Fabrication and electrochemical characterization of super-capacitor based on three-dimensional composite structure of graphene and a vertical array of carbon nanotubes

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Abstract

We have demonstrated a three-dimensional composite structure of graphene and carbon nanotubes as electrodes for super-capacitors. The goal of this study is to fabricate and test the vertically grown carbon nanotubes on the graphene layer acting as a spacer to avoid self-aggregation of the graphene layers while realizing high active surface area for high energy density, specific capacitance, and power density. A vertical array of carbon nanotubes on silicon substrates was grown by a low-pressure chemical vapor deposition process using anodized aluminum oxide nanoporous template fabricated on silicon substrates. Subsequently, a graphene layer was grown by another low-pressure chemical vapor deposition process on top of a vertical array of carbon nanotubes. The Raman spectra confirmed the successful growth of carbon nanotubes followed by the growth of high-quality graphene. The average measured capacitance of the three-dimensional composite structure of graphene-carbon nanotube was $780 \, \mu\mathrm{Fcm}^{-2}$ at $100 \, \mathrm{mVs}^{-1}$.

Introduction

In recent years, nanostructured materials have brought wide scientific and commercial attentions due to their novel physical and chemical properties for their potential energy storage applications.[1,2] However, today's energy storage device do not meet the demand for combined power and energy densities. Conventional capacitors possess a fast response time and high power density, but they are not able to store a large amount of energy. Batteries exhibit a large energy density, but they do not provide fast charge/discharge cycles due to the nature of slow ion diffusion processes. In addition, the overheating of the battery system during fast charge/discharge has raised significant safety concerns.[3] This performance gap between batteries and capacitors has been a major roadblock in electrochemical energy storages. Electrochemical super-capacitors show great un-tapped potential, owing to their high power density, reasonably high energy density and ultra-long cycling stability.[4] The key challenge in fabricating high capacitance super-capacitors lies in being able to effectively maximize the chemically active electrode surface. Thus, to date, researchers have turned to low-dimensional

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materials such as one-dimensional (1D) or two-dimensional (2D) nanomaterials to fabricate super-capacitors with high specific surface area, which are associated with the high aspect ratio.[5,6] In particular, carbon nanotubes (CNTs) and graphenes have generated great interests in energy storage applications due to their large specific surface area and efficient electron transportation mechanism.[7–11] Those electrodes can be coated with CNTs and graphenes through solution dip coating,[12,13] spin coating,[14] vacuum filtration,[14,15] and spray coating.[16,17] However, during the solution-based fabrication process, CNTs and graphene layers tend to self-aggregate and to degrade surface area and conductivity.

In this study, our approach is to overcome natural aggregation of CNTs and graphene by immobilizing vertically grown CNT arrays on graphene sheet that provide space among the nanomaterials. Furthermore, such co-grown CNT-graphene composite structure will facilitate low intrinsic resistance between CNTs and graphene layer.[18–20]

In order to increase the capacitance in the limited size of device and support the graphene layer, a dense and vertical array of CNTs is required to create the large surface area and robust structures. In our previous work, a vertical array of CNTs on silicon (Si) substrates was grown by a low-pressure chemical vapor deposition (LPCVD) process using anodized aluminum oxide (AAO) nanoporous template, which was directly fabricated on Si substrates.[21] With excellent stability and low intrinsic resistance, the three-dimensional (3D) composite structure of the vertically grown CNT array on graphene serves as the scaffold of metal oxide[22,23] or conducting polymer-based[24] pseudo-capacitors to achieve high energy density, power density, and long cycling stability. Further, the graphene-based electrodes eliminate the requirement of the binders and conductive additive, which usually degrade the electrode performance since graphene layer can also act as an excellent current collector.[25–28] Moreover, such 3D composite structure of graphene and CNTs can be used in the stretchable electrodes for super capacitors or batteries since the network of nanomaterials is intrinsically tolerant to the mechanical deformation.[29–33]

