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Graphical Abstract

A Carbon-Based Photocatalyst Efficiently Converting CO_2 to CH_4 and C_2H_2 in Visible Light

Tongshun Wu,[a] Luyi Zou,[b] Dongxue Han,[*a] Fenghua Li,[a] Qixian Zhang,[a] and Li Niu[a]
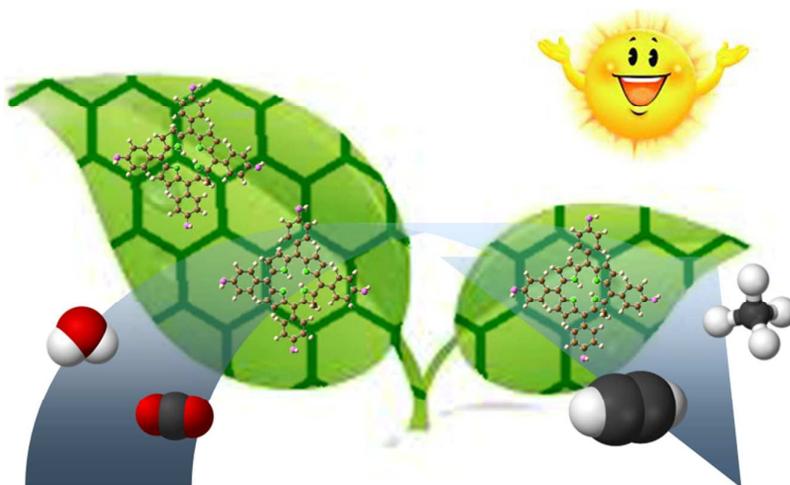
Photocatalysts consisting of porphyrin and graphene have been designed and applied to reduce CO_2 into C_2H_2 in visible light, which is an excellent simulator of natural photosynthesis.

ARTICLE TYPE

A Carbon-Based Photocatalyst Efficiently Converting CO_2 to CH_4 and C_2H_2 in Visible Light

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Novel photocatalysts consisting of porphyrin and graphene have been designed to reduce CO_2 into hydrocarbons in visible light. These catalysts can i) effectively reduce CO_2 to hydrocarbons, particularly to C_2H_2; and ii) selectviely control
10 **the photogenerated electrons transfer from graphene to CO_2 rather than H_2O.**

Introduction

In the past several decades it has performed a significant rise in atmospheric carbon dioxide levels resulting from the combustion
15 of hydrocarbon fuels. In addition, the shortage of hydrocarbon fuels makes it an inevitable problem which has to be faced in the near future. A solar energy-based technology to recycle carbon dioxide into a readily transportable hydrocarbon fuel would help to reduce atmospheric CO_2 levels and partly fulfill energy
20 demands within the present hydrocarbon-based fuel infrastructure.[1] Meanwhile, many efforts have been devoted to convert single-carbon carbohydrates into multi-carbon compounds under mild conditions.[2-5] As a result, through suitable conversion, single-carbon carbohydrates might be used as a
25 substitute for the dwindling petroleum resources as chemical feedstock. Likewise, among various strategies it is a compelling approach using photoenergy to drive the conversion of methane and other single-carbon compounds into more valuable molecules at room temperature.[6, 7]
30 Researches on CO_2 photoreduction has progressed quickly in recent years, and various photocatalysts have been developed. For instance, for organic compounds and transition metal coordination compounds,[8-10] semiconductors,[11-14] metal-organic frameworks,[15] perovskite structure compounds,[16] and hybrid
35 photocatalysts,[17, 18] many trials have been carried out for higher conversion rates and selectivity. However, the photo-reduced products were mostly CH_4, CO, CH_3OH, and some other single-carbon molecules. Till now, reports on derictly converting CO_2 to multi-carbon compounds by photocatalysis are still very few.
40 Even though in some literatures, multi-carbon compounds were detected in the products, the results were only reported as by-products[19-21] but not research target, which have not been carefully investigated yet.
Herein, we described a novel photocatalytic system based on
45 porphyrin and graphene composited, which not only demonstrated a higher conversion rate of CH_4, but also converted CO_2 to acetylene just under visible light irradiation. Due to the

