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Scalable Fabrication of Supercapacitors by Nozzle-Free Electrospinning

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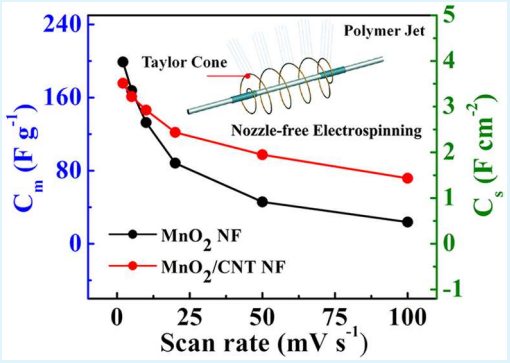
Supporting Information

ABSTRACT: Nozzle-free electrospinning was investigated as a facile technique for producing nanoscale materials for supercapacitors. MnO_2 nanofibers and their composites with multiwalled carbon nanotubes (MWCNTs) were synthesized in a single step, using polyvinylpyrrolidone (PVP) and $Mn(CH_3COO)_2{\cdot}4H_2O$ as starting materials, followed up by heat treatment in ambient air. Nanofibers of relatively uniform diameter were produced at high rates. The nanofibers exhibited good electrical contact between MnO_2 and MWCNT without degradation, which was attributed to the improved stability of MWCNTs in PVP solutions. Electrochemical testing of the composites demonstrated a high capacitance of 1.43 F cm^{-2} at a scan rate of 100 mV s^{-1} in the three-electrode tests. Electrodes and devices produced by nozzle-free electrospinning are promising for practical energy storage applications.



KEYWORDS: *nozzle-free electrospinning, supercapacitors, MnO_2, nanofibers, energy storage devices*

The rapidly growing commercial electrical device market has created an insatiable demand for novel energy storage systems that can provide higher energy and power. Among the various technologies pursued, supercapacitors have attracted much attention due to their high power density and exceptionally long cycle life. The growing interest in employing MnO_2 for supercapacitor electrodes is attributed to its high specific capacitance, relatively large voltage window, and the low cost of this material.[1,2] It has been realized that high electronic and ionic conductivities are necessary in order to utilize the capacitive properties of MnO_2 in supercapacitor electrodes. MnO_2 nanofiber assemblies offer naturally high surface area combined with porosity, allowing for improved electrolyte access to the electrochemically active MnO_2.[3,4] Considerable effort has been spent on optimizing the microstructure and performance of MnO_2 composites with carbon nanotubes (CNTs). The interest in CNTs as an additive derives from the latter's high conductivity and low percolation limit. Co-dispersants were used to improve the electrical contact between CNTs and MnO_2.[5,6] In another scheme, MnO_2-coated CNT was prepared by reduction of Mn^{7+} cations in $KMnO_4$ solutions containing CNTs.[7−9] However, $KMnO_4$ oxidizes CNTs causing structural degradation and reduced electrical conductivity.[10] An active carbon layer was proposed as a sacrificial coating on CNTs.[11] However, a low production rate and nonconformal coverage remain as challenges of the current methods. Additionally, the importance of high material loadings in efficient supercapacitors has been highlighted.[12] Fabrication of MnO_2 electrodes with good capacitive behavior at high material loadings is required for commercial applications.

Nanofibrous materials prepared by the electrospinning method offer high surface area, unique mechanical properties, and low production costs.[13−15] Conventional electrospinning employs a high-voltage-biased needle-like nozzle to dispense a liquid solution, forming a continuous jet that ultimately becomes a nanofiber. Nozzle-based electrospinning setups have a few disadvantages: (1) a narrow operating voltage window, where high voltages must be carefully applied to prevent corona discharges that cause a faulty spinning process, and (2) extremely low production rates.[15] For example, fabrication of MnO_2 nanofibers by conventional electrospinning is slow, producing only a few grams of material per day, which renders it impractical for industrial applications.[16] Nozzle-free electrospinning has emerged as a new electrospinning mode to produce nanofibers on a large scale.[17] Instead of using a nozzle, a rotating drum or coil, partially immersed in the liquid solution to be electrospun, serves as the biased electrode. When the applied electric field exceeds a certain threshold value, the liquid film on the drum or coil deforms enough to cause multiple Taylor cones to form. Thus, multiple jets and nanofibers are produced without the need for nozzles. In previous work, we demonstrated nozzle-free electrospinning in the fabrication of solid acid fuel cell electrodes.[18]

