et al., 2009; Wang et al., 2011). The cZHS was found to be able to degrade pollution highly. Unfortunately, cZHS has a wide bandgap, resulting in UV sources’ requirement for photocatalytic reactions (Kołątaj et al., 2020). Therefore, improving the photoredox-catalytic capacity of cZHS by manipulating its band structure is necessary. Different methods have been deployed and reported in the literature, such as structuring heterogeneous catalysts (BiOI/ZHS, ZnO/ZHS, SnO2/rGO/ZHS, V2O5/TiO2) (Yu et al., 2011; Li et al., 2013; Liu et al., 2015; Fu et al., 2021b) and using surface plasmon resonance (SPR) from noble metals. Recent studies show remarkable achievements in applying the SPR of noble metals to enhance the light absorption of cZHS. For example, the photocatalyst efficiency of ZHS was significantly increased with the help of silver nanoparticles (Ag NPs) (Pham et al., 2022), golden nanoparticles (Au NPs) (Wu and Chen, 2015), bismuth nanoparticles (Bi NPs) (Wang et al., 2017), Ag@Ag3PO4 (Chen et al., 2016), etc. In particular, Au NPs have been reported that it can enhance photoelectricity, photoelectricity, and charge separation of the substrate materials (Subramanian et al., 2004; Gupta and van Huis, 2019). Besides, Au NPs can actively interact with visible light and substrate materials due to the SPR and their stability under many conditions, so it can enhance the photocatalytic performance of the materials (Ibrahim et al., 2018; Gordon et al., 2021).

As reported by Azzazy and co-authors, the SPR band of Au NPs has the absorption maximum at the wavelength of 517 nm and 575 nm with diameters from 9 to 99 nm (Azzazy et al., 2012). Therefore, Au NPs were expected to be suitable for enhancing the visible light absorption of materials. Besides, Au NPs play a role as electron traps and promote charge transfer, which can significantly reduce the fast recombination of electron-hole (Tsai et al., 2013; Meng et al., 2019). In addition, by adding Au NPs, facilitating the interfacial charge transfer can significantly enhance the photocatalytic performances of materials (Kashyap et al., 2021). According to our previous report on Au NPs enhanced SPR ZnSn(OH)3 nanocubes (Au:cZHS) (Pham et al., 2020), Au NPs contribute much to the photoredox-catalytic efficiency of cZHS by creating activation nuclei and transferring electrons within SPR (Liu et al., 2015; Kołątaj et al., 2020; Sergeevskaya et al., 2022).

In this study, the photoredox-catalytic mechanism of Au:cZHS was surveyed and determined via photoredox-catalyzed degradation of NO under solar light. The morphology, surface functional groups, crystallinity, photoredox-catalytic mechanism, and enhancement factors have been investigated logically. Herein, the morphology, lattice fringe, and elements of materials were examined by scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HR-TEM), and scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS mapping), respectively. The molecular vibrations, crystallinity, and reusability were analyzed by Fourier transform infrared spectrophotometer (FTIR) and X-ray diffraction (XRD). The chemical states of Au:cZHS were determined by high-resolution X-ray photoelectron spectroscopy (HR-XPS). The bandgap and the appearance of SPR of samples were determined by differential reflectance spectroscopy (DRS). Significantly, the lifespan of free radicals was evaluated and discussed by electron spin resonance (ESR) spectra. Besides, stability is an essential property of the materials, which affects the application and industrialization. Therefore, the stability of the material was investigated and discussed through recycling experiments and a characteristic technique. On the other hand, the NO conversion in the photocatalytic reaction was also calculated and determined by theory and experiment.

