Bio-nanotextured high aspect ratio micropillar arrays for high surface area energy storage devices

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Abstract. This paper presents fabrication and characterization of bio-nanotextured hierarchical nickel oxide (NiO) supercapacitor electrodes. The hierarchical electrode structure is created through self-assembly of Tobacco mosaic viruses (TMVs) on high aspect-ratio micropillar arrays. Enhanced assembly of the bio-nanoparticles was achieved by increasing TMV solution accessibility into the deep microcavities of the pillar arrays. Electrochemical characterization of the hierarchical NiO supercapacitor electrodes revealed a 25-fold increase in charge capacity compared to a planar NiO, and demonstrated excellent cycle stability over 1500 charge/discharge cycles at 2 mA/cm². This study leverages the unique bio-nanoscaffolds for small scale energy storage devices through further optimization of the hierarchical structures and wetting techniques for significant improvements in micro/nano scale energy storage devices.

1. Introduction
Micro- and nanoscale materials have received significant attention for developing electrical energy storage devices such as Lithium-ion batteries, fuel cells, and supercapacitors. The unique advantages of using materials exhibiting these length-scales comes from their ability to facilitate fast electron/ion transfer kinetics with densely packed high surface-area-to-volume structures, which enable high energy and power density performances through efficient use of energy storage materials [1].

TMV is a biological nanomaterial characterized by its high aspect-ratio structure. Previously, TMVs have been genetically modified to express cysteine residues on their outer most surface to enhance self-assembly and metal binding properties [2]. Subsequent TMV metallization and integration with thin film deposition techniques (atomic layer deposition, sputtering, etc.) enables the demonstration of bio-scaffolds for various energy storage devices [3,4]. The robust metallized TMVs coated with thin film energy storage materials yield a core (metal)/shell (active material) nanoelectrode structure ensuring continuous electrical connectivity between the two electrode components while maintaining the scaffold's nanoscale structure.

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To further increase the electrode surface area, the TMV nanoscaffolds were integrated with gold micropillar arrays to create hierarchical structures. This is one of the most effective ways to create high surface area electrodes, taking advantage of building blocks with different length-scales [5]. However, TMV self-assembly suffers from limitations on high surface area microstructures, showing reduced bio-nanoparticle surface coverage on the vertical and bottom surfaces of high AR geometries [6]. In this work, critical geometric parameters of the microstructures that govern the virus assembly morphology were characterized, thus enabling the use of optimized bio-templated hierarchical architectures. Electrochemical performance of the final hierarchical electrodes was evaluated as NiO supercapacitor electrodes.

2. Methods

2.1. Design and fabrication of micropillar array electrodes

A set of four different micropillar array electrodes was fabricated to study the spacing AR (SAR) dependence of the TMV self-assembly process. As illustrated in figure 1a, a silicon substrate is patterned with an image reversal photoresist (AZ-5214), and etched using deep-reactive-ion-etching (DRIE). The etched wafer was diced into electrodes with dimension of $1 \times 1.7 \text{ cm}^2$ ($1 \times 1 \text{ cm}^2$ pillar array area), and both sides of the electrode were passivated with PECVD Si$_3$N$_4$ (500 nm at 300 $^\circ$C) followed by sputter deposition of Ti (30 nm)/Au (120 nm). All pillars were 70 µm tall and 7 µm in diameter (10:1 AR) (figure 1b), but the spacing between the pillars was varied from 7 to 21 µm corresponding to a SAR of 10:1 to 3.3:1 (figure 1c).

Figure 1. Schematics of micropillar array electrodes structures and fabrication process flow. (a) Fabrication process of micropillar array electrodes. (b) Cross-sectional view of the pillar array. All pillars were 10:1 AR while the SAR varied from 10:1 to 3.3:1, and (c) schematic of the four electrodes with different SAR for varied solution accessibilities.

2.2. TMV nanotexturing on high AR geometries

Three different approaches were tested for nanotexturing the micropillar array electrodes – (1) typical, previously published TMV self-assembly and metallization protocol [5], (2) pre-treatment of the electrodes using isopropyl alcohol (IPA), and (3) ultrasonication after the immersion of the electrode into TMV solution. The typical process involves overnight self-assembly of TMVs after immersion of Au-coated electrode into 0.2 mg/ml TMV solution in 0.1 M phosphate buffer (pH 7). Subsequently, an electroless Ni metallization process follows initial Pd surface activation. For the IPA treatment, the micropillar array electrodes were rinsed and immersed in IPA for 5 minutes followed by the typical
TMV self-assembly and metallization. For ultrasonication, the electrodes were immersed in TMV solution and placed in an ultrasonic bath for 5 minutes prior to overnight self-assembly and metallization. The IPA treatment was expected to increase hydrophilicity of surfaces with hydroxyl groups, which can lead to enhanced wettability of the array structure. The ultrasonication is intended to facilitate TMV diffusion into the microcavities between pillars by agitating the virus solution within the array structure.