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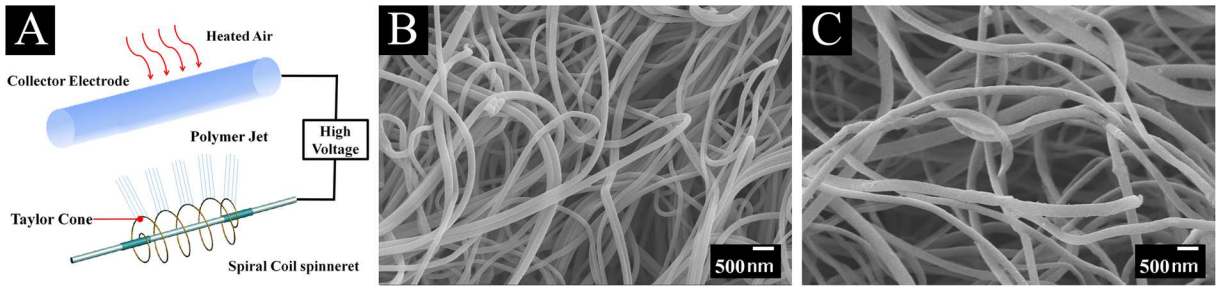

Figure 1. (A) Schematic of the nozzle-free electrospinning process. The coil spinneret is partially immersed in a bath (not shown). SEM images of electrospun nanofibers were obtained from solutions of (B) $Mn(CH_3COO)_2$/PVP, and (C) $Mn(CH_3COO)_2$/MWCNT/PVP.

The goal of this study was to demonstrate nozzle-free electrospinning as a scalable method for manufacturing supercapacitor electrodes. Proof-of-concept experiments targeted the formation of MnO_2 and MnO_2-multiwall CNT (MWCNT) nanofibers. The MnO_2-based nanofibers obtained had small diameters and relatively uniform diameter distribution, which permitted the fabrication of electrodes with good capacitive behavior at high active mass loading and high charge−discharge rates. When producing MnO_2-MWCNT nanofibers by the electrospinning method, MWCNTs are stabilized in the polymer solution used, thus alleviating MWCNT dispersion issues.[10] This work demonstrates that MnO_2-MWCNT nanofibers can be used to fabricate efficient supercapacitor devices with a voltage window of 1.8 V and excellent electrochemical performance.

Figure 1A depicts schematically the nozzle-free electrospinning process. The coil spinneret is immersed partially into a bath, containing a solution of polymer and salt, and rotates at a controlled rate. Numerous Taylor cones form on the coil surface, ejecting multiple nanofibers simultaneously. Compared to the conventional electrospun nanofibers (10−100 mg/h),[19] nozzle-free electrospinning yields high production rates of 435 and 352 mg/h, respectively, for $Mn(CH_3COO)_2$/PVP and $Mn(CH_3COO)_2$/MWCNT/PVP nanofibers (PVP = polyvinylpyrrolidone). SEM images show that the electrospun $Mn(CH_3COO)_2$/PVP nanofibers have a uniform distribution (Figure 1B). $Mn(CH_3COO)_2$/PVP nanofibers have an average diameter of 187 ± 25 nm, which is much smaller compared to pure PVP nanofibers (Figure S2). The changes in the conductivity and viscosity are attributed to variations in fiber diameter. Furthermore, individual MWCNTs were not discernible for PVP/CNT and $Mn(CH_3COO)_2$/MWCNT/PVP composites (Figure 1C). This suggests that the MWCNTs are embedded in the fiber composites. The lack of sediment suggests that the dispersion of MWCNT is considerably improved in the presence of PVP. Without PVP, the suspension is not stable: a black sediment is seen to form immediately after ultrasonication. The improved dispersion emanates likely from PVP wrapping around the nanotubes.[20] Good dispersion of MWCNTs is imperative for their successful incorporation into composites by the electrospinning method.

The microstructure of MnO_2 nanofibers after calcinations, shown in Figure 2A, reveals fibers with relatively uniform diameter < 200 nm. Although the nanofiber aspect ratio changes after heat treatment, the fibers themselves do not agglomerate. Adding carbon nanotubes to form the MnO_2-MWCNT nanofibers produces thicker fibers with exposed MWCNTs (Figure 2B); the fiber diameter increases to 347 ± 116 nm. The crystallinity of these fibers was assessed by XRD.

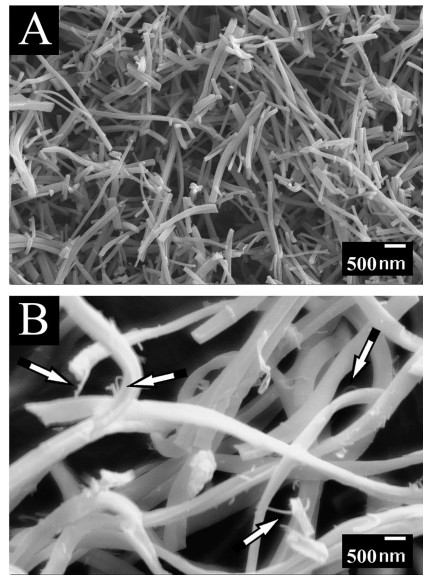

Figure 2. SEM images of (A) MnO_2 and (B) MnO_2-MWCNT nanofibers after calcination. The arrows point to MWCNT.

