Elemental 2D Materials: Progress and Perspectives Toward Unconventional Structures

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Elemental 2D materials have attracted a great deal of interest due to their excellent properties for various applications in catalysis, sensing, photonics, intracellular gene regulation, magnetism, superconductivity, and so on. It is broadly accepted that the physicochemical properties are highly associated with their atomic arrangements and coordination. Recent studies have demonstrated that unconventional structures of elemental 2D materials exhibit unexpected physicochemical properties and innovative applications beyond conventional structures. Those unconventional structures bring new life to elemental 2D materials and deserve special attention. However, there are considerable challenges to controllably prepare them due to their metastable characters. Herein, their synthetic strategies are focused on to shed light on the reasonable design of new structures with special atomic arrangements to open up tremendous opportunities for expanding their functionalities and potential applications. In addition, the correlations among the types of unconventional structures, the element types, and corresponding synthetic strategies are uncovered. Finally, based on the achievements in the representative studies, some prospects and potential opportunities for extending the scope of elemental 2D materials with unconventional structures and potentially distinctive applications are provided.

1. Introduction

Since the production of isolated graphene, 2D materials have been a research focus in various fields owing to unique physicochemical properties resulting from their atomic thickness,[1,2] Among all 2D materials, elemental 2D materials have attracted overwhelming attention and grew rapidly due to their anisotropic structures, unprecedented properties, and promising applications in photoelectric devices, sensors, catalysis, and energy storage.[1,3–6] It is broadly accepted that the physicochemical properties are highly associated with their atomic arrangements and coordination. Recent studies have demonstrated that unconventional structures of elemental 2D materials exhibit novel physicochemical properties and innovative applications beyond conventional structures.[7–11] Unlike bulk boron allotropes known to be semiconductors at normal pressure, unconventionally structured borophene exhibits anisotropic metal properties, which could be attractive for superconductivity.[10,12] Unconventional 4H gold (Au) nanoribbons have been found to produce strong infrared plasmon absorption, and they are quite different from the conventional face-centered cubic (fcc) Au nanoribbons of optical response.[7] Amorphous elemental 2D materials usually reveal extraordinary mechanics and catalytic properties because of the arrangements of atoms absence of long-range periodicity.[8,11] Novel unconventional structures are disclosed, which not only greatly enrich the existing elemental 2D material system, but also provide an addressable platform for studying the structure-dependent property in-depth. In addition, the study of them can provide a deeper understanding of the mechanism of the mutual transformation between thermodynamically stable structures and metastable structures, which is conducive to rationally designing new structures to open up tremendous opportunities for expanding functionalities and potential applications of 2D materials (Table 1).

However, unlike conventional structures, which are inherently easy to synthesize, the synthesis of unconventional structures remains substantial challenges due to their metastable characters. Hitherto, many researchers have made tremendous efforts to synthesize elemental 2D materials with unconventional structures and developed a series of strategies, including surface modification, epitaxial growth, electron beam irradiation, crystal inhibition, and high pressure.[13–18] However, present scientific achievements and systematic understanding of effective synthetic strategies have not been presented yet. It is highly demanded to give a clear guideline of the different strategies for controlling the preparation and reasonable design of unconventional structures of elemental 2D materials.

In this perspective, first we provide a brief overview of experimental and theoretical investigations of representative unconventional structures of elemental 2D materials. Their extraordinary properties and potential applications also have been displayed. Subsequently, we systematically summarize the progress of strategies for the unconventional structures,
specifically, surface modification, epitaxial growth, electron beam irradiation, crystal inhibition, and high pressure. Based on the achievements in these effective synthetic strategies, we present opinions on the key factors for the controllable preparation of the elemental 2D materials with unconventional structures. In addition, correlations among the types of unconventional structures, the element types, and corresponding synthetic strategies are disclosed. Finally, we will provide some prospects and potential opportunities for extending the scope of elemental 2D materials with special atomic arrangements and facilitate their applications.

2. Overview of Unconventional Structures of Elemental 2D Materials

Conventionally, an elemental 2D material adopts the same atomic configuration as its stable bulk counterpart. However, unconventional structures that are not commonly observed in the bulk state have been observed in elemental 2D materials, including not only thermodynamically metastable structures, such as metastable crystal phases, amorphous phases, heterophases, non-close-packed exposed crystal surfaces, and so on, but also many intrinsically kinetically unstable structures which are stabilized by external factors.\[7,8,10,14,15,19–21\] As defined here, unconventional structures of elemental 2D materials are those that adopt different atomic configurations from their stable bulk counterparts.

To prepare the thermodynamically metastable structures successfully, the following two conditions need to be met: 1) the excess enthalpy or excess free energy of a thermodynamic system increases to a certain value by some external process; 2) the metastable structures injected with excess enthalpy and excess free energy cannot be recovered. It is worth noting that the obtained metastable structures are relatively stable, although they tend to transform into thermodynamically stable structures because their Gibbs free energy is higher than that of stable structures. Here, only when the external conditions release their excess enthalpy or excess free energy, such as heating, electron beam irradiation, aging, and so on, the transition can occur.\[22–25\] In addition, a stable phase can also be transformed into a metastable phase under certain external conditions. For example, increasing pressure can move the phase boundary, making a stable phase unstable.\[18\] For an intrinsically kinetically unstable

