



Article Photocatalytic Reduction of CO₂ to Methanol by Cu₂O/TiO₂ Heterojunctions

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Abstract: The conversion of CO₂ to low-carbon fuels using solar energy is considered an economically attractive and environmentally friendly route. The development of novel catalysts and the use of solar energy via photocatalysis are key to achieving the goal of chemically reducing CO₂ under mild conditions. TiO₂ is not very effective for the photocatalytic reduction of CO₂ to low-carbon chemicals such as methanol (CH₃OH). Thus, in this work, novel Cu₂O/TiO₂ heterojunctions that can effectively separate photogenerated electrons and holes were prepared for photocatalytic CO₂-to-CH₃OH. More visible light-active Cu₂O in the Cu₂O/TiO₂ heterojunctions favors the formation of methanol under visible light irradiation. On the other hand, under UV-Vis irradiation for 6 h, the CH₃OH yielded from the photocatalytic CO₂-to-CH₃OH by the Cu₂O/TiO₂ heterojunctions is 21.0–70.6 μ mol/g-catalyst. In contrast, the yield of CH₃OH decreases with an increase in the Cu₂O fraction in the Cu₂O/TiO₂ heterojunctions may lead to less UV light exposure for the photocatalysts, and may decrease the conversion efficiency of CO₂ to CH₃OH.

Keywords: photocatalysis; CO₂; Cu₂O; TiO₂; p-n heterojunctions; methanol



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1. Introduction

In recent years, the significant rise of greenhouse gas CO_2 concentrations on the earth causing serious problems has received much attention. There are major challenges in recycling high-thermal stability CO_2 , which may involve severe reaction conditions (high pressures or high temperatures) with extra energy consumption that may lead to the additional formation of CO_2 . Thus, the recycling of CO_2 into low-carbon chemicals or fuels using solar energy is considered an economically attractive and environmentally friendly route. The desired photocatalysts for the photocatalytic reduction of CO_2 to chemicals or fuels under mild conditions are being developed to achieve the goal of CO_2 recycling [1–3].

Titanium dioxide (TiO₂), an n-type semiconductor, has been used for the photocatalytic reduction of CO₂ to chemicals such as formic acid, formaldehyde, methane and methanol [4,5]. TiO₂ has shown great potential for various photocatalytic reactions, mainly due to its chemical stability, nontoxicity, high oxidation efficiency and environmentally friendly nature [6]. However, because of its fairly wide bandgap (3.2 and 3.0 eV for anatase and rutile phases, respectively), TiO₂ can only be activated by ultraviolet (UV) light, equivalent to about 5% of natural solar light. A variety of strategies, such as metal ion doping, cation or anion doping, and coupling with narrow-bandgap semiconductors, have been developed to extend absorption into the visible light region [7–10]. The doping of anions (e.g., N, F, S, and C) onto TiO₂ could shift the absorption edge to a relatively low energy, and its photo-response into the visible spectrum [11–14]. Cation-, anion- or metal ion-doped TiO₂ could lead to better solar energy harvesting in the visible light region; however, this still suffers from relatively high photogenerated electron and hole recombination rates, causing difficulties in engineering applications [15–17].

 CO_2 may be activated by a one-electron transfer step and form a $\cdot CO_2^-$ radical ion. The $\cdot CO_2^-$ may be reduced to yield a hydroxyformyl radical ($\cdot COOH$), which recombines a hydrogen radical (H^+) and an electron (e^-) to form formic acid [18]. In the following step, formic acid accepts H^+ and e^- to form formaldehyde. Formic acid and formaldehyde seem to be formed prior to methanol generation. Thus, the key points that control the photocatalytic CO₂-to-CH₃OH reaction may include reaction conditions, photocatalyst activity, bandgap energy, light source and process parameters. To effectively suppress the rapid recombination of photoexcited electrons and holes, a heterojunction structure could facilitate electron migration [19,20]. Cuprous oxide (Cu₂O), a typical p-type semiconductor, has wide application prospects in solar cells, photocatalysis, and hydrogen evolution reactions (HER) [21]. Cu₂O, with a bandgap energy of 2.0–2.2 eV, could effectively harvest visible light for photocatalysis. However, while the photocatalytic CO₂-to-CH₃OH reaction facilitated by Cu₂O is thermodynamically feasible, its CH₃OH yield suffers from the low solar conversion efficiency [22]. By the heterojunction between the p-type Cu₂O and n-type TiO₂, the recombination of photo-excited charges could be effectively retarded and facilitate photocatalytic reactions [23,24]. In this work, novel Cu_2O/TiO_2 heterojunctions were thus prepared by a simple soft chemical method as the visible light photocatalysts used for the enhanced photocatalytic reduction of CO₂ to methanol.

