CO_2 Photoreduction

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Photocatalytic Conversion of Diluted CO_2 into Light Hydrocarbons Using Periodically Modulated Multiwalled Nanotube Arrays**

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Solar-energy-driven conversion of CO_2 into hydrocarbon fuels can simultaneously generate chemical fuels to meet energy demand and mitigate rising CO_2 levels. The utilization of the clean and renewable solar power resource is, on a long-term basis, an essential component of solutions to address growing global energy demand, which is projected to be 40 TW by 2050.[1] This is because the solar energy received on the earth's surface in one hour exceeds current total global energy demand. From the perspective of climate change, expansion of the current fossil fuel-based energy infrastructure to meet the projected energy demand is predicted to add 2986-7402 Gt of CO_2 to the atmosphere by 2100, resulting in a mean rise in global temperature of 2.4–4.5 °C.[2]

Since the discovery of the photoreduction of carbon dioxide to form organic compounds using semiconductors by Fujishima and co-workers in 1979,[3] a growing interest in the development of catalysts that are capable of solar-based capture and storage of CO_2 has evolved.[4] Titanium dioxide, which is a cost-efficient, non-toxic and abundant *n*-type semiconductor, has been widely considered in the solar-driven reduction of CO_2. Owing to its large band-gap energy of 3–3.2 eV, TiO_2 without doping or post-synthesis treatments can absorb only the ultraviolet portion of the solar spectrum. To narrow the band-gap of TiO_2 and improve its photocatalytic performance, strategies such as compositional doping or deliberately introducing disorder in crystalline TiO_2 are being investigated.[5] Herein, we demonstrate an approach that is able to achieve high-rate sunlight-driven conversion of diluted CO_2 to light hydrocarbons in which an optimized combination of a Cu-Pt coating and modulated-diameter TiO_2 nanotubes are used as the photocatalyst. We demonstrate at least a fourfold improvement in CO_2 conversion rates over prior art[6] by using a catalyst consisting of coaxial Cu-Pt bimetallic shells supported on a periodically modulated double-walled TiO_2 nanotube (PMTiNT) array core. The photocatalytic reaction occurs at room temperature and generates CH_4, C_2H_4, and C_2H_6 as reaction products. Under AM 1.5 one-sun illumination, using 99.9 % CO_2, we obtained a hydrocarbon production rate of 3.51 $mL\,g^{-1}\,h^{-1}$ or 574 $nmol\,cm^{-2}\,h^{-1}$. A key novelty is the effectiveness of our photocatalyst for the photoreduction of unconcentrated CO_2. When the $Cu_{0.33}$-$Pt_{0.67}$/PMTiNT heterogeneous catalyst was utilized for the photoreduction of diluted CO_2 (0.998 % in N_2) at 25 °C, we found an average hydrocarbon production rate of 3.7 $mL\,g^{-1}\,h^{-1}$ or 610 $nmol\,cm^{-2}\,h^{-1}$. The periodic modulation of the diameters of the nanotube arrays increased the surface area and improved the utilization of light while the bimetallic coating increased catalyst activity and specificity. Our version of a highly active CO_2 reduction system does not require reactant gases with high purities and could potentially be used to photocatalytically capture CO_2 directly from air or from flue gas.

A SEM image (Figure 1 A) shows the top-view of a nanotube array photocatalyst. The average diameters of the outer wall and inner wall are 180 ± 10 nm and 130 ± 10 nm, respectively. High-resolution XPS spectra of the TiO_2-supported Pt-Cu nanotube catalyst (Figure 1 B,C) and energy-dispersive X-ray spectroscopy (EDX) mapping (Figure 1 D) verify that the surfaces of these catalysts are enriched with both copper and platinum. The Pt-Cu coating exists throughout the length of the nanotubes. The peak of $Cu\,2p_{3/2}$ is at 931.2 eV, whereas the peak of $Pt\,4f_{7/2}$ is at 70.5 eV. Details related to the photocatalytic reactor (Figure 1 E) and the measurement of reaction products are given in Supporting Information.

