Supporting Information For

Layer by Layer Assembly of Ultrathin V_2O_5 Anchored MWCNTs and Graphene on Textile Fabrics for High Energy Density Flexible Supercapacitor Electrodes

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~~Experimental Section~~

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The MWCNTs were purchased from Nanokarbon (Korea) and were functionalized by attaching carboxylic groups on the surface using previously developed [1] in which 1.0 g of as purchased MWCNTs were mixed in a conical flask containing a solution of HNO_3 (65%, 100 mL), and H_2SO_4 (98%, 300 mL) and then the mixture was vigorously stirred under reflux for 100 min. The above mixture MWCNTs and acids were further diluted by using deionized water, filtered, and re-dispersed in deionized water. The whole process was continuously repeated until the 7 pH of the filtrate was achieved. MWCNTs Functionalized with carboxylic groups were dried overnight in a vacuum furnace at 80 ^oC. For the synthesis of 3, 10, 15, and 20 nm thin film of V_2O_5 on MWCNTs, modified MWCNTs, and ammonium metavanadate (NH_4VO_3) with the ratio of 1: 0.15, 1: 0.5, 1: 0.7 and 1: 1 were mixed and 1mL of HCl was added to the mixture. The resulting mixture stirred for 1 h at room temperature. The thickness of V_2O_5 on MWCNTs was controlled by varying ratio of NH_4VO_3 in the solution. Finally the NH_4VO_3 treated MWCNTs were filtered and rinsed with water and acetone several times and annealed at 350 ^oC under ambient conditions for 2 h.

The synthesis of monolayer graphene films was achieved by using the previously reported method [2]. 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 naturally to room temperature. 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 x 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 remaining PMMA coated graphene layer was thoroughly washed with deionized water and transferred to a Ni/Cu/Ni/gold coated textile fiber substrate. For LBL assembly the graphene was first transferred to a Ni/Cu/Ni/gold coated textile fiber substrate, in the next step layer of V_2O_5 coated MWCNTs was spray coated on the substrate, followed by the transfer of graphene layers and this is known as one layer. The whole process was repeated for ten times and the overall process involved in fabricating LbL assemblies is shown in Schematic 1.

Material and Electrode Characterization

Morphology was observed using field emission scanning electron microscopy using JEOL JSM-7401F SEM. Transmission electron microscopy and elemental mapping were carried out using JEM 2100F TEM operated at 200 kV. The crystal structure of samples was studied by X-ray diffraction (XRD) analysis using Rigaku Rotaflex D/Max diffractometer with Cu Kα of wavelength λ=1.5418 Å. All electrochemical measurements were carried in a three-electrode assembly consisting of Ag/AgCl as a reference electrode, Pt foil a counter electrode and LBL assembly of graphene and ultrathin V_2O_5 anchored MWCNTs on metal coated textile fiber substrate as a working electrode using Biologic VMP3 potentiostat/galvanostat. To aid the adhesion of samples to the metal coated textile fiber substrate, one percent Nafion solution was used as a binder. Cyclic voltammetry was carried between -1 and 2 V vs. Ag/AgCl for various scan rates ranging from 1 to 50 mV/s. Galvanostatic charge–discharge studies were performed using a Won A Tech Potentiostat/galvanostatic instrument (WPG,100 South Korea).

