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Carbon nanosheets as the electrode material in supercapacitors

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ABSTRACT

Carbon nanosheets are comprised of 1–7 graphene layers that are predominantly vertically oriented with respect to a substrate. The thickness and morphology of the nanosheets can vary depending on the growth precursor and the substrate temperature. They have an ultra-low in-plane resistivity. The capacitance of carbon nanosheets was measured by cyclic voltammetry in a standard electrochemical three-electrode cell, which contains a platinum counter electrode and a standard mercury/mercurous sulfate reference electrode in 6 M H_2SO_4 electrolyte. As a working electrode, the capacitance of carbon nanosheets per area was found to be 0.076 F cm^{-2}. A mathematical model was used to simulate the total possible capacitance of a virtual supercapacitor cell that contains carbon nanosheets as the electrode material and found to be 1.49×10^4 F.

1. Introduction

A supercapacitor (or ultracapacitor) has ultra-high capacitance compared to conventional versions. The supercapacitor establishes capacitance via the electrochemical double-layer (EDLC) [1–3]. Both supercapacitors and batteries are critical energy/power storage devices for portable electronics, wind power and for electrical vehicles (EV) [4]. The development of the EV industry mainly relies on advancement of long life, fast charging, and large capacity batteries. The battery and the supercapacitor are not mutually replaceable and have distinct roles in the EV's power-train system. The battery relies on chemical reaction and electrolyte ion diffusion to generate/store energy and can deliver much more energy than the supercapacitor. A supercapacitor depends on the electrochemical double-layer to store/release energy and can be rapidly charged and discharged by avoiding chemical reactions in devices. The supercapacitor can endure repeated cycles for many years without degradation and contains no heavy ions in the electrolyte/electrode, thus, it is an environmentally friendly device.

The supercapacitor's high capacitance stems from the very high specific surface area of conductive materials. Conventional supercapacitors are comprised of active carbon particles or carbon fibers. These carbon materials are used because they have a high theoretical specific surface area (~1000–2000 $m^2\ g^{-1}$). Correspondingly, the calculated capacitance per unit surface area for active carbon materials is about 10–15 μF cm^{-2}. Therefore, supercapacitors, using active carbon material as electrodes, have a much higher theoretical capacitance (100–300 F g^{-1}) compared to common capacitors (on the order of μF or pF) and have much less internal resistance than that of batteries. Furthermore, as much as 40% of the energy can be recovered, e.g., via braking in a supercapacitor-bus.

According to the reviews of Pandolfo and Hollenkamp [5] and Obreja [6], conventional carbon supercapacitors have a specific energy of 1–10 (Wh kg^{-1}) and specific power of 0.5–10 (kW kg^{-1}). Tens or even hundreds of kilograms of supercapacitors are thus required for one EV. A conventional lead-acid battery is typically 30–40 Wh kg^{-1} and modern lithium-ion batteries are ~120 Wh kg^{-1}, therefore, it is important to improve the EDLC physical limits and to reduce weight.

Two factors limit the capacitance of supercapacitors—the pore distribution and the resistance of the electrode material. To improve electrode performance, the pore distribution of the material should be optimized. The resistance of the electrodes is another common limiting constraint. To increase the specific power, both the bulk resistance and interface resistance of the electrode materials should be minimized.

Several kinds of carbon nanomaterials, i.e. *carbon nanotubes* (CNTs, both single-walled and multi-walled) and *graphene* have attracted research interest as supercapacitor electrode materials [7–9]. Both carbon nanostructures are made up of sp^2-bonded carbon. Graphene is a single atomic-layer of carbon in a hexagonal structure [10,11]. Carbon nanotubes have a tubular geometry

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composed of one or more graphene layers. Both theory and experimental measurements have demonstrated that CNTs and graphene have an ultra-low resistivity for electron transport [12]. At room temperature, the resistivity of the graphene sheet is $\sim 10^{-6}\,\Omega\,cm$ (less than the resistivity of silver). The specific area of a single graphene sheet could approach $2630\,m^2\,g^{-1}$ [7]. Research led by Schindall [13,14] in the MIT LEES project has demonstrated supercapacitors with $30\,Wh\,kg^{-1}$. Studies of the graphene-based supercapacitor, led by Ruoff and co-workers [7,15], recently reported that chemically-modified-graphene (CMG) could gain very high specific capacitance ($137\,F\,g^{-1}$) in an aqueous solution. Nanogate Carbon® [16] is able to obtain 30–75 $Wh\,kg^{-1}$. This carbonaceous material, produced by preheating petroleum coke, has a graphite-structure with an intercalation distance ~0.375 nm.

