

Photocatalytic reduction of carbon dioxide using Co_3O_4 nanoparticles under visible light irradiation

Joseph Albert Mendoza, Hye Kyoung Kim, Hoey Kyung Park, and Kyun Young Park[†]

Department of Chemical Engineering, Kongju National University,
275, Budae-dong, Seobuk-gu, Cheonan, Chungnam 331-717, Korea
(Received 15 January 2012 • accepted 19 July 2012)

Abstract—Photocatalytic reduction of carbon dioxide under visible light irradiation was carried out with Co_3O_4 powders suspended in water. A Pyrex glass batch reactor of 10 mL in volume was used with a 21 W LED lamp of 510 to 620 nm in wave length as light source, and the reaction time was held at 4 h. The major products were formic acid and formaldehyde; the production rates were $4.53 \mu\text{mol g}^{-1}\text{h}^{-1}$ and $0.62 \mu\text{mol g}^{-1}\text{h}^{-1}$ for formic acid and formaldehyde, respectively. Carbon monoxide and methane were detected in trace amounts. The occurrence of the photo-reduction with Co_3O_4 is against the expectation from the valence band edge of Co_3O_4 in the literature. Possible causes for the contradictory result are discussed.

Key words: Photocatalytic Reduction, Visible Light, Carbon Dioxide, Co_3O_4 , Nanoparticles

INTRODUCTION

The increase in the atmospheric concentration of carbon dioxide has been regarded as one of the most severe environmental issues of our time. It has been in the interest of the international research community to find effective and energy-efficient solutions to reduce the CO_2 concentration. Recycling of CO_2 via conversion into a high-energy content fuel is a highly attractive option, but the process is energy intensive and will only be economically feasible if an inexpensive and readily available energy source can be used for conversion [1]. A possible way to meet such requirement is to convert CO_2 at ambient condition into organic compounds such as methane, methanol, ethanol, formic acid, and formaldehyde using semiconductors with the help of solar energy. Many studies have been conducted on the photocatalytic conversion of CO_2 using different catalysts. TiO_2 catalysts showed promising results in efficiently converting CO_2 into hydrocarbons; however, due to its wide band-gap energy of 3.0-3.2 eV, it is effective under only ultraviolet light [2]. Other catalysts with narrower band gap have been investigated [3, 4]. The quantum efficiencies reported so far for the carbon dioxide conversion appear to be short of that required for practical applications [5], calling for further research including the search for new catalyst materials.

Co_3O_4 is a p-type semiconductor that is known to have two band gap energies of 1.44 and 2.06 eV, corresponding, respectively, to edges of $\text{O}^{2-} \rightarrow \text{Co}^{3+}$ and $\text{O}^{2-} \rightarrow \text{Co}^{2+}$ excitations [6]. Cobalt oxides were used as catalyst for water splitting with $[\text{Ru}^{2+}(\text{bpy})_3]/\text{persulfate}$ as photosensitizer [7], and for the degradation of phenols in wastewaters coupled with bismuth vanadate (BiVO_4) [8]. In the present study, bare Co_3O_4 was applied for the first time to a photocatalytic reduction of carbon dioxide with water. Neither hole scavenger nor photo-sensitizer was used.

EXPERIMENTAL

1. Synthesis of Photocatalysts

All chemicals were reagent-grade and used without any further purifications. A solution of 0.25 M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (SIGMA-ALDRICH) was prepared initially. An equivalent amount of 30% $\text{NH}_3 \cdot \text{H}_2\text{O}$ (SIGMA-ALDRICH) was added dropwise into the solution with stirring. The resulting precipitate was separated by centrifugation and washed with water three times. The wet precipitate was then dried and calcined for 2 h in air. The produced powders were characterized with a transmission electron microscope (TECNAL, F20) for morphology and an X-ray diffractometer (SCINCO, SMD-3000) for crystalline structure, and UV-visible spectrometer (SHIMADZU, UV-2450) for light absorption spectra. The diameters of the primary particles in the transmission microscopic image of the Co_3O_4 powder were determined to obtain the average diameter using a computer program by which the number of pixels occupied by a particle was counted and converted into a diameter.

