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Renewable fuel by photohydrogenation of CO$_2$: Impact of the nature of Cu species loaded TiO$_2$

Bo-Ren Chen $^1$, Van-Huy Nguyen $^1$, Jeffrey C.S. Wu $^{1,*}$, Reli Martin $^2$, Kamila Kočí $^2$

$^1$ Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan

$^2$ Institute of Environmental Technology, VŠB-Technical University of Ostrava, 17. listopadu 15/2172, Ostrava – Poruba 708 33, Czech Republic.

* Corresponding author

Phone: +886-2-23631994, Fax: +886-2-23623040, E-mail: cswu@ntu.edu.tw
Efficient gas-phase photocatalytic hydrogenation of CO$_2$ opens a feasible route not only to store H$_2$ by converting into renewable fuel but also to cut down the atmospheric CO$_2$ greenhouse gas.
Abstract

Efficient gas-phase photocatalytic hydrogenation of CO₂ into desired fuel is achieved on Cu-loaded TiO₂ photocatalyst system. Firstly, the enhancing amount of Ti³⁺ rather than Ti⁴⁺ species in Cu-loaded TiO₂, in comparing with TiO₂ photocatalyst, provides an excellent opportunity to promote the photohydrogenation of CO₂. Additionally, the coexistence of Cu and Cu¹⁺ species during the photoreaction could also efficiently enhance photocatalytic activity by prolonging the lifetime of electrons. To achieve the best photoactivity, the content of Cu species must be maintained at an appropriate low concentration (≤ 1wt.%), and the corresponding highest CH₄ yield was 28.72 µmol g⁻¹. This approach opens a feasible route not only to store hydrogen converting into desired renewable fuel but also to cut down the atmospheric CO₂ greenhouse gas.

Keywords: photohydrogenation, carbon dioxide; renewable fuel, photocatalysis; Cu-loaded TiO₂
1. Introduction

Nowadays, hydrogen (H$_2$) is considered as energy for the future because of its clean energy, most abundant, flexible and highly efficient. Although the outlook will inevitably belong to H$_2$, there are still growing concerns about the H$_2$ storage.$^{1,2}$ In details, it requires 11,250 l to achieve 1 kg of H$_2$ under atmospheric pressure and room temperature. Even H$_2$ is compressed at 700 bars; its volumetric energy density is approximately six times lower than that of gasoline (8.8 kWh/l). Meanwhile, the volumetric energy density of natural gas, which mainly consists of methane (CH$_4$), has four- to fivefold higher than that of hydrogen.$^3$ Hence, great efforts have been made to increase the volumetric energy of hydrogen.$^4$ On the other hand, we also concern how to reduce the atmospheric carbon dioxide (CO$_2$), which is the major greenhouse gas in Earth’s atmosphere.$^{5,6}$

To solve these issues, H$_2$ storage through hydrogenation of CO$_2$ to hydrocarbons has been successfully developed.$^{7,8}$ Ideally, this concept provides an alternative and sustainable pathway for H$_2$ storage by considering greenhouse gas CO$_2$ as a potential building block.$^9$ It allows H$_2$ to be converted into renewable fuel, which directly resolves both global environment and H$_2$ storage issues. Among many alternative processes, photohydrogenation of CO$_2$, which is an ideal method for converting CO$_2$ into desired fuels, is considered with much attention.$^{10-12}$ However, it is noted that the quantum efficiency and product yield in the CO$_2$ photohydrogenation are still low and requires a further study. The design of photocatalyst which works efficiently for the photohydrogenation of CO$_2$ has been the subject of several studies. Among the candidates, titania-supported copper catalyst plays a crucial role in promoting the photocatalytic reduction of CO$_2$.$^{13-16}$ Additionally, supported copper is found to be economical and abundant in nature.
Herein, a series of Cu/CuO loaded TiO$_2$ was synthesized and carried out the photohydrogenation of CO$_2$ with H$_2$O in the single photoreactor. It is noticeable that the oxidation state of Cu species is a crucial factor in CO$_2$ photoreduction activity.\textsuperscript{15} Hence, the impact of reducing CuO to Cu and the transition of Cu species during the reaction were carefully evaluated for their potential to hydrogenation. Furthermore, chemical and structural features of photocatalysts were thoroughly characterized by SEM, XRD, UV-vis, XPS and XANES.

2. Experimental

2.1. Preparation of photocatalysts

The whole synthesis procedure is shown in Scheme 1. Titanium dioxide (denoted as TiO$_2$) photocatalyst was prepared by a sol-gel method, which was adapted from Tseng et al.\textsuperscript{15} A typical batch contained 21 ml titanium (IV) butoxide (Ti(OC$_4$H$_9$)$_4$, 99 \%, Fluka), 22 ml n-butanol (C$_4$H$_9$OH, 99.4 \%, J.T. Baker) and 14 ml acetic acid (CH$_3$COOH, 99.7 \%, J.T. Baker). The mixed solution was stirred for 8 h. Then, the transparent sol was dried at room temperature to 423 K for 3 h in an oven, then transferred to a furnace and calcined at 773 K for 5 h to burn off hydrocarbons and consequently produce the desired TiO$_2$ powder photocatalyst.

