# Chemical bottom-up approach for inorganic single-atomic layers aiming beyond graphene

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# Chemical bottom-up approach for inorganic single-atomic layers aiming beyond graphene

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A chemical bottom-up approach for single-atomic layered materials like graphene is attractive due to the possibility of introducing functions. This article includes the synthesis and properties of borophene-oxide and metalladithiolene layers, which are reported as inorganic materials. They have graphene-like two-dimensional networks that enable conjugated structures. Their atomically thin layers are also available by dissolution or synthetic methods. Their two-dimensional electronic features are evaluated from the activation energies for electrical conductions, focusing on the anisotropic features of borophene-oxide layers and the switching abilities of metalladithiolene layers.

## Introduction

Two-dimensional single-layered materials other than graphene have been gathering recent attention due to their unique physical and electronic properties. For example, Xenes, which are monolayered materials of main group elements, are focused as new materials beyond graphene[1-3] including silicene,[4,5] borophene[6,7] and other examples with main group elements.[8-13] Borophene, in which boron atoms are bonded in a two-dimensional network, has received particular attention due to its mechanical flexibility, metallic feature, and superconductivity.[6,14-16] Though Xenes exhibit extremely interesting physical properties, there are still problems to be solved, such as stability, considering their application as materials. In the case of borophene, remarkable progress has been made in recent years, and large-scale synthesis using Cu surfaces has been investigated.[17,18] In addition, bilayer borophene has attracted much attention as a new material that can overcome the stability problem.[19] Stabilization by interlayer bonding of the bilayer borophenes was theoretically predicted,[20] and the synthesis and improved resistance to oxidation have been reported.[21,22] As a result, it is being researched and developed as a promising candidate for practical application as a two-dimensional material.

Chemical bottom-up synthesis of nano- or macro-sized materials is attractive for introducing or tuning the properties by the components. Metal organic frameworks are representative examples, with three-dimensionally constructed structures by metals and ligands. They are expected to have various applications, such as gas storage, gas separation, sensors and reactors by the intended design for the flameworks.[13-26] Considering the case of single-atomic layered materials, chemical synthesis is advantageous since the two-dimensional structure can be simply applied to electronic devices widely utilized in our society. However, the synthesis is more difficult since it requires control of the structure. Thus far, the preparation and functionalization of self-assembled or arranged molecules have been widely investigated.[27,28] In these cases, expression of the two-dimensional electronic or physical properties is difficult since the molecules are weakly connected with van der Waals interaction or hydrogen bonding. Therefore, development of bottom-up fabrication for two-dimensional single-atomic layers with enough electronic interactions is desired to realize design and function tuning toward the applicable materials.

In this article, the synthesis, structure and properties of single-atomic layers or their stacked materials are discussed, which are chemically synthesized from small molecules (Fig. 1). Borophene-oxide[29] and metalladithiolene layers[30] were synthesized in solution phases, and their structures and fundamental properties were clarified, focusing on their similarities and differences with graphene and borophene. The components of the layers were potassium cations and boron species for the borophene-oxide layer, and metal salts and hexathiol ligand for the metalladithiolene layer, respectively. Though the investigated are inorganic materials with boron atoms or metal complexes, they have graphene-like in-plane networks. The boron-boron bonding to form a two-dimensional network of borophene-oxide layer is comparable to that of graphene or borophene, and the structure is different from graphene-oxide possessing a disrupted carbon flame. In the case of the metalladithiolene layer, the network is formed by the connection of flat metal complexes (Fig. 1). This layer is composed of metalladithiolene rings, which have a delocalized electronic structure with resonance forms. The multi-step redox

