Rapid fabrication of supercapacitor electrodes using bio-nanoscaffolds in capillary microfluidics

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Abstract. This paper reports the utilization of capillary microfluidics to rapidly create nanostructure-patterned electrodes for energy storage applications. Using patterned photoresist as open-channel capillary microfluidics, *Tobacco mosaic* virus (TMV) bio-nanoscaffolds suspended in solution are autonomously delivered onto planar gold electrodes over a 1 cm^2 area. The TMVs assemble on the electrode and form a dense bio-nanoscaffold layer due to enhanced evaporation-assisted assembly in the open-channel capillary microfluidic device within an hour. The TMV structures are coated with Ni/NiO through electroless plating and thermal oxidation to form supercapacitor electrodes. The galvanostatic charge/discharge cycle showed a 3.6-fold increase in areal capacitance for the nanostructured electrode compared to planar structures.

1. Introduction

The needs for efficient storage of energy from intermittent sources are driving the development of high efficiency energy storage devices such as battery and supercapacitors [1]. Supercapacitors, which preserve electrical energy through electrochemical reaction, are attractive among various energy storage systems for their higher power and energy densities compared to batteries and conventional dielectric capacitors, respectively [2]. Similarly, nanostructured materials offer significant advantages compared to their bulk counterparts such as improved mechanical stability, faster ion/electron transfer kinetics, higher surface area and higher sensitivity. 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.

Novel functionalities can be engineered on biological molecules such as proteins, DNA and viruses. These mutated biological molecules preserve the nanostructures of nature while exhibiting tailored surface attachments. The *Tobacco mosaic* virus (TMV) is a cylindrical plant virus measuring 300 nm in length with a diameter of 18 nm. It can be genetically modified to include cysteine residues for enhanced binding affinity. These TMV mutants possess the ability to self-assemble onto various

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substrate surfaces and the capability of being metallized as electrodes. TMVs have previously been demonstrated as promising high surface area nanoscaffolds to self-assemble on electrodes for high energy density microbatteries and supercapacitors [3, 4]. However, the TMV self-assembly process was limited by the long assembly time (3-18 hours), low utilization rate of virus samples, and difficulty in localization, preventing its rapid implementation in microdevices.

In this work, a TMV bio-nanoscaffold supercapacitor electrode was rapidly patterned though the integration of capillary microfluidics in the microfabrication process. The integration of capillary microfluidics leverages the autonomous sample delivery of a capillary device as well as the self-assembly of TMVs, and enables rapid coating of TMV nanoscaffolds in specific areas through room-temperature evaporation with optimal utilization of nanoscaffold samples. Subsequently, metallization with Ni from solution and thermal oxidation are easily performed on the TMV structures to form supercapacitor electrodes. The electrochemical performance of the electrodes is tested through galvanostatic charge/discharge cycle.

2. Methods

2.1. Supercapacitor electrodes
The bio-nanoscaffolded supercapacitor electrode leverages the high aspect ratio characteristic and the self-assembly capability of genetically modified TMV, and is aimed at a significant improvement in areal capacity compared to planar electrodes.
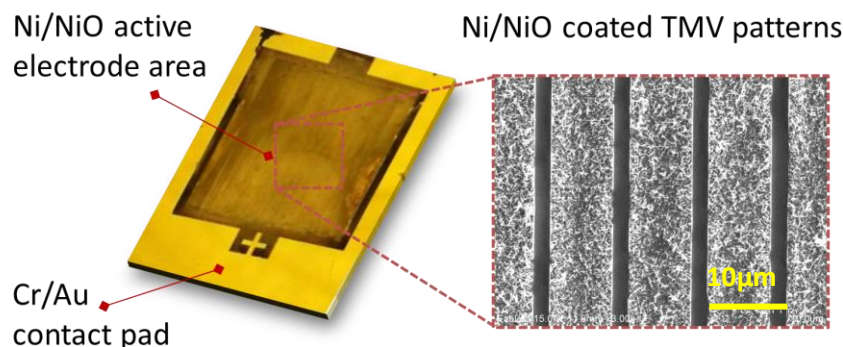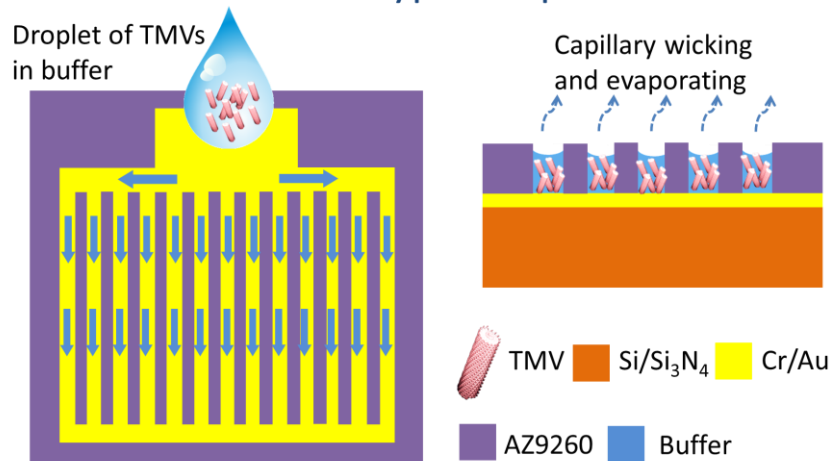

