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Biofabrication of Tobacco mosaic virus-nanoscaffolded supercapacitors via temporal capillary microfluidics

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Abstract

This paper reports the implementation of temporal capillary microfluidic patterns and biological nanoscaffolds in autonomous microfabrication of nanostructured symmetric electrochemical supercapacitors. A photoresist layer was first patterned on the substrate, forming a capillary microfluidics layer with two separated interdigitated microchannels. Tobacco mosaic virus (TMV) macromolecules suspended in solution are autonomously delivered into the microfluidics, and form a dense bio-nanoscaffolds layer within an hour. This TMV layer is utilized in the electroless plating and thermal oxidation for creating nanostructured NiO supercapacitor. The galvanostatic charge/discharge cycle showed a 3.6-fold increase in areal capacitance for the nanostructured electrode compared to planar structures. The rapid creation of nanostructure-textured microdevices with only simple photolithography and bionanostructure self-assembly can completely eliminate the needs for sophisticated synthesis or deposition processes. This method will contribute to rapid prototyping of wide range of nano-/micro-devices with enhanced performance.

Keywords: nanoscaffolds, capillary microfluidics, supercapacitors, self-assembly, nanostructures

(Some figures may appear in colour only in the online journal)

1. Introduction

Batteries and supercapacitors are among the predominately-explored energy storage devices for their high efficiency in preserving energy from intermittent sources [1]. Electrochemical redox supercapacitors usually utilize nanostructured electrodes in faradaic electrochemical redox reactions to preserve electrical energy. These supercapacitors show the advantages of high power and energy densities over batteries and conventional dielectric capacitors, respectively [2–6]. Owing to high surface area and porosity, nanostructures and nanomaterials have been utilized in supercapacitor electrodes

design and fabrication to improve energy storage performance [7]. They offer significant advantages compared to their bulk counterparts such as enhanced mechanical stability, faster ion/electron transfer kinetics, and higher surface area density. These properties make them ideal candidates to be used as electrode materials for redox-based supercapacitors to achieve higher energy density and higher power capability. Many researchers have explored one-dimensional nanostructures (nanotubes, nanofibers, or nanowires) in creation of high surface area electrodes [7, 8]. Apart from improvement in the material, alternative means to achieve similar capacitance increase are to create more sophisticated microstructured

electrodes [9–12]. These methods usually require complex fabrication or synthesis of micro/nano structures on the device, necessitating sophisticated processes to create these high surface area structures. Besides, it is usually critical to perform chemical surface treatment on both device surfaces and nanomaterials in order to create bonds.

The recent advances in bioengineering have provided alternative ways to directly utilize the nanostructures from nature and create nanostructured energy devices in a rapid and autonomous fashion. Biological molecules such as proteins, DNAs and viruses have well-defined biological nanostructures whose functionalities can be mutated through genetic modifications. These mutated biological molecules preserve the inherent nanostructures with extremely high surface to volume ratio while exhibiting tailored surface attachments. One such example is Tobacco mosaic virus (TMV), a cylindrical plant virus measuring 300 nm in length and 18 nm in outer diameter—a highly favorable 1D nanorod structure with high surface to volume ratio. TMV contains 2130 copies of densely arranged identical coat proteins (CPs) with controllable biological affinity to a variety of materials. Recent development in genetic engineering on these TMV protein structures and affinities has enabled the integration of TMV and its virus-like particle mutant as functional materials in microdevices [13–17]. In order to facilitate surface attachment of the TMV molecules on inorganic device surface, TMVs have been genetically modified to let the TMV CPs express cysteine residues for enhanced gold binding affinity. These TMV mutants (TMV1cys) possess the ability to self-assemble onto gold surfaces through thiol-gold interaction. When using these self-assembled TMV1cys particles in supercapacitors, they can serve as nanoscaffolds inner core for creating conductive Ni outer shell through electroless plating while preserving the 1D nanorod structure. This TMV-based fabrication process has been demonstrated as a promising method for high energy density microbatteries and supercapacitors [18, 19]. Currently, the further implements of these TMVs in nanostructured device fabrication are limited by the long TMV assembly time (3–18 h), low utilization efficiency of virus samples, and difficulty in localization. These limitations prevent the use of the TMVs in rapid prototyping of nanostructured energy devices, lower the nanostructure density on electrodes, and compromise the device performance.

