Architecture of $\beta$-Graphdiyne-Containing Thin Film Using Modified Glaser–Hay Coupling Reaction for Enhanced Photocatalytic Property of TiO$_2$

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$\beta$-Graphdiyne ($\beta$-CDY) is a member of 2D graphyne family with zero band gap, and is a promising material with potential applications in energy storage, organic electronics, etc. However, the synthesis of $\beta$-CDY has not been realized yet, and the measurement of its intrinsic properties remains elusive. In this work, $\beta$-CDY-containing thin film is successfully synthesized on copper foil using modified Glaser–Hay coupling reaction with tetraethylbenzene as precursor. The as-grown carbon film has a smooth surface and is continuous and uniform. Electrical measurements reveal the conductivity of $3.47 \times 10^{-4} \text{ S m}^{-1}$ and the work function of 5.22 eV. TiO$_2@\beta$-CDY nanocomposite is then prepared and presented with an enhancement of photocatalytic ability compared to pure TiO$_2$.

The extensive properties and applications of carbon materials depend on the hybridization of carbon atoms, namely, sp, sp$^2$, or sp$^3$.[1] Since the Nobel-Prize-winning discovery of buckminsterfullerene C$_{60}$,[2] tremendous efforts have been devoted to develop new carbon allotropes, such as carbon nanotubes and graphene, which possess extraordinary electrical, mechanical, and optical properties, leading to diverse advanced applications.[3,4] In 1987, Baughman first proposed another kind of 2D carbon allotrope, graphyne (GY), which only contains sp and sp$^2$ hybridized carbon atoms.[5] The presence of acetylenic groups in GY introduces a variety of optical and electronic properties that are quite different from graphene and carbon nanotubes.[6] However, the synthesis of a novel and stable form of GY still remains elusive.

Graphdiyne (GDY), another member of 2D graphyne family, can be described as GY networks, where all acetylenic groups in GY introduce new directions that are synthetically approachable.[5,7] According to the different arrangement of carbon atoms, GDY could be mainly divided into three forms, namely, $\alpha$, $\beta$, and $\gamma$-GDY (Figure S1, Supporting Information).[8] In 2010, Li and co-workers have successfully synthesized $\gamma$-GDY on copper substrates through acetylenic coupling reaction using hexakisethynylbenzene as precursor.[9] $\gamma$-GDY has been predicted to be the most stable structure among the three forms with a band gap of $\approx 0.46$ eV and own unique anisotropic properties.[7] These advantages make $\gamma$-GDY promising for various applications.[10–24]

Different from $\gamma$-GDY, $\beta$-GDY is a zero band gap material and presents a metallic behavior like graphene.[8,25] It contains two diacetylenic linkages ($C\equiv C\equiv C\equiv C\equiv C\equiv C$) that are between two sp$^2$ carbon atoms of ethylene to form a carbon network with uniformly distributed pore structure.[26] Besides its triangular geometries, $\beta$-GDY also has hexagonal geometries, which means larger pore size and lower planer packing density compared to $\gamma$-GDY.[8] These advantages make $\beta$-GDY a promising material to be applied as selective membranes for molecular sieves, lithium or hydrogen storage, heterogeneous catalysis, and electronic chemistry.[27] Calculations of the electronic structure reveal the existence of Dirac points, leading to the intrinsic carry mobility of $\beta$-GDY as high as graphene.[28] Dirac point movement study under rotating uniaxial and shear strains indicates that $\beta$-GDY presents strong anisotropy.[29] Furthermore, $\beta$-GDY has higher percentage of acetylenic linkages (67%) than $\gamma$-GDY (50%), meaning stronger $\pi$-conjunction compared with $\gamma$-GDY.[28] The abundant ring-like diacetylenic linkages are ready to form carbon–metal bond with transition metals.[30–32] These features

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make β-GDY a promising material for electron transportation and charge separation, which could be used in photocatalytic applications. Therefore, developing an approach to synthesize β-GDY and investigating its intrinsic properties and potential applications are highly desirable. However, there has been no available method to prepare β-GDY due to the complicated synthesis of precursors.

