

Photocatalytic Conversion of Carbon Dioxide with Water into Methane: Platinum and Copper(I) Oxide Co-catalysts with a Core–Shell Structure**

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The use of CO₂ for the production of fuels and chemicals has attracted much attention under the current background of the depletion of fossil resources and the increase of emissions of CO₂. However, the activation of CO₂, a very stable molecule, is one of the biggest challenges in chemistry. In the long term, the photocatalytic conversion of CO₂ using solar energy, that is, the artificial photosynthesis, is the most attractive route for the transformation of CO₂ to fuels and chemicals. Since the pioneering work by Inoue et al.,^[1] many studies have been devoted to the semiconductor-based photocatalytic reduction of CO₂ with H₂O and the pace has increased enormously in recent years.^[2] Several kinds of semiconductors such as TiO₂,^[2] Ga₂O₃,^[3] ZnGe₂O₄,^[4] ZnGa₂O₄,^[5] and BaLa₄Ti₄O₁₅^[6] have been reported for the photocatalytic conversion of CO₂, although the activity is still very low.

Co-catalysts are known to play crucial roles in the semiconductor-based photocatalysis.^[2] Enhancing effects of noble or coinage metal co-catalysts such as Pd, Pt, Au, Ag, or Cu have been observed for the photocatalytic conversion of CO₂ with H₂O to hydrocarbons over semiconductors such as TiO₂.^[2,7] It is generally accepted that the noble or coinage metal co-catalyst may facilitate the separation of photo-generated electrons and holes by trapping electrons, enhancing the photocatalytic activity.^[2,7] Because CO₂ is a very stable molecule, it is also highly important to provide catalytically active sites for the activation and conversion of CO₂. Thus, the design of bifunctional co-catalysts with a proper structure is crucial for obtaining high CO₂ conversion activity. To date,

only very limited studies have been devoted to binary co-catalyst systems for the photocatalytic conversion of CO₂ to hydrocarbons (mainly CH₄).^[2b,8,9] Pt and Cu bimetallic co-catalysts coated on N-doped TiO₂ nanotube arrays or periodically modulated multi-walled TiO₂ nanotube arrays showed promising promoting effects.^[8,9] However, the functioning mechanisms and even the chemical states of Pt and Cu in these systems are ambiguous although it seems that Pt may function for the activation of H₂O, while Cu is responsible for the activation of CO₂ to CO.^[8] It can be expected that the reduction of CO₂ through accepting the photogenerated electrons trapped in the co-catalyst is competitive with the reduction of H₂O to H₂. The insight for the rational design of co-catalysts for the efficient reduction of CO₂ is highly deficient. Herein, we present a new strategy for the design and preparation of efficient binary co-catalysts for the preferential reduction of CO₂ in the presence of H₂O.

We prepared TiO₂ (Degussa P25)-loaded Pt and Cu binary co-catalysts by a stepwise photodeposition technique. Pt nanoparticles were first introduced onto TiO₂ by photo-reducing H₂PtCl₆ in an aqueous suspension, providing Pt/TiO₂ with a Pt content of about 0.9 wt % and a mean size of Pt nanoparticles of 3.1 nm (see Figure S1 in the Supporting Information). Then, copper was deposited onto Pt/TiO₂ under irradiation using CuSO₄ as a precursor, and the samples obtained were denoted as Cu/Pt/TiO₂-xh, where xh was the irradiation time for the photodeposition of Cu. We found that the variation of the irradiation time changed the content of Cu (Table S1). Figure 1 shows the high-resolution transmission electron microscope (HRTEM) images for the Cu/Pt/TiO₂-xh series of samples. For the Cu/Pt/TiO₂-1h and the Cu/Pt/TiO₂-2h samples with lower Cu contents (0.59 and 1.1 wt %), although the Cu species were deposited on the Pt nanoparticle, the covering of the Pt nanoparticle was incomplete. As the irradiation time reached 5 h (Cu content = 1.7 wt %), the Pt nanoparticle was covered by a shell of Cu layers, forming a complete core–shell structure. The HRTEM image displayed lattice fringes with an interplanar spacing of 0.211 nm for the shell (Figure 1c), which could be ascribed to the (200) facet of Cu₂O. This suggests that the shell may be in the state of Cu₂O. We have estimated the mean size of the core–shell structured particles in the Cu/Pt/TiO₂-5h sample, and the value is 7.3 nm. It should be noted that the Cu species were preferentially deposited on Pt nanoparticles over these catalysts. We speculate that this is probably because the photogenerated electrons are efficiently extracted onto Pt from TiO₂. For comparison, a sample with Pt and Cu contents