Figure 1. Optical and scanning electron microscopy images showing the TMV nanostructured electrode

The optical and scanning electron microscopy (SEM) images in figure 1 show the morphology of the TMV nanostructured electrode, where Ni/NiO coated TMV nanostructures are patterned in the center of the electrode, forming an active electrode footprint of 1cm^2. The active electrode area is connected to the surrounding Cr/Au contact pad. As shown in the SEM image, the thin film Ni/NiO coating on the TMVs preserves the rod-like structures of the nanoscaffolds, increasing the active surface area compared with a planar electrode. The 8 μm-wide nanoscaffolded electrodes were separated by 2 μm-wide gaps left over from the capillary microfluidics-assisted fabrication process.
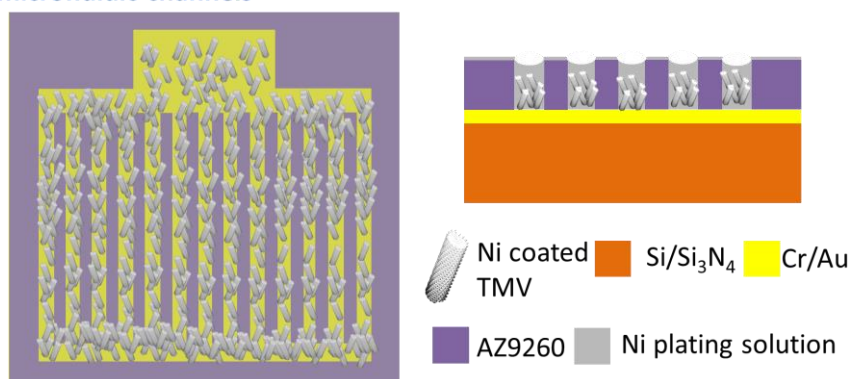
2.2. Capillary microfluidics-assisted nanoscaffolded electrode fabrication
Open-channel capillary microfluidics featuring autonomous liquid sample delivery and enhanced surface evaporation have been demonstrated as a suitable platform for rapid nanostructure assembly in microdevices [5]. The fabrication of the proposed supercapacitor electrodes utilizes a similar capillary microfluidics-assisted process to rapidly pattern nanostructures on a large electrode area with high precision.
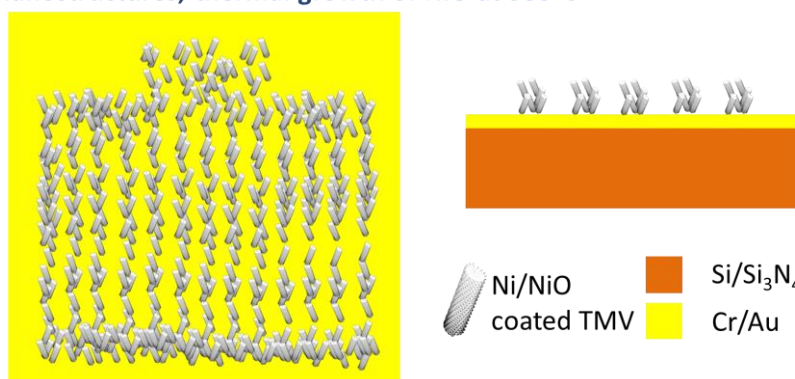
Figure 2. Fabrication process flow of creating TMV nanostructured electrode using capillary microfluidics and one-step photolithography

The microfabrication process flow to create a TMV-nanostructured electrode using temporary open capillary microfluidic patterns is demonstrated in figure 2. One-step photolithography was performed to create microstructured strips with 8 μm of thickness and 2 μm of width on AZ9260 photoresist. The surface was rendered hydrophilic by exposing the surface to O_2 plasma at 50 W for 60 seconds. The

gaps between photoresist strips then served as the open capillary microfluidic channels. TMV nanoscaffolds suspended in deionized water were autonomously delivered on the capillary channel patterns from one end of the electrode over the whole active electrode surface due to capillary effects. 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 (figure 2a). The TMV nanoscaffolds were attached on the active electrode area and concentrated in the capillary microfluidic channels after one hour of room-temperature buffer evaporation. The electrode surface was then metalized though electroless plating of Ni, creating Ni-coated TMV-nanostructured electrode (figure 2b). 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 ºC over 2 hours (figure 2c).