2. Materials and Methods

Cu₂O was prepared by the facile soft chemical method (Figure 1). Briefly, CuCl₂ (97%, Merck, Kenilworth, NJ, USA) (10.1 mmol) was dispersed in a NaCl solution (5 M) (100 mL) with a dispersant (polyethylene glycol 20,000 (Sigma-Aldrich, Burlington, MA, USA) (0.025 mmol)), which was stirred at 298 K for 1 h. Na₃PO₄ (96%, Sigma-Aldrich, USA) (9.76 mmol) was added to the solution and stirred for 1 h. The Cu₂O was centrifuged and cleaned with distilled water and ethanol three times. Titanium butoxide (Ti(OBu)₄) (97%, Sigma-Aldrich, USA) and Cu₂O at the X_{Cu2O} mole fractions (Cu₂O/(Cu₂O + TiO₂)) of 0.1, 0.2 and 0.5 were mixed in deionized water, and were then centrifuged, dried at 378 K for 4 h, and heated at 723 K under N₂ flow (99.99%) (20 mL/min) for 2 h to obtain the Cu₂O/TiO₂ heterojunctions used for photocatalysis experiments.



Figure 1. Preparation procedure for the Cu₂O/TiO₂ heterojunction photocatalysts.

The crystalline structures of the Cu₂O, TiO₂ and Cu₂O/TiO₂ heterojunctions were determined by X-ray diffraction (D8, Discover with Gadds, Bruker AXS Gmbh). The crystalline sizes of the Cu₂O, TiO₂ and Cu₂O/TiO₂ heterojunction photocatlysts were calculated by the Scherrer equation ($t = k\lambda/Bcos\theta$) using the Jade software. The images of the Cu₂O/TiO₂ heterojunctions were investigated by scanning electron microscopy (SEM)

equipped with an energy-dispersive X-ray spectrometer (EDS) (AURIGA) and scanning transmission electron microscopy (JEOL JEM-2100F CS STEM). The room temperature photoluminescence spectra of the photocatalysts were determined on the LabRAM HR (Horiba Jobin Yvon, Palaiseau, France) using the 325 nm excitation wavelength. The diffuse reflection absorption spectra of the photocatalysts at 200–800 nm were studied on a UV-visible spectrophotometer (Varian, Cary 100, Palo Alto, CA, USA). BaSO₄ was used as the standard in the absorption spectroscopic experiments. The bandgap energy was studied via the Kubelka–Munk equation ($\alpha hv = A(hv-Eg)^n$). The specific surface area, pore size and pore volume distribution of the photocatalysts were measured on a nitrogen adsorption–desorption analyzer (Micromeritics, ASAP 2020) using the Brunauer–Emmett–Teller (BET) and Barret–Joyner–Halenda (BJH) model. The zeta potential data were determined from the specific surface areas and active sites of the photocatalysts.

The photocatalytic experiments were carried out in a closed cylindrical quartz reactor to prevent oxygen/air access. The photocatalyst (0.1 g) was dispersed in a sodium hydroxide (0.025 M) aqueous solution (100 mL). Before the photocatalysis experiments, high-purity CO₂ was bubbled through the solution until the pH reached 7.00 at 298 K. A 300 W Xenon arc lamp (Burgeon Instrument Co., Ltd., Taoyuan City, Taiwan) with the light cut off ($\lambda > 400$ nm) by a filter (FSQ-CG400, Newport, Taipei, Taiwan) was used for the experiments on the photocatalytic reduction of CO₂ to methanol. The concentrations of the photocatalytic product methanol were measured by GC-MS (JEOL JMS-700 and Shimadzu, QP2010).

