

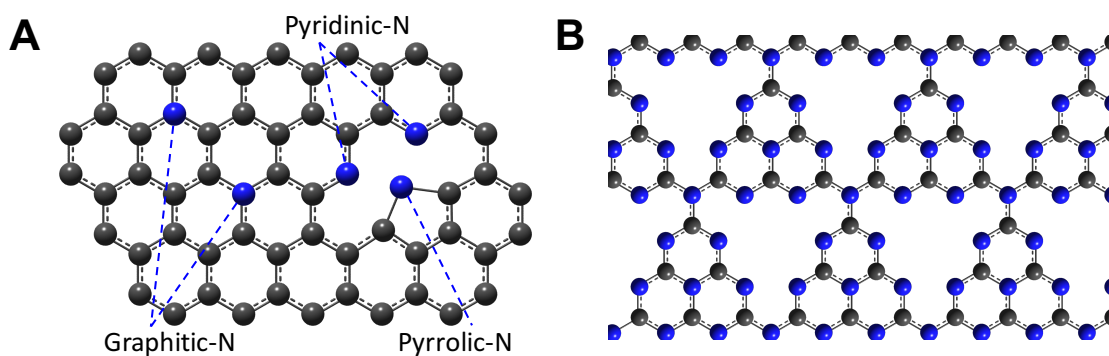
## 論文の内容の要旨

### Development of Novel Synthesis Methods for Carbon-Nitrogen Based Two-Dimensional Crystals (炭素-窒素系二次元結晶の新規成長手法の開発)

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#### 1. Introduction

Two-dimensional (2D) crystals, materials with a thickness of only one or a few atoms thick, have attracted significant research attention due to their intriguing properties and vast field of application recently. Graphene, one atomic layer of graphite with a 2D hybridized carbon structure, is one of the most famous 2D crystals from its unique properties such as high electron mobility of  $200,000 \text{ cm}^2/\text{Vs}$  and high theoretical specific surface area of  $2,630 \text{ m}^2/\text{g}$ . Nitrogen functionalization of graphene is a promising way to bring further fascinating properties to graphene and open the door to its various applications. Substitutional doping of hexagonal carbon lattice with nitrogen atoms enables graphene to modulate the electronic, chemical or structural properties. Three common bonding configurations: graphitic-, pyridinic-, and pyrrolic-N embedded within the carbon lattice, play essential roles in determining the properties (**Fig. 1A**). N-type doping occurs for graphitic-N whereas p-type doping takes place at pyridinic- and pyrrolic-N. Modifying electronic states by such N-doping opens the band gap and enhances the catalytic activity of oxygen reduction reaction while non-doped



**Fig. 1:** Chemical structure of (A) N-Gr and (B) 2D g-C<sub>3</sub>N<sub>4</sub>

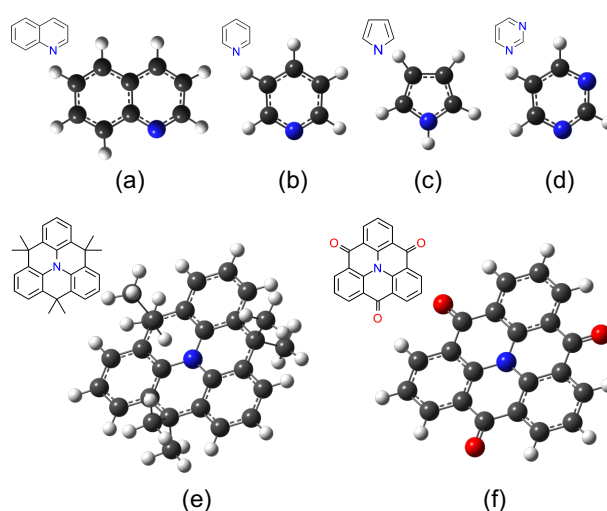
graphene has no band gap. These electronic or catalytic properties of nitrogen-doped graphene (N-Gr) are significantly affected by the doping site of the nitrogen atom. Controlling the doping site is crucial for tuning or tailoring the properties of N-Gr. Therefore it is highly expected to develop methods to realize a selective formation of nitrogen configurations in graphene networks. 2D graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>): crystalline 2D conjugated polymer an analogy to graphene, on the other hand, is also a 2D crystal made of “ubiquitous” carbon and nitrogen atoms (**Fig. 1B**). Bulk material of g-C<sub>3</sub>N<sub>4</sub> is an attractive candidate for a metal-free semiconductor and photocatalyst. Bulk g-C<sub>3</sub>N<sub>4</sub> has an intrinsic bandgap of 2.7 eV suitable for visible light and has the ability for photocatalytic water splitting. The catalytic activity increased as the thickness of g-C<sub>3</sub>N<sub>4</sub> gets decreased because of the increased specific surface area. Therefore, 2D g-C<sub>3</sub>N<sub>4</sub> is expected as a new generation photocatalyst with metal-free, low-cost, outstanding visible-light-driven photocatalyst. Hence, the method for synthesizing 2D g-C<sub>3</sub>N<sub>4</sub> is eagerly anticipated.