| Synthetic strategies          | Elemental 2D materials                  | Unconventional structures                  | References |
|------------------------------|-----------------------------------------|--------------------------------------------|------------|
| Surface modification          | Au square sheets                         | hcp phase                                  | [23]       |
|                              | Au nanoribbons                           |                                            |            |
|                              | Au square sheets                         | 4H phase and (001)-oriented fcc phase      | [7]        |
|                              | Au square-like plates                    | (100)-oriented fcc phase                   | [13]       |
|                              | Pd nanosheets                            | Alternating hcp/fcc phase                  | [57]       |
|                              | Ag nanoplates                            | Amorphous phase                            | [32]       |
|                              |                                        | 4H phase and 2H phase                      | [40]       |
| Epitaxial growth             | Silicene, germanene, and antimonene      | Buckled honeycomb structures               | [26-29]    |
|                              | Borophene                               | Triangular lattice with periodic hexagonal holes | [10,20,21,31] |
|                              | Au@Pt and Au@Pd core–shell nanoplates   |                                            |            |
|                              | Borophene                               | Pure honeycomb structure                   | [14]       |
|                              | Hf                                      | Pure honeycomb structure                   | [65]       |
|                              | Bimetallic Au@M (M = Ag, Pd, Ir, Rh, Os, Ru, and Cu) | 4H/fcc crystal structure                         | [7,19]    |
|                              | core–shell nanoribbons                  |                                            |            |
|                              | Trimetallic Au@PdAg nanoribbons and quarter-metallic Au@PdAg nanoribbons | 4H/fcc crystal structure | [66] |
| Electron beam irradiation    | Monolayer Mo membranes                  | Close-packed hexagonal plane structure      | [68]       |
|                              | Single-atom-thick layer of Fe            | (100)\text{b}                             | [69]       |
|                              | Ultrathin Mo membranes                   | A rectangular (110) crystal face           | [17]       |
| Crystal inhibition           | BP                                      | Amorphous phase                            | [51,71]    |
|                              | Red phosphorus                           | Amorphous phase                            | [9]        |
|                              | Monolayer C                              | Amorphous phase                            | [8]        |
|                              | Si sheets                                | Amorphous phase                            | [53]       |
|                              | Monometal nanosheets (Ir, Rh, and Ru nanosheets), bimetal nanosheets (RhFe and IrRu nanosheets), and trimetal nanosheets (IrRhRu nanosheets) | Amorphous/crystalline heterophase | [22] |
|                              | Pd sheets                                | fcc phase                                  | [18]       |

Table 1. Synthetic strategies of elemental 2D materials with unconventional structures.
structure, the substrate–structure interaction may eliminate its virtual frequency and make it stable.\[10,14,20,21\] Given that the properties of elements and the corresponding synthetic strategies are closely related to their positions in the periodic table and atomic structures, in this section, we will systematically introduce unconventional structures of elemental 2D materials according to the position of the elements in the periodic table.

Graphene is the first planar 2D material with the honeycomb structure adopting \( sp^2 \) hybridization revealed in nature. Subsequently, more and more main group elemental 2D materials have been successfully synthesized. Group IV A elements have four outer-shell electrons made up of the \( sp^2 \) configuration. Unlike carbon (C), which can easily adopt the flat configuration of \( sp^2 \), silicon (Si), germanium (Ge), and stannum (Sn) are more stable and energetically favorable in the \( sp^3 \)-hybridized tetrahedral configuration in bulk than in \( sp^2 \) hybridization because the atomic radius, electronegativity, and energy difference between the \( s \) and \( p \) orbitals are different from those of C. So far, a large number of unconventional buckled honeycomb building blocks and structures of group IV A elemental 2D materials adopting unconventional mixed \( sp^2–sp^3 \) hybridizations have been successfully synthesized by vapor-phase epitaxial growth methods (Figure 1).\[22–29\] The substrate–structure interaction could effectively change their atomic configuration through competing with the intrinsic \( sp^3 \) hybridization, including the tensile stress and electron doping. For group III A elements, all elements are metals except boron. Their 2D metals are currently available in the same atomic configuration as their bulk counterparts. Note that the intriguing element, boron, is the lightest valence-three element, and no 2D planar structure exists in its crystals since they are built from \( B_{12} \) icosahedra.\[10\] However, the intrinsic electron deficiency makes it have the ability to form an enormous number of unconventional 2D polymorphs on different metal substrates. These 2D boron polymorphs commonly consist of triangular grids with periodic holes.\[10,20,21,31\] In addition, the honeycomb structure of 2D boron with true hexagonal configuration as graphene also has been obtained by metal substrate epitaxial growth (Figure 1).\[14\] As for group V A elements, their 2D materials could be easily obtained via exfoliation, which takes the same atomic configuration as their bulk counterparts with

![Figure 1](www.advancedsciencenews.com)
layered structures, and no unconventional structures have been reported yet.\textsuperscript{[12–18]}

For transition metal elemental materials, the metallic atoms tend to form close-packed structures in three dimensions due to the directionless nature of metallic bonds. Generally, 2D transition metal materials typically crystallize with the same phase as their bulk counterparts, such as noble metals (Au, Ag, Pd, Pt, Rh, and Ir) with an fcc phase and nonnoble metals (Fe and Mo) with a body-centered cubic (bcc) phase.\textsuperscript{[19]} Note that some unconventional crystal phases of transition metal materials can be stable in ultrathin 2D materials, such as 2H, 4H 2D Au, Ag materials, alternating hexagonal close-packed (hcp)/fcc 2D Au materials by surface modification, and unconventional multilatellite 4H/fcc 2D materials obtained by solution-phase epitaxial growth on unconventional structured Au materials (Figure 1).\textsuperscript{[7,15,19,23,40]} In addition, the crystallographic direction in the crystalline phases is another degree of freedom for determining the atomic arrangements. Transition metal elemental 2D materials generally expose crystal faces with common (111)_t, (110)_h, and (001)_h.\textsuperscript{[41–43]} Those commonly exposed crystal faces are all the close-packed facets with the lowest surface energy. However, transition metal elemental 2D materials may expose non-close-packed crystal facets through special synthetic methods, which can effectively reduce surface energy resulting in minimizing the total systemic energy. Up to now, a series of 2D transition monometallic and bimetallic materials with non-close-packed facets have been synthesized through surface modification and solution-phase epitaxial growth methods, such as (001)_h-oriented fcc Au nanoribbons, (100)_h-oriented fcc Au square sheets, ultrathin bimetallic (101)_h-oriented fcc Au@Pt and Au@Pd core–shell nanoplates, (100)_h-oriented fcc Au@Pt, and Au@Pd square nanoplates (Figure 1).\textsuperscript{[7,15,16]}