A strong diffraction peak at 23.7° was attributed to the (002) plane of hexagonal graphite structure of pristine MWCNT (Figure 3a). XRD patterns of the MnO_2 nanofiber showed well-resolved peaks corresponding to JCPDS File No. 05-0673 (Figure 3b). The composite nanofibers were found to have additional peaks originating in MWCNT (Figure 3c). Compared to traditional MnO_2 synthesis methods, such as chemical precipitation,[21] hydrothermal growth,[6,22] or sol−gel method,[23] the nozzle-free electrospinning process offers advantages of high production rates and fine morphologies.

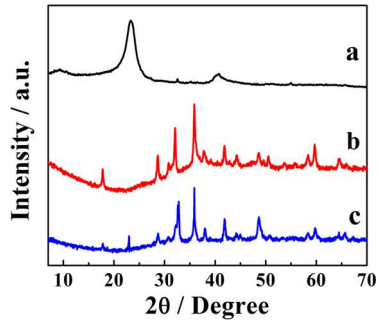

Figure 3. XRD results of (a) pristine MWCNT, (b) MnO_2 nanofibers, and (c) MnO_2-MWCNT composite nanofibers.

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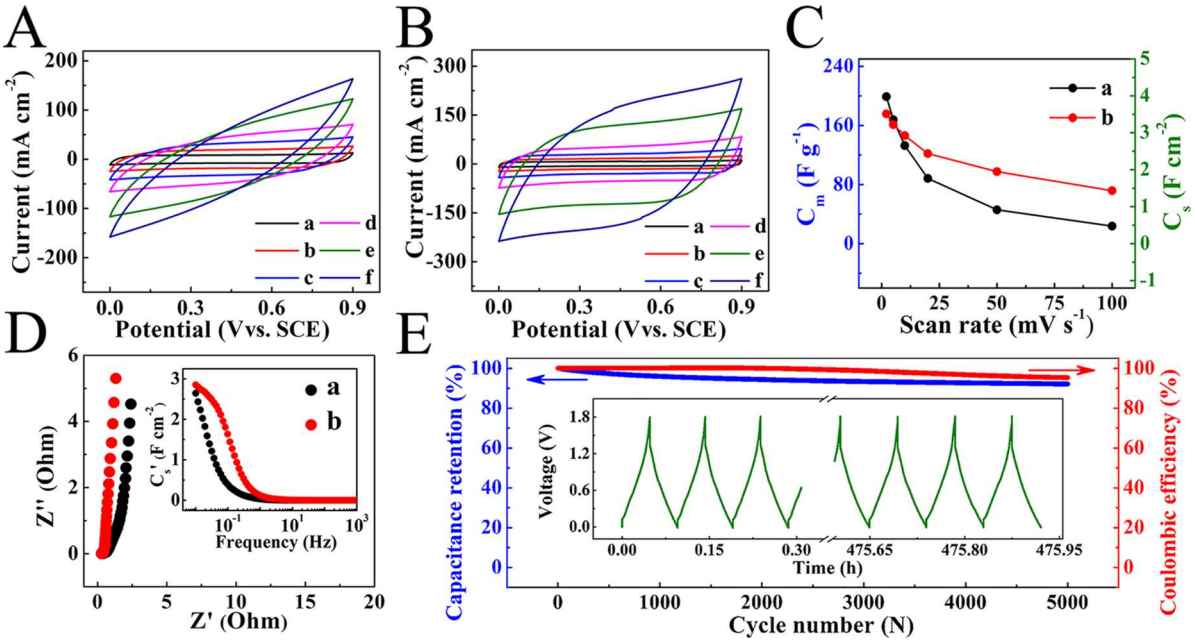

Figure 4. CV curves for (A) MnO_2 and (B) MnO_2-MWCNT nanofibers tested in three-electrode cells at scan rates of (a) 2, (b) 5, (c) 10, (d) 20, (e) 50, and (f) 100 mV s^{-1}. (C) C_m and C_s calculated from CVs versus scan rate and (D) Nyquist plots of complex impedance (the inset shows the C_s' calculated from the impedance data) for (a) MnO_2 and (b) MnO_2-MWCNT nanofibers. (E) Capacitance retention and Coulombic efficiency versus cycle for coin-cell (MnO_2-MWCNT nanofibers+//activated carbon−) based on MnO_2-MWCNT nanofibers. Inset in panel E shows the initial and final charge−discharge curves at a current density of 20 mA cm^{-2}.

