Controllable interfacial synthesis of three-dimensional hierarchical graphdiyne multilayer films

Wenjun Hao, Shan Lu, Zongping Chen*

1State Key Laboratory of Silicon Materials, School of Materials Science and Engineering, Zhejiang University, Hangzhou, China.
E-mail: chenzp@zju.edu.cn

Abstract. Graphdiyne (GDY) is a new type of carbon allotrope. Liquid/liquid interface growth of GDY can be realized in a controllable manner. Herein, three-dimensional hierarchical multilayer GDY films were prepared by polymerization of hexaethynylbenzene at liquid/liquid interface with various thickness. The present approach allows layer-by-layer growth of hierarchical GDY films. The obtained robust GDY multiple layers can be used as support to grow composites which are efficient catalysts for electrochemical reactions.

1. Introduction
In possession of extraordinary electronical, chemical, optical and mechanical properties, non-natural carbon allotropes, including fullerene, carbon nanotubes, graphene, graphyne, and their derivatives, have given rise to various magnificent possibilities in extensive applications in the field of energy, catalysis, environmental, and biomedical domains, etc. In 1987, graphyne was first predicted theoretically by Baughman et al. It is a new type of two-dimensional carbon allotrope which contains sp-sp² hybridized carbon atoms. In 1997, Graphdiyne (GDY) was predicted theoretically by Haley and it is the most investigated graphyne in which two benzene rings are chained by diacetylenic linkages (-C≡C-C≡C-), including α-GDY, β-GDY, γ-GDY. γ-GDY is the most studied GDY due to its stable configuration. In 2010, γ-GDY was experimentally obtained in Li’s group through Glaser-Hay cross coupling by using hexaethynylbenzene (HEB) and copper foil as precursor and substrate, respectively. Then various modified methods have been applied to synthesize GDY with different morphologies, such as nanotubes, nanowires, and nanowalls. In 2018, Gao et al. and co-workers reported a facile van der Waals epitaxial growth method in solution using graphene as substrates. Moreover, chemical vapor deposition (CVD) technique was used to fabricated GDY at 150 °C onto the surface of silver foil. GDY films were also prepared using ZnO nanorod arrays as substrate through a self-catalyzed vapor-liquid-solid method. Furthermore, bulk GDY powders were achieved by using copper powder as catalysts. In 2017, an interfacial strategy was reported for the synthesis of few layers of crystalline GDY through Englinton coupling reaction. Nitrogen doped GDY was prepared successfully by liquid/liquid interface synthetic approach using monomers with different numbers of N atoms. GDY analogues containing H, Me, F were synthesized using different monomers through liquid/liquid interface method. Thus, liquid/liquid interface synthetic approach can provide a large choice of designed monomers and mild reaction conditions for GDY synthesis.

In this work, we design a robust way to fabricate three-dimensional hierarchical multilayer GDY films by polymerization of hexaethynylbenzene at liquid/liquid interface with various thickness. The present approach allows layer-by-layer growth of hierarchical GDY films. The obtained robust GDY
multiple layers can be used as support to grow composites which are promising for energy storage systems.

2. Result and discussion

2.1. Experimental methods

2.1.1. Materials and characterizations
All the reagents and solvents were purchased from Sinopharm and used as received without further purification unless otherwise mentioned. Water was purified by a Milli-Q system. The obtained GDY films were characterized by scanning electron microscope (SEM) using a Hitachi SU-4800 microscope at 5 kV. The GDY samples were also characterized by transmission electron microscope (TEM) and high resolution TEM (HRTEM) using JEOL 2100 F microscope operating at 200 kV. The GDY films were deposited on TEM grids from alcohol dispersion after a sonication step for 2 min. Raman spectra were collected by WITec alpha300R. The surficial chemical stated and composition of the as-synthesized samples were characterized by XPS using a Kratos AXIS Supra spectrometer. The raw XPS data were corrected using the binding energy of the C-C bond at 284.5 eV and fitted with Gaussian-Lorentzian curves.

2.1.2. Synthesis of GDY films with different thickness by liquid-liquid interfacial reaction
HEB was synthesized at the laboratory according to other researchers’ work.22 The synthesis process was operated under N\textsubscript{2} atmosphere in the darkness. Typically, TBAF (1 M in 10 μL of THF) was added into a solution of HEB-TMS (1 μmol) in dichloromethane (10 mL). The mixture was vigorously shaken for 10 min to obtain HEB solution (0.1 nM) in dichloromethane. The HEB solution was poured into a glass weighing bottle (60 mm×30 mm) immediately without further purification. 10 mL ultra-pure water was added gently and spread onto the HEB solution. Then 10 mL copper acetate (0.01 M) and pyridine (0.25 M) aqueous solution was added gently into the water layer. The reaction system was sealed and kept without disturbance for 24 h. A brown GDY film was obtained at the interface. The organic phase was rinsed by dichloromethane and the aqueous phase was cleansed by aqueous HCl (1 M) and ultra-pure water. The GDY films can be transferred to arbitrary substrates. The obtained GDY films were named as GDY-1. GDY-2 was obtained while the reaction time was 72 h. GDY-3 was obtained when the concentration of HEB and copper acetate solutions were 10 times as GDY-1. GDY-4 was named as the same concentration precursors as GDY-3 while the reaction time was 72 h.

