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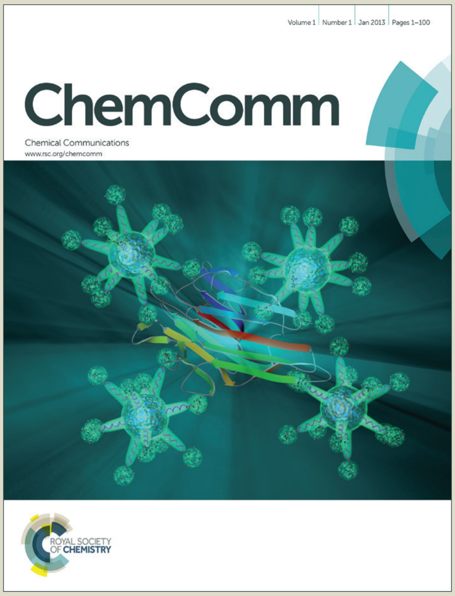

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Bulk graphdiyne powder applied for highly efficient lithium storage

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Here, we prepared bulk graphdiyne (GDY) powder with porous structure and explored its lithium storage properties. The assembled lithium ion batteries exhibited superior electrochemical performance, including high specific capacity, excellent rate performance and long cycle life, which should be attributed to its unique structure, high electronic conductivity and chemical stability.

Rechargeable Lithium-ion-based energy storage devices, such as lithium ion batteries (LIBs) and lithium ion capacitors (LICs), are key components for the increasing demand of the portable, entertainment, computing, telecommunication equipment, and low-emission vehicles required by today's information-rich, mobile society.[1-5] Carbon nanoarchitectures have been employed as important nanoscale advanced materials for application in energy devices to fulfill the increasing needs of low energy consumption and high performance devices. The energy density of traditional LIBs cannot meet current requirements due to the capacity limit of graphite. Carbonaceous materials like fullerenes,[6-8] carbon nanotube,[9-11] graphene[12-15] and graphene-based hybrids[16-18] have been investigated extensively to improve the energy density and performance of batteries. However, there are still numerous issues need to be addressed, for instance, limited Li storage capacity, large irreversible capacity loss, low rate capability, and poor capacity retention upon the charge/discharge cycling, etc.

Graphdiyne (GDY), a novel carbon allotrope comprising *sp*- and sp^2-hybridized carbon atoms, has attracted considerable attention from physical and chemical scientists due to its electronic, optical as well as mechanical properties.[19-22] Since 1997, some small organic diyne segments containing hydrogen atoms were synthesized by Haley et al,[23] but until very recently large-area and all carbon GDY film has been first prepared by Li et al[24] via an in situ cross-coupling reaction on copper foil from hexaethynylbenzene. With respect to GDY, its unique structure owning a large number of triangular-like pores, endows GDY more Li storage sites, and facilities Li ions adsorption, desorption and diffusion both in-plane and out-plane. In terms of graphyne, theoretical studies have shown that it can be used for LIBs anode and the maximum composite of the Li-intercallated graphyne is found to be Li_3C_6, which is three times than that of graphite.[25] Density functional theory[26] and first-principles calculations[27-28] have indicated that the unique atomic arrangement of GDY enables a unique Li triangular occupation pattern: each pore accommodates three Li atoms located at three asymmetric sites and the maximum Li storage capacity of monolayer GDY can be as high as 744 mAh/g (LiC_3),[26] which is twice of the commercial graphite (372 mAh/g, LiC_6).[29] Its considerably high mobility[30] and high Li storage capacity make GDY a promising candidate material employed in rechargeable Li-ion-based energy storage devices.

In this work, we explored bulk GDY powder as an anode material in practical LIBs to evaluate its Li storage properties. GDY powder with microporous and mesoporous structure can be prepared easily according to the cross-coupling reaction and processed to anodes with any shape. The LIBs assembled with GDY-based anodes exhibit high specific capacity, excellent rate performance as well as long cycle life. Those results indicate that GDY is an efficient material for Li storage and has potential to be applied in energy storage applications.

