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Highly stretchable hybrid nanomembrane supercapacitors†

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Supercapacitors that are lightweight, mechanically deformable (stretchable, flexible) and electrochemically stable have potential for various applications like portable, wearable, and implantable electronics. Here we demonstrate a stretchable and high-performing hybrid nanomembrane supercapacitor. The hybrid nanomembrane is prepared by vapour phase polymerization (VPP) based nanoscopic PEDOT coating on carbon nanotube sheets (CNS) transferred onto an elastomeric substrate to form a wavy structure. The resulting wavy structured hybrid nanomembrane based supercapacitor exhibits high electrochemical performance and mechanical stretchability, simultaneously. The high specific capacitances and energy density (82 F g^{-1}, 11 mF cm^{-2}, and 7.28 W h kg^{-1} at 0% strain) are retained under large mechanical deformation (77 F g^{-1} and 6.87 W h kg^{-1} at a biaxial strain of 600%). Moreover, there is only <1% degradation of capacitance ratio after 1000 cycles stretching/releasing and bending/unbending. This high mechanical cyclic stability is shown even during stretching/releasing and bending/unbending measured by dynamic cyclic voltammetry (CV). These results suggest that our supercapacitor is valuable in a wide range of applications that require it to be electrochemically stable under large mechanical deformation, such as strain sensors, wearable electronics and biomedical devices.

Lightweight, stretchable, and flexible supercapacitors have been developed for various applications such as portable electronics,[1] wearable devices,[2] and implantable medical devices.[3,4] The key issue of stretchable and flexible energy storage research is to be deformable active materials with low stretchability, such as graphene,[5] carbon nanotubes, manganese dioxide (MnO_2), silicon (Si)[6–10] and conducting polymers.[11–17] Many related studies have been reported to make stretchable items in terms of structure and material.[18] As for structural approach, interconnect-island mesh, textile configuration, and wavy structure have been reported recently. However, some challenges still remain in these methods.[18–20] Interconnect-island mesh patterns are built by metal interconnects between rigid metal islands. An elaborate lithography technique and winding interconnects are needed to fabricate various patterns. Therefore, interconnect-island mesh patterns need relatively complex and expensive fabrication process, and also the optimization of the patterns to achieve a high stretchability.[18,21] Textile structural configuration concepts are currently attempted in the design of wearable integrated fabrics consisting of up to hierarchical levels which are fibre, yarn, fabric and final product. But it has a high risk of electrical shortage of electrodes.[22] The simple method is to make a wavy structure processed by active materials on pre-stretched substrate then releasing. The stretchability of wavy structure depends on its pre-strain and it is a structural limitation. Stretchability of elastomeric substrate and mechanical property to withstand compression are important factors to decide pre-stain.[19] Therefore, material approach which is the selection of large deformable substrates and active materials is needed to enhance performance. According to the simple equation based on the beam theory: $\varepsilon = h/2r \times 100\%$ (ε is the peak strain of material, h is the thickness, and r is the radius of curvature),[18] active material which has large strain and low thickness has advantage to stretchability.

We previously reported[11] on poly(3,4-ethylenedioxythiophene) (PEDOT)/CNS hybrid nanomembrane with nanoscopic thickness ($\sim$112 nm) obtained by the vapour phase polymerization (VPP) method. This hybrid nanomembrane showed not only improving an electrical sheet resistance as a function of the PEDOT loading amount but also high electrochemical performance. Besides, it is mechanically robust (mechanical strength and modulus were 135 $\pm$ 8 MPa and 12.6 $\pm$ 5.3 GPa, respectively).

In this communication, we report an all-solid-state highly stretchable supercapacitor by using a PEDOT/CNS hybrid nanomembrane that provides a combination of high capacitance and stretchability (82 F g^{-1} and 11 mF cm^{-2} at 0% strain, and 77 F g^{-1} under biaxial strain of 600%). This supercapacitor showed

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a highly stable dynamic CV curve during stretching/releasing and bending/unbending. A capacitance ratio with a high cycle life during mechanical deformation was also observed (<1% degradation after stretching/releasing or bending/unbending during 1000 cycles). Above all, the stretchable PEDOT/CNS hybrid nanomembrane had a combination of high energy density and stretchability. The obtained energy density range was 7.28–6.87 W h kg^{-1} at a stretched strain of 0–600%, respectively, which are considerable values in comparison with recently published thin-film stretchable supercapacitors.[9,15,16]

