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# 研 究 報 告

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富山大学研究推進機構 水素同位体科学研究センター

HYDROGEN ISOTOPE RESEARCH CENTER,

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## 論 文

### C<sub>3</sub>N<sub>4</sub> 光触媒によるヨウ化水素水溶液からの水素生成

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### Hydrogen Production on a C<sub>3</sub>N<sub>4</sub> Photocatalyst from a Hydrogen Iodide Aqueous Solution

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#### Abstract

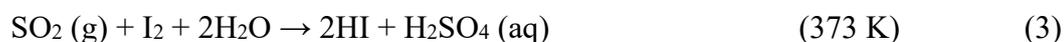
Photocatalytic hydrogen production on graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) from a hydrogen iodide (HI) aqueous solution was investigated with respect to light energy conversion. The photoabsorption and surface

area of g-C<sub>3</sub>N<sub>4</sub> depended strongly on the preparation temperature. The highest photocatalytic activity for HI decomposition was obtained with g-C<sub>3</sub>N<sub>4</sub> prepared at 773 K, which had high photoabsorption capacity. This study revealed that the activity for I<sub>2</sub> formation on the g-C<sub>3</sub>N<sub>4</sub> surface could be improved to achieve efficient HI decomposition with stoichiometric H<sub>2</sub> and I<sub>2</sub> formation.

## 1. Introduction

Hydrogen is considered to be a clean next-generation energy carrier, as it can be produced from various sources and used to generate electrical or thermal energy without CO<sub>2</sub> emission. However, most commercial hydrogen gases are produced from fossil fuels by steam reforming with CO<sub>2</sub> emission [1]. Therefore, hydrogen is currently not a clean energy source. To overcome this situation, various methods of producing hydrogen by water decomposition using renewable energy sources have been studied [2]. Among these, the solar IS (iodine-sulfur) process is a relatively new hydrogen production method [3].

The IS process is a thermochemical water splitting cycle, and the solar IS process employs concentrated solar thermal energy as a heat source [4]. This process comprises three chemical reactions as shown below:



The IS process results in complete thermal decomposition of water into H<sub>2</sub> and O<sub>2</sub> at high temperature. This process was expected to improve HI decomposition for practical use because the low HI decomposition ratio (ca. 20% at 673 K) limits its total efficiency.

To overcome this issue, photocatalytic HI decomposition was investigated in this study. If HI decomposition occurs on photocatalysts under UV or visible light, and sulfuric acid

decomposition is induced by infrared heating in sunlight, the conversion efficiency of the solar IS process would improve. While several studies have been published on photocatalytic HI decomposition [5,6], the photocatalytic activity of graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) for HI decomposition has not yet been investigated. Graphitic carbon nitride is an organic semiconductor photocatalyst, which was reported in 2009, that shows activity for organic pollutants and water decomposition [7]. In this study, g-C<sub>3</sub>N<sub>4</sub> was prepared from melamine at different temperatures, and the photocatalytic activity for HI decomposition was evaluated.

## 2. Experimental

### 2.1. Photocatalyst Preparation and Characterization

All reagents were used without further purification. The g-C<sub>3</sub>N<sub>4</sub> photocatalysts were prepared by heating melamine (99.0%, Wako Pure Chemical Industries, Ltd., Japan) in air. The melamine powder (5 g) was placed in an alumina crucible and calcined at a predetermined temperature (723–973 K) in a muffle furnace. Platinum nanoparticles were employed as co-catalyst for the hydrogen evolution reaction. Pt was loaded on g-C<sub>3</sub>N<sub>4</sub> using an evaporation to dryness method with aqueous tetraammineplatinum(II) nitrate (Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>, 99.995%, Sigma-Aldrich Co., USA). A mixture of C<sub>3</sub>N<sub>4</sub> powder and Pt precursor was heated at 573 K for 2 h under hydrogen gas flow (50 ml min<sup>-1</sup>).

X-ray diffraction (XRD) patterns of the samples were obtained with an X-ray diffractometer (RINT2000, Rigaku Corp., Japan) equipped with Cu K $\alpha$  radiation. The Brunauer-Emmett-Teller (BET) surface area was determined with an adsorption apparatus (BELSORP-mini, MicrotracBEL Corp., Japan). UV–Vis and IR diffuse reflectance spectra were obtained with UV–Vis (UV-3600, Shimadzu Corp., Japan) and FT-IR (Nicolet 6700, Thermo Fisher Scientific Inc., USA) spectrophotometers, respectively. X-ray photoelectron spectroscopy (XPS) was performed with an X-ray photoelectron spectrometer (AXIS-165,

Shimadzu Corp., Japan).