growing energy shortage in the future, this method will become a new, simple and promising path to fabricate multi-carbon
50 chemicals from CO_2. To the best of our knowledge, this is the first time that graphene is usd to facilitate conversion from CO_2 to C_2H_2, and the role of grephene in this system has been also investigated.
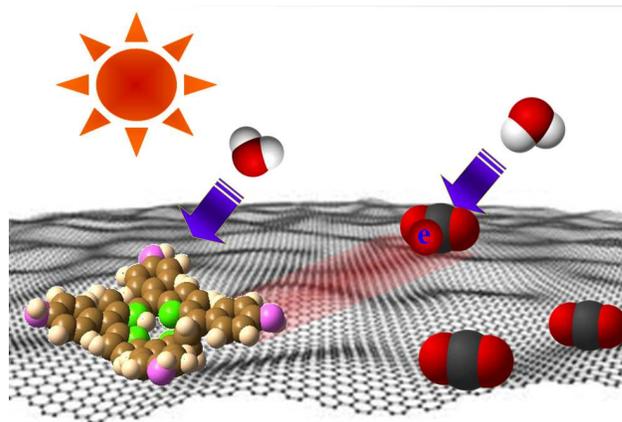
55 **Scheme 1** Proposed transfer process of photo-generated electrons for porphyrin graphene composite. Upon illumination, the photoexcited electrons are injected into graphene from the porphyrin molecules, and then transferred to the adsorbed CO_2. Due to the hydrophobicity of graphene, H_2O molecules are hard to obtain electrons from graphene.

60 ## Results and disscusion

As shown in Scheme 1, cobalt tetrahydroxyphenyl porphyrin (CoTHPP) and meso-tetrahydroxyphenyl porphyrin (THPP) were chosen as the light exciter rather than inorganic materials, because of their preferable ability to absorb light
65 than inorganic materials. Without the effect of surface state and impurity energy levels when compared to inorganic catalyst materials, organic molecules have relatively simple light absorption suitable for study. With absence of surface dangling bonds, which are abundant on the surface of
70 inorganic materials, the interaction between porphyrin and reactants is simpler. Furthermore, these two kinds of porphyrin were chosen due to their excellent photostability.
Considering the high electrical conductivity and tunable band gap properties[22-24], graphene was introduced into this
75 photocatalyst system as a charge transfer mediator. Not only is graphene an excellent electrical material, but also an

outstanding CO_2 absorber, whose theoretical maximum uptake of CO_2 is 37.93 wt%.[25] During the photocatalytic process, the excitons would transfer from the light absorber to CO_2 molecules with an easy passing through graphene component,
5 which will greatly enhance the conversion rate effectively. Moreover, as a hydrophobic material, graphene will not transfer photo-generated charges to H_2O molecule, which thus makes the catalytic reaction occurring on the graphene surface more controllable.

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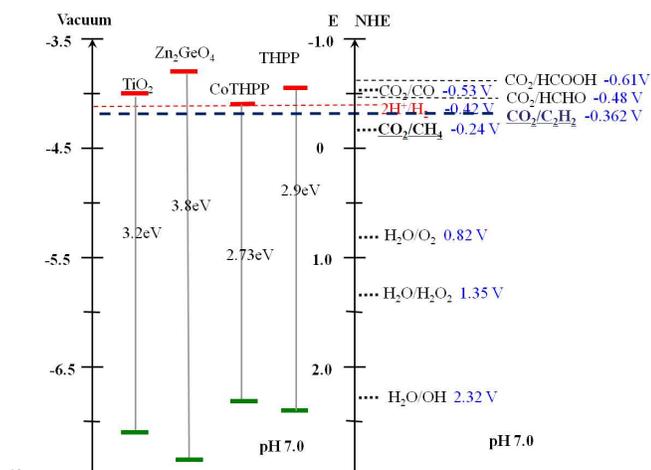
Fig 1 Conduction band and valence band potentials of CoTHPP and THPP (at pH=7.0) in contact with the redox potential for H_2O and CO_2 reactions at pH=7.0 respect to NHE (Normal Hydrogen Electrode) or vacuum. The redox potential of CO_2/C_2H_2 is obtained by calculation
15 through the Gibbs free energy of the electrode reaction with the Nernst equation. And the others are obtained from literatures.

