Transparent, stretchable and high-performance supercapacitors based on freestanding Ni-mesh electrode

Yaoyao Zhao¹, Zhouying Jiang¹, Ya Weng¹ and Yan-Hua Liu¹, ², ³

¹ School of Optoelectronic Science and Engineering & Collaborative Innovation Center of Suzhou Nano Science and Technology, Soochow University, Suzhou, 215006, China
² Light industry institute of electrochemical power sources, Suzhou, Jiangsu 215600, P. R. China
³ Corresponding author’s e-mail: yhliu@suda.edu.cn

Abstract. A high performance transparent and stretchable supercapacitor was formed by the electrochemical deposition of MnO₂ on a freestanding Ni mesh and further integrated with an elastic substrate. The solid-state supercapacitor shows a high transparency of 62% at 550nm and superior areal capacitance of 34.8 mF/cm² at the scan rate of 0.01 v/s. The supercapacitor device possesses a 98.8% capacity retention up to 30% strain. Moreover, the areal capacitance retention rate kept 87% after hundreds of stretching cycles at 30% strain.

1. Introduction

With the rapid development of multifunction wearable consumer electronics, such as wearable display, electronic skin, smart window [1-7], devices that designed to connect human body for operating under continuous mechanical interference such as bending and stretching caused tremendous attentions, it is urgent to develop flexible, transparent and stretchable energy storage units to further promote the development of wearable electronic devices. Owning to the advantages of fast charging time (from a few seconds to a few minutes), long lifetime, high power density, light weight, and no explosion risk, supercapacitors have become a viable candidate for energy storage complementary in wearable electronics, especially for the high coordination of large deformation in general human movement [8-17].

The focus of a transparent stretchable supercapacitor is on the transparent stretchable electrode, the amount of tension in the supercapacitor, and the capacitance retention rate of the supercapacitor in strain. It is very difficult to achieve simultaneously a transparent, stretchable and conductive capacitance device. There are not many reported electrodes and as-built supercapacitors that are both transparent and stretchable [18-24]. To obtain transparent stretchable electrodes, some researchers synthesized new structures. Gong et al. reported a method to fabricate self-assembled monolayer gold nanowires (AuNWs) conductive thin film (2 nm in diameter) as nanostructured electrode for supercapacitors that transparent and stretchable. Although the supercapacitor showed a high optical transmittance of 79% at the wavelength of 550 nm and could be stretched up to 30% strain with no degradation over 80 stretching cycles. The specific capacitance of the supercapacitor was 56.7 μF /cm² [25]. The cyclic stability of the device is poor and the areal capacitance of supercapacitor is relatively small without meeting most practical application. In addition, gold nanowires cannot widely apply owing to high economic cost. In order to obtain the tensile property of supercapacitor, the pre-stretch
substrate method is adopted. Xu et al. reported the applicability of a pre-strain and then buckling method to achieve supercapacitors based on stretchable graphene electrodes [26]. However, in the process of monolayer graphene preparing, the chemical vapor deposition process is relatively complex and the conditions are harsh.

Herein, a transparent and stretchable freestanding hybrid MnO$_2$-Au-Ni mesh electrode has been designed and successfully fabricated via a simple and low-cost method (electrochemical deposition). The supercapacitor fabricated with this hybrid electrodes can simultaneously achieve a high transparency of 62% at 550nm and a stretchability of 30% strain. The supercapacitor gets an areal capacitance of 34.8 mF/cm$^2$ at the scan rate of 0.01 V/s. Meanwhile, the device exhibited superior cyclic stability. The solid-state supercapacitor can remain 98.8% for up to 30% strain.

2. Materials and methods

First, a positive photoresist was spin-coated on the indium tin oxide (ITO) glass that was cleaned (Figure 1(a-i)) as shown in Figure 1(a-ii) and dried in an oven. Next, a hexagon micro pattern is generated on the photoresist by laser direct-writing technique [27]. The period and line width of the pattern structure can be adjusted flexibly. After development, the ITO surface at the micro groove pattern is exposed to the air that provide a conductive layer for later electroplating of metal nickel (Ni) as shown in Figure 1(a-iii). Next, a Ni mesh is formed by electrodeposition as shown in Figure 1(a-iv), and removed the redundant photoresist (Figures 1(a-v)). An ultrathin, transparent and flexible freestanding Ni mesh can be finally achieved by peeling off from the ITO substrate as in Figure 1(a-vi). The electrode thickness is about 7 μm. In the three-electrode working system of the electrochemical workstation, platinum (Pt) wire was used as the pair electrode, saturated calomel as the reference electrode, and Ni mesh was used as the working electrode to realize the electrode with nanoscale structure.

![Fabrication of the hierarchical MnO$_2$-Au-Ni electrode and supercapacitor.](image)

**Figure 1.** a) Fabrication of the hierarchical MnO$_2$-Au-Ni electrode and supercapacitor. b) SEM image of hexagonal structured Ni-mesh electrode. c) Picture of electrode placed on a flower (with electrode inside the dotted line).
Layered electrochemical deposition was performed on a freestanding Ni mesh, as shown in Figure 1(a-vii), a layer of gold (Au) was electrochemically deposited on the surface of the Ni mesh by means of multi-potential deposition (-0.5v, 5s, 0v for 100s), the electrolyte solution was a mixture of 0.1mM HAuCl4 and 0.1M KCl and then the manganese dioxide (MnO2) was further deposited in 0.05M MnSO4 and 0.05M CH3COONa mixed electrolyte solution using the multi-potential deposition method (0.92v for 360s) on the Au layer. The presence of Au increased the deposition of MnO2. In this way, a nanostructured free-standing MnO2-Au-Ni layered electrode as a current collector is completed. Finally, using the PVA/LiCl gel as the electrolyte and the 3M VHB tape as elastic substrate, the above-mentioned stepped electrodes were assembled into a solid supercapacitor, as shown in Figure 1(a-viii). A PVA/LiCl gel electrolyte was completed by mixing 5 g of LiCl and 12 g of PVA powder in 120 mL deionized water under magnetic stirring at 90 °C until the gel became clear, and then cooled down to room temperature. The hierarchical electrodes were laid on the tape plainly, coated with PVA/LiCl gel, and left in the air for several minutes to solidify the gel surface slightly. Finally, the supercapacitor was obtained by assembling the two gel-coated electrodes together and kept in air about one hour until the device was fully solidified. Figure 1(b) is the SEM image of the fabricated hexagonal electrode, showing the connection integrity of the electrode. Figure 1(c) shows the electrode with good self-support and light transmittance that we can still see the details of the flowers clearly through the Ni metal mesh.

