Enhanced photocatalytic CO

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Submission date: 16-Jan-2020 09:41AM (UTC+0700)

Submission ID: 1242462800

File name: Enhanced_photocatalytic_CO.pdf (1.22M)

Word count: 3535

Character count: 18504

Journal of Physics: Conference Series

PAPER • OPEN ACCESS

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To cite this article: C T Handoko *et al* 2019 *J. Phys.: Conf. Ser.* **1282** 012098

Enhanced photocatalytic CO_2 reduction activity of silvered titania prepared by wet deposition method

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Abstract. Titania (TiO_2) was successfully modified with Ag nanoparticles by wet deposition method. The established structures adopt the anatase crystal structure and contain a mixture of Ag^0 and Ag^{1+} species. The Ag loading triggers extended absorption in the visible light region. Furthermore, the Ag loading improves the photocatalytic CO_2 reduction efficiency compared to the pure TiO_2. The optimal Ag loading is 2% molar ratio of Ag versus TiO_2 and the photocatalytic activity will decrease with higher Ag loading. This improved efficiency may be attributed to the synergistic effect between electron trapping and Surface Plasmon Resonance (SPR) phenomenon of Ag nanoparticle on TiO_2 surface.

1. Introduction

The growing consumption of fossil fuels leads to greatly increase the atmospheric CO_2 levels. This fact causes tremendous concerns about the effect of global warming and future energy supply [1]. Thus, the research activity about CO_2 reduction and/or conversion has become a major focus for the scientists. The photocatalytic CO_2 reduction is one of the promising solutions to overcome this problem since it can reduce both of the CO_2 greenhouse gas emissions and solve the energy crisis, in an environmentally friendly manner. The photocatalytic CO_2 reduction produces some useful chemical feedstocks and fuels such as CO, formic acid, CH_3OH, H_2, and CH_4 [2–4].

Titania (TiO_2) is the most widely used photocatalyst material since it has higher photocatalytic activity at $300 \text{ nm} < \lambda < 390 \text{ nm}$, chemical and physical stability, abundance in nature, low cost, and environmental benign [5–7]. However, utilizing pure TiO_2 still has some drawbacks. Some of the drawbacks of using pure TiO_2 in photocatalytic reactions are having a wide band gap (~3,2 eV) [8] and electron-hole recombination [9]. One way to overcome these disadvantages is by noble metal deposition [10].

The noble metals have a lower Fermi level than that of titanium oxide, thus photoexcited electron can migrate from the conduction band of TiO_2 to the deposited metal, while photogenerated holes remain in the valence band of TiO_2. The electron trapping process prevents the electron-hole recombination, thus it can increase the photocatalytic efficiency[10]. The noble metal deposition on the surface of the TiO_2 can also reduce the band gap energy and improve visible light absorption of TiO_2 through the Surface Plasmon Resonance (SPR) phenomenon [11]. Among of the noble metals, the Pt deposition is effective in increasing TiO_2 photocatalytic activity. However, due to a relatively expensive price of Pt, other noble metals are used. Silver is the most promising deposited noble metals due to its low cost, easy preparation, and good composite properties with TiO_2 [12].

Several previous studies based on Ag/TiO_2 materials have been carried out for investigating photocatalytic CO_2 reduction activity. The products are varies depending on the material properties, material preparation, and also the reactor condition. The material properties itself depending on the Ag concentration deposited on TiO_2 surface. On the other hand, the reaction system includes the reactor design, light source, lamp power, wavelength, reactant phase, the amount of catalyst, and material pre-treatment [13–16].

Herein, the Ag nanoparticles are deposited on the TiO_2 surface through wet deposition method due to the easy preparation and low cost. Furthermore, the effect of Ag loading on TiO_2 is studied for the photocatalytic CO_2 reduction to CH_4 in a gas-solid phase under a high-purity system.

2. Experimental Section

2.1. Sample Preparation

The Ag deposited on TiO_2 materials was prepared by simple wet deposition method. In brief, one mol of TiO_2 (Merck, ≥ 99%) and 0.01 mol of $AgNO_3$ (Merck, ≥ 99.9%) were dissolved with 100 mL of distilled water until slurry formed. The Ag loading was count as 1 mol% versus TiO_2. The mixture was stirred continuously for 4 hours and heated at 80 ^{o}C. The obtained slurry was allowed to settle overnight and then heated at 100 ^{o}C for 10 hours to evaporate the water. After 10 hours, the obtained-powder was ground using a mortar and calcined at 500 ^{o}C for 3 hours. The final powder was characterized by XRD and UV-vis spectrophotometer. The similar procedure was carried out for other different Ag loadings (2-4 mol% versus TiO_2). This procedure was similar to previous studies [17,18].

