Printed energy storage devices by integration of electrodes and separators into single sheets of paper

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We report carbon nanotube thin film-based supercapacitors fabricated with printing methods, where electrodes and separators are integrated into single sheets of commercial paper. Carbon nanotube films are easily printed with Meyer rod coating or ink-jet printing onto a paper substrate due to the excellent ink absorption of paper. A specific capacity of 33 F/g at a high specific power of 250 000 W/kg is achieved with an organic electrolyte. Such a lightweight paper-based supercapacitor could be used to power paper electronics such as transistors or displays. © *2010 American Institute of Physics*. [doi:10.1063/1.3425767]

The emerging area of printed electronics has potential applications such as flexible, lightweight displays.[1–5] Plastic substrates such as polyethylene terephthalate (PET), polyethylene naphthalate, or polycarbonate substrates are currently in wide use due to their low cost, flexibility, and smooth surfaces. Building devices on paper, a material which is ubiquitous in everyday life, could take advantage of existing, well developed paper printing technologies. Various types of devices, such as thin film transistors, active matrix displays, sensors, and radio-frequency identification devices[6–11] have been fabricated on paper substrate; these electronics applications take advantage of the low cost and disposability of paper. The major obstacle of using paper for electronics is its rough surfaces; therefore, planarization by surface treatment or surface coating before device fabrications is generally needed. However, the rough surfaces of paper are not problematic for energy storage devices such as Li-ion batteries and supercapacitors. Also, paper-based energy storage devices are necessary for all-paper electronics to operate. Batteries and supercapacitors have been fabricated on paperlike substrates using single walled carbon nanotubes (SWNTs).[12] In this previous study, a cellulose/SWNT composite is used as either the current collector or electrode in devices. However, these devices do not use existing commercial paper and are not printable. Recently, we reported a method for making conductive paper for batteries and supercapacitors based on nanomaterial ink containing SWNTs or Ag nanowires, where conductive paper is either used as the electrodes, current collectors, or both.[13] We also showed that a similar method can be applied for the fabrication of energy storage devices on textile substrates.[14] In our previous report and for the textile devices, nanomaterials are coated separately onto different anode and cathode substrates and are assembled together with a separator. Here we demonstrate an integrated structure, in which the anode, cathode, and separator are integrated on a single sheet of paper. Such an integrated structure allows for the use of high-speed printing, which could lead to low cost, lightweight paper-based energy storage devices for disposable paper electronics. We have fabricated supercapacitors as an example to demonstrate this concept, which can also be extended to batteries. The printing techniques we use in this study include continuous Meyer rod coating and ink-jet printing for generating patterns.

When SWNTs are directly printed onto a paper substrate, the micron-sized pores in paper allow the tubes to penetrate and cause the device to short circuit if all the components are integrated onto a single sheet of paper. To solve this problem, we first treated the paper substrates with polyvinylidene fluoride (PVDF). Overcoating PVDF has been used on both sides of porous membranes to fabricate the separator membrane for Li-ion batteries.[15] 10% PVDF (Kynar® HSV 900) in methylpyrrolidone was dropped onto a paper substrate. A Meyer rod with a coating thickness of 5 μm was pulled over the PVDF ink and the paper was dried at 65 °C in an oven for 20 min. The same coating and drying technique was then applied on the other side of the paper. Thus, coated paper without large holes is achieved [Fig. 1(a)]. The thin layer of PVDF coating on the paper still allows for the transport of electrolytes through the paper, so that the treated paper can still function as an electrolyte membrane and separator without allowing SWNTs to short the device. Figure 1(b) illustrates our supercapacitor device structure with integration of electrodes and separators into single sheets of paper. For coating SWNTs on treated paper, an ink with a concentration

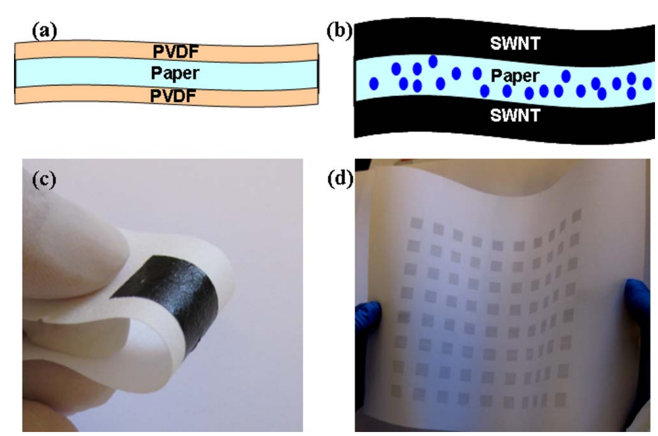

FIG. 1. (Color online) (a) Schematic of Xerox brand printer paper treatment with PVDF; this treatment is used to block the micron-sized pores to avoid short circuiting because of SWNT penetration. (b) Paper supercapacitor structure with SWNT film printed on both sides of the treated Xerox paper. The SWNT film is either Meyer rod-coated or ink-jet printed. (c) A photo of a Meyer rod-coated supercapacitor on Xerox paper. (d) A photo of ink-jet printed supercapacitor on Xerox paper.

