



Photocatalytic conversion of gas phase carbon dioxide by graphitic carbon nitride decorated with cuprous oxide with various morphologies



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ABSTRACT

Submicron cuprous oxide (Cu₂O) crystals with various morphologies were successfully fabricated and incorporated with graphitic carbon nitride (gCN) to evaluate their activity for gas phase CO₂ photoreduction under visible-light illumination. Both the morphology of Cu₂O and the composition of copper species were tunable and were significantly affected by the presence of gCN. The morphology of Cu₂O influenced the band structure and optical property, as well as the efficiency of photo-induced charge transfer within each sample. The compositions of Cu₂O/gCN before and after illumination were compared to evaluate the photostability of samples. In addition to the majority of Cu₂O crystals, other copper species, CuO or metallic Cu, were presented and considered as the assistance for CO₂ adsorption or interfacial charge transfer. Improved conversion of CO₂ to CO was achieved by combining n-type gCN and p-type Cu₂O crystals with an optimum surface composition, and by selecting the Cu₂O crystals with higher photostability.

1. Introduction

Visible light-responsive graphitic carbon nitride (gCN) has attracted numerous attentions since the demonstration of its hydrogen production from water [1]. The unique electronic structure of gCN can be tuned by selecting various carbon- and nitrogen-rich precursors, such as melamine and urea, to achieve various nitrogen contents on gCN [2,3]. However, the low surface area and high carrier recombination rate reduced the photocatalytic activity of gCN [4]. Therefore, the morphology of gCN has been modified or various heterojunctions have been developed to increase surface area or to more effectively separate photoinduced charge carriers on gCN [2,3,5–13]. For example, gCN and TiO₂ composites obtained by Zhou et al. [6] showed better efficiency to photoreduce CO₂ than commercial TiO₂ (P25). In addition to TiO₂, cuprous oxide (Cu₂O) is a potential candidate for the heterojunction with gCN as it is a p-type semiconductor with a narrow band gap of about 2 eV [10,14–17]. Most importantly, the theoretical conduction band position of Cu₂O is more negative than the reduction potential of CO₂ [14,16], indicating the potential capability of Cu₂O to reduce CO₂.

Photoreduction of CO₂ has been considered a promising and beneficial strategy to convert greenhouse gas into valuable products by sunlight. Therefore, a lot of efforts have been focused on the design and modification of photocatalysts to enhance the photocatalytic performance of CO₂ [18–31]. A variety of products of CO₂ reduction were obtained depending on the reaction condition and reduction capability

of catalysts [16,21,23,25,32–34]. Our previous pioneer research discovered the presence of Cu₂O on TiO₂ was favorable to convert dissolved CO₂ into methanol in basic solution [18–20]. Recently, researchers also demonstrated the capability of Cu₂O for CO₂ photoreduction. Wang et al. observed enhanced yields of carbon monoxide and methane from CO₂ over visible-light excited hematite-Cu₂O composite with Z-scheme heterojunction [16]. Yu et al. described the formation of methane and ethylene from CO₂ via visible light-illuminated Cu₂O nanorods [14]. They also found that the coating of carbon layer on Cu₂O nanorods improved the yield of hydrocarbons from CO₂ photoreduction. Ovcharov et al. electrodeposited foam-like Cu₂O nanostructure on substrates to convert CO₂ into methane under visible light [35]. Handoko and Tang also suggested the morphology of Cu₂O was an important role in determining the selectivity of CO₂ photoreduction products [36]. According to the thermal dynamics principle, the formation of carbon monoxide is the easiest 2-electron reduction route from CO₂ [6,14,16,21,26] and CO is also an important feedstock for a series of chemical process [21]. However, the yield of CO may originate from the photodegradation of catalysts, such as graphene oxide (GO)-based materials, which contain carbon and oxygen functional groups. Therefore, the isotope tracing was conducted to confirm the formation of methanol from CO₂ reduction rather than the photodissociation of catalysts [13,37].