Titania-supported copper oxide (denoted as CuO/TiO$_2$) photocatalyst was prepared by an impregnation method. TiO$_2$ powder, which was previously prepared, was added to an appropriate amount of copper (II) chloride solution (CuCl$_2$, 99 \%, Sigma-Aldrich). The solution was then sonicated in an ultrasonic bath and mixed with a magnetic stirrer to get a homogeneous slurry. After wet impregnation, it was dried at 353 K and finally calcined in air at 773 K for 4 h. For titania-supported copper metal (denoted as Cu/TiO$_2$) photocatalyst, it was prepared by reducing
of CuO/TiO$_2$ under a flow of 5% H$_2$/N$_2$ mixture at 573 K for 3 h. In our research, we named each photocatalyst with different Cu/CuO loading weight percentage.

2.2. Characterization of photocatalysts

The light absorption of photocatalysts was fully characterized by UV-visible spectrophotometer (UV-vis, Varian Cary-100). BaSO$_4$ was used as the absorption standard in these measurements. Powder X-ray diffractometer (XRD, Bruker-D8-ADVANCE) with a Cu K$_\alpha$ ($\lambda = 1.5418$ Å) radiation source at 40 kV and 40 mA was used to verify the crystalline structure of the photocatalysts. The BET specific surface area of photocatalyst was determined by N$_2$ adsorption using Physisorption Analyzer (Micromeritics ASAP 2000). Field emission scanning electron microscopy (FE-SEM, JEOL JSM-7000) integrated with energy dispersive spectroscopy (EDS) was operated at an acceleration voltage of 5 kV. The photocatalysts were sputtered with a thin layer of Pt film to prevent surface charging. The X-ray photoelectron spectroscopy (XPS, Thermo Scientific Theta Probe) was used to determine the oxidation states of the elements. The X-ray absorption near-edge structure (XANES) at the Cu K-edge was recorded at the BL17C1 beamline, National Synchrotron Radiation Research Center (NSRRC), Taiwan, where the electron storage ring was operated at an acceleration voltage of 1.5 GeV. All data were acquired at ambient temperature in the fluorescence mode. The K-edge data was normalized to equal the edge jump.

2.3. Photocatalytic hydrogenation of CO$_2$
The gas-phase photocatalytic hydrogenation of CO\(_2\) with H\(_2\)O was carried out in a single Pyrex photoreactor with the volume of 385 ml (as shown in Figure 1). Photocatalyst powder (0.10 g) was evenly packed on the Teflon flat that was fixed in the middle of photoreactor. The bottom of photoreactor was moisturized with 5 ml of deionized water to tune the saturated water vapor pressure in the photoreactor through controlling the reaction temperature. The pen-ray lamp (11SC-1, 254 nm, 12 mW cm\(^{-2}\)) was put from the top of photoreactor to irradiate the UV-light. Before the photoreactions, the reactor was first purged with the CO\(_2\) for 30 min, and tightly closed at an ambient pressure. Then, H\(_2\) (0.01 atm) was added to the photoreactor. After that, the photoreactor was heated up to 363 K by heating tape to generate the gaseous H\(_2\)O, and the lamp was switched on to start the experiment.

The reaction products collected in the gas phase were analyzed every 2 h during the irradiation by gas chromatography (China GC-FID 9800) integrated with the flame ionization detector. To analyze the CO, a methanizer packed with Ni catalyst was connected to GC-FID to convert CO into CH\(_4\) with H\(_2\) at 633 K. A Porapak Q column was installed, and pure N\(_2\) was used as the carrier gas for FID in the detection of hydrocarbons.

The photoreduction quantum efficiency (PQE) is calculated as follows:

\[
PQE (\%) = 100\% \times \left( n \times \frac{\text{product formation rate}}{\text{incident photon rate}} \right)
\]

Here, \(n\) is the number of moles of photoelectrons required to generate one mole of reduction product from CO\(_2\), which includes CH\(_4\) and CO. The incident photon rate is determined from the incident light intensity at \(\lambda = 254\) nm and projected light irradiation area.

The blank experiments were also conducted before performing the photocatalytic reaction. There were almost no products or below the detection limit of gas chromatography with any part
missing, including (a) photocatalysts and (b) UV-light source. Evidently, the photocatalytic hydrogenation of CO\textsubscript{2} is mainly photo-catalyzed.

