Enhancement of Capacitance by Electrochemical Oxidation of Nanodiamond Derived Carbon Nano-Onions

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ABSTRACT

Electrode responsiveness and electrochemical capacitance behavior of nanodiamond-derived carbon nano-onions (N-CNOs) were studied. N-CNOs were prepared by thermal annealing of nanodiamond powders. A thin film of N-CNOs was mounted on glassy carbon (GC) current collector and showed an excellent electrochemical behavior with rectangular voltammetric curves as well as great scan rate dependence of capacitance. The capacitance showed negligible drops over a wide range of scan rates (50 mV/s - 5 V/s) in both KCl and H_2SO_4. This excellent capacitive behavior was attributed to good electrical conductivity and mesoporous nature of N-CNOs. In order to further enhance capacitance, electrochemical oxidation of N-CNOs was carried out by iterating anodic cycling in acidic electrolytes. The capacitance enhancement of oxidized N-CNOs was probed by cyclic voltammetry as well as galvanostatic charging-discharging measurement. This study demonstrates that electrochemical oxidation can be an effective method to improve capacitance and energy density of carbon nanomaterials while maintaining a good scan rate performance.

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1. Introduction

Carbon nano-onions (CNOs) are an emerging class of carbon allotrope that possesses unique microstructural and electronic properties. CNOs have a hollow core surrounded by sp^2-bonded, concentric graphene shells. A variety of approaches have been reported for the synthesis of CNOs, including electron irradiation,[1,2] ion implantation,[3] counter-flow diffusion flames,[4] plasma-enhanced chemical vapor deposition (CVD),[5] thermal treatment of nanodiamonds,[6], and arc discharge of carbon electrode.[7,8]

Among those, CNOs synthesized from nano-diamonds (N-CNOs) have attracted significant attention because of their superb properties including (i) high BET surface area (500 m^2/g), (ii) high electrical conductivity, (iii) high thermal stability, and (iv) appropriate mesoporous structure. N-CNOs showed great potential in several applications including electrochemical energy storage devices[9,10], anti-wear and friction materials[11], hydrogen storage[12], and anode materials for lithium ion batteries[13]. Recently, N-CNOs showed a great promise in electrochemical capacitor and supercapacitor applications with high-power densities, due to excellent electron transports and the easy access of

electrolyte ions to the electrified surface of N-CNO leading to ultra-high power density.[9,10]

In order to meet the demand of supercapacitors with high-energy and high-power densities, the electrochemical capacitance of N-CNOs need to be further improved. Several methods have been popularly tested to enhance the capacitance of carbon nano-materials, including chemical activation with KOH[14] and the utilization of pseudocapacitive materials such as conducting polymers or metal oxides.[10,15,16] Recently, electrochemical oxidation was introduced as an effective route to modify the surface structure of carbon-based electrode materials for the purpose of enhancing the capacitance and electrochemical sensing performance.[17,18] The capacitance enhancement by electrochemical oxidation of carbon materials was mainly attributed to two factors: (i) generation of faradaic current from redox-active chemical groups formed at the graphene edge sites and (ii) enhanced surface electrode area by opening and breakage of graphene layers.

In this study, we explored electrode responses and electrochemical capacitance behaviors of nanodiamond-derived carbon nano-onions (N-CNOs). For electrochemical characterization, N-CNO powders were deposited as a thin film on glassy carbon (GC) current collector. In order to further enhance capacitance, N-CNOs were electrochemically anodized in acidic electrolytes. To the best of our knowledge, this is the first report on the electrochemical oxidation of nanodiamond-derived carbon nano-onions (N-CNOs)

and their subsequent capacitance behavior. This study demonstrates that electrochemical oxidation can be an effective method to improve capacitance and energy density of N-CNO-based electrodes.

2. Experimental

2.1. Chemicals

H_2SO_4 (Sigma-Aldrich) and KCl (Sigma-Aldrich) were used as electrolytes without further purification.

2.2. Synthesis of carbon nano-onions

Carbon nano-onions (N-CNOs) were prepared by thermal annealing of nanodiamond powders (Dynalene NB50) at 1650 °C for 1.0 h under the flow of Helium in a graphitization furnace. To remove any amorphous carbon impurities, as-produced N-CNOs were heated in a furnace at 400 °C for 4 h under air.

2.3. Characterization

2.3.1. X-ray diffraction (XRD)

XRD spectral patterns were obtained with a Bruker D8 Discover diffractometer using Cu-K$_\alpha$ radiation (40 kV, 40 mA) to probe crystallinity and purity of N-CNO. Samples were scanned over a 2θ range from $15°-100°$.

2.3.2. Raman spectroscopy

A micro-Raman characterization was conducted with a DXR Raman Microscope (Thermo Scientific). The excitation wavelength of 532-nm from Nd:YVO$_4$ laser (diode-pumped, frequency-doubled) was focused on the surface of N-CNOs with a 10× objective lens.

