ACS APPLIED MATERIALS & INTERFACES

Letter

Cite This: ACS Appl. Mater. Interfaces 2019, 11, 2734−2739

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Template Synthesis of an Ultrathin β-Graphdiyne-Like Film Using the Eglinton Coupling Reaction

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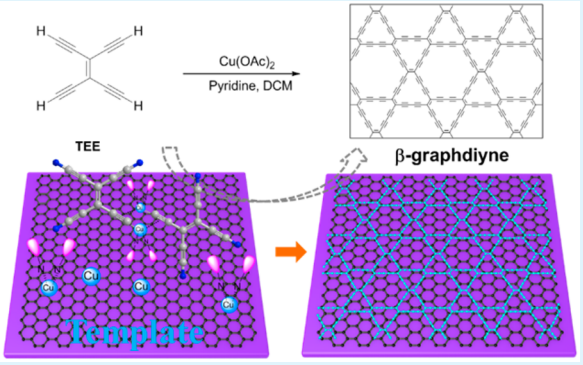
Supporting Information

ABSTRACT: β-Graphdiyne (β-GDY) is a two-dimensional carbon material with zero band gap and highly intrinsic carrier mobility and a promising material with potential applications in electronic devices. However, the synthesis of continuous single or ultrathin β-GDY has not been realized yet. Here, we proposed an approach for ultrathin β-GDY-like film synthesis using graphene as a template because of the strong π−π interaction between β-GDY and graphene. The as-synthesized film presents smooth and continuous morphology and has good crystallinity. Electrical measurement reveals that the film presented a conductivity of 1.30×10^{-2} $S \cdot m^{-1}$ by fabricating electronic devices on β-GDY grown on a dielectric hexagonal boron nitride template.



KEYWORDS: *β-graphdiyne, ultrathin film, graphene, template synthesis, alkyne coupling reaction*

Since the Noble-Prize-winning discovery of two-dimensional (2D) graphene, tremendous effort has been devoted to the discovery of new ultrathin 2D nanomaterials such as hexagonal boron nitride (h-BN), graphitic carbon nitride, transition-metal dichalcogenides, black phosphorus, MXenes, and so on,[1−4] which exhibit versatile properties in the fields of physics, materials science, chemistry, and nanotechnology.[5] Graphdiyne (GDY) is another kind of 2D carbon material constructed with sp- and sp^2-hybridized carbon atoms.[6,7] GDY has aroused great interest because of its unique structure, in which diacetylenic linkages (−C≡C—C≡C−) introduce a variety of optical and electronic properties that are quite different from those of graphene.[8,9] GDY could be mainly divided into three forms, namely, α-, β-, and γ-GDY, depending on the arrangement of sp- and sp^2-hybridized carbon atoms (Figure S1).[10] γ-GDY possesses a natural moderate band gap of 0.46 eV, carrier mobility as high as 10^4−10^5 $V^{-1} \cdot s^{-1}$, a high conjugated structure, and uniformly distributed pores.[11,12] These advantages make γ-GDY promising for various applications such as energy storage and transformation,[13−15] catalysis,[8] sensors, and so on.[16,17]

Different from γ-GDY, β-GDY contains diacetylenic linkages between two sp^2 carbon atoms of ethylene to form a carbon network with a uniformly distributed hierarchical pore structure.[18] β-GDY has a higher percentage of acetylenic linkages (67%) than γ-GDY (50%), meaning a stronger π-conjunction system compared with γ-GDY.[19] Previous work has demonstrated that the synthesized TiO_2@β-GDY composite presents enhanced photocatalytic activity of TiO_2 due to the alkyne-rich framework of β-GDY. Theoretical calculation predicts that single-layer β-GDY is a zero-band-gap material and presents a metallic behavior like graphene.[10] The electronic structure reveals that the existence of Dirac points in β-GDY leads to highly intrinsic carrier mobility.[20] However, the synthesis of continuous single or ultrathin β-GDY is still in infancy. Although previous work has used an alkyne coupling reaction to synthesis a β-GDY-containing film on a copper substrate, the thickness of the synthesized film was larger than 25 nm.[21] This synthetic process forms with difficulty oriented 2D layered β-GDY arising from the weak interaction between monomers and the metallic substrate that inevitably leads to a randomly oriented coupling of the monomer. Moreover, it was difficult to incorporate the synthesized film into devices to harness or quantify the intrinsic properties of β-GDY. Therefore, developing a method to prepare single-layer or ultrathin β-GDY with long-range single-crystalline order is highly desirable.