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activities are investigated in the trinuclear complexes, indicating intense electronic interaction between metals.[31] By using nickel atoms as the metal centre, the metalladithiolene layer can have an atomically flat structure.
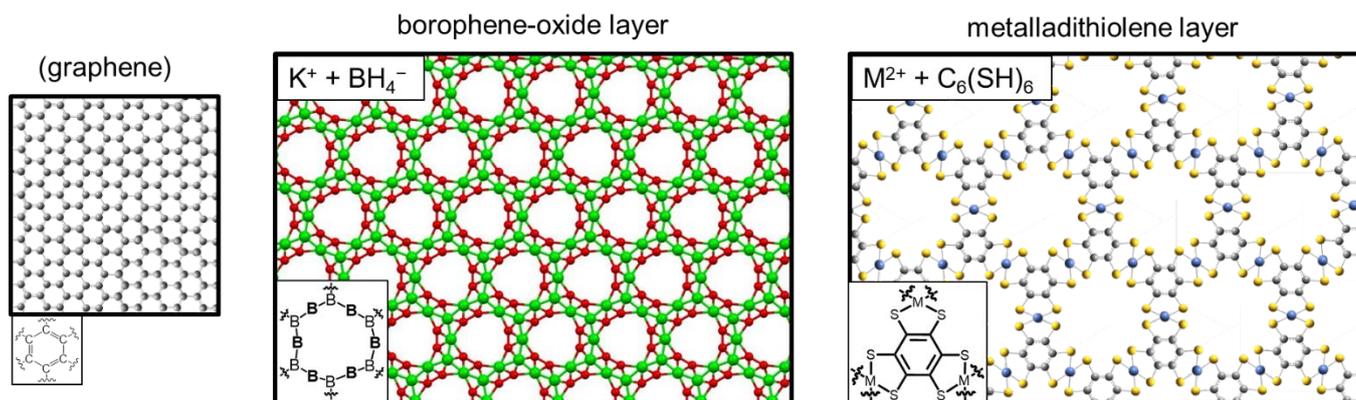


Figure 1. Structures of a) graphene, b) borophene-oxide layer and c) metalladithiolene layer. Gray: Carbon, Green: Boron, Red: Oxygen, Yellow: Sulfur. The occupancy of oxygen in the structure of b) is 50%. Therefore, the oxygen in the chemical structure is omitted, and only the boron skeleton is shown. The blue elements in c) indicate metals such as nickel atoms. Reproduced from ref. 23 with permission from ACS, copyright 2019 and ref. 24 with permission from ACS, copyright 2013.

## Topics

### Synthesis and structures of stacked materials with single-atomic layers

Borophene-oxide layer was synthesized as a layered crystal from a solution of borohydride salts by partial oxidation (Fig. 2a,b). This is a simple and low-cost method for quantitative preparation. Single crystal structure analysis revealed that there is a distorted hexagonal boron network, and the atomically flat borophene-oxide layers and the potassium cations were alternately laminated (Fig. 2c). The single-atomic layers are separated by potassium cations. The revealed distance between boron atoms to form an in-plane network (1.78 Å) was equivalent to that of borophene.
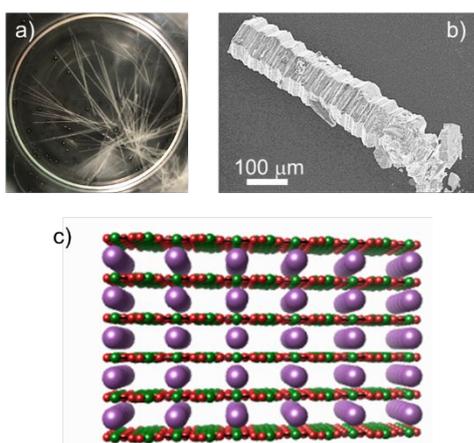


Figure 2. Synthesized borophene-oxide layers with potassium cations. a) A Photograph and b) a SEM image of the obtained crystal. c) Crystal structure of the stacked layers. Green: Boron, Red: Oxygen, Yellow: Purple: Potassium. Reproduced from ref. 23 with permission from ACS, copyright 2019.

The layered structure is also reflected in the appearance of the synthesized crystal. Optical microscope and scanning electron microscope (SEM) observations revealed the stacked form of hexagonal flakes (Fig. 2b). The crystal was easily exfoliated by applying pressure from the side. The emerged surface was smooth, suggesting brittleness between borophene-oxide layers.[29] The weak interaction was revealed by anisotropic extension along the inter-layer direction. Temperature dependency of X-ray diffraction revealed a clear shift of the (001) peak, which is corresponding to the inter-layer distance.[29] Such a feature is totally different from that of magnesium diboride, which is known as a layered material of boron, and is rather similar to that of graphite.