2.2. Results and discussion
The synthetic procedure is illustrated in Fig. 1. Multiple layers of GDY were obtained at the interface between two immiscible solution phases. The upper phase was formed by copper acetate, pyridine and ultra-pure water. The lower phase contained HEB monomer and dichloromethane as solvent. The lower phase was firstly covered by pure water which made sure that the reaction system would remain still while adding the upper solution. The reaction system was kept under inert atmosphere at room temperature for 24 h or 72 h. Multiple layers of GDY were generated successfully at the interface which were insoluble in water or organic phase (Fig. 1). The obtained dark brown to black films were rinsed by water and dichloromethane for several times and transferred to arbitrary substrates.
The obtained GDY films from dilute reagent solutions were named as GDY-1. GDY-2 was obtained while the reaction time was 72 h with the same reagent concentration. GDY-3 was obtained when the concentration of HEB and copper acetate solutions were 10 times as GDY-1. GDY-4 was named as the same concentration precursors as GDY-3 while the reaction time was 72 h. The scanning electron microscope (SEM) image of GDY-1 (Fig. 2a) illustrates that the obtained GDY film is formed with vertical nano-wall structures. The SEM image of GDY-2 (Fig. 2b) shows that the film grows thicker with prolonged reaction time. The SEM image of GDY-3 (Fig. 2c) indicates that the obtained film grows dense when the concentration of the reagents increases 10 times. Furthermore, an interesting phenomenon occurred for GDY-4 (Fig. 2d) when the reaction time increased to 72 h. The cross-sectional SEM image of GDY-4 (Fig. 2e) indicates that its thickness is approximate 15.6 μm. It consists of multiple layers of hierarchical porous structures. When smashing the films into powder, some bubble-like assembly structures can be found in the inner part (Fig. 2f).

The low magnification transmission electron microscope (TEM) images in Fig. 3a,b further indicate the same hierarchical morphologies as SEM images in Fig. 2f. High magnification TEM image (Fig. 3c) exhibit amorphous structure of the obtained GDY. Raman spectroscopy is a powerful technique to reveal the quality and uniformity of carbon materials. Thus, as illustrated in Fig. 3d, the Raman spectrum of
GDY-4 exhibits two strong bands centred at 1356 cm\(^{-1}\) and 1591 cm\(^{-1}\) attributed to D and G band, which are connected to the breathing vibration of sp\(^2\) carbon domain and E\(_{2g}\) stretching vibration mode in aromatic rings. Moreover, two weak bands centred at 1939 cm\(^{-1}\) and 2195 cm\(^{-1}\) are derived from the vibration of the conjugated diyne linkage (-C≡C-C≡C-).23

![Figure 3 a,b) Low magnification transmission electron microscope images of GDY-4; c) High magnification TEM image of GDY-4; d) Raman spectrum of GDY-4.](image)

X-ray photo electron spectroscopy (XPS) is used to determine the chemical composition of the GDY-4. The XPS survey scan spectrum is dominated by strong signal from carbon as illustrated in Fig. 4a. XPS quantitative analysis reveals the atomic ratios of different compositions as 88.9% (C), 10.7% (O), and 0.4% (Cu). The presence of O impurity may due to the contamination from air. The small amount of Cu impurity may due to the reserved catalyst. Narrow scan of C 1s exhibits that the GDY-4 has both sp\(^2\) and sp\(^3\) hybrid carbon. The area ratio of sp and sp\(^2\) is 1.93, which is close to the chemical composition of GDY.24 The presence of C-O and C=O contribution is ascribed to sample handling under ambient condition. The obtained robust GDY multiple layers can be used as support to grow various composites and used as highly efficient catalysts for electrochemical reactions which will be reported elsewhere.

![Figure 4 a) Survey scan of GDY-4; b) Narrow scan for C 1s of GDY-4.](image)

3. Conclusions
In summary, three-dimensional hierarchical multilayer GDY films were prepared by polymerization of hexaethynylbenzene at liquid/liquid interface with various thickness. A hierarchical multilayer GDY film were successfully generated at a controllable manner. SEM and TEM techniques reveal that the...
present approach allows layer-by-layer growth of hierarchical GDY films. XPS and Raman spectrum indicated characteristic compliance with the chemical composition of GDY with good quality. The obtained robust GDY multiple layers with large surface area can be used as support to grow various active nanomaterials and used as highly efficient catalysts for electrochemical energy storage and conversion which will be reported elsewhere.

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