This work presents a capillary microfluidics-based fabrication method for rapid creation of nanostructured symmetric supercapacitor on-chip using TMV bio-nanoscaffolds. The method significantly improves the recently reported work [20] using capillary microfluidics in single electrode fabrication in the aspects of comprehensive electrode morphology study, simultaneous anode and cathode patterning, and characterization of symmetric TMV/NiO supercapacitors. This device fabrication method combines self-assembly of TMV bio-nanoscaffolds with Ni electroless plating on an interdigitated capillary microfluidic pattern created by photolithography. The integration of capillary microfluidics in the fabrication process allows for autonomous sample delivery by capillary forces as well as the self-assembly of TMVs, enabling rapid coating of TMV nanoscaffolds in specific areas through room-temperature evaporation with improved utilization efficiency of the TMV samples. Compared

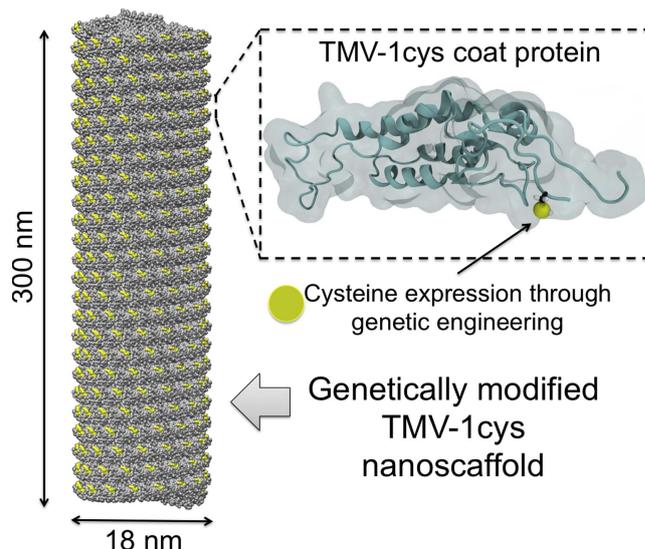


Figure 1. Schematics of the genetically modified TMV1cys bionanoscaffold nanorod, and the enlarged view of its CP structures.

to existing strategies for creating TMV-based energy storage devices, this method enables rapid TMV patterning on the functional device surface, reduces the TMV assembly time from 18 h to less than 1 h, and utilizes 20-fold less amount of TMVs. Using the proposed method, both TMV structured supercapacitor anode and cathode can be fabricated simultaneously in a one-step photolithography process. Cyclic voltammetry and galvanostatic charge/discharge cycle performed on the TMV-nanoscaffolded Ni/NiO supercapacitor have validated the significant electrochemical performance enhancement compared to the planar counterpart. This enhancement is due to the surface area increase through the TMV integration.

2. Methods

2.1. Genetically modified TMV nanoscaffolds

In this work, nanostructured biological molecules—TMVs—are utilized as bionanoscaffolds for creating nanostructured charge storage electrodes. Here, a TMV mutant is genetically engineered to enable self-assembly on gold surfaces and Ni electroless coating.

Figure 1 shows the schematic of a TMV particle genetically modified with cysteine residues on its CPs (TMV1cys). The genetic modification enables the expression of a cysteine residue on the N-terminal end of each identical CP of the TMV. The detailed genetic engineering method for creating TMV1cys has been reported previously [21]. The cysteine carries a thiol (–SH) group that is well known for its high affinity to gold. The exploded view of the single CP model reveals that, due to the spatial location of the relatively small cysteine residue on the N-terminus of the protein, the cysteines on CPs at the ends of each TMV are more exposed to facilitate covalent bindings on the gold surface. This special cysteine expression and spatial location enables the self-assembly of TMV nanorod on gold surface, significantly increasing the area