In this work, we synthesized Cu₂O particles with different morphologies and investigated their effects on photoactivity for CO₂

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photoreduction. As the bandgap of Cu₂O is relatively narrow, a conductive network attached to Cu₂O will enhance its electron-hole separation and increase the concentration of electron on the surface. Therefore, we fabricated gCN from the pyrolysis of melamine as the conductive carbon-based substrate, whose photodegradation was less favorable than GO. In addition, the presence of gCN was found to improve CO₂ adsorption through π - π conjugation or surface basic sites [38–40]. The chemical structures of obtained Cu₂O_gCN samples before and after LED illumination were comprehensively investigated. The influences of chemical structure and morphology of Cu₂O on the formation of free radicals, on the variation of band structure and thus the efficiency of CO₂ conversion was explored and correlated in this work.

2. Experimental

2.1. Materials

Melamine (99%), anhydrous copper(II) chloride (CuCl₂; 98%) and hydroxylamine hydrochloride (NH₂OH·HCl; 99%) were purchased from Alfa Aesar. Sodium hydroxide (NaOH; 97%) was acquired from Showa. Sodium dodecyl sulfate (SDS; \geq 99%) and 5,5-dimethyl-1-pyrroline N-oxide (DMPO, \geq 97%) were supplied from Sigma Aldrich. All chemicals were reagent grade without further purification. Distilled water (18.3 M Ω) was used for all aqueous solution preparation.

2.2. Synthesis of graphitic carbon nitride (gCN)

The precursor of melamine (5 g) decanted in a half-covered crucible was directly heated to 550 °C for 3 h under static air in a muffle oven. The pale-yellow powder was obtained after grinding the resultant product with an agate mortar. The gCN powder was then obtained after water-washing, centrifugation and vacuum-drying at 100 °C.

2.3. Synthesis of Cu₂O_gCN composites

The procedures revealed by Huang et al [41], were applied and modified to synthesize Cu₂O particles. In a typical batch to synthesize Cu₂O_gCN, CuCl₂ solution (100 mL, 0.1 M) was mixed with 1 g gCN-contained aqueous solution (1600–1800 mL), followed by ultra sonication for 10 min to well disperse gCN and assist the adsorption of Cu²⁺ ions on gCN. A vigorous stirring was then applied to mix SDS (17.4 g) with the above solution. Next, NaOH (36 mL, 1 M) was introduced into the mixture and continued stirring. Cu(OH)₂ was then obtained while the solution turned light blue. As different shapes of Cu₂O could be obtained by altering the volumes ratio of H₂O to NH₂OH·HCl, various amounts (80–200 mL) of 0.1 M NH₂OH·HCl solution were stir-mixed with the above mixture at a temperature-controlled water bath (28–30 °C) for at least 1 h. While the color of the solution changed from light blue to clay orange, the crystal of Cu₂O was produced on gCN. The Cu₂O_gCN composites were then obtained after being washed by H₂O/ethanol, filtered, and dried in a vacuum oven at 30 °C overnight. The sample name was decoded xCu₂O_gCN, where x (=c, d, s) indicated the shapes (cube, all-corner-truncated rhombic dodecahedral, or sphere) of Cu₂O formed on g-CN.

2.4. Characterization

The X-ray diffractometer (XRD, Bruker D8 SSS) using Cu K α radiation (λ = 0.154178 nm) at 40 kV and 35 mA was employed to identify the crystallinity of samples. Infrared spectra of samples were recorded by using a Fourier transform infrared (FTIR) spectrophotometer (Nicolet Protégé-460). The morphology of composites was observed via a scanning electron microscope (SEM, Jeol JSM-7401 F) operating at an accelerating voltage 3 kV and a transmission electron microscope (TEM, Jeol JEM-1400) operating at an acceleration voltage of 120 kV. The chemical composition of each sample was investigated