It has been suggested that chemical vapor deposition is the best technique for making high-quality graphene films [10,11], such as the carbon nanosheets developed by Wang et al. [17–19] via rf plasma-enhanced chemical-vapor-deposition. These carbon nanosheets are two-dimensional graphite sheets made up of 1–7 graphene layers (on average three layers) that often terminate in a single graphene sheet [20,21]. The specific surface area of the carbon nanosheet was measured by the BET method [18,19,22] and found to be about $1100\,m^2\,g^{-1}$. By changing deposition time, the CNS height can be varied from 100 nm to >10 μm. The morphology of the CNS, is adjustable via tuning the substrate temperature and by adopting different precursors. The CNS can be synthesized in a substantially pure form (impurity < 100 ppm, as determined by particle-induced X-ray emission, PIXE) [22]. The vertically aligned carbon nanosheets are two-dimensional nanoplates, and represent three-dimensional nanoscale pores. Substrate biasing of the electric field aligns the CNS to an ordered, parallel plane geometry ~300 nm wide and ~1 μm high [22]. In this study, the capacitance of CNS was measured in a standard electrochemical environment containing 6 M H_2SO_4 and the empirical value was used to evaluate a virtual EDLC cell via a math model.

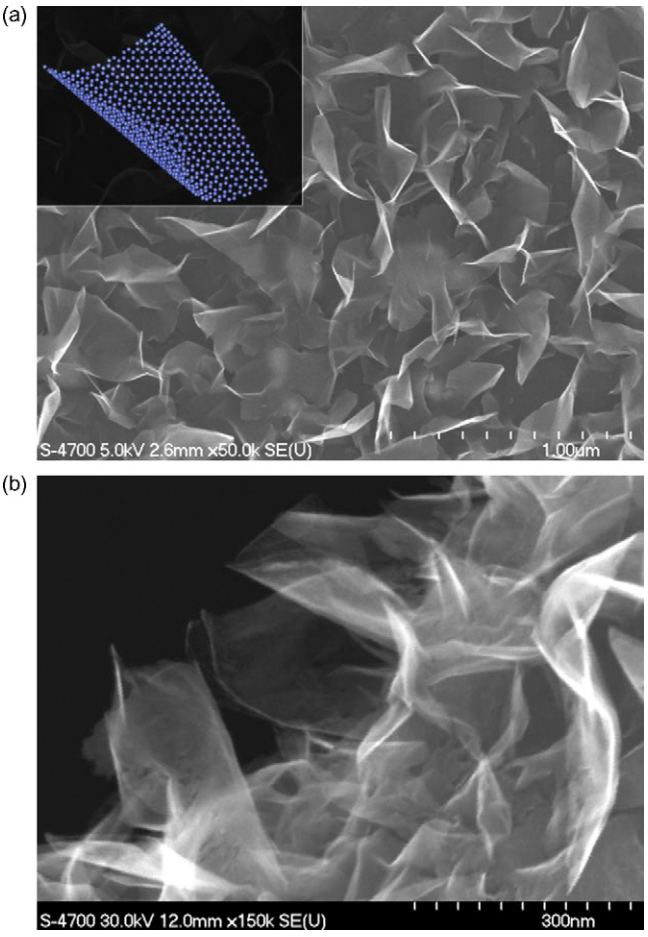

Fig. 1. (a) SEM image of carbon nanosheets (top view). The inset figure shows a schematic diagram of a single graphene sheet. (b) SEM image of carbon nanosheets (cross-section view) shows carbon nanosheets about 0.6 μm tall and less than 1 nm thick.

