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Efficiently Converting CO₂ into C₂H₄ using a Porphyrin–Graphene Composite Photocatalyst

Meihua Piao,^A Nan Liu,^A Yanshu Wang,^A and Chunsheng Feng^{A,B}

^ADepartment of Anesthesiology, First Hospital of Jilin University, Jilin University, Changchun 130023, China.

^BCorresponding author. Email: csfeng@jlu.edu.cn

In this work, a photocatalyst consisting of porphyrin and graphene was designed to reduce CO_2 to hydrocarbons under visible light. This catalyst can (1) effectively reduce CO_2 to hydrocarbons, particularly to C_2H_4 ; (2) selectively control the photogenerated electrons transfer path due to the physico-chemical properties of porphyrin and graphene; and (3) reduce the complexity of investigating this photocatalytic process because the photocatalyst has fewer defects, thus preventing the introduction of interference factors.

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Introduction

Currently, energy and environment are two subjects of considerable importance worldwide. In the past several decades, the level of carbon dioxide in the atmosphere has risen significantly owing to the combustion of hydrocarbon fuels. Accordingly, the shortage of hydrocarbon fuels will be an inevitable problem in the near future. Artificial photosynthesis, a solar energy-based technology, for recycling carbon dioxide into a readily transportable hydrocarbon fuel, would help to reduce atmospheric CO₂ levels and partly fulfil energy demands within the present hydrocarbon-based fuel infrastructure.^[1] Moreover, artificial synthesis, using photoenergy is a compelling approach to drive the conversion of methane and other single-carbon compounds into more valuable molecules at room temperature.^[2,3] For this reason, through suitable conversion, single-carbon carbohydrates may be used as substitutes for the dwindling petroleum resources as chemical feedstock. Therefore, much effort has been devoted to convert single-carbon carbohydrates into multicarbon compounds under mild conditions.[4-7] As a consequence, converting CO₂ into multi-carbon compounds by photocatalytic methods will be of considerable importance, whereby the two processes, i.e. reducing CO₂ to one carbon compound and the subsequent reduction to multi-carbon compounds, are combined.[8]

Research on CO₂ conversion by photocatalytic method has progressed quickly in recent years. And various photocatalysts have been developed and trialled to achieve high conversion rates and selectivity such as organic compounds and transition metal coordination compounds,^[9–11] semiconductors,^[12–18] metal–organic frameworks,^[19] perovskite-structured compounds,^[20] and hybrid photocatalysts.^[21,22] However, the products obtained from the photo-conversion process were mainly CH₄, CO, CH₃OH, and some other single-carbon molecules. In former research, even though multi-carbon compounds were detected in the products, they were only reported as by-products generated in small amounts,^[23–25] and hence were not investigated thoroughly. And reports on directly converting CO_2 to multi-carbon compounds by photocatalytic process are still scarce.^[8] This subject has not gained much attention.

In this work, a novel photocatalytic system based on a porphyrin and graphene composite presented high efficiency of hydrocarbon conversion; not only was a higher conversion rate of CH₄ attained, but also the conversion of CO₂ to ethylene was possible under visible light irradiation. Considering that the conversion of solar energy into chemical energy is becoming the hot spot of future energy investigation, this work provides a simple and promising path to fabricate multi-carbon chemicals from CO₂. Moreover, graphene plays a crucial role in this composite material in facilitating conversion from CO₂ into C_2H_4 that has also been thoroughly investigated.

Experimental

Preparation of Photocatalyst

The preparation of the graphene sheets (GS) was performed according to the method by Wu et al.^[8] The film was prepared by an extremely convenient method involving mist spray. The typical process was as follows: commercially available copper tetra(hydroxyphenyl)porphyrin (CuTHPP, 65 mg) was dissolved in 1,2 dichloroethane (DCE; 100 mL) containing a suspension of GS (0.2 mg mL^{-1}). Then, the dispersion was ejected from a spray lance onto a solid substrate (quartz), driven by N₂ at a certain pressure, while the substrate was maintained at 100°C. The prepared films were then placed in a vacuum drying chamber at 100°C for 2 h to evaporate solvent molecules adsorbed onto the photocatalyst. In addition, a control experiment of porphyrin, in the absence of graphene, was carried out in film form on a quartz substrate. The concentration of porphyrin, size of substrate, and the method employed for film preparation were the same as that used for the preparation of GS/CuTHPP.

Electrochemical Measurement of Porphyrin

CuTHPP was modified on a glassy carbon electrode (GCE) using acetone solution and dried at room temperature. A Pyrex electrolytic cell was employed, filled with Ar-purged 0.5 M Na_2SO_4 (20 mL). A Pt wire and Ag|AgCl electrode were employed as the counter and reference electrodes, respectively. Impedance measurements were recorded using a CHI660 electrochemical workstation.

