



Highly efficient visible-light driven photocatalytic reduction of CO₂ over g-C₃N₄ nanosheets/tetra(4-carboxyphenyl)porphyrin iron(III) chloride heterogeneous catalysts

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ABSTRACT

Photocatalytic reduction of CO₂ into value-added chemicals is particularly attractive as it could produce renewable energy and capture greenhouse gas. Photoreduction of CO₂ can be realized over molecular and inorganic catalysts. The former usually exhibit high activity, but low stability and often inactive under visible-light irradiation; the latter has low activity, but good stability. Here we use g-C₃N₄ nanosheets as the photosensitizer to integrate with Fe tetra(4-carboxylphenyl)porphyrin chloride (FeTCPP) molecular catalyst. Besides π - π stacking between tri-*s*-triazine unit and porphyrin, the carboxyl group modified Fe porphyrin is used for the first time in CO₂ photoreduction so as to form hydrogen bonding with the rich amino groups in g-C₃N₄ nanosheets. g-C₃N₄/FeTCPP heterogeneous catalysts are prepared via a facile self-assembly approach, in which light harvest is separated from catalysis spatially and temporally. The obtained g-C₃N₄/FeTCPP heterogeneous catalysts exhibit high activity for CO₂ reduction under visible-light irradiation, with CO yield of 6.52 mmol g⁻¹ in 6 h and selectivity up to 98%. Fluorescence data indicate that the electrons can efficiently transfer from the g-C₃N₄ nanosheets to FeTCPP. The mechanism for CO₂ reduction over the g-C₃N₄/FeTCPP heterogeneous catalysts is proposed based on the results of quasi in-situ ESR and UV-vis measurements. This work may pave a facile approach for fabricating the high-efficient photocatalysts for CO₂ reduction, as well as better understanding the related mechanism.

1. Introduction

Converting CO₂ into value-added chemicals can mitigate carbon emission and provide alternative energy source [1–3]. Among different approaches, photocatalytic reduction of CO₂ has attracted much interest since late 1970's [4–8]. However, CO₂ reduction is a highly energy demanding process, as formation of CO₂^{·-} via one-electron reduction occurs at a very negative potential ($E_0 = -1.90$ V vs. normal hydrogen electrode (NHE) in solution). The CO₂ reduction can take place via multi-proton-coupled multi-electron reduction reactions, resulting in the formation of many products like CH₄, CH₃OH and CO. The standard redox potential is relatively low for the production of the final products, while with a high overpotential. So the utilization of a catalyst is crucial to initialize and boost the CO₂ photoreduction [9,10].

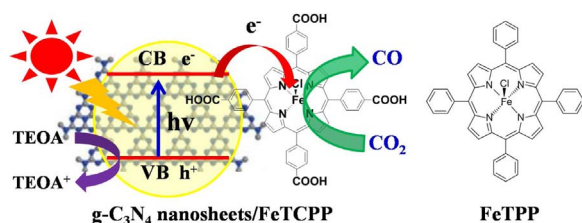
Metal-based molecular complexes have been employed as

homogeneous photocatalysts for CO₂ reduction. Most of them are based on the noble rhenium or ruthenium [11–13], and only few are earth abundant and environmentally benign metals [14,15]. Among them, iron porphyrins play a vital role in catalysis, especially in natural photosynthesis. Robert et al. have used iron porphyrins modified by phenolic group as electro- and/or photo-catalysts to reduce CO₂ to CO with a selectivity > 90% in the homogenous systems [16–20]. It is noted that the molecular catalysts like iron porphyrins suffer from the photodegradation under long-term UV irradiation and most of them are inactive for CO₂ reduction under visible light in case without a photosensitizer [17–19]. Thus, it still remains a big challenge to achieve CO₂ reduction with high efficiency and selectivity over iron porphyrin-based photocatalysts.

