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Short Review

A Short Review of Synthesis of Graphdiyne and Its Potential Applications

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Graphdiyne(GDY), a novel kind of two-dimensional carbon allotrope comprising sp- and sp2-hybridized carbon atoms, was firstly proposed by Baughman group in 1987 and for the first time synthesized by Li group in 2010. The structure of GDY is related to that of graphene, but with the introduction of butadiyne linkages (−C≡C−C≡C−) to form 18-C hexagons, which makes it possess large conjugated system, wide surface spacing, high chemical stability and semiconductor performance. The advanced and unique properties of GDY make it highly promising nanomaterial for applications in energy, catalyst, optoelectronic, separation membrance and sensor, and so on. Herein, we briefly review the recent progresses in the theoretical and experimental researches of GDY's synthesis, particular structure and properties, as well as the applications.

Keywords: GDY, catalyst property, semiconductor material, nanotechnology applications

1. INTRODUCTION

In the past two decades, numerous efforts have been devoted to characterizing, developing and producing new materials built on various allotropes of carbon by researchers from all over the world. Carbon has three hybridization states that include sp3, sp2, and sp, and many naturally existing and man-made carbon allotropes can be produced by different hybridization states, such as graphite (sp2), diamond (sp3), amorphous carbon (sp3), fullerene (sp2), carbon nanotube (sp2), and graphene(sp2), which have been successfully synthesized[1–3] and have become the frontier and focus of international academic research.

Graphdiyne, a new member of all-carbon family, produced by two hybridization states(sp2, sp), was firstly proposed by Baughman and other pioneers in 1987[4], and was synthesized through cross-coupling on the surface of copper foil using hexaethynylbenzen by Li group in 2010 for the first time. As predicted to be the most stable non-natural carbon allotrope, graphdiyne possesses a 2D network of benzene rings connected by diacetylenic linkages[5], and simultaneously owns rich carbon chemical bonds, large conjugated system, wide surface spacing, excellent chemical stability and semiconductor properties, which makes GDY become a hot research area.

Herein, we have to limit our focus on GDY's synthesis, structure, properties, and applications in energy, catalyst, optoelectric, separation membrance, and sensor in this short review.

2. SYNTHESIS

All the time, scientists have been eager to obtain carbon allotropes with SP hybridized due to the advantages of linear structure, without cis-trans isomers and high conjugation of the carbon carbon triple bond with SP hybrid states. Moreover, it is considered that these carbon materials have excellent electrical, optical and optoelectronic properties, and would be the key materials of electronic and optoelectronic devices for the next generation. In 2004, researchers from University of Manchester used a tape to cleave a layer of graphite and eventually got an atom thickness of graphene(GP). Then they found the single layer graphene had high hardness, but also good toughness, which was known as the best conductive material.

In 2010, large-area graphdiyne films were successfully synthesized on the surface of copper by a cross-coupling reaction using hexaethynylbenzene[6] under the efforts of researchers in the Key Laboratory of organic solid Institute of Chinese Academy of Sciences, and in this process, copper foil not only acted as catalyst and substrate for cross coupling reaction, but also provided a large planar substrate for directional polymerization of graphdiyne films. The successful large-area synthesis of graphdiyne film reignited the researchers' interest in graphdiyne. To date, there have been several researches reported about the synthesis of graphdiyne. Zhou group[7] reported a rational approach to synthesize graphdiyne nanowalls through a modified Glaser−Hay coupling reaction. In this paper, hexaethynylbenzene and copper plate were selected as monomer and substrate respectively. By adjusting the ratio of added organic alkali along with the amount of monomer, the proper amount of copper ions was dissolved into the solution to form catalytic reaction sites. With a rapid reaction rate of Glaser−Hay coupling, graphdiyne grew vertically on these sites firstly, then with more copper ions dissolved, uniform graphdiyne nanowalls formed on the surface of copper substrate. Raman spectra, UV−vis spectra, and HRTEM confirmed the features of graphdiyne. In 2016, Wang group[8] fabricated precisely patterned graphdiyne stripe arrays via a direct in situ synthetic method. To reach the strict spacing of reaction process, confined cells at the microscale were regularly created by the integration of a grooved template and a flat copper foil. Due to the superlyophilicity of grooved template, continuous mass transport of raw reactants was allowed into the confined spacing. After the completion of cross-coupling reaction of hexaethynylbenzene, graphdiyne stripes were generated on the copper foil. The geometric pattern and layer thickness of graphdiyne could be manipulated to meet device requirements. However, more researches about graphdiyne are still needed for further exploring its structure, performance, and applications.