A fabrication scheme for stretchable PEDOT/CNS on a Ecoflex rubber film is shown in Fig. 1. First, a 1.25 mm-thick Ecoflex rubber film is biaxially stretched along orthogonal in-plane directions until it reached 850% of the original film area. Overall, 15 CNS layers are then alternatively stacked onto the pre-stretched Ecoflex film as a current collector. Next, the CNS are allowed to densify by ethanol. The prepared 85 wt% PEDOT-loading hybrid nanomembranes are slowly transferred onto the densified CNS in the ethanol bath. No shrinkage or detachment of the hybrid nanomembranes is observed during the ethanol evaporation without a polymer binder.[11] After completely drying, the pre-stretched film is slowly released. The substrate recovers only 600% of the original pre-stretched Ecoflex film because the transferred hybrid nanomembrane (PEDOT/CNS nanomembrane) and CNS as a current collector restrict the full recovery of Ecoflex film substrate. Finally, a highly biaxial wrinkled structure of hybrid nanomembrane is achieved. The specific assembly fabrication process of two symmetric electrodes to make a full cell is explained in detail in the Experimental section. Scanning electron microscope (SEM) images (Fig. 2) show morphologies of the densified CNS and hybrid nanomembrane on the CNS before and after releasing. The densified CNS before the hybrid nanomembrane is transferred has a biaxial alignment of carbon nanotube bundles (see Fig. 2a). The biaxial alignment gives similar electrical conductivity in the biaxial direction for stretchable current collectors. The sheet resistance values of the densified CNS along the x and y directions are similarly 91 and 95 Ω sq^{-1}, respectively. The hybrid nanomembrane containing 85 wt% PEDOT and having an average thickness of ~112 nm (ref. 10) and the thin PEDOT layer provide an electrically conducting connection between individual carbon nanotubes (Fig. 2b). When the pre-stretched hybrid nanomembrane is released uniaxially (~200% relaxes by the x direction), the generated wrinkles show high alignment and a uniform gap (Fig. S1†) overall. Consequently, the following wrinkles by relaxing along the y direction provide compression along the ridges by first relaxation; therefore, a more irregular, bumpy, surface is obtained. Fig. 2c shows the dramatically increased biaxial-wrinkled structure of a hybrid nanomembrane after complete releasing.

Our main challenge is to develop an all-solid-state highly stretchable supercapacitor with high energy density. An all-solid-state supercapacitor is assembled with two symmetric electrodes separately prepared (two-layer CNS/85 wt% PEDOT nanomembranes with elastomeric substrates) and 4.5 M LiCl-based PVA solid electrolyte absorbed nylon panty hose as a stretchable separator. This sandwich structure (an active electrode/separator kept the solid electrolyte/active electrode) is then sealed by Sil-Poxy glue, which makes the electrodes mechanically stable during stretching/releasing and bending/unbending. In addition, the PVA-based LiCl solid electrolytes keep their equilibrium state in the device over 1 month. Fig. 3 shows the electrochemical performance of the all-solid-state stretchable supercapacitor. A photograph of experimental setup of the all-solid-state stretchable supercapacitor is shown in Fig. 3a. The two-layer CNS/85 wt% PEDOT nanomembranes shows stable rectangular CV curves at various strains of 0%, 160%, and biaxial 600% at a scan rate of 10 mV s^{-1} (Fig. 3b). With increasing potential scanned rates (50 and 100 mV s^{-1}), the degradation of the CV area is slightly increased (Fig. S2†).

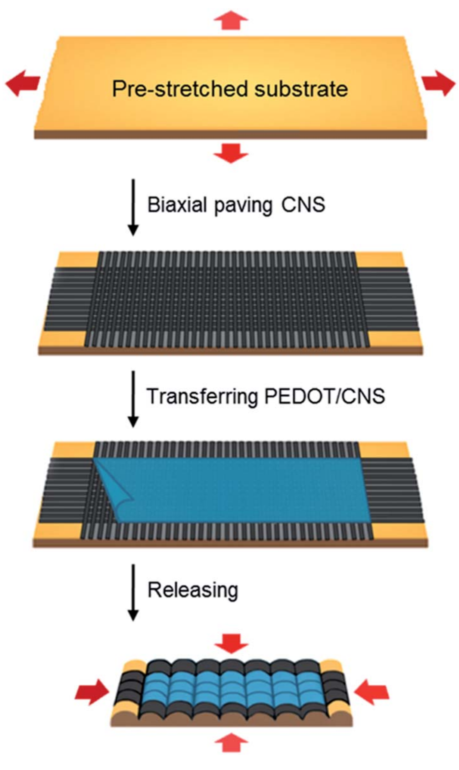

Fig. 1 Schematic diagram of the fabrication process of a stretchable PEDOT/CNS hybrid nanomembrane. (i) Ecoflex rubber (Ecoflex 0050, 1.25 mm thick) is biaxially stretched. (ii) CNS as a current collector are stacked and densified by ethanol. (iii) The PEDOT/CNS hybrid nanomembrane is transferred on the densified CNS in the ethanol bath. (iv) The pre-stretched electrode is slowly released in the biaxial direction.

