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Short communication

Flexible supercapacitor based on polyaniline nanowires/carbon cloth with both high gravimetric and area-normalized capacitance

Ying-Ying Horng[a,b], Yi-Chen Lu[a,b], Yu-Kuei Hsu[c], Chia-Chun Chen[a,c], Li-Chyong Chen[b,*], Kuei-Hsien Chen[b,c,**]

[a] Department of Chemistry, National Taiwan Normal University, Taipei 106, Taiwan
[b] Center for Condensed Matter Sciences, National Taiwan University, 1 Roosevelt Road, Section 4, Taipei 106, Taiwan
[c] Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 106, Taiwan

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ABSTRACT

Flexible supercapacitor is successfully fabricated using polyaniline nanowires/carbon cloth (PANI-NWs/CC) nanocomposite. High gravimetric capacitance of 1079 F g^{-1} at a specific energy of 100.9 Wh kg^{-1} and a specific power of 12.1 kW kg^{-1} is obtained. Moreover, this approach also offers an exceptionally high area-normalized capacitance of 1.8 F cm^{-2}. The diffusion length of protons within the PANI-NWs is estimated to be about 60 nm by electrochemical impedance analysis, which indicates that the electrochemical performance of the electrode is not limited by the thickness of PANI-NWs. The electrochemical performance of PANI-NWS/CC remains without any deterioration, even when the cell is bent under high curvature. These results clearly present a cost-effective and simple method of fabrication of the nanostructured polymers with enormous potential in flexible energy storage device applications.

1. Introduction

The various designs and power needs of soft portable electronic equipment, such as roll-up display, electric paper and wearable systems for personal multimedia require the development of flexible energy devices [1,2]. Flexible supercapacitors have played an increasingly important role in power source applications, since they combine the advantages of high power of conventional capacitors and the high specific energy of batteries [3–6]. Supercapacitors are based on electrostatic charge accommodation at the electrical double-layer and the occurrence of superficial Faradaic reaction [5,7]. The capacitance of a redox supercapacitor consisting of electroactive materials with several oxidation states or structures (e.g. transition metal oxides and conducting polymers) is expected to be higher than that of a double-layer capacitors [3,4]. Among the available metal oxides, RuO_2 shows the best performance, but the high cost inhibits its commercial application [8–10]. Hence, the conducting polymers such as polyaniline (PANI) have advantageous properties with respect to low cost, ease of synthesis, good stability in air as well as relatively high conductivity [11–13]. It is well known that, the materials in the nano-size form are expected to yield significantly improved utilization of supercapacitor electrodes via enhancement in the electrode/electrolyte interface areas and decrease in the cation diffusion length within active materials [14–16]. Recently, synthesis of nano-sized PANI with exceptional conductive properties has been reported to be achieved by using porous carbon, carbon nanotubes, or even graphene as a nano-architectural template that not only increases the specific capacitance to 233–1220 F g^{-1} but also mitigates the cycle degradation issues caused by mechanical problems [14,17–21]. In the real applications, the area-normalized capacitance values (F cm^{-2}) are a better indicator of the performance of supercapacitor, although the gravimetric capacitance values (F g^{-1}) have always been used in the literature for comparison of the performance for supercapacitor. Usually, most electrodes with low amounts PANI loading achieve very high gravimetric capacitance values, but poor area-normalized capacitance values; which restrict their utility in practical applications. Therefore, simultaneously achieving high gravimetric as well as area-normalized capacitance values for electrodes is crucial for their commercial success.