2 EXPERIMENT

2.1 Preparation of Materials

The synthesis process of the materials is shown in Fig. 1. For the preparation of the cZHS, 7.5 mL of SnCl4·5H2O 0.4 M and 7.5 mL of Zn(CH3COO)2·2H2O 0.4 M were mixed by stirring for 15 min. Then, 4 mL of NaOH 3 M, 15 mL of ethanol 40%, and 0.042 g of Pluronic®127 were added and stirred within 30 min under room conditions. The mixing solution was transferred to the hydrothermal system at 100°C for 10 h and cooled down to room temperature. The resultant mixture was washed several times with Deion water (DI) before drying at 80°C for 12 h. For the Au:cZHS preparation, the amount of Au NPs in Au:cZHS composites was selected based on previous studies (Pham et al., 2020). Firstly, the cZHS was fast cooled down by DI; then 2.5 mL of HAuCl4·3H2O was added and stirred in 1 h. Finally, the purple mixture was washed and dried as cZHS to obtain Au:cZHS.
2.2 The Photocatalytic Experiment

The photocatalytic performance of the materials was surveyed by measuring the photodegradation ability of NO gas (500 ppb) in the photocatalytic system. Herein, 0.2 g of the materials were dispersed in 20 mL DI and coated on the Petri dishes (d = 12 cm) before drying at 80°C. The Petri dishes were transferred into a stainless-steel reactor (30 cm L × 15 cm W × 10 cm H) with a quartz window. The flow rate of the experiment was 1.5 L min⁻¹, and the humidity was around 50%. Based on the photocatalytic system design (Pham et al., 2021a, 2022), the humidity is strongly connecting to via control of the flow rate, which means that the humidity of 50% at the flow rate 1.5 L min⁻¹. The 100 ppm of NO gas (N₂ balanced, Ming Yang Co) was diluted with zero air (Model 1001, Sabio Instruments) until it reached 500 ppb. The NO, NO₂, and NOx concentrations were collected and recorded by NOx analyzer (model 42i, Thermo-Scientific). The adsorption–deorption equilibrium was reached in the dark condition. Then, the materials were irradiated under solar light (wavelength from 200 to 1000 nm) by a 300 W Xenon lamp for 30 min.

The photocatalytic mechanism of the Au:cZHS was determined by trapping tests. In the trapping tests, the potassium iodide (KI), isopropyl alcohol (IPA), and dichromate solution (K₂Cr₂O₇) were used for trapping tests to identify factors responsible for the photocatalytic activity (Huy et al., 2019). Herein, the hole (h⁺), hydroxyl radical (·OH), and electron (e⁻) are trapped separately by KI, IPA, and K₂Cr₂O₇, respectively. The photocatalytic-catalytic NO removal efficiency (η), the NO₂ conversion efficiency (γ), and the DeNOx index (α DeNOx) of the materials were calculated by Eq. (1), Eq. (2), and Eq. (3), respectively (Ohtani, 2011). Where \(C_{\text{NO}}\) (ppb) and \(C_{\text{NO₂}}\) (ppb) are the concentrations of NO, and NO₂ in the initial state (i) and final state (f), respectively.

\[
\eta = \frac{C_{\text{NO},i} - C_{\text{NO},f}}{C_{\text{NO},i}} \times 100\% \quad (1)
\]

\[
\gamma = \frac{C_{\text{NO₂},i} - C_{\text{NO₂},f}}{C_{\text{NO},i}} \times 100\% \quad (2)
\]

\[
\alpha_{\text{DeNOx}} = \eta (1 - 3\gamma) C_{\text{NO},i} \quad (3)
\]

The rest concentration of precursor of the reactive oxygen species (ROS) at the time t (min) (\(N_{\text{t, precursor}}\)) was calculated by Eq. (4). Theoretically, the initial concentration of the precursor (\(N_{0, \text{ precursor}}\)) was also the maximum ROS concentration (\(N_{\text{max}}\)). Then, the ROS concentration at the time t (\(N_{\text{t, ROS}}\)) was calculated by Eq. (5–6). Then, the ratio of the (\(N_{\text{t, ROS}}\)) to the maximum ROS concentration (\(N_{\text{max}}\)) was calculated by Eq. (7). Finally, the time when the ROS can reach half of the maximum concentration (\(t_{1/2, \text{ ROS}}\)) was calculated by Eq. (8). Herein, k (min⁻¹) is the rate constant.
\[ N_t^{\text{precursor}} = N_0^{\text{precursor}} e^{-kt} = N_{\text{max}}^{\text{ROS}} e^{-kt} \]  
(4)