A unique synthesis method is used for metalladithiolene layers. The stacked crystalline material was prepared at the interface between an organic layer with organic thiol ligands (benzenehexathiol (BHT)) and an aqueous layer with metal cations. In the case of nickelladithiolene layer, nickel (II) acetate was used. Different from the case of the borophene-oxide layer, the structure of the nickelladithiolene layer is controlled by the reaction field at the flat interface (Fig. 3a). Since the interface is two-dimensionally limited, the growth of the sample in the stacking direction is regulated to form the sheet shape (Fig. 3b). The structure of the dithiolene complex sheet has a 6-fold symmetry similar to that of the borophene-oxide layer, but the lamination state is different. The nickelladithiolene layers are laminated in a zigzag manner, which is in contrast to the borophene sheet in which the layers are completely overlapped (Fig. 3c).
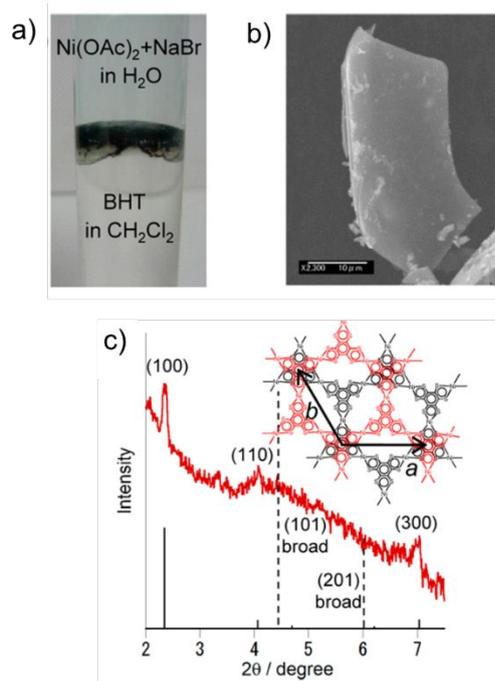
Figure 3. Synthesized nickelladithiolene layers. a) A Photograph and b) a SEM image of the obtained sample. BHT: benzenehexathiol. Powder crystal diffraction peaks and the theoretical simulation. A chemical structure demonstrates the stacked form. Reproduced from ref. 24 with permission from ACS, copyright 2013.

## Preparation of atomically thin layer

Layered materials have enough potential to be atomically thin layers. For example, mechanical exfoliation of graphite enables the preparation of graphene. In the case of the borophene-oxide layer, an atomically thin sheet was prepared from the solution. The borophene-oxide layers have weak inter-layer interactions and are dissolved in organic solvents such as $N,N$-dimethylformamide (DMF) by the solvation of potassium cations between the layers. Therefore, it is possible to prepare atomically thin sheets by casting a solution of the synthesized crystals (Fig. 4a). Such a solution-phase process is difficult in the case of graphene, since graphene and graphite have almost no solubility in solvents. Thin borophene-oxide layers (Thin BoL in Fig. 4b) with a hexagonal diffraction pattern were observed by STEM observation. From an AFM measurement, a thin sheet with a thickness of about 2 nm is reported. This thickness value suggested the formation of a double layer or the attachment of a solvent on the layer or potassium cations. An observation of a thin sheet with a thickness of 0.6 nm, corresponding to a single layer, have also been reported, but the position of the potassium cations that compensate the charges is not precisely determined. Therefore, clear observations, such as scanning tunnelling microscopy (STM) data, are expected.

In the case of the nickelladithiolene layers, since the stacked sample is almost insoluble in organic solvents, the solvation method for atomically thin layers is difficult. In contrast, a growth control method on the solution surface is developed for the atomically thin sheets. An organic solution of the benzenehexathiol ligand was put on the surface of an aqueous