In the present study, we present a simple and convenient route to directly fabricate PANI-NWs onto the surface of carbon cloth (CC) by an electrochemical method. CC was specifically selected as the current collector due to its cost-effectiveness, high conductivity, reasonable chemical stability, and a 3D structure with high porosity (hence high surface area) for PANI-NWs growth. In addition, the flexible nature of CC is also preferable for fabrication of flexible-electrode from the design and packaging perspectives. Moreover, unlike other powdered-type supercapacitors, the PANI-NWs/CC is

* Corresponding author. Tel.: +886 2 33665249; fax: +886 2 23655404.
** Corresponding author at: Center for Condensed Matter Sciences, National Taiwan University, Taipei 106, Taiwan. Tel.: +886 2 33665249; fax: +886 2 23655404.
E-mail addresses: chenlc@ntu.edu.tw (L.-C. Chen), chenkh@pub.iams.sinica.edu.tw (K.-H. Chen).

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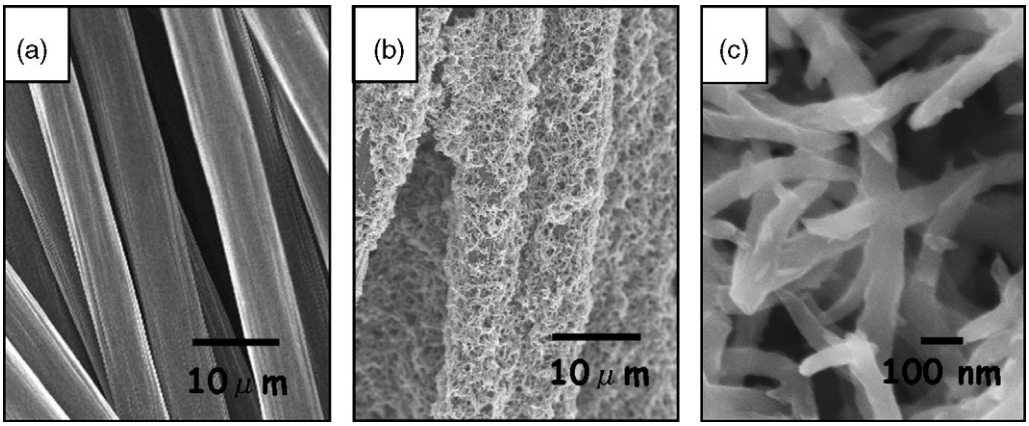

Fig. 1. SEM images of (a) original carbon cloth prior to the deposition of polyaniline, (b) surface of PANI-NWs/CC electrode, and (c) higher-magnification SEM image of the distribution of free-standing, randomly oriented PANI-NWs on carbon cloth.

a binder-free electrode that enables reduction in interfacial resistance and enhances the electrochemical reaction rate. As regards to the porosity of PANI-NWs/CC, the network of comparatively large pore sizes in CC is expected to facilitate the diffusion of electrolyte into the electrode material, thus providing channels for rapid transport of conductive ions. In this work, an excellent capacitive performance of this novel PANI-NWs/CC electrode, that simultaneously exhibits high gravimetric as well as area-normalized capacitance values, is demonstrated.

2. Experimental

2.1. Materials

Carbon cloth (B-1, Designation A: plain-weave, 116 g m^{-2}, 0.35 mm thickness; no wet-proofing) was purchased from E-TEK Division (USA). Aniline, sulfuric acid and hydrochloride were of analytical-reagent grade from Riedel-de Haën (Hannover Germany).

2.2. Fabrication of PANI-NWs/CC electrodes

Deposition of PANI onto CC (geometrical area ~0.375 cm^2) was performed by two-step electrochemical polymerization of aniline (0.2 M) and hydrochloric acid (0.5 M) following the procedure reported in the literature [22]. After deposition, the electrodes were washed free of aniline monomer using 0.5 M hydrochloric acid solution and stored at 4 °C in hydrochloric acid solution. The loading amount of PANI on the CC electrode is determined by the weight difference of the electrode before (without PANI coating) and after polymerization, measured using a microbalance with an accuracy of 10 μg (Sartorius BP 211D, Germany). The area-normalized capacitance values (F cm^{-2}) were calculated from the galvanostatic charge/discharge curves, $Cp = It/\Delta Va$; where I is the discharge current in ampere, t the discharge time in seconds responding to a potential difference of ΔV in volt, and a is the active geometrical area of the electrode in cm^2.