3. Results and Discussion

The XRD patterns of the photocatalysts are shown in Figure 2. The diffraction peaks at 29.6°, 36.5° , 42.4° , 61.4° , 73.6° and 77.5° correspond to the (110), (111), (200), (220), (311) and (222) phases of the crystalline Cu₂O (JCPDS card No. 78-2076), respectively [25]. A high-intensity diffraction peak at 36.4° confirms the existence of Cu₂O in the Cu₂O/TiO₂ heterojunctions. Other diffraction peaks at 25.3° , 37.8° , 48.0° , 53.9° , 55.0° , 62.7° , 68.8° , 70.3° and 75.0° can be indexed to the (101), (004), (200), (105), (211), (204), (116), (220) and (215) planes of TiO₂ (JCPDS card No. 71-1167), associated with the anatase phase [26,27], indicating that the Cu₂O/TiO₂ heterojunctions consist of anatase predominantly. Note that a peak at 38.7° related to the CuO(111) plane is also observed, suggesting the existence of a small amount of CuO. The crystalline sizes of the TiO₂, Cu₂O, and Cu₂O/TiO₂ heterojunctions derived by Scherrer's equation are 50–100, 50–70, and 40–100 nm, respectively.



Figure 2. X-ray diffraction patterns of the (**a**) Cu_2O and Cu_2O/TiO_2 heterojunctions with the X_{Cu2O} fractions of (**b**) 0.5, (**c**) 0.2, (**d**) 0.1, and (**e**) TiO₂ nanoparticles.

The TEM images of the TiO₂ and Cu₂O/TiO₂ heterojunctions are shown in Figure 3. It is clear that the Cu₂O (in the Cu₂O/TiO₂ heterojunction) and TiO₂ have nanoparticle diameters of ~5 and 70–130 nm, respectively. The presence of Cu, Ti, and O in the Cu₂O/TiO₂ heterojunction could be revealed by energy-dispersive X-ray (EDX) spectroscopy (see Figure 3c). The HRTEM image of the sample in Figure 3d shows lattice fringes spacing of 0.212 and 0.237 nm, corresponding to the (200) and (111) planes of Cu₂O, respectively [28]. The TiO₂ with high crystallinity has the d-spacings of 0.352 and 0.246 nm, related to the (100) and (004) planes of anatase TiO₂ [28].



Figure 3. The TEM images of the (**a**) pristine TiO_2 and (**b**) Cu_2O/TiO_2 heterojunctions ($X_{Cu2O} = 0.5$) with (**c**) EDS mapping, and (**d**) the HRTEM image.

The nitrogen adsorption–desorption isothermals of the pristine TiO₂ and Cu₂O/TiO₂ heterojunctions are shown in Figure 4A. The absorption isothermals of the Cu₂O/TiO₂ heterojunctions can be classified as type IV with H1 hysteresis loops, suggesting that they have a mesoporous structure. In Figure 4B, the Cu₂O/TiO₂ heterojunctions have greater pore volumes, with pore diameters between 10 and 40 nm, than the pristine TiO₂, possessing relatively high pore diameters of 30–70 nm. It seems that the smaller Cu₂O nanoparticles may, to some extent, be incorporated into the pores of the TiO₂, which creates more internal surfaces in the interfaces of the Cu₂O and TiO₂ nanoparticles. In Table 1, as expected, the Cu₂O/TiO₂ heterojunctions have relatively high specific surface areas (94–120 m²/g) and small average pore diameters, which may benefit the photocatalytic reduction of CO₂ to CH₃OH.



Figure 4. (**A**) N₂ absorption–desorption isothermals and (**B**) pore size distributions of the Cu₂O/TiO₂ heterojunctions with the X_{Cu2O} fractions of 0.1, 0.2, 0.5, and pristine TiO₂ nanoparticles.

Table 1. The BET surface areas, average pore diameters, and zeta potentials of the pristine TiO_2 and Cu_2O/TiO_2 heterojunctions with the X_{Cu2O} fractions of 0.1–0.5.