solution with nickel ions, and the amount of ligand was limited so as not to exceed a single-atomic layer. The atomically thin sheet was obtained at the surface of the aqueous solution, and it was transferred on substrates (Fig. 4b). The thin sheet (nano-1) was subjected to AFM and STM observations. An atomically thin thickness of about 0.6 nm was demonstrated. In addition, a STM image assigned to be a moiré structure was observed on a HOPG substrate.
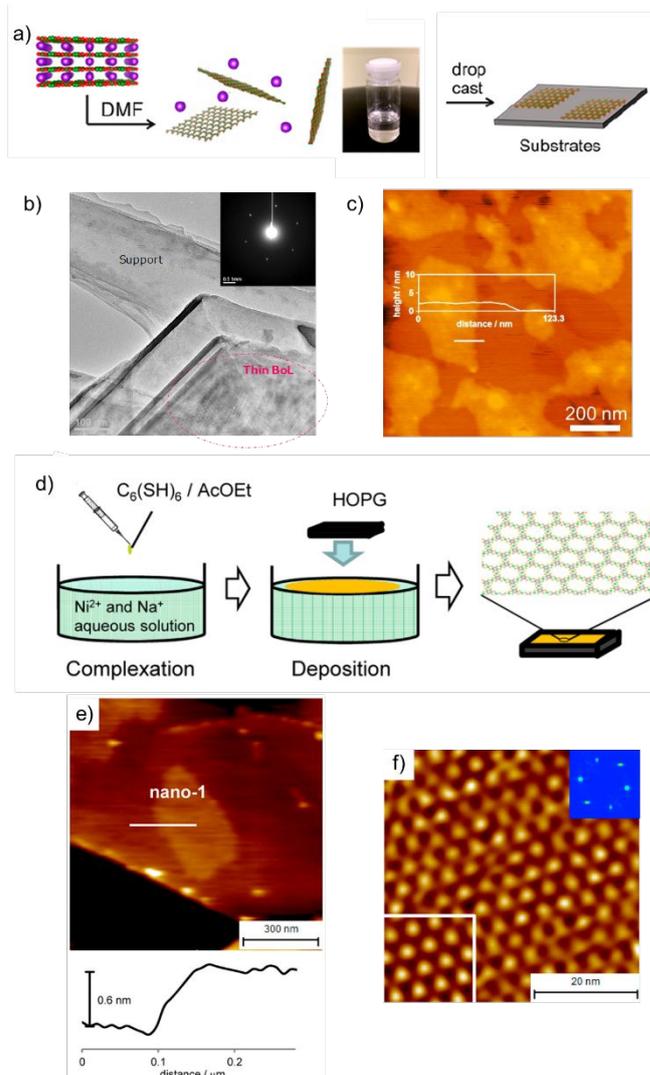


Figure 4. Preparation of atomically thin layers. a) Preparation method, and b) STEM and c) AFM images of borophene-oxide thin layers. d-f) Preparation method (d), and AFM (e) and STM (f) images of nickelladithiolene thin layers (nano-1). Reproduced from ref. 29 with permission from ACS, copyright 2019 and ref. 30 with permission from ACS, copyright 2013.

## Electronic properties

Both borophene-oxide and nickelladithiolene layers have electronic conducting properties different from those of simple metals or semiconductors. Measurements were conducted with the stacked samples (Fig. 5). Borophene-oxide layers were found to have anisotropic conductivity in the stacked crystalline form. The conducting properties are totally different between

the in-plane and inter-plane directions. Temperature dependency measurement of the conductivity revealed that there was almost zero activation energy in the in-plane direction, whereas a certain activation energy (0.2 eV) was in the inter-planar direction (Fig. 5a-c). The in-plane conducting feature with almost zero activation energy inspires the feasibility of high carrier mobility in materials like graphene.