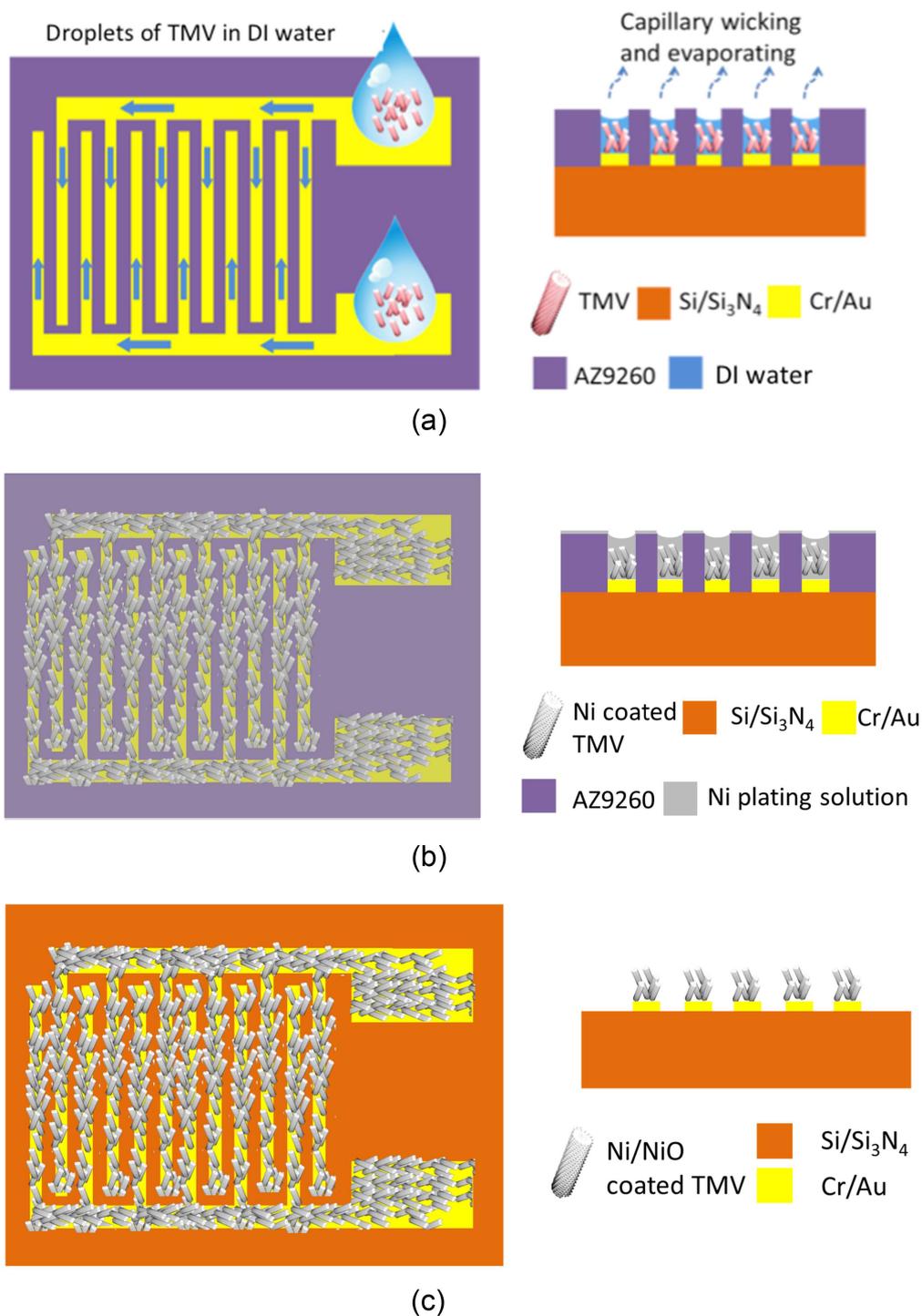


Figure 2. Fabrication process flow of TMV nanostructured electrodes through evaporation-assisted TMV assembly in capillary microfluidics, electroless Ni plating, and thermal oxidation. (a) Delivery and evaporation of TMVs in temporary open capillary microfluidic channels defined by patterned photoresist. (b) Ni electroless deposition on the TMV functionalized capillary microfluidic channels. (c) Stripping off the temporary photoresist capillary microfluidic channel, forming patterned Ni-coated TMV nanostructures; NiO annealed at 300 °C.

on top of the planar surface. The self-assembly process can be achieved by suspending TMV1cys particles in 0.1 M sodium phosphate buffer (pH = 7) and completely immersing the device surface in the TMV-containing buffer at room temperature. Previous studies have demonstrated that the TMVs can self-assemble into a dense nanostructured layer on the surface in an 18 h process [18, 22, 23].

2.2. Capillary microfluidics-based TMV-nanoscaffolded supercapacitor fabrication method

Microfluidics, especially capillary microfluidics with open-channels, have been demonstrated as a suitable platform for rapid nanostructure assembly and biological molecule manipulation in microdevices [15, 24]. The fabrication of the proposed

