

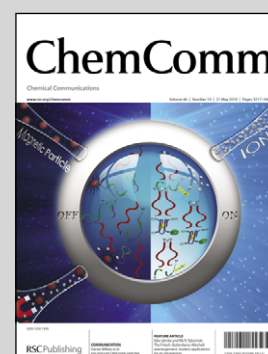
Showcasing research from Yuliang Li's laboratory,
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Architecture of graphdiyne nanoscale films

A new carbon allotrope – graphdiyne – was synthesized and predicted to be the most stable of non-natural carbon allotropes.

Graphdiyne, a new molecular allotrope of carbon, is a two-dimensional layer with one-atom thickness and strongly bonded carbon networks, chemical stability and electrical conductivity.

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Architecture of graphdiyne nanoscale films†

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We have demonstrated a methodology to generate large area graphdiyne films with 3.61 cm² on the surface of copper *via* a cross-coupling reaction using hexaethynylbenzene. The device based on graphdiyne films for measurement of electrical property is fabricated and shows conductivity of $2.516 \times 10^{-4} \text{ S m}^{-1}$ indicating a semiconductor property.

During the past twenty years, scientists have developed synthesis methods for preparing new carbon allotropes for studying specific physical properties. The goal of synthesizing and isolating new stable forms of carbon is the development of a new technology area for focusing mainly on identifying new properties and applications of carbon allotropes.^{1–3} A structural study of carbon is a main fundamental interest in development and is expected to be widely applied to nanosciences and technology. Due to carbon's three hybridization states (sp³, sp², and sp), having numerous combinations by which atoms of this element can be bonded to each other to produce many carbon allotropes; such as graphite (sp²), diamond (sp³) in the nature, and many novel carbon allotropes such as fullerene (sp²), carbon nanotube (sp²), and graphene (sp²), are successfully synthesized.^{1–3} Still, the design and synthesis of new carbon allotropes with definite structure and property is a significant and ongoing challenge within new materials science and there are still a large number of new forms of carbon to be discovered. Several groups have demonstrated a methodology to generate networks of combinations of sp² and sp, or sp³ and sp hybridized carbons.⁴ The carbon–carbon triple bond (sp) is a rather useful connecting unit because of the structural linearity that does not suffer from fluctuation arising from *cis*–*trans* isomerization, it has small steric demands and the facility in connecting a sp carbon to a sp² or sp carbon center. Moreover, carbon networks with delocalized π -systems are of particular relevance owing to the tenability of their properties with clever changes in their electronic, optic and geometric characteristics.⁵ Highly conjugated, carbon-rich organic molecules featuring tunable structural and optoelectronic properties have been recognized as promising candidates for use in next-generation electronic and optoelectronic devices.^{6–9} Graphdiyne proposed (see ESI, Scheme S1†) is a novel structure in the carbon family and

predicted to be the most stable of the various diacetylenic non-natural carbon allotropes and is one of the most “synthetically approachable”.⁴ Graphdiyne was proposed several years ago and great efforts have been dedicated to the preparation of an amount of monomeric and oligomeric substructures toward constricting graphdiyne.^{10–13} However, the synthesizing of a novel, stable graphdiyne form of carbon still remains elusive. In the present work, we aim to demonstrate that large area graphdiyne films can be fabricated on the surface of copper *via* a cross-coupling reaction using hexaethynylbenzene. The approach demonstrated here is remarkable for forming large area films of graphdiyne in a facile way.

The films are composed of graphdiyne multilayers, and are continuous across copper surface and uniformity. The device based on graphdiyne films for measurement of electrical property is fabricated and shows conductivity of $2.516 \times 10^{-4} \text{ S m}^{-1}$ at room temperature indicating a semiconductor property. The excellent semiconductor feature of graphdiyne films is similar to silicon which is a vital candidate, together with graphene, to apply in the fields of electronics, semiconductors and materials.