## 2.2. Photocatalytic Reaction

Photocatalytic HI decomposition was performed in a quartz reactor containing 10 mM aqueous HI. The reactor was irradiated with a Xe lamp ( $2.0 \text{ W cm}^{-2}$ ) with magnetic stirring. The evolved gases were detected using a gas chromatograph (GC-8A, Shimadzu Corp., Japan) with a thermal conductivity detector. After the photocatalytic reaction, the catalyst was collected by centrifugation and separated from the reaction solution by decantation. The amounts of triiodide ( $\text{I}_3^-$ ) and iodide ( $\text{I}^-$ ) ions were determined by titration with aqueous  $\text{Na}_2\text{S}_2\text{O}_3$  and  $\text{AgNO}_3$ , respectively.

## 3. Results and Discussion

Figure 1 shows XRD patterns of carbon nitrides prepared at different temperatures. Most of the diffraction peaks were assigned to g- $\text{C}_3\text{N}_4$ , as reported previously [8]. While g- $\text{C}_3\text{N}_4$  was obtained above 773 K, the sample calcined at 973 K was completely decomposed. The

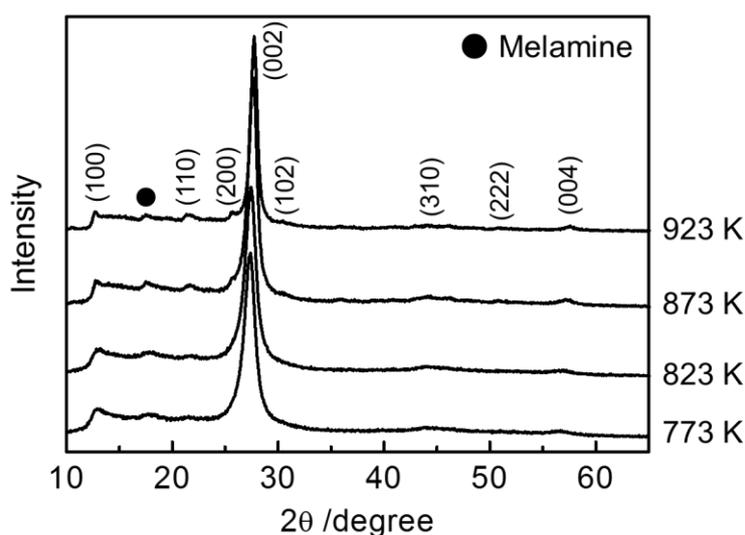


Fig. 1 XRD patterns of synthesized g- $\text{C}_3\text{N}_4$  powders.

Table 1 Weight change and specific surface area of samples calcined at different temperatures.

Calcination temp. /K	Weight of melamine /g	Weight of calcined sample /g	Specific surface area /m <sup>2</sup> g <sup>-1</sup>
773	5.02	2.77	4.7
823	5.00	2.61	9.5
873	5.04	2.21	25.7
923	4.99	1.27	39.9

diffraction peaks of g-C<sub>3</sub>N<sub>4</sub> became sharper as the calcination temperature increased, indicating that the crystallinity of g-C<sub>3</sub>N<sub>4</sub> increased with the calcination temperature.

Table 1 shows the weight of the samples before and after calcination at each temperature. The weight loss during

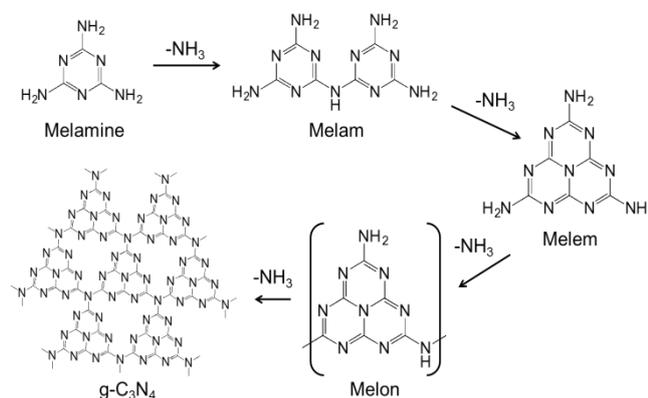


Fig. 2 Formation mechanism of g-C<sub>3</sub>N<sub>4</sub> in thermal decomposition of melamine [9].