Experimental

Fabrication of 3D composite structure of graphene and CNTs

A thin layer of titanium (Ti, 100 nm) and 3-μm thick aluminum (Al) was deposited on a SiO_2 (100 nm thickness)/Si substrate. The fabrication of the 3D composite structure consisting of a vertical array of CNTs under the graphene layer includes the following steps as shown in Figure 1: (a) Al layer was anodized in 0.3 M oxalic acid electrolyte to form a nanometer-scale cylindrical porous AAO template – A constant voltage of 20 V was applied at 20°C; (b) A layer of about 20 nm – 30 nm thick cobalt was deposited by electrodeposition at the bottom of the pores as a catalyst for subsequent growth of CNTs by LPCVD. The LPCVD uses mixture of C_2H_4 and H_2 (8:1 ratio) at pressures of 5 torr for 20 min, and at typical growth temperatures of 410°C–650°C; (c) Fe_3O_4 nanoparticles
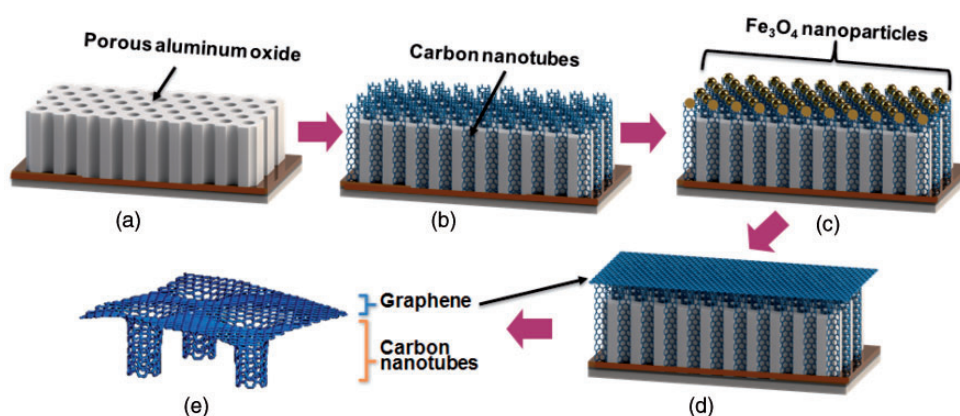

Figure 1. Fabrication process of the graphene on CNT posts: (a) Anodization of 3 μm thick Al deposited on SiO_2/Si substrate in 0.3 M oxalic acid electrolyte to form a nano-porous anodized aluminum oxide (AAO); (b) Electrodeposition of a layer of about 20 nm–30 nm thick cobalt as a catalyst for subsequent growth of CNTs by LPCVD in the pores of AAO template; (c) Deposition of Fe_3O_4 nanoparticles on top of the AAO template by spin coating at 500 r/min for 20 s followed by baking at 300°C; (d) Growth of graphene by LPCVD on Fe_3O_4 NPs-deposited top surface of the AAO under gas mixtures of Ar, H_2 and CH_4; (e) etching AAO by 0.1 M NaOH to result in a vertical array of CNTs topped with graphene.
LPCVD: low-pressure chemical vapor deposition; AAO: anodized aluminum oxide; CNT: carbon nanotube.

(NPs) were spin-coated on top of the AAO template at 500 r/min for 20 s and followed by baking at 300°C for 30 min. The NPs were dispersed in hexane with 7 mg/ml concentration by using ultra sonication; (d) Graphene was grown on Fe_3O_4 NPs deposited on the top surface by using similar LPCVD process used for CNTs. The growth of graphene includes annealing of the catalysts at 800°C for 30 min under gas mixtures of Ar and H_2 and introducing CH_4 in the chamber at 900°C for 20 min; (e) AAO was chemically etched by 0.1 M NaOH to result in the exposed 3D composite structure of vertical array of CNTs and graphene.

Electrochemical characterization of 3D composite structure of graphene and CNTs

The electrochemical behavior of the 3D composite structure of graphene and CNTs was investigated using aqueous electrolyte, 6.0 N KOH. Surface of the entire 3D structure was treated by 0.1 M H_2SO_4 for 5 min in order to improve the wettability to the aqueous electrolyte. Electrochemical measurement of the cell was carried out using a symmetric two-electrode configuration. A heat-treated nickel plate was used to reduce contact resistance and internal resistance of 3D composite structure of graphene and CNTs for electrochemical characterization. In order to obtain the specific capacitance, cyclic voltammograms were acquired by a VERSTAT potentiostat/galvanostat with various scan rates from $10 \, mVs^{-1}$ to $1000 \, mVs^{-1}$. Electrochemical impedance spectroscopy (EIS) was conducted at frequencies ranging from 100 kHz to 10 MHz. The EIS data-fitting program ZVIEW was used to obtain the equivalent circuit parameter, such as equivalent series resistance (ESR). The frequency response of the super-capacitor was examined through the analysis of EIS data.

