

Fabrication and Characterization of 3-D Graphene-CNT Architectures towards Supercapacitor Applications

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ABSTRACT

This work describes the first steps towards fabrication and characterization of a novel hybrid nanostructure comprised of carbon nanotubes (CNTs) grown out-of-plane and in between graphene layers for supercapacitor applications. The structure was characterized by Raman spectroscopy, scanning electron microscopy, and cyclic voltammetry. The results showed improved electrochemical performance for the graphene-CNT structure over the graphene structure. Forthcoming work includes electrochemical testing of a graphene-CNT-graphene architecture.

Keywords: graphene, carbon nanotube, supercapacitor, energy storage

1 INTRODUCTION

Supercapacitors are an important group of energy storage devices having high power density, sufficiently high energy density, fast rate capability and ultra long cycling stability by means of charge accumulation at the electrode/electrolyte interface [1–3]. Thus, high surface area and low intrinsic resistance are important for high performance. Nanostructured carbon materials such as activated carbon (AC) [4], activated carbon fibers (ACF) [5] and carbon nanotubes (CNTs) [6,7] have large surface area and low cost, thus are used for conventional supercapacitor electrodes. In addition, composites using carbon materials and redox materials have also been studied [8].

Recently, graphene has become a promising material for supercapacitors due to excellent electrical conductivity, outstanding theoretical specific surface area (SSA) (~2630 m²/g) [9] and an intrinsic capacitance of up to 21 μF/cm², the theoretical limit of carbon materials [10]. However, supercapacitors composed of graphene alone suffer from loss of active surface area due to aggregation of the material [11–13].

The key idea of this work is to minimize graphene self-aggregation by growing CNTs spacers directly on and between the graphene layers. To this end, we have: 1) fabricated a CNT-graphene architecture in which CNTs were grown out-of-plane on a graphene layer and 2) are currently growing a graphene-CNT-graphene architecture in which CNTs are grown vertically between two graphene layers, as shown in the schematic of Figure 1.

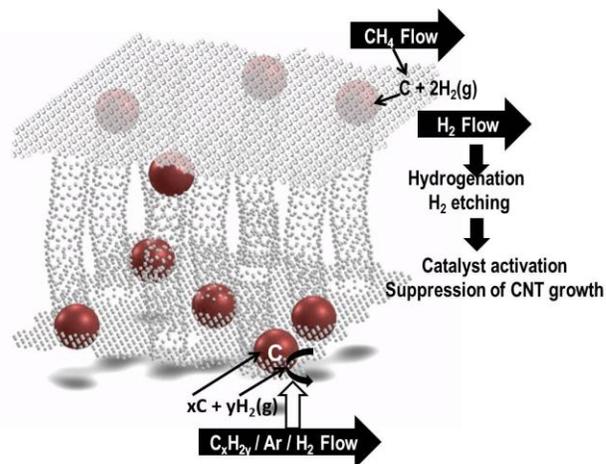


Figure 1: Schematics illustrating direct CNT growth in between planar graphene.

2 EXPERIMENTAL RESULTS AND DISCUSSION

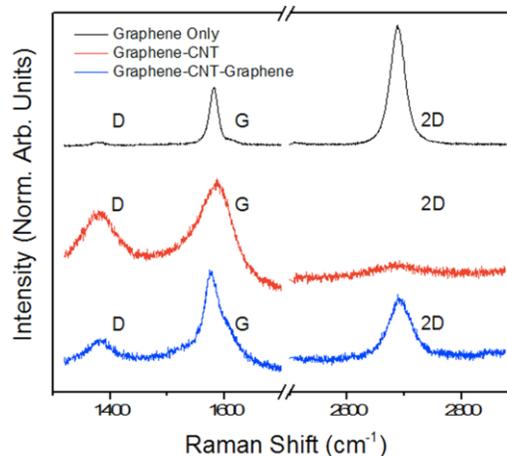


Figure 2: Raman spectra of graphene, graphene-CNT structure, and graphene-CNT-graphene structure.