This thesis aimed to develop the bottom-up synthesis method of these two 2D crystals: N-Gr and 2D g-C<sub>3</sub>N<sub>4</sub>. Among the 2D crystals, these two are exceptionally attractive with its potential for next-generation electronics and energy storage devices. The N-Gr synthesis was focused on controlling the configurations of three doping sites, and fabrication of 2D g-C<sub>3</sub>N<sub>4</sub> was concentrated on creating a large-area crystalline monolayer structure, which has never been done before. Both developed methods were based on direct bottom-up synthesis strategy and different idea from the existing methods of each material.

## 2. Site-Selective Synthesis of Nitrogen-Doped Graphene from Nitrogen-Containing Heterocyclic Compounds

Fabrication approach for N-Gr can be divided into top-down methods: substitute carbon atoms with nitrogen atoms and bottom-up methods: incorporate nitrogen atoms during graphene formation. Top-down synthesis of N-Gr is achieved via nitrogen plasma treatment or ion bombardment while bottom-up synthesis is realized by chemical vapor deposition (CVD) method. In the previous work in our laboratory, N-Gr was formed on Pt (111) from several N-containing molecules as a single-source CVD precursor. The result implies the possibility that the local bonding structure around the N atom of precursor molecule might be preserved and reflected in the formed graphene network. In this work, site-selective synthesis of nitrogen-doped graphene was examined using six kinds of nitrogen-containing heterocyclic compounds as sources (**Fig. 2**). These molecules are used to aim at controlling doping sites with reflecting their N-bonding configurations to graphene.

These six compounds are divided into two groups. The first group consists of four kinds of nitrogen-containing aromatic compounds: quinolone (Fig. 2(a)), pyridine (Fig. 2(b)), pyrrole (Fig.2(c)), and pyrimidine (Fig.2(d)). The second group is composed of remaining two nitrogen-embedded cyclic triarylamines: 4,4,8,8,12,12-hexamethyl-8,12-dihydro-4H-benzo[9,1]quinolizino[3,4,5,6,7-defg]acridine (methyl-form) (Fig.2(e)) and 4H-benzo[9,1]quinolizino[3,4,5,6,7-defg]acridine-4,8,12-trione (ketone-form) (Fig.2(f)). N-Gr were synthesized from these molecules on Pt (111) substrate by single-source CVD. The as-grown films were characterized by X-ray photoelectron spectroscopy (XPS), low-energy electron diffraction (LEED) and Raman spectroscopy measurements. From nitrogen-containing aromatic compounds, each of the molecules deposited on the heated Pt (111) formed N-Gr at 500 °C, which was confirmed with



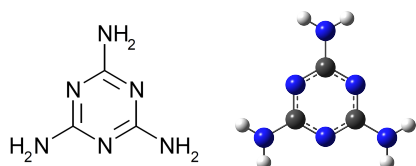
**Fig. 2:** Molecular structures of the source molecules (given in 2D and 3D representations): (a) quinolone, (b) pyridine, (c) pyrrole, (d) pyrimidine, (e) methyl-form, and (f) ketone-form.

LEED and Raman measurements. With respect to N-configurations, which was judged from XPS measurement, the pyridinic-N and pyrrolic-N were exclusively obtained from quinoline and pyrrole sources, while the pyridine-derived and pyrimidine-derived graphenes contained both pyridinic-N and graphitic-N in the graphene lattices. The difference among source molecules suggests that the N doped site in the synthesized graphene depends on the source molecule. As a consequence, the effect of precursors on the doped site was clarified, and site-selective N-doping method by source molecule was developed.

