Graphitic carbon nitride prepared from urea as a photocatalyst for visible-light carbon dioxide reduction with the aid of a mononuclear ruthenium(II) complex

Kazuhiko Maeda*1, Daehyeon An1, Ryo Kuriki1,2, Daling Lu3 and Osamu Ishitani1

Full Research Paper

Address:
1Department of Chemistry, School of Science, Tokyo Institute of Technology, 2-12-1-NE-2 Ookayama, Meguro-ku, Tokyo 152-8550, Japan, 2Japan Society for the Promotion of Science, Kojimachi Business Center Building, 5-3-1, Kojimachi, Chiyoda-ku, Tokyo 102-0083, Japan and 3Suzukakedai Materials Analysis Division, Technical Department, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama 226-8503, Japan

Email:
Kazuhiko Maeda* - maedak@chem.titech.ac.jp

* Corresponding author

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Abstract

Graphitic carbon nitride (g-C3N4) was synthesized by heating urea at different temperatures (773–923 K) in air, and was examined as a photocatalyst for CO2 reduction. With increasing synthesis temperature, the conversion of urea into g-C3N4 was facilitated, as confirmed by X-ray diffraction, FTIR spectroscopy and elemental analysis. The as-synthesized g-C3N4 samples, further modified with Ag nanoparticles, were capable of reducing CO2 into formate under visible light (λ > 400 nm) in the presence of triethanolamine as an electron donor, with the aid of a molecular Ru(II) cocatalyst (RuP). The CO2 reduction activity was improved by increasing the synthesis temperature of g-C3N4, with the maximum activity obtained at 873–923 K. This trend was also consistent with that observed in photocatalytic H2 evolution using Pt-loaded g-C3N4. The photocatalytic activities of RuP/g-C3N4 for CO2 reduction and H2 evolution were thus shown to be strongly associated with the generation of the crystallized g-C3N4 phase.

Introduction

Carbon nitride is one of the oldest synthetic polymers [1], and has several allotropes. Among them, graphitic carbon nitride (g-C3N4) is the most stable form and is an emerging material as an organic semiconductor photocatalyst active for various kinds of reactions such as water splitting, CO2 reduction, and degradation of harmful organic compounds, because of its non-toxic, stable, and earth-abundant nature [2-7].

Our group has developed photocatalytic CO2 reduction systems using g-C3N4-based materials, in combination with functional
metal complexes [8-16]. For example, mesoporous g-C$_3$N$_4$ (mpg-C$_3$N$_4$) modified with a mononuclear Ru(II) complex, such as $\text{trans-}(\text{Cl})\text{Ru}(\text{PO}_3\text{H}_2)_2\text{bpy(CO)}_2\text{Cl}_2$ (bpy: 2,2'-bipyridine), abbreviated as RuP, is capable of photocatalyzing CO$_2$ reduction into formate with high selectivity under visible light irradiation, as confirmed by isotope tracer experiments with $^{13}$CO$_2$ [8-12]. After the first report of a metal complex/ C$_3$N$_4$ hybrid for CO$_2$ reduction, several groups have presented similar reports using cobalt-based metal complexes as reduction cocatalysts [17-20].

In these systems, structural properties of g-C$_3$N$_4$ such as specific surface area and porosity have a strong impact on activity, because they strongly affect the efficiency of electron/hole utilization to the surface chemical reactions [21,22]. Apart from mpg-C$_3$N$_4$ that is usually prepared by a hard-template method with multistep procedures [9,23], g-C$_3$N$_4$ having a relatively higher surface area can be readily prepared by heating urea, which is an inexpensive and readily available precursor, in air [14,24]. In fact, the urea-derived g-C$_3$N$_4$ exhibited an enhanced activity for CO$_2$ reduction compared to mpg-C$_3$N$_4$, when modified with Ag nanoparticles and a binuclear Ru(II) complex [14].

Thermal heating of urea results in decomposition and formation of g-C$_3$N$_4$, whose physicochemical properties should be dependent on the heating temperature. In this work, we investigated photocatalytic activities of g-C$_3$N$_4$, which was synthesized by heating urea at different temperatures, for visible-light CO$_2$ reduction with the aid of a mononuclear Ru(II) complex, RuP (see Scheme 1). As mentioned earlier, g-C$_3$N$_4$ has been studied as a visible-light-responsive photocatalyst mostly for H$_2$ evolution from aqueous triethanolamine (TEOA) solution [2,3,5]. The present work also compares the activities for CO$_2$ reduction with those for H$_2$ evolution in order to obtain a better understanding on photocatalytic activities of g-C$_3$N$_4$ for different kinds of reactions.