The preparations of these two photocatalysts are described in the Supporting Information (SI). Morphologies of the as-prepared thin film photocatalysts were examined by SEM and
20 shown in Figure S1. Through UV-vis measurements, the energy gaps of CoTHPP and THPP were approximately confirmed (CoTHPP 2.73 eV; THPP 2.90 eV), which were shown in Figure S2 (a) and (b). To estimate the conduction band potentials (E_{CB}), Mott-Schottky plots under pH=7.0
25 conditions for CoTHPP and THPP were constructed, as shown in Figure S2 (c) and (d). It was found that the slopes of the plots were positive, suggesting that CoTHPP and THPP were n-type semiconductors. Under illumination the electrons are transferred from porphyrin molecules to graphene while holes
30 remain in the porphyrin, as shown in Scheme 1. The E_{CB} of CoTHPP is approximately -0.62 V vs. Ag|AgCl (-0.42 V vs. NHE), and the E_{CB} of THPP is approximately -0.75 V vs. Ag|AgCl (-0.55 V vs. NHE). In Figure 1, the relationship of the energy bands of the two porphyrins between the energy
35 levels of redox couples can be clearly seen. Theoretically, both CoTHPP and THPP can reduce CO_2 to a carbohydrate and oxidize H_2O to O_2 (as shown in Figure 1), which suggested that these photocatalysts were capable to transform CO_2 to a hydrocarbon molecule.
40 In these composite photocatalysts, the components of graphene are desired to have fewer defects and higher conductivity because it will benefit the photo-generated electrons in transfer from the exciter and diffusion on the

sheets. The conventional methods for preparing reduced
45 graphite oxide (RGO) are not sufficiently effective. Large numbers of defects in the RGO will greatly hinder the transfer of electrons, and the defects will also introduce some trap level in the band gap of graphene. This is disadvantageous to electron diffusion and will cause a difficulty in transferring
50 electrons from graphene sheets (GS) to the adsorbed molecule for reaction.[18]

A series of characterizations were performed to study the quality of the graphehe sheets, shown in Figure 2. SEM measurements were performed to ascertain the exfoliation
55 state of the material (Figure 2a). The SEM image clearly shows that the thickness of the flakes decreased significantly compared to graphite. This indicted that graphene was prepared successfully by this exfoliation method. Transmission electron microscopy (TEM) and electron
60 diffraction (ED) were used to reveal the number of layers in the GS. High-resolution TEM images (Figure 2 c) show that the GS were few-layered in structure, which was further confirmed by ED analysis. As shown in Figure 2b, the diffraction spots from the (1-210) planes were stronger than
65 those from the (0-110) planes. The intensity ratio I(0-110)/I(1-210) was approximately 0.5, suggesting a bi-layer structured graphene.[26,27] More TEM and SEM images are included in the supporting information (Figure S3). The chemical compositions of the as-prepared graphene were examined by
70 X-ray photoelectron spectroscopy (XPS), as shown in Figure 2d. The carbon/oxygen ratio of the sample is 3.1 %. The exfoliation process introduced only small amounts of oxygen, resulting in the sheets being cut small in the exfoliation. Even so, the as-prepared graphene had few defects compared with
75 RGO. The C 1s XPS spectra further support this, only a single peak around 284.5 eV is observed, which is associated with graphitic carbon. Therefore, this is proved to be an effect approach for preparation of graphene through directly exfoliates graphite to graphene sheets without an oxidization
80 process.
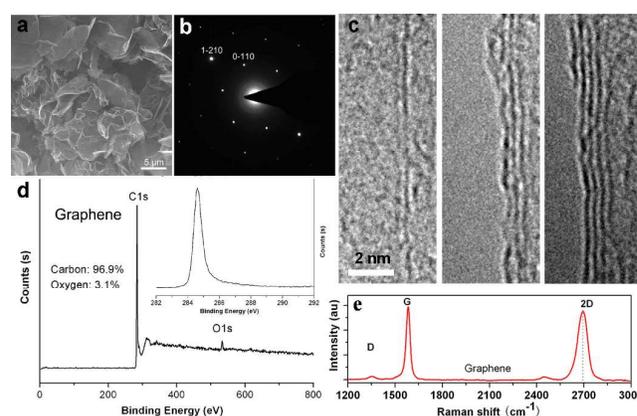
Fig. 2 SEM image of freeze-dried GS (a); HRTEM images of GS with different numbers of layers (c); corresponding ED (b); XPS spectra of GS (d) confirming the admeasurement of oxygen and carbon atoms and
85 corresponding narrow XPS scan of C 1s (insert); and Raman spectra (514.5 nm laser excitation) of graphene on a SiO_2 substrate (e).