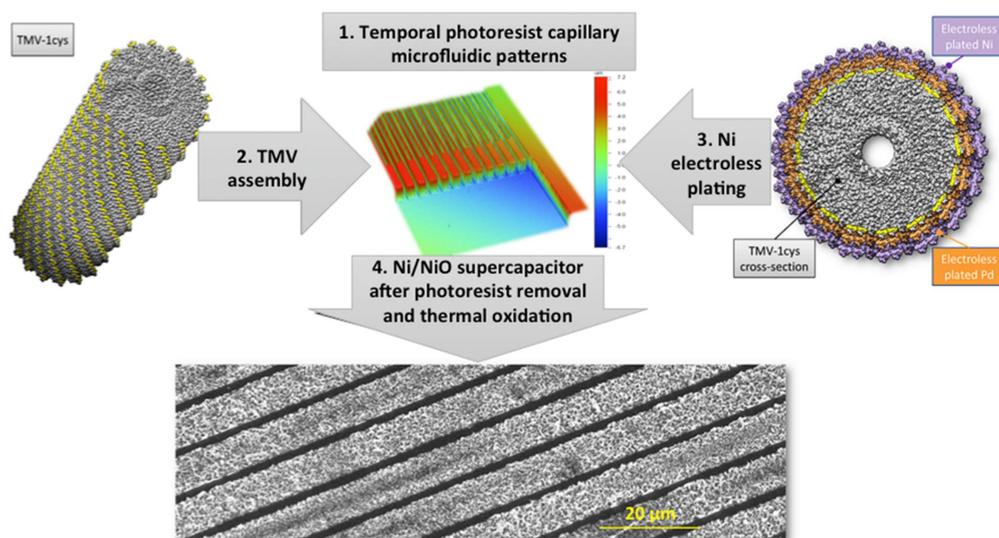


Figure 3. Optical profilometry and scanning electron microscopy (SEM) images showing the TMV nanostructured electrode fabricated through coating of TMVs in photoresist capillary microchannels.

supercapacitor electrodes utilizes a similar capillary microfluidics-assisted process to rapidly pattern nanostructures on a large electrode area with high precision. We have previously demonstrated the use of capillary microfluidics nanoreceptor assembly in a biosensor [25]. In this previous work, one limitation is that the microfluidics needs to be fixed permanently on the sensor, occupying part of the useful device area. Also, the achieved nanostructure is limited to a flat arrangement of nanorods as a monolayer. Here, we are aiming at creating a microscale energy storage device with bulk nanostructured electrodes.

The microfabrication process flow to create a TMV-nanostructured electrode using temporary open capillary microfluidic patterns is demonstrated in figure 2. TMV coating and nickel electroless plating on the same substrate after a one-mask photolithography process formed the symmetric supercapacitor electrode configuration. Before performing capillary-based TMV coating, the photoresist AZ9260 was first patterned with an interdigitated microelectrode (IDME) pair through a photolithography process. With one minute of O_2 plasma treatment, the photoresist pattern displayed hydrophilic characteristic, which can autonomously draw the TMV suspension into the capillary channels.

One-step photolithography was first performed using AZ9260 photoresist to create microstructured trenches with $7\ \mu\text{m}$ in depth and $4\text{--}8\ \mu\text{m}$ in width on Si_3N_4 substrate. Cr/Au layers (20 nm/1800 nm) were then coated on the resist-patterned substrate to form electrical contacts. The Si_3N_4 underneath the Cr/Au layer provides electrical isolation between the two electrodes, and is also able to sustain KOH electrolyte during the subsequent electrochemical testing. The surface was rendered hydrophilic by exposing the surface to O_2 plasma at 50 W for 45 s at 0.5 mTorr. With the enhanced hydrophilicity, the gaps between photoresist strips then served as the open capillary microfluidic channels. TMV nanoscaffolds suspended in deionized water were autonomously delivered on the microfluidic channel patterns from one end of the electrode over the whole active electrode

surface due to capillary effects (figure 2(a)). The capillary microfluidic layer has its top surface exposed to the air, allowing for the rapid evaporation of TMV solution and accelerating TMV assembly on electrodes. The TMV nanoscaffolds were attached on the active electrode area and concentrated in the capillary microfluidic channels after one hour of water evaporation at room temperature. The electrode surface was then metallized through electroless plating of Ni, creating Ni-coated TMV-nanostructured electrode (figure 2(b)). The successive photoresist stripping in acetone removed the temporary capillary microfluidic channels. The NiO layer was formed on the nanostructured Ni surface in a furnace at $300\ ^\circ\text{C}$ over 2 h (figure 2(c)), which has been proven as an effective way to create oxidized outer shells on TMVs [26].

This aforementioned fabrication method aims at creating nanostructured symmetric supercapacitors on-chip in a simplified and accelerated fashion. The integration of TMV nanoscaffolds leverages the high aspect ratio characteristic and the self-assembly capability of genetically modified TMV, which contributes to a significant improvement in areal capacitance compared to bare flat electrodes.

The fabrication method combines nanostructured TMVs and electroless Ni plating on a temporary photoresist capillary microfluidic platform to autonomously create metallized TMV nanostructures on the IDME pair. Such integration significantly increases the electrode surface area that contributes to higher supercapacitor areal capacitance. The optical and scanning electron microscopy (SEM) images in figure 3 show the morphology of the TMV nanostructured IDMEs, where Ni/NiO coated TMV nanostructures are first patterned to form the supercapacitor IDME with the electrode width and spacing of $4\ \mu\text{m}$, and an overall footprint of $4\ \text{mm}^2$. The active IDMEs are connected to Cr/Au contact pads. As shown in the SEM image in figure 3, the thin film Ni/NiO coating on the TMVs preserves the intrinsic rod-like bio-nanostructures of the TMV nanoscaffolds, increasing the

