Hydrazine-modified Zn-oxysulfide nanoparticles for CO₂ reduction under low UV-light illumination

Hairus Abdullahb, Noto Susanto Gultom,a, Dong-Hau Kuo*b, Albert Daniel Saragihb

aDepartment of Material Science and Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan
bDepartment of Industrial Engineering, Universitas Prima Indonesia, Medan, Indonesia

*dhkuo@mail.ntust.edu.tw

Abstract. Photo-catalytically hydrogen-evolved Zn(O,S) nanoparticles (NPs) have been prepared with different amounts of hydrazine (0, 0.25, 0.5, 0.75, 1, 2 mL) to induce more oxygen vacancy sites on catalyst surfaces and utilized to reduce CO₂ with different hole scavenger reagents. The as-prepared catalysts with different hydrazine amounts were first examined with XRD diffractometer, FE-SEM, and electrochemical impedance spectroscopy (EIS). The EIS spectroscopy indicated Zn(O,S) NPs with 0.75 mL hydrazine had the most efficient electron transfer property, therefore it was further used for photocatalytic CO₂ reduction experiment. Some hole scavenger reagents such as Na₂SO₄, ozon, ethanolamine, H₃PO₄, and H₂O₂ were used in this experiment. It was observed that hydrazine and hole scavengers played a critical role to enhance CO₂ reduction. The highest amount of CO₂-converted ethanol was achieved with 0.75 mL-hydrazine-modified Zn(O,S) using Na₂SO₄ and ozon simultaneously as hole scavenger reagents. The proposed mechanism which involved generated oxygen vacancy sites during the photocatalytic session was elucidated with Kröger–Vink notation.

1. Introduction

Nowadays, the main energy source is derived from fossil fuel which is not sustainable for long term application. In addition, the products of fossil fuel combustion such as CO₂, CO, NOₓ, and SO₂ are not friendly to environment. As CO₂ gas is the main product of fossil fuel combustion, the amount of CO₂ in air has significantly increased and caused an elevated global temperature and climate change. To alleviate climate change, Paris Agreement is declared in 2015 to limit global temperature increase below 1.5 °C above the pre-industrial level with net zero greenhouse gas emissions between 2030 and 2050. Therefore, the research on CO₂ reduction is one of the critical works to remediate our environment. CO₂ can be captured in the air and reduced in the photocatalytic process to form useful methanol or ethanol.

In this work, Zn(O,S) NPs which had been reported as hydrogen evolution photocatalysts were modified with additional hydrazine during the preparation process to enhance oxygen vacancy sites. Hydrazine was used as reducing agent and added after Zn(O,S) NPs were formed at 90 °C during the preparation. Oxygen vacancy sites were necessary to trap CO₂ on catalyst surfaces during the reduction reaction to form ethanol. To optimize the oxygen vacancy formation on catalyst, Zn(O,S)
was prepared with different amounts of hydrazine and the as-prepared Zn(O,S) NPs were tested with different hole scavengers to enhance the CO\textsubscript{2} reduction. The proposed mechanism of CO\textsubscript{2} reduction was presented and elucidated in this work.

2. Experimental procedure

2.1. Materials
The materials in this work were commercially obtained and utilized without any purification treatment.

2.2. Synthesis of hydrazine-modified Zn(O,S) powders
The synthesis procedure was modified based on previous works with additional hydrazine monohydrate.\textsuperscript{1,2} To prepare Zn(O,S) NPs, 4.4 g Zn(Ac)·2H\textsubscript{2}O and 0.75 g C\textsubscript{2}H\textsubscript{5}NS were dissolved in a beaker glass containing 500 mL distilled water and heated to 90 °C for 4 h. A specific amount of hydrazine monohydrate (0, 0.25, 0.5, 0.75, 1, and 2 mL) was immediately added into reaction solution after the solution temperature achieved 90 °C and denoted as Zn(O,S)-0, Zn(O,S)-0.25, Zn(O,S)-0.5, Zn(O,S)-0.75, Zn(O,S)-1, and Zn(O,S)-2, respectively. The obtained powders were collected and washed with water for three times and dried in vacuum oven at 80 °C for 12 h.

