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Visible light-induced decomposition of monoethanolamine in water using graphitic carbon nitride as a photocatalyst

Hisao Hori^{a,*}, Shohei Wachi^a, Kentaro Iwamura^a, Taizo Sano^b^a Department of Chemistry, Faculty of Science, Kanagawa University, 2946 Tsuchiya, Hiratsuka 259-1293, Japan^b National Institute of Advanced Industrial Science and Technology (AIST), AIST Tsukuba West, 16-1 Onogawa, Tsukuba 305-8569, Japan

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ABSTRACT

Photochemical decomposition of monoethanolamine (MEA) in the presence of graphitic carbon nitride (g-C₃N₄) in water under visible-light irradiation was investigated. When aqueous MEA was irradiated by visible light (>389 nm) in the presence of either TiO₂ (P25) and O₂ or g-C₃N₄ and argon, virtually no decomposition of MEA was observed. In contrast, when aqueous MEA was irradiated by visible light in the presence of g-C₃N₄ and O₂, the MEA decomposed to produce HCOOH, NO₂⁻, NO₃⁻, and NH₃. Although metal (Ag or Pt)-loading onto g-C₃N₄ enhanced the photocatalytic MEA decomposition slightly, it accelerated the formation of NO₂⁻ and NO₃⁻. After the g-C₃N₄ catalyzed reactions, the recovery of carbon atoms was almost completely accounted for by the remaining MEA and HCOOH formed in the reaction solution, indicating that the carbon atoms in the reacted MEA were predominantly transformed to HCOOH.

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1. Introduction

Alkanolamines, which have an amino group and a hydroxyl group on an alkane backbone, have been used as components for surfactants, emulsifiers, lubricants, polishes, corrosion inhibitors, pharmaceuticals, and so forth [1]. In addition to these traditional usages, alkanolamines are increasingly used for post-combustion CO₂ capture technology aimed at mitigating climate change [2]. In CO₂ capture plants, aqueous amines are employed as capture solvents of CO₂ from combustion flue gases. Monoethanolamine (HOCH₂CH₂NH₂, MEA), a primary amine, is the most common amine used for this purpose, although secondary and tertiary amines are also used or planned to be used in CO₂ capture [2–4].

With the blossoming of post-combustion CO₂ capture technology, the sites where the technology is introduced (e.g., coal-fired power plants) are potentially major sources of the amines and their degradation products in the environment [4–6]. These amines are lost from the CO₂ absorber column through evaporation and entrainment in the plants; aqueous and solid wastes from the plants also contain these amines and their degradation products [6]. Consequently, the presence of amines in surface waters has been reported, although available data are limited so far [4]. These amines can degrade to form potentially carcinogenic nitrosamines

and nitramines [4–8]. Nitrosamines are mostly derived from secondary amines [5]. However, they can also be generated from primary and tertiary amine solutions used for CO₂ capture because these amines transform to secondary amines in the capture solvent [7]. In fact, nitrosamines were detected in regenerated MEA solvent from a post-combustion CO₂ capture plant at a coal-fired power station [8]. MEA is also used as a stripper in the manufacturing of thin-film transistor liquid crystals and as a corrosion inhibitor in metal working fluid; the wastewater from these processes is also a cause for concern [9–12]. Accordingly, there is a need to develop techniques to decompose MEA in water to harmless species under mild conditions to protect against emissions from stationary sources. Among the techniques aimed at decomposition of MEA in water or solid, biodegradation has been extensively investigated [9–18]. Photocatalytic approaches are also attractive. However, we found only two reports about the photocatalytic decomposition of MEA in water: use of titanium silicalite-1 (TS-1) zeolite [19] or TiO₂-loaded clinoptilolite [20]. In both reports, the decomposition of MEA was driven by UV light irradiation, and the common photocatalyst TiO₂ plus UV light irradiation served as a comparator, although TiO₂ showed less photocatalytic activity than TS-1 zeolite and TiO₂-loaded clinoptilolite.

* Corresponding author.

E-mail address: h-hori@kanagawa-u.ac.jp (H. Hori).