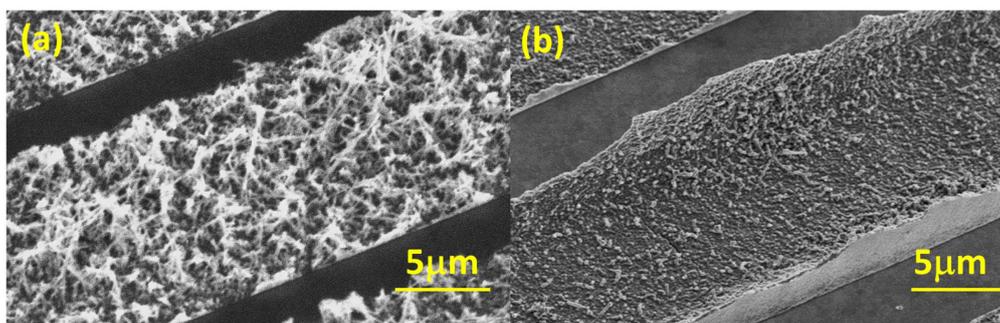


Figure 4. SEM images showing TMV nanoscaffolded Ni/NiO electrodes fabricated by evaporation of (a) 0.2 mg ml^{-1} and (b) 2 mg ml^{-1} of TMVs in capillary microfluidic channels [21].

active supercapacitor electrode surface area compared to a planar electrode.

2.3. Electrochemical test equipment and setup

The electrochemical performance of the fabricated Ni/NiO nanoscaffolded supercapacitor electrodes was tested in both cyclic voltammetry and galvanostatic charge/discharge cycling. For single electrode characterization, a three-electrode setup was utilized, composed of the fabricated TMV Ni/NiO working electrodes, a commercial Ag/AgCl reference electrode (1 M KCl), and a Pt-foil (2 cm^2) as a counter electrode. Galvanostatic charge/discharge cycling was performed under constant current density of $500 \mu\text{A cm}^{-2}$. In the characterization of the symmetric TMV Ni/NiO supercapacitor performance, both cyclic voltammetry and galvanostatic charge/discharge were performed at a range of scan rates and current densities, respectively. All the electrochemical tests used 2 M KOH solution as electrolyte, and were performed with a VSP-300 potentiostat (Bio-Logic Science Instruments SAS, France).

3. Results and discussions

TMV Ni/NiO supercapacitor electrode surface was studied using SEM to understand the influence of capillary forces on the morphology of the nanostructured electrode. This provided guidance for creating highly porous and high surface area electrode with uniformly coated nanostructures. The charge storage performance of the symmetric TMV Ni/NiO supercapacitor was characterized using electrochemical methods introduced above.

3.1. TMV-coated single electrode and concentration dependency

The metallized TMV-nanoscaffolded electrode patterns fabricated in the capillary microfluidics are shown in figure 4. Figure 4(a) is the SEM image showing the morphology TMV Ni/NiO electrode fabricated using 0.2 mg ml^{-1} TMV in $50 \mu\text{l}$ of DI water. Delivered automatically by capillary force and evaporated at room temperature, the TMV-containing solution

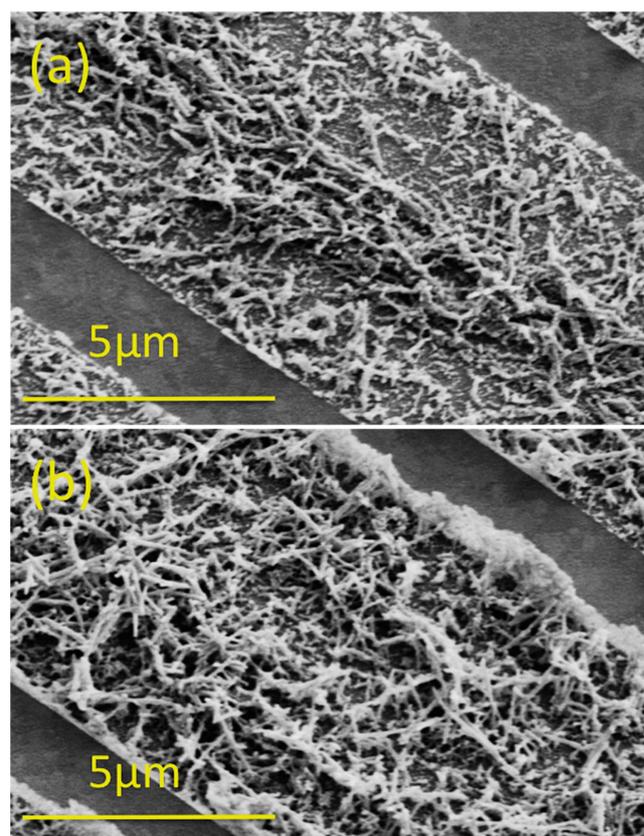


Figure 5. SEM images showing the TMV distribution (a) close to the inlet of the channel, and (b) in the center of the microfluidic channel.

coated the gold electrode surface with highly porous TMV structures. However, as the TMV concentration was further increased to 2 mg ml^{-1} , the TMV nanorods were closely stacked after evaporation, forming a thick film with reduced porosity after metallization (figure 4(b)). The reduction in porosity devalues the use of nanostructures, and will eventually lead to lower areal capacitance. Therefore, to make the supercapacitor electrode to show high surface area, the TMV suspension with the concentration of 0.2 mg ml^{-1} is adopted to create porous TMV Ni/NiO electrode in the following electrochemical tests.