heat treatment was caused by sublimation of melamine and desorption of ammonia, which are driven by both deamination and the formation of aromatic units [9], as shown in Fig. 2. These reactions accelerate as the temperature increases. Therefore, melamine polymerization increased with the calcination temperature, and the weight of the prepared sample decreased due to deammoniation. These results were consistent with the XRD results. The specific surface area of the g-C<sub>3</sub>N<sub>4</sub> samples, obtained by nitrogen gas adsorption, is also summarized in Table 1. The surface area increased with the calcination temperature, and that of a sample calcined at 923 K was about 40 m<sup>2</sup> g<sup>-1</sup>. Furthermore, hysteresis loops were observed in the adsorption-desorption isotherms of all samples, which were identified as IUPAC type H3 [10]. It was thus confirmed that the carbon nitrides prepared in this study were agglomerates of plate-like crystals such as graphite.

Figure 3 shows UV–Vis diffuse reflectance spectra of the prepared g-C<sub>3</sub>N<sub>4</sub> samples. The absorption edge was 450 nm for the g-C<sub>3</sub>N<sub>4</sub> calcined at 773 K, and this shifted to a shorter wavelength after heating at a higher temperature. The band gap energy of the samples can be determined from a plot of  $(F(R)hv)^{1/2}$

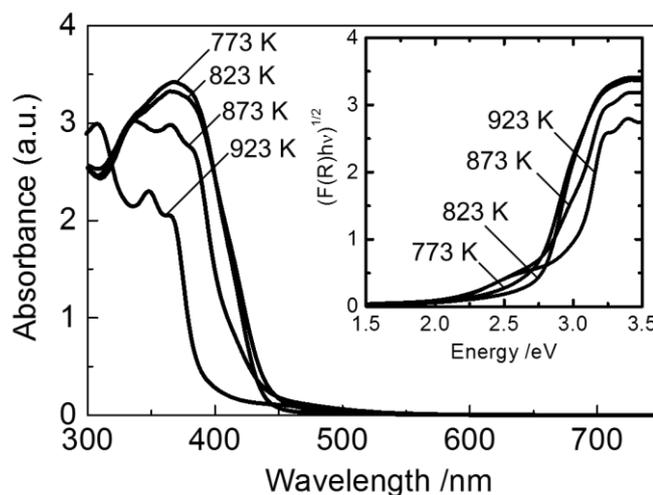


Fig. 3 UV–Vis DR spectra of g-C<sub>3</sub>N<sub>4</sub> samples.

versus light energy (Fig. 3 inset), where  $R$ ,  $h$ , and  $\nu$  are the reflectance coefficient, Planck's constant, and the light frequency. The optical band gaps of g-C<sub>3</sub>N<sub>4</sub> calcined at 773, 823, 873, and 923 K were estimated as 2.7, 2.75, 2.8, and 3.0 eV, respectively. As the prepared g-C<sub>3</sub>N<sub>4</sub> samples can absorb visible light, they are more favorable for solar energy conversion than TiO<sub>2</sub> photocatalysts.

Photocatalytic decomposition of HI on Pt/g-C<sub>3</sub>N<sub>4</sub> was performed under Xe lamp irradiation. The control experiments showed that no detectable product was formed in the absence of either the photocatalysts or light irradiation. The main products of the photocatalytic HI decomposition were H<sub>2</sub> and I<sub>3</sub><sup>-</sup>, which was produced by reaction between I<sub>2</sub> and I<sup>-</sup>. As shown in Fig. 4, the photocatalytic activity of the g-C<sub>3</sub>N<sub>4</sub> depended on the calcination

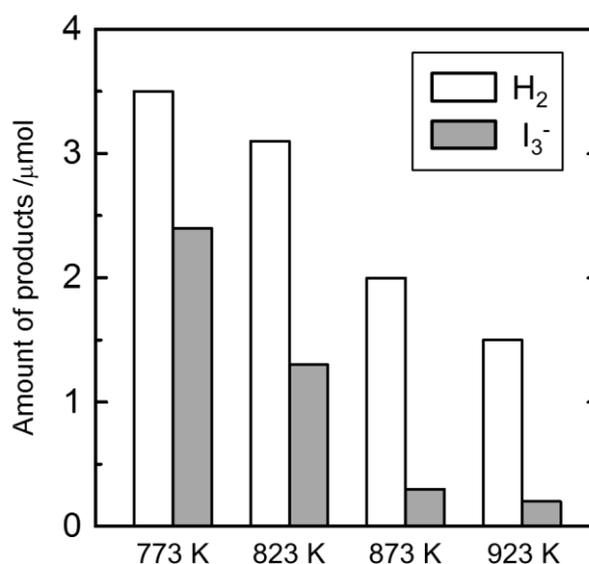


Fig. 4 Amounts of H<sub>2</sub> and I<sub>3</sub><sup>-</sup> formed on Pt/g-C<sub>3</sub>N<sub>4</sub> photocatalysts after HI decomposition for 12 h.

