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Stretchable and transparent supercapacitors based on aerosol synthesized single-walled carbon nanotube films

Evgenia P. Gilshteyn,^a Tanja Kallio,^{*b} Petri Kanninen,^b Ekaterina O. Fedorovskaya,^{cd} Anton S. Anisimov^e and Albert G. Nasibulin^{*afg}

Stretchable all-solid supercapacitors based on aerosol synthesized single-walled carbon nanotubes (SWCNTs) have been successfully fabricated and tested. High quality SWCNT films with excellent optoelectrical and mechanical properties were used as the current collectors and active electrodes of the stretchable supercapacitors. A transmittance of up to 75% was achieved for supercapacitors made from the assembly of two PDMS/SWCNT electrodes and a gel electrolyte in between. The transparent supercapacitor has a specific capacitance of 17.5 F g⁻¹ and can be stretched up to 120% with practically no variation in the electrochemical performance after 1000 stretching cycles and 1000 charging–discharging cycles.

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1. Introduction

Transparent energy conversion and storage devices have recently attracted increasing attention due to their great potential as integrated power sources for displays and windows in buildings, automobiles and aerospace vehicles.^{1–3} On the other hand, mechanical stretchability coupled with optical transparency of the energy storage devices is required for many other applications, ranging from self-powered rolled-up displays to self-powered wearable optoelectronics. The design of highly stretchable devices is an essential element in the development of many unprecedented applications such as electronic skin^{4,5} and smart energy storage clothes.^{6–8} Portable and wearable supercapacitors, coupled with either self-healability or stretchability,^{7,9,10} have particularly become mainstream in personalized electronics.^{11,12} However, the development of both transparent and stretchable supercapacitors (TSSs) is still a challenge, because typical existing

electrodes are neither stretchable nor transparent (*e.g.*, metal oxide on carbon-based electrodes), even though they might possess either stretchability with low transmittance (*e.g.*, conducting polymers) or transparency with poor mechanical properties (*e.g.*, ITO and other metal oxides). To our best knowledge, no optoelectronic nor energy-related devices have been reported to show both good transparency and high stretchability, though many devices with only one function have been reported elsewhere *e.g.* ref. 13 and 14.

SWCNTs possess many unique properties, which are advantageous for a wide variety of applications, including stretchable electronics. They have exceptionally high Young's modulus of elasticity and tensile strength and are the strongest known material.^{15,16} The porosity and specific surface area of SWCNT films are very large, and they possess high transparency and flexibility.¹⁷ In addition, SWCNTs can withstand extremely high currents (up to 10⁹ A cm⁻²) making them an ideal replacement for copper and aluminum in fast integrated charge/discharge circuits. SWCNT films are thought to be excellent replacement for traditional transparent electrodes, such as indium-tin oxide (ITO), which suffers from several serious drawbacks including limited flexibility and chemical resistance, rare raw material and high refraction and haze.¹⁸ SWCNT networks show improved performance and reduced fabrication cost compared to ITO and organic materials that have been studied as low-cost alternatives.¹⁹ Particularly, aerosol synthesized and collected on a filter SWCNTs can be effectively transferred to any substrate, including stretchable substrate materials such as PDMS (polydimethylsiloxane). They fulfil all the requirements for low-cost, stretchable and transparent electronics.^{20–22}

^aSkolkovo Institute of Science and Technology, Laboratory of Nanomaterials, 100 Novaya str., Skolkovo, Moscow Region, 143025, Russia. E-mail: a.nasibulin@skoltech.ru

^bResearch Group of Electrochemical Energy Conversion and Storage, Department of Chemistry, School of Chemical Technology, Aalto University, P.O. Box 16100, FI-00076 Aalto, Finland. E-mail: tanja.kallio@aalto.fi

^cNikolaev Institute of Inorganic Chemistry, Siberian Branch of Russian Academy of Sciences, 3, Acad. Lavrentiev Ave., Novosibirsk, 630090, Russia

^dNovosibirsk State University, 2 Pirogov str., Novosibirsk, 630090, Russia

^eCanatu Oy, Konalankuja 5, FI-00390 Helsinki, Finland

^fDepartment of Applied Physics, School of Science, Aalto University, P.O. Box 15100, FI-00076 Aalto, Finland

^gSaint-Petersburg State Polytechnical University, Department of Material Science, Polytechnicheskaya 29, 195251, Saint-Petersburg, Russia