**Results and Discussion**

**Synthesis of g-C$_3$N$_4$ by thermal heating of urea at different temperatures**

Figure 1 shows XRD patterns of g-C$_3$N$_4$ samples synthesized at different temperatures. Two peaks are observed at 2theta = 13 and 27.4°, which are assigned to an in-planar repeating motif and the stacking of the conjugated aromatic system, respectively [25]. In fact, the urea-derived g-C$_3$N$_4$ exhibited an enhanced activity for CO$_2$ reduction compared to mpg-C$_3$N$_4$, when modified with Ag nanoparticles and a binuclear Ru(II) complex [14].

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**Scheme 1:** Synthesis of g-C$_3$N$_4$ by thermal heating of urea and application to photocatalytic CO$_2$ reduction with a mononuclear Ru(II) complex (RuP).
at the present temperature range examined. With increasing temperature, the intensity of these peaks became stronger, indicating that the formation of g-C$_3$N$_4$ was facilitated at higher temperatures. It is, however, noted that the high-temperature heating also caused the loss of the product mass due to the decomposition of g-C$_3$N$_4$ itself [25].

FTIR spectra for the same set of the samples are shown in Figure 2. Characteristic peaks can be seen in the 1650–1200 cm$^{-1}$ region. The peaks at 1322 and 1243 cm$^{-1}$ are assigned to the stretching vibration of connected units of C–N(–C)–C (full condensation) or C–NH–C (partial condensation) [26,27]. The leftovers of 1641, 1569, 1462 and 1412 cm$^{-1}$ are assigned to stretching vibration modes of heptazine-derived repeating units, and are sharper with increasing temperature. This further indicates the production of g-C$_3$N$_4$ at elevated temperatures, consistent with the XRD analysis (Figure 1). The 812 cm$^{-1}$ peak is attributed to the out-of-plane bending vibration characteristic of heptazine rings.

The results of elemental analyses for the as-prepared g-C$_3$N$_4$ samples were listed in Table 1. In all cases, not only carbon and nitrogen, which are the main constituent elements of g-C$_3$N$_4$, but also hydrogen and oxygen were detected. As the synthesis temperature increased, the compositions of carbon and nitrogen became closer to the ideal values, although the carbon content was obviously lower. The hydrogen and oxygen impurities were also reduced with an increase in the synthesis temperature. These results indicate that rising temperature is important to obtain purer g-C$_3$N$_4$ in terms of the chemical composition.

TEM images of the same samples are shown in Figure 3. The sample synthesized at 773 K had a lot of circular voids having 50–100 nm in size. At 823 K, this void structure was less prominent, and sheet-like morphology started to appear. With a further increase in the synthesis temperature, the synthesized samples consisted of disordered nanosheets. This change in par-

**Table 1: Results of elemental analysis and specific surface area measurements.**

| synthesis temperature [K] | composition [wt %] | specific surface area [m$^2$ g$^{-1}$] |
|---------------------------|--------------------|--------------------------------------|
|                           | C  | N  | H  | O  |                             |
| 773                       | 32.68 | 59.60 | 1.78 | 4.98 | 38                        |
| 823                       | 33.29 | 59.97 | 1.53 | 4.58 | 36                        |
| 873                       | 33.64 | 60.38 | 1.26 | 4.15 | 56                        |
| 923                       | 34.29 | 61.14 | 1.09 | 2.90 | 54                        |
| ideal C$_3$N$_4$          | 39.13 | 60.87 | 0    | 0    | –                         |
Figure 3: TEM images of g-C$_3$N$_4$ synthesized at different temperatures.

Particle morphology is in qualitative agreement with that in the specific surface area (see Table 1).

Figure 4 shows the UV–visible diffuse reflectance spectra of g-C$_3$N$_4$ synthesized at different temperatures. All of the samples exhibited an absorption edge at 420–450 nm, attributed to electron transitions from the valence band formed by nitrogen 2p orbitals to the conduction band formed by carbon 2p orbitals [25]. The band gaps of the synthesized g-C$_3$N$_4$ were estimated to be ca. 2.8–3.0 eV, from the onset wavelength of the diffuse reflectance spectra. This value is consistent with that reported previously [24]. As the synthesis temperature increases, the onset wavelength is shifted to longer wavelengths (i.e., band gap is decreased), with more pronounced tailing absorption extending to 550 nm that is assigned to n–π* transitions involving lone pairs on the edge nitrogen atoms of the heptazine rings [28,29]. While the n–π* transitions are forbidden for perfectly symmetric and planar heptazine units, they become partially allowed with increasing the condensation of layers in g-C$_3$N$_4$, which results from an increase in the synthesis temperature.