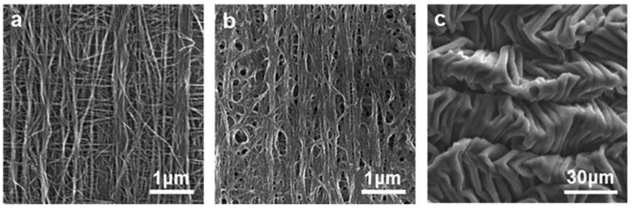

Fig. 2 (a) SEM images of the densified CNS as a current collector before transferring the hybrid nanomembrane. (b) The PEDOT/CNS hybrid nanomembrane transfer on the current collector before releasing. (c) The biaxial wrinkled structure of the PEDOT/CNS hybrid nanomembrane after releasing.

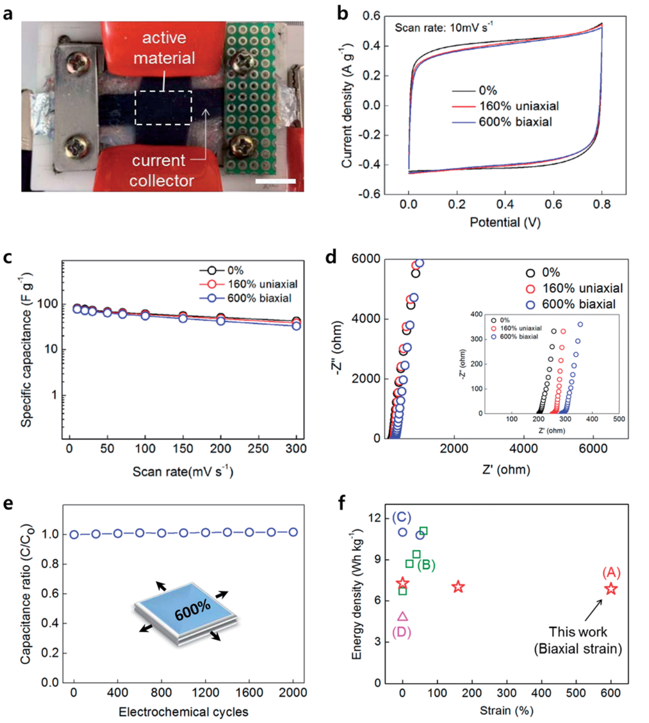

Fig. 3 (a) Photograph showing the completely assembled experimental setup of the all-solid-state stretchable supercapacitor. Scale bar: 10 mm. (b) CV curves at strains of 0%, 160%, and biaxial 600% at the scan rate of 10 mV s^{-1}. (c) Gravimetric capacitance of the supercapacitor with increasing scan rate. (d) Nyquist plot for the sandwich structure of all-solid-state stretchable supercapacitor at various strains of 0%, 160%, and biaxial 600%, showing the imaginary part *vs.* the real part of impedance. Inset: magnified diagram for high frequencies. (e) Cyclic stability of all-solid-state stretchable supercapacitor at the biaxial strain of 600% (scan rate: 300 mV s^{-1}). (f) Results of energy densities (W h kg^{-1}) of our highly stretchable supercapacitor (A) and comparison with other stretchable pseudocapacitors providing both energy density (W h kg^{-1}) and strain (%). (Polypyrrole/nylon lycra fabric[15] (B), polyaniline/multi-walled carbon nanotubes[16] (C), and MnO_2/carbon nano particles[9] (D)).

The areal and gravimetric capacitance of the stretchable PEDOT/CNS hybrid nanomembrane is obtained using the formula: $C = I/(\mathrm{d}V/\mathrm{d}t)$, where I is the discharge current. The single-electrode gravimetric (or areal) capacitance (C_{sp}) is calculated with the following equation:[23] $C_{sp} = 4C/M$, where M is the sum weight of the active material in both electrodes (when we normalize the active materials area, we use the surface area at the measured situation). The gravimetric capacitances of stretchable hybrid nanomembranes are 82 and 43 F g^{-1}, respectively, going from 10 to 300 mV s^{-1} (Fig. 2c) at 0% strain. When the hybrid nanomembrane stretches to a biaxial strain of 600%, the gravimetric capacitances are 77 and 33 F g^{-1}, going from 10 to 300 mV s^{-1}. Capacity retention (C/C_0) of 0.94 is maintained at biaxial strain of 600% (Fig. S3†). The Nyquist plot in the frequency range of 100 kHz to 10 mHz shows ESR increasing as a function of strain of the hybrid nanomembrane (Fig. 3d), which supports the structural change during stretching/releasing. Our stretchable hybrid nanomembrane has a high cycle life during charging and discharging at the prestretched strain until 600% biaxial strain (Fig. 3e), showing that the capacitance ratio is fully maintained for 2000 cycles. Not only the cycle life at 600% biaxial strain, but also the cycle life at 0% and 160% linear strain shows good performance during 2000 cycles (Fig. S4†). The Ragone plot in Fig. 3f and Table S1† show energy densities at various stretchability values of PEDOT/CNS hybrid nanomembrane and comparison results of other flexible and stretchable film-type pseudocapacitors (normalizing with active material). The energy density (E, W h) of the stretchable PEDOT/CNS hybrid nanomembrane is obtained by equation: $E = CV^2/2$, where C represents the specific capacitance and V is the potential range of the CV plot. The PEDOT/CNS hybrid nanomembrane at a strain of 0% – biaxial 600% has an energy density of 7.28–6.87 W h kg^{-1}, which are considerable values compared with other recently published supercapacitors (polypyrrole/nylon lycra fabric: 6.7–11.1 W h kg^{-1} at 0–60% strain,[15] polyaniline/multi-walled carbon nanotubes: 11–10.78 W h kg^{-1} at 0–50% strain,[16] and MnO_2/carbon nano particles: 4.8 W h kg^{-1} flexible, but not stretchable[9]). Here, the biggest challenge we overcame is the fabrication of a highly stretchable hybrid nanomembrane supercapacitor with high energy density. To our knowledge, we are the first to report such a highly stretchable (biaxial strain of ~600%) all-solid-state symmetric supercapacitor.