In this study, we present a feasible synthetic route to prepare β-GDY-containing thin film on copper foil with thickness about 25 nm using tetraethynylethene (TEE) as the precursor. Our synthetic strategy was derived from the Glaser–Hay coupling reaction that provides an efficient procedure for preparing symmetric diyne compounds in relatively high yields (Scheme 1).\(^{[33–35]}\) The schematic illustration of synthetic strategy is depicted in Figure 1. First, TEE was prepared and used immediately from tetra[(trimethylsilyl)ethynyl]ethene (TEE-TMS) which was synthesized according to previous reported work.\(^{[36]}\) Then, the monomer TEE was added into a three-neck flask containing acetone, pyridine, \(N,N,N',N'\text{-tetramethylethylenediamine} \) (TMEDA), and pretreated copper foils. The four terminal alkyls on TEE have high reactivity and are easily coupled with each other to form an uniform carbon network structure. Taking into account the volatile property of TEE, we adopted a modified Glaser–Hay coupling reaction to synthesize the β-GDY-containing network structure.\(^{[33–35,37]}\) In this process, the copper foil plays the roles of both a substrate and the source of catalyst,\(^{[38,39]}\) where a Glaser–Hay reaction took place efficiently with the aid of organic base. As a result, a carbon film of 25 nm thickness on the surface of copper foil was obtained. Electrical measurement of the film showed the conductivity of \(3.47 \times 10^{-6} \text{ S m}^{-1}\). This film could be used as a metal-free electron transfer layer to fabricate TiO\(_2@\beta\)-GDY composite which greatly enhanced the photocatalytic activity of TiO\(_2\).

The bonding structure and the elementary composition of β-GDY were studied systemically by Raman spectroscopy, Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), and UV–vis absorption spectroscopy. Figure 2a shows typical Raman spectrum of β-GDY. As shown in the Raman spectrum, four dominant peaks appeared at 1460.1, 1577.1, 1902.8, and 2173.1 cm\(^{-1}\), respectively. The peak at 1460.1 cm\(^{-1}\) comes from the vibration of carbon–carbon double bond that is consistent to the theoretical calculation.\(^{[40]}\) The peak at 1577.1 cm\(^{-1}\) comes from the stretching vibration of \(sp^2\) carbon domains in aromatic rings. The peak at 2173.1 cm\(^{-1}\) can be attributed to the stretching vibration of conjugated diyne links (\(-C=C-C=C-\)).\(^{[9,37]}\) The Raman peak of diyne linkage presents an obvious hypochromatic shift compared to the Raman peak of monomer (Figure S2, Supporting Information), that is consistent with theoretical predictions (Figure S3, Supporting Information). The peak at 1902 cm\(^{-1}\) could be assigned to carbon–carbon triple bond according to previous works.\(^{[9,37]}\) We note that no obvious changes of the β-GDY film were observed during the Raman spectroscopy characterization by 514 nm laser (0.09 mW) for 20 s, indicating the good stability of the synthesized β-GDY in air. FT-IR spectrum of as-grown GDY film on copper foil was displayed in Figure 2b. The band observed at 1060 cm\(^{-1}\) could be attributed to the stretching vibration of carbon–oxygen bond. The band of 2191 cm\(^{-1}\) is the typical carbon–carbon triple bond stretching vibration, that is in agreement with the result of Raman spectrum.\(^{[45]}\)

![Scheme 1. The Glaser–Hay coupling reaction.\(^{[33–35]}\) TMEDA = \(N,N,N',N'\text{-tetramethylethylenediamine}\).](image)

![Figure 1. Schematic illustration of the experimental setup for the β-GDY-containing film growth on copper substrate.](image)
XPS measurements indicated that the GDY is mainly composed of carbon element (Figure 2c). The existence of oxygen might result from the absorption of oxygen from air or the inevitable defects. Energy-dispersive spectrum results further confirmed the nearly pure carbon element (Figure S4a, Supporting Information). The peak at 285.0 eV shows essentially identical binding energy for the C1s orbital that can be deconvoluted into four subpeaks at 284.5, 285.3, 286.8, and 288.2 eV that are assigned to the C1s orbital of C=C, C≡C, C=O, and C=O bonds, respectively (Figure 2d). UV–vis absorption spectroscopy was also used to investigate the optical properties of as-prepared γ-GDY film (Figure S4b, Supporting Information). According to the UV–vis absorption measurements, there is an obvious bathochromic shift in the UV–vis spectra of the as-grown sample compared to monomers, which indicates that the extendedly conjugated π system formed due to alkynyl coupling enhanced electron delocalization.[37,42]