One approach to address the aforementioned problems is to incorporate an organic photosensitizer with the iron porphyrin for CO₂

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Scheme 1. Structure of $g\text{-C}_3\text{N}_4/\text{FeTCPP}$ heterogeneous catalyst system and FeTPP.

reduction under visible-light irradiation [17]. Considering inorganic materials usually show superior stability to the organic counterparts and exhibit fairly strong light absorption, inorganic nanomaterials can be used as the light absorber to incorporate with the molecular catalysts [21–24]. In this case, the hybrid systems have the strengths of not only high efficiency and selectivity from the molecular catalysts, but also high stability, easy recycling and visible-light activity from the inorganic nanomaterials. More important, the light harvest is separated from catalysis spatially and temporally, resulting in efficient separation and transfer of charge carriers. Graphite carbon nitride ($g\text{-C}_3\text{N}_4$) has been studied for various applications by virtue of visible-light absorption, rich marginal amino groups, high stability and earth-abundant nature [25–35], which has also been used as the photosensitizer to incorporate with metal based molecular catalysts [36,37].

Here we have synthesized a carboxyl group modified iron porphyrin catalyst, tetra(4-carboxyphenyl)porphyrin iron(III) chloride (FeTCPP), and fabricated a highly efficient $g\text{-C}_3\text{N}_4$ nanosheets/FeTCPP ($g\text{-C}_3\text{N}_4/\text{FeTCPP}$) heterogeneous catalyst for photoreduction of CO_2 to CO under visible light (Scheme 1). The $g\text{-C}_3\text{N}_4/\text{FeTCPP}$ heterogeneous catalyst was fabricated by integrating FeTCPP with $g\text{-C}_3\text{N}_4$ nanosheets via a simple self-assembly approach, in which the cost effective $g\text{-C}_3\text{N}_4$ nanosheets act as the light-harvesting unit and environment-friendly iron-based FeTCPP works as the catalytic center. Two molecular catalysts with and without the carboxyl groups, i.e., the FeTCPP and Fe meso-tetraphenylporphyrin chloride (FeTPP) have been used to study the influence of carboxyl groups. Fairly strong interaction can exist between the $g\text{-C}_3\text{N}_4$ nanosheets and FeTCPP via both hydrogen bonding and $\pi\text{-}\pi$ stacking through the marginal amino groups of $g\text{-C}_3\text{N}_4$ nanosheets with the carboxyl groups on FeTCPP and tri-s-triazine units with porphyrins, respectively, which can facilitate the charge transfer between them. More important, the CO_2 reduction mechanism using $g\text{-C}_3\text{N}_4/\text{FeTCPP}$ heterogeneous catalysts is proposed based on the results of quasi in-situ electron spin resonance (ESR) and ultraviolet–visible spectroscopy (UV-vis) measurements. This is the first report that carboxyl-group modified iron porphyrin is employed as the photocatalyst for CO_2 reduction.

2. Experimental

2.1. Chemicals

All of the chemicals and solvents used were analytical grade or chromatographic grade. Dicyandiamide, N,N -dimethylformamide (DMF) and tetraethylammonium tetrafluoroborate (Et_4NBF_4) were obtained from Sigma-Aldrich. N,N -dimethylacetamide (DMA), triethanolamine (TEOA) and acetonitrile (MeCN) were purchased from Shanghai Aladdin Bio-chem Technology. Carbon dioxide gas (super grade purity 99.999%) was bought from Beijing Beiwen Gases Company. FeTPP was purchased from Alfa. Ultrapure water (Millipore Milli-Q grade with a resistivity of 18.2 $\text{M}\Omega\text{ cm}$) was used in all the experiments.

2.2. Synthesis of FeTCPP

Metal-free tetra(4-carboxyphenyl)porphyrin (TCPP) was used as received and the corresponding FeTCPP was synthesized according to previous report [38]. Briefly, FeTCPP was synthesized by refluxing

0.33 mmol of TCPP with 1.82 mmol of FeCl_3 in DMF solvent under Ar for 2 h and was monitored by thin layer chromatography analysis. Then, after cooling to room temperature, DMF was removed by distillation and FeTCPP was precipitated by adding excess water. The solid sample was obtained by being dried under vacuum and characterized by high resolution mass spectra (Fig. S1, HR ESI⁺). $[\text{M-Cl}]^+$ ($\text{C}_{48}\text{H}_{28}\text{FeN}_4\text{O}_8$) Calculated: 844.1257; Observed: 844.1258.