Recently, graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) has received much attention because it can be easily prepared by heating nitrogen-rich organic compounds, such as melamine, and acts as a photocatalyst when induced by visible-light irradiation [21–23]. Since $g\text{-C}_3\text{N}_4$ was reported to have photocatalytic water splitting activity under visible-light irradiation [24], there have been numerous studies on water purification using $g\text{-C}_3\text{N}_4$ or a composite as a photocatalyst. Although many of these reports focused on the degradation of model contaminants such as organic dyes [25–33], there have been an increasing number of reports on the degradation of real contaminants such as phenols [30,34,35]. Studies focused on air purification, for example, the removal of NO [36] and methyl mercaptan [37] induced by the photocatalytic activity of $g\text{-C}_3\text{N}_4$, have also been reported.

In the present work, we report the photocatalytic decomposition of MEA in water by use of $g\text{-C}_3\text{N}_4$ or metal (Ag or Pt)-loaded $g\text{-C}_3\text{N}_4$. To the best of our knowledge, this is the first report on the visible light-induced photocatalytic decomposition of MEA in water.

2. Materials and procedures

2.1. Materials

MEA (>99%) and other chemicals were purchased from Wako Pure Chemical Industries (Osaka, Japan). Powdered TiO_2 (Degussa P25, BET surface area, $50\text{ m}^2\text{ g}^{-1}$) was obtained from Nippon Aerosil (Tokyo, Japan). We used four kinds of $g\text{-C}_3\text{N}_4$: $g\text{-C}_3\text{N}_4$ prepared by a standard method (Std- $g\text{-C}_3\text{N}_4$), $g\text{-C}_3\text{N}_4$ obtained from hydrothermal treatment of Std- $g\text{-C}_3\text{N}_4$ (HT- $g\text{-C}_3\text{N}_4$), silver-loaded $g\text{-C}_3\text{N}_4$ (HT- $g\text{-C}_3\text{N}_4\text{-Ag}$), and platinum-loaded $g\text{-C}_3\text{N}_4$ (HT- $g\text{-C}_3\text{N}_4\text{-Pt}$). Std- $g\text{-C}_3\text{N}_4$ was synthesized from melamine by heating at $550\text{ }^\circ\text{C}$ for 2 h; additional details are described elsewhere [36]. HT- $g\text{-C}_3\text{N}_4$ was prepared from Std- $g\text{-C}_3\text{N}_4$ by hydrothermal treatment with 0.1 M NaOH at $110\text{ }^\circ\text{C}$ for 18 h [36]. The synthesis scheme for all catalysts is shown in Scheme S1 in Supplementary materials. Detailed characterization of these species was described in the reference [36]. HT- $g\text{-C}_3\text{N}_4\text{-Ag}$ was obtained by photodeposition of silver onto HT- $g\text{-C}_3\text{N}_4$ by use of aqueous AgNO_3 and UV light irradiation from a

high-pressure mercury lamp, as reported previously [37]. Likewise, HT- $g\text{-C}_3\text{N}_4\text{-Pt}$ was prepared by photodeposition of platinum onto HT- $g\text{-C}_3\text{N}_4$ by use of aqueous H_2PtCl_6 and UV light irradiation. The amount of silver and platinum in HT- $g\text{-C}_3\text{N}_4\text{-Ag}$ and HT- $g\text{-C}_3\text{N}_4\text{-Pt}$, respectively, was 1.0 wt%. The specific surface areas of Std- $g\text{-C}_3\text{N}_4$ and HT- $g\text{-C}_3\text{N}_4$, measured by using the BET method with nitrogen absorption, were 7.7 and $65\text{ m}^2\text{ g}^{-1}$, respectively.

