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Improved the Light Adsorption and Separation of Charge Carriers to Boost Photocatalytic Conversion of CO₂ by Using Silver Doped ZnO Photocatalyst

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Abstract: This work developed a strategy to enhance the photocatalytic activity of ZnO by doping it with silver nanoparticles (Ag) to improve the light adsorption and separation of charge carriers, which further increases the conversion of CO₂. The loading of Ag over ZnO (Ag-ZnO) was confirmed by characterization methods (SEM, XRD, and XPS), and the photocatalytic activities of Ag-ZnO were significantly enhanced. As the result, the production rates of CO and CH4 by doped Ag-ZnO were 9.8 and 2.4 μmol g⁻¹ h⁻¹, respectively. The ZnO that had the production rate of CO was 3.2 μmol g⁻¹ h⁻¹ and it is relatively low for the production of CH4 at around 0.56 μmol g⁻¹ h⁻¹. The doping of Ag over ZnO displayed a high conversion rate for both CO and CH4, which were 3 and 4.2 times higher than that of ZnO. The doped Ag-ZnO photocatalyst also had high stability up to 10 cycles with less than 11% loss in the production of CO and CH4. The improvement of photocatalytic activities of Ag-ZnO was due to the Ag doping, which enhanced the light adsorption (400–500 nm) and narrowed band gap energy (2.5 eV), preventing the charge carrier separation. This work brings an efficient photocatalyst for CO₂ conversion in order to reduce carbon dioxide concentration as well as greenhouse gas emissions.

Keywords: ZnO photocatalyst; Ag doping; CO₂ conversion; stability; renewable energy

1. Introduction

In recent years, the effect of climate change and global warming are becoming more serious with the number of natural disasters around the world [1,2]. Wildfires, droughts, tornados, hurricanes, floods, and landslides have appeared everywhere with negative effects on both humans and the environment. In terms of greenhouse gas emission, in particular, carbon dioxide is the main factor contributing to climate change at more than 79%, followed by methane at 11%, nitrous oxide at 7%, and fluorinated gases at 3% [2–5]. Due to the increase in population, as well as industrial activities, the concentration of carbon dioxide has also increased rapidly from 380 ppm in 2010 to 410 ppm in 2020.

Therefore, finding a way to reduce the concentration of carbon dioxide (CO₂) is urgent in order to help our people avoid natural disasters and face environmental problems. Growing more trees, using public traffic, reducing waste, and replacing fossil fuels with green energy like H₂, methanol, or renewable energy (solar light) are popular methods, nowadays [6–8]. However, each strategy has some limitations such as needing a long time, high cost, or being uncomfortable to use. In addition, the rising CO₂ levels are coming from industrial activities; thus, we need to develop an efficient way to reduce or capture
the big amounts of carbon dioxide. CO2 capture by adsorbent or amine solution was developed previously, but it requires additional materials or chemicals as well as high energy or temperature during capturing process [1,3,7,9–12]. It also can be easily released back into the environment, due to the weak bonding between the adsorbent and CO2.

The conversion of CO2 using catalysts or photocatalysts has been rapidly growing, especially since the conversion of CO2 into valuable chemicals or fuels attracted scientists from around the world. Photocatalytic conversion of carbon dioxide brings more advantages by utilizing natural solar light and reusing catalysts for a long time [13–15]. It could help to reduce to operation cost of the CO2 conversion process and decrease the negative effect of greenhouse gas emissions [3,6,16].

The common inorganic and organic photocatalysts materials like TiO2, ZnO, CdS, WO3, and g-C3N4 based have been investigated for conversion of CO2 [15–18]. Among them, ZnO-based material was widely applied due to its availability, non-toxic, and cheap material. Patial and co-workers have investigated that among works published about ZnO-based photocatalysts, more than 200 papers have been done with CO2 reduction in the years 2020 and 2021 [19]. The hetero-structured ZnO is the highest method used for CO2 reduction at 36%, followed by defect-engineered ZnO (32%), plasmonic metal-loaded ZnO (18%), and 14% assigned to the doped ZnO. Therefore, the development method for doping ZnO is interesting to extend the application of ZnO-based photocatalyst for the conversion of carbon dioxide [11,13,15,18,20,21].

Doping with metals like Ca, Mg, Al, Fe, Cu, La, Ce, Pt, and Ag has been investigated to improve the ZnO photocatalytic activities by narrowed bandgap energy and enhanced photogenerated separation, as well as extended light adsorption [15,18,20,22–24]. Silver is one of the cheapest, most stable, and non-toxic of the noble metals; with surface plasmon resonance it also can support enhancing light adsorption as well. The doped Ag onto ZnO was determined to improve the photocatalytic decomposition of methylene blue [13,15,25].

