



Surprisingly advanced CO₂ photocatalytic conversion over thiourea derived g-C₃N₄ with water vapor while introducing 200–420 nm UV light



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ABSTRACT

200–420 nm UV light was for the first time introduced for CO₂ photocatalytic reduction over graphitic carbon nitride (g-C₃N₄). It was surprisingly found that thiourea derived g-C₃N₄ (TCN), which showed inferior activity in CO₂ reduction under visible light irradiation, exhibited more remarkable CO₂ conversion efficiency under >200 nm light irradiation compared to g-C₃N₄ synthesized from urea (UCN) and commercial TiO₂ (P25). Also, the highest selectivity to CO₂ conversion was observed over TCN while P25 showed the most prominent H₂ production followed by UCN. Through a series of characterizations, the more abundant –NH_x species that were responsible for CO₂ activation, the enhanced reducing ability of photo-excited electrons under UV light and the higher photo-excited electron-hole separation efficiency were supposed to contribute to the excellent CO₂ photocatalytic reduction activity of TCN under >200 nm UV–vis light irradiation, whilst its visible-light activity was relatively weak because of its limited surface area. Further, TCN performed a wonderful stability with a good record of circle tests in this irradiation condition.

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1. Introduction

The growing amount of carbon dioxide (CO₂) in the atmosphere has become a great concern worldwide [1,2]. Photocatalytic reduction of CO₂, which aims at converting CO₂ into energy fuels through utilization of extensive solar light, has recently received a growing amount of attention as a promising technique to reduce the atmospheric CO₂ amount and mitigate energy crisis at the same time [3]. Since Inoue et al. [4] discovered that semiconductors (TiO₂, GaP, ZnO, ZnS etc.) with appropriate band structures were able to photocatalytically reduce CO₂ into hydrocarbons such as HCOOH, CH₃OH and CO in water, a great number of semiconductor photocatalysts have been investigated for their application in CO₂ photocatalytic reduction [5,6]. However, most of the catalysts showed apparent shortcomings. For example, the confined light absorption of large-band-gap photocatalysts (TiO₂, ZnO etc.) [7–9], photo-corrosion of sulphides photocatalysts (CdSe,

BiS etc.) [10,11] and limited electron reducing ability of photocatalysts with a relatively low conduction band (Bi₂WO₆, WO₃ etc.) [12,13]. Besides, with the deposition of noble metals or combined structures, many of the photocatalysts turned out to be instable, environmentally-harmful and costly [11,14–16].

One of the recent materials in the spotlight, Graphitic carbon nitride (g-C₃N₄), is an environmental-benign metal-free polymeric compound with special semiconductor properties. It shows exceptional catalytic activity for a variety of chemical reactions [17,18]. This fascinating material can be easily obtained by polymerization of various organic precursors containing both carbon and nitrogen such as cyanamide [19], melamine [20] and other cheap feedstock such as urea [21], and thiourea [22]. Since the seminal application of g-C₃N₄ in photocatalysis was led by Wang et al. [19] for H₂ generation from water under visible light, this low-cost material with excellent thermal and chemical stability and an easily tuneable electronic structure has been regarded as a highly promising visible-light responsive photocatalyst [19,23]. For CO₂ photocatalytic conversion, besides its robustness, suitable band structure and cost-effectiveness, g-C₃N₄ showed advantages in possessing –NH_x residual which will

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facilitate CO₂ absorption and reduce the conversion energy [16,24–29]. Thus, the utilization of g-C₃N₄ for CO₂ reduction has received great attention recently [18]. Zhang et al. [24] firstly reported that g-C₃N₄ could photocatalytically convert CO₂ to CO in solid-gas system. Mao et al. [25] and Niu et al. [27] suggested the influence of the morphology especially layer thickness of g-C₃N₄ on the selectivity to different products during the multiple-electrons-and-protons CO₂ reducing process. More recently, many hybrid structures based on g-C₃N₄ such as SnO_{2-x}/g-C₃N₄ [30], Ag₃PO₄/g-C₃N₄ [15], g-C₃N₄/Bi₂WO₆ [14], B₂C/g-C₃N₄ [31] and NaNbO₃/g-C₃N₄^[16] have been synthesized and found to show enhanced activity for CO₂ reduction under visible light. All the studies implied the promising application of engineered g-C₃N₄ for the envisioned green conversion of CO₂.

Interestingly, as g-C₃N₄ is a visible-light responsive photocatalyst, the activity of g-C₃N₄ under UV light (200–400 nm) seemed to be overlooked [32]. In 2012, Sastre and his coworkers [33] suggested that 185 nm deep UV could be utilized to achieve photolysis of CO₂ in the presence of H₂O or H₂ and the activity and the selectivity to methane was further improved at the presence of basic solid. With the basic –NH_x groups on the surface of g-C₃N₄, studying the performance of its diverse members under UV light in CO₂ photocatalytic reduction could be of interest. But as far as we concerned, getting into UV light as strong as 185 nm is not suitable not only as it consumes a large amount of energy to get UV light with that short wavelength but also because such a strong light beam should have high requirement for the reaction unit and show considerable health risks. Thus in this research, we just considered the part of UV light (200–420 nm) that is available from the solar spectrum and investigate the CO₂ photocatalytic reduction performance of g-C₃N₄ prepared from two different common precursors with and without the UV light portion. The results turned out to be very interesting and detailed characterizations were carried out to elucidate the phenomenon observed. Commercial TiO₂ (P25) was also introduced to compare with g-C₃N₄ under the setting UV–vis light.