The MnO_2 and MnO_2-MWCNT nanofibers were used for fabrication of electrodes for supercapacitor tests. Electrodes with mass loading of 20 mg cm^{-2} were prepared by impregnation of Ni foam using a suspension of active materials in ethanol, containing 5 wt % polyvinyl butyral (PVB) binder. Panels A and B of Figure 4 compare the CV of three-electrode tests for MnO_2 and MnO_2-MWCNT nanofibers. These electrodes exhibited nearly rectangular shaped CV with the magnitude of current being proportional to scan rate, indicating good capacitive behavior. The MnO_2-MWCNT nanofibers allowed further improvement in capacitance retention at high scan rates. The C_s calculated from CV at a scan rate of 2 mV s^{-1} was 3.91 and 3.51 F cm^{-2} for MnO_2 and MnO_2-MWCNT nanofibers, respectively (Figure 4C). At a scan rate of 100 mV s^{-1}, the C_s of MnO_2 nanofibers was 0.48 F cm^{-2} (24 F g^{-1}), while the value for MnO_2-MWCNT nanofibers was 1.43 F cm^{-2} (72 F g^{-1}). It is known that MWCNT has relatively low SC (~20 F g^{-1}).[24,25] Therefore, the contribution of MWCNT to the capacitance of the composite electrode should be relatively small. The C_s of MnO_2 and MnO_2-MWCNT nanofiber electrodes, prepared by nozzle-free electrospinning, was significantly higher compared to data reported in the literature.[26,27] The EIS measurements (Figure 4D) show that the MnO_2 nanofibers have a larger electrode resistance Z' compared to the MnO_2-MWCNT nanofibers. C' values, calculated from the impedance data (Figure 4D inset), indicate improved capacitance retention with increasing frequency for MnO_2-MWCNT versus MnO_2 electrodes. The relaxation frequency corresponding to the maximum of C'' shifted from 16 mHz for MnO_2 nanofibers to 115 mHz for MnO_2-MWCNT nanofibers. The C'' measurements reveal improved rate capability for MnO_2-MWCNT versus MnO_2 nanofibers.

The advantage of nanofibers for fabrication of efficient supercapacitors is well-known. However, increased material loading is needed for achieving high C_s, which leads to increased resistance and reduced electrolyte access to the bulk of the active material.[27] Limited electrolyte access causes poor capacitive performance. Increasing the material loading reduces the C_s value.[28] Our results show that MnO_2-based nanofibers, produced by nozzle-free electrospinning, permit the fabrication of electrodes with high C_s and good capacitance retention at high material loading. Furthermore, the MnO_2-MWCNT electrode shows good cycling stability with 97.5% capacitance retention after 1000 cycles (Supporting Information Figure S5). The CV shape, electrochemical impedance, and alternating current (AC) capacitance remained practically unchanged during cycling.

The MnO_2-MWCNT electrodes were combined with activated carbon negative electrodes for the fabrication of coin-cell devices (Figure S6). The galvanostatic charge−discharge tests were performed in a voltage window of 1.8 V (Figure S7). The high voltage window of the Na_2SO_4 electrolyte is attributed to an overpotential related to the hydrogen sorption mechanism at the negative electrode. The symmetric shape of the curves indicates good capacitive performance of the cell. Figure 4E shows the cyclic behavior of the coin cells and corresponding charge−discharge curves, which exhibit a similar triangular shape in the beginning and end of cycling. The capacitance retention and Coulombic efficiency were 92.1 and 95.3% after 5000 cycles, respectively. The test results indicate that the supercapacitor devices produced by nozzle-free electrospinning are promising for practical applications.

CONCLUSIONS

Nozzle-free electrospinning was performed for the manufacture of MnO_2-based nanofibers. After heat treatment, the nanofibers showed relatively uniform distribution, with an average diameter of 205 ± 42 and 347 ± 116 nm for MnO_2 and MnO_2-MWCNT, respectively. The heat-treated fibers were

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ACS Appl. Energy Mater. 2018, 1, 296−300

incorporated into supercapacitor electrodes, which registered a capacitance of 1.43 F cm^{-2} at a scan rate of 100 mV s^{-1} based on three-electrode tests. The nanofiber production method developed in this investigation offers promise for large-scale manufacturing of supercapacitors.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsaem.7b00227.

Experimental details, electrospinning setup, sedimentation tests, and additional morphological and electrochemical characterization (PDF)

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Notes

The authors declare no competing financial interest.

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