Enhancing the Supercapacitor Performance of Graphene/MnO$_2$-Nanostructured Electrodes by Conductive Wrapping

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Materials & Methods

Preparation of Graphene/MnO$_2$ Nanostructured Textiles. Polyester textiles (Cloud 9 dream fleece, Wal-Mart) were dipped into the graphene ink (~0.15 mg/mL in water with sodium cholate surfactant) and subjected to 'dip and dry' coating cycles to make conductive graphene-coated textiles (sheet resistance ~700 Ω/sq). MnO$_2$ nanomaterials were deposited on graphene-coated textiles by electrodeposition process. Briefly, graphene-coated textiles were immersed into the plating solution containing 20 mM Mn(NO$_3$)$_2$ and 100 mM NaNO$_3$, and subjected to 90 min deposition under constant current of 100 μA/cm^2 for conformal coating of MnO$_2$ nanostructures on textile fibers. After electrodeposition, the textiles were taken out and washed with DI water to remove excessive electrolyte, and then dried in vacuum oven at 60 °C to let dry for 2 hr.

SWNT Solution Preparation. To form a CNT ink solution, SWNTs grown by laser ablation and SDBS (Sigma–Aldrich) were mixed and dispersed in DI water. The concentrations for SWNTs and SDBS surfactant were 2 and 0.2 mg/mL, respectively. The CNT dispersion was first sonicated in bath sonicator for 5 min, and then placed for probe-sonication for 30 min at 200W (VC 505; Sonics).

Conductive Wrapping of Graphene/MnO₂-Textiles. For conductive wrapping with SWNTs, the graphene/MnO₂ nanostructured textiles were directly dipped into the 0.2 mg/mL SWNT ink solution and immediately removed. The 'wet' textiles were then placed in the vacuum oven for 10 min drying at 100 °C to remove the water. The dry textiles were then rinsed with copious DI water to remove SDBS surfactant, and re-subjected to drying process. The mass of SWNTs coated was estimated by weight difference before and after CNT coatings on textiles. For wrapping with conducting polymer PEDOT-PSS, graphene/MnO₂ nanostructured textiles were dipped into the commercially available polymer solution (Clevios, 1:10 diluted PH1000 solution) and subjected to the same drying step. The 'dip and dry' process was repeated for 2-3 times to get ~0.2 mg/cm² polymer coating in our studies.

Electrochemical Measurement. The electrochemical characterization was carried out based on three-electrode system using a BioLogic VMP3 potentiostat-galvanostat multichannel equipped with electrochemical impedance spectroscopy (EIS) board. Besides the working electrode (different composite electrodes), a Ag/AgCl reference electrode (Fisher Scientific) and a Platinum counter electrode (Fisher Scientific) were used in the measurement. Cyclic voltammetries (CVs) were performed in the potential range of 0 V to 0.85 V vs. Ag/AgCl reference electrode under a sweep rate of 5~100 mV/s. Galvanostatic charge-discharge tests were performed by cycling the voltage from 0 to 0.85 V at different current densities (0.1~5 mA/cm²).

Data Analysis.

The specific capacitance C_s (F/g) of hybrid nanostructured electrodes was calculated based on galvanostatic charge-discharge curves according to the following equation:

$$C_s = i / -[(\Delta V/\Delta t)m] = i / -(\text{slope} \cdot m),$$

where i is the applied current, m is the total mass of active electrode materials, $[\Delta V/\Delta t]$ is the slope of the discharge curves after the initial voltage drop (iR drop) at the beginning of each discharge.