by an X-ray photoelectron spectroscope (XPS, Ulvac-Phi 5000 VersaProbe) using Al K α radiation. XPS valence band spectra obtained at lower binding energy region were applied to estimate the valence band edge of samples. The UV–vis diffuse reflectance spectra of powder samples were acquired on a spectrophotometer (Jasco V-650) equipped with an integrating sphere (ISV-722). The photoluminescence (PL) of samples were probed on a fluorescence spectrophotometer (Hitachi F-7000) using an excitation wavelength of 350 nm. Each sample before PL measurement was vacuum dried overnight to reduce the influence of water adsorption on PL. A high-resolution surface area and porosimetry analyzer (MICROMERITICS, ASAP2020) was utilized to determine the BET surface area of samples. Electron paramagnetic resonance (EPR) spectra of samples were obtained on a spectrometer (Bruker EMX-10/12) equipped with an SHQE cavity. All EPR spectra of samples at ambient condition were recorded at a resonant frequency around 9.8 GHz. In order to identify the radicals generated from illuminated sample, each sample suspension was mixed with the spin trap (DMPO) solution just before EPR measurements. The fresh stock solution contained each sample and the DMPO with a concentration of 40 ppm and 2000 ppm, respectively. For each run, 1 mL of the stock solution was withdrawn into a Suprasil aqueous flat cell (Wilmad, TE-102). The EPR spectra were recorded upon the irradiation of the sample-filled standard cell in the cavity. The *in-situ* illumination system was a 150-Watt Xenon lamp (Labguide, Xe-150).

2.5. Photocatalytic reduction of carbon dioxide

The photocatalytic reduction of CO₂ was conducted in a batch reactor (300 mL) at ambient temperature. After sprinkling vacuum-dried powder sample (1 g) on the bottom of the glass reactor, the reactor was covered with a double manifold glass lid with an opening outlet and placed in a vacuum oven at 30 °C for 1 h to remove gaseous impurity from the reactor. High purity CO₂ (99.999%) was then purged through a water bubbler at room temperature into the reactor at a flowrate of 60 mL per min for 30 min. The outlet and inlet of the reactor were then closed and ready for the illumination. Three LED light bulbs (Philips, 14 W) were placed symmetrically outside the reactor to provide the radical illumination. The emission spectrum of this LED light bulb shown in the inset of Fig. 1 indicated visible light-only irradiation. A gas chromatography (YL Instrument, YL6500) equipped with a highly sensitive pulsed-discharge helium ionization detector (PDHID) was employed to analyze the products of photoreduction. The carrier gas was He, and two separation columns from Ohio Valley Specialty, including Porapak N for the detection of H₂, O₂, CO and CH₄, and Molecular Sieve 5A for CO₂, H₂O and other C₁-C₂ hydrocarbons, were connected in series to simultaneously analyze all possible products from one injection. The volume of each injection was 1 mL of gas product withdrawn from the photoreactor by a gas-tight syringe.

3. Results and discussion

3.1. Characteristics of xCu₂O_gCN

The chemical structure of gCN was examined by FTIR and XPS analysis. The characteristic stretching vibration mode of C=N groups at 1643 and 1558 cm⁻¹ and C–N stretching at 1242, 1319 and 1404 cm⁻¹ were observed from the FTIR spectrum of gCN depicted in Fig. 1(a) [4–612,17]. The appearance of the peak at 810 cm⁻¹ suggested the presence of triazine ring of gCN [5, 12]. A broad band in the range of 2900 to 3300 cm⁻¹ corresponded to the stretching vibration modes of terminal NH or NH₂ groups [17]. The XPS spectra of gCN in C1s region was shown in Fig. 1(b). The characteristic carbon species of gCN, including sp-bonded C in N-containing aromatic rings (N=C–N) and sp² graphitic carbons C-(N)₃ and C–C, appeared at the binding energy of 288.0 eV, 286.0 eV and 284.7 eV, respectively [17,42–44]. The weak peak centered at 293.5 eV was originated from the

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