Table 1 Literature review of stretchable and/or transparent supercapacitors based on carbon nanotubes

Material	Transparency at 550 nm (%)	Stretchability (%)	Capacitance	Reference
Aligned MWCNT forest/PVA ^a -H ₃ PO ₄ /PDMS	75%	Linear strain 30%	7.3 F g ⁻¹	23
CNT@MnO ₂ /Na ₂ SO ₄ -hydrogel electrolyte	Nontransparent	Linear strain 150%	478.6 mF cm ⁻²	24
SWCNT arrays/ion-gel electrolyte/Ti-Au/PDMS	Transparent	Linear strain 30%	8 mF cm ⁻²	25
MWCNT fiber/PVA-H ₂ SO ₄ electrolyte	Transparent	Strain 100% on fiber direction	4.8 mF cm ⁻²	26
Acid treated CNT@PANI ^b film/PVA-H ₂ SO ₄ electrolyte	Nontransparent	Uniaxial, biaxial strain 200%	1147.1 mF cm ⁻²	27
CNT/MnO ₂ /polymer fiber supercapacitor	Nontransparent	Strain 150% on fiber direction	2.4 mF cm ⁻²	28
CNT ink/metal/PDMS/PVA-ion-gel electrolyte	Nontransparent	Strain 20%	52.2 F g ⁻¹	29
Buckled SWCNT film/PDMS/TEABF ₄ in PC ^c	Nontransparent	Pre-strain 30% and strain 30%	52 F g ⁻¹	30
SWNT macrofilm/polyurethane/organic electrolyte	Nontransparent	Strain 31.5%	34 F g ⁻¹	31
PPy ^d electrodes/SWCNTs/polymer electrolyte	Nontransparent	Strain 30%	18.8 F g ⁻¹	32
Aerosol synthesized CNT films/PVA-H ₂ SO ₄ gel/PDMS	75%	Linear strain 120%	17.5 F g ⁻¹ or 47.5 μF cm ⁻²	Present work

^a PVA - poly(vinyl alcohol). ^b PANI - polyaniline. ^c TEABF₄ in PC - tetraethylammonium tetrafluoroborate in propylene carbonate. ^d PPy - polypyrrole.

In this work, we applied dry deposited thin films of aerosol CVD synthesized SWCNT as the electrodes to fabricate TSSs. Remarkably high specific capacitance and stability are reached with the SWCNT electrodes in test cells and they are used to construct various TSS prototypes.

Such devices have attracted much attention from researchers and show promising application potential in the field of wearable energy storage. As can be seen from Table 1, where we collected the results devoted to transparent and stretchable supercapacitors based on carbon nanotubes, so far either high transparency or stretchability can be simultaneously achieved in devices. The transparent and stretchable supercapacitors developed in this work, showed a superior specific capacitance of 17.5 F g⁻¹ compared to previously reported transparent devices based on CNTs. They can be stretched up to 120% elongation without any significant change in electrochemical performance under 1000 stretching cycles.

2. Experimental

2.1 Experimental methods and materials

SWCNTs were synthesized by an aerosol (floating catalyst) CVD method based on ferrocene vapor decomposition in a CO atmosphere described elsewhere.^{33,34} Briefly, the catalyst precursor was vaporized by passing ambient pressure and temperature CO through a cartridge filled with a ferrocene powder.

The flow containing ferrocene vapor was then introduced into a high-temperature zone. In order to obtain stable growth of SWCNTs, a controlled amount of carbon dioxide was added together with the carbon source.³⁵ SWCNTs were collected downstream of the reactor by filtering the flow through nitrocellulose membrane filters.

SWCNT film morphology was investigated by FEI Helios Nanolab 660 scanning electron microscope with the maximum accelerating voltage of 30 kV. TEM images were obtained with a Tecnai G2 F20 transmission electron microscope with a point resolution of 0.24 nm at 80 kV. Raman spectrometer Horiba Jobin-Yvon Labram HR with a 633 nm laser was used to investigate the quality of the SWCNT film. Optical transmittance was measured with a Perkin Elmer Lambda 1050 UV-Vis-NIR spectrophotometer in a wide range from 150 to 3200 nm, and usually referred to 550 nm.

PDMS substrates with the thickness of about 1 mm were prepared by pouring the mixture of "base" and "curing" agents at a ratio of 10 : 1 (Sylgard 184, Dow Corning) into a circle mold, followed by thermal curing at 70 °C for 45 minutes. Then, the PDMS film was cut into required size pieces.