2. Photocatalytic Reaction

A batch-type 10 mL Pyrex glass reactor was used. 25 mg of the Co_3O_4 powder was put in the reactor and spread on the bottom by shaking the reactor gently. 250 μL of distilled water was then injected to wet the powder. A stream of carbon dioxide was passed through a bubbler containing water and the reactor in series for 10 min at a rate of 300 ml/min away from light. Afterwards, the reactor was transferred into a plastic chamber, 0.20 m in diameter and 0.55 m in length and placed on the bottom. The chamber is equipped with a green 21 W LED light on its ceiling; the wavelength of the light ranges from 510 to 620 nm. The reaction was initiated by turning on the LED light and continued for 4 h. After reaction, the product gas in the reactor was sampled with a syringe and analyzed by gas chromatography. A gas chromatograph (HP, 5890) equipped with

[†]To whom correspondence should be addressed.
E-mail: kypark@kongju.ac.kr

molecular sieve column and thermal conductivity detector was used for hydrogen. For methane, a gas chromatograph (SHIMADZU, GC-2014) with GS ALUMINA column and flame ionization detector was used. For carbon monoxide, a gas chromatograph equipped with a methanizer (YOUNG LIN, YL6100) was used. The water in the reactor was diluted by distilled water and separated from the catalyst particles by filtration in the dark. The filtrate was then analyzed by liquid chromatography (FUTECS, AT-300) for formaldehyde and formic acid and by gas chromatography (SHIMADZU, GC-2014) using HP INNOWAX column for methanol.

RESULTS AND DISCUSSION

Fig. 1 shows the TEM image of the synthesized cobalt oxide nanoparticles. The number average diameter of the primary particles in the image was determined to be 18.5 nm with the standard deviation at 5.6 nm. The BET area was measured to be 36.1 m²/g. The surface-area equivalent diameter was calculated at 27 nm using the BET area and particle density of 6.1 g/cm³. Fig. 2 shows the XRD

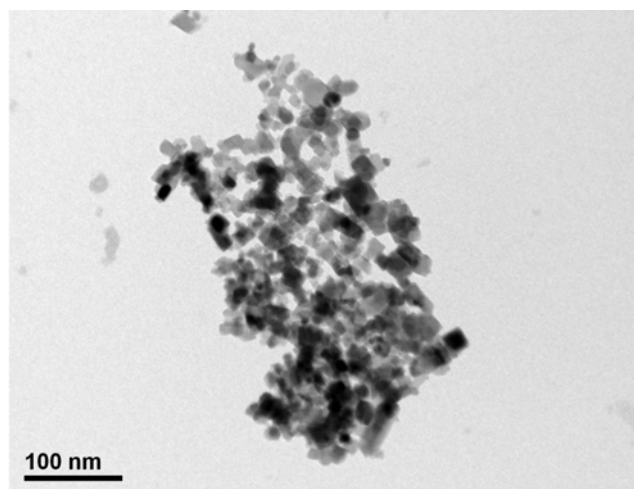


Fig. 1. Transmission electron microscopic image for the Co₃O₄ synthesized from CoCl₂·6H₂O precursor.

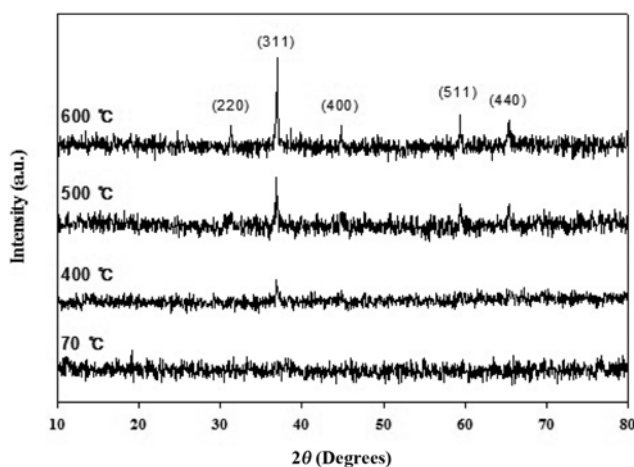


Fig. 2. X-ray diffraction patterns for the synthesized Co₃O₄ particles.

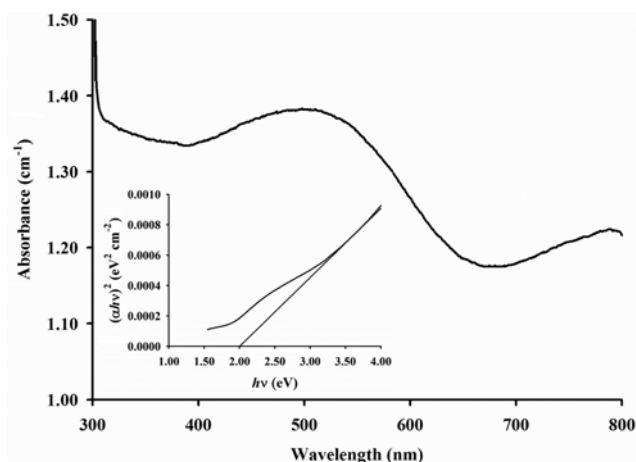


Fig. 3. UV-Vis spectra for the synthesized Co₃O₄ particles.