3. STRUCTURE AND PROPERTIES

The phylogenetic method of graphdiyne sp and sp2 hybrid state determines its unique molecular structure. According to the number of acetylenic bonds between the benzene rings, their names are slightly different. There is only an acetylenic bond between the benzene rings called graphyne(GY), that two acetylenic bonds called graphdiyne(GDY). It should be noted that by far GDY is the only prepared graphite alkyne allotrope in laboratory. In general, there are three types of C-C bonds[9-12]in the graphdiyne molecule: C (sp2) -C (sp2) bond on the central aromatic benzene ring with a bond length is about 0.143 nm, the C (sp2) -C (sp) bond to C=C and C≡C, whose bond length is about 0.140 nm, and the bond length of C (sp) -C (sp) bond to C≡C is 0.123 nm. The acetylenic bond formed by hybridization of sp and sp2 and benzene ring constitute graphdiyne molecule with the two-dimensional planar structure of a single atomic layer. In order to maintain the stability of GDY structure in infinite plane extension process, GDY monolayer two-dimensional planar structure would form a certain fold. The two-dimensional planar graphdiyne molecules are stacked through van der Waals force and π-π interaction to form a layered structure. The large triangular ring of 18 C atoms forms a three-dimensional channel structure in the layered structure. The planar sp2 and sp hybrid structure endues GDY a high degree of π conjugation, a uniformly dispersed pore configuration and a tunable electronic structure property. Therefore, strictly speaking, graphdiyne not only has characteristic of monolayer two-dimensional planar materials similar to graphene, but also the characteristic of three-dimensional porous materials. Such a rigid planar structure, uniform sub-nanometer pore and other unique properties make GDY very suitable for the storage and separation of molecules and ions.

Considering the molecular structure of graphdiyne, it would be an effective way to adjust its electronic, chemical, mechanical and magnetic properties by changing the width of the nanobelts, the morphologies and the functional modification of molecular plane edges. For double and three layers GDY, the electronic structure and optical absorption properties may also change under an external electric field. As the first-principles calculations shown, graphdiyne possesses natural band-gap energy compared with the graphene with zero band-gap energy [9,13-15], which makes GDY directly apply to the actual optoelectronic devices. Meanwhile, GY and GDY both are semiconductors, and they have direct transitions respectively in the M and G points of the Brillouin zone. Smith group [16] predicted that graphdiyne's band-gap energy could reach 1.22 eV similar to that of silicon, which makes GDY possible as a complementary alternative in existing silicon electronic devices. More interestingly, the electronic properties of GDY could be significantly changed through hydrogenation or halogenation. Thereby GDY could be applied to meet different requirements of optoelectronic devices by adjusting its band-gap energy. In addition, with a highly conjugated structure and uniformly distributed sharp walls, graphdiyne is reported to exhibit superior field-emission performance. Zhou group [7] had demonstrated the extraordinary and stable field-emission properties of GDY by calculating the typical plot of emission current density J versus the applied electric field (J−E curve) ,E_{to} (turn-on field) and E_{thr} (threshold field) and Fowler−Nordheim (F−N) plots.

4. APPLICATIONS

According to the structure and properties of graphdiyne mentioned above, it could envision that GDY may be extensively used in energy, optoelectronics, catalyst, the separation membrane, sensors and so on.

5. ENERGY

GDY owns both characteristics of monolayer two-dimensional planar material similar to graphene and three-dimensional porous material, which makes graphdiyne own a large specific surface area. Moreover, GDY's porous channel could accommodate a large number of particles such as lithium ions, or small molecules such as hydrogen, etc. Consequently, GDY could be used as the electrode material of energy storage and conversion.

To meet the increasing demand for today's information-rich society, rechargeable lithium-ion-based energy storage devices are widely used as pivotal components. Carbon materials like fullerenes [17-19], multi-walled carbon nanotubes [20-22], and graphene[23-26] have been explored extensively to improve performance of batteries and the energy density. However, numerous issues are still needed to be addressed, such as low rate capability, large irreversible capacity loss and limited Li storage capacity, etc. The appearance of graphdiyne provides a new choice for carbon material for lithium storage. Some studies have shown that the assembled GDY-based LIBs exhibit excellent electrochemical properties, including a highly stable specific capacity and fabulous rate performance [27]. GDY owns such a unique structure with numerous micropores and mesopores, which endows GDY with more Li storage sites. It is expected that the designing and preparation of new carbon materials such as GDY may provide a way to exploit novel electrode materials with excellent performance and further satisfy the future requirements of lithium ion-based energy storage devices.