The details of the synthesis experiments are described in the electronic supplementary information.† In brief, the monomer of hexaethynylbenzene was synthesized in good yield (62%) by addition of tetrabutylammonium fluoride (TBAF) to THF solution of hexakis[(trimethylsilyl)ethynyl]benzene for 10 min at 8 °C. The graphdiyne was successfully grown on the surface of copper foil in the presence of pyridine by a cross-coupling reaction of the monomer of hexaethynylbenzene for 72 h at 60 °C under nitrogen atmosphere. In the process of forming graphdiyne, the copper foil is not the only catalyst for the cross-coupling reaction but also is the substrate for growing graphdiyne film. In fact, copper is easy to transfer to Cu(II) ion in alkaline solution. In our experiment, trace amounts of Cu(II) ions can be produced in the presence of pyridine resulting in catalyzing the cross-coupling reaction.^{14,15}

Fig. 1a shows a scanning electron microscope (SEM) image of graphdiyne film on a copper substrate. The film is uniform which indicates that the graphdiyne film is continuous. The higher magnification image of graphdiyne film on copper foil (Fig. 1b) displays the particles attached on the surface of the graphdiyne film. Fig. 1c shows the presence of a split film with curling on the brim of the copper foil, which indicates that the graphdiyne film is flexible. From Fig. 1d, the thickness of graphdiyne film is about 1 μm . The result of energy-dispersive X-ray (EDX) spectrum analysis (see ESI, Fig. S1b†) indicates that the graphdiyne film consists of only elemental carbon.

Fig. 2a and b show transmission electron microscope (TEM) images of graphdiyne. Fig. 2a displays a cracked graphdiyne film with a smooth surface. The high resolution

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† Electronic supplementary information (ESI) available: EDX spectrum analysis, FT-IR spectrum of graphdiyne film and the experimental preparation for graphdiyne nanoscale films. See DOI: 10.1039/b922733d

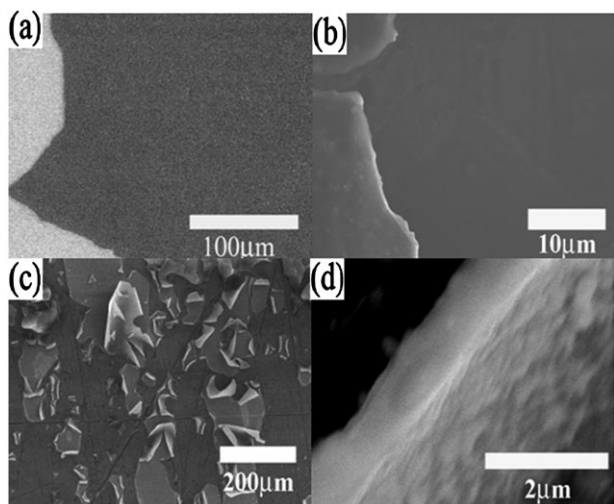


Fig. 1 The SEM images of graphdiyne films grown on the surface of copper foil, (a) large-area graphdiyne film, (b) higher magnification image, (c) cracked film on the brim of copper foil, (d) a turned up film.

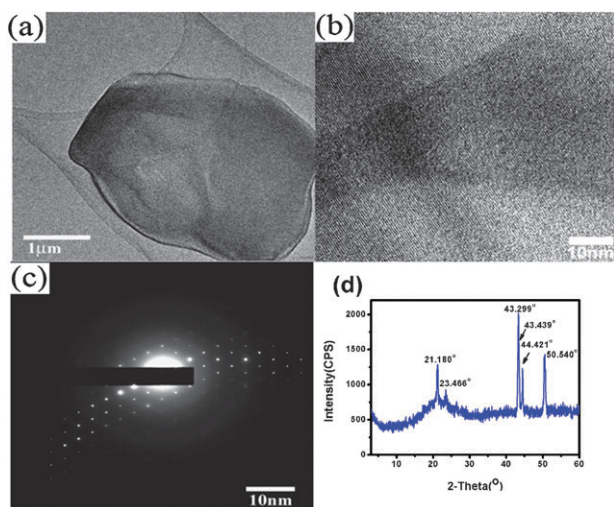


Fig. 2 The TEM images of graphdiyne films grown on the surface of copper foil, (a) low-magnification TEM images showing graphdiyne film, (b) high-magnification TEM images showing the edges of film regions of a. (c) SAED pattern. (d) XRD pattern of graphdiyne film.

TEM image (Fig. 2b) recorded from the blue circled area in Fig. 2a exhibits clear lattice fringes of 4.1913 Å without defects and dislocations, which is larger than that of graphene 2.32 Å and graphite 2.46 Å.¹⁶ The selected area electron diffraction (SAED) pattern in Fig. 2c confirms the nature of high crystallinity. The X-ray diffraction (XRD, Cu-K α radiation) pattern in Fig. 2d further confirms that the graphdiyne film is crystalline. The strong diffraction peak at 10.59° corresponds to the diffraction spacing of 4.1913 Å, other peaks at 21.72°, 22.21° and 25.27° can also be observed.