3. Results and discussion

3.1. Photocatalyst characterization

All photocatalysts were fully characterized by BET, FE-SEM, EDS, UV-vis, XRD, XPS and XANES to reveal their structure, surface morphology and chemical state of the species. Firstly, the morphology of the synthesized TiO\textsubscript{2} and Cu-loaded TiO\textsubscript{2} is examined by FE-SEM, as shown in Figure 2. It clearly indicates that loading of Cu obviously could not change the shape and modify the morphology of supported TiO\textsubscript{2}. However, the dispersion of Cu species might decrease with increasing loading amount. The mapping photograph for 2\%CuO/TiO\textsubscript{2} photocatalyst and their corresponding elemental mapping of Ti, O and Cu was shown in Figure 3. It clearly shows that a part of the Cu-loaded could be aggregated. It is not beneficial for the photocatalytic activity. By the elemental EDS analysis, the weight percentages of Cu species in 1\%Cu/TiO\textsubscript{2} and 2\%Cu/TiO\textsubscript{2} are 0.95 and 2.31 wt\%, respectively, which is consistent with the composition as planned.

Figure 4 depicts the XRD patterns of the TiO\textsubscript{2} along with Cu-loaded TiO\textsubscript{2} photocatalysts. All the photocatalysts exhibited similar XRD patterns. A very sharp and intense peak was observed at 2\theta = 25.28° corresponds to the (101) planes of the anatase TiO\textsubscript{2}, while few small peaks were also observed at 2\theta values of 36.95°, 37.80°, 38.58°, 48.05°, 53.89°, 55.06°, 62.69°, 68.76°, 70.31°, 75.03°, and 76.02°, respectively. These values are in good agreement with anatase phase (JCPDS, No. 21-1272), suggesting that crystallite structure of TiO\textsubscript{2} exists mostly as anatase phase. The
inset of Figure 4 shows the shift of the (101) planes of the anatase TiO$_2$ peaks toward lower 2θ values in the patterns of Cu-loaded TiO$_2$, suggesting that Ti sites in the TiO$_2$ lattice were occupied by Cu species.$^{17}$ Although we have observed the (101) planes of the anatase TiO$_2$ peaks changed significantly in intensity, only a slight change in half width was observed. The TiO$_2$ crystallite sizes were estimated from the half bandwidth of the corresponding X-ray spectral peak by the Scherrer formula:

$$D = \frac{k \lambda}{\beta \cos \theta}$$  

Here, $\lambda$ is the X-ray wavelength ($\lambda = 1.5418\text{Å}$), $\beta$ is the half width of the (101) planes, $\theta$ is the Bragg diffraction angle, and $k$ is a correction factor ($k = 0.9$).

In this study, the TiO$_2$ crystallite sizes were about 31.4-34.0 nm (Table 1), which is consistent with SEM result. It is noted that there are no apparent peaks for CuO in the XRD patterns of CuO/TiO$_2$. The reason is that the amount of Cu species is very low, in the range of 1-2 wt%; hence, it could not be ruled out due to limitations of the experimental technique. For Cu/TiO$_2$, the peak at 2θ values of 43.3° and 50.4°, corresponding to Miller indices (111) and (200) planes of metallic Cu species, respectively.$^{18}$

The optical properties of the TiO$_2$ together with Cu-loaded TiO$_2$ photocatalysts are measured by UV-vis spectra. As displayed in Figure 5, it clearly shows that all the photocatalysts performed the absorption peak of 360 nm, assigned to TiO$_2$. The Cu-loaded TiO$_2$ photocatalysts have an extended absorption edge in the region of 400-800 nm. Interestingly, the UV-Vis spectroscopic studies could gain information on the state of Cu species in these catalysts.$^{19}$ As expected, the upward shift of intensity absorbance in this region increased with the loading amount of Cu species. It is noticeable that the broadband of CuO/TiO$_2$ photocatalysts in the range of 600-800
nm corresponds to d–d transitions of Cu$^{2+}$ in Oh symmetry with a tetragonal distortion$^{17}$. This observation implies that Cu$^{2+}$ species was mainly presented on CuO/TiO$_2$ photocatalysts. Additionally, pretreatment the photocatalyst by H$_2$ to reduce the CuO to Cu will raise the band located at 410-590 nm, which corresponds to metallic Cu$^0$ species$^{19,20}$. It is noted that this range is also associated with the three-dimensional Cu$^{1+}$ clusters in the CuO matrix due to incomplete reduction$^{19}$.