Figure 4: UV–visible diffuse reflectance spectra of g-C$_3$N$_4$ synthesized at different temperatures.
Photocatalytic activities for CO₂ reduction and H₂ evolution

Using the as-prepared g-C₃N₄, CO₂ reduction was conducted with the aid of RuP cocatalyst and Ag promoter in a N,N-dimethylacetamide (DMA)/TEOA mixed solution under visible light (λ > 400 nm). Here TEOA works as an effective electron donor that scavenges holes generated in the valence band of g-C₃N₄ [25]. The use of DMA as the solvent for CO₂ reduction using RuP/mpg-C₃N₄ has previously been shown to be the best choice of solvents to maximize the photocatalytic activity [10]. Because RuP does not absorb visible light efficiently, the g-C₃N₄ component can be activated selectively by visible light [10]. Our previous study also indicated that the amount of a molecular cocatalyst is very important in this kind of mononuclear-complex/C₃N₄ hybrid photocatalyst for visible-light CO₂ reduction [8]. To eliminate any other effects other than heating temperature of urea, we fixed the amount of RuP in this study. Ag nanoparticles loaded on mpg-C₃N₄ serves as a promoter of electron transfer from mpg-C₃N₄ to RuP, as discussed in our previous work [13]. TEM observation indicated that the loaded Ag is in the form of nanoparticles of 5–10 nm in size (Figure 5). Without Ag (i.e., RuP/g-C₃N₄), formate production was clearly observable, but the activity was typically 20% that of RuP/Ag/g-C₃N₄. Hence we employed Ag as an additional promoter in all cases. It should be also noted that no reaction took place using only g-C₃N₄.

As listed in Table 2, the main product during the reaction was formate with 90–95% selectivity. Minor products were CO and H₂. With increasing the synthesis temperature, the formate generation activity was improved to reach a maximum at 873–923 K, while almost unchanging the CO and H₂ evolution. The catalytic turnover number of formate generation calculated based on the mole amount of RuP at the optimal conditions reached 650, which confirms the catalytic cycle of the reaction.

H₂ evolution was also conducted in a mixed solution of water and TEOA. It is also noted that Pt was in situ loaded on g-C₃N₄ as a cocatalyst to facilitate H₂ evolution. As listed in Table 2, all of the synthesized samples produced H₂. Similar to the trend in CO₂ reduction, the H₂ evolution activity was enhanced as the synthesis temperature was increased.

The results of the photocatalytic reactions thus indicated that photocatalytic activities of g-C₃N₄ derived from urea were dependent on the heating temperature of urea. The trend of activity observed in both CO₂ reduction and H₂ evolution could be explained in terms of the formation of the g-C₃N₄ structure. Physicochemical analyses indicated that increasing the synthesis temperature of g-C₃N₄ promotes conversion of urea into g-C₃N₄ (Figure 1 and Figure 2), which has even better visible-

Table 2: Photocatalytic activities of g-C₃N₄ synthesized at different temperatures for CO₂ reduction and H₂ evolution under visible light (λ > 400 nm)a.

| synthesis temperature [K] | CO₂ reductionb [µmol] | H₂ evolutionc [µmol] |
|---------------------------|-----------------------|---------------------|
|                           | formate | CO   | H₂ |                           |                        |
| 773                       | 2.8     | 0.2  | 0.1| 7.0                        |
| 823                       | 3.0     | 0.2  | 0.1| 9.7                        |
| 873                       | 5.2     | 0.1  | 0.1| 17.9                       |
| 923                       | 5.1     | 0.1  | 0.1| 18.6                       |

aReaction conditions: photocatalyst (4.0 mg); reactant solution (4.0 mL); light source, 400 W high-pressure Hg lamp with a NaNO₂ aqueous solution filter. Reaction time: 5 h. bWith 2.0 µmol g⁻¹ RuP and 5.0 wt % Ag. Performed in a DMA/TEOA mixed solution (4:1 v/v). cWith 3.0 wt % Pt. Performed in a water/TEOA mixed solution (9:1 v/v).
light absorption (Figure 4). The better light absorption profile as well as higher specific surface area of the g-C₃N₄ samples synthesized at elevated temperatures would have a positive impact on the activity to a certain extent. It is also noted that the photocatalytic activity for CO₂ reduction was much lower than that for H₂ evolution, even though the same electron donor, TEOA, was employed. This in turn implies that there still remains much room for the improvement of CO₂ reduction activity, for example, if a proper modification method, which allows for more efficient electron transfer, is developed. This is now under investigation in our laboratory.

Conclusion

Heating urea in air at 773–923 K resulted in the formation of g-C₃N₄, which exhibited photocatalytic activity for CO₂ reduction into formate under visible light with the aid of a molecular Ru(II) cocatalyst. Experimental results highlighted that higher heating temperature for the synthesis led to the production of more crystallized g-C₃N₄ with higher specific surface area and more pronounced visible-light absorption, which was preferable for photocatalytic reactions of both CO₂ reduction and H₂ evolution. However, too high synthesis temperature causes a mass loss of g-C₃N₄ due to thermal decomposition, which is not practically desirable.