The results of X-ray photoelectron spectroscopy (XPS) (Fig. 3) are consistent with EDX analysis indicating unambiguously that graphdiyne films are composed of only elemental carbon. The C 1s peak at 284.8 eV in Fig. 3a shows essentially identical binding energies for the C 1s orbital. The presence of an O 1s peak at 532 eV is due to the absorption of air in graphdiyne.

In the graphdiyne, the extra alkyne units between benzene rings increase the pore size of the network to approximately 2.5 Å,¹⁷ which results in air adsorption in the pores when the sample is exposed to air. Fig. 3b presents a high resolution asymmetric C 1s XPS spectrum of graphdiyne. After the subtraction of a Shirley background followed by fitting with a mixture function of Lorentzian and Gaussian, the C 1s peak can be mainly deconvoluted into four sub-peaks at 284.5, 285.2, 286.9 and 288.5 eV, which have been assigned to a C 1s orbital of C–C (sp²), C–C (sp), C–O and C=O, respectively.^{18,19} The area ratio of sp/sp² is 2, which confirms that the benzene rings link with others by diene in as-prepared graphdiyne.

Raman spectroscopy was used to evaluate the quality and uniformity of graphdiyne on the surface of copper foil. Fig. 4 shows typical Raman spectra of graphdiyne at different positions. All the Raman spectra from different positions display four prominent peaks at 1382.2 cm⁻¹, 1569.5 cm⁻¹, 1926.2 cm⁻¹, and 2189.8 cm⁻¹, respectively. The peak at 1569.5 cm⁻¹ corresponds to the first-order scattering of the E_{2g} mode observed for in-phase stretching vibration sp² carbon domains in aromatic rings, which is red shift comparing to the G band of graphite (1575 cm⁻¹).²⁰ The peak at 1382.2 cm⁻¹ is attributed to the breathing vibration of sp² carbon domains in aromatic rings, which is a hypsochromic shift compared to

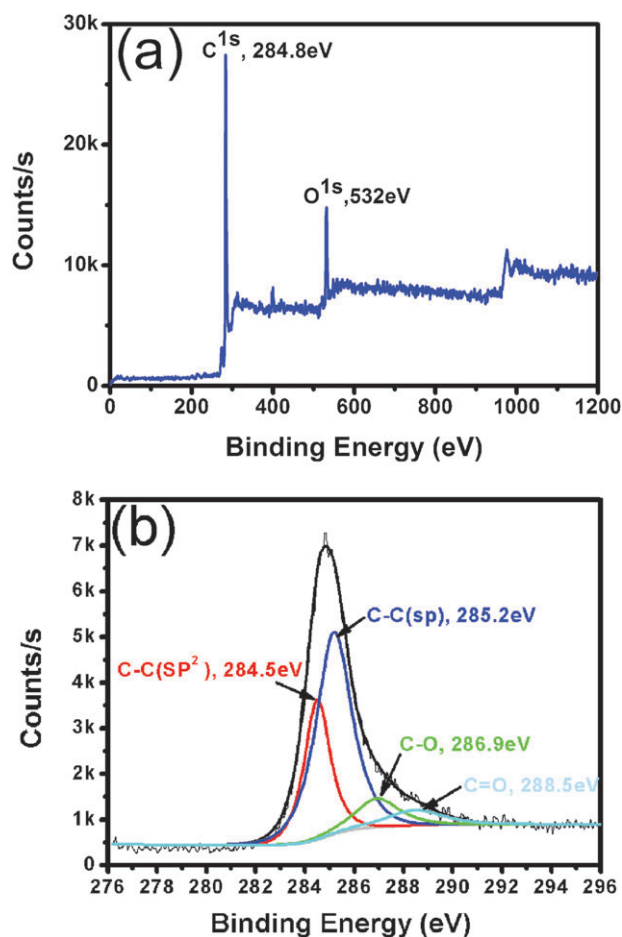


Fig. 3 XPS spectra of graphdiyne film: (a) survey scan, (b) narrow scan for element C.