The almost zero activation energy was also observed in the oxidized nickelladithiolene layers. The metallic electronic state of the as-prepared nickelladithiolene layers (ap-1) was revealed by the photoelectron spectroscopy on highly oriented pyrolytic graphite (HOPG). A Fermi edge was detected at 300 K, and the Fermi edge was clearer at 17 K (Fig. 5d).[32] In the case of nickelladithiolene layers, the redox activity of the metal complex is advantageous for functionalization. The oxidized and as-prepared states (ox-1 and ap-1, respectively) can be tuned by chemical oxidation or reduction treatment. The activation energies were revealed by the van der Pauw method under the control of scanning electron microscopy (Fig. 5e,f). Considering the metallic electronic state, the detected activation energies were considered to be derived from the boundary of sheet grains. The as-prepared sample (ap-1) with a mixed valence electronic state was found to have a larger activation energy (26 meV) than that of the oxidized sample (ox-1, 10 meV). In addition, changing conductivity by two orders of magnitude is also demonstrated.[32] Such electronic and physical properties observed by the two-dimensional networks are generally unavailable in simple graphene or aligned small molecules.
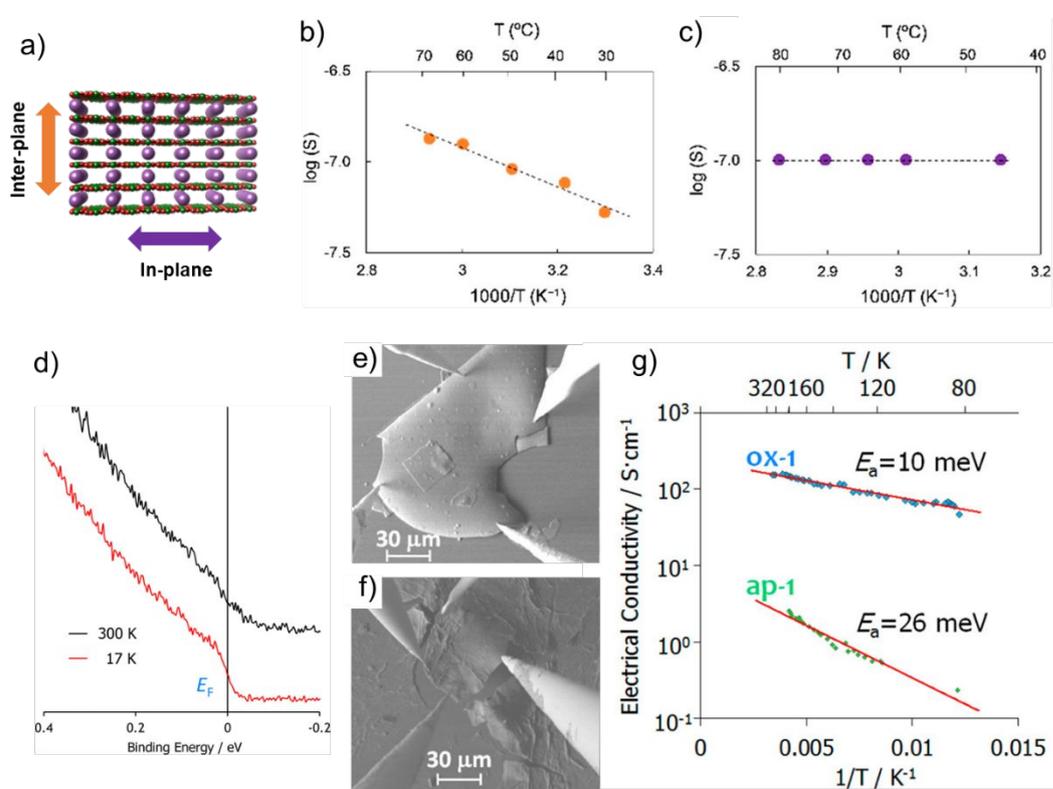


Figure 5. Temperature dependency measurements for electronic conducting properties. a) Structure of the stacked borophene-oxide layers. The temperature dependence of the b) inter-plane and c) in-plane directions. d) Photoelectron spectroscopy of as-prepared nickelladithiolene layers (ap-1). e,f) Conductivity measurements with the van der Pauw method for the oxidized nickelladithiolene layers (ox-1) and the as-prepared nickelladithiolene layers (ap-1), respectively. g) Temperature dependence of the conductivity. Reproduced from ref. 29 with permission from ACS, copyright 2019 and ref. 32 with permission from ACS, copyright 2013.

Table 1. Conductivity measurement and activation energies.[23,24]

| sample | | sample form | measurement direction | method | $E_a$ / eV |
|---|---|---|---|---|---|
| borophene-oxide layers | | crystal | in-plane | AC impedance | $\simeq 0$ |
| | | crystal | inter-plane | AC impedance | 0.2 |
| nickelladithiolene layers | oxidized | stacked sheet | in-plane | van der Pauw method | 0.010 |
| | as-prepared | stacked sheet | in-plane | van der Pauw method | 0.026 |

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## Conclusions and outlook

This article describes chemically prepared two-dimensional single-atomic layered structures with in-plane bonding networks, focusing on borophene-oxide and metalladithiolene layers. Such bottom-up synthesis has enough possibility to design the functions of the materials for the application. In the case of borophene-oxide layers, it is expected that tuning the amount of metal cations between layers will lead to the control of physical and electronic properties. It was recently reported that the weak interaction between layers via potassium cations makes this material an active liquid crystal.[33] The wide active range of the liquid crystal was revealed due to its inorganic and two-dimensional structure. The relatively flexible feature derived from the single-atomic layered structure is considered to support the realization of the liquid crystalline state.

The structure control synthesis used for metalladithiolene layers[30] is already developed for various kinds of two-dimensional materials. Expansion of the ligands and metals has been investigated, and two-dimensional coordination nanosheets (CONASHs) with optical or redox active functions have been widely reported.[34-40] Such variation in the building blocks expects further development not only for functional electronic devices but also for high-performance batteries and catalyst systems that utilize the wide surface areas.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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