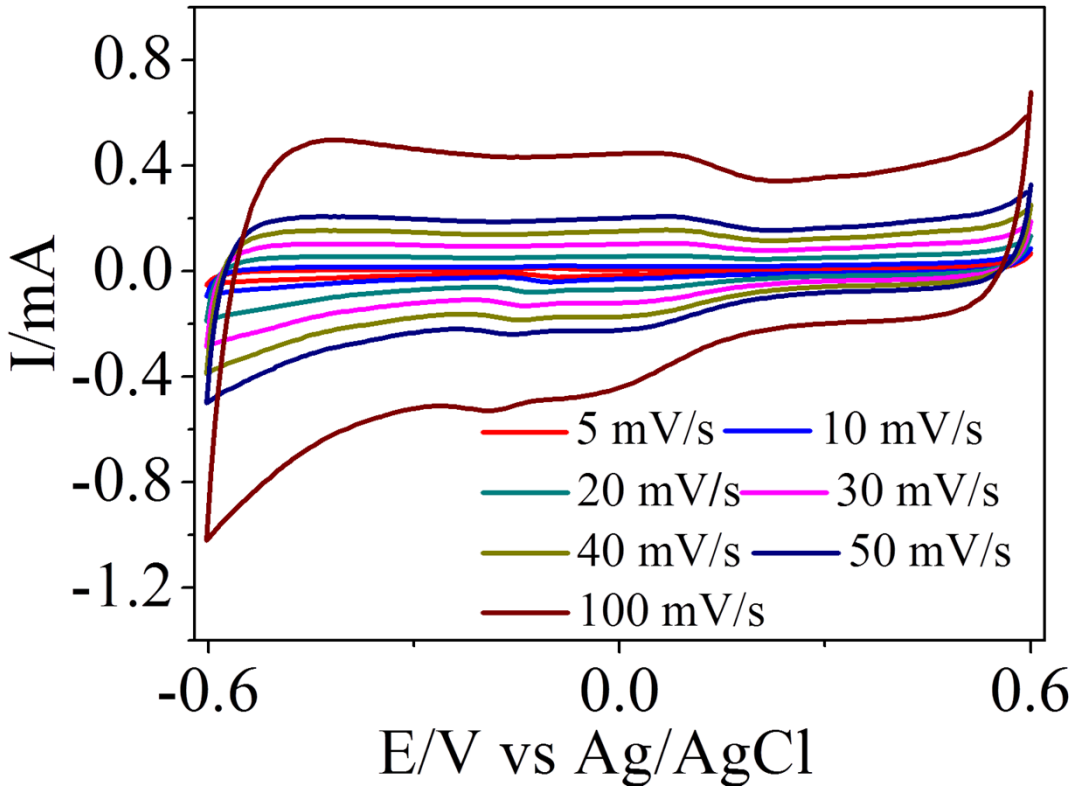

Figure S1: Cyclic voltammograms (CV) of LBL assembled MWCNTs with ten layers electrode at various scan rates from 5 to 100 mV s^{-1} in a 2 M KCl aqueous solution at room temperature.

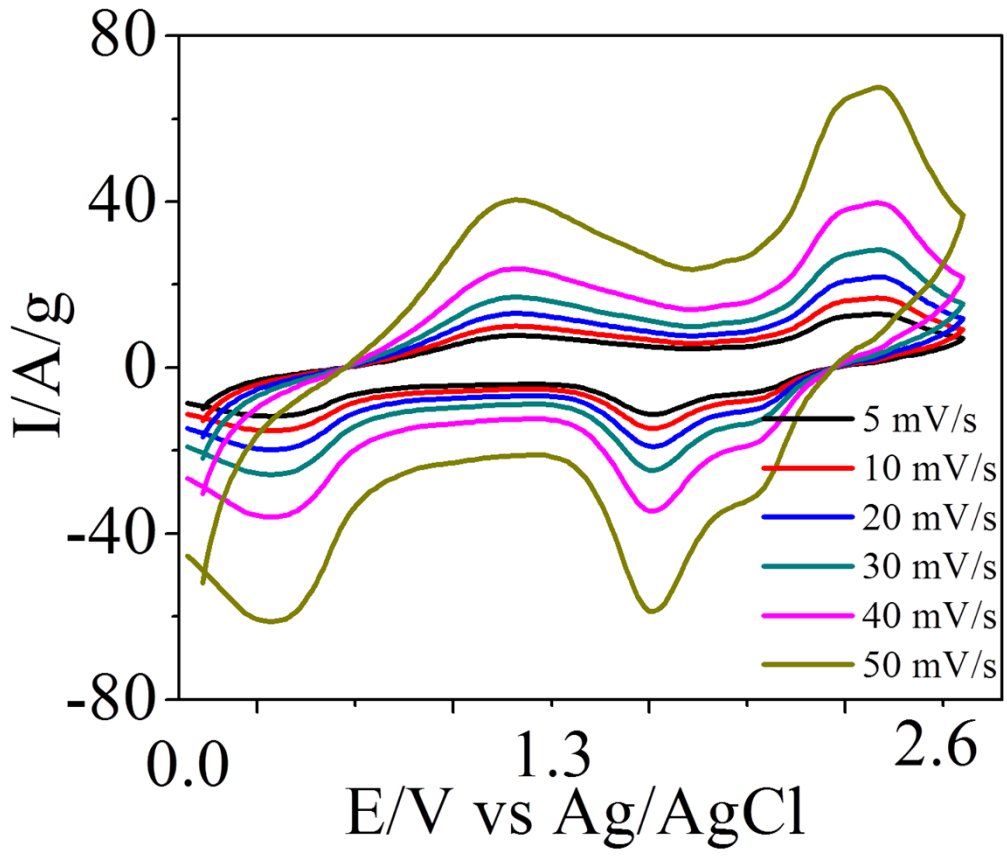

Figure S2: Cyclic voltammograms (CV) of LBL assembled electrode with 3 nm V_2O_5 deposited MWCNTs and graphene at various scan rates from 1 to 50 mV s^{-1} electrode in a 1 M $LiClO_4$ solution at room temperature.

Reference:

[1] Gao, C.; Vo, C. D.; Jin, Y. Z.; Li, W.; Armes, S. P., Multihydroxy polymer-functionalized carbon nanotubes: Synthesis, derivatization, and metal loading. *Macromolecules* 2005, 38, 8634-8648.

[2] Güneş, F.; Shin, H. J.; Biswas, C.; Han, G. H.; Kim, E. S.; Chae, S. J.; Choi, J. Y.; Lee, Y. H., Layer-by-layer doping of few-layer graphene film. *ACS Nano* 2010, 4, 4595-4600.