Anodization of pure titanium provides an effective and facile way to generate TiO_2 nanotube arrays with high surface area and controllable dimensions, leading to wide-ranging applications that include solar cells, photocatalysts, and supercapacitors.[7] In many cases, however, the photoactivity of TiO_2 nanotubes is limited because of their exclusive absorption of the ultraviolet range of the solar spectrum. The sensitivity of Cu-coated TiO_2 to visible light is partly explained by the interfacial charge-transfer (IFCT) mechanism.[8] TiO_2 nanotube arrays with periodically modulated diameters and coaxial bimetallic coatings also function as defect-doped one-dimensional photonic crystals[9] that trap light and improve its utilization in photocatalysis. The fabrication of such PMTiNTs was enabled by the application

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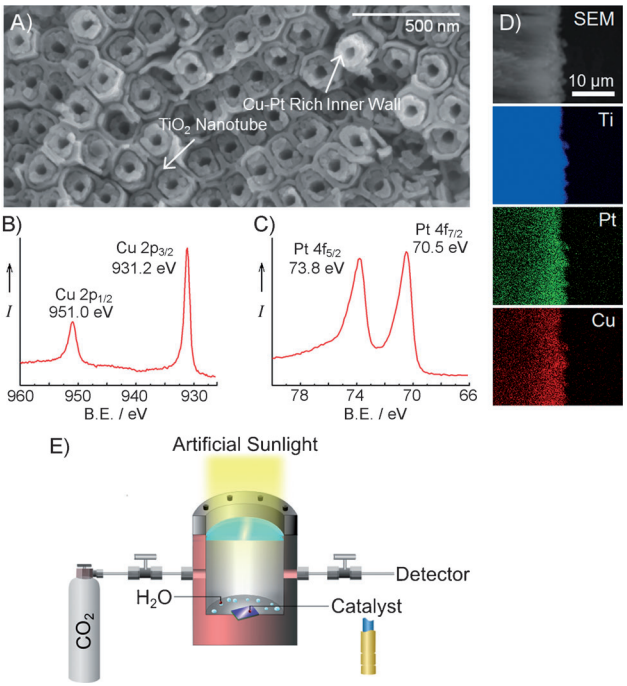

Figure 1. A) SEM image taken several μm deep from the top of a 15 μm-thick PMTiNT-supported Cu-Pt nanocatalyst for solar-driven CO_2 reduction. A Cu-Pt coated inner wall and a PMTiNT are indicated. B) Cu 2p and C) Pt 4f XPS spectra taken on a Cu-Pt/PMTiNT nanocatalyst. D) Cross-sectional SEM and EDX mapping of Cu-Pt-loaded PMTiNTs. E) Illustration of solar-driven conversion of CO_2 at room temperature (25 °C) using a high-pressure reaction chamber connected directly to a gas chromatograph sampling loop for compositional analysis.