Graphene and CNTs were grown under atmospheric pressure chemical vapor deposition (APCVD), and characterized by Raman spectroscopy, scanning electron microscopy (SEM) for morphology study, and cyclic

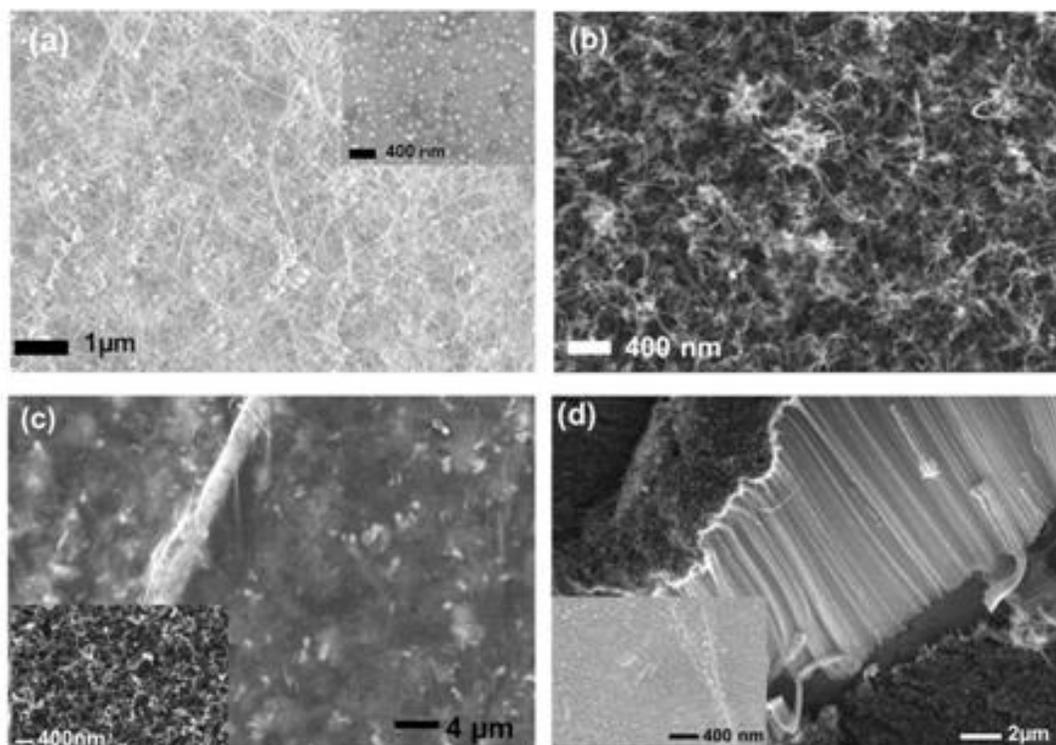


Figure 3: SEM images of direct growth of CNTs using (a) CH_4 and (b-d) C_2H_4 gas; (a and b) CNT array on graphene layer and (c) spaghetti-like and (d) vertical arrays of CNTs in between two graphene layers. Ni catalyst array on (inset of a) and in between (inset of d) graphene layers during H_2 heat treatment.

voltammetry (CV) for electrochemical testing.

The graphene only, graphene-CNT and graphene-CNT-graphene structures were characterized by Raman spectroscopy, as shown in Figure 2. As the figure shows, in the graphene only spectra, the I_{2D}/I_G ratio of 2, minimal D peak and FWHM of 28 cm^{-1} of the 2D peak indicates that the sample is monolayer. The appearance of a shifted D peak, broadening and decreased intensity of the 2D peak and I_D/I_G ratio of 0.5 in the graphene-CNT spectra confirms the presence of CNTs grown under CH_4 flow. Point spectra on a graphene-CNT-graphene 3-D structure detail the presence of the second graphene layer on the CNT array. Each peak is a convolution of both CNT and graphene characteristics.

In order to find the optimal conditions for CNT growth between graphene layers, we first studied direct growth of CNTs on graphene. Variation of CH_4 , H_2 and Ar flow rates balanced the competing processes of hydrogen etching and carbon formation during growth [13,14]. Under intermediate CH_4 conditions, the rate of CH_4 decomposition, carbon diffusion/formation and hydrogen etching was well optimized, growing densely packed, long CNTs. The SEM image is shown in Figure 3a.