The structure of GDY sheet is shown in Fig. 1A, where the unit cell is drawn with green line. As two dimension (2D) atomic layers consisting of two adjacent *sp*-bonded carbon atoms and sp^2-bonded carbon atoms, GDY exhibited excellent chemical stability and high electrical conductivity,[19] and was predicated to be the most stable of the various diacetylenic non-natural carbon allotropes as well as one of the most synthetically approachable. Containing two acetylenic linkages between repeating patterns of carbon hexagons, the unique structure endows GDY with high degrees of π-conjunction, uniformly distributed pores, and tunable electronic properties. For graphene, the highly inherent anisotropic nature of Li diffusion limits the rate capability of the charge/discharge reactions. Both experimental and theoretical investigations have confirmed that Li diffusion in defect-free graphene is restricted in the interlayer space (in-plane diffusion) because Li hopping between adjacent layers through a carbon hexagon is energetically extremely unfavorable (~10 eV).[29,31-32] Instead, as reported by many researchers,[19,27-28] the atomic arrangement of GDY composed of *sp*- and sp^2-hybridized carbon atoms leads to a unique Li triangular occupation pattern, i.e., each pore accommodates three Li atoms located at three symmetric sites. The continuous Li diffusion across a single GDY layer can be achieved by overcoming an energy barrier of 0.52 eV. Li can easily penetrate GDY plane with an energy barrier of 0.35 eV, which enables Li atoms to be well dispersed on both sides of single-layer GDY. Therefore, the maximum Li storage capacity of GDY monolayers can be expected as high as LiC_3 with triangular-patterned Li atoms distributing alternately on both sides of GDY which is twice the capacity of graphite.

However, until now, there were no reports on applying GDY as a practical battery application, for the quantities and qualities of GDY sample were hard to control and achieve. In order to work as electrode in a battery, GDY must be available in large quantities. Collaborated with Li's group,[19,24] who firstly developed an in situ cross-coupling reaction on to fabricate large-area ordered films, we prepared bulk GDY powder with microporous and mesoporous structure and applied as anode materials in LIBs. The preparation details of the GDY powder was described in the supplementary information according to the cross-coupling reaction as reported.[24]

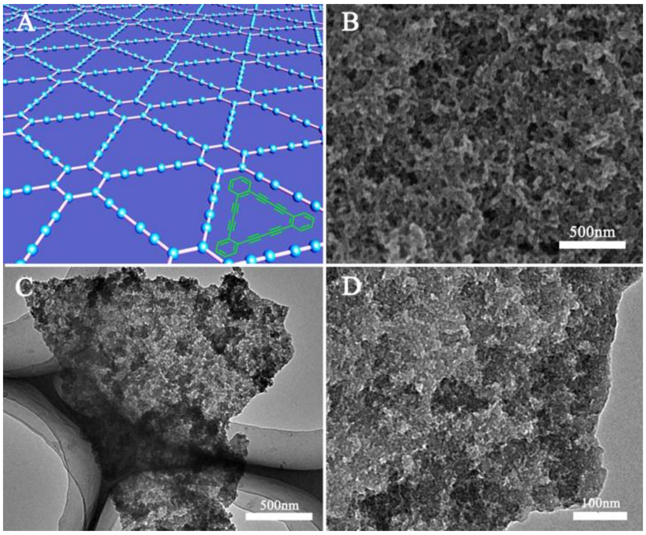

Fig. 1 (A) Ball-and-stick model of GDY structure, the inset is the unit cell of GDY. (B) SEM and (C, D) TEM images of GDY.

The morphology of GDY powder was investigated using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Fig. 1B shows that GDY powder is composed of 3D microporous and mesoporous structure. TEM images (Fig. 1C, D) further confirm this porous structure. The porosity of GDY was further characterized by Nitrogen adsorption/desorption experiment and the isotherm is shown in Fig. 2A. Pore size distribution analysis clearly indicates that the pore-size is mainly in a range among 0.81, 1.56, 2.98 and 8.12 nm, demonstrating the microporous and mesoporous structure of GDY, which is considered to be beneficial for the rapid transport of electrons and ions. Nitrogen adsorption-desorption measurement also shows a high specific surface area of 320.9 m^2/g, which endows GDY more active sites for Li storage.

In agreement with previously reported data,[24] the Raman spectra of Bulk GDY powder (Fig. 2B) exhibit two prominent peaks: a D band at 1363.3 cm^{-1} and a G band at 1582.1 cm^{-1}. The intensity of the D band is strongly associated with structural defects, including disordered carbon atoms and edges; the G band corresponds to first-order scattering of the E_{2g} stretching vibration mode observed for sp^2-hybridized carbon atom domains in aromatic rings. For GDY, the ratio of the intensities of the D and G bands was 0.66, suggesting bulk GDY powder possess high order and low content of defects.[19,24] The peak at 2161.5 cm^{-1} was contributed by the vibration of acetylenic linkages (−C≡C−C≡C−).