Special Issue: Graphdiyne Materials: Preparation, Structure, and Function

Received: February 20, 2018
Accepted: March 30, 2018
Published: March 30, 2018

DOI: 10.1021/acsami.8b03028
ACS Appl. Mater. Interfaces 2019, 11, 2734−2739

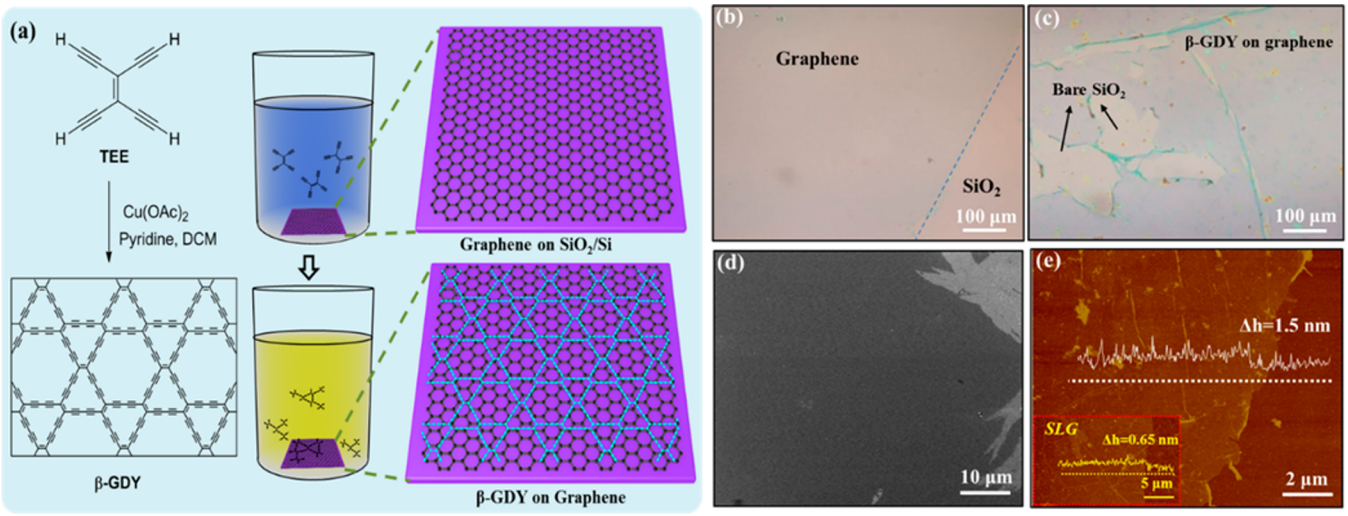


Figure 1. (a) Schematic illustration of the experimental setup for the ultrathin β-GDY-like film grown on graphene. (b) OM image of bare graphene. OM (c), SEM (d), and AFM (e) images of the film grown on graphene. The AFM image of SLG is shown in the inset.