In recent years, organic-inorganic hybrid perovskite solar cells, due to its various advantages, has caused a high degree of concern [28-40]. It is well known that enhancing power conversion efficiency (PCE) of perovskite solar cells is a major limitation[41]. Yang group [42] achieved the higher PCE of 19.3% by building electron transport layer (ETL). So it is very important to improve the electrons transport properties in perovskite solar cells. N-type organic molecule such as phenyl-C_{61}-butyric acid methyl ester (PCBM)[43] or metal oxides such as ZnO[44] and TiO_2[45,46] are usually employed as the ETLs to achieve the higher efficiencies of perovskite solar cells. However, there are still several problematic issues such as low coverage, leakage currents, interfacial recombination needed to be resolved, which result in relatively poor photovoltaic performance. Therefore, doping or modification of the PCBM layer ought to be made to achieve higher photocurrents and better coverage for high-performance perovskite solar cells. Kuang group[47] for the first time built the electron transport layer composed of PCBM doped with GDY in planar heterojunction (PHJ) $CH_3NH_3PbI_{3-x}Cl_x$ solar cells. This introduction of GDY led to the improved performance of PHJ perovskite solar cells with the PCE increased from 13.5 to 14.8% and the J_{sc} increased from 22.3 to

23.4 mA/cm^2. It was found that the doping GDY increased electrical conductivity, electron mobility, and charge extraction ability in the ETL layer as well as improved the ETL film coverage on perovskite layer that was very important for the data repeatability. All results explained the origin of enhanced J_{SC} and FF. So the introduction of carbon materials such as GDY into perovskite solar cell applications would become a simple and effective strategy for improving device performances in the future.

In addition, due to electrochemical energy systems' environment friendliness and sustainable nature, they have become an ideal choice in terms of the clean energy technologies[48]. Among them, supercapacitors have received more concern among other electro-chemical energys due to their outstanding performance[49,50]. Supercapacitors are divided into two categories, scilicet, the pseudocapacitors and the electrochemical double layer capacitors (EDLCs) [51]. Owing to the advantages of compatibility with various electrolytes, low cost and high conductivity compared with pseudocapacitive electrodes, EDLCs are more attractive in terms of practical applications[52]. All kinds of carbon related materials, including porous carbon, carbon nanotubes, graphene and its derivatives have been extensively investigated as an electrode material for EDLCs [53]. However, due to the urgent needs of the energy system, new materials for supercapacitor electrode applications are still needed. Karth group [54] prepared the graphdiyne nanostructures via a cross-coupling reaction and studied their electrochemical properties via electrochemical impedance spectroscopy and other methods for exploring their applications. The results demonstrate that graphdiyne electrode owns capacitance retention of about 97% over 1000 cycles, which implys its potential applications as an electrode material for supercapacitor. The application of graphdiyne in supercapacitor should be further promoted.