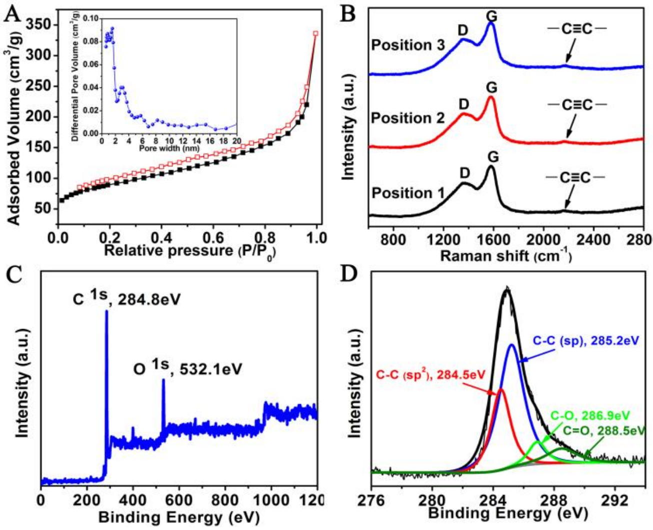

Fig. 2 (A) N_2 adsorption/desorption isotherms, and the inset is the pore-size distribution of GDY. (B) Typical Raman spectra of GDY. (C) Survey and (D) C 1s binding energy profiles of GDY.

X-ray photoelectron spectroscopy (XPS) displayed unambiguously that the GDY samples were composed of only elemental carbon (Fig. 2C and D). The C 1s peak that appeared at 284.8 eV, can be assigned to the binding energy of a C 1s orbital. The presence of a signal for O 1s at 532.1 eV arose from the adsorption of O_2 when GDY was exposed to air. After subtraction of the Shirley background, followed by fitting with a mixture function of Lorentzian and Gaussian, the C 1s peak could be divided into four mainly sub-peaks at 284.5, 285.2, 286.9, and 288.5 eV, which could be assigned to orbitals in C–C (sp^2), C≡C (sp), C–O, and C=O bonds, respectively. The area ratio of the sp- and sp^2-hybridized carbon atoms was 2, confirmed the structure of GDY comprising benzene rings linked together through two acetylenic linkages.

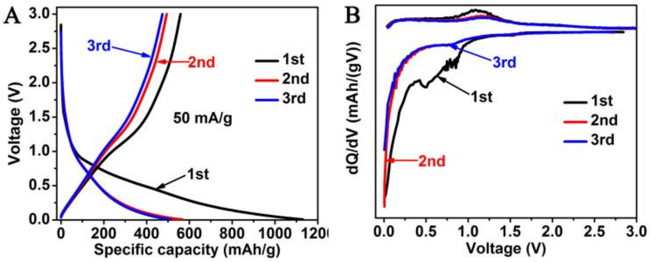

Fig. 3 (A) Galvanostatic charge/discharge profiles and (B) Differential curves of charge/discharge profiles of GDY based electrode under 50 mA/g.

Coin cells were fabricated to evaluate the electrochemical Li storage capacity of GDY-based electrode using Li foil as the counter electrode. The schematic structure of the coin cell can be found in Fig. S1. The electrochemical performance of GDY was shown in Fig. 3 and Fig. 4. As shown in Fig. 3A, the charge/discharge profiles of GDY electrode were consistent with cyclic voltammogram (CV) curves (Fig. S2) without distinguishing plateau. During the initial cycle, a large irreversible capacity emerged and the initial coulombic efficiency was as low as 53.6%, which could be attributed to the formation of solid electrolyte interphase (SEI) layer on the GDY electrode surface. In the subsequent cycles, the differential voltage curves (Fig. 3B) obviously showed that the larger part of specific capacity (＞70%) in the region below 0.5 V, corresponding to the Li intercalation into GDY layers.[33] While, the capacity above 0.5 V could be ascribed to the faradic capacitance on the surface or on the edge sites of GDY.[13,33]