The sample was further measured by Raman and the spectra are shown in Figure 2e. The G band (~1580 cm^{-1}) and 2D

band ($\sim$2700 cm^{-1}) were clearly visible in the graphene samples, and a weak signal for the D peak ($\sim$1350 cm^{-1}) was observed which is attributed to edge effects.[28] It is found that the graphite powder used as the raw material in this study also exhibited a weak D peak in its Raman spectrum (data not shown here). Thus, it is speculated that the defects observed in the final products might be originated from the starting graphite material. In addition, the signal intensities of the D peaks show an obvious difference from the RGO reported in the literature, which demonstrated that the process does not introduce a significant amount of additional structural defects, such as epoxides covalently bound to the basal plane.[29] In the Raman spectra of graphene, the 2D peak can be used to ascertain the number of sheets layers.[28] As shown in Figure 2 e, the 2D band of the as-prepared graphene had clearly shifted to lower energy. On the basis of the peak profile and position, it can be concluded that the graphite has been successfully exfoliated to few-layer graphenes (FLG) with a thicknesses of less than 5 layers.[28]
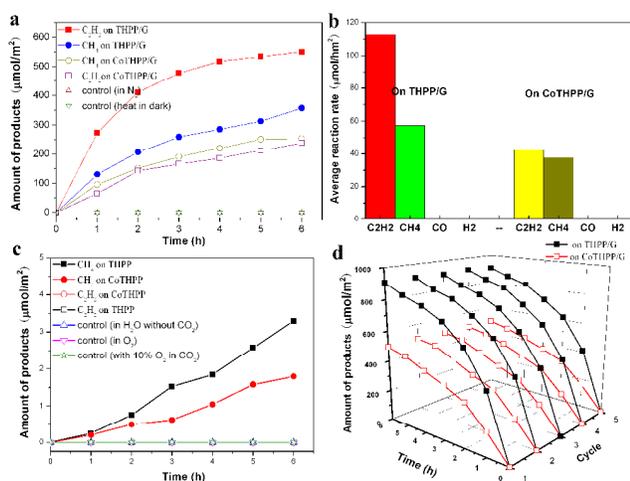
Fig. 3 Plots of hydrocarbon generation vs. time for porphyrin/G catalyst by gas-solid phase reduction method (a); and corresponding hydrocarbon generation rate (b); control experiments on THPP and CoTHPP, and control experiments of our as-prepared catalyst in O_2 or in H_2O (c); measurements of the activity stability (d).
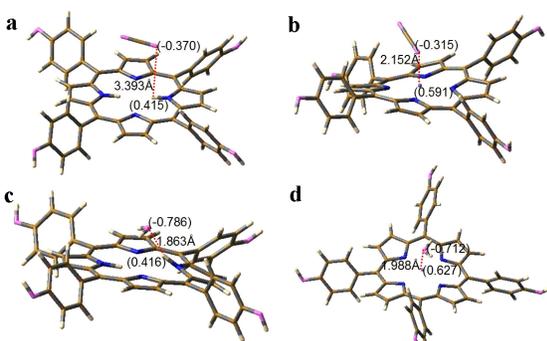
Fig. 4 The charge distribution and distance between the positive charges and molecules: (a) THPP$^+$ with CO_2, (c) THPP$^+$ with H_2O, (b) CoTHPP$^+$ with CO_2, and (d) CoTHPP$^+$ with H_2O.