6. CATALYST

Firstly, graphdiyne itself is a class of excellent non-metallic oxygen reduction electro-catalyst. Caj [55] suggested that the graphdiyne could catalyze the oxidation of CO at low temperatures through the calculations of the density functional theory. Moreover, GDY's nature can be increased by atom doped. Zhang group[56] demonstrated that N-doped GDY own excellent electro-catalytic performances for Oxygen Reduction Reaction (ORR) with a equivalent electro-catalytic activity to commercial Pt/C catalysts, which is expected to be the substitution of precious metal platinum catalyst. What's more, N-doped GDY possesses a better stability and tolerance to the crossover effect than Pt/C catalysts. Furthermore, GDYO, the oxidation form of GDY, is observed to be an even excellent substrate for depositing ultrafine Pd clusters to form Pd/GDYO nanocomposite which shows a high catalytic performance toward the reduction of 4-nitrophenol[57]. Secondly, there are also numerous researches about application of GDY as a support material in catalysis. Yang group[58] calculated and compared the electronic properties and chemical structure of TiO_2-GDY and TiO_2-GR composites with different TiO_2 facets by first-principles density functional theory, and found that TiO_2(001)-GDY composites have stronger electronic structure, charge separation, and the oxidation ability than pure TiO_2(001) or TiO_2(001)- graphene composites. In addition, the rate constant of the TiO_2(001)-GDY composites is 1.63 times that of the pure TiO_2(001) and 1.27 times that of the TiO_2(001)- graphene composites for photocatalytic degradation of methylene blue. All of these suggested that TiO_2(001)-GDY composites could be a promising and excellent high-efficiency photocatalyst candidate. Sakthivel group [59] found that the hybrid material formed by graphdiyne and ZnO nanoparticles had an efficient degradation effect on azo dyes, which was twice as much as that of ZnO nanoparticles. Chen group [60] made GDY crosslinked with graphene oxide(GO) and further hybrided with Ag/AgBr, and the results show that Ag/AgBr/GO/GDY composites exhibits much stronger photocatalytic performance than Ag/AgBr, Ag/AgBr/GO, or Ag/AgBr/GDY for degradation of methyl orange contaminants under visible light irradiation. Recently, Li group[61] fabricated a novel kind of nanostructured nonprecious metal ORR catalyst (Fe-PANI@GD-900) via one-step carbonization of iron and polyaniline (PANI) co-modified on GDY nanocomposite under nitrogen atmosphere. The as-prepared Fe- PANI@GD-900 showed high selectivity for the direct four-electron ORR pathway, and promising long-term stability in alkaline medium. Unexpectedly, Fe-PANI@GD-900 still exhibited excellent ORR property in both alkaline and acidic electrolytes although its mass ORR activity is low compared with that of Pt/C catalyst. As far as we know, this is the first experiment report on the utilization of GDY material as a carbon nanosupport for synthesis of Fe-based NPMCs with high ORR catalytic activity and durability in alkaline medium. Therefore, GDY is a highly competitive potential material in photocatalytic and photoelectric applications of two-dimensional carbon materials.

7. OPTOELECTRIC

As the first principle calculation shown that GDY owns natural band-gap energy compared with graphene whose band-gap energy is zero, which makes GDY could be directly applied to the actual optoelectronic devices. As we all known, ultraviolet(UV) thin–film photodetectors(PDs) have been widely used in commercial and military fields owing to the advantages of low-cost fabrication, structural simplicity and room-temperature, and ZnO nanostructures are usually used for preparing ZnO PDs. Jin group[62] made great efforts to use GDY to cap the surface of ZnO to achieve high-performance UV photodetectors. Hereafter, GDY nanoparticles(GDY NP) were assembled onto the surface of the propylamine(PrA)-modified ZnO nanoparticles(ZnO NP) to fabricate GDY:ZnO nanocomposites which then were used for the preparation of UV PDs. With the introduction of GDY, the photoresponse was significantly enhanced due to the junction formed between GDY NP and ZnO NP. Li group [63] assembled to obtain CdSe-GDY composites by strong π-π interactions between GDY and 4-mercaptopyridine surface-functionalized CdSe quantum dots which then were used as the hole transfer layer of photoelectrochemical water splitting cell (PEC), and the experimental results suggested the integrated photocathode could generate a current density of nearly -70 μA cm(-2) in neutral aqueous solution. Meanwhile, the photocathode evolves H2 with 90 ± 5% faradic efficiency and shows good stability within 12 hours. Meng group [64] introduced GDY into the poly-3-hexylthiophene (P3HT) hole transport layer of perovskite solar cell for the first time. The strong π-π stacking between GDY and P3HT greatly improved the hole transport and battery performance. The transient photoluminescence spectra also confirmed that the introduction of GDY significantly improved the properties of hole separation and transport of the battery device. Due to the improvement of hole transport performance and the additional scattering properties of GDY, the average photoelectric conversion efficiency of the Perovskite batteries was observed with 20% enhancement, and achieved a maximum efficiency of 14.58%. It's well known that organic-inorganic perovskite solar cells have recently been the research hotspot in the field of photovoltaics. There was a study that employed phenyl-C61-butyric acid methyl ester(PCBM) as the electron transport layer(ETL) to achieve the high efficiencies of perovskite solar cells, which still exist several disadvantages[65]. Kuang group[47] introduced GDY into PCBM ETL layer of perovskite solar cells as a dopant, and observed that the average power conversion efficiency (PCE) of PCBM:GD-based devices increased to 28.7% compared to that of pure PCBM-based ones. Moreover, GDY can also greatly improve the PCE of dye-sensitized solar cell [66]. In summary, GDY shows its great potential and prospect for applications in the field of photovoltaic.

8. SEPARATION MEMBRANE

The unique structure of GDY endues it a rigid planar, uniform sub-nanometer pore and other particular properties, which makes GDY very suitable for the storage and separation of molecules and ions.