2.3.3. Electrochemical measurements

Electrochemical characterization of N-CNO was conducted with a CH Instruments (CHI) potentiostat (660D, Austin, TX) using a single compartment, three-electrode glass cell. A platinum wire was used as the counter electrode and a commercial Ag/AgCl electrode (3 M KCl) served as the reference electrode. For the working electrode, a commercially available glassy carbon (GC) disk electrode (CHI) was modified with a thin film of N-CNO powders in the following way. First, N-CNO powders were dispersed in deionized water (10 μg/mL) and sonicated for 30 min to make a homogeneous dispersion. Afterwards, a droplet of the dispersion (typically 10 μL) was placed onto a freshly polished GC disk. Then, the electrode was dried in an oven at 40 °C for 1 h. After drying, N-CNOs formed a thin and relatively smooth film on the GC surface. Electrochemical oxidation of N-CNOs was made by sweeping a potential from 1.0 V to 2.0 V (vs. Ag/AgCl, sweep rate: 50 mV/s) in 1 M H_2SO_4. Prior to each oxidation step, the solution was purged with oxygen gas for 10 min to maintain the constant level of oxygen concentration. After electrochemical oxidation, capacitance of N-CNOs was evaluated by cyclic voltammetry and galvanostatic charging-discharging measurement in either 1 M H_2SO_4 or 1 M KCl.

3. Results and Discussion

Fig. 1a and 1b are low resolution and high resolution TEM images of N-CNOs, respectively. As shown in Fig. 1a, as-grown N-CNOs have a uniform size distribution (diameter of 4-7 nm). Fig. 1b shows that N-CNOs are spherical and composed of concentric nano-graphene layers surrounding a hollow core. The number of spherical graphene layers is 4-8, depending on the diameter

of N-CNOs. Fig. 1c shows a representative powder X-ray diffraction (XRD) pattern of N-CNOs. Two broad peaks are observed at $2\theta = 25.5°$ and $43.4°$. These peaks are assigned to the (002) and (100) planes of graphite, respectively. Two additional broader reflections are observed at $2\theta = 53.0°$ and $79.0°$, which can be assigned to (004) and (110) planes of graphite, respectively. All of these peaks are the characteristics of graphitic materials. The most pronounced reflection in the XRD pattern is the (002) line at 25.1° and is reflective of the spacing between concentric graphene layers in N-CNO particles. Based upon the 2θ line position of 25.1°, the spacing between two graphene layers, d, was calculated to be 0.357 nm ($d = n\lambda/2\sin\theta$). This value is quite larger than the interlayer spacing of bulk graphite, 0.335 nm, indicating a widened spacing in the (002) plane of N-CNOs due to their strain and microstructural disorder.

The micro-Raman spectrum of as-grown N-CNOs is presented in Fig. 1d. Raman spectroscopy is a powerful analytical tool to probe the microstructure and the structural disorder of sp^2- and sp^3-bonded carbon materials such as graphite, glassy carbon, carbon nanotube, graphene, and diamond.[19,20] The Raman spectrum of N-CNO revealed two dominant peaks at 1350 and 1580 cm^{-1}. The peak positioned at 1580 cm^{-1} (G-band, graphitic) is assigned to the scattering due to the lattice phonon. The peak at 1350 cm^{-1} (D-band, disorder-induced) arises from scattering by disorder-activated edge phonon. The peaks with weaker intensities located at ~2600 cm^{-1} represent 2D phonon band. The peak intensity ratio of I_D/I_G is an important parameter to represent the degree of microstructural order and the density of edge planes existing in sp^2-bonded carbon material. As seen in Fig. 1d, as-produced N-CNOs showed a high I_D/I_G (>1) with broad D and G bands indicating that N–CNO is very disordered and rich in edge planes. The microstructural disorder and defects play important roles in chemical reactivity and electrochemical properties.[21] To probe the chemical composition and the chemical state of N-CNO sample, X-ray photoelectron spectroscopic characterization (XPS) was conducted. Fig. 1e and 1f show the representative XPS survey and high resolution spectra for as-grown N-CNOs, respectively. As shown in the survey spectra (Fig. 1e), N-CNOs have a decent content of oxygen in addition to carbon (O/C ratio of 3.27%). This indicates that oxygen-related functional groups are formed at the terminated edge of nanographene layers in N-CNOs. According to the high resolution XPS analysis, the C1s peak can be de-convoluted to C-C (sp^2) (284.6 eV) and carbons bounded to three different types of oxygen (C-OH (285.7 eV), C = O (286.6 eV), and O-C = O (289.1 eV)).

The electrochemical responsiveness and capacitance behavior of as-prepared N-CNOs were studied. Fig. 2a and 2b are representative cyclic voltammograms of N-CNOs recorded in two electrolytes, 1 M KCl and 1 M H_2SO_4, respectively. In both electrolytes, cyclic voltammetric curves were recorded at different scan rates (50 mV/s, 100 mV/s, 250 mV/s, 500 mV/s, 1 V/s, and 5 V/s). In order to determine specific capacitance (C, F/g), voltammetric current was normalized by the mass of N-CNOs (typically ~10 μg) mounted on GC current collector and the scan rate. The capacitance was calculated based on the following equation,

$$C = \frac{i}{\upsilon \cdot m}$$

where C_{dl} is specific (gravimetric) capacitance (F/g), i is current intensity (A) at the given potential, υ is the scan rate of potential (V/s), and m is the mass (g) of N-CNO.

The cyclic voltammetric (CV) curves of N-CNOs in 1 M KCl (Fig. 2a) show flat and featureless currents in the potential window between -0.2 V and 0.8 V vs. Ag/AgCl. At the scan rates from 50 mV/s to 1 V/s, N-CNOs showed rectangular cyclic voltammetric curves, indicating that N-CNOs have a good electrical conductivity. Calculated capacitance was 38 F/g at 50 mV/s and 32 F/g at 5 V/s, respectively, showing about 15% capacitance drop at the 100x faster