N-Gr with dominant pyridinic- and pyrrolic-N was successfully synthesized from source molecules with two-coordinated N atom. However, synthesis of exclusively graphitic-N doped graphene remains challenging. In this work, molecules with three-coordinated N were used to fabricate such N-Gr. Each of two nitrogen-embedded cyclic triaryl amines was deposited on Pt(111) respectively. At 400°C, the graphene with nitrogen atoms exclusively doped at a graphitic site was synthesized from the methyl-form, while not from the ketone-form at any temperature. From the XPS N 1s region spectra of films fabricated from methyl-form, the original chemical structure around N atom of the molecule was preserved until 300 °C (**Fig. 3A**). The peak at 401.0 eV observed for the film formed at 400 °C belongs to graphitic N species (**Fig. 3A**). The conjugation occurred locally at that temperature leading to N-doped graphene (**Fig. 3B**). The ketone-form molecule did not form N-Gr at any temperature. The interaction with a Pt surface seems to remove C-O from the ketone-form molecules at a temperature as low as 300 °C. The present result indicates that the structure of a source molecule is quite important for controlling the N-doped site in the graphene lattice.

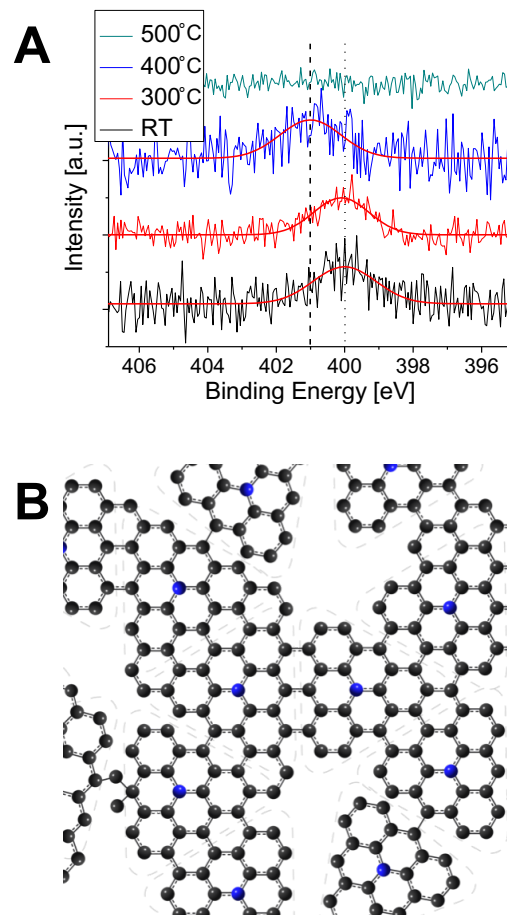
### 3. Approaches Towards the Chemical Vapor Deposition Synthesis of Graphitic Carbon Nitride: Critical Role of the Substrate and Annealing Temperature on the Thermal Behavior of Melamine

In this part, the synthesis of monolayer g-C<sub>3</sub>N<sub>4</sub> was challenged by using single-source CVD methods which is the same method as the previous part (Part 2). In the method, melamine was chosen as a source molecule and deposited on Pt



**Fig. 4:** Molecular structures of melamine represented in 2D and 3D view.

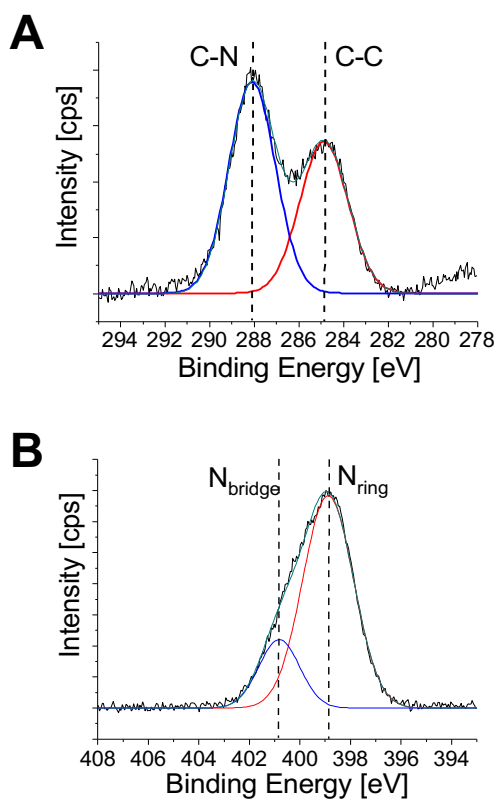
(111) and Cu (111) at different temperatures (**Fig. 4**). On Pt (111) substrate, melamine was already decomposed at room temperature, indicates strong catalytic activity of the substrate. On the other hand, a self-assembled 2D network of melamine was observed for the first time on Cu (111) at 400 °C and graphene were formed at 500 °C. Even though the g-C<sub>3</sub>N<sub>4</sub> was not formed, valuable findings were obtained from the results.



**Fig. 3:** (A) XPS N 1s spectra of films fabricated from methyl form. (B) Schematic illustration of the formation of graphitic-N doped graphene from methyl-form.