Unconventional structures of elemental 2D materials aforementioned are all crystalline phases, as for the amorphous phase structures, which are the most thermodynamically unstable phase and exist in both metallic and nonmetallic materials. Impressively, compared with crystalline materials, amorphous materials usually possess unique physicochemical properties, due to their arrangements of atoms absence of long-range periodicity.\textsuperscript{[44,45]} In recent years, diverse amorphous 2D materials, such as elemental materials, transition metal dichalcogenides, metal oxides, metal hydroxide, and metal phosphates, have been successfully synthesized and demonstrated surprising performance in the fields of mechanics, magnetism, catalysis, energy storage, and biosensors.\textsuperscript{[46–50]} Here, preparing amorphous 2D element materials presents enormous challenges owing to their strong interatomic bonding and the metastable character greatly hampering their widespread researches and applications. At present, some amorphous elemental 2D materials have been successfully synthesized by ligand exchange and crystal inhibition, including nonmetallic black phosphorous (BP), red phosphorus, monolayer C, Si sheets, monometal nanosheets (Pd, Ir, Rh, and Ru nanosheets), bimetal nanosheets (RhFe and IrRu nanosheets), and trimetal nanosheets (IrRhRu nanosheets) (Figure 1).\textsuperscript{[8,9,13,51–53]}

3. Properties and Potential Applications of Unconventional Structures

Importantly, those unconventional structures have endowed the intriguing physicochemical properties for various potential applications in plasmonic, catalysis, photonics, mechanics, and so on. Unlike bulk boron known to be semiconductors at normal pressure, unconventionally structured borophene exhibits anisotropic metal properties, which could be attractive for superconductivity (Figure 2a).\textsuperscript{[10,12]} Zhang et al. revealed that unconventional 4H Au nanoribbons had very strong infrared plasmon absorption and quite different optical response from conventional fcc Au nanoribbons, which might have promising plasmonic applications (Figure 2b,c).\textsuperscript{[7]} Significantly, amorphous elemental 2D materials usually reveal extraordinary mechanics, electrical and catalytic properties because of the arrangements of atoms absence of long-range periodicity. Amorphous 2D BP presents an amazing high exciton diffusion coefficient and long exciton lifetime and has the prospect of low-cost and high-performance optoelectronic devices.\textsuperscript{[51]} Monolayer amorphous C has been found to exhibit unique mechanical and insulation properties recently.\textsuperscript{[52]} Li’s group performed a divided oxygen evolution reaction (OER) to evaluate the electrocatalytic performance of amorphous Ir nanosheets.\textsuperscript{[13]} Compared with the crystalline Ir nanosheets, commercial RuO$_2$ and IrO$_2$ catalyst, the amorphous Ir nanosheets display the lowest overpotential for a current density of 10 mA cm$^{-2}$ and the smallest Tafel slope (Figure 2d,e). They attributed this superior OER activity to abundant active sites and faster charge transfer (Figure 2f).

In addition to the experimentally realized unconventional structures of element 2D materials, several structures are theoretically predicted, which would inject fresh blood into a wide variety of applications. Penta-graphene is entirely composed of pentagons structure, which displays a negative Poisson’s ratio, a large bandgap, and ultrahigh mechanical strength.\textsuperscript{[54]} Popgraphene, which is another new 2D planar carbon allotrope consisted of 5-8-5 carbon rings, might be a promising anode material for Li-ion batteries with fast charge/discharge rates.\textsuperscript{[55]} Tetra-silicene, which has a similar puckered configuration to that of phosphorene constituted of only Si tetragons, would have an indirect bandgap (0.19 eV) and admirable carrier mobility.\textsuperscript{[56]}

For the moment, there are few studies on the properties and applications of unconventional structures. The in-depth study of unconventional structures can contribute to the flourishing of 2D materials and more efforts will need to be devoted in the future.

As aforementioned, the unconventional structures of elemental 2D materials might bring about extraordinary physicochemical properties and innovative applications due to the distinct atom arrangements. In the following section, we will give a systematic overview of the achievements of representative synthetic strategies to inspire researchers to rationally design new materials with special structures and facilitate their applications.
4. Synthetic Strategies of Unconventional Structures

4.1. Surface Modification

Recent studies have demonstrated that wet-chemical synthesis is an effective method to synthesize 2D metal materials.\(^7,15,23,43,57,58\) Conventionally, thermodynamic nonstable phases and non-close-packed crystal surfaces are not available due to their high systemic energy. In ultrathin 2D element materials, the surface energy becomes dominant in the total systemic energy. The significance of adsorption of adsorbent in the solution can realize surface modification, which can effectively control phase and growth direction through effectively reducing surface energy highlighted by Zhang’s group in their recent articles.\(^7,15,23,52,57\) A schematic diagram for the formation of elemental 2D materials with unconventional structures by surface modification is shown in Figure 3a.