\[ N_t^{\text{ROS}} = N_0^{\text{precursor}} - N_t^{\text{precursor}} \]  
(5)

\[ N_t^{\text{ROS}} = N_{\text{max}}^{\text{ROS}} (1 - e^{-kt}) \]  
(6)

\[ \frac{N_t^{\text{ROS}}}{N_{\text{max}}^{\text{ROS}}} = 1 - e^{-kt} \]  
(7)

\[ t_{1/2}^{\text{ROS}} = \frac{\ln(2)}{k} \]  
(8)

### 2.3 Characterization

The FTIR was established in 400–4000 cm⁻¹ to determine the phase composition of materials. The XRD (Bunaciu, Udrishtioiu, and Aboul-Enein 2015 X-ray) was used to analyze the crystallinity of the materials. The morphology of the materials was determined by SEM (Hitachi FE-SEM S-4800N) and TEM (JEOL JEM 2000FXI model). The XPS analysis was also invested in determining the surface elemental composition and elemental states. The optical properties were examined by DRS spectra. The ESR spectra was invested to determine the generation and signals of the radicals. The SEM-EDS was provided to identify the surface chemistry of the materials.

### 3 RESULTS AND DISCUSSIONS

The XRD pattern of the materials is shown in Fig. 2(a). The peaks at 19.8, 22.8, 32.6, 36.6, 38.4, 40.2, 46.7, 52.6, 58.2, 62.3, 68.2, 73.2, and 77.8° correspond to the (111), (200), (220), (310), (311), (222), (400), (422), (511), (440), (531), and (600) plane of cZHS, respectively [JCPDS74-182] (Dillip et al., 2020). Besides, the peaks at 38.4 and 43.6 correspond to the (111) and (200) planes of Au NPs, respectively [JCPDS 01-1172] (Yadav et al., 2022). However, the intensity of those peaks is too low. The intensity of the characteristic peaks of cZHS is dramatically decreased with the appearance of Au NPs. In addition, the molecular vibrations of the materials were determined by FTIR spectra, which are shown in Fig. 2(b). The peaks at 540 and 783 cm⁻¹ correspond to the vibrations of Sn–O–Sn (Busca et al., 1994). The peaks at 1088 and 1178 cm⁻¹ correspond to the vibration of Zn–OH and Sn–OH, respectively (Odeh, 2015). The peaks at 1643 and 3100–3500 cm⁻¹ correspond to the stretching and scissoring of –OH (Zeng et al., 2008). The molecular vibrations of the material were decreased by adding the Au NPs. However, the peaks of Au NPs are difficult to detect by XRD patterns and FTIR spectra. The molecular vibrations of the cZHS shifted after adding Au NPs, the characteristic molecular vibrations of cZHS shifted after adding Au NPs. These results indicated that the cZHS is successfully synthesized via the hydrothermal method. In addition, the crystal structure and molecular vibrations of cZHS were also affected by Au NPs.

The SEM images of samples are shown in Figs. 3(a, b). The cube shape of the material was easily identified. However, there were some morphological differences between cZHS and Au:cZHS. Figs. 3(a, b) show that the cZHS has a smooth surface with sharp edges. In contrast, the cube shape of Au:cZHS could be seen clearly, but the surface and edges were not as smooth as cZHS. The surface modifications confirmed the loading of Au NPs on the surface of cZHS as in our previous study (Pham et al., 2020). The HR-TEM images of the Au:cZHS are shown in Figs. 3(c–f). The cube shapes of the materials were observed by TEM. In addition, the d-spacing values detected at 0.246 nm and 0.259 nm revealed the presence of the (310) and (220) plane of the ZHS, respectively (Fig. 3(e)) (Duan et al., 2017). The d-spacing values at 0.246 might correspond to the (111) plane of Au NPs (JCPDS: 4-784) (Torres-Mendieta et al., 2016). These results were consistent with the SEAD (inset
Fig. 2. The (a) XRD pattern and (b) FTIR spectra of the materials.