2.2. Photocatalytic CO_2 Reduction Test

The photocatalytic CO_2 reduction was performed under ultra-high vacuum high-purity gas-phase photoreactor [19–22]. The gas source was 6.0 He (99.9999% He) and 1.5% CO_2/He. The gas and H_2O mixture was obtained by passing the gas through the water saturator at 5 ^{o}C. The 200 W Hg/Xe lamp with the water filter was used as the light source. Before starting the CO_2 reduction measurement, the cleaning procedure was performed to make sure that the samples were free from carbon-containing species. The cleaning steps including pre-heated at 400 ^{o}C for 3 hours with a tubular furnace, batch cleaning, and flow cleaning. The batch cleaning was conducted by passing pure He through the water saturator until the reactor pressure reached 1500 mbar, and then the light was turned on for 6 hours. While the flow cleaning was done in the same way, but the He-H_2O mixture was only passed in the reactor. The photocatalytic CO_2 reduction experiment was performed with the similar procedure as batch cleaning step, except for the use of CO_2 gas as the reactant. Thus, the reactant consisted of 1.5% CO_2/He and H_2O. The products were analyzed using Shimadzu Tracera GC 2010 plus which was equipped with a barrier ionization discharge (BID) and flame ionized (FID) detector.

3. Results and Discussion

The XRD patterns (Figure is not shown) show that all samples adopt anatase crystal structure (JCPDS File No. 83-2243), indicating that Ag species is only deposited on TiO_2 surface and not incorporated into TiO_2 structure. The reflexes of Ag species peaks are appeared at $2\theta \sim 33^{o}$ and $\sim 44^{o}$. The first corresponds to the characteristic of Ag^{0} species with lattice plane of (200) (JCPDS File No. 04-0783), while the latter corresponds to the diffraction pattern of (111) planes of Ag_2O species (JCPDS File No. 41-1104). Furthermore, the UV-Vis investigation reveals that the Ag loading triggers the material absorption in the visible light region (400-700 nm) compared to the bare TiO_2. The broad absorption band from 400 nm to 700 nm attributes to the characteristic of Surface Plasmon Resonance (SPR) of Ag nanoparticle [23].

The products analysis are only focused on methane (CH_4) production, which is the most dominant product of the reaction, although the reaction also produces ethane (C_2H_6) and ethane (C_2H_4) in relatively small amounts. The material produces CH_4 even though CO_2 gas is not added as a reactant. This indicates that there are CO_2 species adsorbed on the surface of photocatalyst material. In addition to adsorbed CO_2 species, it is likely that the materials also contain several carbon impurity species which are adsorbed during material preparation. The light irradiation at high temperatures can eliminate the adsorbed hydrocarbon [24]. The cleaning process can reduce unwanted CH_4 product around 50%. Thus, we ensure that the next CH_4 product originally comes from photocatalytic CO_2 reduction.

The CH_4 is only obtained when the materials are exposed to the light source. Figure 1 clearly shows the evolution of CH_4 during light irradiation. As depicted in Figure 1, all of Ag loading improves the photocatalytic efficiency in CO_2 reduction compared to the pure TiO_2. The final CH_4 evolution after 6 hours of radiation is 12.03 ppm, 17.20 ppm, 19.75 ppm, 14.01 ppm, and 13.18 ppm for the bare TiO_2, Ag/TiO_2 1%, Ag/TiO_2 2%, and Ag/TiO_2 4%, respectively. The highest photocatalytic activity is found in Ag/TiO_2%. Further increase in Ag concentration (3% and 4%) leads to a gradual decrease in photocatalytic activity.