2.3. Assembly of symmetrical PANI-NWs/CC capacitors

Symmetrical capacitors (see Fig. 5a), PANI/cellulose/PANI (hereafter referred to as PANI capacitor) were assembled with cellulose film as separator by sandwiching the PANI-NWs/CC electrodes. Cellulose film is the main constituent of paper and an inexpensive insulting separator. Before assembly, the PANI-NWs/CC electrodes were soaked in an electrolyte of 1 M H_2SO_4 for about 10 min. This step allowed filling of the pores of polymer matrix by the aqueous electrolyte.

2.4. Measurements of PANI-NWs/CC electrode characteristics

The morphologies of PANI-NWs/CC electrodes were investigated using field-emission scanning electron microscopy (FESEM, JEOL-6700). In order to evaluate the electrochemical capacitance performance of PANI-NWs/CC, cyclic voltammetry (CV), galvanostatic charge/discharge method and AC impendence analysis were employed. Electrochemical measurements were performed using a potentiostat (Autolab/PGSTAT12) at ambient temperature in 1 M H_2SO_4 aqueous solution as electrolyte, using a conventional three-electrode system consisting of the PANI-NWs/CC electrode as working electrode, platinum wire as auxiliary electrode, and Ag/AgCl (3 M KCl) as reference electrode.

3. Results and discussion

3.1. Characteristics of PANI-NWs/CC composite

SEM observations, as shown in Fig. 1b, elucidate a distribution of dense but randomly oriented nanostructured PANI on the surface of CC. For comparison, the morphology of the original CC is also shown in Fig. 1a. The high-magnification SEM image in Fig. 1c illustrates free-standing wire-like structures of PANI-NWs, with 60–80 nm in diameter and several microns in length. Such nanostructure of PANI can be expected to provide significant enhancement in the active-surface area for high performance electrochemical capacitors. Moreover, the reasonably binder-free interface between the PANI-NWs and CC further benefits a rapid electron-transfer, resulting in improved charge storage and delivery.

3.2. Capacitive performance

The results of the CV measurements using a conventional three-electrode system on PANI-NWs/CC and bare CC electrodes are shown in Fig. 2a within the potential window of −0.2 to 0.8 V, at the scan rates of 5, 10, 25 and 50 mV s^{-1} in 1 M H_2SO_4 electrolyte. Notably, the CV results of PANI-NWs/CC are almost three orders of magnitude higher than that of bare CC recorded in the same electrolyte at a scan rate of 10 mV s^{-1}. This improvement in the capacitive performance of PANI-NWs/CC electrode is, hence, believed to have resulted from the PANI-NWs not the CC. Further, as can be seen from the SEM images, deposition of PANI uniformly covers the entire surface of CC. In this case, the weight of PANI-NWs on the CC is considered in the calculation of specific capacitance for PANI-NWs/CC electrode in order to deduce a meaningful capacitive performance. It may be noted from Fig. 2a that with an increase in scan rate, the current density also increases.