The morphology of the as-prepared β-GDY film was characterized by scanning electron microscopy (SEM). Figure 2e is a high magnification image of β-GDY film that displays the margin between β-GDY film and copper foil, which means that the copper substrate was uniformly covered by β-GDY film. Low magnification images of β-GDY film on a copper substrate (Figure S5, Supporting Information) show that the carbon film has a smooth surface and is continuous. Transmission electron microscopy (TEM) image indicates the layer-like structure of as-obtained β-GDY film (Figure S6, Supporting Information). High-resolution TEM (HRTEM) characterization clearly reveals curved streaks with a lattice parameter of 0.369 nm, which could be assigned to the interlayer distance of β-GDY (Figure 2f).[43] Corresponding selected area electron diffraction (SAED) pattern was shown in the inset of Figure 2f and its intensity integrating over 360° was also presented in Figure S6b (Supporting Information). This value is slightly higher than that of graphene owing to a more delocalized system of GDY and is close to that of γ-GDY.[13,44]

Atomic force microscopy (AFM) characterization of β-GDY film on SiO2 plate indicates that the film has a smooth surface with a roughness about 2 nm and the thickness is about 25 nm (Figure 3a). The electrical properties of the β-GDY films on substrate were measured by peak force tunneling AFM, a variant of AFM using a conductive cantilever tip, which could indicate
the current–voltage (I–V) characteristics as well as the surface contour of potential difference of the β-GDY film (Figure 3b). The I–V curves were measured on more than 100 sites at a bias voltage from −0.500 to +0.500 V. As shown in Figure 3c, the I–V relationship is highly linear in the voltage range between −0.200 and +0.200 V, which suggests the Ohmic behavior of β-GDY film. The conductivity was calculated as 3.47 × 10^{-6} S m^{-1}, indicating that the as-grown β-GDY is conductive, similar to γ-GDY. To further explore the properties of β-GDY, the work functions were also investigated with Kelvin probe force microscopy using Pt–Ir-coated tip (Pt–Ir Φ = 4.86 eV) in ambient conditions and are shown in Figure 3d. The value of 5.22 eV of β-GDY is slightly higher than that of γ-GDY (Φ = 5.20 eV), which suggests the existence of alkyne-rich framework in β-GDY. For further proof of alkyne-rich architecture in β-GDY, we calculated the work functions of several GY family materials including α-, β-, and γ-GY or GDY (Table S1, Supporting Information). On account of high electron density around carbon–carbon triple bond, the higher percentage of alkyne in structure is and the stronger electrostatic potential in the material exists.

In terms of structure, β-GDY has a higher percentage of acetylenic linkages than that of γ-GDY, and has strong π-conjugation as γ-GDY. Moreover, β-GDY owns a conductive property because of its metallic behavior according to the theoretical predication. These advantages imply that β-GDY might be of potential use in the fields of photocatalysis and photovoltaics. Previous reports have revealed that TiO_2@γ-GDY nanocomposite presented a higher photocatalytic activity compared to pure TiO_2^{[45,46]} Theoretical analysis demonstrated that Ti–C π bond is formed in TiO_2(001)@γ-GD composite because the high π-conjugation system of γ-GDY would make TiO_2 anchor to the GDY layer tightly and is beneficial for the charge transfer. Considering the highly π-conjugated system and the conductive property of the synthesized β-GDY-containing film, we applied it as an electronic transfer layer to enhance the photocatalytic performance of TiO_2. TiO_2@β-GDY composite was prepared through hydrothermal method. Its photocatalytic activity was evaluated by the degradation of organic dye methylene blue (MB). For comparison, TiO_2@γ-GDY was also prepared using the same method.

Figure 4a is the diagram of the catalytic processing. Briefly, electron–hole pairs were primarily formed on the semiconductor surface under light irradiation. β-GDY-containing film was used as an electron acceptor to prevent the electron–hole recombination of TiO_2. The holes were with high oxidability that can degrade 

![Figure 3. a) AFM image of β-GDY film transferred onto Si/SiO_2 substrate. b) Current AFM image. c) I–V curve of β-GDY film. d) Work functions of GY and GDY from theoretical predications and experimental measurements.](image-url)