patterns of Co₃O₄ with varying calcination temperature. The crystalline peaks appeared at 400 °C and increased in intensity as the temperature was further increased to 600 °C. In the preliminary photo-reaction study to follow, the calcination temperature was fixed at 400 °C, considering that the surface area of the Co₃O₄ should collapse at higher temperatures due to sintering between neighboring particles. The UV-visible spectra of the cobalt oxide particles calcined at 400 °C are shown in Fig. 3 over the wavelength 300 to 800 nm. The high background may be unavoidable because Co₃O₄ absorbs light over broad wavelength, including the light longer than 800 nm in wavelength. The band gap energy of the Co₃O₄ particles was determined to be 2.0 eV by plotting $(\alpha h\nu)^2$ vs. $h\nu$ in the inset where α is the measured absorption coefficient, h is the Planck constant, and ν is the wave frequency. The obtained band gap energy is comparable to 2.06 eV reported for Co₃O₄ thin films [6].

The products detectable in significant quantity at room temperature were formaldehyde, formic acid, and methane. Elevated reaction temperature would bring higher production rates. In the present study, however, the temperature was fixed at room temperature because a disposal of carbon dioxide through elevated-temperature reaction would produce another carbon dioxide associated with the energy supplied for temperature elevation. None of the products was detected in the absence of either catalyst or carbon dioxide, indicating that the products are due to the photocatalytic reaction. Carbon monoxide was detected, but neglected because the measured concentrations were not significantly different from the concentration of carbon monoxide present as impurity in the carbon dioxide charged to the reactor. Methanol, ethanol, and hydrogen were not detected. The product concentrations in ppm and the production rates in $\mu\text{mol}/(\text{g}\cdot\text{h})$ are shown in Table 1; the rates were

Table 1. Measured product concentrations and calculated production rates

Product	Concentration, ppm	Production rate, $\mu\text{mol}/(\text{g}\cdot\text{h})$
Formic acid	2.87 ± 0.93	4.53
Formaldehyde	0.25 ± 0.02	0.62
Methane	8.13 ± 1.17	0.033

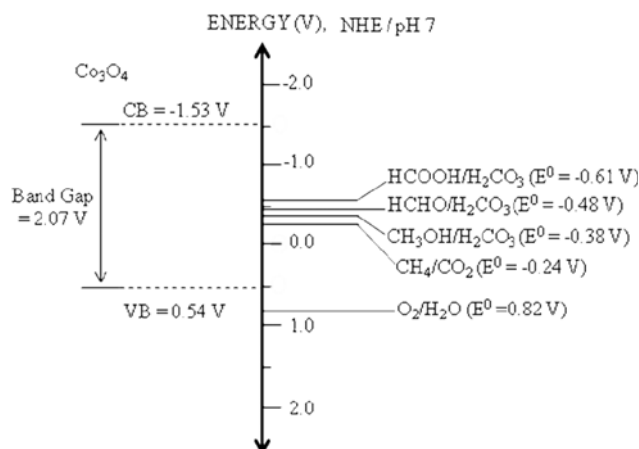
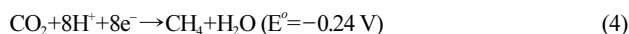
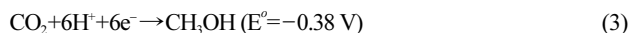
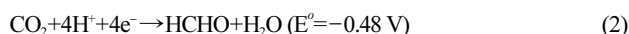
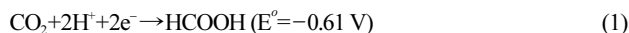


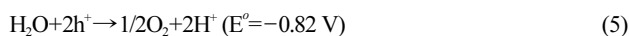
Fig. 4. Band edge positions of Co_3O_4 and the potential levels of the redox reactions involved in CO_2 conversion.

calculated using the measured concentrations averaged for two duplicate runs and information on catalyst mass, reaction time, and reactor volume. The production rates were 4.53, 0.62 and 0.033 $\mu\text{moles}/(\text{g}\cdot\text{h})$ for formic acid, formaldehyde and methane, respectively. No experimental data in the literature are available that can be compared with our data under similar reaction conditions.

The reduction of carbon dioxide is known to occur as follows [9]:



The protons are provided by the oxidation of water represented by



All potentials are presented as reduction potentials in reference to NHE at pH 7. Fig. 4 shows the band positions of Co_3O_4 along with the potential levels of Eqs. (1) to (5). The conduction and valence band edge positions of Co_3O_4 , quoted from the work of Long et al. [8], were -1.53 V and 0.54 V , respectively.