Photocatalytic Measurement

A double-sided photocatalytic film with an appropriate area of $2 \times 10 \text{ cm} \times 20 \text{ cm}$ was introduced into a 1-L quartz chamber equipped with valves for evacuation and gas feeding. Following loading of the sample, the chamber was evacuated and sealed to ~10 mTorr using a mechanical pump. Carbon dioxide (CO₂, 99.99 % pure) was forced to pass through a bubbler containing deionized water before entering the reaction chamber. These two processes of evacuation and CO₂ pumping were repeated thrice. The approximate excess pressure is less than 1.0 psi. All CO₂ conversion experiments were performed under irradiation of a solar simulator. The light power density was 100 mW cm⁻². The equilibrium temperature of the samples was ~40°C (±5°C). Although the experiments have also been conducted at lower temperatures (~35°C), no definite influence of temperature on product formation rates has been found.

Results and Discussion

In order to construct an outstanding photocatalyst with high selectivity, two types of special materials were used as shown in Scheme 1. CuTHPP was chosen as the antenna (light exciter) rather than inorganic materials because CuTHPP has a greater ability to absorb light than inorganic materials. Compared with inorganic catalyst materials, organic molecules possess relatively simple light absorption suitable for investigating, with no interference from the effect of surface state and impurity energy levels. More importantly, organic molecules as catalysts do not possess surface dangling bonds, which are otherwise abundant on the surface of inorganic materials. Thus, the interaction between porphyrin and reactants is simpler to control. All above characteristics are beneficial to improve the selectivity of photocatalysts. Another important reason to choose such porphyrin molecule as antenna is its excellent photostability.

Graphene was introduced into this photocatalyst system as a charge transfer mediator for its high electrical conductivity and tuneable band gap properties.^[26–28] Moreover, graphene is an outstanding CO₂ absorber according to literature reports, of which the theoretical maximum uptake of CO₂ is 37.93 wt-%.^[29] After combining these two components, under light irradiation, the excited electrons would move from the antenna to the CO₂ molecules while easily passing through the graphene component, thus greatly enhancing the conversion rate effectively. Moreover, the hydrophobic property of graphene allows the catalytic reaction to proceed on the surface in a more controllable fashion because H₂O molecules are unable to accept photogenerated charges from the graphene surface. Therefore, these two materials were combined to realize hydrocarbon photogeneration, as shown in Scheme 1.

In order to confirm whether this photocatalyst can reduce CO_2 into hydrocarbon, the energy level of this material was investigated using the Mott–Schottky method and UV-visible measurement technique (Fig. 1a, b). Through the UV-visible measurements, the energy gap of CuTHPP was estimated as



Scheme 1. Transfer process of photogenerated electrons for CuTHPP/ graphene composite. Under illumination, the photoexcited electrons are transferred from the porphyrin molecules passing through graphene sheets. Due to the hydrophobicity of graphene, the transfer of electrons from graphene to H_2O molecules is difficult.

2.72 eV, as shown in Fig. 1b. To estimate the conduction band potential (E_{CB}), Mott-Schottky plot for CuTHPP was constructed under the condition of pH = 7.0, as shown in Fig. 1a. It can be seen that the slope of the plot was positive, thus suggesting that CuTHPP is an n-type semiconductor. When illuminated, the generated electrons are transferred from the porphyrin molecules to graphene, while the holes remain in the porphyrin because of the properties of these two materials mentioned above. The ECB of CuTHPP was approximately -0.74 V versus Ag|AgCl (-0.54 V versus NHE (normal hydrogen electrode)). According to the band gap and E_{CB} of CuTHPP, we can achieve the relationship between the energy bands of this porphyrin and the energy levels of the redox couple, as clearly seen in Fig. 1. In this case, theoretically, CO₂ can be reduced to a carbohydrate, and H₂O can be oxidized to O₂ using the present photocatalyst.

Owing to the large number of defects in reduced graphite oxide (RGO), the transfer of electrons will be greatly hindered, and the defects will also lead to the introduction of some trap levels in the band gap of graphene. These traps will result in a difficulty in transferring electrons from the GS to the adsorbed molecule for following reactions.^[22] In consequence, the preparation of graphene using conventional methods (graphite oxide reduction) is not sufficiently effective. Therefore, the presence of fewer defects and the higher conductivity of graphene are desirable in this photocatalytic composite.

