1

Introduction

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1.1 The Development of Carbon Materials

The pursuit of new materials with nontraditional architecture is one of the hot spots in current research [1-3]. Carbon-based nanomaterials (such as fullerenes, carbon nanotubes, and graphene) have attracted much attention due to their special structures and chemical and physical properties [4-7]. Carbon materials have experienced a long history of development. The contact of carbon materials with humans can be traced back to the earliest appearance of humans on the earth.

| 1

The first known existence of carbon was charcoal and soot. Diamond is a famous allotype of carbon, which was discovered by humans as early as 4000 BCE. Graphite is the most widely used allotrope of carbon and was found in the sixteenth century. Although carbon is one of the oldest elements, it is surprising that it constantly shows great vitality for the discovery of new allotropes (Figure 1.1), such as fullerene (1985), carbon nanotubes (1991), graphene (2004), and graphdiyne (GDY) (2010). The application of carbon materials can even be considered to promote the progress of human society and the development of other materials. In fact, the unique valence bond hybrid forms of carbon molecules, namely sp, sp^2 , and sp^3 , ensure that carbon allotropes can be constructed in various possible forms and exhibit different intrinsic properties. Diamond is composed of sp³-hybridized carbon, while graphite, fullerene, carbon nanotubes, and graphene are composed of sp²-hybridized carbon. sp² hybrid carbon can enhance the conjugation of materials and exhibit good electrical conductivity, while sp³ hybrid carbon has three-dimensional (3D) spatial configuration in carbon materials, which can further improve the rigidity of related materials. The sp hybrid carbon has a linear structure, which can improve the porosity and provide enough active or storage sites for other atoms. At present, the reasonable design of carbon materials and the full use of the advantages of the three hybrid carbon materials are of great significance in many research fields.

An interesting family of carbon allotropes is represented by the so-called graphynes (GYs) and GDYs. In general, these allotropes are flat one-atom-thin carbon



Figure 1.1 The development of carbon materials.



Figure 1.2 Schematic structures of graphene, carbyne, and graphynes, which comprise exclusively sp-atoms, sp²-atoms, and both types: $(sp + sp^2)$ atoms, respectively.

networks (such as graphene), which can be constructed by replacing some =C=C= bonds in graphene by uniformly distributed acetylenic bonds —C=C— (graphynes) or diacetylenic bonds —C=C—C=C— (GDYs). In both cases, the resulting network consists of two nonequivalent types of carbon atoms: threefold coordinated sp²-hybridized atom and twofold coordinated sp-hybridized atom. In this context, these flat carbon networks can be regarded as the "intermediate" (sp² + sp) systems between two famous carbon allotropes: graphene (containing only sp²-like atoms) and carbyne (containing only sp-like atoms) [8], see Figure 1.2. We can simply classify these materials according to the number of "—C=C—" bonds connecting two adjacent sp²-hybridized carbon atoms. As shown in Figure 1.2, they are called graphyne, GDY, and graphyne-*n* [9].

The history of systematic study of $(sp + sp^2)$ allotrope family began in 1987, when Baughman et al. [10] first proposed the structural model of graphynes and discussed some macrocyclic subunits suitable for creating these networks. Ten years later (1997), the structure of GDY was predicted and many small diacetylene molecules had been synthesized, which had become the "hot" spot of synthetic chemistry for a period of time. These studies started in the mid-1990s and continued into the new millennium. The chemists began some computational simulation and theoretical studies during this period, and the related materials with different sizes and dimensions [11–16], as well as some of their B–N and B–C–N analogues [15, 17–19] were also experimented by theoretical simulation. On the other hand, the experimental efforts in the synthesis of subunits of these systems were closely related to organic chemistry, that is, new synthetic routes in annulene chemistry [20]. However, research in these areas has not advanced much because of the serious lack of innovation in synthetic methods, leading to the study of the synthesized GDY in the synthesis and properties of some small-molecule diacetylene. It was in 2010 that the synthesized bottleneck of GDY was broken, and this was a great success. A new allotrope of carbon was born, which opened up a new field for research in carbon materials.

1.2 Models and Nomenclature

In 1968, Balaban et al. first proposed a rich and diverse planar carbon network (consisting of only sp²-bonded atoms with a threefold coordination) [21]. The search line was actively extended, and then a large number of related two-dimensional periodic carbon networks were constructed from non-C6 carbon polygons. For example, so-called pentaheptites [22, 23] (formed by periodically distributed pentagons C5 and heptagons C7) or haeckelites [24] (including pentagons C5, hexagons C6, and heptagons C7, see Figure 1.3), as well as some other related types of carbon networks, sometimes referred to as graphene allotropes [9, 27–35], were proposed and successfully investigated. Here, the so-called two-dimensional supracrystals [25, 36] can also be mentioned, Figure 1.3. These hypothetical low-stable polycyclic networks are composed of strained cycles such as C3, C4, and C12; therefore, their synthesis seems very suspicious. The recently studied 2D "square carbon" [25] also belongs to this category.