Fig. 3. SEM images of (a) cZHS and (b) Au:cZHS. (c, d) TEM images, (e, f) HR-TEM images, and SAED pattern (inset e) of Au:cZHS.
Fig. 3(e)). Besides, Fig. 3(f) also shows the d-spacing value of 0.209 nm corresponding to the (200) plane of Au NPs. In addition, the particle edge length of the cube shape of the Au:cZHS is shown in Fig. 4(a), the average particle edge length of the cube shape was 244.1 nm. Li and co-authors (Li et al., 2020) reported that the electro-optical characteristics of photocatalysts are intimately linked to particle size. The photocatalytic rate constant declines exponentially with particle size, which relates to the charge transfer (Lin et al., 2006). Based on the DRS and photocatalytic results, the electron-hole recombination was reduced by the support of the Au NPs, and the \( h^+ \), \( e^- \) can move to the catalyst surface for the photocatalytic reactions. The EDS spectra and element mapping

![Graph showing particle length distribution](attachment:image.png)

![SEM-EDS mappings](attachment:image.png)

**Fig. 4.** (a) The particle length, SEM-EDS mapping of (b) O, (c) Zn, (d) Sn, (e) Au, and (f) SEM-EDS spectra of the Au:cZHS.
of the samples are shown in Figs. 4(b–f). The wt% of O, Zn, Sn, and Au were 15.4, 31.3, 49.3, and 3.9%, respectively. The results indicated that F127 successfully reduced the Au NPs at 100°C.

The compositions of the samples were determined by XPS (Fig. 5(a)). The peaks at 87, 530, and 1021 eV were assigned to the Au 4f, O 1s, Zn 2p3 (Dong et al., 2019; Shi et al., 2019). The HR-XPS of the material are shown in Figs. 5(b–e). The peaks at 1021 and 1023 eV were assigned to the Zn 2p3/2 of the Zn$^{2+}$ state of the material (Fig. 5(b)) (Platonov et al., 2019; Caban et al., 2021). The peaks at 530 and 533 eV were assigned to the Sn–O, and Zn–O bonds of the material (Fig. 5(d)). As shown in Fig. 5(d), the peaks at 485 and 494 corresponded to the Sn 3d of material. The peaks at 485 and 488 eV were assigned to the Sn 3d5/2, and the peaks at 494, 496 eV were assigned to the Sn 3d3/2 of the Sn$^{4+}$ state (Wang et al., 2011). The peak at 82 eV was assigned to the Au 4f7/2 of Au$^0$, while the peaks at 87 and 91 eV were assigned to the Au 4f5/2 of Au$^{3+}$ (Fig. 5(f)) (Sylvestre et al., 2004; Dillip et al., 2020; Tran Vu et al., 2021). The optical absorption properties of the samples

![XPS survey](a)

![HR-XPS Zn 2p3](b)

![O 1s](c)

![Sn 3d5](d)

![Au 4f](e)

**Fig. 5.** (a) XPS survey, (b) HR-XPS Zn 2p3, (c) O 1s, (d) Sn 3d5, and (e) Au 4f orbital of Au:cZHS.
Fig. 6. (a) DRS spectra and (b) Kubelka-Munk plots of cZHS and Au:cZHS.

are shown in Fig. 6. As shown in Fig. 6(a), the samples strongly absorb photons with a wavelength in the range of UV and visible light ($\lambda > 200$ nm). In addition, the peaks in the range of UV light ($\lambda \sim 340$ nm) and visible light ($\lambda \sim 550$ nm) of Au:cZHS can indicate the presence of Au NPs with the surface plasmon resonance (Fu et al., 2021a; Pham et al., 2022). The bandgap of samples was calculated by the Kubelka–Munk plots (Fig. 6(b)). The bandgap of cZHS was 5.2 eV, while that of Au:cZHS was 3.9 eV. The Au NPs support decreasing the bandgap of cZHS. The smaller bandgap of Au:cZHS promises better photoresponsibility.