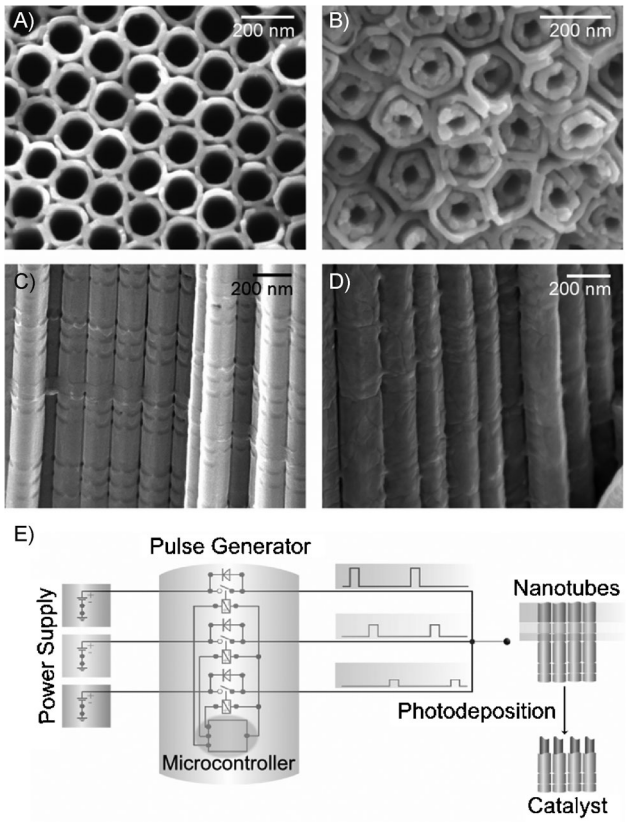

Figure 2. A, B) Plan-view and C, D) cross-sectional SEM images of the as-prepared PMTiNT platform (A, C) and Cu-Pt loaded nanotubes (B, D). E) Illustration of the pulse generator employed for the fabrication of PMTiNTs with three repeating segments of 200 nm, 60 nm, and 60 nm in length.

of a sequence of current pulses generated by a switching operation between different individual power supplies during the anodization of titanium (Figure 2 and the Supporting Information, Figure S1).[9] PMTiNTs with three repeating segments (200 nm, 60 nm, and 60 nm in length) were fabricated. Note that in galvanostatic pulse anodization, the length of anodized segments was determined by both pulse duration and current magnitude. These freshly formed amorphous TiO_2 nanotubes, which were subsequently annealed to anatase at 505 °C, exhibit high photoactivity.

Along with the development of PMTiNTs, a broad range of Cu-Pt compositions of nanotube structures deposited on the calcined TiO_2 nanotube supports were explored. Core–shell nanotubes with bimetallic coatings on the double-walled TiO_2 nanotubes were formed by selective photodeposition of Cu-Pt on the inner walls of anatase nanotube arrays in a precursor solution consisting of Cu^{2+}, Pt^{2+}, and methanol with different ratios. TiO_2 nanotube arrays grow with a double-walled structure (Figure 1 A and 2 B), which manifests itself during rapid thermal annealing but can also be fused by slow heating to temperatures > 550 °C to show single walls.[10] When processing conditions corresponding to single-walled structures were used, double walls were still observed, suggesting that the conditions of fabricating PMTiNTs generated the double-walled structures in our case (Supporting Information, Figures S2, S3).

The ability of bimetallic alloys to improve catalytic activity and selectivity has resulted in their use as electrocatalysts in fuel cells and as catalysts in a variety of organic syntheses.[11] The combination of noble-metal bimetallic alloys with ordered TiO_2 nanotube arrays of tunable diameter and wall thickness in core–shell structures offers new possibilities in controlling the shape, size, and composition of the photocatalysts. To investigate the role of Cu-Pt bimetallic coatings in the photocatalytic system, a series of Cu-Pt/TiO_2 nanocatalysts were prepared and compared to pure copper and platinum-loaded TiO_2 reference samples in the reduction of CO_2. A large number of individual catalysts in which the ratio of Cu/Pt was gradually changed from 1:6 to 5:1 were tested, and the averaged catalytic activity was quantified by the total yield of hydrocarbons (in either molar or volumetric units) per unit catalyst (mass of catalyst or surface area of catalyst wafer) per unit time. Figure 3 A shows a plot of the rate of production of hydrocarbons as a function of Cu/Pt composition in Cu-Pt/TiO_2 nanocatalysts for a one-hour photoreduction reaction using 0.998 % CO_2, wherein the overall hydrocarbon production rate was maximized (3.73 $mL\,g^{-1}\,h^{-1}$) when $Cu_{0.33}$-$Pt_{0.67}$/TiO_2 was employed. In this plot, one distinguishable region was observed in the range from Cu-50 % to Cu-85 %, which exhibits a minimum hydrocarbon production rate at Cu-75 %. The rate of CH_4 produced