3. Result and discussion
The excellent conductivity, stretchability and light transmittance of Ni metal mesh provide excellent fluid collection for the transparent and stretchable supercapacitor. Stretchable substrate, fluid collection and gel electrolyte determine the transparent and stretchable properties of supercapacitors. The rough Au layer with convex pellets can act as nucleation sites for the uniform deposition of MnO2 [28]. The electrodeposition of Au nanoparticle particles on Ni metal mesh not only enhances the conductivity of fluid collection, but also increases the deposition amount of MnO2 and increases the specific surface area of MnO2. It’s more favorable for gel electrolyte ions to enter and undergo REDOX reactions. The capacitance, charging-discharging, light transmittance and tensile properties of the hybrid electrode are tested respectively in liquid and solid state. Comparing to the Ni mesh electrode (85%), the transmittance of the hybrid MnO2-Au-Ni mesh electrode (73%) decreased slightly in Figure 2(a). A three-electrode system was used to test the liquid state of the mixed electrode. Using Pt electrode and saturated calomel electrode as the pair electrode and the reference electrode respectively, the working electrode was mixed electrode and the solution was 1M Na2SO4. The electrode gets an areal capacitance of 408 mF/cm² at the scan rate of 0.01 V/s (Figure 2(b)).

The CV curve of the hierarchical electrode in Figure 2(b) shows a large enclosed. Galvanostatic charging-discharging (GCD) at current density from 0.25 to 2.5 mA/cm² for hybrid electrode were measured as showing in Figure 2(c). The GCD curves has triangular symmetry, indicating the stability of charging and discharging. Meanwhile, the charge and discharge time also indirectly explains the large areal capacitance. The areal capacitance shows almost no attenuation after 5000 cycles (Figure 2(d)). Two symmetrical hybrid electrodes were assembled into a supercapacitor using a PVA/LiCl gel electrolyte. The CV curves with scan rate varying from 0.01 V/s to 1 V/s for one device are showing in Figure 3(a). The MnO2 loading shows a closed and relatively symmetric region at every scan rate. It is suggested that the hybrid electrode has good capacitance. Galvanostatic charging-discharging (GCD) at current density from 0.25 to 2.5 mA/cm² for device were measured as showing in Figure 3(b). At a current density of 0.25 mA/cm², the charging and discharging time is about 300s, indicating that the areal capacitance of the supercapacitor is large. The transmittance of supercapacitor prepared was measured as in Figure 4(a).

In the range of visible light, the overall transmittance of the device is above 62%. Figure 4(b) shows the CV curves at a scan rate of 50 V/s during the stretching process. The curves at each scan rate are almost identical, which further indirectly indicates the stability of the areal capacitance of the supercapacitor during the stretching process. From its original length to 30% of its original length and
then restoring to its original length, the minimum retention rate of areal capacitance is 98.8%, as shown in Figure 4(c). During the whole stretching process, the areal capacitance of the device almost keeps unchanged, implying the tensile stability of the supercapacitor. When the tensile degree is 30%, the minimum areal capacitance retention rate of the device is about 87% (Figure 4(d)) after 200 cycles of stretching, indicating good tensile properties of the devices.

**Figure 2.** a) The transmittance of the freestanding Ni mesh and the hierarchical MnO$_2$-Au-Ni mesh electrode. b) The areal capacitance of the hybrid electrode at varying scan rate of 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1V/s, with CV curves insert. c) GCD curves of the hybrid electrode at current density of 0.25, 0.5, 1, 2, 2.5mA/cm$^2$. d) Areal capacitance retention rate under cycling number up to 5000, with CV curves insert.
Figure 3. Electrochemical performance of the solid-state supercapacitor. a) CV curves of the device at scan rate of 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1.0 V/s. b) GCD curves of device at current density of 0.25, 0.50, 1.00, 2.00, 2.00, 2.50 mA/cm².

Figure 4. Transmittance and stretchability performance of the solid-state supercapacitor. a) Transmittance of the device. b) CV curves of the device in different tensile state (0%-10%-20%-30%-20%-10%-0%). c) Areal capacitance retention of device in different tensile state (0%-10%-20%-30%-20%-10%-0%). d) The capacitance retention of 200 cycles under maximum tensile 30%.
4. Conclusions

In summary, a high performance transparent stretchable supercapacitor was developed by electrochemical deposition of MnO$_2$ on a freestanding Ni metal net and employing with a stretchable substrate. What’s more, the line width and period of the collection fluid can be adjusted flexibly. Systematically investigation has been carried out about the optical and electrochemical properties of the prepared samples. The obtained transparent and stretchable supercapacitor based on Ni meshes and tape achieve a high optical transparency (62% at 550 nm), excellent stretchability (30% strain), and good electrochemical stability. The supercapacitor can be widely applied in flexible optoelectronic devices with superior performance and a controlled solution fabrication process.

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