The electrochemical measurements and stability of TSSs was studied with an Autolab PGSTAT100 potentiostat (Metrohm) at various scanning rates. Cyclic voltammograms in the range from -0.8 and 0.8 V and speed 200 mV s⁻¹ were recorded with an Elins Potentiostat-galvanostat P-40X.

2.2 Properties of aerosol SWCNT films

SWCNTs produced by the aerosol CVD method are of a high quality, which can be confirmed with the help of scanning and transmission electron microscope (SEM, TEM) and optical investigations of the produced samples. Thus, the SWCNTs are immediately suitable for many applications without any additional treatment after their deposition on a substrate by a dry press transfer technique.³⁶

SEM imaging (Fig. 1a) reveals that the SWCNTs form a random network. This allows to use the SWCNT film as an electrode due to high connectivity resulting in highly conductive



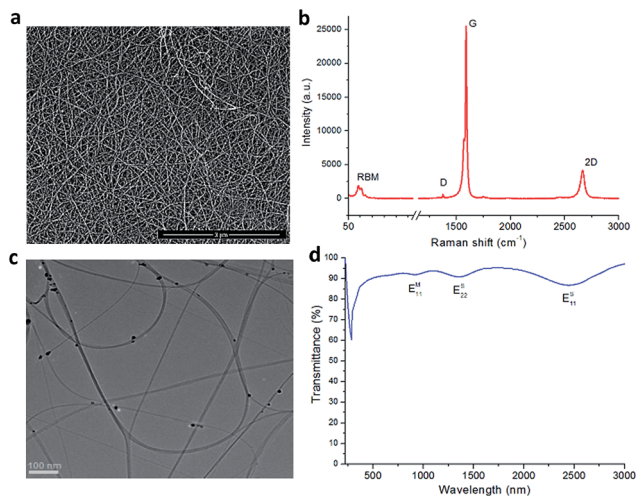


Fig. 1 (a) SEM image of a SWCNT film, (b) Raman spectrum of the SWCNT film with peaks observed: RBM, D, G, 2D, (c) TEM image of the SWCNTs, (d) transmission spectrum of the SWCNT film used for fabrication of TSS electrodes.

surface area readily accessible for ion absorption. Moreover, this kind of an entangled SWCNT network structure allows stretching the electrode so that connections between the mechanically strong SWCNTs remain. Consequently, conductivity is also preserved during stretching and release. TEM images confirmed that the produced tubes are single-walled carbon nanotubes with some iron catalyst nanoparticles (Fig. 1b).

Raman spectrum of the tubes deposited on a quartz substrate demonstrates typical peaks for SWCNTs (Fig. 1c). The D-band around 1350 cm^{-1} corresponds to defective structures, while the G-band around 1580 cm^{-1} is indicative of graphitic structures.³⁷ The low intensity ratio between D and G bands ($I_D/I_G = 0.029$) shows that the structure of the as-produced SWCNTs is highly crystalline and consequently, these nanotubes have good mechanical and electrical properties. In addition, typical Raman peaks for SWCNTs are present: RBM (radial breathing mode), associated with vibration of carbon atoms in a radial direction and 2D band, the result of two phonon lattice vibrational process.

Van Hove singularities corresponding to electronic transitions in semiconducting (E_{11}^S and E_{22}^S) and metallic (E_{11}^M) SWCNTs can be clearly observed in the transmission spectrum (Fig. 1d). The mean diameter of SWCNTs estimated from the spectrum is about 2.5 nm ,³⁸ which corresponds to the results obtained from the analysis of the TEM images. Optical transmittance of the film is usually referred to the wavelength of 550 nm (middle of the visible light range – 380 to 780 nm) and the quartz substrate contribution is subtracted as the background. Since absorbance, A , is a linear function of the SWCNT film thickness, h , the latter can be calculated using $h\text{ (nm)} = 417 \times A$.³⁹ Therefore, for a film with the transmittance of 90% the calculated thickness is about 19 nm .