Herein, this study uses Ag as a doping agent to increase the photocatalytic activities of ZnO by extending the light adsorption range and enhancing the charge transfer and separation, which are favorable for the reduction in CO2. The characterizations of photocatalysts before and after doping with silver have been done by various methods to determine the influence of Ag over ZnO. Photo-reduction in CO2 was also investigated under dark and solar light conditions. The light-harvesting, as well as surface morphology, crystal phase, chemical state, and their effect on CO2 conversion, were discussed.

2. Results and Discussions

2.1. Photocatalysts Properties

The morphologies of ZnO and Ag-doped ZnO were observed by SEM images which are shown in Figure 1. ZnO had a uniform nanorod shape, while the surface of Ag-ZnO contained some small nanoparticles loading onto the nanorods of ZnO. The result from SEM analysis confirmed that the silver nanoparticles were loaded over ZnO [13,21,25].
The XRD patterns of ZnO and Ag-doped ZnO are shown in Figure 2. The diffraction peak of ZnO displayed with high crystalline of ZnO with $2\theta$ was found at 31.2, 32.9, 34.5, 46.1, 54.8, 61.9, and 70.1° [10,11,15,18,20]. It can be seen that after loading Ag nanoparticles, the XRD peaks intensity if ZnO were reduced and a new peak at $2\theta = 40.8^\circ$ appeared, demonstrating that Ag was loaded onto ZnO [13,16,22]. The intensity of the main peaks which belonged to ZnO was decreased by the doping of Ag due to the reduction in crystallinity by the defects that were derived during the modification process. In addition, the result from the XRD analysis did not show any peak of AgO, indicating that silver was loaded on the surface of ZnO [21,22,26].

Figure 3 shows that the XPS survey of ZnO and Ag-ZnO with the presence of Zn (2p, 3d, 3p, 3s), O (1s), and Ag (3d) elements, determined the loaded of Ag over ZnO [13,14,20]. It also displayed the high spectrum intensity of O 1 s in the doped photocatalyst; thus, the loading of Ag would form more oxygen vacancies or functional groups and it may influence the CO$_2$ conversion performance [6,9,12,24].
Figure 3. XPS survey of ZnO (blue) and Ag-ZnO (black).

Further, the high-intensity spectrum of Zn 2p, Ag 3d, and O 1s was discovered and the results are listed in Figure 4.

The spectrum of Zn 2p had two peaks including Zn 2p_{1/2} (at 1040 eV) and Zn 2p_{3/2} (1025 eV) [9,11,13,15,18,20]. It clearly showed that the intensity of peaks of Zn 2p from the doped sample (Ag-ZnO) was higher than that of undoped ZnO (Figure 4a). Ahmad and co-workers have confirmed that the loading of Ag could reduce the electron density and result in an increase in the binding energy. They also explained the intensity of Zn 2p from Ag-ZnO increased due to more diffuse atoms on the surface of the doped sample rather than undoped ZnO [26]. The Ag 3d spectrum of Ag-ZnO was given in Figure 4b with the characteristic peak of 3d_{5/2} and 3d_{3/2} at binding energy 368.76 and 374.8 eV, demonstrating...
that silver presented in the sample as metallic silver clusters [13,22]. The binding energy of O 1s peaks from ZnO in Figure 4 c was deconvoluted into two peaks at a binding energy of 532.4 and 535.2 eV, which are assumed to be Zn-O and O-H, respectively [14,20].

However, the O 1s peaks from Ag-ZnO displayed three peaks at the energy levels of 531, 532.1 and 533.2 eV, which belonged to lattice oxygen of ZnO, oxygen vacancies, and O-H, respectively. The oxygen vacancies were enhanced after doping with Ag, indicating more photocatalytic reactions could happen between Ag-ZnO and CO₂, rather than undoped ZnO [13,16,18].

2.2. Optical Properties of ZnO and Ag-ZnO

The UV-vis absorbance spectrum of ZnO and Ag-ZnO was shown in Figure 5, respectively. The light absorption edge of ZnO was mostly in the range of 300–400 nm, while the Ag-ZnO showed gradually extend to the visible light (300–500 nm) [13,14,16,20,23]. The adsorption edges of ZnO and Ag-ZnO were at ~400 and 497 nm along with the bandgap energy of 3.1 and 2.5 eV, respectively. The Tauc plots were employed (Figure S1) to determine the band gap energy of ZnO and Ag-ZnO [26–28]. The results from the Tauc plots demonstrated that the loading of Ag onto ZnO narrowed its band energy from 3.1 eV to 2.5 eV. The result further confirmed that Ag-ZnO had wide light adsorption from UV to visible light with narrow band gap energy, which contributes to the enhancement of CO₂ conversion efficiency [6,13,18,20,29–31].