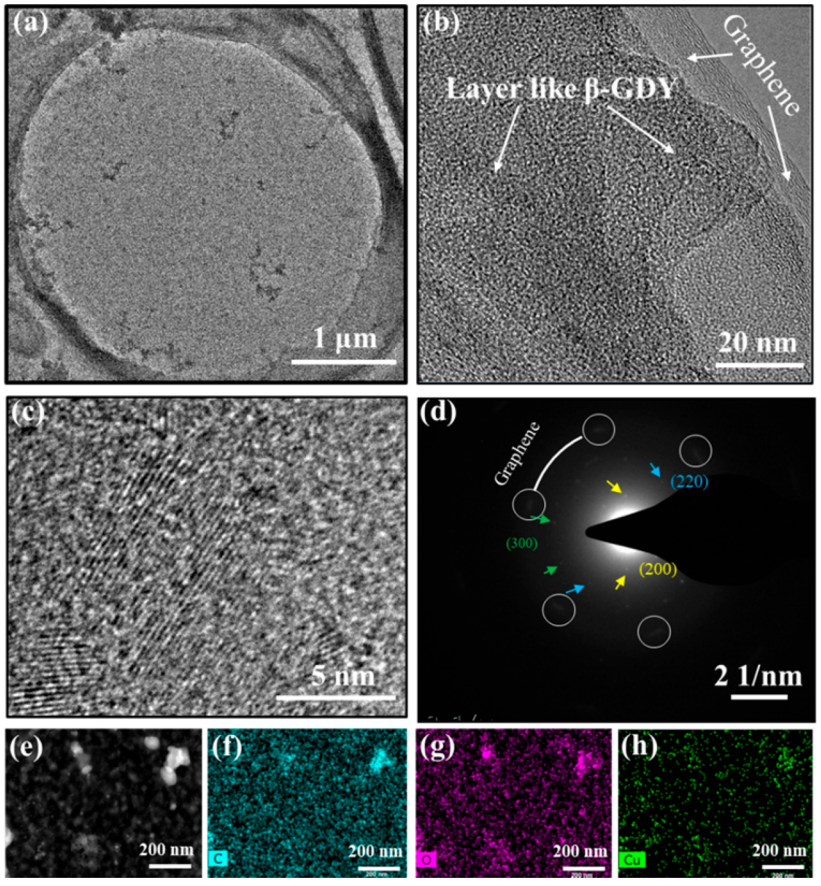


Figure 2. TEM image (a), HRTEM images (b and c), SAED pattern (d), and elemental mapping images (e–h) of the β-GDY-like film on graphene.

In essence, GDY was constructed by an organic coupling reaction between organic molecules, which means that the orientation of the organic molecules plays a key role in forming the long-range-ordered GDY structure. Using a template as the grown substrate can control the orientation of the organic molecules by taking advantage of template–molecule interaction, and this has been demonstrated as an effective method to synthesize oriented 2D materials.[22] However, the orientation of the organic molecules at the interface is highly susceptible to the nature of the substrate because of the competition between the molecule–interface and intermolecular interactions.[23] Therefore, selecting an appropriate template is very important. Graphene is a layered structure constructed with sp^2-hybridized carbon atoms. It has been demonstrated as an ideal candidate as a template for the synthesis of 2D covalent organic framework materials because of its highly conjugated system and chemical stability.[23] The alkyne-rich framework endows β-GDY with strong π-conjugation system that would have strong interaction

DOI: 10.1021/acsami.8b03028
ACS Appl. Mater. Interfaces 2019, 11, 2734–2739

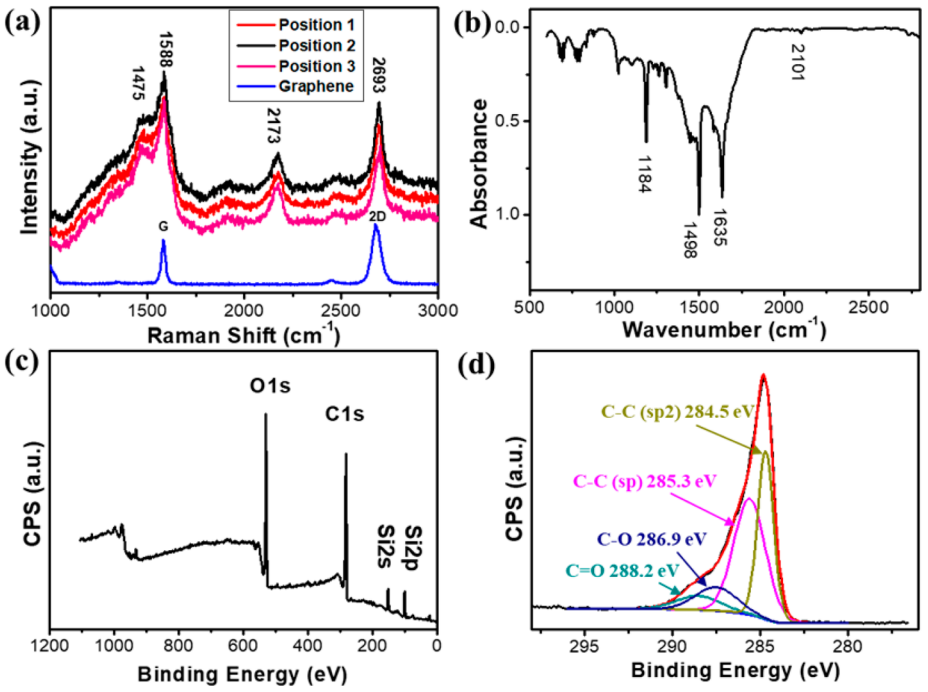


Figure 3. (a) Raman spectra of the β-GDY-like film on graphene and SLG. (b) FTIR spectrum of the β-GDY-like film exfoliated from a SiO_2 plate. XPS spectra of the β-GDY-like film on graphene: (c) survey scan; (d) narrow scan for C 1s.

with graphene. Moreover, both graphene and β-GDY are hexagonally symmetrical structures, meaning good lattice matching between them. Our structural model simulation reveals that six unit cells of graphene match well with one unit cell of β-GDY (Figure S2). Regarding the strong interaction and good lattice matching between graphene and GDY, graphene could be a promising template for oriented 2D-layered β-GDY film synthesis.

