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High Energy Density based Flexible Electrochemical Supercapacitors from Layer-by-Layer Assembled Multiwall Carbon Nanotubes and Graphene

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ABSTRACT

Thin film electrodes for high energy density based flexible supercapacitors are fabricate using layer-by-layer (LBL) assembly of MWCNTs and graphene. The addition of conductive spacer of MWCNTs between the layers of graphene prevents the agglomeration between each other and therefore facilitates the maximum number of active sites for electrolyte ion intercalation. The supercapacitor devices based on this flexible LBL assembly show very high electrochemical capacitance (390 Fg^{-1}) and exhibit excellent cycling stability, retaining over 97% of its initial charge after 25,000 cycles. The addition of MWCNTs between the layers of graphene raised the energy density by 31% and power density by 39% more than the bare graphene electrodes. The LBL films of MWCNTs-graphene yield ultra-high energy density of 168 $Whkg^{-1}$ which is very promising for future potential application in high performance flexible energy storage devices.

1. Introduction

The recent development in flexible and portable electronic devices with multi-functionalities is limited as they required flexible, lightweight and highly efficient energy storage devices [1–5]. The conventional charge storage devices, such as batteries are bulky and have limitations of short cycle life with relatively slow charging/discharging rates are not suitable for use in portable electronic devices [6–8]. Consequently, electrochemical capacitors have emerged as one of the most promising candidates to fulfill future energy storage needs for wearable electronics as they can provide a higher power density, fast charge and discharge rates and longer life cycles than batteries, and higher energy density than dielectric capacitors [5–9]. Much effort has been dedicated to use various carbon based materials for flexible energy storage devices due to their light weight and flexibility [6]. Among the various carbon based materials, graphene based materials have gained considerable attention due to its many intriguing characteristics, such as high surface 2630 $m^2 g^{-1}$, light weight, electronic conductivity and theoretical specific capacitance 526 Fg^{-1} [5,9–12]. However, their experimental specific capacitance is much lower due to its irreversible agglomerates through the van der Waals interactions since the stacked material cannot be completely accessible to the electrolyte [10–13]. The issue at hand is how to design the electrode structure with graphene which prevent the agglomeration between each layers and therefore facilitate the maximum number of active sites for capacitance. In this work, we report conceptually different approach to solve the agglomeration and accessibility problems of graphene by utilizing layer-by-layer (LBL) assembly in which MWCNTs have been alternated with in the layers of graphene. The MWCNTs not only prevent agglomeration between each other of graphene, but also improve the accessibility for electrolyte ions. As the future development of higher performance energy storages devices not only depends on the employment of new and lighter electrode materials, but also on the new materials for the substrates. Here we also designed and used a new flexible substrate based on LBL deposited metal on non-woven wiper because of its soft and robust mechanical characteristics. The flexible supercapacitors assembled from LBL assembly of MWCNTs and graphene on this newly designed substrate showed superior rate capability, improved specific capacitance (390 Fg^{-1}) and cyclic stability compared with other electrodes.

2. Experimental Methods

The MWCNTs are purchased from Nanokarbon (Korea). The well dispersed MWCNTs were acheived by attaching carboxylic groups on their surface using a reported method.[14] The synthesis of

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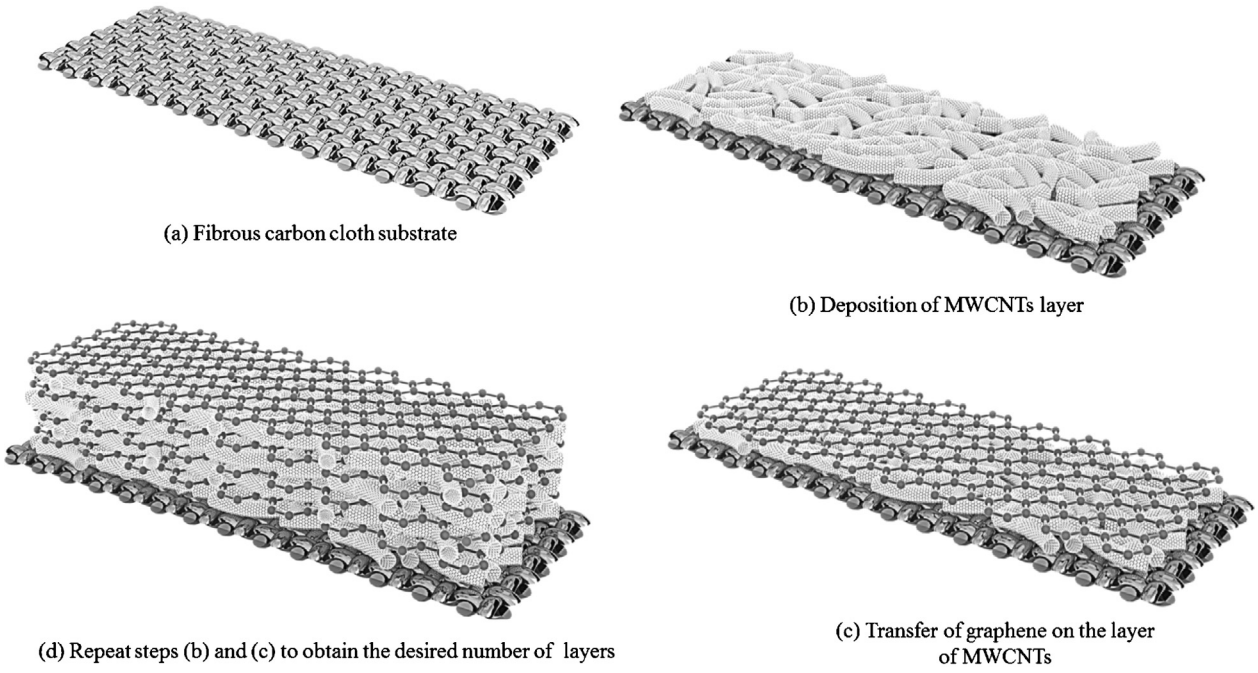