Fig. 7(a) shows the photoredox-catalytic NO degradation efficiency over the materials under solar light for 30 min. The photoredox-catalytic NO degradation efficiency increased rapidly in the first 5 min of the photoredox-catalytic reaction. As shown in Fig. 7(a), photoredox-catalytic NO degradation efficiency of the blank samples was 9%. The photoredox-catalytic NO degradation efficiency of Au:cZHS was 75% higher than cZHS (58%). This result indicated that the photoredox-catalytic activity of the cZHS significantly increased with the support of Au NPs by SPR. The relationship between the NO degradation and NO$_2$ conversion was calculated and shown in Fig. 7(b). The results showed that Au:cZHS has the lowest NO$_2$ conversion (2%) compared to cZHS (6%). Besides, the generation of other nitrogen products of Au:cZHS and cZHS were 72% and 52%, respectively. Table 1 shows the studies on the SPR that enhance the photocatalytic performance of ZHS, which relates to this study. This study is the first study on removing NO via the Au:cZHS in the gas phase. This study does not only show the high photoredox-catalytic NO degradation efficiency and the photocatalytic NO removal pathway. Besides, the photocatalytic mechanism of the Au:cZHS are logically discussed via the characteristic analysis. On the other hand, for the effect of the single metal to support the photoredox-catalytic NO degradation, our previous study showed a high removal efficiency from the support of Ag NPs. In comparing the previous research and this study, the Au NPs offer higher stability and lower toxical production (Pham et al., 2022). However, the NO removal efficiency of the Au:cZHS was lower than Ag:cZHS. The lower NO removal efficiency may be caused by the low amount of Au NPs loaded on the surface of the materials was confirmed by EDS mapping (Fig. 4(f)). Similarly, the SEM and TEM images also confirmed that the dispersion of gold particles is not uniform. The charge transfer in the materials could be affected by the amount of Au NPs. Besides, the accumulation of the by-products on the surface of the materials was also a cause of the lower NO removal efficiency.

As shown in Fig. 7(c), the photoredox-catalytic NO degradation efficiency of the materials with adding KI, IPA, and K$_2$Cr$_2$O$_7$ was 53, 70, and 29%, respectively. The photoredox-catalytic NO degradation efficiency significantly decreased by adding KI. It indicated that the e$^-$ was a main factor for the photoredox-catalytic activity of Au:cZHS. In addition, the reusability of Au:cZHS was demonstrated by repeating the photoredox-catalyzed degradation of NO experiment 5 times, the results were presented in the XRD sample and FTIR spectra (Fig. 5) (Li et al., 2019). The photoredox-catalytic efficiency of Au:cZHS slightly decreased from 75% to 70% for the 5th time (Fig. 7(d)). The decrease in the photoredox-catalytic NO degradation efficiency is due to the accumulation of the by-products on the surface of the materials, which inhibits the activity sites
Fig. 7. (a) Photoredox-catalytic NO degradation efficiency, (b) photoredox-catalytic NO conversion of cZHS and Au:cZHS, and (c) trapping results, (d) recycling test of Au:cZHS.