In this study, we present a graphene-templated synthetic route to prepare an ultrathin β-GDY-like film by the Eglinton coupling reaction using tetraethynylethene (TEE) as the precursor. The schematic illustration of the synthetic strategy is depicted in Figure 1a. First, TEE was prepared and used immediately from tetrakis[(trimethylsilyl)ethynyl]ethene, which was synthesized according to a previously reported work.[24] Then, the monomer TEE was added into the reactor containing dichloromethane (DCM), pyridine, toluene, copper acetate [$Cu(OAc)_2$], and a SiO_2/Si-plate-supported single-layer graphene (SLG). DCM and toluene were used to assist the deprotection process and enhance the solubility of $Cu(OAc)_2$ in pyridine, respectively. The four terminal alkynyls on TEE have high reactivity and are easily chemically coupled with each other to form a uniform network structure of carbon on the graphene surface. As a result, a carbon film of about 1.5 nm thickness containing β-GDY and SLG on the SiO_2/Si substrate was obtained. In order to investigate the electronic property of the as-prepared β-GDY-like film, electronic devices were fabricated on the film grown on a dielectric h-BN template. Electrical measurement revealed that the film presented a conductivity of 1.30×10^{-2} $S \cdot m^{-1}$, which is much larger than the β-GDY film synthesized on a copper foil (3.47×10^{-6} $S \cdot m^{-1}$).[21]

The morphology of the as-prepared film was characterized by optical microscopy (OM), scanning electron microscopy (SEM), and atomic force microscopy (AFM). Figure 1b shows the SiO_2-plate-supported SLG with an undefined surface. After the synthetic process, the OM image shows a different optical contrast compared to bare SLG (Figure 1c), indicating the formation of a thin film. The SEM image shows that the film grown on graphene has a smooth surface and is highly continuous (Figure 1d). The thickness of transferred SLG was about 0.65 nm (Figure 1e, inset). AFM characterization of the as-grown film reveals a flat surface, and the total thickness containing SLG was about 1.5 nm (Figure 1e). A thickness survey at different positions shows that the film thickness ranged from 1.1 to 1.7 nm, whereas most of them were about 1.5 nm (Figure S3).

Transmission electron microscopy (TEM) was employed to verify the in-plane periodicity of the synthesized film on graphene. Figure 2a shows a typical low-magnification TEM image, where a free-standing film containing graphene was supported by a molybdenum grid through an in situ synthetic route. High-resolution TEM (HRTEM) characterization clearly presents the layerlike film supported by graphene (Figure 2b). A further HRTEM image exhibits some uniform lattice fringes, which reflects the ordered structure of the film (Figure 2c). The selected-area electron diffraction (SAED) pattern shown in Figure 2d displays several diffraction spots, which demonstrates the moderate crystallinity of the film. The innermost diffraction spot series is indexed as a set of (200) diffractions derived from a hexagonal 2D lattice with $a = b = 1.46$ nm of the β-GDY structure. The corresponding (220) and (300) spacings of β-GDY can also be indexed, which are in good agreement with the theoretical results of β-GDY (Figure S4a). The completely hexagonal diffraction spots are not observed, which may be attributed to the limited domain size and inevitable defects of the β-GDY film. Thus, the term β-GDY-like was used instead in this work. The intensity integration over 360° was also presented in Figure S4b, where (200), (220), and (300) spacings of β-GDY can be easily identified. Energy-dispersive spectroscopy (EDS) elemental mapping associated with the TEM image shows that carbon was located on the whole film