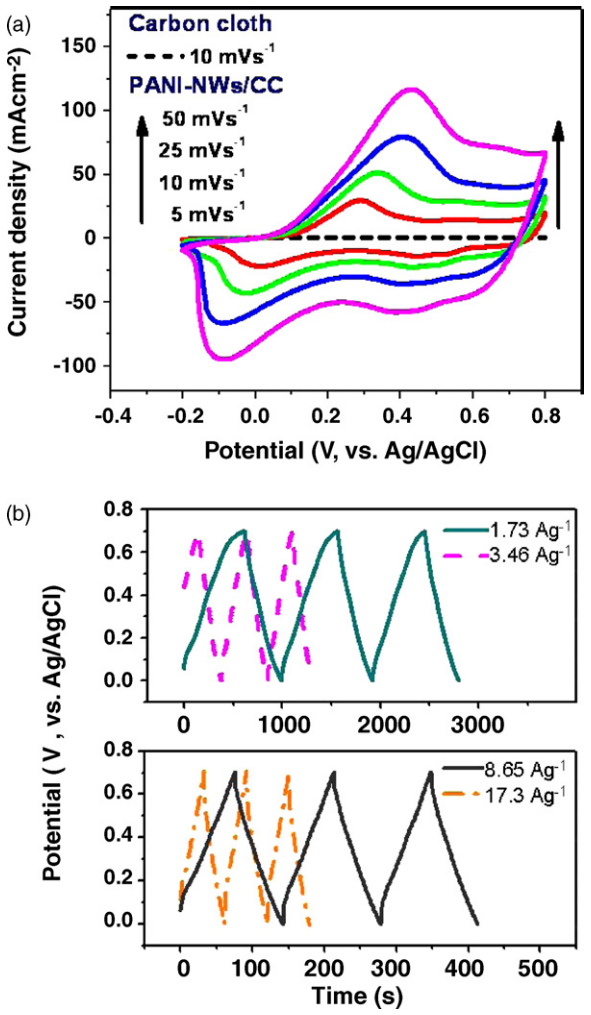

Fig. 2. The electrochemical capacitance performance of PANI-NWs/CC electrodes in 1 M H_2SO_4, using a conventional three-electrode system. (a) Cyclic voltammetry of PANI-NWs/CC (solid line) and carbon cloth (dash line) electrode at different scan rates. (b) Charge–discharge tests within the potential window of 0–0.7 V vs. Ag/AgCl.

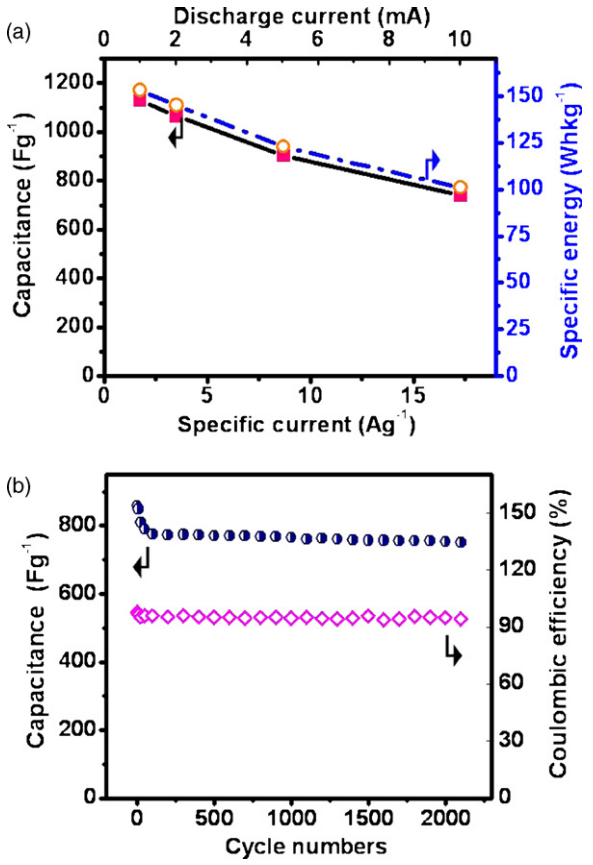

Fig. 3. (a) Gravimetric capacitance (square data points) and specific energy (circular data points) as functions of charge–discharge current density. (b) Stability tests of the PANI-NWs/CC electrode at a current density of 8.65 A g^{-1} for 2100 cycles (circular data point: capacitance; diamond data point: coulombic efficiency).