For the TSS fabrication we utilized the films with different transmittances, *i.e.* thicknesses. SWCNT films with 90% transmittance were used for fabrication of transparent electrodes (CNT_1 in Fig. 2), while 80% transmittance (40 nm thick) films

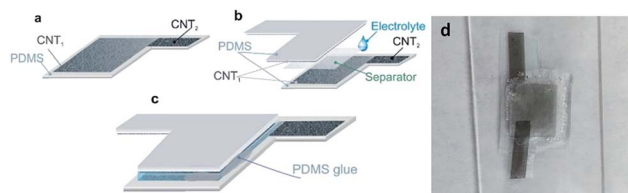


Fig. 2 Scheme of TSS fabrication process: (a) deposition of CNT_1 and CNT_2 films on PDMS, (b) assembling the TSS by adding the separator and acid electrolyte, (c) gluing two substrates with the liquid PDMS, (d) photograph of the SWCNT based TSS with H_2SO_4 electrolyte and a nontransparent separator.

for current collectors (CNT_2 in Fig. 2), due to the higher conductivity of the thicker SWCNT network.

3. Results

3.1 Fabrication of TSS based on liquid H_2SO_4 /separator

Fig. 2 schematically shows the procedure for preparing transparent and stretchable supercapacitors with liquid H_2SO_4 /separator. The pristine SWCNTs were first deposited onto a preformed PDMS substrate (Fig. 2a) and then heated to $200\text{ }^\circ\text{C}$ in order to anneal the surface and to desorb oxygen and organic impurities. After that $2\text{ mol dm}^{-3}\text{ H}_2\text{SO}_4$ solution was dropped on top of one of the SWCNT films and covered with a paper separator (Fig. 2b). Finally, we constructed the supercapacitors by assembling another PDMS-supported SWCNT electrode on top of the newly formed separator/liquid H_2SO_4 /SWCNT/PDMS multilayer film and glued this structure with liquid PDMS at the edges. Fig. 2 shows the fabricated stretchable and semi-transparent device. The fabricated supercapacitor is flexible as it can be seen from Fig. 2d and can be stretched at least up to 50% strain (Fig. 4b), as will be demonstrated further.

Immediately after the liquid PDMS glue was solidified, cyclic voltammogram characteristics were measured at different scan rates from 10 to 500 mV s^{-1} (Fig. 3). The current increased with the increasing scan rate, as is characteristic for adsorption-controlled reactions, implying that no mass transfer or kinetic limitations can be observed and all the SWCNT surface sites are readily accessible even with the

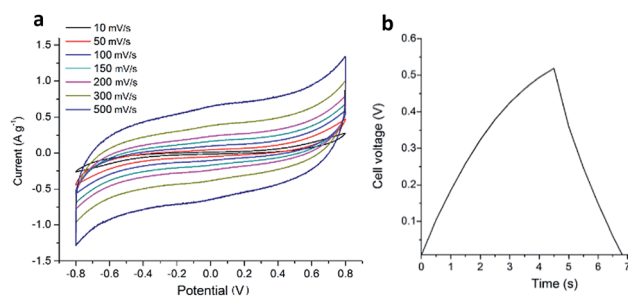


Fig. 3 Electrochemical characterization of the SWCNT stretchable supercapacitors with acid H_2SO_4 : (a) cyclic voltammograms at various scan rates (numbers indicates scan rates in mV s^{-1}), (b) constant current charging and discharging at 0.25 A g^{-1} .



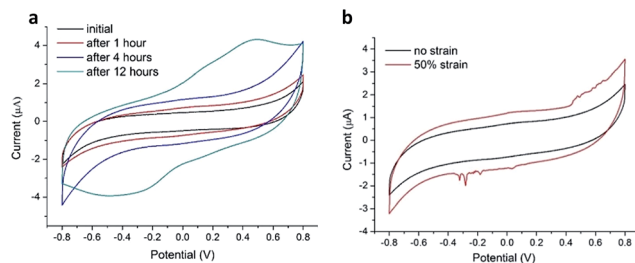


Fig. 4 (a) Cyclic voltammograms of TSS with liquid acidic electrolyte at different periods of time after the fabrication, (b) cyclic voltammograms of TSS before stretching and being stretched at 50%.

higher scan rates. Thus, the same capacitance is achieved in the studied scan rate range.

Due to the fact that we used water based electrolyte and SWCNTs exhibit hydrophobic behavior, cyclic voltammograms measured at different periods of time (Fig. 4a) showed the time dependence. To follow the wetting behavior of the electrodes, the voltammograms were measured immediately after the fabrication process, after 1, 4 and 12 hours. It can be easily seen that after letting the device be impregnated in electrolyte for 12 hours the current increased 6 times.