DOI: 10.1021/acsami.8b03028
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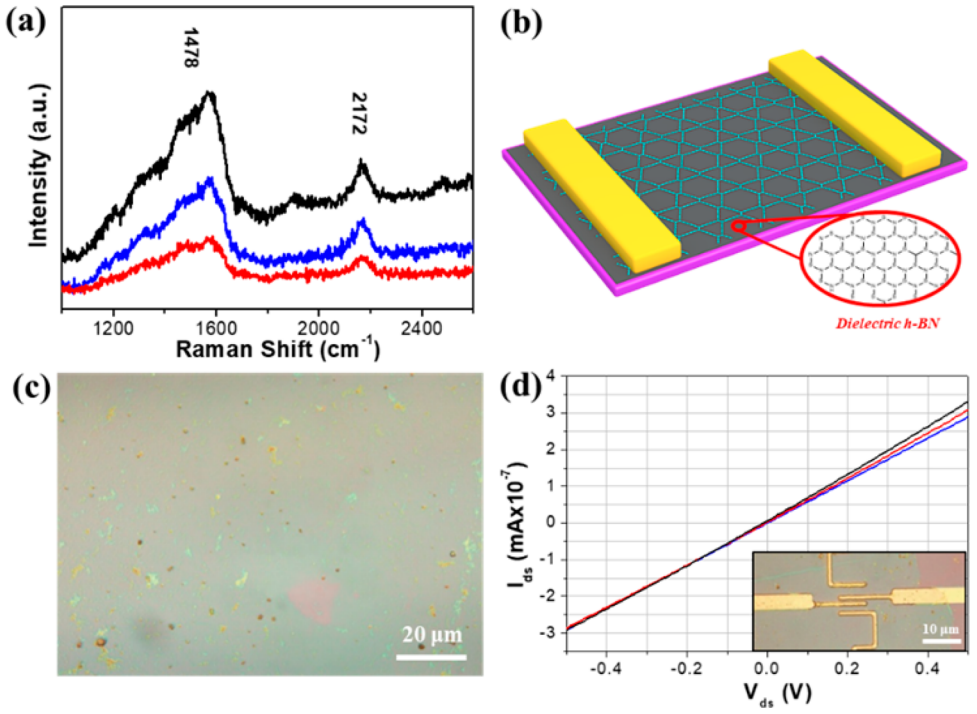

Figure 4. (a) Raman spectra of β-GDY on h-BN. (b) 3D view of β-GDY growth on a dielectric h-BN device. (c) OM image of β-GDY on h-BN. (d) $I-V_{ds}$ characteristic for the device and the OM image of the device (channel width: 2 μm).

(Figure 2e–h). The existence of oxygen might result from the adsorption of oxygen from air or the inevitable defects, which is consistent with single-point analysis of the EDS (Figure S5), and the copper might come from a small quantity of residual catalyst.

The bonding structure and elementary composition of the β-GDY-like film were studied systemically by Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and UV–vis absorption spectroscopy. Figure 3a shows the typical Raman spectra of the β-GDY-like film on graphene at different positions and of bare SLG. In the Raman spectra of the β-GDY-like film on graphene, four dominant peaks appeared at 1475, 1588, 2173, and 2693 cm^{-1}, respectively. The peak at 1475 cm^{-1} comes from the vibration of C=C bonds.[25] The peak at 2173 cm^{-1} is attributed to the stretching vibration of conjugated diacetylenic linkages.[26] A higher intensity and a narrower full width at half-maximum (fwhm) are observed compared to previous work.[21] Figure S6a shows the experimental and calculated Raman spectra of the monomer (TEE). From the experimental results, the two domain peaks at 1485 and 2070 cm^{-1} come from the stretching vibration of C=C bonds and C≡C bonds, respectively. An obvious hypochromatic shift of the Raman peak of diacetylenic linkages and a bathochromic shift of the Raman peak of C=C bonds are observed compared to the monomer (Figure S6b). All of the results are consistent with theoretical predictions of the Raman spectra of β-GDY. The bottom curve in Figure 3a is the typical Raman spectrum of SLG, where the peaks at 1588 and 2693 cm^{-1} correspond to the G and 2D bands of graphene. Figure 3b shows the FTIR spectrum of a synthesized β-GDY-like film, where four major bands are observed at 1184, 1498, 1635, and 2101 cm^{-1}, respectively. The bands located at 1498 and 1635 cm^{-1} are assigned to the skeletal vibrations of C=C bonds of β-GDY and graphene, respectively. The band of 2101 cm^{-1} is the typical C≡C stretching vibration, and its intensity is slightly weak because of molecular symmetry.[26] XPS measurements indicate that the film is mainly composed of the carbon element (Figure 3c). The existence of oxygen might result from the SiO_2/Si substrate, the adsorption of oxygen from air, or the inevitable defects, which is in agreement with the EDS elemental mapping results. A high-resolution XPS scan discerns the chemical environment of the carbon element (Figure 3d). The peak at 285.0 eV shows an essentially identical binding energy for the C 1s orbital, which can be deconvoluted into four subpeaks at 284.5, 285.3, 286.9, and 288.2 eV, assigned to the C 1s orbital of C=C, C≡C, C–O, and C=O bonds, respectively.[21] UV–vis absorption spectroscopy was used to investigate the optical properties of the β-GDY-like film (Figure S6c). According to the UV–vis absorption measurements, there is an obvious bathochromic shift in the UV–vis spectrum of the as-grown film compared to the monomer, which indicates the formation of a large π-conjugated system due to alkyne-coupling-enhanced electron delocalization.