After preparation, a series of characterizations were performed to investigate the quality of the graphene sheets, as shown in Fig. 2. The exfoliation state of the material was first ascertained by scanning electron microscopy (SEM) measurements (Fig. 2a). After exfoliation, the thickness of the flakes decreased significantly when compared with that of graphite, as clearly shown in the SEM image. Transmission electron microscopy (TEM) was used to reveal the number of layers in the GS. The high-resolution TEM image (Fig. 2b) shows that the structure of GS consisted of a few layers.

The structure of graphene was further investigated by Raman spectroscopy, as shown in Fig. 2c. The G band (\sim 1580 cm⁻¹) and 2D band (\sim 2700 cm⁻¹) were observed clearly in graphene, and a weak peak for D band (\sim 1350 cm⁻¹) was visible that is attributed to edge effects.^[30] However, the signal intensities of the D peak are obviously different from that of the RGO reported



Fig. 1. (a) Mott–Schottky plot for the conduction band of CuTHPP by investigating the relationship between impedance and potential change at a fixed frequency in 0.5 M Na₂SO₄ at pH = 7.0. (b) UV-Visible measurements of the band gaps of CuTHPP, graphene (G), and their composite. (c) Band potentials of CuTHPP (at pH = 7.0) in contact with the redox potential for H₂O and CO₂ reactions at pH = 7.0 with respect to NHE or vacuum.



Fig. 2. (a) SEM image of GS. (b) High-resolution TEM image of GS with few layers. (c) Raman spectrum (using a laser excitation wavelength of 514.5 nm) of graphene on a SiO₂ substrate. (d) XPS spectrum of GS confirming the presence of oxygen and carbon atoms and corresponding narrow XPS scan of C 1s. (e) SEM image of GS/CuTHPP composite.

in the literature, thereby demonstrating that the exfoliation process did not introduce significant amounts of additional structural defects such as epoxides covalently bound to the basal plane.^[31] In the Raman spectrum, the 2D peak can be used to

ascertain the number of layers of the graphene sheets.^[30] As shown in Fig. 2c, the 2D band of the as-prepared graphene shifted clearly to lower energies. Based on the peak profile and position, the as-prepared graphene can be classified as a



Fig. 3. (a) Plots of hydrocarbon generation as a function of time over porphyrin/G catalyst via gas-solid phase reduction method and associated control experiments. (b) Hydrocarbon generation rate. (c) Activity stability measurements. The red closed markers represent CH_4 generation, open markers stand for C_2H_4 generation.

few-layer graphene (FLG) with a thickness corresponding to 5 layers. $^{[30]}$

X-Ray photoelectron spectroscopy (XPS) was used to examine the chemical composition of the as-prepared graphene, as shown in Fig. 2d. The oxygen content of the sample is 3.1 %. The exfoliation process introduced only small amounts of oxygen, resulting from the small cut sheets in the process. Nevertheless, the as-prepared graphene had few defects compared with RGO. This can be further confirmed from the C 1s XPS spectrum, whereby only a single peak at \sim 284.5 eV, which is associated with graphitic carbon, can be observed. Therefore, the result indicted that graphene was prepared successfully by the exfoliation method mentioned above.

The morphology of the as-prepared thin film photocatalysts was examined by SEM and shown in Fig. 2e. As observed, the nano-sized CuTHPP crystal grew on the graphene sheets, resulting in a roughened surface, which indicated the integration of the two components in the photocatalyst. Because of the large size (50-100 µm) and wrinkle of GS, the composite sheets cannot spread smoothly. Consequently, this film was uneven; the thickness is not uniform and varies from 100 nm to $30 \mu \text{m}$ (from the flat region to the crinkled region) based on the SEM and optical microscopy analyses. This structure means that the photogenerated electrons can be transferred from CuTHPP to graphene efficiently. It is worth noting that after combining CuTHPP with GS, the UV signal of CuTHPP did not shift (as shown in Fig. 1b) that suggested that the intermolecular ordering of porphyrin was the same as that of porphyrin without graphene. Additionally, CuTHPP contains a large amount of hydrophilic OH groups, which result in slight adsorption of water onto the film. However, this hydrophilic property is not inconsistent with the hypothesis mentioned above. Although the OH groups of porphyrin make the film hydrophilic, the hydrophobic character of graphene remains unchanged. We hypothesized that the hydrophobicity of graphene and hydrophilicity of porphyrin could be used to achieve individual adsorption (water or CO₂) onto different components of the graphene-porphyrin composite, consequently resulting in separated reactions via different mechanisms.