3. Results and discussions

3.1. XRD pattern analysis

![XRD patterns of as-prepared hydrazine-modified Zn(O,S) NPs.](image)

To identify the crystal structures of as-prepared Zn(O,S) powders, XRD measurements were carried out for each of the powders with different hydrazine amounts. Fig. 1 shows the XRD patterns of as-prepared Zn(O,S) powders with different hydrazine amounts. The major peaks were located between
those of ZnO (PDF #65-2880) and ZnS (PDF #05-0566), indicating the formation of Zn(O,S) solid solution. However, the secondary phase of ZnO hexagonal was formed at high amount of hydrazine. The data suggested after Zn precursor was reduced at high concentration to metal by hydrazine,\(^3\) the formation of oxy-sulfide phase for Zn metal was not thermodynamically favorable.\(^4\) As the result, hexagonal ZnO phase was finally formed as it was easier to precipitate at 90 °C.

3.2. Scanning electron microscopy (SEM) analysis

![Fig. 2](image1)

**Fig. 2** FE-SEM images of Zn(O,S) NPs with (a) 0 mL, (b) 0.25 mL, (c) 0.5 mL, (d) 0.75 mL, (e) 1 mL, and (f) 2 mL hydrazine monohydrate for their preparations.

![Fig. 3](image2)

**Fig. 3** (a) FE-SEM image and its elemental mapping of (b) Zn, (c) O, (d) S in Zn(O,S) NPs indicated with the depicted yellow rectangle in the image.
Fig. 2 indicates the morphology of as-prepared Zn(O,S) NPs with different hydrazine amounts. The particle size was decreased as the amount of hydrazine was increased. The observed particle size was decreased from approximately 300 nm (without hydrazine) to less than 100 nm (with hydrazine). The additional hydrazine in preparation process might increase the surface area of Zn(O,S) NPs, thus enhancing the catalytic sites.

To ensure all the elements were present in Zn(O,S) NPs, elemental mapping of Zn(O,S) NPs was examined with FE-SEM and it revealed all the elements were present and well distributed as shown in Fig. 3, in which the observed area was indicated with depicted yellow rectangle. The element mapping revealed Zn had the highest signal which was indicated with high contrast in Fig. 3a. Furthermore, the signal density of sulfur was higher than that of oxygen as seen in Fig. 3b and 3c, therefore sulfide phase was dominant as indicated with XRD patterns which showed the characteristic of zinc blende structure with peak shifts.

3.3. Electrochemical impedance spectroscopy (EIS) analysis
The electron-transfer property of capacitive double-layer in the interfaces between catalysis surface and electrolyte during the photo reaction was probed with EIS analysis. The measurement was carried out in 0.1 M KCl solution containing 10% ethanol with Zn(O,S)-modified glassy carbon electrode (GCE), Pt, and Ag/AgCl were used as working, counter, and reference electrodes, respectively. Fig. 4 shows the electrochemical impedance spectra of as-prepared Zn(O,S) with different amounts of hydrazine.

Fig. 4 Electrochemical impedance spectra of as-prepared Zn(O,S) with different amounts of hydrazine.

The smaller arc of EIS spectra indicated the lower resistance to transfer electron during photocatalytic reaction. Based on the EIS data in Fig. 4, Zn(O,S) with 0.75 mL hydrazine had the lowest resistance for electron transfer property and was probably great for photocatalytic reaction. Therefore, it was further used for CO\(_2\) reduction in this work.

3.4. Photocatalytic CO\(_2\) reduction
The reduction of CO\(_2\) was conducted in a 500 mL reactor with 4 x 4 watt blacklight UV tube lamps which were inserted in the middle of reactor. The experiment was done by dispersing Zn(O,S)-0.75 in 400 mL distilled water with CO\(_2\) gas bubbling during the reaction. To easily observed the CO\(_2\)-
reduced ethanol in reaction solution, the experiment was done in 24 h under UV light illumination. An aliquot was taken out and examined with GC-FID to exactly determine the concentration of produced ethanol in solution. The photocatalytic CO$_2$ reduction experiments were carried out with different hole scavengers. To enhance the reduction performance and to increase the photo carrier lifetime, hole scavengers were necessary to be employed for this experiment. Table 1 shows the amount of produced ethanol after 24 h photocatalytic reaction with different hole scavengers. The best production rate of ethanol, approximately 11.80 ppm/g·h was achieved with hydrazine-modified Zn(O,S) in the presence of Na$_2$SO$_3$ and ozon as hole scavenger reagents.