2.3. Electrochemical characterization

The enhanced energy storage performance of the bio-nanotextured hierarchical structures was characterized using a NiO supercapacitor system. The NiO supercapacitor electrodes were prepared by annealing Ni-coated hierarchical electrodes at 300 °C for two hours in a box furnace (details of the NiO electrode preparation and characterization have been published elsewhere [7]). The electrodes were characterized using galvanostatic (2 mA/cm²) charge/discharge cycles in 2 M KOH aqueous electrolyte in a three-electrode electrochemical cell (working: hierarchical NiO, counter: Pt foil, reference: Ag/AgCl).

3. Results and analysis

3.1. TMV coverage on high AR micropillar arrays

The cross-section scanning electron microscope (SEM) images in figure 2 show results from the typical TMV self-assembly and Ni metallization process on the micropillar array electrodes. As clearly shown in the images (figure 2a-d), uniform nanotexturing of the vertical sidewalls is observed on the pillars located at the edge of all four electrodes. However, on the pillars located in the center of the electrode, a gradual reduction of virus surface coverage towards the bottom of the pillars is observed as the SAR decreases (figure 2e-g). Uniform TMV assembly was only achieved only on pillar arrays with 3.3:1 SAR (figure 2h). This, combined with the TMV assembly profile from the edge towards the center of the pillar arrays (figure 3, 7:1 SAR), is evidence that the reduced TMV assembly density can likely be attributed to the surface tension of the TMV solution on the structurally hydrophobic pillar.
arrays, thereby reducing surface wettability at the base of the pillar arrays that are located in the center of the electrode.

**Figure 3.** Cross-sectional SEM image taken from the edge of the center-cleaved electrode (7:1 SAR) after typical TMV self-assembly and Ni metallization protocol.

The cross-sectional SEM images shown in figure 4 are from pillar arrays (7:1 SAR) located at the center of electrodes treated with ultrasonication (figure 4a) and IPA (figure 4b,c,d). When compared with figure 2f for the same SAR, an obvious improvement of the virus coating is observed from both methods. A homogeneous TMV coating is achieved at the bottom of pillar sidewalls, while TMV was hardly observed in figure 2f. Low uniformity along the pillar sidewalls, showing less TMV at the bottom (figure 4c) compared to more complex clusters toward the top (figure 4d) – especially for the case of IPA treatment – shows the need for further study and improvements. For the electrochemical characterization experiments, IPA treatment method was selected due to localized breakdown of the micropillars during the ultrasonication.

**Figure 4.** Cross-section SEM images taken from the center area of 7:1 SAR electrodes after the TMV and Ni coating process using (a) ultrasonication and (b) IPA treatment. The angled SEM images taken from the (c) top and (d) bottom of the electrodes treated with IPA.

### 3.2. Electrochemical performance of the hierarchical electrodes

Electrochemical characterization results of the hierarchical NiO electrodes are shown in figure 5. Based on the results above, micropillar array electrodes with 5:1 SAR were used to ensure a highly uniform coverage of the microstructures with TMV, and to be able to characterize the surface area enhancement factor from the microstructures under that assumption. Figure 5a shows the areal capacitance of the hierarchical NiO electrodes measured from 1500 galvanostatic (2 mA/cm²) charge/discharge cycles. This shows excellent cycle stability with coulombic efficiency remaining above 99 % for the entire cycle duration. When comparing the areal capacitance between the hierarchical and planar NiO electrodes, a significant improvement from 18mF/cm² to 450mF/cm² is achieved. The 25-fold increase in areal capacitance is accompanied by highly stable NiO charge/discharge characteristics up to at least the 1500th cycle (figure 5b). Considering the calculated 3.5 surface area enhancement factor from the micropillar array, the remaining factor of 7 due to
nanotexturing alone compares favourably with previously reported enhancement factors on flat surfaces in the range of 7–9.

![Figure 5](image-url)  
**Figure 5.** Electrochemical characterization of hierarchical NiO electrode. (a) Areal capacitance and coulombic efficiency for 1500 galvanostatic charge/discharge cycles at 2 mA/cm². (b) Stable galvanostatic charge/discharge plot of last 10 cycles.

4. **Summary**

This work studies the essential parameters of micropillar array geometries which govern the TMV nanotexturing quality over high surface area microstructures. It was found that there is a trade-off between SAR of micropillar arrays vs uniform TMV coating. This is attributed to structural hydrophobicity of densely packed micropillar arrays resulting in limited wetting of TMV solution into deep microcavities. IPA treatment for enhanced wettability resulted in increased surface coverage of TMVs on the high SAR array structures. However, uniformity of the coverage along the pillar sidewalls still requires further optimization and improvement. The electrochemical characterization results suggest a great advantage of this unique bio-nanoscaffolds for small scale energy storage devices with significant improvements in energy storage performance.

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