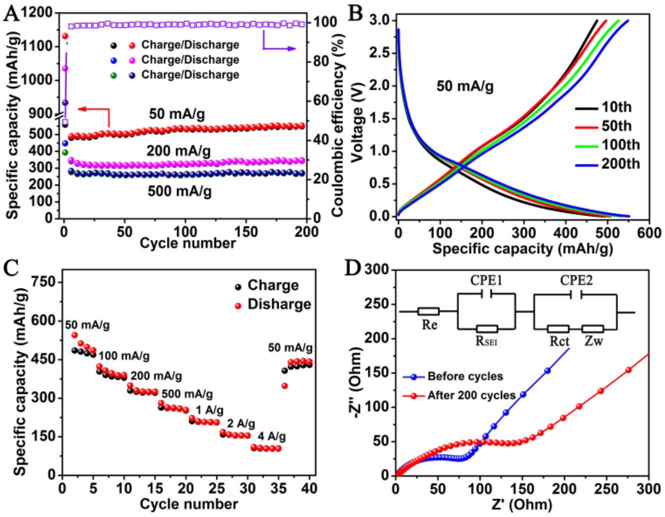

Fig. 4 (A) Cycle performance and coulombic efficiency, (B) charge/discharge profiles and (C) rate performance of GDY electrode. (D) Nyquist plots of GDY-based electrode before and after 200 cycles, and the inset is the equivalent circuit.

With the increasing demand for LIBs in current society, it is highly desirable to exploit electrode materials with high capacity and excellent cycling stability for LIBs. Graphene has been widely investigated as anodes for LIBs, showing a high specific capacity above 1000 mAh/g in the initial discharge/charge process. Although pristine graphene show a high specific capacity and power density, its relatively poor cycle stability and short cycle life limit the application in LIBs. The capacity of graphene droped dramatically to lower than 500 mAh/g after 20 or 30 cycles.[18-19,33] Here, the batteries with GDY based electrode exhibited a constant high specific capacity and outstanding cycle stability as shown in Fig. 4A, with a reversible capacity of 552 mAh/g achieved even after 200 cycles at a current density of 50 mA/g and a high coulombic efficiency > 98% obtained from 10th. The charge/discharge curves (Fig. 4B) clearly illustrate that the charge and discharge capacities at the 200th cycle are close to those at the 10th cycle. It is striking to note that even at a higher current density of 200 and 500 mA/g, the reversible capacity up to 345 and 266 mAh/g (Fig. 4C) could be obtained after 200 cycles respectively without any capacity reduction from 10th cycle. The high specific capacity and long cycle life are attributed to the high specific surface area and excellent chemical stability of microporous and mesoporous GDY powder. The surface of GDY-based electrode was smooth before cycles, but after 200 cycles (ESI, Fig. S4) the surface became a little rough with small particles formed, which may be responsible for the slightly increase of capacity during cycling. Furthermore, according to the electrochemical impedance spectroscopy (EIS) of GDY before and after cycling, Nyquist plots (Fig. 4D) revealed that the diameter of the semicircle for GDY electrode after 200 cycles in the high-medium frequency region is larger than that for the electrode before cycling, suggesting the increased charge-transfer resistances (Rct). The long cycling performance (more than 200 cycles) and detailed information of kinetic parameters can be referred in Fig S5 and Tab. S1 of ESI, respectively.

For the LIBs application, one of challenging problems is the limited rate performance at high charge/discharge rates. The porous structures have been demonstrated to be beneficial for improving the rate performance of LIBs. The unique structure of GDY with numerous microporous and mesoporous, and the low barriers of Li ions diffusion are helpful for the rapid transport of electrons and ions on GDY, thus making the GDY suitable as Li storage even at high charge/discharge rates. As can be seen in Fig. 4C, the rate performance of GDY powder was further evaluated at different current densities ranging from 50 to 4000 mA/g. Even at a larger current density of 1, 2 and 4 A/g, there was still reversible capacity of 210, 158 and 105 mAh/g, which are superior to those of graphite. When the current density was reset to 50 mA/g, the capacity increased to 444 mAh/g, exhibiting outstanding rate performance which benefits from the high electronic conductivity, excellent chemical stability of GDY, and fast diffusion of Li ions in its microporous and mesoporous structure. All these results demonstrate that GDY is a promising anode material for LIBs with high capacity, outstanding rate capability and long cycle life.

In conclusion, GDY powders were successfully synthesized and applied as electrode materials for lithium storage. The assembled GDY-based LIBs exhibit excellent electrochemical performance, including high stable specific capacity of 552 mAh/g, for as long cycle life as 200 cycles, and outstanding rate performance. The unique structure of GDY with numerous microporous and mesoporous endows GDY more Li storage sites and facilitates the rapid transport of electrons and ions. We believe that designing and preparing novel carbon-based materials with porous structure might open up an approach to develop new electrode materials with high capacity and excellent cycling stability for satisfying the future requirements of Li-ion-based energy storage devices.

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