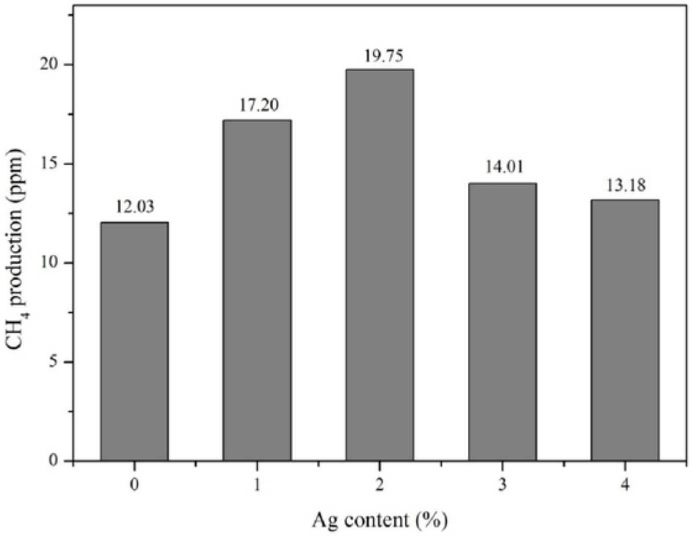

Figure 1. Photocatalytic CO_2 reduction over Ag/TiO_2 materials

This phenomenon can be described as follows. The Ag species act as electron trapping due to the lower Fermi energy level compared to TiO_2. Thus, the photogenerated electron located in the conduction band of TiO_2 is quickly transferred to Ag species deposited on the surface of TiO_2 and prevent the electron-hole recombination [25]. Furthermore, the Schottky barrier energy is formed between TiO_2 surface and Ag metallic. This Schottky barrier blocks the retransferring electron process from Ag to TiO_2, thus the electron remains in the Ag species [26]. These processes improve the electron-hole separation and finally increase the photocatalytic activity.

In addition, the SPR also contributes to improve photocatalytic activity of as-prepared materials. The SPR effect boosts electron energy in Ag nanoparticle when exposed to the visible light. The strong electron field of SPR triggers the fast reactions with the electron acceptor from reactant [13]. A synergistic effect between SPR and electron-hole separation gives a significant impact to the photocatalytic activity improvement.

Increasing the Ag loading after 2% blocks the active site of the photocatalyst, thus decreases the photocatalytic activity. Bensouici et al. (2015) investigated that an increase of Ag loading caused agglomeration phenomenon of Ag nanoparticles and eventually limit the contact between photocatalyst and the light source. Furthermore, the interface between Ag species and TiO_2 has high defect density and known as one of electron-hole recombination center [27].

The reaction possibility which occurs during the photocatalytic CO_2 reduction using Ag/TiO_2 material can be proposed following these equations.

$$TiO_2 + hv \longrightarrow h_{VB}^{+} + e_{CB}^{-} \tag{1}$$

$$h_{VB}^{+} + e_{CB}^{-} \longrightarrow \text{heat} \tag{2}$$

$$e_{CB}^{-} \longrightarrow e_{Ag}^{-} \tag{3}$$

$$e_{Ag}^{-} + hv\ (\text{visible}) \longrightarrow e_{SPR}^{-} \tag{4}$$

$$h_{VB}^{+} + H_2O \longrightarrow HO^{-} + H^{+} \tag{5}$$

$$HO^{-} + h_{VB}^{+} \longrightarrow HO^{\cdot} \tag{6}$$

$$H^{+} + e_{SPR}^{-} \longrightarrow H^{\cdot} \tag{7}$$

$$CO_2 + e_{SPR}^{-} \longrightarrow \cdot CO_2^{-} \tag{8}$$

$$CO_2^{-\cdot} + h_{VB}^{+} \longrightarrow CO + OH^{-} \tag{9}$$

$$CO + e_{SPR}^{-} \longrightarrow \cdot CO^{-} \tag{10}$$

$$\cdot CO^{-} + H^{\cdot} \longrightarrow C + OH^{-} \tag{11}$$

$$C + H^{\cdot} \longrightarrow \cdot CH \tag{12}$$

$$\cdot CH + H^{\cdot} \longrightarrow CH_2 \tag{13}$$

$$CH_2 + H^{\cdot} \longrightarrow \cdot CH_3 \tag{14}$$

$$\cdot CH_3 + H^{\cdot} \longrightarrow CH_4 \tag{15}$$

Where:

h_{VB}^{+} is the hole generated in valence band of TiO_2

e_{CB}^{-} is the photoexcited electron occurred in conduction band of TiO_2

e_{Ag}^{-} is the electron transferred from TiO_2 to Ag

e_{SPR}^{-} is SPR effect of Ag

When a photon with the energy higher than the band gap energy of TiO_2, the electron will be excited to the conduction band (CB) of TiO_2, while the hole is formed in the valence band (VB) (equation 1). The photogenerated electron and hole can also react together releasing heat (equation 2). This phenomenon is called recombination of electron-hole which makes the limitation of photocatalytic activity. The other non-recombined electron transferred from TiO_2 CB to the Ag surface as an electron acceptor (equation 3). SPR effect of Ag nanoparticle enhances the activity of trapped electron in Ag surface (equation 4). Active hole further can react with adsorbed water to produce HO^{-} and H^{+} (equation 5). The formed HO^{-} and H^{+} react with hole and electron, respectively to form hydroxyl radical and hydrogen radical (equation 6-7). At the same time, the adsorbed CO_2 species react with e_{SPR}^{-} for producing $\cdot CO_2^{-}$ (equation 8). CO intermediate is generated from the reaction between $\cdot CO_2^{-}$ and hole according to equation 9. Furthermore, the reaction between CO and e_{SPR}^{-} produces carbonyl radical as shown in equation 10. The C residue or surficial C is produced from the reaction between carbonyl radical and hydrogen radical (equation 11). Further reaction of this C residue with hydrogen radical produces intermediate species according to equation 12-14. The last step is the formation of CH_4 from the methyl radical and hydrogen radical (equation 15).

As described above that the Ag/TiO_2 materials consist of Ag^0, Ag^{1+}, and TiO_2. This composite combines the heterojunction properties of Ag_2O/TiO_2 and also electron trap-SPR characteristic of Ag^0. Figure 2 shows the schematic photocatalytic CO_2 reduction using Ag/TiO_2.

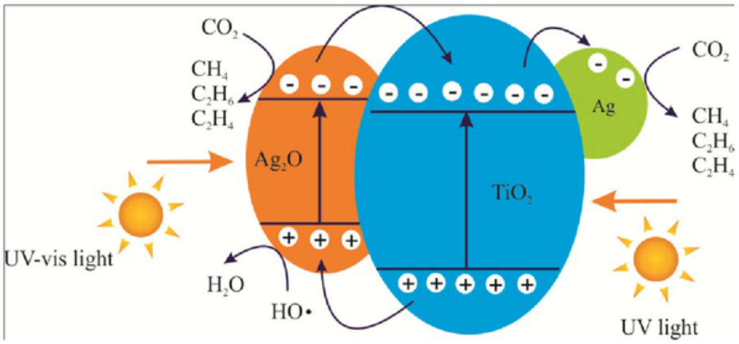

Figure 2. Scheme of photocatalytic CO_2 reduction over Ag/TiO_2 material

The electron trapping mechanism of Ag^0 and formation of CH_4 over Ag/TiO_2 photocatalyst have been discussed in equations 4-18. The CO_2 gas is more strongly adsorbed on Ag_2O species compared to Ag^0. Stuve et al. (1982) revealed that the metallic Ag^0 requires pre-adsorption of O_2 molecules to adsorb CO_2 molecules. Therefore, the CO_2 cannot be adsorbed properly on Ag^0 species [28]. The photocatalytic mechanism in the presence of Ag_2O on TiO_2 surface is described as follows.

The Ag_2O/TiO_2 is the type II p-n heterojunction. When reaching equilibrium, TiO_2 (n-type semiconductor) has a positive charge, while Ag_2O (p-type semiconductor) has a negative charge. When a suitable photon energy exposes the material, several photoexcited electrons in the conduction band of Ag_2O migrates to the conduction band of TiO_2. The photogenerated hole moves from valence band of TiO_2 to the valence band of Ag_2O. This electron-hole transfer occurs due to the formation of an electric field at the p-Ag_2O/n-TiO_2 heterojunction and eventually retards the electron-hole recombination [29]. Most electrons in the conduction band of TiO_2 directly contribute to the formation of CH_4 through the equations 11-18.

4. Conclusion

The Ag/TiO_2 in different loading (1-4%) was successfully synthesized by a simple wet deposition method. All of Ag loading show improvement in photocatalytic CO_2 reduction activity compared to the bare TiO_2. This improved efficiency due to the synergistic effect between electron trapping of Ag^0 species and also SPR phenomenon occurred in Ag^0 species. Furthermore, the mixed valence of Ag^0 and Ag^{+1} offers beneficial for photocatalytic performance due to the formation of both p-Ag_2O/n-TiO_2 heterojunction and electron trapping phenomenon of Ag/TiO_2 materials.

Acknowledgment

This research was funded by the Ministry of Research, Technology and Higher Education of Indonesia (grant number: 2064.31/D3/PG2017) and the German Ministry of Education and Research (BMBF) in the scope of the funding scheme CO_2Plus (Project-No. 033RC033, PROPHECY). The authors would like to thank colleagues from Heterogenous Photocatalyst Department of Leibniz Institute for Catalysis at the University of Rostock (LIKAT) for providing the photocatalytic CO_2 reduction measurement.

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