This implies that the redox reaction is not kinetically limited at least within the scan rates of 5–50 mV s^{-1}, thus, indicating a significant rate capability. Fig. 2b shows the charge–discharge curves of PANI-NWs/CC electrodes at different discharge currents within a potential window of 0–0.7 V. The gravimetric capacitance of PANI-NWs/CC electrode, as calculated by the specific capacitance relationship reported in the literature [23], at a discharge current of 1.73 A g^{-1} is 1079 F g^{-1}, which corresponds to the area-normalized capacitance of 1.8 F cm^{-2}. This value of area-normalized capacitance is normalized by the geometric area of the electrode. To the best of our knowledge, this value of area-normalized capacitance is the highest reported to date for the PANI-based supercapacitors. The gravimetric capacitance of the PANI-NWs/CC electrode as a function of different discharge currents is shown in Fig. 3a. The gravimetric capacitance of the electrode (square data points) can be seen to decrease with increasing charge–discharge current. The capacitance retention is about 70%, with increase in current density from 1.73 A g^{-1} to 17.3 A g^{-1}. Similarly, the specific energy (circular data points in Fig. 3a) of the electrode also decreases with increasing charge–discharge current. From the above measurements, a maximum power density of 12.1 kW kg^{-1} is obtained for the PANI-NWs/CC electrode at a specific energy of 100.9 Wh kg^{-1} [24].

The cycling performance of the PANI-NWs/CC electrode was also studied at a current density of 8.65 A g^{-1} in 1 M H_2SO_4 aqueous electrolyte. As shown by circular data points in Fig. 3b, the gravimetric capacitance of the electrode in the first cycle is 858 F g^{-1}, which slowly decrease to 752 F g^{-1} in the 2100th cycle corresponding to 14% decrease from initial capacitance. A small decrease in the gravimetric capacitance value can also be seen in the first 100 cycles, while the capacitance remains almost constant thereafter, which indicates that this electrode has a long-life electrochemical stability. Furthermore, during the cycling process, the coulombic efficiency which is the ratio of charge capacitance and discharge capacitance, exhibits retention of as high as 98% (see diamond data points in Fig. 3b). Thus, the superior performance of PANI-NWs/CC obtained here confirms the advantages of the loosely packed structure of PANI-NWs/CC that facilitate the fast penetration of the electrolytes through PANI-NWs to allow rapid electron-transfer for charge storage and delivery.

3.3. Estimation of diffusion length in the PANI-NWs/CC electrodes

In order to understand the optimum diameter of PANI-NWs in PANI-NWs/CC electrodes for effective cation diffusion, we estimated the diffusion length of protons in PANI-NWs using the impedance analysis. Fig. 4 shows the typical characteristics of the PANI-NWs/solution interface, the generalized equivalent circuit, and the Nyquist plot simulated for the equivalent circuit of the PANI-NWs/CC. The diffusion length L of ions within the electrode during the charge–discharge process can be estimated as $(D \times \tau_d)^{1/2}$, where D and τ_d are the diffusion coefficient and time, respectively [25]. The charge transport in a thin polymer film is limited by the finite film thickness [26]. Therefore, for the nanometer-size active material, the reduced diffusion length