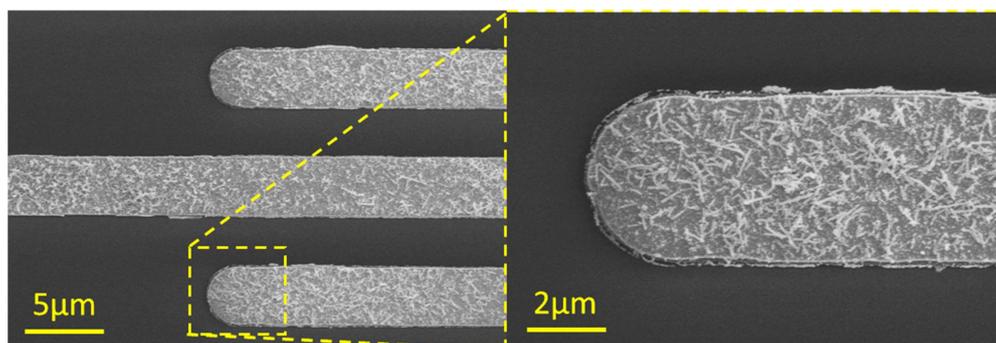


Figure 6. SEM images showing the planar symmetric NiO supercapacitor fabricated in the photoresist capillary microfluidic channel. The minimum electrode feature size is $4\ \mu\text{m}$.

3.2. TMV distribution in the microfluidic channel

1 cm long temporary photoresist microfluidic channels were utilized to study the distribution of TMVs across the channel. Figure 5(a) shows the TMV distribution close to the inlet of the channel where the velocity in the center of the channel is very large ($>1\ \text{mm s}^{-1}$ for liquid meniscus moving). As a result, the TMV rods accumulate in the center of the channel and form an orientation along the channel. Figure 5(b) shows the TMV distribution near the end of the channel where the flow velocity is very low. In this case, the capillary forces on the sidewalls of the channel are more dominant than inertial forces, pulling more TMVs to the side of the channel as the liquid evaporates. This resulted in higher density TMVs on the two sides of the channel.

Both the above circumstances were resulted from the unbalanced capillary forces and inertial forces across the long capillary microfluidic channel. In order to create more uniform and high-density TMV coating, shorter and smaller channels ($2\ \text{mm}$ in length, $4\ \mu\text{m}$ in width and $7\ \mu\text{m}$ in depth) were utilized in creating symmetric Ni/NiO supercapacitors aiming at more balanced force distributions in the channel and high quality TMV coating.

3.3. TMV-nanoscaffolded symmetric supercapacitor electrodes

Figure 6 shows the SEM images of the TMV nanoscaffolded Ni/NiO symmetric supercapacitor full device fabricated using the capillary microfluidics-assisted method. Because two isolated comb-shape trenches form the IDME photoresist pattern, there were isolated capillary microfluidic channels created in one photolithography process. Thus, the two independent microfluidic channels can be used to create TMV-template symmetric NiO supercapacitor. Figure 6 shows that the interdigitated NiO supercapacitor electrodes have very clear edges after stripping of photoresist and oxidation of Ni. Due to the shorter and smaller microfluidic channels, the distribution of TMV in the channel is much more uniform than what was demonstrated in section 3.2 with long channels. The accumulation of TMVs in the center or edge is not clearly observed in this case.

3.4. Electrochemical characterization in a three-electrode setup

The electrochemical performance of the NiO supercapacitor electrodes was first characterized in a three-electrode system. The energy storage performance of the nanostructured NiO electrodes was examined by comparing with planar NiO electrodes. A comparison of galvanostatic discharge plots between the two electrodes is shown in figure 7(a). The nanostructured NiO electrode exhibits a 3.6-fold increase in areal capacitance ($59\ \text{mF cm}^{-2}$) versus the planar one ($16\ \text{mF cm}^{-2}$) at $0.5\ \text{mA cm}^{-2}$, which is a significant enhancement in performance from the simplistic fabrication method. The nanostructured NiO electrodes fabricated via evaporation-assisted process in capillary microfluidics showed excellent charge/discharge cycle stability over 30 cycles maintaining stable discharge plot characteristic with the areal capacitance of $59\ \text{mF cm}^{-2}$ at $0.5\ \text{mA cm}^{-2}$ current density (figure 7(b)). The electrochemical characterization validates the new process using temporal capillary microfluidics for fabrication of TMV-based high surface area electrodes.