### Table 1. The studies on the SPR enhance the photocatalytic performance of ZHS.

<table>
<thead>
<tr>
<th>Material</th>
<th>Pollutants - concentration</th>
<th>Irradiation time (min)</th>
<th>Dosage (g)</th>
<th>Removal efficiency (%)</th>
<th>By-products</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au/ ZHS</td>
<td>Rhodamine B - 10 ppm</td>
<td>20</td>
<td>N/A</td>
<td>100</td>
<td>N/A</td>
<td>(Zhang et al., 2019)</td>
</tr>
<tr>
<td>Au:cZHS</td>
<td>Formaldehyde - 1 ppm</td>
<td>30</td>
<td>0.1</td>
<td>70</td>
<td>CO₂ and H₂O</td>
<td>(Pham et al., 2020)</td>
</tr>
<tr>
<td>Ag:cZHS</td>
<td>NO - 500 ppb</td>
<td>30</td>
<td>0.2</td>
<td>87</td>
<td>NO₂, others nitrogen species</td>
<td>(Pham et al., 2022)</td>
</tr>
<tr>
<td>Ag@Ag₃PO₄@ZHS</td>
<td>Rhodamine B - 10 ppm</td>
<td>20 - 40</td>
<td>0.05</td>
<td>93</td>
<td>CO₂ and H₂O</td>
<td>(Chen et al., 2016)</td>
</tr>
<tr>
<td>Ag@Ag₃PO₄@ZHS</td>
<td>Methyl orange - 10 ppm</td>
<td></td>
<td></td>
<td>96.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag@Ag₃PO₄@ZHS</td>
<td>Methylene blue - 10 ppm</td>
<td></td>
<td></td>
<td>99.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag@AgCl/ZHS</td>
<td>Rhodamine B - 10 ppm</td>
<td>60</td>
<td>0.04</td>
<td>99.8</td>
<td>CO₂ and H₂O</td>
<td>(Chen et al., 2015)</td>
</tr>
<tr>
<td>Ag@AgCl/ZHS</td>
<td>Crystal violet - 10 ppm</td>
<td>60</td>
<td>0.1</td>
<td>98.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag@AgCl/ZHS</td>
<td>Phenol - 10 ppm</td>
<td>120</td>
<td>0.1</td>
<td>91</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi/BiOCl/ZHS</td>
<td>Rhodamine B - 48 ppm</td>
<td>120</td>
<td>0.1</td>
<td>91.4</td>
<td>N/A</td>
<td>(Wang et al., 2017)</td>
</tr>
<tr>
<td>Au:ZHS</td>
<td>NO - 500 ppb</td>
<td>30</td>
<td>0.2</td>
<td>75</td>
<td>NO₂, others nitrogen species</td>
<td>This study</td>
</tr>
</tbody>
</table>
of the materials (Huang et al., 2016). Besides, the DeNOx index of the cZHS and Au:cZHS was 226 and 375 ppb, respectively (Fig. S2). The DeNOx index confirmed that the Au:cZHS is the green-selective photocatalyst. These results indicated that Au:cZHS have a good performance for NO degradation.

The time-dependent ESR signals were determined from 0 min to 10 min under the dark and UV conditions to survey the generation and contribution of ·O₂ and ·OH radicals to the photoredox-catalytic reactions. As shown in Figs. 8 (a, b), the signals of ·O₂ and ·OH radicals appeared markedly after 10 min under UV conditions while there were no signals in the dark condition. The ESR results indicated that Au:cZHS generated ·OH radicals more than ·O₂ radicals; ZHS might contribute to those ·OH radicals. Besides, the ROS were determined and shown in Fig. 8(c). At the beginning of the photoredox-catalytic reactions, the maximum concentrations of ROS forming of ·OH and ·O₂ radicals over the Au:cZHS were 0.396 and 0.263, respectively. In addition, the ·OH formation rate of ROS was higher than that ·O₂ radicals formation rate of ROS over Au:cZHS, which was 1.892 and 0.109 min⁻¹, respectively. Therefore, the factors of photoredox-catalyzed reaction (h⁺, e⁻) react with O₂ and H₂O to form ·OH radicals more than ·O₂ radicals throughout the photoredox-catalytic reactions. Based on the ESR results, the ·OH radicals contributed the most to the photoredox-catalytic reactions.