Figure 1.3 Structural motifs of some 2D carbon networks: **1.1**: pentaheptites [22, 23], **1.2**: haeckelites [24], and **1.3 – 1.7**: some hypothetical so-called 2D carbon supracrystals – polycyclic networks (based on Kepler's nets) composed of strained cycles such as C3, C4, and C12 [25]. Source: Ivanovskii [26]. © 2013, Elsevier.



Figure 1.4 Ideal atomic models [10] of possible graphynes (GV1–GV7). The threefold coordinated sp² atoms (forming hexagons, pairs, or as isolated atoms) are marked. On the left: thermal ripples of GV1 network according to molecular dynamics (MD) simulation at T = 300 K [37]. Source: Ivanovskii [26]. © 2013, Elsevier.

Graphynes are a series of stable two-dimensional crystalline carbon allotropes composed of sp- and sp²-hybridized carbon atoms. Their structural models were first proposed by R. H. Baughman et al. [10]. They have a two-dimensional structure similar to graphite and contain acetylenic linkages (sp components), referred to as graphyne. Accordingly, sp- and sp²-hybridized carbon atoms can be connected to each other according to certain hybrid rules, producing a variety of 2D structures [26]. Some of such GYs are depicted in Figure 1.4. These (and related) networks fall into four categories: I-IV, see Figure 1.4. Therefore, the structure of group I (GY1) includes hexagons C6, which are connected to each other by $-C \equiv C - C$ linkages. The two networks (GY2, GY3) of the second family consist of hexagonal C6 and a pair of sp² atoms (C=C bonds), which are interconnected by $-C\equiv C-$ linkages. The three networks of group III (GY4-GY6) have no hexagonal C6 and only contain paired sp² atoms (C=C bond). They are connected by $-C\equiv C$ —bonds (GY4, GY5), or by paired sp² atoms and isolated sp² atoms (GY6). Finally, the network of group IV (GY7) consists of isolated sp² atoms, which are connected to each other by $-C \equiv C - \text{linkages}$. This network (so-called supergraphene) can be seen as a graphene-like structure, in which all C=C bonds are replaced by acetylenic linkages $-C \equiv C$. Therefore, GY7 has the same hexagonal *p6m* symmetry as graphene.

Today, there is still no standard classification of such graphyne systems. In the first work, Baughman et al. [10] designated the GY networks to be considered in the simplified nomenclature, which defines the number of carbon atoms in different rings forming a given network. According to this method, graphynes can be named as a, b, and g-graphyne, where a and b represent the number of carbon atoms in the smallest ring of the graphynes (a ring) and number of carbon atoms in the adjacent smallest ring of the graphynes (b ring), respectively. Among them, rings a and b are connected by $C(sp^2)C(sp)C(sp)C(sp^2)$. The index g is the number



Figure 1.5 Some possible atomic motifs of graphyne-like structures, which are termed in the text as GY1'-GY5'. Source: Ivanovskii [26]. © 2013, Elsevier.

6 1 Introduction

of carbon atoms in the third ring of graphynes, which is connected to ring b by $C(sp^2)C(sp)C(sp)C(sp^2)$. For example, GY2 network is called 6,6,12-graphyne, GY4 is named 12,12,12-graphyne, and supergraphene (GY7) is called 18,18,18-graphyne. In addition, for convenience, several kinds of graphynes are commonly named after the Greek alphabet [36], which can be called as the customary nomenclature: α -graphyne (GY7) [38], β -graphyne (GY4) [39], and γ -graphyne (GY1) [12].

Coming back to possible types of graphynes, the structures of GY1' and GY2' (Figure 1.5) can be easily constructed from pentaheptite or haeckelite networks by simple replacement of all C=C bonds by acetylenic linkages $-C\equiv C-$; the structures of GY3 and GY4' are graphyne-like analogues of some 2D carbon supracrystals depicted in Figure 1.3. Besides, various graphene/graphyne "hybrids" can be supposed. A simple example is GY5', which includes "stripes" of hexagons C6 bonded