![Figure 5. UV-vis spectra of (a) ZnO and (b) Ag-ZnO.](image)

The result further confirmed that Ag-ZnO had wide light adsorption from UV to visible light with narrowed band gap energy from 3.1 to 2.5 eV, which contributes to the enhancement of CO₂ conversion efficiency [6,13,18,20,26].

In addition, the charge separation efficiency of ZnO and Ag-ZnO photocatalysts was evaluated by photoluminescence analysis (Figure S2).

The photoluminescence spectra of Ag-ZnO significantly reduced in intensity as compared to ZnO, demonstrating the low possibility of recombination between electron and hole or the chance of charge separation is higher than ZnO. In addition, the shape of Ag-ZnO was wider than that of ZnO, indicating the charge transport was rapidly improved or doped catalysts had higher efficient charge carrier transfer than undoped ZnO [13,21].
2.3. CO₂ Conversion by ZnO and Ag-ZnO under Solar Light

Figure 6 presented the photocatalytic activities of ZnO and Ag-ZnO for CO₂ conversion into different products including CO and CH₄.

Under the dark condition, there are no photocatalytic activities for CO₂ conversion was observed for both ZnO and Ag-ZnO.

With the presence of solar light, the production rate of CO was 3.2 and 9.8 μmol g⁻¹ h⁻¹ by ZnO and Ag-ZnO, respectively. The production rate of CH₄ was lower than CO with 2.4 μmol g⁻¹ h⁻¹ by Ag-ZnO and 0.56 μmol g⁻¹ h⁻¹ by undoped ZnO. The undoped ZnO photocatalyst provided a low CO₂ conversion rate into CO and CH₄ due to its rapid charge recombination, larger band gap (3.1 eV), and narrow light adsorption range [11,13–15,20,30]. However, after loading Ag over ZnO, the CO₂ conversion rate significantly improved, which was 3 and 4.2 times higher than that of ZnO. As we determined in the characterizations section, the Ag loading over ZnO brings more light adsorption range and improved the charge separation rate, which is correlated with enhancing the photocatalytic CO₂ conversion [8,15,18,19,21,25,30].

Further, the CO₂ conversion efficiency was compared to other materials which are listed in Table S1. Under the solar light, the Ag-ZnO presented a good capacity for the production rate of CO and CH₄. However, it still needs to develop more to enhance the production rate of CH₄ and other valuable chemicals.

The stability of ZnO and Ag-ZnO photocatalysts was quantified for 10 cycling tests of CO₂ conversion (Figure 7). There is negligible change in the reproduction of CO and CH₄ by Ag-ZnO photocatalysts as shown in Figure 7, indicating that prepared catalysts are stable for CO₂ conversion [12,21,25,31,32].
In detail, the production rates of CO and CH₄ remained at 81.3 and 72% in the 10th cycle by using Ag-ZnO. The unmodified ZnO photocatalyst displayed as a little unstable after being 10 times reused as compared to Ag-ZnO. For example, the production rate of CO after 10 recycling experiments was 58.2% and the CH₄ production rate was also relatively low at around 51.3%.

In addition, the XRD of reused Ag-ZnO was analyzed to investigate the change in the phase structure and crystalline of the photocatalyst. The result in Figure S3 suggested that the reused Ag-ZnO photocatalyst had a similar structure and crystalline as the original material.

2.4. Proposed Mechanism

Based on the collected data from characterizations of photocatalysts and experiments for CO₂ conversion, a proposed photocatalytic mechanism was proposed in Figure 8.

During the solar light irritation, the photo-induced electrons are excited from VB to CB of ZnO, producing a number of photoelectrons. The produced electrons will transfer to CB of Ag, which acts like an electron acceptor or electron conductor to increase the
electron-hole pair separation rate [13,14,16,23,33]. Therefore, more charge carriers provide for an effective CO₂ conversion rate based on the inhibited recombination of electron-hole. The electrons and holes above will act as reducing agents for the conversion of CO₂ into CO and CH₄ as following the reaction [6,19]:

\[
\begin{align*}
\text{Ag-ZnO} + hν & \rightarrow h^+ + e^- \quad (1) \\
2\text{H}_2\text{O} + 4h^+ & \rightarrow 4\text{H}^+ + \text{O}_2 \quad (2) \\
\text{CO}_2 + 2\text{H}^+ + 2e^- & \rightarrow \text{CO} + \text{H}_2\text{O} \quad (3) \\
\text{CO}_2 + 8\text{H}^+ + 8e^- & \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad (4)
\end{align*}
\]

3. Materials and Methods

3.1. Chemicals Use and Photocatalysts Preparation

This work used zinc oxides (ZnO), silver nitrate (AgNO₃), ethanol (C₂H₅OH), Zinc nitrate (Zn(NO₃)₂), sodium hydroxide (NaOH), and carbon dioxide gas (CO₂). All chemicals are analytical grade from Merck (Merck Millipore, Darmstadt, Germany) and can be used directly.