The oxidation state of Cu species is a key factor that determines their photocatalytic activity in the photoreduction of CO$_2$$^{15}$. X-ray photoelectron spectroscopy (XPS) was conducted to determine further the chemical environment of Cu species. XPS spectra of the Cu2p region for TiO$_2$, 2%Cu/TiO$_2$, and 2%CuO/TiO$_2$ photocatalysts are reported (Figure 6(a)). There is no peak observed in the range of 925-965 eV for TiO$_2$ photocatalyst. In contrast, the Cu2p$_{3/2}$ and Cu2p$_{1/2}$ binding energy values of 2%CuO/TiO$_2$ photocatalyst appeared at 933.9 eV and 953.6 eV, respectively, confirming the presence of Cu$^{2+}$. It is noted that pretreatment the 2%CuO/TiO$_2$ photocatalyst by H$_2$ to successfully reduce the Cu$^{2+}$ to Cu$^0$. The Cu2p$_{3/2}$ and Cu2p$_{1/2}$ binding energy values of 2%Cu/TiO$_2$ photocatalyst appeared at 931.6 eV and 951.8 eV, respectively. These results are in accordance with an earlier report$^{21}$. Due to the low amount of Cu species on 1%CuO/TiO$_2$ and 1%Cu/TiO$_2$ samples, its XPS spectra of the Cu2p region could not be observed clearly. Figure 6(b) shows the Ti2p region for TiO$_2$, 2%Cu/TiO$_2$, and 2%CuO/TiO$_2$ photocatalysts. The binding energy values appeared at 458.7 eV and 457.3 eV corresponded to Ti$^{4+}$ and Ti$^{3+}$, respectively$^{22}$. There is a significant amount of Ti$^{3+}$ rather than Ti$^{4+}$ observed in the Ti2p XPS spectra of 2%Cu/TiO$_2$, and 2%CuO/TiO$_2$, in compared with TiO$_2$ photocatalysts. On the other hand, we also observed a shift to higher binding energy for O1s spectra when Cu species was introduced to the TiO$_2$ (Figure 6(c)). The O1s binding energy of TiO$_2$ was at 529.9
eV while those of Cu-loaded/TiO$_2$ was at 530.6 eV. The loading Cu could modify the surface
dioxy (OH) content of photocatalyst.$^{23}$

To have a clearer image of the Cu state on 1%Cu/TiO$_2$ and 1%CuO/TiO$_2$ photocatalysts, Cu K-
edge XANES was characterized. Figure 7(a) shows the Cu K-edge XANES spectra of
1%Cu/TiO$_2$ and 1%CuO/TiO$_2$ photocatalysts, in compared with the Cu foil, Cu$_2$O and CuO
references. The good resemblance spectra of 1%Cu/TiO$_2$ and 1%CuO/TiO$_2$ with that of Cu foil
and CuO references indicates that their local structure in 1%Cu/TiO$_2$ and 1%CuO/TiO$_2$
photocatalysts are mainly in Cu$^0$ and Cu$^{2+}$, respectively. There are four types of peaks in a range
of 8960-9040 eV, including 1s-3d transition (A), 1s-4p$_z$ (1s-4p$\pi^*$) transition (B), 1s-4p$_{x,y}$ (1s-
4p$\sigma^*$) transition (C), and multiple scattering (D).$^{24}$ The spectrum of 1%CuO/TiO$_2$ exhibits a
well-separated weak pre-edge band A due to the 1s-3d transition and an intense band B and C
due to the 1s-4p transition. However, the band B, which could be observed as a shoulder of the
intense band C, is not clearly separated. Additionally, with the presence of a band D (multiple
scattering), it suggests that the Cu species on 1%CuO/TiO$_2$ are aggregated.$^{24}$ For the 1%Cu/TiO$_2$
spectrum, there are no peaks attributed to the band A and D. More importantly here, the Fourier
transforms (FTs) of the $k^3\chi(k)$ EXAFS for 1%Cu/TiO$_2$ and 1%CuO/TiO$_2$ photocatalysts along
with Cu foil, Cu$_2$O, and CuO references were also compared in Figure 7(b). Phase shift function
was used as reference files to analyze the EXAFS data. In the 1%Cu/TiO$_2$ photocatalyst, the FT
peak appearing at 2.45 Å is assigned to Cu-Cu bond. In the 1%CuO/TiO$_2$ photocatalyst, the first
FT peak appearing at 1.84 Å is assigned to Cu-O bond. However, different from the above
XANES result, the FT for 1%CuO/TiO$_2$ photocatalyst in the range of 2-4 Å is not similar to that
for the CuO reference but is somewhat similar to that for the Cu$_2$O reference. In particular, it
exhibits only one peak appearing at 3.00 Å, which is assigned to Cu-Cu bond.
In summary, Cu species were successfully loaded on TiO$_2$ using the incipient wetness impregnation method. Based on the UV-vis, XRD, XPS, and XANES results, the Cu$^{2+}$ mainly exists on CuO/TiO$_2$ photocatalyst. Importantly, most Cu species in the photocatalysts was stable in Cu$^0$ after reduction by H$_2$. The presence of Cu species exhibits outstanding the optical properties. It expects that Cu-loaded TiO$_2$ can significantly influence the photoreduction of CO$_2$.