2. Method

The carbon nanosheets were fabricated in a plasma enhanced chemical vapor deposition (PECVD) system reported previously [18–23]. Briefly, during deposition, 400–1200 W radio frequency (RF, 13.56 MHz) power was inductively coupled into the deposition chamber through a planar-coiled RF antenna sitting on a quartz window. A precursor gas, methane (CH_4) was used as the carbon source and mixed with hydrogen (H_2) as the carrier gas. The density of the inductive plasma is ~10 times greater than that of capacitive-coupled systems. Other typical deposition parameters were the substrate temperature, varied between 600 and 950 °C, and the chamber pressure, varied between 20 and 200 mTorr. Carbon nanosheets have been successfully coated on Si, W, Mo, Zr, Ti, Hf, Nb, Ta, Cr, 304 stainless steel, SiO_2, and Al_2O_3, etc., without any special pre-treatment or catalyst. Fig. 1a shows a scanning electron microscope (SEM) image of typical carbon nanosheets deposited with 40% CH_4 in 60% H_2, at 100 mTorr total pressure, 680 °C substrate temperature, and 900 W RF power. The inset figure in Fig. 1a is a schematic diagram of graphene. Fig. 1b shows nanosheets are roughly vertical to the substrate and, in this growth, ~0.6 μm high. As shown in Fig. 1b, the edges of the nanosheets are extremely thin (<1 nm), also confirmed by a high-resolution transmission electron microscope [17–19,22]. Fig. 2a demonstrates carbon nanosheets uniformly coated on carbon fibers. The inset figure in Fig. 2a is a carbon cloth made up of a multitude of carbon fibers. Fig. 2b is an SEM image of a carbon fiber with carbon nanosheet coating. The CNS coatings substantially enlarge the carbon fibers' specific surface area. In this work, CNS were deposited on a conventional carbon paper (see Fig. 3a and b) as a working electrode for the capacitance measurements. The carbon paper was made of polyacrylonitrile (PAN) carbon fibers. Between the fibers are carbonized binders (residue adhesive), which were used in the paper pulping process.

Cyclic voltammetry (CV) is an efficient technique to evaluate new materials for EDLC capacitors. In this study, CV experiments involved scanning a potential (V) between a working electrode, where carbon nanosheets were attached, and a reference electrode, simultaneously recording time-dependent current (i) running through the working electrode. The charging/discharging current (i) is related to capacitance (C) and scanning rate (dV/dt) as $C = i/(dV/dt)$. In real applications, EDLC capacitors are two-electrode devices. However, in order to understand materials performance on individual electrodes (anode or cathode), it is a scientific necessity to use a reference electrode. The potential applied to either working electrode or counter electrode can be separated. Horowitz and Hill [24] had a concise explanation of the potentiostatic electrochemistry circuit (also called *voltage clamp*), which is based on the feedback of an operational-amplifier. A commercial potentiostat made by *Gamry*™ was utilized for this study. Carbon nanosheets were mounted to a customized working electrode made up of PTFE plastics. The sample exposure area is $0.78\,cm^2$ (1 cm diameter). The counter electrode was made of platinum foil. The reference electrode is a standard mercury/mercurous sulfate electrode (abbreviated "MSE", $Hg–Hg_2SO_4–SO_4^{2-}$) and the electrolyte is 6-mole sulfate acid (H_2SO_4).