Table 1 Photocatalytic CO$_2$ reduction to ethanol in the presence of Zn(O,S)-0.75 NPs with different hole scavenger agents under blacklight UV tube lamp illumination in 24 h

| Catalyst            | Hole scavenger          | Ethanol amounts (ppm) |
|---------------------|-------------------------|-----------------------|
| Zn(O,S)             | Na$_2$SO$_3$            | 2.53                  |
| Zn(O,S) + N$_2$H$_4$| Na$_2$SO$_3$            | 11.16                 |
| Zn(O,S) + N$_2$H$_4$| Na$_2$SO$_3$ + ozon     | 56.81                 |
| Zn(O,S) + N$_2$H$_4$| Ethanolamine             | 42.32                 |
| Zn(O,S) + N$_2$H$_4$| H$_2$PO$_4$             | 29.28                 |
| Zn(O,S) + N$_2$H$_4$| H$_2$O$_2$              | 9.67                  |

3.5. Photocatalytic mechanism

The photocatalytic initiation with water valence band of Zn(O,S) which was supported with the availability of surface oxygen anion from material defect and photo-generated hole as shown in Eq. (1). The as-produced oxygen vacancy sites were crucial for H$_2$O trapped on catalyst to weaken OH bonding which could further use to attract CO$_2$ to initialize the reduction. The overall reactions were proposed as follows:

$$H_2O + V_{O,surf}^{2+} \rightarrow 2H^+ + O_{O,surf}^{0+}$$

$$12H^+ + 2CO_2 \rightarrow C_2H_5OH + 3H_2O$$

$$H_2O + O_{O,surf}^{2+} + 2h^+ \rightarrow 2OH_{aq}^- + V_{O,surf}^{2+}$$

Fig. 5 Photocatalytic mechanism of CO$_2$ reduction involving the oxygen vacancy formation to enhance water reduction.

The CO$_2$-reduced ethanol would also possibly be oxidized by photo-generated holes, therefore to block the back reaction mechanism, hole scavenger agent was necessary to add in the solution during the photocatalytic reduction of CO$_2$. Besides using for water oxidation, oxygen vacancy sites were also crucial for H$_2$O trapped on catalyst surfaces to weaken OH bonding which could further use to attract CO$_2$ to initialize the reduction. The detailed CO$_2$ reduction mechanism was schematically depicted in Fig. 6.
Fig. 6 Kinetic mechanism of photocatalytic CO$_2$ reduction to form ethanol in water

CO$_2$ reduction reaction was competitive with H$_2$ evolution reaction. After H$^+$ ions were generated from water oxidation by oxygen vacancy, they were ready for CO$_2$ reduction. However, more H$^+$ ions were needed to undergo the CO$_2$ reduction compared to H$_2$ evolution reaction, therefore to enhance the amount of generated H$^+$ ions, an appropriate hole scavengers were required.

4. Conclusions
Zn(O,S) NPs have been successfully synthesized with different hydrazine amounts and characterized with XRD, SEM, and EIS to determine their structures, morphology, and electron transfer properties. EIS spectra indicated Zn(O,S) with 0.75 mL hydrazine had the lowest resistance to transfer electron in the interfaces between catalyst surfaces and KCl electrolyte. The improved electrochemical property was related with oxygen vacancy formation as hydrazine was added in Zn(O,S) synthesis. Furthermore, the Zn(O,S) with the lowest resistance in EIS measurement was used for photocatalytic CO$_2$ reduction with different kinds of hole scavenger reagents. It was found the highest amount of ethanol (56.81 ppm) was achieved with Na$_2$SO$_4$ and ozon in 24 h photocatalytic reaction.

Acknowledgements
This work was supported by Ministry of Science and Technology of Taiwan with the grant numbers of MOST 106-2633-E-011-002 and MOST 107-2811-E-011-008.

5. References
[1] Abdullah, H.; Kuo, D.-H.; Chen, X., High Efficient Noble Metal Free Zn(O,S) Nanoparticles for Hydrogen Evolution. *International Journal of Hydrogen Energy* 2017, 42, 5638-5648.
[2] Abdullah, H.; Kuo, D.-H., Utilization of Photocatalytic Hydrogen Evolved (Zn,Sn)(O,S) Nanoparticles to Reduce 4-Nitrophenol to 4-Aminophenol. *International Journal of Hydrogen Energy* 2018.
[3] Abdullah, H.; Gultom, N. S.; Kuo, D.-H.; Saragih, A. D., Cobalt-Doped Zn(O,S)/Ga$_2$O$_3$ Nanoheterojunction Composites for Enhanced Hydrogen Production. *New Journal of Chemistry* 2018.
[4] Molefe, F. V.; Koao, L. F.; Dejene, B. F.; Swart, H. C., Phase Formation of Hexagonal Wurtzite ZnO through Decomposition of Zn(OH)$_2$ at Various Growth Temperatures Using Cbd Method. *Optical Materials* 2015, 46, 292-298.