Theoretically, β-GDY has good conductivity because of the presence of diacetylenic linkages and unique Dirac points.[21] Therefore, investigating the electronic properties of β-GDY is extremely important. However, it is difficult to observe the intrinsic electronic properties of β-GDY if the film is on graphene, which might overwhelm the properties of β-GDY. In order to solve this problem, we employed dielectric h-BN as the template to synthesize a film of β-GDY, on which electrodes were fabricated. h-BN is naturally comprised of layered structures with an interlayer spacing of ~0.33 nm. Although h-BN has good mechanical strength and thermal conductivity, the large band gap (~4–6 eV) makes it an insulator,[27] which means that h-BN can be used as a dielectric layer in electronic devices. Moreover, h-BN, which structurally resembles graphene, has been proven to be helpful for assembling 2D organic molecules.[28,29] Previous work has demonstrated that

DOI: 10.1021/acsami.8b03028
ACS Appl. Mater. Interfaces 2019, 11, 2734–2739

only negligible perturbation exists when the active layer is supported on h-BN.[30] Here we use the CVD-grown h-BN as the template instead of graphene to synthesize β-GDY through the same synthetic procedures. The β-GDY film grown on h-BN shows Raman features similar to those grown on graphene (Figure 4a). A fundamental two-electrode device was fabricated to evaluate the conductivity of the β-GDY film. The schematic depiction of the device is shown in Figure 4b, and the OM image of the device is presented in Figure 4c, in which h-BN was used as both a synthetic template and a dielectric layer. The $I-V$ curves were measured at a bias voltage from −0.500 to +0.500 V (Figure 4d). As shown in Figure 4d, the $I-V$ relationship is highly linear in the voltage range between −0.5 and +0.5 V, which suggests the ohmic behavior of the β-GDY film. The conductivity was calculated as 1.3×10^{-2} S·m^{-1}, which is similar to that of γ-GDY but higher than that of the β-GDY film synthesized on a copper foil, indicating the good conductivity of the as-grown β-GDY film.

In conclusion, we developed a novel graphene-templated method to synthesize an ultrathin β-GDY-like film on graphene by taking advantage of the strong π−π interaction between β-GDY and graphene. The as-synthesized GDY film presents smooth and continuous morphology and has good crystallinity. Electronic devices were fabricated on β-GDY grown on a dielectric h-BN template, and electrical measurement reveals that the film presented a conductivity of 1.30×10^{-2} S·m^{-1}. After further optimization of the synthesis parameter, the template method could be promising to prepare single-crystalline β-GDY of a single layer.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b03028.

Experimental details (monomer synthesis, β-GDY-like film synthesis, etc.), details of characterizations (SEM, AFM, EDX, XPS, UV−vis absorption, and FTIR), considered stacking structures of β-GDY−graphene from top-view and simulated TEM/SAED patterns, and calculations of work functions (PDF)

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Funding

Ministry of Science and Technology of China (Grants 2016YFA0200101 and 2016YFA0200104), National Natural Science Foundation of China (Grants 51432002, 51720105003, and 21790052), and Beijing Municipal Science and Technology Project (Project 161100002116026).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Congwei Tan for guidance in device fabrication, Luzhao Sun and Zhepeng Zhang for CVD growth of graphene and h-BN, and Zhenzhu Li for valuable discussion from the perspective of theoretical calculation.

■ ABBREVIATIONS

GDY, graphdiyne; 2D, two-dimensional; h-BN, hexagonal boron nitride; TEE, tetraethynylethene; DCM, dichloromethane; SLG, single-layer graphene; OM, optical microscopy; SEM, scanning electron microscopy; AFM, atomic force microscopy; TEM, transmission electron microscopy; HRTEM, high-resolution TEM; SAED, selected-area electron diffraction; EDS, energy-dispersive spectroscopy; FTIR, Fourier transform infrared spectroscopy; XPS, X-ray photoelectron spectroscopy

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