temperature. The g-C<sub>3</sub>N<sub>4</sub> sample calcined at 773 K showed the highest hydrogen production during photocatalytic HI decomposition. This can be explained by differences in the light absorbed by the prepared g-C<sub>3</sub>N<sub>4</sub> photocatalysts. However, the amounts of I<sub>2</sub> formed were below the stoichiometric amounts in all cases. To determine the reason for non-stoichiometric H<sub>2</sub> and I<sub>2</sub> (I<sub>3</sub><sup>-</sup>) formation,

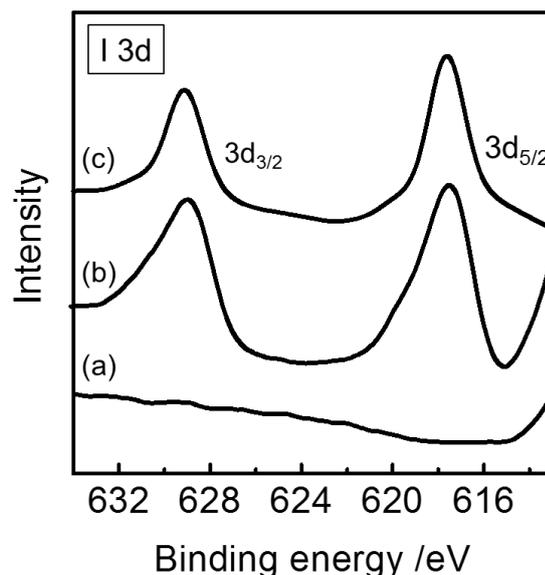


Fig. 5 XPS spectra of Pt/g-C<sub>3</sub>N<sub>4</sub> prepared at 773 K (a) before and (b) after HI decomposition. (c) NaI reference data.

XPS was performed. Figure 5 shows XPS spectra of the catalyst before and after photocatalytic HI decomposition with NaI as a reference. Despite washing several times with pure water, I 3d peaks were observed from the Pt/g-C<sub>3</sub>N<sub>4</sub> catalyst after the reaction. This indicates the presence of strongly adsorbed iodine on the g-C<sub>3</sub>N<sub>4</sub>. Liu et al. reported that products accumulated on a g-C<sub>3</sub>N<sub>4</sub> photocatalyst and inhibited photocatalytic reactions [11]. For HI photodecomposition on Pt/g-C<sub>3</sub>N<sub>4</sub>, no co-catalyst was used for I<sub>2</sub> formation, while a Pt co-catalyst was used for H<sub>2</sub> formation. Therefore, it appeared that I<sub>2</sub> formation on the g-C<sub>3</sub>N<sub>4</sub> catalyst surface proceeded less easily than H<sub>2</sub> formation. Since the surface areas of the g-C<sub>3</sub>N<sub>4</sub> catalysts prepared at a high calcination temperature tended to be large, it is believed that inhibition of the photocatalytic reaction also increased, due to iodine accumulation. Consequently, it is considered that g-C<sub>3</sub>N<sub>4</sub> calcined at 773 K with a high photoabsorption capacity and a small surface area showed the highest photocatalytic activity for HI decomposition.

#### 4. Conclusions

Photocatalytic hydrogen production on Pt/g-C<sub>3</sub>N<sub>4</sub> from aqueous HI was investigated in this study. XRD, UV–Vis absorption spectra, and BET surface area measurements revealed that the crystallinity, photoabsorption properties, and surface area of the prepared g-C<sub>3</sub>N<sub>4</sub> strongly depended on the calcination temperature. The highest photocatalytic activity for HI decomposition was obtained with g-C<sub>3</sub>N<sub>4</sub> prepared at 773 K, due to its high photoabsorption capacity. Compared to H<sub>2</sub> formation, the activity of the Pt/g-C<sub>3</sub>N<sub>4</sub> surface for I<sub>2</sub> formation appeared low; thus, co-catalysts should be employed for I<sub>2</sub> formation to improve the photocatalytic activity of g-C<sub>3</sub>N<sub>4</sub> for HI decomposition.

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