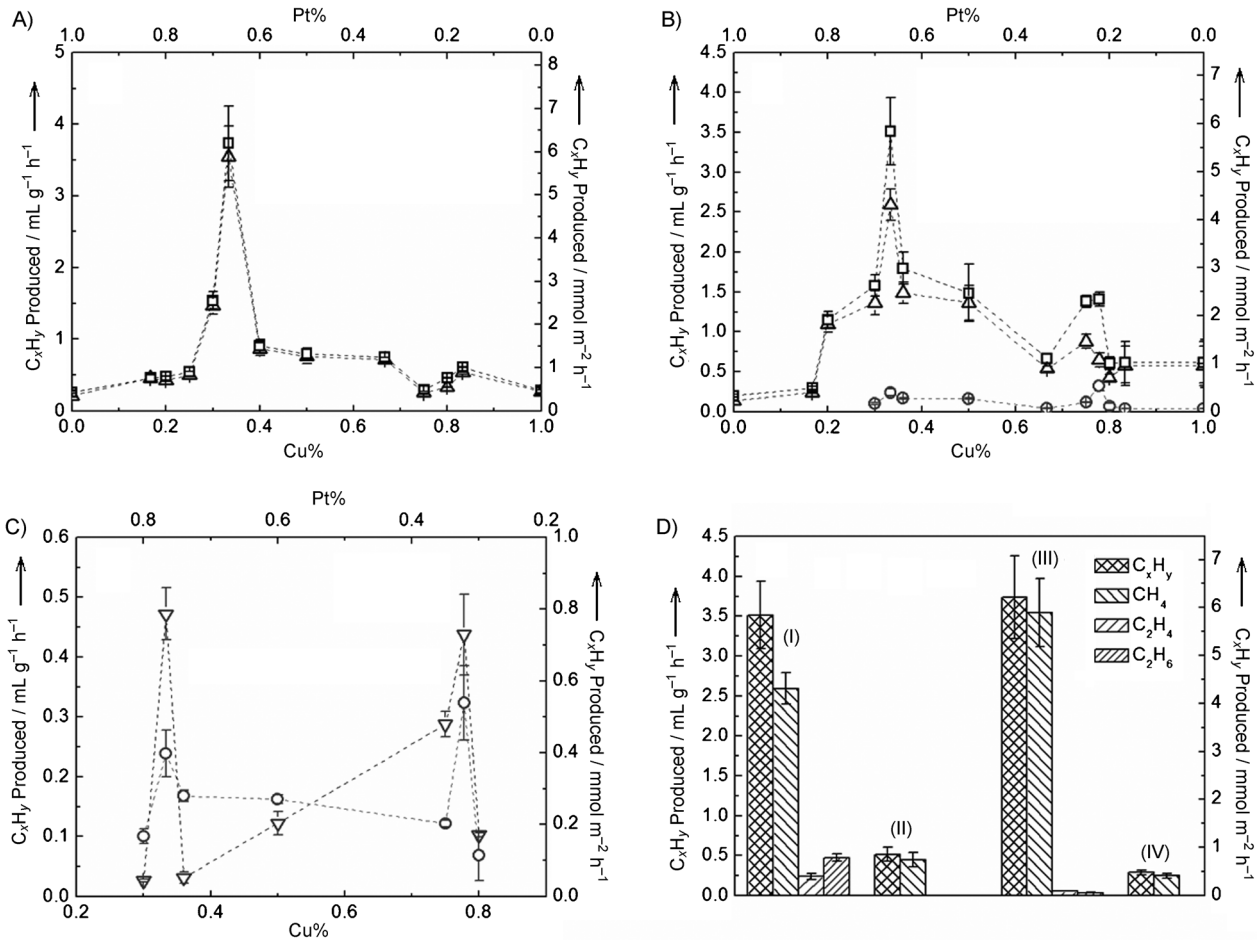

Figure 3. A, B) Plots of hydrocarbon (□), CH_4 (△), and C_2H_4 (○) solar-driven generation rates against fraction of Cu in Cu-Pt bimetallic system using 0.998% (A) and 99.9% (B) CO_2. C) Comparison of the C_2H_4 (○) and C_2H_6 (▽) solar-driven generation rates against fraction of Cu in the Cu-Pt bimetallic system using 99.9% CO_2. D) Comparison of hydrocarbon generation activities of $Cu_{0.33}$-$Pt_{0.67}$ nanotube-loaded PMTiNTs (I, III) and regular TiNTs (II, IV) using 99.9% (I, II) and 0.998% (III, IV) CO_2.

during the one-hour reduction of 0.998% CO_2 reached a maximum at $Cu_{0.33}$-$Pt_{0.67}$ (3.55 mL g^{-1} h^{-1}), whereas $Cu_{0.75}Pt_{0.25}$ gave the lowest CH_4 production rate (0.26 mL g^{-1} h^{-1}). The hydrocarbon production trends are qualitatively the same when using 99.9% CO_2, with the exception of a local peak observed close to Cu-75% (Figure 3B). The maximum production rates of hydrocarbons and CH_4 were also obtained for the higher purity CO_2 with $Cu_{0.33}$-$Pt_{0.67}$ (3.51 mL g^{-1} h^{-1} and 2.60 mL g^{-1} h^{-1}, respectively), which confirms that the $Cu_{0.33}$-$Pt_{0.67}$ was the most reactive catalyst in the Cu-Pt/TiO_2 series for the photocatalytic reduction of CO_2. More importantly, considerable amounts of C_2H_4 and C_2H_6 were produced when 99.9% CO_2 was