3.5. Electrochemical characterization in symmetric NiO configuration

The performance of the NiO supercapacitor in symmetric configuration was characterized as a full supercapacitor. The kinetics of the charge storage mechanism are based on the opposite redox reaction on the two sides of the interdigitated NiO electrodes. NiO on one side of the device is being oxidized to NiOOH while the other side gets reduced from NiOOH to NiO. To enable this system, the fabricated supercapacitor device required initial kinetic balancing redox cycles until the clear corresponding redox peaks are revealed and reach their saturation. These initial cycles are shown in figure 8(a) which required 90 cyclic voltammetry cycles at $20\ \text{mV s}^{-1}$ to form symmetric redox peaks centered at 0 V. After a sufficient number of kinetic balancing cycles and reaching the saturation of the cyclic voltammetry current peaks, the charge storage performance characterization continued using galvanostatic charge/discharge tests. Figure 8(b) shows the charge/discharge configuration of the symmetric

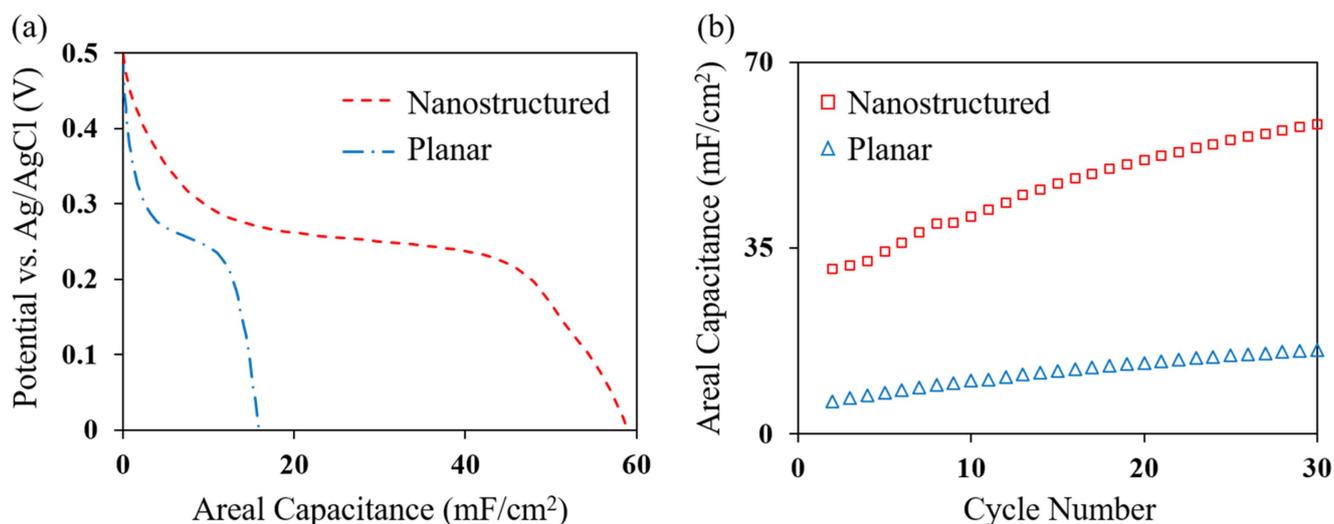


Figure 7. Electrochemical characterization of the TMV nanostructured NiO electrodes: (a) comparison of galvanostatic discharge plot and (b) areal capacitance increase by the TMV nanoscaffolds in different cycles.