Experimental

Materials and reagents

g-C₃N₄ samples were synthesized by heating 10 g of urea (99.4%, Wako Chemicals Co.) in air at a ramp rate of 2.3 K min⁻¹ to a given temperature (773–923 K), keeping that temperature for 4 h, then cooling without temperature control.

Ag (5.0 wt %) was loaded as a promoter onto the surface of g-C₃N₄ by an impregnation method using AgNO₃ (>99.8%, Wako Pure Chemicals Co.) as the precursor according to the previous method [13]. g-C₃N₄ (50 mg) was dispersed in an aqueous AgNO₃ solution (10 mL). The water content was subsequently removed under reduced pressure at 317 K. The resulting solid sample was heated under a H₂ stream (20 mL min⁻¹) at 473 K for 1 h.

RuP was synthesized according to methods reported in our previous paper [10]. Adsorption of RuP onto Ag/g-C₃N₄ was conducted by dispersing 40 mg of Ag/g-C₃N₄ in an acetonitrile (MeCN) solution (20 mL) of RuP. The suspension was stirred overnight at room temperature in the dark to allow for the adsorption/desorption equilibrium, followed by filtration and washing with acetonitrile. The filtrates were collected and concentrated to a volume of 30 mL. The amount of the ruthenium complex absorbed was calculated based on the UV–vis spectrum of the filtrate, using Equation 1:

\[
\text{adsorbed amount (mol g}^{-1}\text{)} = \frac{A_{\text{before}} - A_{\text{after}}}{A_{\text{before}}} \frac{C \cdot 20 \times 10^{-3} \cdot (\text{L})}{40 \times 10^{-3} \cdot (\text{g})},
\]

where \(A_{\text{before}}\) and \(A_{\text{after}}\) are the absorbance of the solution before and after the adsorption procedure, respectively, and \(C\) is the initial concentration of RuP.

Organic solvents used in this work were subject to purification prior to use. DMA was dried over molecular sieves 4 Å (which was heated at 373 K under reduced pressure (<1 Torr) overnight for several days), and distilled under reduced pressure (10–20 Torr). MeCN was distilled over P₂O₅ twice, and then distilled over CaH₂ prior to use. TEOA was distilled under reduced pressure (<1 Torr). The distilled DMA and TEOA were kept under Ar prior to use.

Characterization

The prepared materials were characterized by X-ray diffraction (XRD) (MiniFlex600, Rigaku; Cu Kα radiation), Fourier-transform infrared (FTIR) spectroscopy (FTIR-610, Jasco), transmission electron microscopy (TEM) (JEM-2010F, JEOL), and UV–visible diffuse reflectance spectroscopy (DRS) (V-565, Jasco). The Brunauer–Emmett–Teller (BET) surface area of each specimen was determined using a BELSOEP-mini instrument (BEL Japan) at liquid nitrogen temperature. The amount of carbon, nitrogen, hydrogen and oxygen were determined by elemental analysis (MICRO CORDER JM10, J-SCIENCE) by Suzukakedai Materials Analysis Division, Technical Department, Tokyo Institute of Technology.

Photocatalytic reactions

Reactions were performed at room temperature (298 K) using an 8 mL test tube containing 4 mL of solution by dispersing 4 mg of photocatalyst powder. For H₂ evolution, a mixed solution of water and TEOA (9:1 v/v) was used as the reactant solution, which was in prior purged with Ar for 20–30 min to remove residual air. Pt (3.0 wt %) was loaded in situ using H₂PtCl₆ (98.5%, Wako Pure Chemicals Co.) as the precursor. For CO₂ reduction, a mixed solution of DMA and TEOA (4:1 v/v) was used. Prior to irradiation, the suspension was purged with CO₂ (Taiyo Nippon Sanso Co., >99.995%) for 20–30 min. A 400 W high-pressure Hg lamp (SEN) was used as a light source, in combination with a NaNO₂ solution as a filter to provide visible light irradiation (λ > 400 nm). The gaseous reaction products were analyzed using a gas chromatograph with a thermal conductivity detector (GL Science, Model GC323). The formate generated in the liquid phase was
analyzed via a capillary electrophoresis system (Otsuka Electronics Co., Model CAPI-3300).

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ORCID® iDs
Kazuhiro Maeda - https://orcid.org/0000-0001-7245-8318
Ryo Kuriki - https://orcid.org/0000-0002-3843-2867
Daling Lu - https://orcid.org/0000-0002-9084-480X
Osamu Ishitani - https://orcid.org/0000-0001-9557-7854

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