#### 4. Synthesis of Large-Area Atomically Thin Graphitic Carbon Nitride Film via Interfacial Thermal Polymerization of Melamine

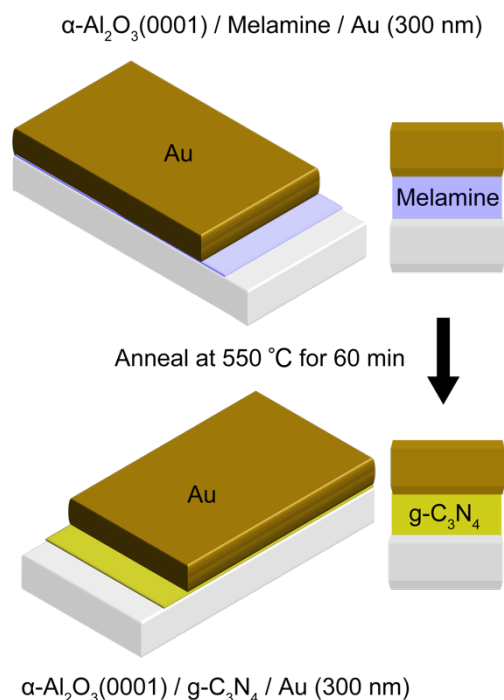
Recently, attempts for 2D g-C<sub>3</sub>N<sub>4</sub> synthesis has been growing its number. Most of them are based on a top-down method which separates monolayer g-C<sub>3</sub>N<sub>4</sub> via chemical or physical exfoliation of layered bulk g-C<sub>3</sub>N<sub>4</sub>. Such method has an advantage of facile, rapid and low-cost synthesis of g-C<sub>3</sub>N<sub>4</sub> nanosheets. However, the delamination process causes structural damage or doping of impurities to synthesized 2D g-C<sub>3</sub>N<sub>4</sub>. The exfoliation process affects not only the interlayer interaction but also intralayer  $\pi$ -conjugated polymeric networks of layered g-C<sub>3</sub>N<sub>4</sub>. The top-down method limits the grain size of 2D g-C<sub>3</sub>N<sub>4</sub> below 1  $\mu\text{m}$  and gives the g-C<sub>3</sub>N<sub>4</sub> a porous structure. Thus, bottom-up synthesis methods are desperately demanded a large scale and impurity free 2D g-C<sub>3</sub>N<sub>4</sub> production. In this work, an entirely new approach using solid/solid interface to fabricate 2D g-C<sub>3</sub>N<sub>4</sub> was devised. To create the 2D conjugated polymer



**Fig. 6:** (A) XPS C 1s region, (B) XPS N 1s region spectra of synthesized 2D g-C<sub>3</sub>N<sub>4</sub>

#### 5. Conclusion

Synthesis methods of two carbon-nitrogen based two-dimensional (2D) crystals are developed in this thesis. In the site-selective synthesis of N-Gr, three doping sites are successfully controlled by using the structure of molecular precursors. Large-scale monolayer g-C<sub>3</sub>N<sub>4</sub> was synthesized from a novel method using solid/solid interface. These works contribute to developing methods optimized for 2D crystal synthesis and are beneficial for the future application of 2D crystals.



**Fig. 5:** Schematic diagram of solid/solid interfacial synthesis of 2D g-C<sub>3</sub>N<sub>4</sub>

structure, atomically thin film of precursor: melamine (C<sub>3</sub>N<sub>6</sub>H<sub>6</sub>) was sandwiched between two solids: sapphire crystal and Au thin-film (**Fig. 5**). The confined melamine thin-film in the sapphire/Au interface was annealed and polymerized to form g-C<sub>3</sub>N<sub>4</sub> at 550 °C. After annealing, Au thin-film was etched with diluted aqua regia, and exposed thin-film on the sapphire substrate was characterized by XPS and AFM. XPS C 1s region spectra showed two configurations of carbon atoms: C-N and C-C bond (**Fig. 6A**). N 1s spectra also consisted of two peaks which can be assigned as sp<sup>2</sup>-N within an aromatic ring (N<sub>ring</sub>) and nitrogen atom bonded to three aromatic rings (N<sub>bridge</sub>) judging from its binding energy. The intensity ratio of C-N component of C 1s and N 1s (0.78) is close to the expected ratio of g-C<sub>3</sub>N<sub>4</sub> (0.75). Also, AFM measurement revealed that the fabricated film was atomically flat, and the thickness was around 1 nm. From these results, the direct synthesis of 2D g-C<sub>3</sub>N<sub>4</sub> was achieved with the novel method.