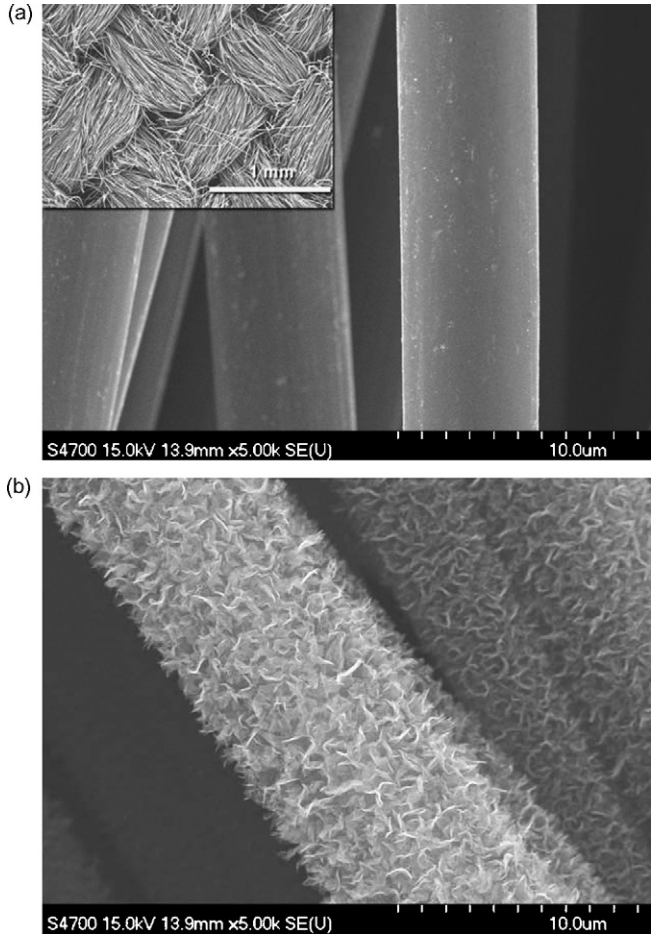

Fig. 2. (a) SEM of pristine carbon fibers before coating. Inset on left-top corner shows the woven carbon fiber cloth. (b) SEM of carbon fibers in the cloth with carbon nanosheets after coating. The CNS coating substantially increased the carbon fibers' specific area.

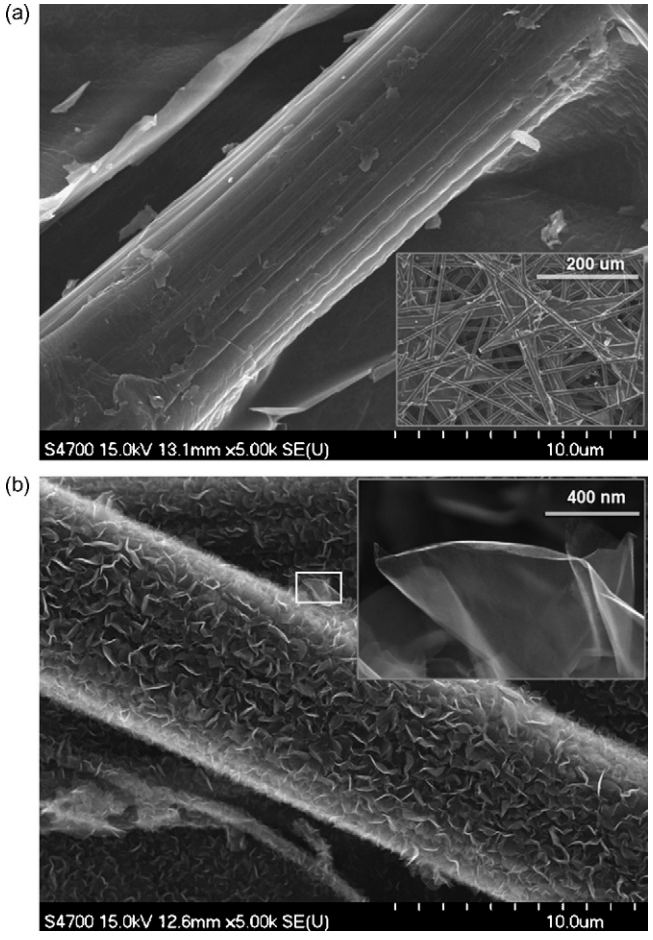

Fig. 3. (a) SEM of a pristine carbon paper before coating. Inset shows lower magnification. (b) SEM image of PAN-based carbon fibers embedded in the carbon paper; the paper is coated with carbon nanosheets. Inset shows higher magnification of sheets.

3. Results and discussion

Fig. 4 shows CV plots of a carbon nanosheets sample attached to working electrode (anode) at various scan rates (25, 50, 100, 150, 200, 250 and 300 mV s^{-1}). The *X*-axis is the differential voltage (*V*) between working electrode and reference electrode. The *Y*-axis is the measured electric current (*i*) running through the working electrode. Theoretically, an ideal capacitor will generate a perfect rectangular profile, since the capacitance *C* (or *i*) should keep constant at a linear charging/discharging rate (dV/dt = constant). The profile of the cyclic voltammograph in low scan rate (25 mV s^{-1}) is close to rectangular shape, which suggests it approaches an ideal EDLC capacitor. In this experimental series, the materials went through charging/discharging cycles by stopping at 0.6 V. The CV plots kept semi-rectangular shapes at 300 mV s^{-1}. The materials' capacitance is almost the same at different scan rates. This behavior indicates the materials might have good performance in fast charging/discharging applications. At high scan rate (>50 mV s^{-1}), the materials capacitance increased from low to high voltage. In other words, the materials capacitance depends on the applied voltage, thus deviating from an ideal capacitor. The maximum discharging current (*I*) is 3 mA at a scan rate (dV/dt) of 50 mV s^{-1}, thus giving $C = I/(dV/dt) = 0.06$ F. The carbon nanosheets were deposited on a carbon paper of exposure area $S = 0.782\ cm^2$. Hence the CNS yields $C/S = 0.0764\ F\ cm^{-2}$ on the testing area *S*.