Results and discussion

The morphology and nanostructure of the 3D composite structure of graphene and CNTs were investigated by a field emission scanning electron microscope (FESEM). Figure 2 shows (a) a top-view of the 3D structure after etching AAO partially (only about 50 nm deep from the top surface of AAO), (b) a cross-sectional view of the 3D structure before etching AAO, and (c) a side-view after the wet etching by 0.1 M NaOH. After the wet etching of AAO, CNTs were packed and bundled due to the surface tension. Although the CNTs are not maintained in an ordered manner after the etching, the surface area of the electrode still dramatically increased by the near-vertical CNT bundles.

In order to characterize the 3D composite structure of graphene and CNTs, Raman spectra were taken at an excitation wavelength of 532 nm. Figure 3 shows the Raman spectrum of the 3D composite structure after AAO etching. As shown in the Figure 3, the spectra shows a broad G band, a suppressed 2D band and a large defect peak of D band at $\sim 1380 \, cm^{-1}$ arising from the addition of the CNTs. In addition, the G bandwidth increases compared with the G bandwidth of graphene. It was also found that no radial breading mode (RBM) was observed in the 3D composite structure of graphene and CNTs, which may be attributed to either the presence of too many walls or > 2 nm inner diameter for each CNT. The results confirmed the successful growth of CNTs followed by the growth of graphene.

Figure 4 shows the cyclic voltammetry (CV) curve of 3D composite structure of graphene and CNTs at the scan rate of $100 \, mVs^{-1}$. The CV curve of the super-capacitor electrodes based on 3D composite structure of graphene and CNTs exhibits close to an idea rectangular shape even at a high scan rate of $100 \, mVs^{-1}$, indicating a small ESR. A specific power density of as high as 28 kW/kg was obtained. The average measured
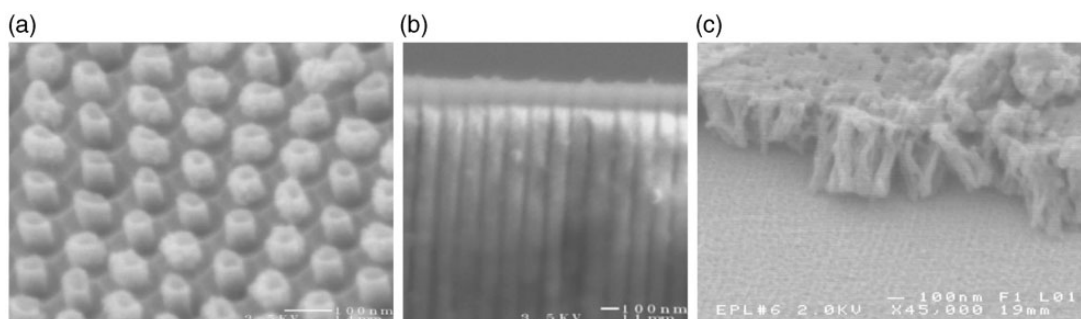

