Nitrogen and oxygen co-doped graphene quantum dots with high capacitance performance for micro-supercapacitors

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ABSTRACT

The applications of carbon-based micro-supercapacitors (MSCs) based on the electrical double layer capacitance mechanism are usually limited by the extremely low specific capacitances and energy storage densities of carbon electrodes fabricated from less active, large-size carbon materials. As a promising alternative, high-activity N and O co-doped graphene quantum dots (N-O-GQDs) offer a combination of advantages, such as ultrasmall sizes, rich active sites, high hydrophilicity, and facile assembly into conductive carbon films. Here we report the facile electrophoresis construction of carbon-based MSCs for ultrahigh energy density storage using N-O-GQDs as the initial electrode material. The N-O-GQD MSCs show extremely high volumetric capacitances of 325 F cm^{-3} in H$_2$SO$_4$ due to their high pseudocapacitive activity, high loading density, and enhanced electrolyte wettingability ascribed to a large amount of doped nitrogen and oxygen functional groups. They deliver an ultrahigh volumetric energy density, superior to that of thin-film lithium batteries. Three connected all-solid-state N-O-GQD MSCs can light a red light–emitting diode. Furthermore, the pseudocapacitive MSCs maintain high power densities, and cycling stability owing to improvements in electrical conductivity and electrolyte penetration. The important results highlight the promising applications of high-activity nanographenes in on-chip power sources for driving diverse micro-devices.

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1. Introduction

The rapid development of portable electronic equipment, implantable medical devices, wireless sensor networks and other micro-electromechanical systems has stimulated an increasing demand for micro-energy storage devices [1—4]. Micro-supercapacitors (MSCs) with electrode sizes of tens to hundreds of micrometers are promising energy storage systems for miniaturized devices due to their excellent rate capability, high power density, and long cycle life [5—9]. Usually, carbon-based MSCs are fabricated based on the electrical double layer capacitance (EDLC) storage mechanism using large-size carbon materials as electrode materials, including carbon fibers (CF) [9], activated carbon (AC) [10], carbide derived carbon (CDC) [2,11], carbon nanotubes (CNT) [7], and graphene sheets [4—6,8]. These carbon-based MSCs

possess light weight, high power density, and excellent cycle life, but their practical applications are limited by low volumetric energy densities (0.6—9 mWh cm^{-3}) due to the EDLC storage limitations and the low packing density of these carbon materials with large specific area. In this context, metal oxides (RuO$_2$ [12] and MnO$_2$ [13]) and conductive polymers (polyaniline [14] and polypyrrole [15]) are extensively explored as pseudocapacitve materials to enhance the energy densities of MSCs. For example, MSCs based on polyaniline networks and nanofibers were reported to show volumetric energy densities of 5.83 and 16.4 mWh cm^{-3}, respectively [16,17]. However, the miniaturization applications of pseudocapacitve MSCs are limited by poor cycle lifetimes and low power densities owing to the low electrical conductivity and sluggish Faradic reaction dynamics of pseudocapacitve materials. The limited enhancement in volumetric energy densities is compromised by poor cycle lifetimes and low power densities, presenting a great challenge in the fabrication of MSCs with comprehensive superior electrochemical performances.

In recent years, ultrasmall nanographenes called graphene

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quantum dots (GQDs) with lateral sizes of several nanometers have attracted increasing attention in electrochemical, photoelectronic, biomedical, and other fields owing to their unique structure and superior properties [18—31]. With rapid development towards device miniaturization, GQDs are more suitable than large carbon materials for the design and fabrication of micro-devices and micro-powers because of their ultrasmall sizes. Moreover, ultrasmall GQDs have much higher edge/core atomic ratios than usual carbon materials, which could greatly enhance electrochemical activities of carbon electrodes, given that edge carbon atoms are typical electrochemically active defects in sp^2 hybrid carbon materials. Many studies have also revealed that the electrochemical activities of carbon materials can be further increased by introducing N or/and O heteroatoms [32—37]. For example, doping carbon materials with N or O heteroatoms could induce additional pseudocapacitive activities in carbon-based supercapacitors and thus greatly increase specific capacitance. Moreover, N or O doping is favorable for improving the interface wettability of the carbon electrode for the aqueous electrolyte and thus enhancing Faradic reaction dynamics. Therefore, N/O co-doped GQDs (N-O-GQDs) with a ultrahigh overall doping concentration are expected to offer ultrahigh specific capacitances and energy storage densities for MSCs owing to their more pronounced edge and doping effects compared with usual carbon materials. Because of these advantages, GQD-based electrodes have recently been assembled for fabrication of symmetric GQD//GQD MSCs and asymmetric (GQD//MnO$_2$ and GQD//PANI) MSCs. However, reported GQD-based MSCs in aqueous electrolyte showed rather low areal capacitance (0.5—3.0 mF cm^{-2}) and energy densities (0.07—0.41 μWh cm^{-2}) [22,24,25], and their all-solid-state MSCs (GQD//PANI) exhibited poorer performances (0.2 mF cm^{-2}; 0.03 μWh cm^{-2}) [25]. These unexpected performances are largely ascribed to the low doping level of GQDs and their poor loading ability on micro-electrodes.

