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Edge effects in vertically-oriented graphene based electric double-layer capacitors

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HIGHLIGHTS

- Comprehensive research on the edge effects in VG based EDLCs was first reported.
- VGs with diverse edge-to-basal ratios and edge densities were obtained.
- Edges play a predominant role on the charge storage behavior of VG based EDLCs.
- The underlying mechanism was elucidated with combination of DFT and MD simulation.
- The roles of edges on the EDLC microstructures insides VG channels were unveiled.

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ABSTRACT

Vertically-oriented graphenes (VGs) have been demonstrated as a promising active material for electric double-layer capacitors (EDLCs), partially due to their edge-enriched structure. In this work, the 'edge effects', i.e., edges as the promoters of high capacitance, in VG based EDLCs are investigated with experimental research and numerical simulations. VGs with diverse heights (i.e., edge-to-basal ratios) and edge densities are prepared with varying the plasma-enabled growth time and employing different plasma sources. Electrochemical measurements show that the edges play a predominant role on the charge storage behavior of VGs. A simulation is further conducted to unveil the roles of the edges on the separation and adsorption of ions within VG channels. The initial charge distribution of a VG plane is obtained with density functional theory (DFT) calculations, which is subsequently applied to a molecular dynamics (MD) simulation system to gain the insights into the microscope EDLC structures. Compared with the basal planes, the edges present higher initial charge density (by 4.2 times), higher ion packing density (by 2.6 times), closer ion packing location (by 0.8 Å), and larger ion separation degree (by 14%). The as-obtained findings will be instructive in designing the morphology and structure of VGs for enhanced capacitive performances.

1. Introduction

Oriented nanostructures with a uniform spatial alignment can outperform their non-oriented or randomly dispersed counterparts in specific applications [1,2]. Typically, vertically-oriented graphenes (VGs) are a class of networks of few-layer graphenes that are perpendicular to a substrate surface. Compared with stacks of horizontal graphenes (*e.g.*, chemically-converted graphenes or reduced graphene oxide stacks), VGs own a series of unique features such as vertical orientation to the substrate, open inter-sheet channels, and exposed ultrathin graphene edges, which are advantageous in a wide range of applications [3,4].

In particular, VGs have been demonstrated as a promising active material for electric double-layer capacitors (EDLCs, or the so-called 'supercapacitors' and 'ultracapacitors'), a type of advanced electrochemical devices for energy storage that requires frequent charge-discharge cycles at a high power and over a short period of time [5–7]. For example, VG electrodes fabricated with a hand-rolling and cutting process exhibited a 5.25-fold higher in electric charge than the reduced graphene oxide powder counterpart [8]; VGs synthesized *via* a plasma-enabled route presented a high

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specific capacitance of 230 F g^{-1}, which is among the best values of various three-dimensional (3D) graphene-based EDLC electrodes [9].

The numerous exposed edges of VGs are considered to play a crucial role on the enhancement of charge storage capability [9–11]. It is well known that the electronic properties of graphene are strongly related to the edge properties, such as edge states, chirality, edge structure, and edge chemistry [12–14]. It will further affect the formation of EDLC microstructure nearby the edge region and eventually influence the electrochemical behaviors (*e.g.*, capacitance and frequency response) [14–17]. In fact, such an 'edge effect', i.e., edges work as promoters of high capacitance, has been widely noticed on many carbonaceous electrodes [18–23]. Randin et al. reported that the edge planes of an annealed pyrolytic graphite presented a much higher specific capacitance (50–70 μF cm^{-2}) than that of the basal planes (~3 μF cm^{-2}) [18]. Zhang et al. split a vertical multiwalled carbon nanotube carpet to a graphene nanoribbon carpet and found a 4-fold increase in the specific capacitance due to the increase of edge sites [19]. Shi et al. reported a 4 orders of magnitude higher specific capacitance of the edges than that of the basal plane region on a monolayer graphene [20]. Hassan et al. fabricated activated micrometer-sized few layer graphene sheets with edge-enriched planes, resulting in about 2 time increase in the specific capacitance [21]. The above experimental observations with improved capacitance are strongly related to the edge effects. As a consequence, a comprehensive research on the edge effects in VG based EDLCs is timely.

Molecular dynamics (MD) simulation is a powerful technique to describe the motion of particles (*e.g.*, ions and molecules) in EDLC systems at atomic scale [24]. We have previously reported the MD simulation results on the EDLC microstructures insides VG channels, on the basis of an approximation that VGs were initially charged at a uniform state [25]. However, due to the presence of exposed graphene edges, the real initial charge distribution on a VG plane should be inhomogeneous. On the other hand, density functional theory (DFT) based on quantum mechanical calculations has been widely used for explicitly capturing the electronic degrees of freedom presented in the system and the quantum behavior of atoms and molecules, *e.g*, band structure, density of states, electronic structure, and magnetic properties [14,26,27].