2.3. Equipment and test setup

The performance of the fabricated Ni/NiO nanoscaffolded supercapacitor electrodes was tested using redox cycling in a three-electrode setup. The test setup utilized the fabricated Ni/NiO working electrodes, commercial Ag/AgCl reference electrode (CH Instruments, TX, USA) and 2 cm^2 of platinum foils as the counter electrode. The constant current density charge and discharge tests were performed in 2 M KOH solution with a VSP-300 potentiostat (Bio-Logic Science Instruments SAS, France).
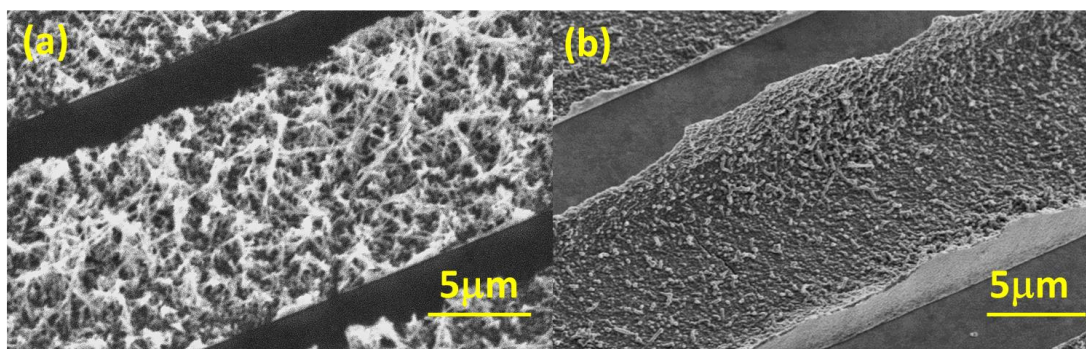
3. Results and discussions

Figure 3. SEM images showing TMV nanoscaffolded Ni/NiO electrodes fabricated by evaporation of (a) 0.2 mg/ml and (b) 2 mg/ml of TMVs in capillary microfluidic channels

The SEM images in figure 3 show the metallized TMV-nanoscaffolded electrode patterns fabricated in the capillary microfluidics. The SEM images in figure 3a shows the morphology of nanostructured Ni/NiO electrode fabricated using the TMV nanoscaffolds in 50 µl of DI water at the concentration of 0.2 mg/ml. After autonomous delivery and the subsequent evaporation of the TMV solution, the electrode surface demonstrates clear porous structures composed of TMV nanorods in random orientations. However, as the TMV concentration further increases (2 mg/ml), the nanorods are closely stacked during evaporation, forming a thick film with much lower porosity after metallization (figure 3b). This would likely yield a decreased areal capacitance. Therefore, to ensure an enhanced surface area of the supercapacitor electrode, the TMV suspension with the concentration of 0.2 mg/ml is adopted to create porous TMV Ni/NiO electrode in the following electrochemical tests.
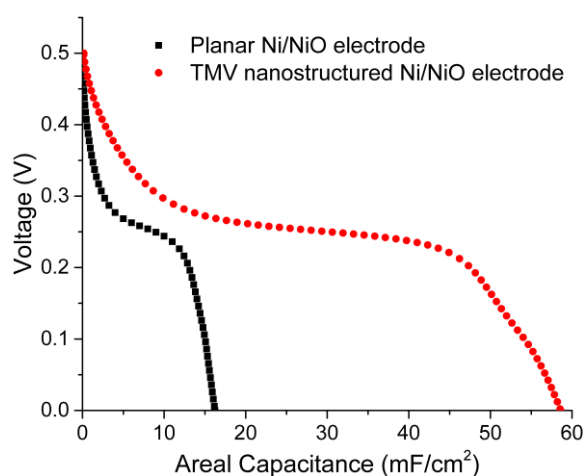
Figure 4. Discharge characteristics of the Ni/NiO coated planar and TMV nanostructured electrodes

The electrochemical performance of the NiO supercapacitor electrodes was tested by charge and discharge cycles at constant current of 500 µA (active electrode area of 0.8 cm^2). Figure 4 shows the discharge characteristics of both the planar and TMV nanostructured Ni/NiO electrodes at the 30th cycle. The TMV nanostructured electrode showed an approximate 3.6-fold increase in areal capacitance compared to the planar Ni/NiO electrode, validating the significant increase in the active surface area of NiO using the nanostructured electrode fabricated in capillary microfluidics. The capacitance increase is lower than the reported 7-fold increase [4]. This is caused by the occupation of microfluidic channel sidewalls on chip which results in the reduction of active electrode area, and the possible degradation in porosity of TMV layer during evaporation.

4. Summary

This is the first demonstration of using capillary microfluidics as an enabling technology to rapidly fabricate nanostructure-patterned electrodes for energy applications. The TMV bio-nanoscaffolds were autonomously delivered in temporary photoresist-patterned open capillary microfluidic channels, and functionalized the planar electrode with patterned high-surface-area nanostructures within an hour. This technology enables higher areal capacitance within a small footprint, efficiently utilizes minimum amount of nanostructure samples to functionalize a device surface, and will contribute to rapid fabrication of nanostructured energy storage devices in symmetric/asymmetric configurations using one-step photolithography.

References

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