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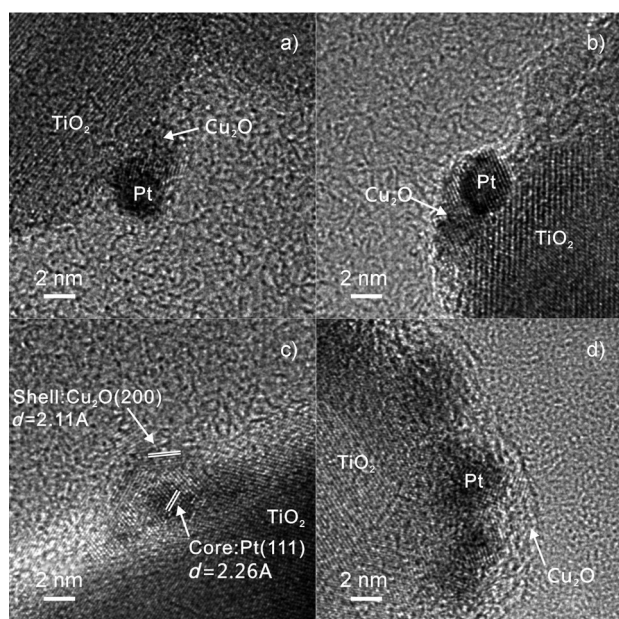


Figure 1. Typical HRTEM micrographs for the Cu/Pt/TiO₂-xh series of catalysts. a) Cu/Pt/TiO₂-1h, b) Cu/Pt/TiO₂-2h, c) Cu/Pt/TiO₂-5h, d) Cu/Pt/TiO₂-10h.

of 0.90 and 1.6 wt %, which were similar to those in the Cu/Pt/TiO₂-5h, was also prepared by a hydrazine-reduction method. TEM measurements suggested that this sample was composed of Pt and Cu₂O nanoparticles (denoted as Pt-Cu/TiO₂ hereafter; Figure S2).

The chemical states of Pt and Cu in our samples were further characterized by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Only diffraction peaks ascribed to TiO₂ were observed for each sample (Figure S3), implying that no larger platinum or copper-related crystallites were formed. XPS measurements revealed that the binding energies of Pt 4f_{7/2} were about 70.9 eV for the Pt/TiO₂, Cu/Pt/TiO₂-5h, and Pt-Cu/TiO₂ samples (Figure S4), confirming that Pt was in metallic state in these samples.^[10] The binding energies of Cu 2p_{3/2} for the Cu/TiO₂, Cu/Pt/TiO₂-5h, and Pt-Cu/TiO₂ samples were about 932.5 eV (Figure S5A), which could be attributed to either Cu⁰ or Cu^I.^[11] The positions of the Cu L₃VV Auger lines for these samples were centered at 916.6–917.1 eV (Figure S5B), corresponding to that of Cu^I.^[11] Considering that Cu⁰ may be easily oxidized into Cu^I after exposure to air,^[12] we further performed in situ CO-adsorbed Fourier-transform infrared studies. The results suggested that the Cu species in our catalysts after the irradiation ($\lambda = 320$ –780 nm) existed in the state of Cu^I or Cu₂O (Figure S6).

To further confirm the formation of the core-shell structure in the sample prepared by the stepwise photo-deposition technique, we have performed high-sensitivity low-energy ion scattering (HS-LEIS) studies, which have been proven to be powerful for providing the atomic composition of the outmost atomic layer of the surface.^[13] The HS-LEIS spectra for the Cu/TiO₂, Pt/TiO₂, Pt-Cu/TiO₂, and Cu/Pt/TiO₂-5h are displayed in Figure 2. It is known that the He⁺ ions can give an overview of almost all elements on the outer surface with poor sensitivity for heavier elements,