To date, by surface modification, the abundant unconventional structures of 2D transition metals have been obtained, including metastable crystal phases, amorphous phases, and heterophases, non-close-packed crystal facets. Zhang et al. first reported hcp Au square sheets on graphene oxide (GO) sheets capped by oleylamine via the wet-chemical synthetic method.\(^23\) The crystallographic models and the high-resolution transmission electron microscopy (HRTEM) image of as-obtained Au square sheets indicate that the Au square sheets grow along the normal [110] direction with adopting ABAB stacking along the [001] direction (2H phase) (Figure 3b,c). It is the presence of oleylamine on the surface of Au square sheets that reduces the surface energy and enables it to exist stably, even though the fcc phase is more stable than the hcp phase in the bulk Au. Subsequently, they also successfully synthesized another new metastable hexagonal 4H phase of Au nanoribbons by colloidal synthesis.\(^7\) Different from the hcp (2H type) Au, 4H phase Au nanoribbons have the "ABCB" stacking order along the close-packed [001] direction (Figure 3d). Note that another surface 1,2-dichloropropane molecules are important presenting in this colloidal synthesis to obtain 4H phase Au nanoribbons. They found that only twinned fcc Au nanoribbons and a small amount of Au nanowires were acquired without 1,2-dichloropropane molecules.

The fact that phase transitions can be achieved by surface ligand exchange further confirms that surface modification is an effective strategy for the successful synthesis of the 2D metal materials with unconventional structures. For instance, Zhang et al. reported that (100) oriented fcc Au square sheets were acquired by converting the hcp Au square sheets with the aid...
of ligand. The selected area electron diffraction (SAED) pattern of a typical Au square sheet obtained by octadecanethiol (ODT) exchanging oleylamine initially capped on the Au square sheet demonstrates that the Au square sheets are fcc phase with the unique (100) orientation (Figure 3e). And the Au square sheets possess a square lattice pattern (Figure 3f). In addition to ODT, they also found other various kinds of thiol molecules could be used for the fcc phase Au sheets with the (100) orientation, including benzene, monothiol, carboxylic acid, dithiol, and hydroxide. Surprisingly, ligand exchange can also induce the common fcc phase Pd nanomaterials to transform into an unusual amorphous phase (Figure 3g, h).

Here, ligand exchange destroys the original crystal structure resulting in lattice distortion of fcc phase Pd nanomaterials. The adsorption of ligand plays an important role in controlling not only the crystal phase but also the growth direction. For example, (001)-oriented fcc Au nanoribbon could be obtained from (110)4H-oriented 4H Au nanoribbon by ligand exchange-induced phase transformation. However, the reason for the oriented transformation is still unrevealed.

Apart from single-phase 2D metal materials with unconventional structures, 2D metal materials with heterophases can also be obtained by surface modification. Zhang et al. obtained Au square-like plates possess alternating hcp/fcc phases in the center and fcc phases at the edges through a secondary growth method. The difference between the thickness of the center and the edge confirms the existence of surfactants (1-aminooctadecene) on both sides of the Au square-like plates. In addition to Zhang’s research group, Zheleva et al. also demonstrated surface modification by capping agents could stabilize the metastable structures and was an important determinant of the crystal structure through the synthesis of Ag nanoplates with different phases.

Surface modification is a promising strategy for unconventional phases and crystal facets of elemental 2D metal materials by effectively reducing surface energy. However, except for 2D Au and Ag, other unconventional structures of elemental 2D metal materials are rarely reported by this strategy. Maybe it is attributed to the absence of appropriate surface modifiers. Therefore, more efforts are needed to prepare other elemental 2D metal materials with unconventional phases and crystal facets.

4.2. Epitaxial Growth

Epitaxial growth has been proved to be an effective method for preparing unconventional structures of element 2D materials,
including vapor-phase epitaxial growth and solution-phase epitaxial growth.

The substrate in the vapor-phase epitaxial growth plays a vital role in the growth of elemental 2D materials, which is not only as the growth template but also affects the nucleation and surface diffusion.\(^{[59,60]}\) In addition, the structures of elemental 2D materials strongly depend on the substrates because the interactions can effectively change their atomic configuration.\(^{[12,61]}\) The tunability of the interaction between the different substrates and 2D sheets could bring about diverse unconventional structures. It has been well documented that numerous unconventional structures of 2D elemental materials could be synthesized owing to the tensile stress and electron doping deriving from the interaction between the substrates and sheets, including the majority of group IV A elemental 2D materials, 2D boron sheets, and a few transition metals. A schematic diagram for the formation of elemental 2D materials with unconventional structures by vapor-phase epitaxial growth is shown in Figure 4a.

Si, Ge, and Sn are more stable when adopting the \(sp^3\)-hybridized tetrahedral configuration in bulk. Pure 2D Si, Ge, and Sn materials could only be obtained by substrate–structure interaction which can compete with the intrinsic \(sp^3\) hybridization to make them take \(sp^2–sp^3\) hybridizations. For example, Wu et al. demonstrated that a variety of 2D silicon, including the H phase, T phase, and silicene, could be obtained on the Ag(111) substrate. Figure 4b shows the high-resolution scanning tunneling microscope (HRSTM) image of the obtained monolayer silicene.\(^{[26]}\) The evolution of those monolayer super-structured silicons on the Ag(111) substrate relies on the coverage and the growth temperature. These phases are all honeycomb structures different from any known surface structures of bulk silicon. In addition, those honeycomb structures are buckled, on account of the interaction between silicon sheets and the Ag substrate. The top and side views of the atomic structure model of silicene are shown in Figure 4c.