The prepared photocatalyst was tested in an enclosed quartz chamber with a Xenon lamp as the light source using a highpass filter with a 'cut-on' wavelength of 400 nm to remove the UV component. Reaction products were analyzed using a gas chromatograph equipped with a flame ionization (FI) detector for the detection of hydrocarbons and a thermal conductivity (TC) detector for the detection of hydrogen. Each interval data is an average result obtained from the detection measurements conducted thrice. Gas sample analysis of the reaction products revealed that ethylene was predominant, whereas methane was found in relatively lower concentrations. Fig. 3 shows the yield and rate of hydrocarbons generation on this composite photocatalyst. The production rates of ethylene $(\sim 23.17 \,\mu\text{mol g}^{-1} \,\text{h}^{-1})$ and methane $(\sim 14.94 \,\mu\text{mol g}^{-1} \,\text{h}^{-1})$ were obtained from the CuTHPP/graphene (CuTHPP/G) sample. In the most recent studies, nanoparticles have been primarily employed as photocatalysts.^[12,13,15,19,20,22] Compared with our composite systems, porphyrin molecules were used as the antenna; its high absorbance enhanced the conversion of CO₂ to a certain extent. The lifetime of photogenerated carriers can be greatly increased by the low-defect graphene present in this photocatalyst, thereby providing a large surface for capturing abundant CO₂ molecules. Consequently, this photocatalyst presented excellent hydrocarbon generation owing to the synergistic effect of the two components. Regarding the overall yield of hydrocarbon, our photocatalyst exhibited comparative performance to noble metal co-loaded nanocatalysts (<25 $\mu mol~g^{-1}~h^{-1}).^{[15]}$ The absence of H_2 signals indicated that the amount of H₂ evolved in this work was not significant or non-existent. This result can be attributed to the hydrophopic property of graphene, which hindered reduction of H₂O. Signals associated with some other potential products with larger molecular weights, such as HCO₂H, CH₂O, and CH₃OH, may be neglected as they are probably difficult to form.

To confirm that the hydrocarbons were generated through catalytic reaction rather than through organic decomposition of the photocatalysts themselves, control experiments were performed. The dark control experiment was conducted by heating the catalysts at 50°C in the presence of CO₂, and hydrocarbons were not detected after 8 h of reaction. The photocatalyst films were also irradiated under an N₂ atmosphere in the chamber for 8 h, and no hydrocarbons was detected either (as shown in Fig. 3a). Similarly, as shown in the Fig. 3a, another control experiment was carried out in H₂O and O₂ atmosphere. In this case, no CH₄ or C₂H₄ was detected, thereby confirming that the



Fig. 4. Proposed mechanism of the photo-reduction of CO₂ to C₂H₄ on graphene.

products were generated by the photocatalytic process. With the aim of investigating the role of graphene in this photocatalytic process, a control experiment was conducted involving CuTHPP and no graphene (Fig. 3a). In this control experiment, only CH₄ was detected in trace amounts; C_2H_4 was not detected. This result suggests that the generation of C_2H_4 was determined by graphene in this composite system that can be likely ascribed to the outstanding ability of graphene as an excellent electron transfer mediator and adsorber for CO₂. Furthermore, the process was successively repeated for five times, and no obvious decay in activity could be observed (Fig. 3c) that demonstrates that the photocatalysts are stable.

The potential mechanism of the photocatalytic conversion of CO_2 into C_2H_4 over graphene can be deduced as illustrated in Fig. 4. According to the mechanism of catalytic reduction of CO_2 on Cu surface, ^[32–34] the key step in the conversion of CO_2 into bi-carbon compounds is the self-coupling of CH_2O^{\bullet} radicals, HCO_2^{\bullet} radicals, CHO^{\bullet} radical, CO_2^{-} radical, or intercoupling of other radicals. As assumed by Wu et al., ^[8] in the reaction process, all the intermediates have a delocalized

electronic structure, which can be attached to the graphene through $\pi-\pi$ non-covalent bond and receive electrons continuously. Under this circumstance, the potential of the transition states can be greatly decreased, as well as the stability of the intermediates.

Conclusion

In summary, due to the synergistic effect of porphyrin and graphene, the as-prepared photocatalyst presented a high CO_2 conversion rate and reaction selectivity of H_2O and CO_2 molecules. In particular, C_2H_4 was produced in a remarkable amount under visible light. Because the present porphyrin–graphene composite as photocatalyst for converting CO_2 into multicarbon compounds is a novel system, experimental trials involving different porphyrins would benefit the enrichment of the current developed system. Changing the central metallic ion and grafting branch is expected to enhance the catalytic activity and selectivity. Converting single-carbon inorganic compounds into multi-carbon compounds via photocatalysis if of significant

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