3. Photocatalytic hydrogenation of CO$_2$

3.1 The presence of hydrogen and reaction temperature

Figure 8 shows the time profiles of the photocatalytic reduction of CO$_2$ with H$_2$O in the presence/absence of H$_2$ under different temperature on 1%Cu/TiO$_2$ photocatalyst. Firstly, we conducted the photoreduction of CO$_2$ with H$_2$O at 333 K without H$_2$. The result shows that only 0.07 µmol g$^{-1}$ of CH$_4$ and no CO product were formed after 8 h in condition.

By increasing the reaction temperature to 363 K, both CH$_4$ and CO are detected. Their product yields are 5.32 and 0.26 µmol g$^{-1}$ for CH$_4$ and CO, respectively, after 8 h of reaction. It is accepted that photon irradiation is the primary source of energy in photocatalysis to generate the electron-hole pairs at an ambient temperature. However, the photocatalytic reactions proceed more efficiently at high temperatures because the surface reaction can be accelerated by raising the collision frequency and diffusion rate. Furthermore, products do not easily be desorbed at low temperatures; on the contrary, it desorbs more readily at high temperatures. It should be mentioned that H$_2$O vapor plays a crucial role in the photocatalytic activity. Further raising the reaction temperature also increases the generated gaseous H$_2$O, resulting in the enhancement of photocatalytic activity. Several studies have focused on the reaction temperature dependence of
Note that Anpo et al. also carried out the photoreduction of CO\textsubscript{2} with H\textsubscript{2}O on various TiO\textsubscript{2} catalysts.\textsuperscript{26} They reported that their enhancement of product yields corresponds to the reaction temperature and amount of gaseous H\textsubscript{2}O, which is highly consistent with this study.

Investigation of photohydrogenation of CO\textsubscript{2} at 363 K in the presence of H\textsubscript{2} was also conducted. The result shows that it took 2 h for CO to reach a maximum yield (5.47 µmol g\textsuperscript{-1}), and then it gradually decreased. In general, CO is thermodynamically more favorable than CO\textsubscript{2}.\textsuperscript{11} Hence, it might be consumed by reacting with either H\textsubscript{2} or H\textsubscript{2}O to produce CH\textsubscript{4}, resulting in the observed decrease of CO yield. For the yield of CH\textsubscript{4}, it is in a good linear relationship with the irradiation time. The CH\textsubscript{4} yield reaches to 28.72 µmol g\textsuperscript{-1} after 8 h in reaction. Such significant improvement of photocatalytic reaction is attributed to the presence of H\textsubscript{2}, which is used immediately for the hydrogenation of CO\textsubscript{2}. The reason is that hydrogenation of CO\textsubscript{2} is thermodynamically favorable and is a spontaneous reaction.

3.2 The amount Cu-loaded and its oxidation state on TiO\textsubscript{2} supports

The influence of amount CuO-loaded TiO\textsubscript{2} on photohydrogenation of CO\textsubscript{2} with H\textsubscript{2}O was also examined at 363 K. As expected, Figure 9 shows that the catalysts with a CuO loading of 1 and 2 wt.% exhibited photocatalytic reactivity to produce CO and CH\textsubscript{4} with a yield of 4.0-5.0 and 19.3-14.6 µmol g\textsuperscript{-1}, respectively. Note that only 1.33 µmol g\textsuperscript{-1} of CO and 11.94 µmol g\textsuperscript{-1} of CH\textsubscript{4} were produced over TiO\textsubscript{2} under the same condition. It is well known that the recombination of the electron-hole pair will be reduced when Cu species is loaded on TiO\textsubscript{2}. Hence, the photoactivity will be enhanced with the loading of Cu species. Additionally, Ti\textsuperscript{3+} species are an important
factor that influences the photocatalytic activity in the photohydrogenation of CO$_2$. The reason is that the electron-rich Ti$^{3+}$ species might transfer spontaneously an electron to surface adsorbed CO$_2$ leading to an intermediate CO$_2$$^{•−}$ species.$^{28}$ As it can be noticed, CO$_2$$^{•−}$ species is supported as the precursor of CO formation. It is important to emphasize that following the loading Cu species on TiO$_2$ support, the ratio of Ti$^{3+}$ species, which is shown in Figure 6(b), will increase dramatically compared with TiO$_2$. Hence, the observed yield of CO was increased more than threefold by Cu-loaded species. On the other hand, the surface hydroxyl content of photocatalyst was observed to increase with the presence of Cu-loaded (Figure 6(c)). It is noted that the surface hydroxyl is the crucial role to enhance the photocatalytic activity by generating the active hydroxyl radicals.$^{29}$