Similarly, diverse unconventional structured 2D borophene sheets have been experimentally realized on the Ag, Au, Cu, and Al metal substrates.\(^{[10,14,20,21,31]}\) Typically, owing to electron deficiency of boron, the 2D borophene sheets commonly exhibit a triangular lattice but with different arrangements of periodic

Figure 4. Vapor-phase epitaxial growth for elemental 2D materials with unconventional structures. a) Schematic illustration of the formation of elemental 2D materials with unconventional structures by vapor-phase epitaxial growth. b) HRSTM image of silicene on Ag(111). c) Top and side views of the atomic structure model of silicene. The red, gray, and green balls represent the upper buckled, in-plain, and lower buckled Si atoms, respectively. Reproduced with permission.\(^{[26]}\) Copyright 2012, American Chemical Society. d,e) HRSTM image of \(\beta_{12}\) borophene and \(\chi_3\) borophene on Ag(111). Reproduced with permission.\(^{[21]}\) Copyright 2016, Springer Nature. f,g) Structural models and electron density of honeycomb borophene on Al(111) and Ag(111). Reproduced with permission.\(^{[14]}\) Copyright 2018, Elsevier. h) HRSTM image of Hf layer on an Ir(111) surface. i) The close-up image of Hf adlayer with honeycomb lattice and a height profile taken along the blue line in the close-up image. Reproduced with permission.\(^{[65]}\) Copyright 2013, American Chemical Society.
hexagonal holes (Figure 4d,e).\textsuperscript{[21]} The freestanding $\delta_6$ and $\beta_{12}$ borophene are unstable due to possessing imaginary modes around the $\Gamma$ point.\textsuperscript{[62,63]} However, for $\beta_{12}$ borophene, only 1% in-plane tensile strain can make it stable.\textsuperscript{[62,64]} As a result, $\beta_{12}$ borophene could be obtained on both Cu(111) and Ag(111) surface owing to the tensile stress of the interaction between the substrates and sheets.\textsuperscript{[10,20,21]} Apart from tensile stress, electron doping can also stabilize 2D borophene structures. There is a particularly striking example of pure honeycomb borophene. As we aforementioned, the boron with the electron deficiency tends to form triangular lattices with periodic hexagonal holes instead of true hexagonal configuration due to its instability. However, Wu et al. recently synthesized the honeycomb borophene on Al(111) substrate.\textsuperscript{[14]} Through density functional theory studies, they asserted that the stability of honeycomb borophene was attributed to about 0.7 electrons transferred from Al(111) substrate to each boron atom. The Al(111) substrate has a high electron density and a relatively low work function resulting in a more efficient charge transfer from the substrate to boron than other metal substrates, such as the aforementioned Ag(111) substrate. According to theoretical calculations on honeycomb borophene on Ag(111) substrate, there is little electron accumulation at the interface between Ag(111) substrate and honeycomb borophene, suggesting negligible charge transfer between the Ag(111) substrate and borophene (Figure 4fg).

Apart from the main group elements, Gao et al. successfully prepared transitional elements Hf honeycomb on Ir(111) by vapor-phase epitaxial growth, which was the first example of transition metal honeycomb structures (Figure 4h,i).\textsuperscript{[65]} Previously, all of the 2D honeycomb materials were reported consisting of elements with $p$ orbitals electronic structure without $d$ electrons. Compared with vapor-phase epitaxial growth, solution-phase epitaxial growth has attracted enormous attention for effectively obtaining bimetallic or multimetallic 2D metallic materials with unconventional single- or heterostructure phases without ultrahigh vacuum and high temperature.\textsuperscript{[7,15,16,19,66]} A schematic diagram for the formation of bimetallic or multimetallic 2D metallic materials with unconventional structures by solution-phase epitaxial growth is shown in Figure 5a.

Here, Au or Au-based composite materials with unconventional structures usually were used as the templates, including 4H Au nanoribbons, hcp Au square sheets, and 4H/fcc Au@Ag nanoribbons. For example, a series of bimetallic Au@M ($M = \text{Ag, Pd, Ir, Rh, Os, Ru, and Cu}$) core–shell nanoribbons with an unusual 4H/fcc crystal structure have been obtained by using 4H Au nanoribbons as the template.\textsuperscript{[7,19]} Interestingly, all aforementioned 4H/fcc crystal structures have an alternating 4H and fcc crystal structure along with the close-packed directions of $[001]_{\text{fcc}}$/$[111]_{\text{hcp}}$ (Figure 5b). The 4H phase of M could be stabilized via this epitaxial growth process, and the deposition of M on the surface of Au nanoribbons resulted in the original 4H Au transforming into 4H/fcc polytypic structure. Impressively, with the help of galvanic reaction, multilayer 4H/fcc 2D materials could be successfully synthesized by epitaxial growth of expected metals on alternating 4H/fcc Au@Ag nanoribbons, including but not limited to 4H/fcc trimetallic Au@PdAg nanoribbons and quarter-metallic Au@PtPdAg nanoribbons (Figure 5c).\textsuperscript{[66]} In addition, the unique (100)-oriented fcc bimetallic Au@Ag core–shell square sheets could be obtained by using hcp Au square sheets as the template (Figure 5d).\textsuperscript{[35]} Here, the epitaxial growth mechanism of bimetallic Au@Ag nanosheets was identified due to continuous lattice fringes from the Au core to the Ag shell (Figure 5e). They also reported that ultrathin bimetallic fcc Au@Pt and Au@Pd core–shell nanoplates with a unique (101)$_3$ orientation were synthesized through the solution-phase epitaxial growth method (Figure 5f).\textsuperscript{[16]} Interestingly, in addition to the obtained fcc Au@Pt and Au@Pd with a unique (101)$_3$ orientation rhombic nanoplates, there were a small amount of (100)$_1$-oriented Au@Pt and Au@Pd square nanoplates (less than 10% yield) in the final products. Through experimental and theoretical studies, the reason for phase transformation was revealed attributing to the interplay between the epitaxial strain, surface energy, and phase stability when the Pt or Pd shell epitaxially grew on hcp phase Au square sheets surface. However, the reason for the oriented transformation is also still unrevealed.

