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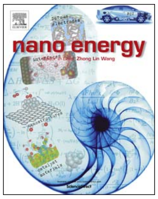

Microscopic vertical orientation of nano-interspaced graphene architectures in deposit films as electrodes for enhanced supercapacitor performance[☆]

Gyoung Gug Jang[a,1], Bo Song[b], Liyi Li[b], Jong Kahk Keum[c], Yongdong Jiang[d], Andrew Hunt[d], Kyoung-sik Moon[b], Ching-Ping Wong[b], Michael Z. Hu[a,*,1]

[a] Energy and Transportation Science Division, Oak Ridge National Laboratory (ORNL), Oak Ridge, TN 37831, United States
[b] School of Material Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332, United States
[c] Center for Nanophase Materials Sciences, Chemical and Engineering Materials Division, ORNL, United States
[d] nGimat Co., Norcross, GA 30093, United States

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ABSTRACT

This work reported a novel two-step process to fabricate high-performance supercapacitor films that contain microscale domains of nano-interspaced, re-stacked graphene sheets oriented perpendicular to the surface of current collector substrate, *i.e.*, carbon fiber paper. In the two-step process, we first used ligand molecules to modify the surface of graphene oxide (GO) sheets and manipulate the interspacing between the re-stacked GO sheets. The ligand-modified GOs, *i.e.*, m-GOs, were then reduced to obtain more conductive graphene (m-rGO), where X-ray diffraction measurement results indicated well-controlled interlayer spacing between the restacked m-rGO sheets up to 1 nm. The typical lateral dimension of the restacked m-rGO sheets were ~40 µm. Then, electrical field was introduced during m-rGO slurry deposition process to induce the vertical orientation of the m-rGO sheets/stacks in the film deposit. The direct current electrical field induced the orientation of the domains of m-rGO stacks along the direction perpendicular to the surface of deposit film, *i.e.*, direction of electric field. Also, the applied electric field increased the interlayer spacing further, which should enhance the diffusion and accessibility of electrolyte ions. As compared with the traditionally deposited "control" films, the field-processed film deposits that contain oriented structure of graphene sheets/stacks have shown up to ~1.6 times higher values in capacitance (430 F/g at 0.5 A/g) and ~67% reduction in equivalent series resistance. The approach of using electric field to tailor the microscopic architecture of graphene-based deposit films is effective to fabricate film electrodes for high performance supercapacitors.

1. Introduction

Graphene-based energy-storage devices such as supercapacitors have attracted rapidly growing attention due to graphene's superior properties (*e.g.* electrical conductivity, high theoretical surface area and chemical resistance) resulting in high energy density, high rates of charge/discharge, and long cyclic lives [1]. Currently, various engineered graphene electrode platforms have been developed to effectively utilize these intrinsic graphene properties. It can be categorized mainly into two approaches: surface functionalization and structure modification. For surface functionalization, graphene oxide (GO) is mostly used as a precursor for high quality graphene. GO resulting from liquid-phase exfoliation of graphite is suitable for low-cost and mass production of graphene-based particulate materials that contains single or few layer sheets in each particle [2]. However, GO sheets tend to either form irreversible agglomeration or restack during solution reduction process, resulting in significant loss of the surface area. Therefore, various additional ligand molecules, such as surfactant [3], redox-active functional group molecules [4–6], conductive polymer [7,8], and transition metallic nanoparticle [9], have been introduced to prevent the restacking of graphene sheets and increase interlayer spacing (*i.e.* porous gap) between restacked graphene sheets. Such interspace tailoring for various electrolytes is a strategy to improve the charge storage capability and the wettability of the graphene electrode surface.

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[*] Corresponding author.
E-mail address: hum1@ornl.gov (M.Z. Hu).

[1] Authors of equal contribution.

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However, most structures of these graphene electrode materials including reduced GOs (rGOs) are limited to the horizontally aligned film because of intrinsic orientation of two-dimensional graphene sheets. The close restacking of lamellar sheet structure that exists in a dried film retards diffusion of electrolyte ions due to long transport path, resulting in a relatively slow kinetic response [10].

For structure modification, three dimensionally architectured graphene films, *e.g.,* porous/holey [11–13] and vertically aligned sheets [10,14–18], have been reported to exhibit high performance supercapacitor electrodes because their enhanced kinetics of electrons and electrolyte ions in their unique structures. Especially vertically-aligned graphene sheets exhibit high kinetic performance due to (1) open edge structure to enhance electron transfer between an active carbon material and a current-collector, (2) a suitable pore size and distribution to facilitate mobility of electrolyte ions, and (3) short paths and ease of electrolyte ions to the graphene layers. Despite these advantages, the fabrication methods for "vertical graphene (VG)" structures such as plasma-enhanced chemical vapor deposition [14–18] and cutting of graphene oxide sheet roll [10] have difficulty in reducing fabrication cost and scale-up for large sized or large amount of films. Furthermore, a low gravimetric capacitance (less than rGO films and powders) because of porosity in free-standing films [10] or densely stacking may limit highly efficient supercapacitors.