To analyze the stretchability of the transparent supercapacitors, cyclic voltammetric measurements were performed under mechanical deformations, such as stretching after the fabrication process (Fig. 4b). It was observed that the

capacitance of the TSS was improved by stretching up to 50% strain. This can be explained by the fact that stretching process led to better wetting of the SWCNTs by the electrolyte, thus increasing the area available for the ion absorption.

The specific capacitance of this device (C_{sp}) can be calculated using the charge integrated from the area of the cyclic voltammogram graphs according to:^{30–32}

$$C_{sp} = \frac{1}{2mV\nu} \int_{V_-}^{V_+} I(V)dV, \quad (1)$$

where m is the mass of the active material in both electrodes, $V = 0.8$ V is the potential window between the positive and negative electrodes, $\nu = 200$ mV s⁻¹ is the scan rate. The mass density of the electrodes was determined to be 5 $\mu\text{g cm}^{-2}$. This type of TSSs has demonstrated the capacitance C_{sp} of 3.2 F g⁻¹, and can be taken as a basis for the comparison with the results obtained with improved structures.

One of the main issues impeded the fabrication of highly stretchable supercapacitors with high performance is the leakage of the electrolyte while applying force to the TSSs.

This problem is arisen from the configuration of the stretchable supercapacitor device wherein liquid electrolyte is sandwiched by two electrodes. Our further experiments were devoted to improvement of TSS configuration by replacing the liquid electrolyte, which might suffer from leakage of a harmful liquid, and consequently the non-transparent separator with a conformable gel electrolyte.

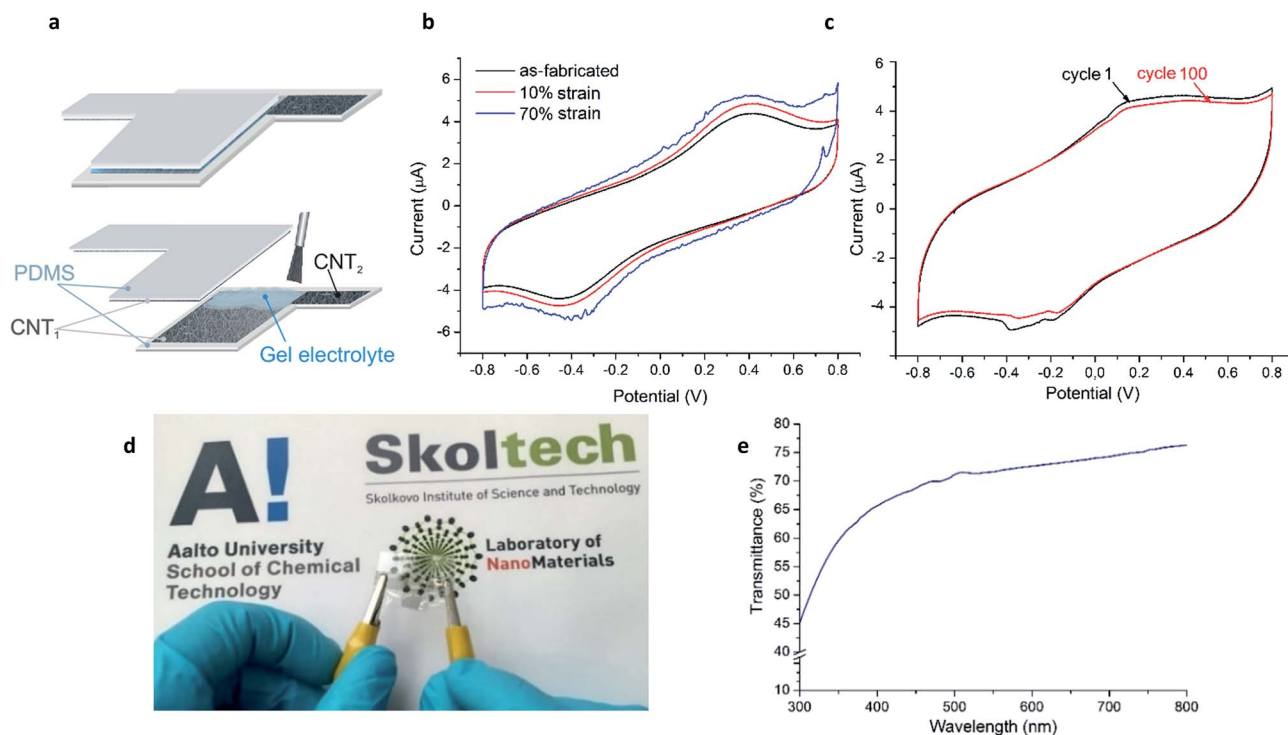


Fig. 5 The optical and electrochemical properties of the TSSs based on gel electrolyte: (a) schematic image of TSS fabrication process by deposition of gel electrolyte, (b) electrochemical performance of as-fabricated TSS and under applied 10% and 70% strain, (c) CV curves for the first and hundredth stretching cycles, (d) photograph of the transparent and stretchable supercapacitor, (e) transmittance spectrum of the assembled TSS.