The substrates or seeds used for epitaxial growth, on one hand, provide growth templates for epitaxial structures and, on the other hand, can stabilize unconventional structures through the substrate–structure interactions, including the tensile stress and electron doping. However, these unconventional structures can only stably exist when attached to the growing substrates, which limits the applications on any substrates.

4.3. Electron Beam Irradiation

Electron beam irradiation, which is often considered negative for 2D materials, has been considered to be a reliable technique for achieving single-atom manipulation in recent years. A schematic diagram for elemental 2D materials with unconventional structures by electron beam irradiation is shown in Figure 6a. When suitably energetic electron beam irradiates metal compounds, the low-Z element (e.g., C, Se, etc.) might be removed due to knock-on effect and ionization.\textsuperscript{[67]} As a result, the rest of the high-Z element (metal) will transform into unconventional structures of elemental 2D materials. For example, Pennycook et al. successfully obtained monolayer Mo membranes via selectively ionizing Se atoms in monolayer MoSe$_2$, and Mo atoms reserved the close-packed structure of the sandwiched Mo layer in MoSe$_2$ nanosheets, which is a symmetrical hexagonal plane of crystals different from the bcc structure of bulk Mo metal (Figure 6b).\textsuperscript{[68]} Rummeli et al. synthesized a free-standing single-atom-thick layer of Fe with a square (100) crystal face instead of (110) crystal face suspended in graphene pores, which is the bcc phase close-packed facets with the lowest surface energy (Figure 6c,d).\textsuperscript{[69]} The interaction between graphene and 2D Fe stabilizes the square (100) crystal face.

Apart from single-atom manipulation in the irradiation process, adsorption control can also be achieved to obtain some unconventional structures. Recently, our group revealed that ultrathin Mo membranes with a low-symmetry rectangular (110) crystal face could be synthesized successfully by an adsorption-free reaction (Figure 6e).\textsuperscript{[70]} It is the first time that the low-symmetry lattice structure of 2D transition metals has been experimentally realized, although the rectangular lattice structure exists some transition metals crystal faces. Image simulations verify that the obtained rectangular lattice structure
is AB stacked Mo(110) with even atom thickness (2, 4, etc.), as shown in Figure 6f. Theoretical calculations indicate that the (100) face possesses the lowest energy, followed by the (110) face, and finally the (111) face after the adsorption of C or O (Figure 6g). In addition, a common symmetrical square lattice structured Mo(100) could be obtained in the majority of the regions when using amorphous Mo with C and O adsorption, and the 2D α-Mo2C/graphene vertical heterojunction as the starting material (Figure 6h,i). These results powerfully confirm the claim that no foreign atoms being adsorbed is a key factor for the successful preparation of the (110) faced bcc phase 2D transition metal. Here, because the continuous electron beam irradiation will proceed and sputtered C atoms continuously entering the vacuum of the microscope, C atoms will not undergo secondary adsorption. Therefore, adsorption free can be achieved in this electron beam irradiation-induced special process.
In short, electron beam irradiation sheds new light on single-atom manipulation and adsorption control for generating unconventional structures of elemental 2D materials. Regrettfully, this method is only suitable for particular starting materials, whose low-Z element (e.g., C, Se, etc.) is removed due to knock-on effect and ionization and the rest of the high-Z element (metal) will transform into unconventional structures of elemental 2D materials.

4.4. Crystal Inhibition

Common methods for the synthesis of 2D materials often yield crystalline structures. To get the most thermodynamically unstable amorphous phase, crystal inhibition becomes an effective method. Hereon, crystal inhibition is usually achieved by introducing atomic irregular arrangement factors, such as rapid reactions and insufficient energy modulated by the reaction time and temperature. A schematic diagram for the fabrication of amorphous elemental 2D materials by crystal inhibition is shown in Figure 7a.

2D amorphous BP materials are usually synthesized by laser deposition. For example, the amorphous ultrathin BP films were synthesized by conventional pulsed laser deposition (PLD) technique at 150 °C low temperatures due to the focused energy provided by the laser. However, the energy is not enough to impel the ordered arrangement of atoms at this low temperature. And so, as a consequence, the amorphous nature can be reserved. Özyilmaz et al. recently obtained amorphous monolayer carbon by laser-assisted chemical vapor deposition (CVD) with the substrate temperatures as low as 200 °C (Figure 7b). Generally, the reaction temperature of CVD for growing crystalline graphene should reach 1000 °C or higher. The large-area HRTEM image shows that there is lack of any long-range order structure, but a connected and distorted structure of five-, six-, seven-, and eight-member rings (Figure 7c). And heavily distorted crystallites with oriented randomly of monolayer amorphous carbon were demonstrated.
by large-scale atom-by-atom mapping of the selected region (green regions) about 1 nm across (Figure 7d). Impressively, this is the first time to definitely disclose the atomic arrangements of amorphous materials.