In practical applications such as stretchable and flexible energy storage devices, various measurements of the electrochemical performance during structural deformations such as stretching/releasing and bending/unbending should be considered. Fig. 4 shows the mechanical stability of a PEDOT/CNS hybrid nanomembrane supercapacitor. The results in Fig. 4a and b show little change in the capacitance ratio when the hybrid nanomembrane is stretched to 160% (~0.3% for 1000 cycles), and bent with a bending angle of 135° (~0.3% for

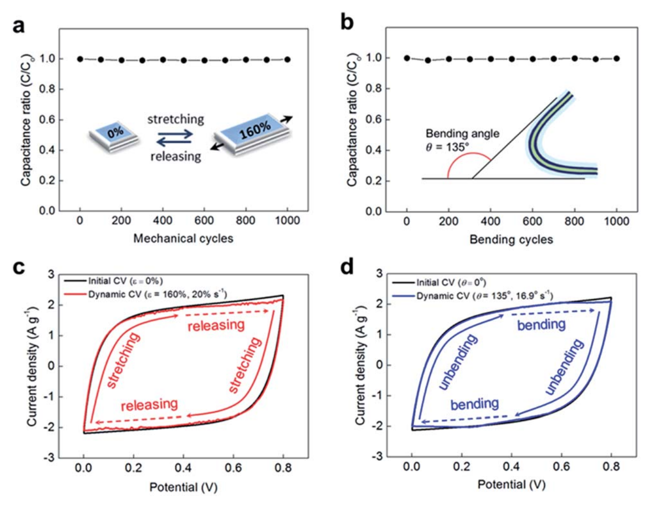

Fig. 4 (a) Dependence of the capacitance ratio on the mechanical cycle number (uniaxial 160% areal strain). (b) Dependence of the capacitance ratio on the bending cycle number (bending angle: $\theta = 135°$). (c) Dynamic CV curve (scan rate: 50 mV s^{-1}) measured during stretching/releasing cycle to 160% strain at a strain rate of 40% s^{-1} (d) dynamic CV curve (scan rate: 50 mV s^{-1}) measured during the bending/unbending cycle to 135° at a bending rate of 16.9° s^{-1}.

1000 cycles), respectively. The CV curves of the hybrid nanomembrane under static and dynamic stretching/releasing and bending/unbending (Fig. 4c and d) demonstrate that the initial CV curve area is maintained. These results support the electrical connection between current collector and active material is strongly adhered and no degradation under dramatic large deformation.

Conclusions

In summary, we have developed a highly flexible and stretchable all-solid-state supercapacitor based on a PEDOT/CNS hybrid nanomembrane. The hybrid nanomembrane shows high capacitance and stretchability (82 F g^{-1} and 11 mF cm^{-2} at 0% strain, and 77 F g^{-1} at a biaxial strain of 600%). There is no observation of shrinkage or detachment of the hybrid nanomembrane during deforming (stretching/releasing and bending/unbending) after densifying the hybrid nanomembrane to the pre-stretched rubber. A high cyclic stability and a dynamic CV curve during stretching/releasing and bending/unbending are also observed. The PEDOT/CNS hybrid nanomembrane has a high combination of energy density and stretchability (7.28–6.87 W h kg^{-1} at a strain of 0% to biaxial 600%), which are considerable values compared with other recently published supercapacitors. Based on these results, these stretchable hybrid nanomembranes seem to be applicable in pressure and strain sensors,[24] stretchable circuit,[25] and implantable medical devices,[26] as well as electrochemical capacitors.[27]

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