Photocatalysts	X _{Cu2O} Fractions	BET Surface Area (m²/g)	BJH Average Pore Diameter (nm)	Zeta Potential (mV)
Pristine TiO ₂	0	48	50	52.7
	0.1	94	23	-21.1
Cu_2O/TiO_2	0.2	105	15	-26.6
	0.5	120	15	-39.1

According to the linear regression analysis, the relationship between the zeta potentials (see in Table 1) and BET surfaces of the Cu₂O/TiO₂ heterojunctions and TiO₂ nanoparticles was well fitted ($R^2 > 0.9$). The zeta potential data were determined by the specific surface areas and active sites of the photocatalysts. The Cu₂O/TiO₂ heterojunctions with negative potential can provide more active sites for CO₂ reduction, suggesting that the Cu₂O/TiO₂ heterojunctions.

The diffuse reflectance ultraviolet–visible spectra of the photocatalysts were also determined. In Figure 5, the absorbance of the Cu_2O/TiO_2 heterojunctions in the range of 200–800 nm can be observed. Compared with TiO₂, the fundamental absorbance cuts at 400 nm, and the TiO₂ mixed with Cu_2O reveals a significantly enhanced absorption in the visible light region. It is clear that TiO₂ with Cu_2O causes a red-shift to 400–800 nm in the visible light range, possibly due to the forming of the Cu_2O/TiO_2 heterojunctions [28].

In Figure 6, the bandgap energies of the photocatalysts were determined by the Kubelka–Munk transforms [29]. The direct bandgaps of the TiO₂, Cu₂O and Cu₂O/TiO₂ heterojunctions with the X_{Cu2O} fractions of 0.1, 0.2 and 0.5 were estimated to be 3.20, 2.09, 3.03, 3.0 and 2.94 eV, respectively. It seems that the coupling of Cu₂O with TiO₂ can effectively decrease the bandgap energies of both. The Cu₂O/TiO₂ heterojunctions turn out to be more photoactive than TiO₂ under visible light irradiation.



Figure 5. UV-Vis DR spectra of the Cu_2O/TiO_2 heterojunctions with the X_{Cu2O} fractions of 0.1–0.5.



Figure 6. The Tauc plot of the Cu_2O/TiO_2 heterojunctions with the X_{Cu2O} fractions of 0.1–0.5.

The charge separation efficiency of photoinduced electrons and holes is also one of the important factors in photocatalysis. The photoluminescence spectra can provide information on charge carrier trapping, migration and transfer [30]. The photoluminescence spectra of the Cu₂O/TiO₂ heterojunctions are shown in Figure 7. The photoluminescence intensity of the Cu₂O/TiO₂ heterojunctions is less than that of TiO₂. A clear quenching of the photoluminescence emission of the Cu₂O/TiO₂ heterojunctions of 0.2, which showed maximum quenching. Such quenching of the photoluminescence suggests that the separation of photogenerated electron and hole pairs in the Cu₂O/TiO₂ heterojunctions has been effectively improved. Cu₂O can transfer the photogenerated holes from TiO₂ to inhibit the recombination of photogenerated electrons and holes significantly, and this may consequently lead to enhanced photocatalysis.



Figure 7. The photoluminescence spectra of the Cu_2O/TiO_2 heterojunctions with the X_{Cu2O} fractions of (a) 0.1, (b) 0.2 and (c) 0.5, and (d) pristine TiO₂ nanoparticles.

Figure 8A shows the yield of CH₃OH from the photocatalytic reduction of CO₂ by the Cu₂O/TiO₂ heterojunctions under visible light irradiation. After 6 h of visible light irradiation, the yields of CH₃OH photocatalyzed by the Cu₂O/TiO₂ heterojunctions with the X_{Cu2O} fractions of 0.1, 0.2, and 0.5 are 9.29, 11.44, and 13.06 µmol/g-catalyst, respectively. Note that, as expected, TiO₂ is not very effective for the photocatalytic CO₂-to-CH₃OH reaction. Additionally, more visible light-active Cu₂O in the Cu₂O/TiO₂ heterojunctions favors the formation of methanol. On the other hand, under UV-Vis irradiation for 6 h, the CH₃OH yielded from the photocatalytic CO₂-to-CH₃OH reaction by the Cu₂O/TiO₂ heterojunctions is 21.0–70.6 µmol/g-catalyst (see Figure 8B). It is clear that the yields of CH₃OH under UV-Vis irradiation are greater than those under visible irradiation. In contrast, the yield of CH₃OH decreases with an increase in the Cu₂O fraction in the Cu₂O/TiO₂ heterojunctions. It seems that excess Cu₂O in the Cu₂O/TiO₂ heterojunctions may lead to less UV light exposure for the photocatalysts, and may reduce the conversion efficiency of CO₂ to CH₃OH.