3.2 Fabrication of TSS based on a PVA-H₂SO₄ gel electrolyte

Nonetheless, most reports on stretchable supercapacitors have focused on the development of stretchable electrode materials and their designs while little attention is paid on the choice of an electrolyte. Widely used electrolytes are generally liquid. However, the liquid electrolytes are not appropriate for stretchable supercapacitors because of the intrinsic leakage problem. In order to improve the TSS performance we utilized another type of an electrolyte, polyvinyl alcohol-H₂SO₄ gel.

The first two fabrication steps were similar to the ones described in the previously reported section (Fig. 2a and b). A gel containing polyvinyl alcohol (PVA) powder (5 g) and H₂SO₄ (5 g, 95% concentration) in water (50 mL) was used as the electrolyte. It is worth noting that the strength of the H₂SO₄ was 95%. Then, the viscous solutions were cast onto the SWCNT electrodes, subsequently the two electrodes coated with the gel electrolyte were dried in the air at room temperature for 10 h. While the solution was still viscous, one of the electrolyte-coated electrodes was firmly pressed on the other electrolyte-coated electrode and the whole assembly was treated at 40 °C for 5 h, while the whole supercapacitor became solidified but still fully stretchable (Fig. 5a). Finally, the TSS contacting pads were connected to the potentiostat-galvanostat for subsequent characterization of the device performance (Fig. 5b and c). The whole device can be bent, folded, and even stretched at least up to 70% strain without any obvious performance change, as it can be seen from Fig. 5b. Additional advantages of this supercapacitor is its high transparency – 75% (Fig. 5e) and absence of harmful liquid compounds, since the TSS is solid.

4. Discussions

The current values can be compared with the values obtained with the acid liquid electrolyte, but the shape of this graph looks better, which indicates better operating parameters of such TSSs. This can be attributed to excellent properties of the PVA-H₂SO₄ electrolyte, less overall resistance because of a thinner

electrolyte layer and high tensile strength after solidification, in comparison with TSS based on the liquid electrolyte.³⁴ The capacitance of the device, C_{sp} , calculated according to eqn (1) achieves the value of 7.4 F g⁻¹.

Thus, the problems in fabrication of highly stretchable supercapacitors, leakage of the electrolyte, was solved by using the gel electrolyte. For further improvement of TSS characteristics under applied strain we developed pre-stretching approach (Fig. 6a), which is based on spreading of gel electrolyte on the SWCNT film under applied strain. We achieved TSS structure, which can be stretched up to 120% of strain without significant change of the capacitance even after 1000 stretching cycles (Fig. 6b). The gel electrolyte is viscous and thus stretching improves the contact between the SWCNT electrodes and the electrolyte. Better wetting of the SWCNTs increases the active surface area and consequently, enhances mass transfer and double layer structuring resulting in the observed higher specific capacitance. In Fig. 6c the cyclic voltammograms of the TSS before and after 1000 cycles between -0.8 and 0.8 V are shown and surprisingly, a small improvement in current is seen. This is attributed to better wetting of the hydrophobic SWCNT during the successive potential cycles and indicates excellent stability for the SWCNT electrodes and the TSS device.