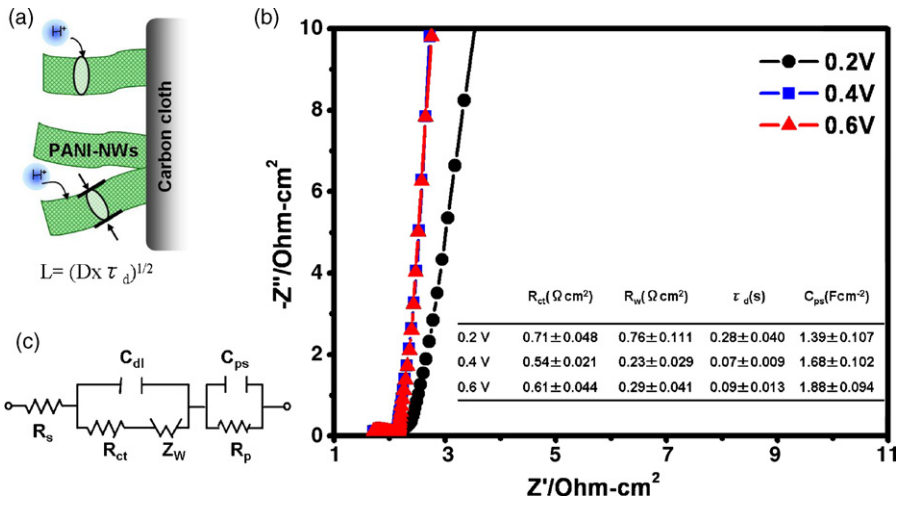

Fig. 4. (a) Schematic representation of how the required diffusion length is reduced in the PANI-NWs/CC electrode. (b) The Nyquist plot of the PANI-NWs/CC at various applied potentials. Insert: the best fitting values of the equivalent circuit parameters. (c) The equivalent electric circuit used in fitting the experimental data.

(L) will ensure high utilization of the electrode material. The impedance spectra measured for PANI-NWs/CC electrode at different applied potentials, with amplitude of 10 mV, from 100 kHz to 50 mHz, are shown as Nyquist plots in Fig. 4b. The equivalent circuit for the electrodes is also presented in Fig. 4c which consists of the following elements: the bulk solution resistance (R_S), double-layer capacitance (C_{dl}) which is expected to exist in parallel to the charge transfer resistance (R_{ct}), and a Warburg diffusion element (Z_W) attributable to the diffusion of ions and relative to τ_d [25,27,28]. Moreover, the capacitive nature of the PANI-based electrode in the low-frequency domain could be reasonably represented by a pseudocapacitance (C_{ps}), which is mainly attributable to the faradaic process of PANI redox transition, in parallel with a PANI resistance (R_p). The values of R_{ct}, R_w, τ_d and pseudocapacitance C_{ps} were calculated from the CNLS fitting of the experimental impedance spectra. Based on the fitting results in Fig. 4, the maximum capacitance of PANI-NWs/CC can be obtained as $1.88 \pm 0.094\,F\,cm^{-2}$. Here, the normalized factor of the capacitance is the geometric area of the electrode since the capacitance performance is contributed from the NW + CC composite electrode. This result is consistent with the area-normalized capacitance of $1.8\,F\,cm^{-2}$ from charge/discharge method of PANI-NWs/CC electrode. The effective diffusion length was estimated to be about 60 nm at the 0.4 V, based to the equation $(D \times \tau_d)^{1/2}$; $D = 5 \times 10^{-10}\,cm^2\,s^{-1}$ [29]. Since the average diameter of these NWs is about 60–80 nm, the diffusion length of about 60 nm implies that the electrochemical performance of PANI-NWs/CC electrode is not limited by diffusion process (i.e. by the thickness of PANI-NWs).

