Chemically synthetic graphdiynes: application in energy conversion fields and the beyond

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The discovery of graphene in 2004 brings a new era of two-dimensional (2D) materials research [1]. Together with previous carbon nanotubes and fullerene, the carbon series nanostructures seem an endless story that always astonishes the world. In this means, the first chemical synthesis of graphdiynes by Chinese chemists Yuliang Li *et al.* continues the brilliant age of carbon research [2].

Proposed by Haley and coworkers, graphdiyne (GD) is a 2D carbon allotrope containing planar sp and sp² carbon atoms, which is predicted to be the most stable carbon allotrope containing diacetylenic linkages [3]. Density functional theory (DFT) calculations coupled with Boltzman transport equation show that GD sheet is a semiconductor with a band gap of 0.46 eV and an in-plane electron mobility on the order of 10⁵ cm² V⁻¹ s⁻¹ at room temperature, with a hole mobility about an order of lower magnitude [4]. Considering that, GD is anticipated to exhibit outstanding electronic properties and hold the great promises in applications where high charge carrier mobility is preferred, such as photocatalysis, solar cells and energy storage. For example, Wang's group published the first paper studying the photocatalytic process enhanced by GD [5]. In this work, GD was firstly chemically modified with titania nanoparticles (P25) by a facile hydrothermal treatment to form a nanocomposite photocatalyst. And the P25-GD nanocomposite showed better photocatalytic activity than P25-carbon nanotube composite and P25-graphene composite. It was proposed that the interactions between P25 and GD decreased the bandgap of P25, which thus extended its absorbable light range. Additionally, Wang's group also showed that TiO₂(001)-GD composites possessed superior charge separation and oxidation properties to GD- or graphene-based composites with different faceted TiO₂ from both first-principles DFT and experimental studies [6]. Besides, GD was also introduced to different counterparts for oxygen reduction reactions, perovskite solar cells and lithium-ion batteries, and its unique structure and semiconductor property endow them with superior performance, even compared with the prevalent graphene

[7–9]. These studies further excavated the deep application potential of GD. However, the GDs used in the above studies are mostly bulk or thick materials so that the excellent surface properties and electron mobility cannot be well exploited. Thin GD is believed to exhibit better performance since the surface area will be enlarged and contacts thoroughly with other materials.

In a recent online publication of *Advanced Energy Materials*, Professor Ranbo Yu from the University of Science and Technology Beijing, China, and her collaborators reported a new nanocomposite of graphdiyne nanosheet (GDNS) modified by Pt nanoparticles (PtNP) via a facile ion-beam sputtering method for the first time (Fig. 1) [10]. Thick GD was exfoliated by a lithium-ion intercalation/exfoliation method into much thinner GDNS. Moreover, based on DFT calculations, they revealed that Pt and C atoms of GD interacted via the d_z orbital of Pt and the p_z orbital of C. As a result, the PtNP-GDNS composite showed outstanding catalytic activity towards the reaction of I₃⁻/I⁻ redox pairs, the best among reduced graphene oxide/PtNP composite (PtNP-rGO), PtNP and Pt foil. This can be ascribed to the enhanced charge transfer ability resulting from the chemical interaction between Pt and the triple bond of GD. The dye-sensitized solar cells (DSSCs) using PtNP-GDNS as counter electrode showed much higher efficiency due to their superior catalytic ability than the PtNP and PtNP-rGO based DSSCs, even rival to that using Pt foil. This is the first study using GD-based material as the counter electrode for DSSCs.

With more interesting findings or research in energy conversion fields, the theoretical stage of GD could be further promoted to a new stage of application. The proposed high charge carrier mobility and intrinsic semiconductor properties of GD will guarantee its great potential in more fields in the future. It is believed that chemically synthetic GD will become a superb competitor among the 2D carbon materials available for energy conversion and catalysis.

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Figure 1 (a) Localized orbital locator (LOL) maps and Mayer bond order analysis for the Pt₂-GD fragment (off-center adsorption site). (b) TEM image of PtNP-GDNS. (c) Cyclic voltammetry curves of different counter electrodes. (d) Photocurrent density-voltage (J-V) curves of dye-sensitized solar cells using different counter electrodes. Adapted with permission from Ref. [10], Copyright 2015, Wiley.

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