![Figure 4. a) Schematic structure of TiO_2@β-GDY and tentative processes of the photodegradation of methylene blue (MB). b) HRTEM image of TiO_2@β-GDY. c) Photocatalytic degradation of MB over TiO_2 and different loading amount of β-GDY. d) Photocatalytic degradation of MB over TiO_2, TiO_2@γ-GDY, and TiO_2@β-GDY.](image-url)
organic dye into carbon dioxide, water, or other products after several steps. The XPS survey spectra of the \( \text{TiO}_2@\beta\text{-GDY} \) composite indicated the presence of Cls, Ti2p, and O1s groups at binding energies 285, 459, and 530 eV, respectively (Figure S7a, Supporting Information). The Cls spectrum (Figure S7b, Supporting Information) can be deconvoluted into C–Ti, C–C (sp\(^2\)), C–C (sp), and C–O, and at binding energies 284.3, 284.7, 285.8, and 288.2 eV, respectively. Notably, the Ti–C bond at 284.3 eV was discerned, indicating the anchoring of \( \text{TiO}_2 \) on GDY that is beneficial to the electron transfer and would enhance the photocatalytic ability of \( \text{TiO}_2 \) according to previous work.\(^{[46]}\) SEM and TEM images displayed the morphology characteristics of nanosheets and the SAED pattern could be indexed as [001] zone of \( \text{TiO}_2 \) (Figure S8a–c, Supporting Information). HRTEM image clearly showed the composition of \( \text{TiO}_2 \) and \( \beta\text{-GDY} \) (Figure 4b).\(^{[47]}\) Moreover, the continuous atomic planes with a lattice spacing of 3.7 Å corresponding to the (100) planes of anatase \( \text{TiO}_2 \) single crystals were also shown (Figure S8d, Supporting Information).\(^{[48]}\) The X-ray diffraction patterns and Raman spectrum of the products are shown in Figure S9 (Supporting Information).

The photocatalytic ability of \( \text{TiO}_2@\beta\text{-GDY} \) composite was evaluated by degrading MB under UV–visible light. According to the Beer–Lambert Law, the normalized temporal concentration change \( \left( \frac{A}{A_0} \right) \) of MB is proportional to the normalized maximum absorbance \( A_0 \) which is used to investigate the degradation speed of MB. The blank test showed that the concentration of MB did not decrease without light irradiation. Bare \( \text{TiO}_2 \) owned a moderate catalytic ability for MB degradation. In order to optimize the photocatalytic ability of \( \text{TiO}_2@\beta\text{-GDY} \), the composition ratio was controlled. As a result, \( \text{TiO}_2@\beta\text{-GDY} \) composites presented a superior photocatalytic efficiency than bare \( \text{TiO}_2 \) and the efficiency of different compositing ratio followed the order: 0.6 wt% > 0.8 wt% > 0.4 wt% of \( \beta\text{-GDY} \) (Figure 4c). For comparison, the optimized \( \text{TiO}_2@\gamma\text{-GDY} \) with 0.6 wt% carbon materials was also prepared and investigated (Figure 4d). The results showed that \( \text{TiO}_2@\beta\text{-GDY} \) had higher catalytic activity than \( \text{TiO}_2@\gamma\text{-GDY} \) composite and bare \( \text{TiO}_2 \). This is possibly due to the relative higher π-conjugated system in \( \beta\text{-GDY} \) that induced preferable synergistic effects between \( \text{TiO}_2 \) and \( \beta\text{-GDY} \).\(^{[49,50]}\) As mentioned above, the high π-conjugation system of GDY contributes to form of Ti–C π bond that is beneficial for the charge transfer. Compared to \( \gamma\text{-GDY} \), the large ring-like frameworks of \( \beta\text{-GDY} \) provides a suitable coordination site for Ti atoms and the higher acetylenic linkages percentage of \( \beta\text{-GDY} \) (about 1.2 times to \( \gamma\text{-GDY} \)) would provide more Ti–C π bonds that can capture the photogenerated electrons from \( \text{TiO}_2 \) via a percolation mechanism. Hence, \( \beta\text{-GDY} \) acts as a preferable electron acceptor to suppress the charge recombination effectively, leaving more holes to form reactive species that promote the degradation of dyes.

In conclusion, we have developed a novel method to prepare \( \beta\text{-GDY} \)-containing thin film on copper foil using a modified Glaser–Hay coupling reaction where the copper foil acted as the role of both a substrate and the source of catalyst. The synthesized film presented a smooth and uniform surface. The electronic property measurements of \( \beta\text{-GDY} \) film showed a conductivity of \( 3.47 \times 10^{-6} \text{ S m}^{-1} \) and a work function of 5.22 eV, which agreed well with theoretical calculations.