Although the adding CuO species improves significantly the activity, the addition of excess CuO to TiO$_2$ was undesirable for the photoreaction. Firstly, one of the influential factors of this dependence may be the CuO dispersion on TiO$_2$. The CuO dispersion usually decreases with increasing loading amount because of the aggregation of some small CuO particles, resulting in the reduced surface illumination of the photocatalyst. Note that BET surface area of 1%CuO/TiO$_2$ and 2%CuO/TiO$_2$ photocatalysts are 6.1 and 3.8 m$^2$ g$^{-1}$, respectively (Table 1). A loss of 38% of BET surface area was observed by increasing the loading CuO amount from 1% to 2%. The previous study observed that CuCl$_2$ precursor, which was also used in this study, led to being well-dispersed Cu at low loading only.$^{30,31}$ At high loading, a significant amount of CuO species aggregated on the surface of the support and obscured the pores of TiO$_2$. Secondly, excess CuO might act as the recombination centers for electron-hole pairs, resulting in reduced photoactivity.
The oxidation state of Cu species is also a key factor that determines their CO$_2$ photoreduction activity.$^{15}$ In this study, the pretreatment 1%CuO/TiO$_2$ by reducing CuO to Cu was found to be more efficient to generate CH$_4$ than that without pretreatment (Figure 10). The yield of CH$_4$ for Cu/TiO$_2$ was 28.72 µmol g$^{-1}$, which was enhanced 48.5% compared with that for CuO/TiO$_2$. To gain further insight into the transition of the nature of the copper species during the reaction, the photocatalysts was collected after the experiment for further XPS and UV-vis analysis. Figure 11 shows that the Cu2p peaks for spent CuO/TiO$_2$ photocatalyst, which was collected after the reaction, were shifted to lower binding energy than those for fresh CuO/TiO$_2$ photocatalyst. On the other hand, the Cu2p peaks for spent Cu/TiO$_2$ photocatalyst were shifted to higher binding energy than those for fresh Cu/TiO$_2$ photocatalyst. This result reveals that Cu$^{1+}$ species could be generated during UV-light irradiation from a part of either Cu$^{0}$ or Cu$^{2+}$ species.

\begin{equation}
\text{Photocatalyst} + h\nu \rightarrow h^+ + e^- \tag{3}
\end{equation}

\begin{equation}
\text{Cu}^0 + h^+ \leftrightarrow \text{Cu}^{1+} + e^- \tag{4}
\end{equation}

\begin{equation}
\text{Cu}^{2+} + e^- \leftrightarrow \text{Cu}^{1+} + h^+ \tag{5}
\end{equation}

During the photoreaction, the holes and electrons from TiO$_2$ can be transferred to Cu$^{0}$ and Cu$^{2+}$ species to keep a certain amount of their species oxidized and reduced, respectively, to Cu$^{1+}$.\textsuperscript{32} The UV-vis analysis of above photocatalysts is also shown in Figure 11. In details, the UV-vis spectrum of the spent Cu/TiO$_2$ photocatalyst shows an increased intensity in the range of 410-590 nm, in compared with that of the fresh Cu/TiO$_2$ photocatalyst. This change indicates that a part of Cu$^{0}$ was oxidized to Cu$^{1+}$ species.\textsuperscript{19} Similarly, we also observed this phenomenon for spent CuO/TiO$_2$ photocatalyst, confirming the presence of Cu$^{1+}$ species. The UV-vis result agrees with the XPS result. We final note that CuO-Cu$_2$O/TiO$_2$ and Cu-Cu$_2$O/TiO$_2$
photocatalysts system could be formed under UV-light irradiation (Figure 11). Briefly, the coexistence of different nature of Cu species has a significant influence on the photocatalytic activity by the enhanced separation and inhibited recombination of photogenerated electron-hole pairs. Moreover, it also exhibits outstanding the optical properties. Especially, the Cu-CuO/TiO$_2$ structure is proposed can also further prolong the lifetime of electrons. The reason is that the electrons, which is generated by UV-light irradiation on the Cu$_2$O valence band, need to transfer to the media Cu first, and then further transfer to the valence band of TiO$_2$. As a result, Cu-Cu$_2$O/TiO$_2$ had the highest photocatalytic performance, among candidate photocatalysts. Interestingly, Cu-Cu$_2$O/TiO$_2$ also performed an excellent selectivity to CH$_4$ yield. The reasons are that Cu$^0$ species could efficiently suppress the formation of CO, while Cu$^{1+}$ species is noted as an active site to promote the formation of CH$_4$ efficiently.