In this study, a mathematical model was developed to evaluate the material in an ideal supercapacitor. As shown in Fig. 5, the supercapacitor with a radius *R* and a height *H*, can be formed by wrapping up the carbon nanosheet in a "sandwich-pad" following the Archimedean spiral. The sandwich-pad has a centric symmetric geometry. The pad contains two current collectors, which are connected to the reversed polarized voltage. It has one insulating layer as an ion permeable separator. Carbon nanosheets are filled in as electrode material. The left corner inset shows the cross-section schematic of the pad (screening zone in the middle of the figure). The thickness of the sandwich-pad is *d* and its rolling path follows an Archimedes spiral pattern. If we assume the inner-wall and outer-wall current collectors are electrically insulated and the winding is fully compressed, the number of turns (*N*) can be estimated by the ratio of the capacitor radius and the pad thickness, i.e. R/d. To evaluate the capacitance of a supercapacitor, we can apply the following simplified model to represent the cross-section of the wrapped pad-structure: the contour of the inner surface of the nanosheet satisfies the equation of an Archimedean spiral starting from the origin where *r* and θ denote the distance and angle from the start point, respectively and $a = d/2\pi$ is a constant. Hence, we can estimate the total length of the sandwich pad by calculating the integral length of the Archimedean spiral using the following formula:

$$L = \frac{a}{2}\varphi\sqrt{1+\varphi^2} + \frac{a}{2}\ln(\varphi + \sqrt{1+\varphi^2}), \quad (1)$$

where $\varphi = 2N\pi$, $N = R/d$. A Matlab script was developed to evaluate *L* for various inputs.