![Time-dependent ESR spectra of Au:cZHS](image)

Fig. 8. Time-dependent ESR spectra of Au:cZHS under (a) dark condition and (b) UV condition. (c) Lifespan evaluation for Au:cZHS.
According to the experiments and ESR results, the photoredox-catalytic reactions is proposed and shown in Fig. 9 and Fig. 10 (Ângelo et al., 2013; Pham et al., 2022; Van Pham et al., 2022). The photoredox-catalytic NO conversion pathway (Fig. 9) was proposed based on the report from Wang and coauthors (Wang et al., 2018). Herein, Wang and coauthors reported that there are two reaction pathways for the photocatalytic NO transformation, and the final by-products may include NO2, N2O3, NO7, NO5, and also N2O (Nguyen et al., 2020). In addition, as shown in Fig. 10, the e−–h+ pairs were formed under solar irradiation for the photoredox-catalytic reactions. Firstly, the e− move from VB to CB of cZHS to create excess e− and excess h+. At the same time, the e− of Au NPs is excited under solar light, then migrates to the CB of the cZHS, creating an additional e− at the CB of the cZHS, and vice versa. The e− transport between cZHS and Au NPs reduces the recombination of the e−–h+ pairs. Herein, Au NPs do not only work as the e− donor but also as e− traps. Secondly, the h+ in VB reacts with H2O to produce ·OH radicals (high proportion), and the e− reacts with O2 to produce ·O2 radicals (low proportion). Through intermediate reactions, the ·O2 produced the hydroperoxyl radical (·HO2), then the ·HO2 could produce the ·OH. Finally, the ·O2 and ·OH radicals degraded NO to generate NO2 and other nitrogen pieces (Pham et al., 2021a).

Fig. 9. Photoredox-catalytic NO conversion pathway.

Fig. 10. Schematic photoredox-catalytic mechanism of the Au:ZHS to treat NO gas.
4 CONCLUSION

In this study, the photoredox-catalytic mechanism and the reusability of the Au:cZHS were investigated and discussed thoroughly by experimental and analytical evidence. The photoredox-catalytic NO degradation of the cZHS increased from 58% to 75% with the support of SPR from Au NPs. The improving photoredox-catalytic activity of Au:cZHS is supported by SPR from Au NPs, which is confirmed by DRS spectra. However, the lower NO removal efficiency (compared to others) may cause by the low amount of the loaded Au NPs. Besides, the NO conversion to NO₂ and other nitrogen species of the Au:cZHS and cZHS was calculated to determine the by-products via the photocatalytic reaction. The Au:cZHS has shown a low NO₂ generation efficiency (2%), and the other nitrogen species generation efficiency was 72%, while the NO conversion to NO₂ and the other nitrogen species generation of the cZHS were 6 and 52%, respectively. These results confirmed that the cZHS generate more harmful gases than Au:cZHS. The photoredox-catalytic efficiency of Au:cZHS decreased 5% after five-time recycling. On the other hand, the XPS and HR-TEM confirmed that F127 successfully formed the Au NPs at 100°C. The photoredox-catalytic mechanism of Au:cZHS was clarified by ESR and trapping test. The trapping test and ESR results show that the e⁻ and ·OH radicals are the main factor for photocatalytic reaction. Overall, this study gave a first discussion on the photoredox catalyst of Au:cZHS. It also indicated that Au:cZHS could be considered more for air pollutants treatment application. In the scientific aspect, this study provides an understanding of the mechanism and efficiency of the charge transfer between the noble metal and semiconductor and also the effect of the SPR on the photocatalytic performances.

ACKNOWLEDGMENT

This work was supported by Department of Civil Engineering Chung Yuan Christian University, Taoyuan City, 32023, Taiwan; Department of Environmental Engineering, Chung Yuan Christian University, Taoyuan City, 32023, Taiwan; Center for Environmental Risk Management, Chung Yuan Christian University, No. 200, Taoyuan City, 32023, Taiwan.

FUNDING

This research was financially supported by the Chung Yuan Christian University, Taiwan (Project No: 109609432).

SUPPLEMENTARY MATERIAL

Supplementary material for this article can be found in the online version at https://doi.org/10.4209/aaqr.220355

REFERENCES