2.3. Preparation of $g\text{-C}_3\text{N}_4$ nanosheets and $g\text{-C}_3\text{N}_4/\text{FeTCPP}$ heterogeneous catalysts

Bulk $g\text{-C}_3\text{N}_4$ was prepared by typical thermal polymerization of dicyandiamide, simply heated 5 g dicyandiamide to 550 °C in muffle furnace with a ramp rate of 2.3 °C min^{-1} , and kept at this temperature for 4 h in ambient atmosphere. The $g\text{-C}_3\text{N}_4$ nanosheets were prepared by direct thermal oxidation etching of bulk $g\text{-C}_3\text{N}_4$ at 500 °C for 2 h as reported previously [39]. The $g\text{-C}_3\text{N}_4/\text{FeTCPP}$ heterogeneous catalysts were prepared by integrating FeTCPP with $g\text{-C}_3\text{N}_4$ nanosheets via a simple self-assembly approach via mechanical mix under stirring.

2.4. Characterization

The morphology of $g\text{-C}_3\text{N}_4$ was observed with a Hitachi SU8200 scanning electron microscope (SEM). Transmission electron microscopy (TEM) was operated on a FEI Tecnai G2 T20 electron microscope. Powder X-ray diffraction (XRD) was measured on a Bruker D8 diffract meter with Cu $K\alpha$ radiation ($\lambda = 0.15406\text{ nm}$). Nitrogen adsorption–desorption isotherm curves were analyzed on a Micromeritics TriStarII 3020. UV–vis diffuse reflectance spectroscopy (DRS) and UV–vis absorption spectra were recorded on a Lambda 750 UV/Vis/NIR spectrophotometer (Perkin-Elmer, USA). The quasi in-situ UV–vis absorption spectra were measured in a well-sealed quartz cell under visible-light irradiation (Xenon lamp, $420\text{ nm} < \lambda < 780\text{ nm}$, 220 mW cm^{-2}) with various time (0 min ~ 1 h), the solution (acetonitrile: water: TEOA, 3:1:1, v:v:v) were purged with Ar or CO_2 at least for 1 h before irradiation. Fourier transform-infrared spectra (FT-IR) were recorded on a Spectrum One Spectrometer (Perkin-Elmer, USA).

Photoluminescence (PL) and time-resolved PL decay spectra were collected on a NanoLOG-TCSPC spectrophotometer (Horiba Jobin Yvon, USA) by being excited at 390 nm. ESR measurements were carried out on a JEOL JES-FA-200 spectrometer (JEOL Ltd., Tokyo, Japan), the solution were prepared in DMA and TEOA mixed solution (volume, 4:1) under both Ar and CO_2 atmosphere in dark and with visible-light irradiation ($420\text{ nm} < \lambda < 780\text{ nm}$, 5 min), respectively. Cyclic voltammetry (CV) of the Fe porphyrin complexes was performed in DMF solution containing Et_4NBF_4 (0.1 mol L^{-1}) as the supporting electrolyte with the CHI 660D potentiostat in a standard three-electrode cell at room temperature under Ar or CO_2 atmosphere. Glassy carbon electrode, Pt plate and Ag/AgCl electrode were used as working, counter and reference electrode, respectively. The concentration of the Fe porphyrin catalyst was 1 mmol L^{-1} and the scan rate was 100 mV s^{-1} . Finally the redox potential values were converted to the values vs. normal hydrogen electrode (NHE).

2.5. Photocatalytic reduction of CO_2

The photocatalytic reduction of CO_2 was carried out in a photo-reaction system (Labsolar-IIIAG, Beijing Perfectlight Technology Co., Ltd.) saturated with 26 kPa CO_2 at 15 °C as reported previously [5,30]. The $g\text{-C}_3\text{N}_4/\text{FeTCPP}$ heterogeneous catalysts were prepared by mechanical mix of 50 mg $g\text{-C}_3\text{N}_4$ nanosheets and different amount (0.1, 0.25, 0.5, 1.0, and 2.0 mg) of FeTCPP in 100 mL solution of acetonitrile/water/TEOA (3:1:1, v:v:v) under stirring. The whole system was vacuumed and purged with Ar for three times to remove the air. The high purity CO_2 gas was bubbled into the quartz reactor for at least 90 min before illumination. The light source ($420\text{ nm} < \lambda < 780\text{ nm}$)

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