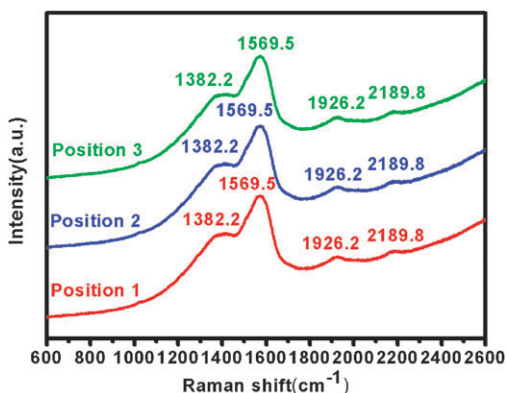


Fig. 4 Raman spectra of graphdiyne films on three positions.

the D band of graphite,¹⁸ and the pronounced D band is a disordered band associated with structural defects, amorphous carbon or edges that can break the symmetry and selection rule.²¹ The intensity ratio (the peak of 1382.2 cm⁻¹ to the peak of 1575 cm⁻¹) is 0.729, which indicates the high order and low defects in the graphdiyne films, and the graphdiyne films are composed of multilayers.²¹ The peaks at 2189.8 cm⁻¹ and 1926.2 cm⁻¹ can be attributed to the vibration of conjugated diene links (-C≡C-C≡C-).¹⁷

Fig. 5 shows the typical atomic force microscopy (AFM) images of as-grown graphdiyne films on copper substrate. The

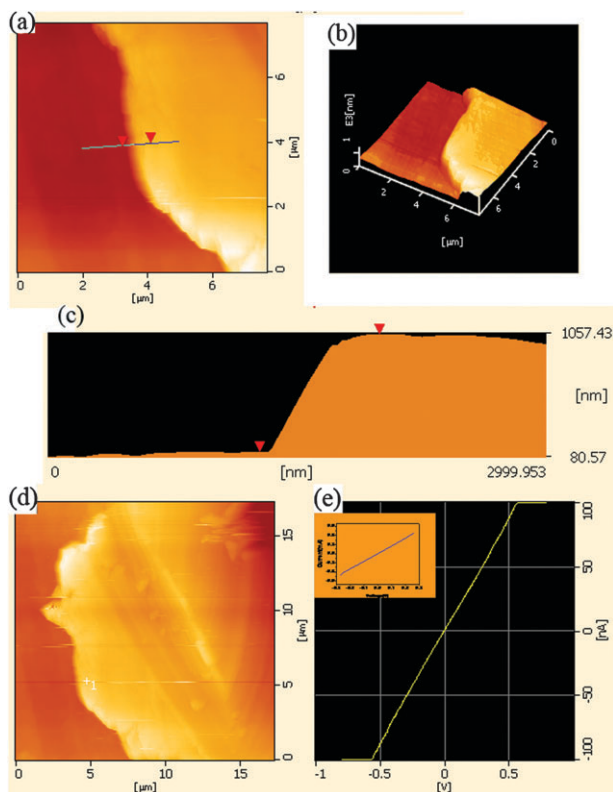


Fig. 5 AFM images of graphdiyne film (a) the morphology, (b) Tapping mode 3D height AFM image. (c) The profile of the graphdiyne film height taken along the line marked in a. (d) Current AFM image, (e) I - V curve of graphdiyne film, and the inset is I - V curve of graphdiyne films measurement on the device.

cross-sectional view of the AFM image (Fig. 5a-c) indicates that the average thickness of graphdiyne films is 970 nm, which is coincident with SEM observation. The electrical properties of the graphdiyne films on copper foil are investigated by AFM using a conductive cantilever under application of a bias voltage, where a conductive cantilever was contacted with the graphdiyne film. The electrical characteristics of the graphdiyne film are investigated by recording typical current-voltage (I - V) curves at a bias voltage of -0.800 V to +0.800 V at a number of sites (Fig. 5d and e). As shown in Fig. 5e, the I - V curve behavior in the range of bias voltage between -0.500 V and +0.500 V is highly linear. The devices based on graphdiyne films on the Cu foil for conductivity study are fabricated and are measured at room temperature. The graphdiyne films are grown on Cu foils as bottom electrodes, and Al films (20 mm²) are prepared as top electrodes.²² The inset of Fig. 5e shows that the I - V curve of the graphdiyne film is linear, which exhibits Ohmic behavior, and the slope of the line is 2.53×10^{-3} . The conductivity is calculated as 2.516×10^{-4} S m⁻¹, which compares with silicon, and demonstrates that the graphdiyne film exhibits excellent semi-conducting properties.

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