used, with the production rates of C_2H_4 (0.33 mL g^{-1} h^{-1}) and C_2H_6 (0.47 mL g^{-1} h^{-1}) maximized at Cu-75% and Cu-33%, respectively (Figure 3B,C). For comparison, even at Cu-33%, there was only 0.06 mL g^{-1} h^{-1} C_2H_4 and 0.04 mL g^{-1} h^{-1} C_2H_6 produced when reducing 0.998% CO_2. Overall, the Pt-Cu/TiO_2 catalysts exhibited high catalytic activity for the photoreduction of CO_2 and gave rise to significant hydrocarbon production at specific Cu-Pt compositions. In contrast, pure copper and pure platinum-loaded periodically modulated nanotube catalysts led to relatively low hydrocarbon production rates (0.28 and 0.26 mL g^{-1} h^{-1} using 0.998% CO_2, 0.61 and 0.20 mL g^{-1} h^{-1} using 99.9% CO_2, respectively). A series of experiments were also performed using regular, smooth-sided TiO_2 nanotube arrays loaded with $Cu_{0.33}$-$Pt_{0.67}$ with the same dimensions of the periodically modulated nanotubes to distinguish the effect of such nanostructures on the catalysts. Figure 3D obviously shows that by using these reference samples, the production rate of hydrocarbons dropped 92% and 86% in 0.998% CO_2 and 99.9% CO_2, respectively, whereas the production rate of CH_4 decreased by 93% and 83%, respectively. In the case of $Cu_{0.33}$-$Pt_{0.67}$-loaded regular TiO_2 nanotubes, no C_2H_4 or C_2H_6 products were observed.