In addition, Li’s group presented a simple and universal approach for preparing various amorphous noble metal nanosheets, including monometal nanosheets (Ir, Rh, and Ru nanosheets), bimetal nanosheets (RhFe and IrRu nanosheets), and trimetal nanosheets (IrRhRu nanosheets), through directly annealing the mixture of alkali salts and metal acetylacetonate. They clearly demonstrated that annealing temperature was of great importance for the formation of an amorphous phase. The annealing temperature should both drive the reaction and ensure that the relative low diffusion rate to facilitate the formation of amorphous rather than crystalline phases during the nucleation process. A series of control experiments implemented shows that annealing temperature must be situated between the melting point of metal acetylacetonate and alkali salt. The as-prepared Ir nanosheets have considerable lateral dimensions about a few micrometers (Figure 7e). The disordered atomic structure and characteristic diffuse halo verify the amorphous nature of Ir nanosheets (Figure 7f). High-angle annular

Figure 7. Crystal inhibition for elemental 2D materials with unconventional structures. a) A schematic diagram for the fabrication of amorphous elemental 2D materials by crystal inhibition. b) Large-area monolayer amorphous carbon onto a SiO$_2$/Si wafer. c) HRTEM image of monolayer amorphous carbon. d) Large-scale atom-by-atom mapping of the selected region. Reproduced with permission.[8] Copyright 2020, Springer Nature. e) TEM image of amorphous Ir nanosheets. f) HAADF-STEM image of amorphous Ir nanosheets. The inset in (c) shows the corresponding SAED pattern. g) HAADF-STEM image and the corresponding EDS elemental mapping of amorphous Ir nanosheets. Reproduced under the terms of a Creative Commons Attribution 4.0 International License.[13] Copyright 2019, The Authors, published by Springer Nature.
dark-field scanning transmission electron microscope (HAADF-STEM) image and the corresponding energy-dispersive X-ray spectrum (EDS) elemental mapping indicate that Ir and C evenly distributed on the whole nanosheet (Figure 7g). Here, the authors claimed that the existence of Ir–C bonds might contribute to the stabilization of amorphous structure based on extended X-ray absorption fine structure and X-ray photoelectron spectroscopy results. In addition, many amorphous/crystalline heterophase 2D metal materials have been also synthesized using reaction temperature to control their crystal processes, such as amorphous/crystalline heterophase Pd.$^{[22,74]}$ The reaction temperature is generally not higher than 150 °C. The amorphous ratio of these nanosheets could also be easily tuned by simply changing the reaction temperature.$^{[22]}

In brief, crystal inhibition appears to be a universal way to synthesis unconventional amorphous 2D materials through introducing atomic irregular arrangement factors, such as rapid reactions and insufficient energy modulated by the reaction time and temperature. In addition, more types of amorphous–crystalline heterophases might be successfully prepared by carefully controlling atomic irregular arrangement factors.

4.5. High Pressure

Apart from the aforementioned chemical methods, unconventional structures of elemental 2D materials could be obtained by physical methods, such as high pressure. For example, Lei et al. revealed that the metastable face-centered tetragonal (fctl) phase Ag nanoplates could be obtained through transforming from the stable fcc phase Ag nanoplates under nonhydrostatic pressure (12 GPa).$^{[18]}$ Although the synthesis of unconventional structures of elemental 2D materials by high-pressure induction is relatively rare, high pressure is a conventional physical method to realize the crystal phase control of noble metal nanomaterials under harsh conditions.$^{[77–79]}$ It is well documented that high pressure-induced crystal phase transformation is relevant to the internal crystallinity and surface capping organic layers, which provides a valuable reference for exploration and development of other unconventional structures of elemental materials.$^{[18,77]}

In a word, high pressure is a conventional physical method to realize unconventional structures of elemental 2D noble metal materials by crystal phase transformation. In addition, high pressure-induced crystal phase transformation is relevant to the internal crystallinity and surface capping organic layers. At present, the unconventional structures of elemental 2D materials are rarely synthesized by the high pressure due to harsh conditions.

5. Conclusions and Perspectives

Unconventional structures of elemental 2D materials have received great interest in recent years owing to potentially derived extraordinary physicochemical properties and innovative applications. Controlled preparation of elemental 2D materials with unconventional structures is helpful to understand the structure–dependent property and rationally design new structures with special atomic arrangements for facilitating their promising applications. This perspective starts with the brief introduction of the representative unconventional structures of elemental 2D materials, including thermodynamically unstable structures and intrinsically kinetically unstable structures which are stabilized by external factors. Subsequently, aiming to give a clear guideline of the different strategies for controlled preparation and reasonable design unconventional structures of elemental 2D materials, we systematically summarize the progress of strategies for unconventional structure, specifically, surface modification, epitaxial growth, electron beam irradiation, crystal inhibition, and high pressure.

Remarkably, by careful exploring the isolated region of the periodic table as shown in Figure 1b, which contains unconventional structures and synthetic strategies of elemental 2D materials, valuable information about correlations between the types of unconventional structures, elements types, and corresponding synthetic strategies is available: 1) The types of unconventional structures of elemental 2D materials depend on the element types. Unconventional buckled honeycomb building blocks and structures adopting unconventional mixed sp$^2$–sp$^3$ hybridizations focus on the group IV A elements (Si, Ge, Sn), which all adopt the sp$^3$-hybridized tetrahedral configuration in bulk. The noble metals whose stable bulk counterparts are fcc phases in VIII, I B, and II B group appear to be more likely to acquire metastable phase structures, such as hcp and fct phase. The metals whose stable bulk counterparts are bcc phases in group VI B and VII B are not easy to obtain other metastable phases. These clearly show that the unconventional structures are correlated with the electron configuration of atoms, which can be used as a reference for expanding the unconventional structured system. 2) Elements shown in white, which have not been experimentally verified to obtain elemental 2D materials with unconventional structure, can be divided into three categories: i) chemical activity (Al, Ga, In, etc.), these elemental materials are easily oxidized, and there is a huge challenge for the preparation of corresponding 2D materials, thus hindering the exploration of their unconventional structures; ii) chemical inertness (Ti, V, Gr, W, etc.), their chemical inertness often makes them useful as a substrate, and their corresponding 2D materials have not even been explored; iii) bulk solids with layered structures (P, As, Sb, etc.), their corresponding 2D materials could be easily obtained by exfoliation which take the same atomic configuration as their bulk counterparts, and no unconventional structures have been reported yet. 3) There is also a correlation between synthetic strategies and the element types. Due to the absence of d electrons in main group elements, the configuration of the element will be affected and changed when the transition metals with abundant d electrons are used as epitaxial substrates. Thus, vapor-phase epitaxial growth can obtain a large number of unconventional structures of the group IV A elements and boron due to the substrate–structure interaction. As for transition metals, because the stable crystalline phase of the metal is directly related to the valence electron configuration of the metal atoms, the same crystalline phases may be obtained by the same preparation methods. For example, a series of metals (Ag, Pd, Ir, Rh, and Cu) whose stable bulk counterparts are fcc phases can be grown externally on 4H Au nanoribbons to form unconventional 4H/fcc crystal structures.