Figure 8. Photocatalytic reduction of CO₂ to methanol under (**A**) visible and (**B**) UV–visible irradiation by the Cu₂O/TiO₂ heterojunctions with the X_{Cu2O} fractions of (a) 0.1, (b) 0.2, (c) and 0.5, and (d) TiO₂ nanoparticles.

The schematic diagram of the charge separation in the Cu_2O/TiO_2 heterojunction structure is depicted in Scheme 1. When the Cu_2O/TiO_2 heterojunctions are irradiated by visible light, only the electrons of Cu_2O can be excited to the conduction band, and then move to the TiO_2 , leading to the better separation of electron and hole pairs. However, photoexcited electrons in Cu_2O and TiO_2 are excited to the conduction band when irradiated under UV–visible light, whereas the holes of TiO_2 may quickly transfer to the Cu_2O , which may reduce the recombination of photogenerated holes and electrons and promote the photocatalytic activity.



Scheme 1. The charge separation with the Cu_2O/TiO_2 heterojunctions under (a) ultraviolet–visible and (b) visible light irradiation.

 CO_2 can be activated by a one-electron transfer step to form $\cdot CO_2^-$, which may be reduced to yield the hydroxyformyl radical (COOH), which recombines with a hydrogen radical (H⁺) and an electron (e⁻) to form formic acid and formaldehyde (which seem to be formed prior to the CH₃OH generation) [18]. Thus, the key points that control the photocatalytic CO₂-to-CH₃OH reaction may include reaction conditions, photocatalyst activity, bandgap energy, light source and process parameters, and the comparison between different methods is shown in Table 2 [31–38]. It is clear that the Cu₂O/TiO₂ heterojunctions prepared in this work offer much better CH₃OH yields under visible light irradiation.

Photocatalyst	Light Source	Bandgap Energy (eV)	Reactions	CH3OH Yield (µmol/g/h)	Ref.
Cu ₂ O/TiO ₂	UV	2.9–3.0	100 mg photocatalysts,	9–13 12–70	This work
	Vis		CO_2 in deionized water		
Co/TiO ₂	UV	-	CO_2 in NaHCO ₃ (1 M)	0.05	[31]
Anatase TiO ₂	Vis	2.9–3.2	500 mg photocatalysts, CO ₂ in deionized water	2.74	[32]
$SnO_2/g-C_3N_4$	UV	-	20 mg photocatalysts, CO_2 in water vapor	0.02	[33]
rGO/ZnO	Vis	2.8	100 mg photocatalysts, CO_2 in water vapor	0.42	[34]
rGO/Cu ₂ O	UV	2.7–2.8	100 mg photocatalysts, CO ₂ in NaOH (1 M)	8.77	[35]
CQDs/Cu ₂ O	Vis	2.4–2.6	150 mg photocatalysts, CO ₂ in deionized water	1.96	[36]
ZnTe/SrTiO ₃	UV	2.8–3.4	20 mg photocatalysts, CO ₂ in deionized water	0.75	[37]
$ZnO/g-C_3N_4$	UV	2.6–3.0	10 mg photocatalysts, CO ₂ in deionized water	0.06	[38]

Table 2. Method comparison for photocatalytic CO₂-to-CH₃OH reaction.

4. Conclusions

The novel Cu₂O/TiO₂ heterojunction photocatalysts prepared by a simple soft chemical method have relatively high specific surface areas and small average pore diameters, which may benefit the photocatalytic reduction of CO₂ to CH₃OH. The Cu₂O in conjunction with TiO₂ decreases its bandgap energy, and extends the absorption to the visible light region. The p-n-type heterojunction can effectively suppress charge carrier recombination. After the 6 h photocatalytic reduction, 9–13 and 21–76 µmol/g-catalyst of methanol can be yielded under visible and UV-Vis irradiation, respectively. The comparison between different methods suggests that the Cu₂O/TiO₂ heterojunctions prepared in this work offer much better CH₃OH yields under visible and UV light irradiation.

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