2. Experimental

2.1. Chemical

Urea and thiourea were purchased from Aladdin Industrial Corporation (Shanghai, China). HNO₃ was from Sinopharm Chemical Reagent Corporation (Shanghai, China). All of the chemicals were of analytical purity and used without any further purification.

2.2. Sample preparation

Urea and thiourea were used as precursors to obtain two different kinds of g-C₃N₄ and denoted as UCN and TCN, respectively. Typically, 20 g precursors in a 100 ml crucible with a cover was heated to 550 °C with a ramping rate of 20 °C/min and kept at this temperature for 2 h. After the reaction, the resulted powders were washed with 0.1 M HNO₃ and deionized water and dried at 60 °C overnight.

2.3. Characterization methods

The crystal phases of as-prepared catalysts were analyzed by X-ray powder diffraction (XRD) on an X-ray diffractometer (Model D/max RA, Japan) with Cu K α irradiation. FTIR spectra were recorded on an FTIR spectrometer (Bruker Alpha, Germany) equipped with a deuterated triglycine sulfate (DTGS) detector with sample discs prepared with dried KBr. Elemental analysis (EA) result was obtained with an Elementar Vario Micro Cube. X-

ray photoelectron spectroscopy (XPS: Thermo ESCALAB 250Xi, USA) measurements were performed with a monochromatized Al K α source (150 W, 500 μ m, $h\nu$ = 1486.6 eV) to investigate the surface chemical compositions and states. The carbonaceous C 1s line (284.8 eV) was used as the reference to calibrate the binding energies. The morphologies and microstructures of the as-prepared samples were investigated by transmission electron microscopy (TEM: FEI TECNAI G² F20 S-TWIN, USA). The Brunauer-Emmett-Teller (BET) specific surface area was calculated from a multipoint BET method and the pore distribution curves were determined with a BJH desorption method on a physisorption analyzer (Micromeritics ASAP 2020, USA). The UV–vis diffuse reflection spectra (UV–vis DRS) were obtained with a scan UV–vis spectrophotometer (TU-1901, China) equipped with an integrating sphere assembly and BaSO₄ was used as a reflectance standard. The photoluminescence spectra were measured with a fluorescence spectrophotometer (RAMANLOG 6, USA) using 256 nm lasers as excitation source.

Photocurrents under the irradiation of light with different wavelengths ranges were measured on an electrochemical system (CHI 660B, Shanghai, China) using a three-electrode photoelectrochemical cell. The electrolyte solution was 0.2 M Na₂SO₄. Platinum wire was used as the counter electrode and saturated calomel electrode (SCE) used as the reference electrode. The working electrode was prepared as follows: 20 mg of a powder sample was dispersed in 2 ml ethanol. After 30-min supersonic treatment, the suspension was dip-coated onto a piece of ITO glass electrode to make a film of 1 \times 1 cm². Then the electrode was exposed to UV-light for 30 min and subsequently annealed at 200 °C for 10 h.

2.4. Photocatalytic reduction of CO₂

Photocatalytic reduction of CO₂ was conducted using a continuous-flow system as described in our precious paper [34]. Typically, 40 mg catalyst was dispersed at the bottom of a stainless-steel-made reactor with a quartz window on the top. A 300 W Xe lamp (PLS-SXE300UV, Beijing Trust-tech Co. Ltd., China) was used as the light source to provide two ranges of wavelengths, namely, >420 nm visible light and >200 nm UV–vis light with the help of two light filters.

At the beginning of a typical experimental process, pure CO₂ gas was purged into the reactor through a water bubbler at 120 ml/min for 1 h in order to get rid of any impurity gases. Then the flow rate was adjusted to 3.0 ml/min and stabilized for another 1 h before the light was tuned on. During the reaction, the effluent gas was introduced to a gas chromatography (Agilent 7890A, USA) through auto-valves at a certain time interval to detect the instant concentration of H₂, CO, CH₄ and other hydrocarbons. Control experiments without any photocatalyst, using pure Ar instead of CO₂ and at dark were also conducted in the same system. CO₂ conversion was calculated by summing up the amount of C in the main C-contained products as shown in Eq. (1):

$$\text{Amount of CO}_2 \text{ conversion in 5 h} = n(\text{CO}) + n(\text{CH}_4) + 2 \times n(\text{CH}_3\text{CHO}) \quad (1)$$

in which, n stood for the 5-h yield of the corresponding product in the unite of $\mu\text{mol/g}_{\text{cata}}$.

The selectivity to CO₂ conversion under > 200 nm UV–vis light was simply deduced according to Eq. (2):

$$\text{Selectivity to CO}_2 \text{ conversion}(\%) = \frac{8 \times n(\text{CH}_4) + 2 \times n(\text{CO})}{8 \times n(\text{CH}_4) + 2 \times n(\text{CO}) + 2 \times n(\text{H}_2)} \times 100\% \quad (2)$$

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