In fact, Jiao group[67] explored the diffusion of hydrogen (H_2), carbon oxide (CO), and methane (CH_4) through graphdiyne and found that GDY is a good hydrogen separation membrane. Apart from hydrogen separation, graphdiyne is thought to be an efficient membrane for He^3/He^4 isotope separation [68]. Meng group [69] ascertained that graphdiyne was difficult to oxidize via detailed first-principles calculations (needs 1.97eV to break the C-C bond) and meanwhile demonstrated that graphdiyne coule be a perfect membrane for O_2 separation from Cl_2, HCl, HCN, CNCl, SO_2, H_2S, NH_3, and CH_2O in terms of selectivity and permeability. Therefore, one-atom-thick graphdiyne with natural uniform pores and mechanical robustness would be a very bright membrane for oxygen separation or oxygen purification from other gases, which would be of great interest and wide applications in scientific research, for industrial and medical areas, as same as the daily life .

Gao group [70] proposed an ingenious design to fabricate a uniform layer of graphdiyne-based ordered nanostructure that was successfully made via situ Glaser–Hay coupling. Then coating with PDMS, the obtained PGDCF displayed excellent super-hydrophobicity. In addition, the deliberately selected copper foam also endues the PGDCF with high abrasion resistance, which is important for practical applications to integrate both superhydrophobicity and high mechanical strength in one material. Moreover, as an example, PGDCF exhibited both high efficiency and good recyclability when used for oil/water separation.

9. SENSOR

The interplay between materials and biological molecules is a significant topic in material science research and condensed matter physics. When designing bio-devices, especially nano-biosensors, exploring the physical mechanism of the interactions between biological molecules and material surfaces is a fundamental problem. Graphene(GP), a promising material for various applications in engineering and medicine, is considered a flexible substrate for functionalization with peptides, proteins and small biomolecules[71,72]. Zeng group [73] built a graphene-based electrochemical immunosensor for detection of cytomegalovirus phosphoprotein，which is proved to be highly specific with acceptable precision, good stability and repeatability. However, as a semi-metal with zero band-gap[74-76], GP still has limitations in sensitive detection for biomolecules. And in terms of semiconducting C material, GDY is more suitable than GP for manufacturing nanoelectronic devices. Moreover, GDY may possess strong adsorption to biomolecules owning to its unique structure of larger pores.

The interactions between single-layer GDY and typical AAs theoretically was studied by ab initio calculations and compared with the interactions between GP and AAs[77]. The results displayed that the adsorption energy of each AA molecule on GDY was larger compared with that on GP. The current-bias curves of GDY-AA systems displayed different reaction of GDY to various AAs. According to the results above， GDY is a promising nano-material for sensitive AA/protein biosensors.

In addition, GDY and its oxide could be used to establish a novel and effective fluorescent sensing platform for highly selective and sensitive detection of biomolecules had been demonstrated for the first time by Wang group[78]. Their study offered a new fluorescent sensing platform based on 2D nanostructure, which is technically simple, robust, and easily operated. Moreover, this study also consigned a first extension of GDY into fluorescent sensing community, which would definitely stimulate more interests in researches on fluorescence sensing area with 2D nanomaterials.

What’s more, Wang group [8] developed a stretchable sensor based on the graphdiyne stripe arrays to monitor the human finger motion and demonstrated that the geometric pattern and layer thickness of graphdiyne could be manipulated to meet device requirements.

10. CONCLUSION AND FUTURE PERSPECTIVES

This paper reviews the recent progress in the theoretical and experimental research of polymer two-dimensional material graphdiyne from its synthesis, structure, properties, and applications. The study of GDY has attracted close attention of scientists from different fields. Scientists have carried out a lot of research work on the theoretical prediction, synthesis method and application of GDY, developed the method of characterization to confirm its structure, and explored its electronic structure and properties. It is an effective method to adjust the properties of electronic, chemical, optoelectronics, mechanical, semiconductor and magnetic fields through changing its width of nanobelts, morphology and functional groups of the edge. Graphdiyne possesses important and potential application prospects in electronics, optoelectronics, semiconductor, separation membrane, energy storage materials and sensor. Theories and practices results have shown that GDY shows a very peculiar properties and performance in various areas, GDY may develop into a key material in the future high-tech field. GDY’s special chemical and electronic structure makes it occupy considerable position in the scientific research of possible future, with a strong competitive edge. Especially during to its superior semiconductor performance, GDY would have a extensive prospective application in biomedicine and biological devices.

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The first two authors are equally contributed to this work, they are considered as co-author.

CONFLICTS OF INTEREST
The authors declare no conflict of interest.

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