In summary, the results reported herein highlight the exploration of easily prepared periodically modulated TiO_2 nanotubes with remarkable photoactivity. Relatively high CO_2-to-hydrocarbon conversion rates were achieved by coupling bimetallic coatings with these TiO_2 nanotube arrays as catalysts in the photoreduction of CO_2 and H_2O to hydrocarbons at room temperature. Direct control over TiO_2 nanotube structures using programmed pulse anodization has opened a feasible route to enhance their photocatalytic efficiency, which also benefited the development of the reported catalyst. By varying the fraction of one component

in this bimetallic system, $Cu_{0.33}$-$Pt_{0.67}$ has been found to be the most reactive catalyst in its family to generate light hydrocarbons at room temperature using low-concentration CO_2.

Experimental Section

Catalyst Preparation: Grade 2 pure titanium substrates were degreased in an ultrasonic bath of reagent-grade ethanol for 10 min and tried with nitrogen gas. Electropolishing of titanium was preformed at 0°C in perchloric acid (0.100 M in glacial acetic acid, Ricca Chemical) for 10 min using constant voltage (125 V). The substrates were then removed from the polishing solution, cleaned ultrasonically with isopropyl alcohol for 5 min, and dried with a nitrogen gas flow.

Periodically modulated titania nanotube (PMTiNT) platforms were synthesized by pulse anodization of pre-electropolished titanium substrates in a two-electrode anodization setup using a graphite counter electrode. Before anodization, these titanium substrates were cleaned ultrasonically with acetone and isopropyl alcohol, and then dried by a stream of nitrogen gas. Pulse anodization of titanium that has been discussed in the paper was carried out at 15°C in an EG electrolyte, which consists of a mixture of NH_4F (0.25%, w/w), deionized water (3%, v/v), and ethylene glycol. Constant applied currents were used during the anodization. After anodization, the substrates were removed from the electrolyte solution, rinsed with isopropyl alcohol, and dried with nitrogen gas. The annealing of as-prepared PMTiNTs was carried out at 505°C for 8 h with a ramping rate of 1.3 °C min^{-1} in a 3-zone tube furnace (Lindberg/Blue M, Thermo Scientific).

A growth solution was prepared by mixing $K[PtCl_4]$ (0.5–2 mM, aq)/$[Pt(acac)_2]$ (0.5–2 mM, in methanol), $[Cu(acac)_2]$ (0.5–2 mM, in methanol), methanol, and deionized water at room temperature using ultrasonication. A teflon reaction cell was designed and constructed to match the dimension of the sample. To prepare the catalysts, annealed PMTiNT platforms were soaked in the growth solution and the photodeposition of metallic nanotubes was carried out for 45–60 min under the irradiation of a 4 W 365 nm screen-inspection UV lamp (1000 μw cm^{-2}). The PMTiNT platforms were then removed from the growth solution and rinsed thoroughly with isopropyl alcohol, dried by nitrogen gas.

Samples were characterized by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The SEM images were taken with a Hitachi S-4800FE-SEM. XPS measurements were carried out under UHV conditions ($< 10^{-8}$ Torr) on a Kratos Analytical, Axis-Ultra instrument. Wide angle X-ray diffraction data (Supporting Information, Figure S4) were collected using a Rigaku Ultima IV diffractometer.

The photoreduction of CO_2 was carried out at room temperature in a dark room. A Newport solar simulator (91160–1000) equipped with Class A filters was employed as the light source. The distance between the catalyst surface and the lens of the solar simulator is 32 cm. AM 1.5 sunlight was used for all experiments. Catalyst film area: circa 1.8 cm^2; mass of the catalyst film (Cu-Pt + TiO_2): circa 6.7 mg. To measure the mass of the catalyst, the Cu-Pt-coated PMTiNT thin films were detached from the titanium substrate using mechanical forces and carefully weighed.

Gas chromatography determinations were carried out by a Varian Star (Varian, CA, USA) equipped with a Porapak QS column (12 Ft; 366 cm; 3.2 mm OD, 2 mm ID). A TCD detector and a FID detector were employed. The detector temperature was held at 180°C and 250°C for TCD and FID, respectively. The column temperature was held at 70°C. Helium was used as the carrier gas.

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