The ZnO was synthesized by adding the NaOH (concentration of 0.5 M) into a 50 mL solution of ZnCl₂ (1M), the NaOH was slowly added until the precipitation process to form (ZnOH)₂ has done. Then the precipitated material was separated from the solution, dried at 80 °C for 24 h, then heated at 200 °C for 5 h to collect ZnO.

Ag-doped ZnO was done following by adding an amount of ZnO and AgNO₃ into 100 mL solution containing DI water and ethanol (1:1 vol.%) then stirring for 5 h, dried by the oven for 24 h at 80 °C, then pyrolyzed under N₂ gas for 2 h at 500 °C. The final product collected after the pyrolysis process was Ag-ZnO.

3.2. Characterizations

Morphology of ZnO and Ag-ZnO photocatalysts was observed with a Field-emission scanning electron microscope (SU800-SEM,Hitachi, Tokyo, Japan). UV-vis diffuse adsorption spectroscopy was performed by Shimadzu UV-1200 UV-Vis spectrometer (Kyoto, Japan). XRD patterns were recorded by X-ray diffractometer (Hitachi, XRD-9KW diffractometer, Tokyo, Japan) using Cu Kα radiation. The chemical states of the catalysts were obtained from X-ray photoelectron spectroscopy (XPS, Thermo Fisher, 260-EC, Kandel, Germany). Photoelectrochemical studies were carried out by the photoluminescence spectra (PL) of synthesized materials which were obtained from Fluoromax-4 fluorescence spectrometer (Horiba, Kyoto, Japan).

3.3. Photocatalytic Conversion of CO₂

The photocatalytic activity of CO₂ conversion was done by loading 0.05 g photocatalyst on a Teflon photocatalyst holder. The pure gas CO₂ was passed through the reaction system for 30 min to remove the air. The DI water (5 mL) was injected into the system to start the conversion process; before turning on the light, the system was checked under dark conditions for 1 h. The light source was provided by a Xenon arc lamp (250 W, Guangdong, China) for the photocatalytic reaction.

During irradiation, 0.2 mL of the gas sample was continually collected from the reaction and analyzed by FID detector with the help of Tech, GC-7980 gas chromatograph (Techomp, Kwai Chung, Hong Kong, China) to determine the concentration of CO and CH₄.

To investigate the stability of ZnO and Ag-ZnO, the catalysts were collected after the cycling experiment, dried at 80 °C for 12 h after washing several times with DI, and then used for other cycle experiments. For a recycled experiment, the photocatalyst was collected after each cycle test, washed, and dried at 100 °C for 5 h, and then reused for the next cycles.
4. Conclusions

This work was aimed to synthesize ZnO and Ag loaded over ZnO photocatalysts for improvement of CO2 conversion rate into CO and CH4 gas.

The loading of Ag leads to increased light adsorption of Ag-ZnO in the visible light regions (400–500 nm). The photoluminescence analysis indicated effective charge separation of Ag-ZnO due to the loading Ag, where it acts like an electron conductor to inhibit the recombination between electron-hole. The surface morphology, X-ray directions, and chemical statements analysis further confirmed the Ag successfully loaded over ZnO and it existed as metallic silver clusters.

The Ag–ZnO had a production rate of CO and CH4 up to 9.8 and 2.4 μmol g⁻¹ h⁻¹, which were 3- and 4.2-times higher than that of undoped ZnO. The modified photocatalyst Ag-ZnO also showed good stability up to 10 cycles with the production rates of CO and CH4 remaining at 81.3 and 72%, respectively. This work brings a new way to modify the ZnO in order to expand its application for energy conversion. The high conversion rate of CO: also can use for further development to reduce greenhouse gas emissions.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal12101194/s1, Figure S1: Touc plot of (a) ZnO and (b) Ag-ZnO; Figure S2. Photoluminescence analysis of ZnO and Ag-ZnO; Figure S3. XRD patterns of Ag-ZnO and reused Ag-ZnO photocatalysts; Table S1: The photocatalytic CO2 conversion of different photocatalysts [34–39].

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