The conduction band edge of Co_3O_4 is more negative than the potentials of the CO_2 reduction reactions. This favors spontaneous transfer of the photo-generated electrons to the reductions. The valence band edge position is less positive than the potential level of the water oxidation, which is not favorable for the transfer of the holes to the water oxidation. Overall, the reduction of carbon dioxide with Co_3O_4 appears not to be feasible thermodynamically due to the barrier in hole transfer. On the contrary, there occurred an appreciable reduction as experimentally observed. This contradictory result is discussed in the following section.

The actual potential (E) of Eq. (5) at a given operating condition can be represented by

$$E = E^\circ - \frac{RT}{nF} \ln \frac{1}{[\text{H}^+]^2 p_{\text{O}_2}} \quad (6)$$

where E° is the standard potential, R is the gas constant, T is the

temperature, n is the number of electrons involved in the reaction, F is the Faraday constant, $[\text{H}^+]$ is the molar proton concentration, and P_{O_2} is the oxygen pressure. By substituting $8.314 \text{ J}/(\text{mol}\cdot\text{K})$ for R , 298.15 K for T , 2 for n , $96485 \text{ coulomb/mol}$, 10^{-7} mol/L for $[\text{H}^+]$, and 1.23 V for E° , one obtains the following relationship between E and P_{O_2} :

$$E = 0.82 - 0.0591 \log \frac{1}{p_{\text{O}_2}^{1/4}} \quad (7)$$

The water oxidation potential, 0.82 V in Fig. 4 is that at the oxygen pressure of 1 atm . By Eq. (7), the actual potential should be lower than 0.82 V because the photocatalytic reduction was carried out nearly oxygen-free. The oxygen pressure that can shift the potential in Fig. 4 up to the level of valence band edge is calculated to be $1.2 \times 10^{-19} \text{ atm}$. It is difficult to say, however, that the oxygen pressure at the operation condition of this study was that low indeed. The oxygen-pressure effect alone may not be able to explain the experimental observation that the reduction occurred with the unfavorable energy positions.

There may be other causes that can be suspected. The valence band edge of Co_3O_4 in the literature may be underestimated. The bicarbonate ion (HCO_3^-) produced by the dissolution of carbon dioxide in water may have played a role as hole scavenger, as was pointed out earlier by Dimitrijevic et al. [10].

CONCLUSION

We have demonstrated the photocatalytic reduction of carbon dioxide into formic acid and formaldehyde using bare Co_3O_4 nanoparticles in water under illumination at $510\text{--}620 \text{ nm}$ with a 21 W LED as light source. The occurrence of the photocatalytic reduction with Co_3O_4 is against the expectation from the valence band edge of Co_3O_4 reported in the literature. Possible causes for the contradictory result were suspected, but further investigation is necessary to find the causes that can be accepted. The present study being in the preliminary stage, the activity of Co_3O_4 can be further improved through variation of operating variables such as the particle size and the calcination temperature of the as-prepared Co_3O_4 .

ACKNOWLEDGEMENT

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MEST) (No. 2010-000923). One of the authors, Kyun Young Park, acknowledges the financial support by Kongju National University for the research during his leave of absence.

REFERENCES

1. C. C. Lo, C. H. Hung, C. S. Yuan and J. F. Wu, *Sol. Energy Mater. Sol. C.*, **91**, 1765 (2007).
2. R. Thiruvengatachari, S. Vigneswaran and I. S. Moon, *Korean J. Chem. Eng.*, **25**, 64 (2008).
3. Y. Liu, B. Huang, Y. Dai, X. Zhang, X. Qin, M. Jiang and M. Whangbo, *Catal. Commun.*, **11**, 210 (2009).
4. C. Wang, R. L. Thompson, J. Baltrus and C. Matranga, *J. Phys. Chem. Lett.*, **1**, 48 (2010).

5. S. C. Roy, O. K. Varghese, M. Paulose and C. A. Grimes, *ACS Nano*, **4**, 3, 1259 (2010).
6. J. Patil and P. Chauhan, *Mater. Charact.*, **61**, 575 (2010).
7. F. Jiao and H. Frei, *Angew. Chem.*, **121**, 1873 (2009).
8. M. Long, W. Cai, J. Cai, B. Zhou, X. Chai and Y. Wu, *J. Phys. Chem. B*, **110**, 20211 (2006).
9. M. M. Halmann and M. Steinberg, *Greenhouse gas carbon dioxide mitigation*, Lewis Pub., Boca Raton, FL (1999).
10. N. M. Dimitrijevic, B. K. Vijayan, O. G. Poluektov, T. Rajh, K. A. Gray, H. He and P. Zapol, *J. Am. Chem. Soc.*, **133**, 3964 (2011).