

## Letter

Enhanced CO<sub>2</sub> photoreduction under electrostatic field induction

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## ARTICLE INFO

## Article history:

Received 18 August 2013

Received in revised form

1 July 2015

Accepted 7 July 2015

## Keywords:

Electrostatic force

TiO<sub>2</sub>

CO<sub>2</sub> photoreduction

## ABSTRACT

A highly efficient electrostatic induced CO<sub>2</sub> photoreduction system is introduced. When 45 kV of electrostatic force was applied, 6.26% of quantum yield of CO<sub>2</sub> photoreduction reaction was achieved (equivalent to 184.44 μmol/g h) using pure TiO<sub>2</sub> nanorods that grown on FTO glass as the photocatalyst.

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## 1. Introduction

Solar energy is an unlimited energy source but its applications are limited by the location, season and time, that restrict the conversion of solar energy to another kind of energy form, such as electricity and chemical energy. In an effort to mitigate the greenhouse effect and fossil fuel shortage, there is wide interest in converting the greenhouse gas carbon dioxide (CO<sub>2</sub>) into organic molecules such as carbon monoxide (CO), methane (CH<sub>4</sub>), formic acid (HCOOH), formaldehyde (HCHO) or methanol (CH<sub>3</sub>OH) by chemical routes [1–3]. CO<sub>2</sub> photoreduction process, also known as “artificial photosynthesis”, is a clean and green process because it uses solar energy and converts CO<sub>2</sub> into CO and hydrocarbon fuels at ambient temperature and pressure without giving hazardous by-product [4–8]. Therefore, studies are essential in order to realize its practical applications, because once fossil fuel supplies are exhausted, only natural energy sources, e.g., solar energy, will be available [9–11].

In the CO<sub>2</sub> photoreduction process, products with low molecular weight, such as CO and CH<sub>4</sub> can be easily produced within a short period of time. These products can be used as the feedstock for various synthetic processes, such as the *d*-metal catalyzed Fischer-Tropsch process, and Monsanto and Cativa (both acetic acid) processes. Additionally, CO has significant fuel value ( $\Delta_c H^\circ = -283.0 \text{ kJ mol}^{-1}$ ) that can be converted into methanol

(e.g., by the CuO/ZnO/Al<sub>2</sub>O<sub>3</sub>-catalyzed ICI-process) as liquid fuel [12,13]. Therefore, more effort is required to develop the CO<sub>2</sub> photoreduction process so that we can utilize solar energy efficiently and ultimately reduce the dependence on fossil fuels.

Titanium dioxide (TiO<sub>2</sub>) is a non-toxic, stable, cheap material, thus it is one of the most widely used photocatalyst including CO<sub>2</sub> photoreduction process. However, current achievable CO<sub>2</sub> photoreduction rate of TiO<sub>2</sub> is still low, due to the narrow light response range and low quantum efficiency of TiO<sub>2</sub> [14–17]. The highest conversion rates per gram of TiO<sub>2</sub> in an hour of UV irradiation so far are ~250 μmol and ~36 μmol of CO [18] and CH<sub>4</sub>[19] respectively. Therefore, considerable effort has been made to enhance TiO<sub>2</sub> photoactivity under both UV and visible light, such as by doping [20–22], surface sensitization [19,23,24], metal deposition [25–28], and coupling of composite semiconductors [29,30]. For instance, the Ag deposited TiO<sub>2</sub> sample reported by Wang et al. managed to obtain ~1361 μmol of CH<sub>4</sub> from a gram of catalyst after an hour of Xe lamp irradiation [18].

Though the above efforts have significantly promoted the conversion of CO<sub>2</sub> into CH<sub>4</sub>, we realize that a combination of chemical and physical enhancements would be able to perfectize the whole CO<sub>2</sub> photoreduction system. For instance, the application of high gas pressures during the CO<sub>2</sub> photoreduction process, which achieved 20.2% of Faradaic efficiency for methane [31], while the combination of solar energy with electrochemistry to perform photoelectrochemical CO<sub>2</sub> reduction reported the highest Faradaic efficiency of 97% [32,33].

The CO<sub>2</sub> photoreduction process is a heterogeneous catalysis process which involves other factors such as the random motion of gas molecules [34] and the adsorption at a gas–solid interface

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[35,36]. During the gas–solid interaction in the CO<sub>2</sub> photoreduction process, the gas molecules in the reactor move freely, through Brownian motion. The collision between gas molecules and a solid TiO<sub>2</sub> semiconductor provides a chance for TiO<sub>2</sub> to reduce CO<sub>2</sub> to CO and CH<sub>4</sub> under UV light irradiation. Therefore, the effective collision probability, which is the collision probability of gas molecules with TiO<sub>2</sub> at the correct orientation resulting in a chemical reaction between CO<sub>2</sub> molecules and TiO<sub>2</sub> photocatalyst, is one of the most important factors in the CO<sub>2</sub> photoreduction process. When comparing the collision probability and the effective collision, the effective collision probability is usually low that leads to low reaction rate.

Herein, we attempt to increase the effective collisions probability of CO<sub>2</sub> molecules with TiO<sub>2</sub> in order to increase the photoreduction rate of CO<sub>2</sub>. We propose the use of electrostatic field induction which requires only an external application of electrostatic generator to the CO<sub>2</sub> photoreduction system. The electrostatic field induction not only increases the conversion yield but also induces the reaction to produce usable CO and CH<sub>4</sub> in a short period of time.