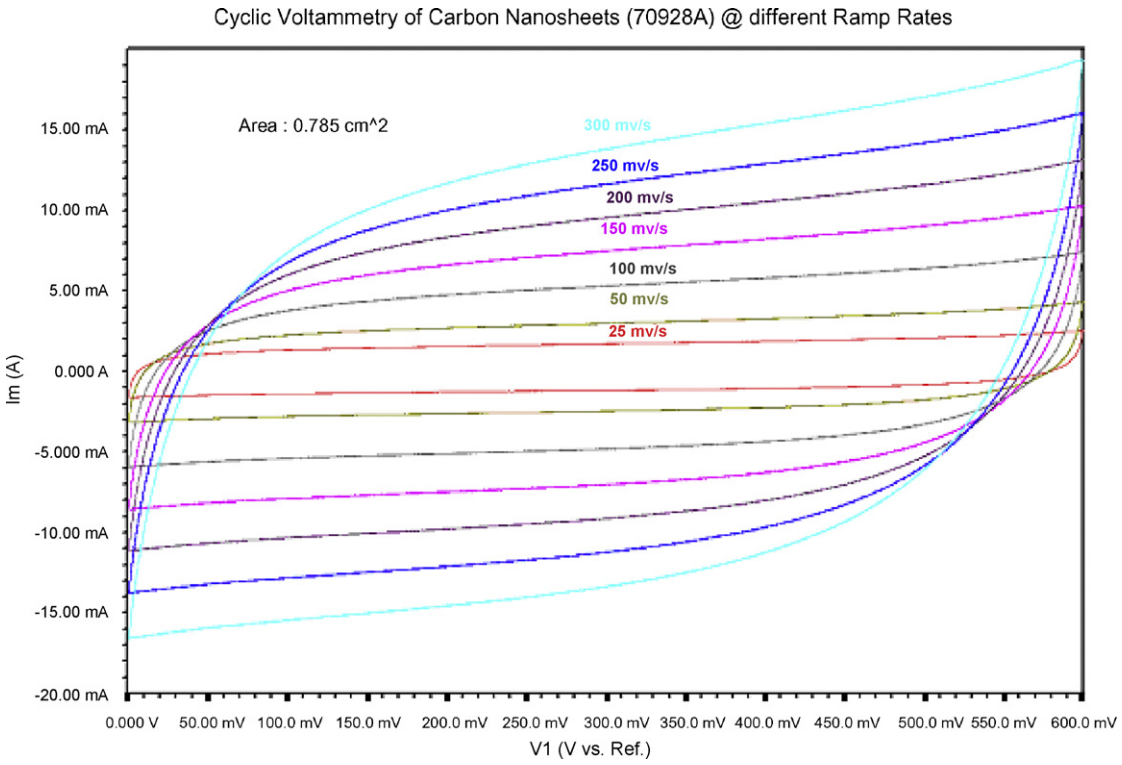

Fig. 4. A cyclic voltammogram (CV) of carbon nanosheets (label 70928A) at various scan rates (25, 50, 100, 150, 200, 250 and 300 mV s^{-1}) with 6 M H_2SO_4 as electrolyte. The material keeps good ultracapacitance performance at fast charging/discharging rates.

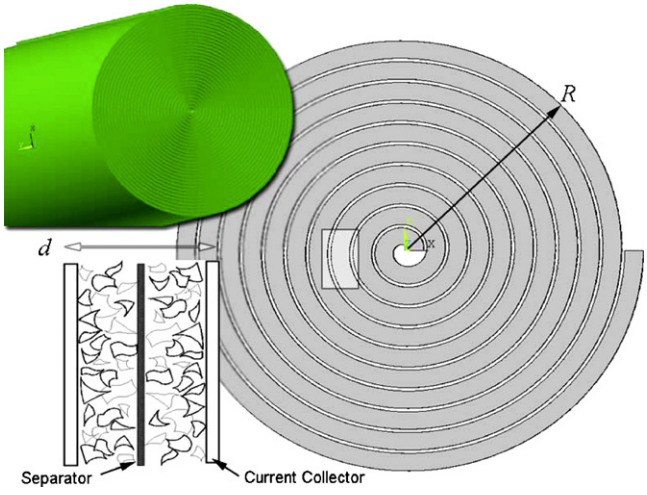

Fig. 5. A virtual supercapacitor-cell containing carbon nanosheets as the electrode material. A rolled sandwiched-pad forms the supercapacitor. The sandwich-pad contains two conductive electrodes as current collectors. It has one insulating layer as an ion permeable separator. Carbon nanosheets are filled in as electrode material. Left corner inset shows the cross-section schematic of the pad (screening zone in the middle of the figure).

For a supercapacitor device with $R = 3$ cm, $H = 13.8$ cm, which is rolled in a sandwich pad with $d = 100$ μm, the capacitance value of the device needs to be calculated as two capacitors. Device capacitance is 1/2 the capacitance of each electrode since the two are in series. This gives,

$$C_{total} = \left(\frac{1}{2}\right) HL \left(\frac{C}{S}\right) = 1.49 \times 10^4 \text{ F}. \quad (2)$$

For reference, a commercial supercapacitor device (*Maxwell Boostcap*® Ultracapacitor, BCAP3000-P270-T04) with a cylinder height of $H = 13.8$ cm and an outer diameter OD = 60.0 mm, has a capacitance of 3000.0 F, however, direct comparison of the commercial product to this new concept is not appropriate. By using an aqueous electrolyte (sulfur acid), the maximum CV testing voltage (0.6 V) is much lower than practical working voltage. Commercial devices, like *Boostcap*®, using non-aqueous organic electrolyte (such as acetonitrile) can sustain a working voltage of 2.5 V. Since the energy storage is a goal to evaluate EDLC devices, it is meaningful to compare electrode materials capacitance at the same working voltage.

4. Summary

This study evaluates carbon nanosheets as an electrode material for an electrochemical double-layer capacitor (EDLC). Carbon nanosheets are made of graphene, or 1–7 layers of sp^2 carbon-bonded graphite structure. They can grow to an area greater than 1 μm × 1 μm and a thickness less than 1 nm. Carbon nanosheets were coated on a conventional carbon paper or carbon fiber cloths via inductive-coupled plasma enhanced chemical vapor deposition (ICP-CVD). Cyclic voltammetry demonstrated that carbon nanosheets yield 0.076 F cm^{-2} in an inorganic electrolyte (H_2SO_4) if measured by nominal electrode area. A geometrical model (using the Archimedes spiral as rolling pattern) was developed to evaluate the specific virtual device capacitance. A value of 14,900 F at maximum working voltage of 0.6 V was determined.

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