In this work, the edge effects in VG based EDLCs were investigated with experimental research and numerical simulations. VGs with diverse edge-to-basal ratios were prepared with adjusting the growth time in a microwave plasma-enhanced chemical vapor deposition (M-PECVD) system. VGs with different edge densities were obtained with employing two types of plasma sources, i.e., M-PECVD and radio frequency (rf) inductively coupled plasma enhanced chemical vapor deposition (ICPECVD). Electrochemical measurements were then conducted on the EDLCs employing VGs with different edge-to-basal ratios and edge densities as the active materials. Calculations with combining DFT and MD simulations were carried out to unveil the underlying mechanism of the edge effects on the capacitive performance of VG based EDLCs. Specifically, the initial charge distributions on the VG electrode were evaluated by a DFT calculation, followed by a comprehensive MD simulation on the EDLC structures (*e.g.*, accumulating density, packing location, and separation degree of ions) within the charged VG channels.

2. Experimental and simulation methods

2.1. M-PECVD growth of VGs

VGs with diverse heights (meanwhile, diverse edge-to-basal ratios) were fabricated in a M-PECVD system. A 2.45 GHz microwave source was coupled to the synthesis reactor vessel with a cylindrical quartz tube. A nickel film (pure > 99%, XFNANO Materials Tech) was placed on the surface of a stainless steel holder as the growth substrate. Prior to the growth, the system was heated to 650 °C by a 350 W H_2 microwave. Subsequently, CH_4/H_2 mixture (flow rate H_2: CH_4 = 5: 1) was introduced into the reactor for VG growth. During the entire growth process, the pressure in the reactor was maintained at 350 Pa. Besides, a 50 V bias was applied to the growth substrate during the growth process.

2.2. ICPECVD growth of VGs

VGs with relatively dense edges were grown in an ICPECVD reactor. An 800 W rf power was inductively coupled into the deposition chamber through a planar-coiled antenna sitting on a quartz window. A gas mixture of CH_4 and H_2 was fed into the chamber with a constant pressure of 6 Pa. VGs with relatively high density were then obtained with a 20-min growth at 800 °C.

2.3. Material characterization

The surface morphologies and crystal structures of VGs were inspected by a SU-70 scanning electron microscope (SEM, Hitachi) and a Tecnai G2 F30 STwin transmission electron microscopy (TEM, Philips-FEI). A DXR 532 Raman spectrometer (Thermo Fisher Scientific) was applied to obtain the Raman spectra with an excitation wavelength of 532 nm. X-ray photoelectron spectroscopy (XPS) measurements were performed in a VG Escalab Mark II system employing a monochromatic Mg Kα X-ray source (1253.6 eV, West Sussex).

2.4. Electrochemical measurements

VG based EDLCs were assembled in a two electrode system with a layered structure and all the components were sandwiched between two pieces of plastic sheet. Two pieces of VG electrodes (~15 mm in diameter) were separated by a porous polypropylene film in a 6 M KOH aqueous electrolyte solution. Electrochemical performances of the VG based EDLCs were tested by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) on an electrochemical workstation (PGSTAT302N, Metrohm Autolab B.V.) at room temperature. EIS was recorded from 100 kHz to 10 mHz, with an amplitude of 5 mV.

2.5. DFT calculations

Different with our previous practice that a uniform charge was assigned to the electrodes [25], in the current work, the initial charge distribution on an individual VG plane was first obtained with a DFT calculation. As shown in Fig. 1a, a zigzag VG plane terminated by H atoms was constructed [10]. The lattice constant of graphene was set as 2.466 Å, close to the experimental value of 2.461 Å [15]. The length of the VG plane along X direction was set as L = 11.4, 19.9, 28.5, 41.3, 49.8, 62.6, 84.0, 105.4, 126.7 and 148.1 Å, respectively. The width of the VG plane in Y direction was fixed as 4.932 Å. A sufficient large vacuum layer with a thickness of 20 Å was set along X and Z direction to avoid the interactions between adjacent periodic systems. A surface charge density of 5 μC cm^{-2}, fell in the range of −20 μC cm^{-2} to 30 μC cm^{-2} for typical EDLCs employing aqueous electrolytes, was applied to the VG surface [28].

The charge distribution on the as-built zigzag VG plane was then calculated with the DFT method [29], using a Quantum ESPRESSO package [30] with the Predew-Wang91 (GGA-PW91) exchange-correlation function [31]. A projector augmented wave (PAW) method was applied to describe the interactions between ion core