Figure 1.6 Graphdiyne with special properties and the related potential applications. EMI; 1-ethyl-3methylimidazolium, PVdF; poly(vinylidene fluoride), BF_4 ; tetrafluoroborate, GD NS; Graphdiyne nanosheets, P3HT; poly(3-hexylthiophene-2,5-diyl), HOMO; highest occupied molecular orbital, LUMO; lowest unoccupied molecular orbital. Source: (a) Gao et al. [40]. © 2016, John Wiey & Sons, (b) Xue et al. [41]. ©2018, Springer Nature/CC License 4.0, (c) Wang et al. [42]. ©2012, John Wiley & Sons, (d) Xiao et al. [43]. ©2015, John Wiley & Sons, (e) Jia et al. [44]. ©2017, Elsevier, (f) Parvin et al. [45]. John Wiley & Sons, (g) Lu et al. [46]. ©2018, Springer Nature/CC License 4.0.

by acetylenic linkages $-C \equiv C$, etc. On the other hand, in all of the described graphynes, the sp² atoms are bonded by "single" $-C \equiv C$ — linkages. Therefore, one more way of construction of graphyne-like networks is to increase the length of linear carbine-like atomic chains between sp² atoms, i.e. to replace ($-C \equiv C$ —) by ($-C \equiv C - C \equiv C$ —) or ($-C \equiv C - C \equiv C - C \equiv C$ —) chains, etc. which connect either hexagons C6, or pairs of sp² atoms, or individual sp² atoms.

1.3 Brief Introduction of Graphdiyne

The chemical study of carbon-rich molecules has and will continue to produce significant structures in size, topology, and spatial direction. Nevertheless, the achievements of early chemists were indeed remarkable in the current synthetic and analytical techniques that modern chemists take for granted. Advanced synthesis methods for alkyne chemistry have been developed through Sonogashira cross-coupling reactions or oxidative acetylenic coupling reactions catalyzed by Cu-[47, 48] or Pd/Cu [49]. The on-surface chemistry also provides a new way for the development of GDY.

GDY has butadiyne linkage between two adjacent aromatic rings. The development of GDY prepared by in situ Glaser coupling reaction of hexaethynylbenzene (HEB) monomers on a copper (Cu) substrate by Professor Yuliang Li's group [50] in 2010, is widely recognized as a great breakthrough regarding the structure of carbon materials. One of the most important features of the chemical structure of GDY is the presence of quantitative sp carbon, which gives it some characteristics that other carbon materials do not have [51, 52].

Theoretical analysis shows that GDY has a direct natural bandgap (0.46 eV) [53] and a Dirac cone structure, which can be attributed to the inhomogeneous π -bonding between the sp and sp²-hybridized carbon (Figure 1.6). GDY has excellent electrical properties, such as high carrier mobility and small carrier effective mass, which make it promising for nanoelectronics [54]. Both the intrinsic holes and electrons mobility of GDY at room temperature can reach up to $10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [55]. As the number of GDY layers increases, the band gap of GDY decreases and the direct band gap remain unchanged. The mechanical properties of GYs are considered as a function of the number and arrangement of acetylenic linkages [9, 56]. The expanded pores surrounded by the butadiyne linkers and benzene rings in the structure provide additional space for the storage and diffusion of metal atoms such as lithium and sodium. Moreover, the uniformly distributed in-plane pores of GDY can also promote the vertical transfer of ions [57].

Another unique feature of GDY -based materials is that they can be prepared by chemical methods, which is conducive to adjusting and optimizing their morphology and some fundamental chemical properties, including the conductivity, size and distribution of the pores, and affinity to certain metal atoms. In addition, the position and number of heteroatoms introduced in GDY can be well controlled by this preparation method [58]. GDY has been synthesized under different experimental

8 1 Introduction

conditions in the forms of films, nanowires, nanotube arrays, nanowalls, 3D foams, nanosheets and ordered stripe arrays, etc.

The above structural features and performance advantages make it possible and convenient to adjust and optimize the electrochemical properties of GDY, leading to the wide application of GDY in efficient separation, energy storage, photoelectric and energy conversion (Figure 1.6). The abundant distribution of alkyne bonds makes the charge distribution on the GDY surface extremely uneven, which endows it with more active sites, leading to higher intrinsic activity, which can effectively promote the catalytic reaction process. Therefore, GDY should be a valuable complement to popular sp²-hybridized carbon materials for constructing new concepts and highly active metal-free catalysts and understanding their catalytic mechanisms.

In Chapters 2–4, we will introduce the fundamental characteristics of GDY in terms of experiment and theory, namely electrical, mechanical, and optical properties [51, 52, 58, 59]. More importantly, we will focus on the application of GDY in catalysis [41, 42] (Chapter 5), energy conversion and storage [43, 44] (Chapters 6, 7), electronic devices [46] (Chapter 8), detectors, biomedicine and treatment [45], and water purification [40] (Chapter 9).

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