Based on the aforementioned present scientific achievements, systematic understanding of effective synthetic strategies, and correlations between the types of unconventional structures,
the element types, and corresponding synthetic strategies, we can see that there is still much work to be done, despite significant progress has been made in the area of unconventional structures of elemental 2D materials. First, the variety of unconventional structures of elemental 2D materials is limited. The unconventional structures of elemental 2D materials are mainly concentrated in boron element, the group IV A elements (Si, Ge, Sn), and the metastable phases Au (4H, 2H), the unconventional structures derived from the epitaxial growth of metastable phase Au, and a small number of amorphous materials, including amorphous C, BP, Si, Pd, Ir, multilayer nanosheets, and so on. Other metastable crystalline phases of the main group, transition metal, and a wide variety of amorphous elemental 2D materials are seldom reported so far. In addition, the preparation of more complex heterogeneous monometal or multimetal is also of great importance and promising for enriching the diversity of unconventional structures of elemental 2D materials and disclosing the unique physical and chemical properties. Second, the mechanism for the acquired unconventional structure is unclear. Moreover, high-index facets usually exhibit much higher chemical-reaction activities due to their high density of atomic steps, ledges, kinks, and dangling bonds. However, it is very challenging to prepare transition metal 2D materials with exposed high-index facets owing to high surface energy. Until now, no transition metal 2D materials with exposed high-index facets have been successfully synthesized, even though there has been a great deal of experience for noble metal nanoparticles. Third, improving the stability of unconventional structures elemental 2D materials requires attention. Although considerable unconventional structures of elemental 2D materials have been revealed and exhibit unique properties, a short period of stability limits their further application. Therefore, based on the achievements in the representative studies in this perspective, we will provide some prospects and potential opportunities for the controlled preparation of various elemental 2D materials with unconventional structures.

Advanced in situ observation techniques will contribute to a deeper understanding of formation mechanisms and provide crucial insights regarding the preparation of other unconventional structures. At present, many emerging in situ techniques have been developed and implemented in a variety of catalytic reactions, batteries system, and other fields, such as in situ X-ray diffraction (XRD), Raman, and TEM. Note that more advanced synchrotron X-ray radiography techniques with the ultrahigh spatial resolution and grazing-incidence wide-angle X-ray scattering (GIWAXS) with ultrafast time resolution can provide information on atomic-scale arrangements of materials. These techniques are expected for in situ study of the forming causes of the unconventional crystal phase and the crystal surface by surface modification.

The developments of theoretical calculation and modeling will pave a new way of identifying surface modification effects, structural formation energy, reaction intermediates, structural formation pathways, and so on. In addition, theoretical calculation and modeling could help to predict new unconventional materials and suggest potential strategies for their stabilization. At present, theoretical modeling prevailing focuses on reaction energetics and thermodynamics; kinetic modeling should be further developed to better reveal the various influencing factors of structure formation due to the variability of the reaction conditions. Future investigation of the unconventional structures by the combination of in situ data and the theoretical calculation and modeling must be a promising research direction, which will accelerate the development of the unconventional structures of elemental 2D materials.

There is plenty of room to extend the scope of elemental 2D materials with unconventional structures and to study extraordinary physicochemical properties and innovative applications. First, unconventional structures that may be stable under certain conditions can be predicted theoretically, as aforementioned. Second, the aforementioned synthetic strategies might be useful to prepare new unconventional structures of elemental 2D materials. For example, surface modification and crystal inhibition methods might facilitate the formation of amorphous materials. In addition, as aforementioned, there is a correlation between synthesis strategies and element locations. The synthetic strategies may be suitable for elements with similar external electron arrangements. Aluminum, which also lacks electrons like B, may form a similar various unconventional 2D structures by epitaxial growth.

In addition, transition metal 2D materials with exposed high-index facets are always highly anticipated and there are already signs of a successful synthesis. Recently, many types of high-index single-crystal Cu and Ni foil were reported by Liu et al.\textsuperscript{[80]} They claimed that the facet selection is determined randomly by the maximum size grain surface, not the surface energy minimization as is usually the case. This report provides new insights into the growth of high-index facets and inspires the growth of the 2D transition metals with high-index facets.

It is particularly important to improve the stability of unconventional structures of elemental 2D materials for further application research, not only due to the sensitivity of their 2D surface to the environment but also due to the timeliness of the strategy to maintain their original metastability. Here, the reported strategies to stabilize other unstable 2D materials might be useful for improving the stability of unconventional structured elemental 2D materials, such as heteroatom doping, protective layer coating, chemical functionalization, and hybridization with other chemicals.\textsuperscript{[81–85]} In addition, considerable efforts will be also required for exploiting other effective stabilization strategies.

**Acknowledgements**

The research was supported by the National Natural Science Foundation of China (grants nos. 21673161 and 21905210) and the Sino-German Center for Research Promotion (grant no. 1400).

**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

amorphous phases, elemental 2D materials, heterophases, metastable crystal phases, unconventional structures
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