Here, we report the first application of heavily co-doped N-O-GQDs in MSCs. N-O-GQDs containing 17.8 at% N and 21.3 at% O were synthesized by a modified molecular fusion method and their loading on interdigital finger gold electrodes was made by electrophoresis. Through the N/O enhanced interaction between the N-O-GQDs and the Au surface of electrodes, the GQDs can be facilely deposited on the micro-electrodes to form dense carbon films (3.57 g cm^{-3}) containing self-assembled microtubes. Symmetric MSCs based on the N-O-GQD material offer superior performances in both aqueous and solid electrolytes. Their all-solid-state MSCs in PVA/H$_3$PO$_4$ show extremely high volumetric capacitance (56.1 F cm^{-3}) and volumetric energy density (7.8 mWh cm^{-3}), while their areal capacitance is also high (9.99 mF cm^{-2}) and high cycling stability is maintained. The encouraging results make the N-O-GQD material promising for the next generation of high-performance MSCs.

2. Experimental

Materials: gold interdigital finger electrodes (20*10*0.635 mm) were purchased from Changchun Megaborui Technology Co., Ltd., China. All other chemicals were of analytical grade and commercially available from Shanghai Chemical Reagent Co. Ltd. and used as received without any further purification.

Fabrication of N-O-GQDs: In a typical procedure for synthesis of N-O-GQDs, pyrene (4 g) was nitrated into trinitropyrene in hot HNO$_3$ (320 ml) at 80 °C under refluxing and stirring for 48 h. After cooled to room temperature, the mixture was diluted with deionized (DI) water and filtered through a 0.22 μm microporous membrane to remove the acid. The resultant yellow 1, 3, 6-trinitropyrene was dispersed in DI water (640 mL) by ultrasonication for 2 h. The suspension (40 mL) was transferred to a poly (tetrafluoroethylene) (Teflon)-lined autoclave and 4 ml hydrazine hydrate was added, then heated at 200 °C for 12 h. After cooled to room temperature, the product containing water-soluble N-O-GQDs was filtered through a 0.22 μm microporous membrane to remove insoluble carbon product. N-O-GQDs powder was obtained by further dialysed in a dialysis bag (retained molecular weight: 3500 Da) for 2 days to remove sodium salt and unfused small molecules and dried at 80 °C.

Fabrication of N-O-GQD electrodes: N-O-GQD/Au electrodes were prepared by a facile electrodeposition method with a two-electrode setup, where gold interdigital finger electrodes and Pt foil were used as working electrode and counter electrode, respectively. An aqueous precursor solution with N-O-GQDs (4.5 mg ml^{-1}) and deionized water (40 mL) was used as the electrolyte, and the deposition was performed at a constant potential of 2—4 V for 1—4 h. After the deposition, the electrodes were washed with distilled water and then dried at air, and obtained the N-O-GQD microelectrodes. In order to explore the contribution of N and O groups of the N-O-GQDs to the pseudocapacitive performance, we annealed the N-O-GQD microelectrodes in argon atmosphere to vary the N and O contents. The microelectrodes treated at 400 and 800 °C for 1 h were labeled as N-O-GQD-400 and N-O-GQD-800, respectively.

Fabrication of all-solid-state N-O-GQD MSCs: polyvinyl alcohol (PVA)/H$_3$PO$_4$ hydrogel, as an electrolyte, was synthesized by mixing 6 g of PVA (wt.99.9%) powder, 6 g of H$_3$PO$_4$ (wt.85%) and DI water (60 mL). The mixture was heated at 85 °C under stirring until the solution turned clear. By casting the hydrogel onto the prepared N-O-GQD micro-electrodes and drying naturally, an all solid-state N-O-GQD MSCs was obtained.

Material characterizations: Scanning electron microscopy (JEOL FESEM-6700F, 15 KV) images were obtained on a field emission scanning electron microanalyzer at an acceleration voltage of 5 kV. Transmission electron microscope (TEM) was operated on a Hitachi H7650 transmission electron microscope with CCD imaging system on an acceleration voltage of 120 kV. XRD patterns were obtained with a Rigaku 18 KWD/max-2550 using Cu Kα radiation. FT-IR spectra of dried samples were recorded with a Bio-Rad FTIR spectrometer FTS165. Raman spectra were recorded on a Renishaw in plus laser Raman spectrometer with λexc = 785 nm. XPS spectra were collected using a Kratos Axis Ultra DLD X-ray photoelectron spectrometer.

Electrochemical measurements: All electrochemical tests, including cyclic voltammetry (CV), galvanostatic charge−discharge (GCD), and electrochemical impedance spectroscopy (EIS), were carried out using an electrochemical working station (CHI660D, Shanghai, China) at room temperature. In a three-electrode system, N-O-GQD/Au, Ag/AgCl electrode and Pt wire were respectively used as work electrode, the reference electrode, and the counter electrode. The CV tests were measured with the potential window from −0.2 V to 0.8 V in a three-electrode system and from 0 V to 1.0 V in a two-electrode system. The EIS measurements were carried out in the frequency range from 0.01 Hz to 1000 kHz with 5 mV ac amplitude.

In a three-electrode system, the capacitance values of electrodes were calculated from the CV data according to the following foumula:

$$C_{electrode} = \int idV/v\Delta V \tag{1}$$

Where v is the scan rate (V s^{-1}), ΔV is the operating potential window in volts (1.0 V), and i is the current (A).

In a two-electrode system, the capacitance of each device was