These as-prepared photocatalysts were tested in an enclosed quartz chamber with a Xenon lamp as the light source using a high-pass filter with a "cut on" wavelength of 400 nm to remove the UV component, and the experimental details can be found in the SI. Reaction products were analyzed using a gas chromatograph equipped with flame ionization (FI) and thermal conductivity (TC) detectors. The FI detector enabled detection of most hydrocarbons, and the TC detector was used for the amounts of carbon oxides or hydrogen (if any). Each interval detection is repeated 6 times to get an average value. Gas sample analysis of the reaction products predominately showed acetylene, while methane was also found in relatively low concentrations. Figure 3 shows the yield and rate of hydrocarbons generation on these composite photocatalysts. Production rates of acetylene ($\sim$112.89 µmol/m^{2}h) and methane ($\sim$57.38 µmol/m^{2}h) were obtained from the THPP/G sample, and the total hydrocarbon generation rate was about 170.27 µmol/m^{2}h. Comparing with literatures, most previous works have been performed using nanoparticles primarily under UV illumination.[11, 12, 14-16, 18] In our composite systems, the porphyrin molecules accomplished visible-light irradiation, and high absorbance of porphyrin enhanced the conversion of CO_2 to a certain extent. Low defected graphene in these photocatalysts can greatly increase the life of photo-generated carriers, and provid a large surface which can capture abundant CO_2 molecules. Since a synergistic effect of the two components exists, this kind of photocatalyst presented excellent hydrocarbon generation. Concerning on methane production, our photocatalysts had a comparative achievement with the Ru and noble metal co-loaded nano-catalyst.[14] H_2 could not be detected indicating that the amount evolved in this work was not significant or not produced at all. The hydrophopic property of graphene also hinders reduction of H_2O. CO was not detected in the photocatalytic systems due to the energy levels of porphyrin (as shown in figure 1). Signals of some other potential products with larger molecular weights, such as HCO_2H, CH_2O, and CH_3OH, may be neglected as they are probably hardly to be formed.

Control experiments were performed to confirm that the hydrocarbons were generated through catalytic reaction rather than through organic decomposition of the photocatalysts themselves. The dark control experiments by heating the catalysts at 50 ˚C were also done in the presence of CO_2, and after 8 hours hydrocarbons were not detected. The photocatalyst films were irradiated in an enclosed chamber under an N_2 atmosphere for 8 hours, and no hydrocarbons were detected either (as shown in Figure 3a). Similarly, as shown in the Figure 3c, the control experiments were carried out in H_2O and O_2 atmosphere, respectively. In these circumstances, no CH_4 and C_2H_2 can be detected, which suggested that the products were definitively generated by the photocatalytic process. It is noticeable that this photocatalytic reaction do not occur when 10V-V% O_2 is added into the photoreduction system (shown in Figure 3c). According to the delocalized electronic structure, O_2 is able to be adsorbed on the GS same as CO_2, and then be reduced to $O_2^{-\cdot}$, which can oxidize the reducing products of CO_2. Therefore, O_2 will hinder the photocatalytic conversion of CO_2, which is the main reason for the reaction rate declining. Moreover, the measurements of the activity stability demonstate that the photocatalysts are stable as well, after five cycles of detection,

for no obvious decay of activity can be observed. In order to investigate the role of graphene in this catalytic process, a control experiment without graphene was evaluated on THPP (Figure 3c). In this experiment, only very small amounts of CH_4 were detected and with trace amounts of H_2, while C_2H_2 was not detected , it can be deduced that graphene dominate the generation of C_2H_2 in this composite system, which should be probably ascribed to the outstanding ability of graphene as excellent electron transfer mediator and adsorber for CO_2. The potential mechanistic steps in photo-reduction of CO_2 to C_2H_2 on graphene can be seen in the Figure S4. The first steps of the mechanism may be similar as those reported by Amatore et al., where oxalate can be formed through self-coupling of $CO_2^{-\cdot}$ anion radicals, or via CO_2 coupling with the $CO_2^{-\cdot}$ anion radical.[30] In the steps shown in Figure S4, all the intermediates are in delocalized electronic structure, and can be attached on graphene through π-π non-covalent bond and receive electrons uninterruptedly. Moreover, in this case, the potential of the transition states can be greatly decreased, and the stability of the intermediates.