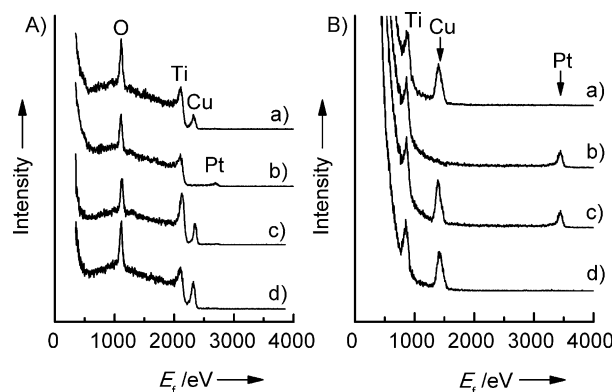


Figure 2. HS-LEIS spectra for a) Cu/TiO₂, b) Pt/TiO₂, c) Pt-Cu/TiO₂, and d) Cu/Pt/TiO₂-5h catalysts. A) 3 keV ⁴He⁺, B) 5 keV ²⁰Ne⁺.

whereas the Ne⁺ ions can provide better sensitivities for heavier elements although it is unsuitable for the measurement of lighter elements. Figure 2B clearly shows that Pt and Cu co-exist on the outmost surface of the Pt-Cu/TiO₂ sample, whereas only Cu is present on the outer surface of the Cu/Pt/TiO₂-5h sample. We further measured the HS-LEIS spectra for the Cu/Pt/TiO₂-xh series of samples and found that, with an increase in the irradiation time, the intensity of the Cu signal increased and that of the Pt signal decreased gradually (Figure S7). When the irradiation time was ≥ 5 h, the signal of Pt disappeared. Therefore, our HS-LEIS results provide further evidence for the formation of the core-shell structure in the Cu/Pt/TiO₂-5h and the Cu/Pt/TiO₂-10h samples.

The photocatalytic reduction of CO₂ with H₂O over our catalysts provided CO and CH₄ as two main products (Table 1). The formation of H₂ was also observed at the

Table 1: Photocatalytic conversion of CO₂ with H₂O over TiO₂-loaded single or binary co-catalysts.^[a]

Catalyst	Formation rate [$\mu\text{mol g}^{-1} \text{h}^{-1}$]			Selectivity for CO ₂ reduction [%]
	H ₂	CO	CH ₄	
TiO ₂	4.9	2.5	1.2	60
Pt/TiO ₂	66	2.2	11	41
Cu/TiO ₂	9.9	5.4	8.7	80
Pt-Cu/TiO ₂	51	5.9	9.8	47
Cu/Pt/TiO ₂ -5h	25	8.3	33	85

[a] Reaction conditions: photocatalyst, 0.020 g; CO₂ pressure, 0.2 MPa; H₂O, 4.0 mL; light source, 320–780 nm; irradiation time, 4 h.

same time. We further confirmed the formation of O₂ over our catalysts (see the Supporting Information for experimental details). These suggest the occurrence of the following reductive reactions through photogenerated electrons and the formation of O₂ by photogenerated holes over our catalysts [Eqs. (1)–(4)]:

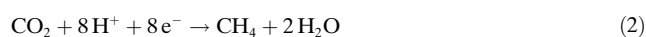




Table 1 shows that the loading of either Pt or Cu (existing as Cu_2O) single co-catalysts onto TiO_2 can promote the formation of CH_4 . The formation of CO was also improved by Cu. The enhanced electron–hole separation through trapping electrons by the noble or coinage metal co-catalyst with a lower Fermi energy level is believed to be a main reason. The increased electron density on the co-catalyst may favor the formation of CH_4 , which requires eight electrons. Our present work further clarified that the formation of H_2 was also enhanced by loading Pt or Cu onto TiO_2 , and such an enhancement was much more significant in the case of Pt co-catalyst. Considering that the reduction of H_2O to H_2 is a competitive reaction with the reduction of CO_2 to CO and CH_4 ,^[2c] we have evaluated the selectivity for CO_2 reduction on an electron basis (Supporting Information, experimental details). It becomes clear that the Pt co-catalyst decreases the selectivity, whereas the selectivity for CO_2 reduction increases from 60 to 80% by loading Cu onto TiO_2 .