3.3 Comparison of the photoreduction efficiency

The dependencies of products yield and PQE on different photocatalysts are shown in Figure 12. The results suggest that Cu-loaded TiO$_2$ reduces CO$_2$ more efficiently than TiO$_2$. The photohydrogenation activity is intensively related to the amount Cu-loaded and its oxidation state on TiO$_2$. The increased photocatalytic activity with the presence of Cu species can be explained as Cu species acting as electron traps responsible for accumulating the photo-generated electrons, and resulting in minimizing charge recombination electron-hole pairs. Additionally, the ratio of Ti$^{3+}$ species in Cu-loaded TiO$_2$ was higher than that in TiO$_2$. This observation is attributed to the enhancement of CO formation. However, adding excess CuO/Cu to TiO$_2$ may face the low dispersion issue resulting in the activity inhibition. In the present, we observed that PQE achieved highest over 1%Cu/TiO$_2$ photocatalyst (0.13%).
Although the conditions for conducting experiments are different, it is worth comparing the photocatalytic activity regarding product rate in the literature (Table 2).\textsuperscript{17, 35-41} We see that CO and CH\textsubscript{4} were formed as the main products. Despite substantial efforts have been devoted to improving the efficiency of this photocatalytic process, it is still lower than in natural photosynthesis. Hence, further research in this field is needed for enabling photohydrogenation / photoreduction of CO\textsubscript{2} in the future.

4. Conclusions

Cu species (Cu\textsuperscript{0} and Cu\textsuperscript{2+}) were successfully loaded on the TiO\textsubscript{2} support and then evaluated for their potential to hydrogenation of CO\textsubscript{2}. There might exist the interaction between the Cu species and TiO\textsubscript{2} support that enhancing a significant amount of Ti\textsuperscript{3+} rather than Ti\textsuperscript{4+} species in Cu-loaded TiO\textsubscript{2}, in compared with TiO\textsubscript{2} photocatalysts. This property provides a chance to generate an intermediate CO\textsubscript{2}•− species, leading to the enhancement of CO\textsubscript{2} hydrogenation activity. Notably, CuO-Cu\textsubscript{2}O/TiO\textsubscript{2} and Cu-Cu\textsubscript{2}O/TiO\textsubscript{2} photocatalyst system, which was formed under UV-light irradiation, significantly enhanced photocatalytic activity by prolonging the lifetime of electrons. The co-existence of Cu\textsuperscript{0} and Cu\textsuperscript{1+} species was beneficial to catalysis involving hydrogenation of CO\textsubscript{2} into desired renewable fuel (CH\textsubscript{4}). Although the adding Cu species improves the activity significantly, the excess content of Cu to TiO\textsubscript{2} was undesirable for the photoreaction. To achieve the enhanced photocatalytic activity, the content of Cu species must be maintained at an appropriate low concentration (≤ 1wt.%), and the corresponding highest CH\textsubscript{4} yield was 28.72 µmol g\textsuperscript{-1}.
Acknowledgments

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References


## Tables and Figures

**Table 1.** The properties of TiO$_2$ supports

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<th>Entry</th>
<th>Photocatalysts</th>
<th>BET (m$^2$ g$^{-1}$)</th>
<th>TiO$_2$ crystalline size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TiO$_2$</td>
<td>5.2</td>
<td>31.4</td>
</tr>
<tr>
<td>2</td>
<td>1% CuO/TiO$_2$</td>
<td>6.1</td>
<td>32.6</td>
</tr>
<tr>
<td>3</td>
<td>2% CuO/TiO$_2$</td>
<td>3.8</td>
<td>32.6</td>
</tr>
<tr>
<td>4</td>
<td>1% Cu/TiO$_2$</td>
<td>6.3</td>
<td>34.0</td>
</tr>
<tr>
<td>5</td>
<td>2% Cu/TiO$_2$</td>
<td>5.1</td>
<td>33.9</td>
</tr>
</tbody>
</table>
Table 2. The performance comparison of photocatalytic activity