The photocatalytic process was further studied through theoretical simulations, and the computational details of which are shown in the SI. Unlike the nano-material catalysts, which have many defects on the surface due to the imperfections of the surface lattice, the interaction of porphyrin particles with the molecules in the catalytic system is no longer complicated. As shown in the electronic density contours of the HOMO and LUMO orbitals (in Figure S5), electronic density is higher at the central ring of the porphyrin molecule, and increases further after excitation. This central ring is the active center for electrons transfer in catalytic process. As shown in Figure 4, the optimal geometric structure can intuitively explain that the center of the porphyrin molecule is most active. Then, it is necessary to know which molecule will act on this center more easily in this photocatalytic system, CO_2 or H_2O. Therefore, a transition state model, an electropositive porphyrin molecule, has been designed, which generated transfer of the electrons to graphene sheets after exciting an n-type porphyrin molecule. The electropositive porphyrin molecules are named $THPP^+$ and $CoTHPP^+$. Through calculation of the total binding energies, it was found that the values of $THPP^+$ with CO_2 and H_2O were 1.79 kcal/mol and 5.25 kcal/mol, respectively. This result suggested that the H_2O bound with $THPP^+$ more easily than CO_2. That is, the major reaction occurring on THPP is oxidization of H_2O to OH radicals and further to O_2, rather than CO_3^{2-} to $CO_3^{-\cdot}$.[13] Moreover, the distance between $THPP^+$ and H_2O was 1.863 Å, which was much shorter than $THPP^+$ to CO_2 (3.393 Å), demonstrating that $THPP^+$ bound with H_2O directly (as shown in Figure 4). The reaction occurred as designed: the redox processes were separated, H_2O was oxidized on porphyrin, and CO_2 was reduced on graphene. Just like $THPP^+$, $CoTHPP^+$ presented similar properties, wherein the total binding energies were 5.45 kcal/mol (with CO_2) and 25.44 kcal/mol (with H_2O), and the bond distances were 1.988 Å (to H_2O) and 2.152 Å (to CO_2) respectively. Therefore, the major oxidation occurring on CoTHPP was H_2O to O_2 as mentioned above. As shown in Figure 3, the CoTHPP/G showed lower conversion rates compared to THPP/G, although the total binding energies to H_2O of CoTHPP were higher than THPP to H_2O. This may be caused by the central ring of CoTHPP which is not a planar structure (as shown in Figure 4). In such status, the large π structure will be broken, and it is further adverse for transfer of electrons to graphene for reducing CO_2.

Conclusions

In summary, the combination of porphyrin and graphene made the photocatalysis occuring on each component more simply, it also allowed greater ease of investigation, and further enhancment in selectivity. Moreover, due to the synergistic effect of these two materials, the presented photocatalysts demonstrated a high CO_2 conversion rate. In particular, C_2H_2 was produced in a remarkable amount in visible light. It is of great significance for converting single-carbon source to multi-carbon compounds via photocatalysis. The research on which were still very few till now,[1—20] although the mechanism needs to be further investigated. This work will introduce a new thread to convert CO_2 to chemicals, and new materials to effectively store solar energy into chemical energy. It will be an improvement on artificial photosynthesis, and provide a potential way of solving the carbon emission and energy shortage simultaneously.

Acknowledgements

Notes and references

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† Electronic Supplementary Information (ESI) available: details of preparation and measurement, more TEM and SEM images of graphene and photocatalyst. See DOI: 10.1039/b000000x/

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