In this present work, we report a facile method for depositing VG structured films onto a carbon fiber paper (CFP, as current collector for supercapacitor) by drop-casting and evaporating liquid slurry of molecular ligand composited rGO (m-rGO) under an electrical field (E-field). The graphene surface was first engineered by modifying molecular ligands on GOs and chemically reduced. Four different functional ligand molecules (*e.g.* 2,5-diamino-1,4-dihydroxyl benzene dihydrochloride (DDDC), octadecyltrichlorosilane (ODTS), *p*-phenylenediamine (PPD), polyaniline (PANI)) were studied. The molecular ligands serve as "spacer" to preserve interspace in restacked m-rGO sheets after the film deposits are dried up. The ligand-controlled interspacing increases graphene surface accessibility of electrolytes. The slurry materials of m-rGO dispersed in suitable solvents were drop-casted evaporatively on various substrates (like CFP) under E-field (Fig. 1). The E-field induced vertical orientation of graphene sheets/stacks during the film deposition/drying. In principle, when a thin 2D graphene sheet is brought into an E-field, electric polarization effects could induce a moment of force which tends to align the graphene sheet along the field direction [19]. As described in Fig. 1, the appropriate E-field can result in the formation of a stable vertically-oriented three-dimensional conducting network that avoids intrinsically tight restacking of graphene sheets due to functionalized ligands. Furthermore, we observed E-field-tailored interlayer spacing (*i.e.* widen interspacing relative to baseline m-rGO films without E-field orientation). These structural and morphological tailoring (at both nanoscopic and microscopic scales) have led to higher specific capacitance, faster kinetics and better contact of active material/current collector, compared with a baseline film deposit (*i.e.,* horizontally restacked graphene film electrode under no E-field).

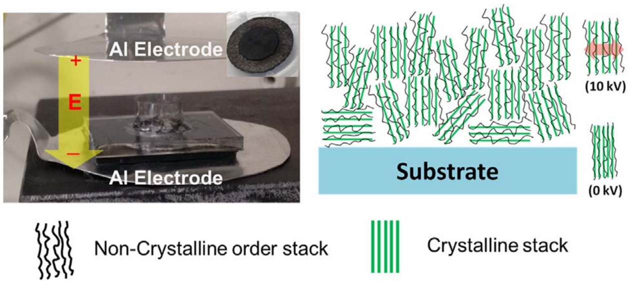

Fig. 1. Two-step process to deposit graphene films that contain controlled nano-interspacing and microscopic "vertical graphene" domains (i.e., non-crystalline order stack or crystalline stack). Vertical structures evolve during electrical field-assisted deposition of m-rGO films under electric field at 10 kV.

2. Experimental

All the chemical reagents in this work were commercially available and used as received. GO was synthesized from natural graphite powders (230U from Asbury Carbons, PA) by a modified Hummers method [20]. The 230U is micron sized (~40–50 µm) powder. Carbon fiber paper (CFP, Spectracarb 2050A −1050) was purchased from FuelCellsEtc (College Station, TX).

2.1. GO reduction to rGO

GO and rGO are baseline materials. 100 mg GO was dispersed in 100 ml H_2O and sonicated for 1 h, then 1 ml hydrazine (as reducing chemical) was added to the solution and stirred at 80 °C for 24 h. The resulting solution was filtrated and washed with H_2O repeatedly. The powder was then dried at 55 °C for overnight.

2.2. Synthesis of ligand-grafted graphene: m-rGOs (DDDC-rGO & ODTS-rGO)

GO slurry contains 120 mg of GO solid sheets in 40 ml of 200-proof ethanol and was sonicated for 2 h to homogenize. 52 µl HCl was added into the slurry and mixed with 150 mg 2,5-diamino-1,4-dihydroxylbenzene dihydrochloride (DDDC) or 200 mg octadecyltrichlorosilane (ODTS) in a reaction vessel sealed with a cap. The reaction mixture was allowed to react at 120 °C in an oven overnight for 16 h. The reacted slurry was cooled down to room temperature. For chemical reduction of the ligand-grafted GO, 0.436 ml NH_3 and 35.9 µl hydrazine was dropped into the reaction vessel and the mixture was held at 95 °C for 3 h. After cooling at room temperature, the slurry was transferred and centrifuged for 10 min at 12,000 rpm. Supernatant was decanted. The ethanol (~50 ml) washing and centrifugation was repeated 3 times to wash out the residual un-reacted DDDC (purple color) or ODTS.

2.3. Synthesis of m-rGOs (PPD-rGO & PANI-rGO)

PPD-rGO [21] and PANI-GO composite [22] were synthesized by previously reported procedures. For the synthesis of PANI-rGO, reduction was followed by the method of rGO procedure.

2.4. Electric field assisted deposition of particulate films of m-rGO materials

A m-rGO was re-dispersed in ethanol or hexane (only for ODTS-rGO) with sonication for 1 h to form a homogeneous suspension slurry (~3 g/L). The graphene slurry was drop-casted onto the top surface of a horizontally placed CFP (12 mm of diameter) at the bottom of a "sealed" or "unsealed" glass cell (10 mm of diameter of cylindrical tube), which sits in a vertically oriented E-field at 10 kV (Fig. 1 & Fig. S1, for the deposition cell configuration). The high voltage was supplied by a high voltage DC power supply (Series ER/DM, Glassman High Voltage, Inc.). The two horizontal parallel electrode plates for generating E-field were ~6 cm diameter of Al foils. The air gap between electrode plates was ~2.5 cm. The slurry of ODTS-rGO or DDDC-rGO was evaporatively deposited onto the CFP top surface in the "sealed" glass cell. (Fig. S1) Once the sealed cell was assembled with a CFP, the drop-casted thin film was formed on the selective area by upward solvent drying under E-field. Other m-rGO material slurries were deposited in the "unsealed" glass cell to reduce deposition rate. (Fig. S1). At the beginning of deposition, the porous CFP was drained out some graphene slurry. A continuous graphene film formed on the surface of the CFP via continuous deposition. Once a continuous thin film formed on the porous CFP, the permeate rate of graphene solution was slow down and the film was mainly formed by solvent drying