For this pre-stretching approach, the calculated specific capacitance value of C_{sp} is 17.5 F g⁻¹, which is higher than that obtained for the liquid or gel electrolyte without pre-stretching. It ought to be remarked that recently we have fabricated transparent and flexible electrochemical double-layer capacitor (EDLC) prototype from our SWCNT films.¹⁷ The supercapacitor showed extremely high mass specific capacitance of 178 F g⁻¹ compared to other carbon-based flexible and transparent EDLCs. However, that supercapacitor had higher values of the capacitance due to the fact that material properties were tested in a test cell, and the lateral conductivity of the SWCNT film was not an issue. Therefore, the TSS fabricated here demonstrated relatively high capacitance in a prototype cell being stretchable and transparent. Thus, we optimized and eventually fabricated highly stretchable TSS by combining our SWCNT films pre-

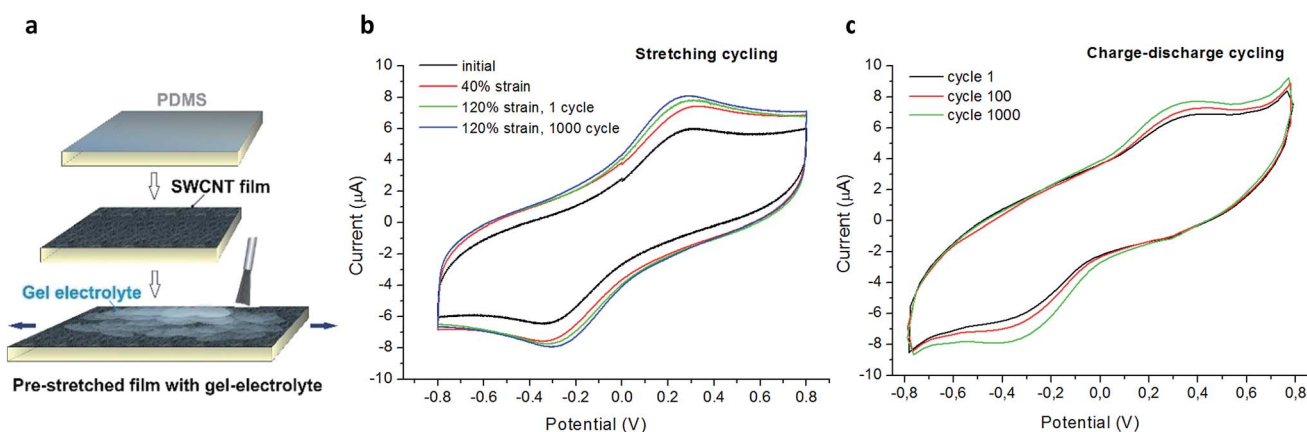


Fig. 6 (a) Scheme of gel electrolyte deposition on pre-stretched SWCNTs on PDMS. (b) Cyclic voltammograms of TSS made of pre-stretched electrodes at zero applied strain, 40% strain, at first cycle of stretching to 120% and after 1000 cycle of stretching to 120% (scan rate – 200 mV s⁻¹), (c) cyclic voltammogram of the supercapacitor before and after 1000 cycles between -0.8 and 0.8 V.



strained on the PDMS substrate and using of a gel electrolyte. The capacitance of these pre-strained TSSs remained nearly unchanged, even under the strain up to 120%. This configuration enabled stretching of the supercapacitor as an integrated unit and overcame the limitation of conventional stretchable supercapacitor configuration wherein two electrodes move relative to the separator under strain. The performance of the stretchable supercapacitors remained nearly unchanged under 120% strain even under stretched conditions and after 1000 stretching cycles. Superior stretchability of the aerosol synthesized SWCNT films may find broad applications in stretchable electronics, energy storage electrodes and sensors. Such high stretchability, combined with transparency and high specific capacitance confirmed that fabricated supercapacitor has a great potential for broad practical applications.

5. Conclusions

In summary, we successfully developed highly stretchable supercapacitors, based on SWCNT films with 80% transmittance as current collectors and 90% transmittance films, as electrode material. Our first fabricated and tested TSSs with liquid 2 mol dm⁻³ H₂SO₄ electrolyte showed capacitance about 3.2 F g⁻¹ and allowed to apply 50% of strain. This limitation can be explained by the presence of non-stretchable separator and leakage of liquid electrolyte. In order to solve this problem, TSS based on PVA-H₂SO₄ gel electrolyte was developed, which showed specific cell capacitance of 7.4 F g⁻¹. In order to increase durability to stretching of such TSS another technique was performed based on pre-stretching of the electrodes with the deposited gel electrolyte. This approach allowed using the effect of better electrolyte diffusion and electron transport through the electrode layers and obtain the capacitance value of 17.5 F g⁻¹, significantly higher than previously reported. Furthermore, TSS based on pre-stretching approach demonstrated stretchability up to 120% with excellent stability even after stretching for 1000 cycles in addition to electrochemical stability after 1000 charging–discharging cycles.

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