Then, we also studied the graphene/CNT growth using C_2H_4 , and found the use of C_2H_4 reduced the incidence of graphene etching (as seen with CH_4), likely due to the

greater concentration of dissociated carbon for similar flow rates. Building on these results, gas flow rates of C_2H_4 , H_2 , and Ar were varied at $700 \text{ }^\circ\text{C}$ to grow CNTs between graphene layers. The SEM images are shown in Figure 3b-d. A metal catalyst film deposited between two graphene layers was thermally treated to breakdown into a CNT catalyst array. Using C_2H_4 , long, densely-packed, vertically aligned CNTs were grown on graphene, which implies large surface areas for charge storage, reduced self-aggregation, and efficient charge transfer between the CNTs and graphene, as shown in Figure 3d.

The electrochemical behavior of the graphene-CNT structure was characterized by cyclic voltammetry (CV). A standard rectangular shape of the CV curves (Figure 4) indicates that electron transfer was unrestricted during the accumulation of charged ions on the surface of the graphene-CNT-graphene electrode.

The measured average capacitance of the graphene-CNT sample, $653.7 \mu\text{F}/\text{cm}^2$ at $10 \text{ mV}/\text{s}$, considerably higher than a graphene-only electrode ($99.6 \mu\text{F}/\text{cm}^2$ at $10 \text{ mV}/\text{s}$), is attributed to the extra surface area provided by CNTs. The graphene-CNT capacitance was maintained at $490.3 \mu\text{F}/\text{cm}^2$ at charging and discharging rates of $300 \text{ mV}/\text{s}$, implying very rapid current response on voltage reversal at each end potential [15].

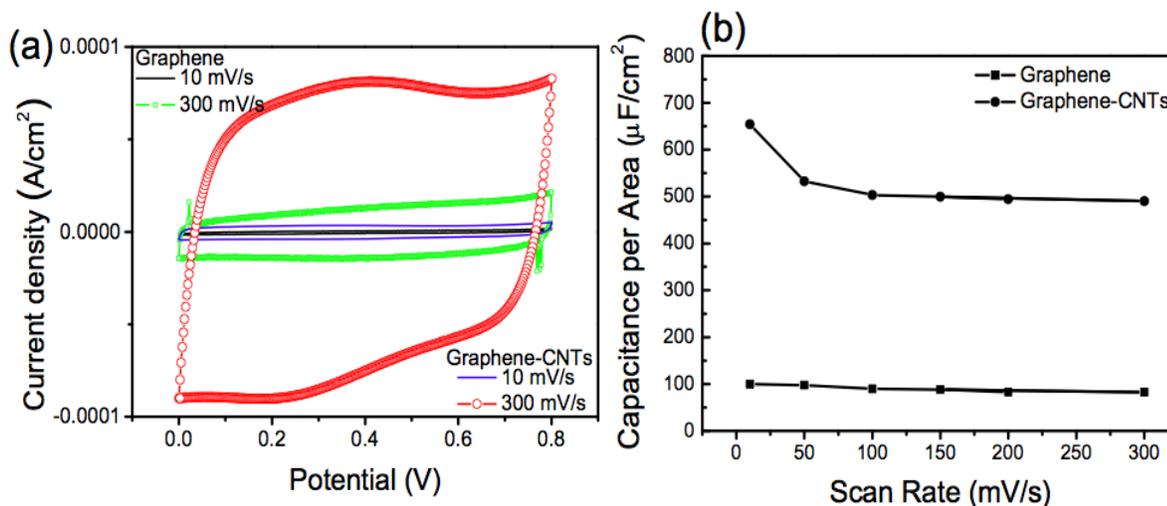


Figure 4: Cyclic voltammograms for CVD grown graphene without CNTs and graphene-CNT hybrid electrode at (a) different scan rates in 0.1 M H₂SO₄ at room temperature, and (b) capacitance per area obtained at scan rates of 10-300 mV/s. Images are from our previous work [14].

3 CONCLUSIONS

The growth of novel graphene-CNT and graphene-CNT-graphene architectures is a milestone towards fabricating structures of alternating graphene and CNT layers for 3D hybrid electrode architecture. Electrochemical tests performed on the CNT-graphene structure resulted in outstanding measured capacitance, thus cementing the suitability of 3-D architecture in high performance energy storage applications. Forthcoming work includes electrochemical testing of a graphene-CNT-graphene architecture.

4 ACKNOWLEDGEMENT

This work has been supported in part by National Science Foundation (EECS-1040007, ECCS-1104870, ECCS-1202269 and EEC-1138244) and Air Force Office for Scientific Research (FA9550-11-1-0272, FA9550-12-1-0326).

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