Figure 2. FESEM images showing (a) top-view of a vertical array of CNTs exposed as a result of etching AAO partially (only about 50 nm deep from the top surface of AAO) before spin coating Fe_3O_4 NPs; (b) cross-sectional view of the 3D composite structure of graphene and CNTs grown by two separate LPCVD processes; (c) side-view of the 3D composite structure of graphene and CNTs released after etching AAO completely by NaOH (scale bar in the SEM images is 100 nm).
FESEM: field emission scanning electron microscope; LPCVD: low-pressure chemical vapor deposition; AAO: anodized aluminum oxide; CNTs: carbon nanotubes.
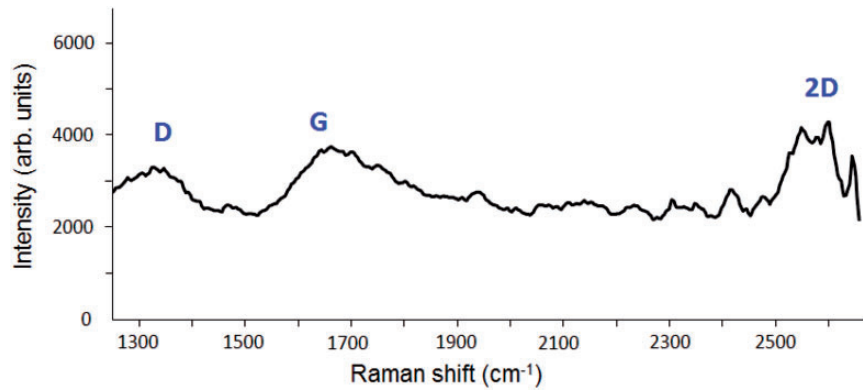
Figure 3. Raman spectra of the 3D composite structure of graphene and CNTs grown by LPCVD. The spectra show a broad G band, a suppressed 2D band and a large defect peak of D band at $\sim$1380 cm^{-1} arising from the addition of the CNTs. In addition, the G bandwidth increases compared with the G bandwidth of graphene.
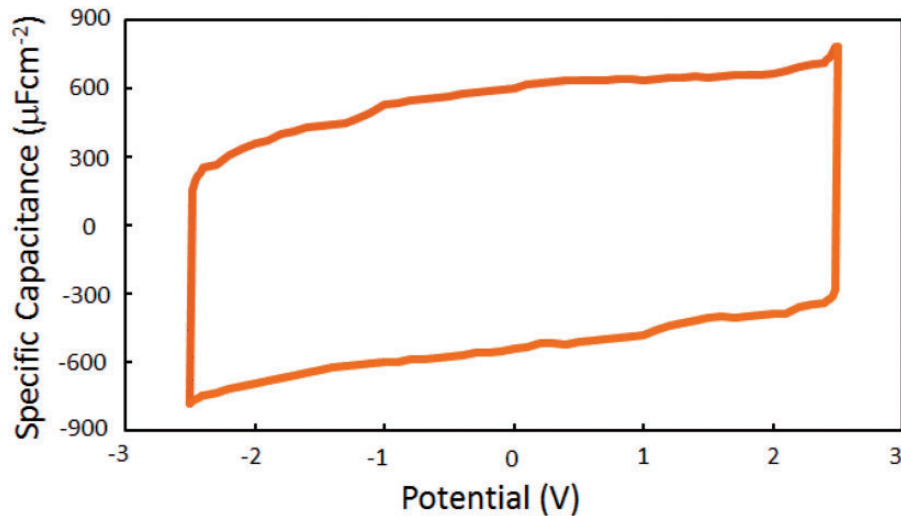LPCVD: low-pressure chemical vapor deposition; CNTs: carbon nanotubes.

Figure 4. Cyclic voltammetry curve of the 3D composite structure of graphene and CNTs at the scan rate of 100 mVs^{-1}. The average measured capacitance of the 3D composite structure of graphene and CNTs was 780 μFcm^{-2}.
CNTs: carbon nanotubes.

capacitance of the 3D composite structure of graphene and CNTs was 780 μFcm^{-2} at a scan rate of 100 mVs^{-1}. It is noteworthy that high power density of the electrodes is critical for minimizing the size of power cell for miniaturized devices. Therefore, such 3D composite structure of graphene and CNTs as high power density electrodes has the potential to pave the way for a new generation of energy delivery system.

Conclusion

The 3D composite structure of graphene and CNTs was fabricated via the two-step CVD processes using AAO nanoporous templates. Raman spectra of the 3D composite structure of graphene and CNTs indicate the

successful growth of CNTs followed by the growth of graphene layer on top of a vertical array of CNTs. Characterization of the super-capacitor performance of the 3D composite structure of graphene and CNTs indicated that the average measure capacitance of the fabricated structure was 780 μFcm^{-2} at 100 mVs^{-1} with a standard rectangular CV curve. These results indicate that such 3D composite structure of graphene and CNTs has potential towards 3D graphene-CNT multi-stack structure for high power density super-capacitors. Further, the fabrication of 3D composite electrode is compatible with the processes for micro-electromechanical systems (MEMS). The super-capacitor and batteries integrated in the MEMS devices will be our future study. As a continued study, the investigations on

number of graphene layer, graphene-CNT junction characteristics including defects, effects of the electrical and thermal annealing, and repeatability of the electrochemical characterization at various working conditions based on the statistical analysis will be conducted.

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