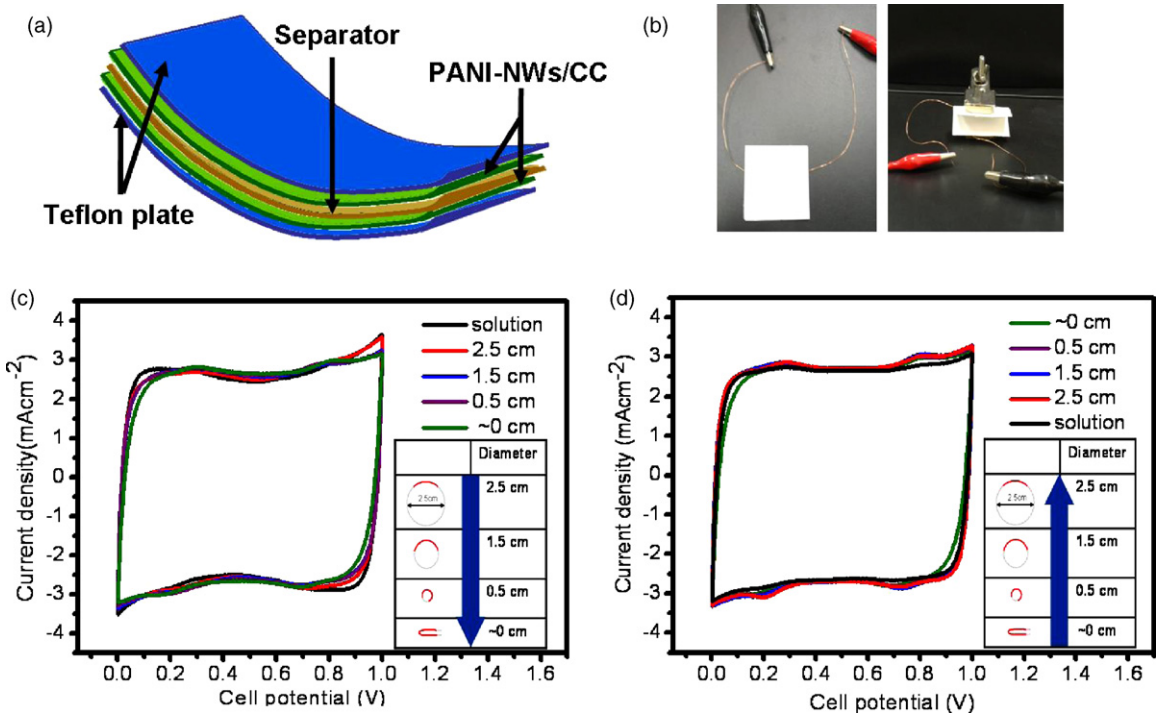

Fig. 5. (a) Schematic of the flexible supercapacitor made of PANI-NWs/CC, using a conventional two-electrode system. (b) Photographs demonstrating mechanical flexibility of PANI capacitors. Flat sheet (left), and curvature cells (right) are shown. Comparison of cyclic voltammograms. (c) PANI capacitor bended with diameters of curvatures from 2.5 cm to 0 cm. (d) PANI capacitor returned the diameters from 0 cm to 2.5 cm at a scan rate of $10\,mV\,s^{-1}$.

3.4. Flexibility test

The schematic diagram of the flexible supercapacitor made of PANI-NWs/CC with cellulose film as separator by sandwiching the PANI electrodes and 1 M H_2SO_4 as the electrolyte is shown in Fig. 5a using a two-electrode system. Optical photographs (left: flat sheet and right: curvature cells) were taken to demonstrate the mechanical flexibility of PANI capacitors. Comparison of PANI capacitors bended with diameters of curvature from 2.5 cm to 0 cm (Fig. 5c) and PANI capacitors returned the diameters from 0 cm to 2.5 cm (Fig. 5d) at a scan rate of 10 mV s^{-1} showed similar capacitive behavior with capacitance loss only of 0.05%, indicating their highly flexible and completely recoverable properties. Recently, several routes toward the energy storage devices with improved mechanical flexibility to meet the requirements of soft portable electronic equipment have been demonstrated [1,2,30]. To the author's knowledge, such superior flexibility has not been systematically and quantitatively demonstrated for other flexible batteries or supercapacitors.

4. Conclusions

In summary, we have successfully fabricated flexible-electrode by direct growth of PANI-NWs via electrochemical deposition onto CC surface and also demonstrated excellent capacitive performance in both gravimetric as well as area-normalized capacitance values for these PANI-NWs/CC electrodes. According to the galvanostatic charge/discharge analysis, the gravimetric capacitance of 1079 F g^{-1} was obtained at a specific energy of 100.9 Wh kg^{-1} and a specific power of 12.1 kW kg^{-1}. Significantly, extremely high magnitude of the area-normalized capacitance (1.8 F cm^{-2}) can be achieved in this novel nanocomposite wherein the architecture is favorable for effective cation diffusion. Furthermore, the present study also suggests the potential of large-scale application of PANI-NWs/CC electrodes as flexible and electrochemically stable supercapacitor.

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