Although Cu (existing as Cu_2O) is a more selective co-catalyst for the reduction of CO_2 , the rate of CH_4 formation over Cu/TiO_2 is lower than that over the Pt/TiO_2 . Our transient photocurrent response measurements showed that the photocurrent for Cu/TiO_2 was significantly lower than that for Pt/TiO_2 (Figure 3), clarifying the lower efficiency of

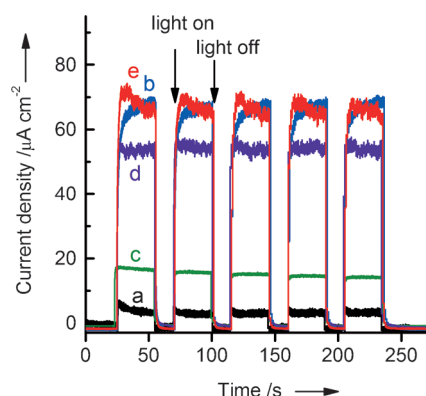


Figure 3. Transient photocurrent responses for a) TiO_2 , b) Pt/TiO_2 , c) Cu/TiO_2 , d) Pt-Cu/TiO_2 , and e) Cu/Pt/TiO_2 -5h catalysts.

the separation of photogenerated electron–hole pairs in the Cu/TiO_2 catalyst. The combination of Cu_2O responsible for the selective activation of CO_2 and Pt capable of effectively extracting the photogenerated electrons is expected to increase the photocatalytic activity for CO_2 reduction. However, the use of the Pt-Cu/TiO_2 catalyst, which was composed of Pt and Cu_2O nanoparticles, did not show synergistic effects for CO and CH_4 formation. The rate of CH_4 formation over this catalyst was even lower than that over the Pt/TiO_2 . The selectivity for CO_2 reduction was also low over this catalyst. On the other hand, the Cu/Pt/TiO_2 -5h catalyst containing core–shell-structured $\text{Pt@Cu}_2\text{O}$ nanoparticles demonstrated a significantly enhanced activity for the formation of CH_4

(Table 1). The rate of CH_4 formation over this catalyst was about 28 times higher than that over TiO_2 alone, and was 3.0 and 3.8 times higher than those over the Pt/TiO_2 and Cu/TiO_2 , respectively. The formation of CO over the Cu/Pt/TiO_2 -5h catalyst was also higher than that over Cu/TiO_2 or Pt/TiO_2 . We performed a blank reaction over the Cu/Pt/TiO_2 -5h catalyst. In the absence of CO_2 , the formation of CO and CH_4 was negligible, confirming that CO and CH_4 were formed from CO_2 . The rate of H_2 formation in the absence of CO_2 was $32\text{ }\mu\text{mol g}^{-1}\text{ h}^{-1}$, only slightly higher than that ($25\text{ }\mu\text{mol g}^{-1}\text{ h}^{-1}$) in the presence of CO_2 . The transient photocurrent response measurement showed that the Cu/Pt/TiO_2 -5h catalyst exhibited a photocurrent similar to Pt/TiO_2 (Figure 3), indicating that the $\text{Pt@Cu}_2\text{O}$ core–shell structure could keep the higher ability of Pt nanoparticles for trapping the photogenerated electrons from TiO_2 . All these observations allow us to exclude the possibility that CH_4 is formed via the hydrogenation of CO_2 or CO adsorbed or formed on the Cu site by the atomic H species generated on the Pt site.^[2b,8] Instead, our results clearly demonstrate that the covering of Pt by Cu_2O with a core–shell structure suppressed the reduction of H_2O to H_2 and preferentially accelerated the reduction of CO_2 to CO and CH_4 . The selectivity for CO_2 reduction reached 85%.