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalysts</th>
<th>Conditions</th>
<th>Light source</th>
<th>Temp. (K)</th>
<th>Products (µmol g⁻¹ h⁻¹)</th>
<th>PQE (%)</th>
<th>Ref. / Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cu/TiO₂</td>
<td>H₂O (5 mL), H₂ (0.01 atm), saturated CO₂ (1 atm)</td>
<td>11SC-1 pen-ray lamp: 254 nm; 12 mW cm⁻²</td>
<td>363</td>
<td>CO: 0.54</td>
<td>0.13</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CH₄: 3.59</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Cu/TiO₂</td>
<td>H₂O (5 mL), saturated CO₂ (1 atm)</td>
<td>–</td>
<td>–</td>
<td>CO: 0.03</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CH₄: 0.67</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Cu/TiO₂</td>
<td>H₂O (200 mL), saturated CO₂ (1 atm)</td>
<td>8 W UVA: 3.25 mW cm⁻²</td>
<td>–</td>
<td>CH₄: 0.03</td>
<td>–</td>
<td>35 / 2012</td>
</tr>
<tr>
<td>4</td>
<td>Cu₂O/TiO₂</td>
<td>H₂O (100 mL), saturated CO₂ (1.25 atm)</td>
<td>300 W xenon lamp (PLS-SXE300, λ ≥ 420 nm)</td>
<td>288</td>
<td>CH₄: 0.16</td>
<td>–</td>
<td>36 / 2015</td>
</tr>
<tr>
<td>5</td>
<td>3.0Cu-TiO₂</td>
<td>H₂O (25 mL) under a CO₂ atmosphere (1.4 bars)</td>
<td>Hg lamp (125 W)</td>
<td>298</td>
<td>CO: 0.3</td>
<td>–</td>
<td>17 / 2016</td>
</tr>
<tr>
<td></td>
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<td>CH₄: 0.3</td>
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<tr>
<td>6</td>
<td>LiTaO₃</td>
<td>CO₂ (150 µmol), H₂ (50 µmol)</td>
<td>200 W Hg-Xe lamp (UVF-204S Type C)</td>
<td>303</td>
<td>CO: 0.42</td>
<td>–</td>
<td>37 / 2010</td>
</tr>
<tr>
<td>7</td>
<td>RuO₂ –Pt/ Zn₁.₇GeN₁.₈O</td>
<td>H₂O (0.4 ml), saturated CO₂ (1 atm)</td>
<td>300 W Xe arc lamp (λ &gt; 420 nm)</td>
<td>–</td>
<td>CH₄: 4.58</td>
<td>0.03</td>
<td>38 / 2012</td>
</tr>
<tr>
<td>8</td>
<td>TiO₂-GCM</td>
<td>H₂O (5 ml), saturated CO₂ (1 atm)</td>
<td>300 W Xe arc lamp</td>
<td>303</td>
<td>CH₄: 2.06</td>
<td>–</td>
<td>39 / 2013</td>
</tr>
<tr>
<td>9</td>
<td>C,N-TNT06</td>
<td>CO₂ and H₂O vapors (80% humidity)</td>
<td>100 W Xenon with an AM 1.5 filter</td>
<td>–</td>
<td>CH₄: 9.75</td>
<td>–</td>
<td>40 / 2015</td>
</tr>
<tr>
<td>10</td>
<td>Co-doped TiO₂</td>
<td>H₂O (3 ml), a pure CO₂ gas (80 kPa)</td>
<td>300 W xenon arc lamp with an L-42 glass filter</td>
<td>–</td>
<td>CO: 0.34</td>
<td>–</td>
<td>41 / 2015</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CH₄: 0.18</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**Abbreviation:** PQE: Photoreduction quantum efficiency, –: lack of information.

**Scheme 1.** The flow chart for synthesis procedure of photocatalysts.

**Figure 1.** The diagram of a single Pyrex photoreactor system.
Figure 2. SEM images of (a) TiO$_2$, (b) 1%CuO/TiO$_2$, (c) 2%CuO/TiO$_2$, (d) 1%Cu/TiO$_2$, and (e) 2%Cu/TiO$_2$ photocatalysts.

Figure 3. SEM mapping photograph for 2%CuO/TiO$_2$ photocatalyst: (a) SEM image of 2%CuO/TiO$_2$ with Cu mapping, and elemental mapping images of (b) Ti, (c) O, and (d) Cu.
**Figure 4.** XRD patterns of TiO$_2$, 1%CuO/TiO$_2$, (c) 2%CuO/TiO$_2$, 1%Cu/TiO$_2$, and 2%Cu/TiO$_2$ photocatalysts. The inset depicts the shift of the (101) planes of TiO$_2$ supports.
Figure 5. UV-vis spectra of TiO$_2$, 1%CuO/TiO$_2$, (c) 2%CuO/TiO$_2$, 1%Cu/TiO$_2$, and 2%Cu/TiO$_2$ photocatalysts.
Figure 6. XPS spectra of (a) Cu2p, (b) Ti2p and (c) O1s for TiO$_2$, 2%Cu/TiO$_2$, and 2%CuO/TiO$_2$ photocatalysts.
Figure 7. (a) Normalized Cu K-edge XANES spectra and (b) Fourier transforms of Cu K-edge EXAFS spectra for 1%Cu/TiO$_2$ and 1%CuO/TiO$_2$ photocatalysts, together with Cu metal foil, Cu$_2$O, and CuO references.
Figure 8. Reaction time profiles of the photocatalytic reduction of CO$_2$ with H$_2$O in the presence/absence of H$_2$ under different temperature to produce (a) CH$_4$ and (b) CO on 1%Cu/TiO$_2$ photocatalyst.

Figure 9. Reaction time profiles of the photocatalytic reduction of CO$_2$ with H$_2$O and H$_2$ to produce (a) CH$_4$ and (b) CO on different amount of CuO loaded TiO$_2$ photocatalysts.
Figure 10. Reaction time profiles of the photocatalytic reduction of CO\(_2\) with H\(_2\)O and H\(_2\) to produce (a) CH\(_4\) and (b) CO on different Cu oxidation state photocatalysts.

Figure 11. The transition of the nature of Cu species during the photoreaction.
Figure 12. Performance comparison of the products yields (after 8 h in reaction) and the quantum efficiency on different photocatalysts.