2.2. Photocatalytic reactions

$g\text{-C}_3\text{N}_4$ powder (Std- $g\text{-C}_3\text{N}_4$, HT- $g\text{-C}_3\text{N}_4$, HT- $g\text{-C}_3\text{N}_4\text{-Pt}$, or HT- $g\text{-C}_3\text{N}_4\text{-Ag}$; 30 mg), an aqueous solution of MEA (5.00–5.18 mM, 22 mL), and a polytetrafluoroethylene stirring bar were introduced into a gold vessel (25-mL volume, 3.8-cm o.d.), which was stable to corrosive MEA solutions. The vessel was inserted into a column-shaped pressure-resistant photochemical reactor made of Inconel alloy (205-mL volume, 3.8-cm i.d.). The reactor had a sapphire window on the top to receive the light and had gas inlet and outlet ports on the side. After the reactor was pressurized to 0.5 MPa with oxygen gas through the gas inlet port, the mixture in the vessel was irradiated with visible light ($>389\text{ nm}$) while stirring. The reason for using pressurized oxygen is ease of gas collection after the reaction. Under the pressurized conditions, the gas in the reactor after the reaction can be spontaneously transferred to the gas sampling bag by opening the valve which connects the reactor and the sampling bag. The irradiation light was generated by a combination of a long-pass filter (LU0400, Asahi Spectra, Tokyo, Japan) and a 500 W xenon short-arc lamp (UXL 500D, Ushio, Tokyo, Japan). The light from the lamp was introduced to an optical fiber, passed through a water filter, the long-pass filter, the sapphire window of the reactor, and then reached the reaction mixture. The irradiation light intensity of this system was low: the irradiance at the center of the light spot on the sample position was $120\text{ }\mu\text{W cm}^{-2}$ at 405 nm, as measured by a power meter (FieldMaster, detection head, LM-2VIS, Coherent, Santa Clara, CA, USA) with a band-pass filter (HB0405, Asahi Spectra, half bandwidth, 10 nm). During the photochemical reaction, the temperature of the reaction mixture was kept constant at $25\text{ }^\circ\text{C}$ by use of a circulation water bath. Control reactions using TiO_2 instead of $g\text{-C}_3\text{N}_4$ were also carried out.

At the end of the irradiation time period, a gas-sampling bag (CEK-1, GL Sciences, Tokyo, Japan) was connected to the gas outlet port of the reactor. The gas in the reactor was transferred to the sampling bag by releasing the pressure, and the collected gas was subjected to gas chromatography-mass spectrometry (GC-MS). The reaction mixture was separated by centrifugation, and the collected solution was analyzed by ion chromatography and high-performance liquid chromatography (HPLC). The collected solid was dried under vacuum and subjected to X-ray photoelectron spectroscopy (XPS) to examine the $g\text{-C}_3\text{N}_4$ for degradation.

2.3. Analytical procedures

An ion chromatograph (IC 2010, Tosoh, Tokyo, Japan) with an automatic sample injector (injection volume, $30\text{ }\mu\text{L}$), a separation column (Tosoh TSKgel SuperIC-CR, i.d., 4.6 mm; length, 15 cm), a column oven, and a conductivity detector in cationic mode was used to quantify the MEA in the reaction solution. The temperature of the column oven was kept constant at $40\text{ }^\circ\text{C}$. The mobile phase was an aqueous solution containing methanesulfonic acid (1.0 mM) and 18-crown-6 (1.0 mM). A second ion chromatograph (Tosoh IC 2001) was used to quantify the NO_2^- and NO_3^- . In this system, analyte separation was performed by a combination of a guard column (Tosoh TSKgel Super IC-A, i.d., 4.6 mm; length, 1 cm), a separation column (Tosoh TSKgel Super IC Anion, i.d., 4.6 mm;

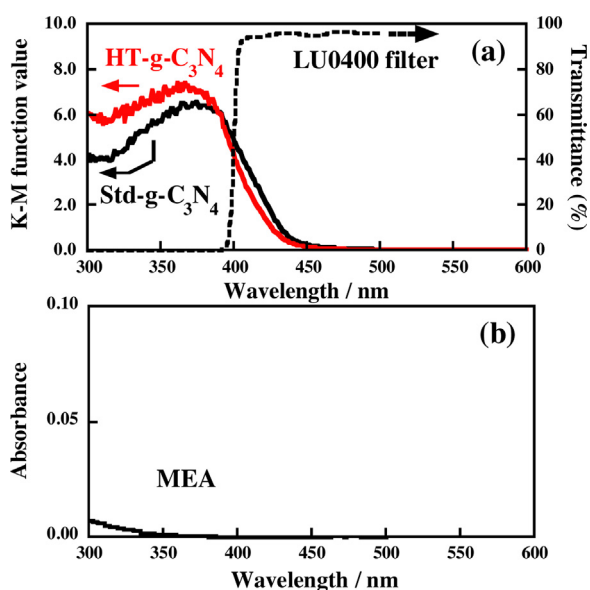


Fig. 1. (a) Diffuse reflectance UV–visible absorption spectra of Std- $g\text{-C}_3\text{N}_4$ and HT- $g\text{-C}_3\text{N}_4$, and transmittance of the LU0400 long-pass filter, and (b) UV–visible absorption spectrum of MEA in water (5.0 mM; path length, 1.0 cm). In panel b, the MEA concentration is the same as that used in the photochemical reactions.

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