The photocatalytic behavior of the Cu/Pt/TiO_2 -xh series of catalysts depended on the content of Cu, which had been regulated by changing the irradiation time used for Cu photodeposition. At a Cu content of < 1.7 wt %, the increase in Cu content significantly decreased the formation of H_2 and increased that of CH_4 and CO (Figure 4). At the same time, the selectivity for CO_2 reduction increased remarkably. TEM

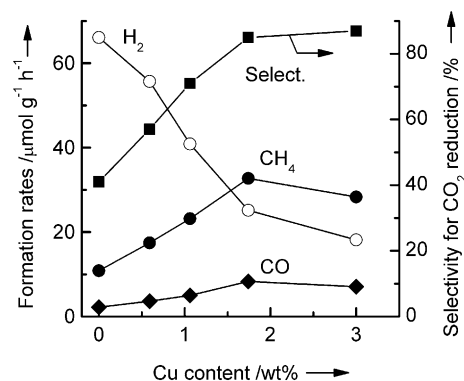


Figure 4. Dependence of the photocatalytic behavior on the Cu content in the Cu/Pt/TiO_2 -xh catalysts for the reduction of CO_2 with H_2O . Reaction conditions: photocatalyst, 0.020 g; CO_2 pressure, 0.2 MPa; H_2O , 4.0 mL; light source, 320–780 nm; irradiation time, 4 h.

images of these samples showed the gradual covering of Pt nanoparticles by Cu layers. For the sample with a Cu content of 1.7 wt %, over which the core–shell structure was formed, the rates of CH_4 and CO formation reached the maximum values. A further increase in Cu content slightly decreased the rates of CH_4 and CO formation, suggesting that a too thick Cu_2O shell was unfavorable to the reduction of CO_2 . These systematic changes further demonstrate the favorable role of

the core-shell-structured Pt@Cu₂O co-catalyst in the preferential reduction of CO₂ by the photogenerated electrons.

It is worth mentioning that a few core-shell-structured co-catalyst or catalyst systems such as Rh@Cr₂O₃,^[14] Ni@NiO,^[15] and Cu@TiO₂^[16] have been reported to be efficient for photocatalysis. In the case of the Rh@Cr₂O₃ co-catalyst for the photocatalytic splitting of H₂O, the metal oxide shell has been proposed to be capable of avoiding the reoxidation of H₂ formed on metal nanoparticles.^[14] Our present work has demonstrated that the preparation of a core-shell-structured Pt@Cu₂O co-catalyst can significantly promote the photocatalytic reduction of CO₂ with H₂O to CH₄ and CO. It is proposed that the Cu₂O shell provides sites for the preferential activation and conversion of CO₂ molecules in the presence of H₂O, while the Pt core extracts the photogenerated electrons from TiO₂. The deposition of a Cu₂O shell on Pt markedly suppresses the reduction of H₂O to H₂, a competitive reaction with the reduction of CO₂. We expect that further optimization of the chemical compositions of the core and the shell may further improve the photocatalytic activity for CO₂ reduction with H₂O in the future.

Experimental Section

The Cu/Pt/TiO₂ catalyst was prepared by a stepwise photodeposition method. Pt was first loaded onto TiO₂ (Degussa P25) by photo-reducing H₂PtCl₆ in an aqueous suspension, which was irradiated with a 300 W Hg lamp for 1 h. The Pt/TiO₂ was then dispersed in an aqueous solution of CuSO₄. After evacuation, the suspension was exposed to irradiation with the Hg lamp to deposit Cu species onto Pt/TiO₂. The final product was washed thoroughly with deionized water and dried overnight in vacuum. The content of Cu was regulated by varying the irradiation time in the second step, and the obtained sample was denoted as Cu/Pt/TiO₂-xh. For comparison, a Pt-Cu/TiO₂ sample was also prepared by a hydrazine-reduction method, in which hydrazine was used for the reduction of the mixed aqueous solution of Pt and Cu precursors in the presence of TiO₂. The contents of Pt and Cu in each sample were analyzed by inductively coupled plasma mass spectrometry (ICP-MS). XRD, XPS, TEM, CO-adsorbed FT-IR, and HS-LEIS techniques were used for catalyst characterizations. Photoelectrochemical measurements were carried out with an Ivium CompactStat (Holland). Photocatalytic reactions were performed in a stainless-steel reactor with a quartz window on the top of the reactor. The light source was a 200 W Xe lamp ($\lambda = 320\text{--}780\text{ nm}$). The photocatalyst was placed on a Teflon catalyst holder without being immersed in water. Typically, 4.0 mL of H₂O was charged in the bottom of the reactor, and the pressure of CO₂ was regulated to 0.2 MPa. The photocatalytic reaction was typically carried out at 323 K for 4 h. The products were analyzed by gas chromatography. See the Supporting Information for the experimental details.

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