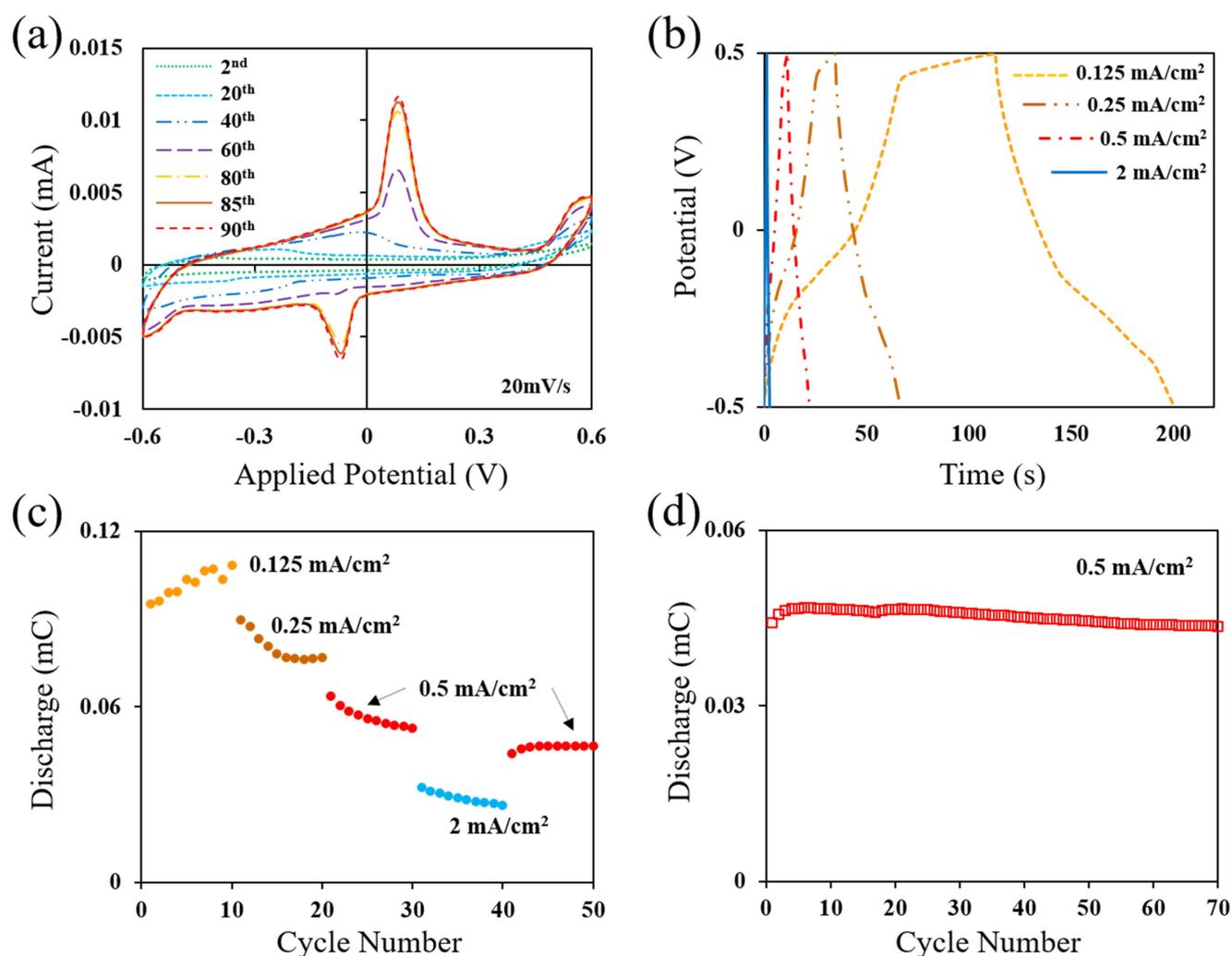


Figure 8. Electrochemical characterization of the symmetric NiO supercapacitor. (a) Cyclic voltammetry (CV) characterization of the symmetric NiO supercapacitor showing initial redox balancing cycles. (b) Galvanostatic charge/discharge plot at different current densities showing pseudo-capacitive characteristic of the device. (c) Current rate dependant discharge capacity retention with excellent dynamic performance. (d) The symmetric NiO supercapacitor was stable up to 70 charge/discharge cycles without any significant performance fading.

NiO supercapacitor at different current densities. The pseudocapacitive behavior is clearly confirmed in the semi-triangular charge discharge plot over a wide range of current levels ($0.125\text{--}2\text{ mA cm}^{-2}$). Also, the dynamic stability of the symmetric supercapacitor is characterized in figure 8(c) showing the generally accepted rate dependent charge capacity characteristic of supercapacitors with good charge capacity recovery (85%) performance at the last 0.5 mA cm^{-2} cycles after previous high power operations. The symmetric NiO Supercapacitor was stable over 70 cycles without any significant capacity fading (figure 8(d)). The areal capacitance of the symmetric supercapacitor devices are measured much lower compared to the results from the three electrode characterization, and this is attributed to lower conductivity NiO as a charge provider when compared with the Pt-foil counter electrodes limiting the overall current rate capability.

4. Conclusions

Capillary microfluidics is demonstrated as an enabling technology for rapid fabrication of microscale energy storage devices featuring biotemplate-based nanostructures. Utilizing temporal photoresist patterns as open capillary microfluidic channels, genetically modified TMV particles (TMV1cys) are rapidly delivered on designed microelectrode area by capillary force, creating bio-nanoscaffolds in the Ni/NiO supercapacitor electrode fabrication. This technology significantly reduces the TMV coating time from 18 to 1 h, enables higher areal capacitance within a limited device footprint, and utilizes efficient amount of nanostructure samples to functionalize a device surface. This temporal capillary microfluidic fabrication method is fully compatible with existing photolithography, and will further contribute to rapid and simple fabrication process of nanostructured devices and surfaces in a wide range of applications.

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