## 2. Experimental

### 2.1. Materials & Methods

Fluorinated tin oxide (FTO) pieces (F:SnO<sub>2</sub>, Tec 15, 10 Ω m, Hartford Glass Company) which were ultrasonically cleaned for 60 min in a mixed solution of deionized water, acetone, and 2-propanol with volume ratios of 1:1:1, were employed as substrates for the growth of the nanorods. In a Teflon-lined stainless steel autoclave (500 mL volume, Jinan Henghua Sci. & Tec. Co. Ltd.), deionized water and concentrated hydrochloric acid (36.5–38% by weight) were mixed (ratio 1:1) to reach a total volume of 300 mL, and stirred at ambient conditions for 5 min before the addition of 6 mL of titanium butoxide (97% Aldrich). After stirring for another 5 min, 180 drops of surfactant polyethylene imine (PEI, China Midwest Group, Beijing) with a molecular weight of 5000 were added to the solution, and FTO substrates were placed at an angle against the wall of the Teflonliner with the conducting side facing down. The hydrothermal synthesis was then conducted at 120 °C for 20 h. The details of TiO<sub>2</sub> film preparation on fluorine-doped tin oxide (FTO) coated glass were reported in our previous paper [37].

### 2.2. Characterizations

The samples were characterized using Scanning Electron Microscopy (SEM, Hitachi S4800) to observe the microstructures of the TiO<sub>2</sub> films. Transmission Electron Microscope (TEM) images were obtained by a Tecnai G2 F30 S-TWIN transmission electron microscope, which was operated at an accelerating voltage of 200 kV. X-ray diffraction (XRD) patterns of the TiO<sub>2</sub> films were recorded at room temperature, using a Bruker X'Pert PRO X-ray diffractometer with Cu Kα radiation and 2θ scan rate of 4 min<sup>-1</sup>. Diffraction patterns were taken over the 2θ range of 20–80°.

Photoreduction of CO<sub>2</sub> was carried out under irradiation of four 8-watt UVA lamps at room temperature in a stainless steel photo-reactor equipped with two quartz windows. Prior to each photoreduction test, the TiO<sub>2</sub> film deposited on FTO glass was fixed with a pair of supports in the photo-reactor, and then purged with CO<sub>2</sub> and water vapor which was generated through a water bubbler, and introduced into the reactor at 100 ml/min for 1 h. The flow rate of CO<sub>2</sub> and water vapor was then reduced and maintained at 50 ml/min during the entire photoreduction process. After 30 min, when the flow was stabilized, the UV lamp and DC voltage of the electrostatic generator were turned on and the concentration of

effluent gas as a function of irradiation time was recorded. The photoreduction of CO<sub>2</sub> analysis was also carried out in the dark to ensure no other organic substances were present or generated other than by the photoreduction reaction.

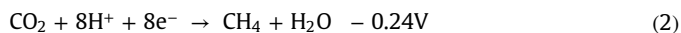
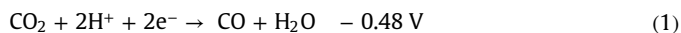
## 3. Results and discussion

The novel and facile development of CO<sub>2</sub> photoreduction under an electrostatic field to enhance its photocatalytic activity was performed using nanorod structured TiO<sub>2</sub> thin film that grown on FTO substrate as shown in Fig. 1a and b. This simple photocatalyst possessing anisotropic-shaped nanostructures is able to overcome the drawbacks such as aggregation of nanoparticles which could otherwise adversely affect catalyst efficiency.

The nanorod structured TiO<sub>2</sub> films used in this study possess a large specific surface area (117 m<sup>2</sup>/g) [37]. Therefore, factors such as low surface area and grain boundaries that resist electron mobility and limit the efficiency of TiO<sub>2</sub> in CO<sub>2</sub> photoreduction could be eliminated in this case. When the samples were irradiated with UV lamps, the P25 as the control sample showed the lowest methane production rate. The nanorod structured TiO<sub>2</sub> sample showed the methane production rate of only ~3 μmol/g h, while TiO<sub>2</sub> supplemented with copper nanoparticles reached a peak methane production rate of 13 μmol/g h (refer to Supporting information).

When the pure TiO<sub>2</sub> nanorod structured sample was exposed to the electrostatic field (Fig. 2), the negative electrode was connected to the wall of the stainless-steel reactor, while the positive electrode was connected to the TiO<sub>2</sub> thin film. The TiO<sub>2</sub> thin film were exposed to 25 kV, 35 kV and 45 kV of electrostatic force respectively and they achieved the maximum methane production rates of ~120, 150 and 180 μmol/g respectively as shown in Fig. 3. These results showed significant improvement on the CO<sub>2</sub> photoreduction performance over the documented literature values that used pure TiO<sub>2</sub> as photocatalyst under UV light irradiation so far. Although application of higher applied electrostatic forces could promote even higher CO<sub>2</sub> photoreduction quantum yields, values > 45 kV could cause system breakdown. Improvements to this aspect of the method will be examined in future studies.

CO<sub>2</sub> is a very stable molecule and is difficult to be reduced and oxidized, therefore, it is important to study the basic processes occurring at the surface of the photocatalyst. After absorption of photons with energy equal to, or greater than, the bandgap, photogenerated electrons are excited and moved to the conduction band, leaving holes in the valence band. The photogenerated electrons and holes then undergo photoreduction and photo-oxidation, respectively. The photo-oxidation of water then leads to the formation of hydroxyl radicals (OH·) and H<sup>+</sup>. While the photoreduction of CO<sub>2</sub> is performed through a multi-electron transfer process, as shown in the equations below:



According to our results as shown in Fig. 3, the CH<sub>4</sub> yield increased with irradiation time and reached a peak value of ~184 μmol/g h at around the 19th hour of irradiation. The quantum yield from these conditions was calculated to be 6.26% (see Supporting information S3). To the best of our knowledge, this value is, to date, the highest CH<sub>4</sub> yield compared to other values

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