Scheme 1. Schematic 1 Schematic illustration of the fabrication process of the layer by layer assembly of MWCNTs and graphene on fibrous carbon cloth substrate for flexible supercapacitor applications.

monolayer graphene films was achieved by using the previously reported method [15]. Briefly, a Cu foil with a thickness of 25 μm was placed into a vacuum chemical vapor deposition (CVD) quartz chamber. Prior to processing, the foil was annealed at 950 °C in H_2 atmosphere for 2 hrs to remove any residual oxygen and water present in the system. The growth of graphene was carried out at the same temperature in an atmosphere of H_2/CH_4, 80/250 sccm, for 30 mins, and then the system was cooled down to room temperature naturally. In the next step, Polymethyl methacrylate (PMMA) was spin-coated on top of the graphene layer and the Cu foil was cut into small pieces ($4 \times 4\,cm^2$) which were then dissolved in 1 M iron (III) chloride. The etching of Cu foil was achieved by immersing it into 1 M iron (III) chloride ($FeCl_3$) solution.

The graphene layer was thoroughly washed with deionized water and transferred on different substrates such as ITO and fibrous carbon cloth substrate. The layer of MWCNTs was deposited by using spin-spray layer-by-layer self-assembly (SSLBL) method. In this method, the MWCNTs solution was spray onto a substrate spinning at a constant rate of 2000 rpm. This cycle makes one bilayer (BL) of MWCNTs and graphene, denoted (LBL of MWCNTs-graphene). The cycle was repeated to reach the desired number of bilayers of LBL of MWCNTs-graphene thin films. After each bilayer, the as-prepared LBL of MWCNTs-graphene films were heat-treated at 80 °C for 10 minutes in vacuum to improve the stability of the films. Any LBL of MWCNTs- graphene films over 5 bilayers were heat-treated for 20 minutes to control the inter diffusion. By controlling the dilution and quantity of the MWCNTs solution being applied to the substrate, the spin speed, layer thickness of MWCNTs can be precisely controlled. The electrode with LBL assembled graphene layers is achieved in the similar way as described above except the addition of MWCNTs layers. The mass of the LBL assembled electrode with different layers of MWCNTs and graphene on fibrous carbon cloth substrate was determined by weighting substrate before after deposition of each layer which was heat-treated at 80 °C and the weight of the substrate was subtracted to get the weight of active material. The loading mass of each single layer of MWCNTs and graphene electrode was approximately ~ 2.65 $\pm 0.02\,mg\,cm^{-2}$.

3. Results and Discussion

To prepare high performance flexible supercapacitor electrodes on a fibrous carbon cloth substrate while overcoming the aforementioned limitations, we developed a facile LBL assembly of graphene and MWCNTs as shown schematically in schematic 1. The LBL assemblies of graphene and MWCNTs consist of a series of four basic steps: (1) MWCNTs solution is spin coated on fibrous carbon cloth substrate transfer, (2) drying to remove water molecules on a substrate, (3) transfer of graphene on MWCNTs coated fibrous carbon cloth substrate and (4) drying of the second LBL component at 80 °C under vacuum to improve the mechanical stability of the assembly. These basic steps are then repeated as many times as necessary to reach a desired thickness of the film. FE-SEM was used to obtain in-depth information regarding the LBL assembly of MWCNTs-graphene and the results using MWNCTs solution with mono and ten layers are shown in Fig. 1. The FE-SEM image obtained from the monolayer graphene-MWCNTs assembly indicates that with appropriate density of MWCNTs, a long-range close-packing of MWCNTs with small voids and without aggregation was formed on the graphene by using this technique. Furthermore, this highly interconnected microstructure can act as an ideal support for the transfer of second graphene layer. On the other hand, highly dense MWCNTs show aggregation and alignment of bundles of MWNCTs due to van der Waals interactions and capillary forces. The LBL assembly constructed by using densely packed MWCNTs exhibit weak mechanical integrity, poor control of thickness and dense packing, leading to diminishment of the available surface area of the MWNCTs. However, the LBL assembly constructed by using graphene and diluted MWCNTs solution yield randomly oriented individual MWNCTs with well-developed nanoscale pores, making LBL of MWCNTs-graphene films thin films an ideal electrode structure with mixed ionic/electronic conducting channels. The FESEM results of LBL of MWCNTs- graphene films having ten layers show that a highly interpenetrated and porous structure is created (Fig. 1(b)). The synthesized LBL assembly makes as ideal structure for energy storage devices, as MWCNTs have intrinsically high electrical conductivity, high surface area and act as a spacer