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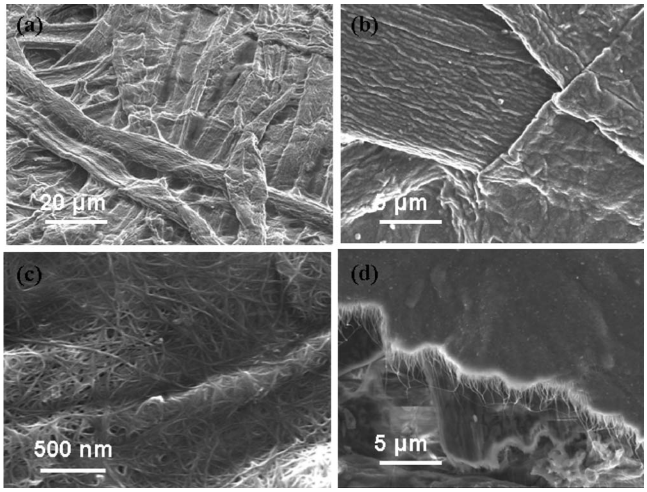

FIG. 2. (a) SEM image of Xerox brand printer paper surface showing rough surface morphology on the micron scale. The paper fibers have a diameter of 10–20 μm. (b) SEM image of SWNT film coating on 50 nm PVDF-treated Xerox paper. SWNTs are conformally coated on paper fibers, bridging the fiber gaps which lead to high electrical conductivity. (c) Zoom of (b) to show the conformal coating of SWNTs. (d) Cross section of SWNT film on PVDF-treated Xerox paper. There are no SWNTs protruding into the paper to short the supercapacitor device.

of 2.0 mg/mL SWNT in water was prepared, and 1% sodium dodecylbenzenesulfonate (SDBS) surfactant is used. The ink was coated by using the Meyer rod method on both sides of the PVDF-treated paper.[16] The thickness of the wet SWNT film can vary from 4 to $\sim$100 μm depending on the choice of Meyer rod. We observed that a high concentration of SWNTs helps to avoid device short circuiting due to the high density of SWNT junctions on the paper substrate. When 0.5 mg/mL SWNTs in water is used, we found that the devices are occasionally shorted. Figure 1(c) shows a printed supercapacitor using the Meyer rod coating method. The well-defined area of SWNTs coating is achieved by using tape to protect the uncoated area.

For certain devices, such as sensor arrays on paper, miniaturized power devices are needed. We used an ink-jet printing method to print the supercapacitor arrays on paper. For this process, an ink-jet printer (Dimatix Materials Printer DMP-2800) with 16 nozzles was used. The spacing of individual dots is 50 μm with an overlap of 30 μm. It takes about one minute to print the patterns shown in Fig. 1(d) onto one side of the paper. The same ink was used for ink-jet printing and Meyer rod coating. Due to the high liquid absorption of paper, ink-jet printing is easily carried out without causing lines or defects in the pattern. In our comparison experiment, ink-jet printing of the same ink onto a plastic PET substrate causes line defects along the direction of nozzle movement.

As when writing with a pen or pencil on paper, the SWNT coating experiences strong binding forces which allows the coating to pass the tape or rubbing test.[13] Figure 2(a) shows an SEM image of the morphology of Xerox brand printer paper. The rough surface is detrimental in paper-based electronic devices such as transistors or thin film solar cells; however, it is not problematic for energy storage devices. The rough surface could be advantageous for energy storage devices due to a greater degree of electrolyte absorption and increased access of the electrolyte to the electrode material; in this case, the SWNT coating. Figure 2(b) shows an SEM image of the conformal coating of SWNTs on paper with a thickness of $\sim$3 μm. The sheet resistance measured by a four-point probe is $\sim$10 Ω/sq. Due to the large aspect ratio and the excellent flexibility of SWNTs, the SWNTs bend over the rough surface and follow the surface of paper fibersconform to the surface of the paper fibers, which leads to the high electrical conductivity [Fig. 2(c)]. To confirm that there are no SWNTs that penetrate the paper membrane, SEM images of the cross sections of coated paper were taken, as shown in Fig. 2(d). In Fig. 2(d), the SWNTs form a film on the paper surface. This may be due to the high viscosity of the SWNT ink and the agglomeration of SWNTs even in the solution. Occasionally, SWNTs were found in the paper if a diluted SWNT ink was used. The highly conductive, nonshorted membrane and the large binding between the SWNT ink and the paper surface lead to mechanically stable supercapacitor devices that can be fabricated through this simple printing process.

We also coated SWNTs on different types of paper after PVDF treatment, which include Kodak brand color printing paper, newspaper, and grocery advertisement papers. We found that the electrical conductivity is similar when 2.0 mg/mL SWNT ink is used, although the surface roughness for different papers is dramatically different. Figure 3(a) shows a printed supercapacitor with newspaper as both the substrate and the separator. The thickness of the entire device is $\sim$30 μm. To test the supercapacitor performance, coffee bag cells were made with platinum wire used for electrical connections. In such devices, the SWNT films act as both the current collectors and the electrodes. Therefore, there are only two following materials in the whole device: SWNTs and newspaper. The electrolyte is 1 M $LiPF_6$ in ethylene carbonate; diethylene carbonate=1:1 v/v (Ferro Corp.). The final device was tested with a MACCOR 4300 battery analyzer. The active area overlapped by both SWNT conductive paper substrates was 1 cm^2 and the mass was $\sim$0.3 mg/cm^2. The devices with an area of 1 cm^2 were tested with different currents, as shown in Fig. 3(b). The applied voltage was $0 < V < 3.0$ V. The linearity of the potential curve indicates excellent charge-discharge supercapacitor behavior. Based on the IR drop, the device impedance is found to be $\sim$30 Ω, which is mainly due to the SWNT current collector and the organic electrolyte. Based on the voltage profile and the mass density, the specific capacitance is calculated [Fig. 3(c)]. The specific capacitance is 33 F/g at a specific power of 250 000 W/kg, which is a reasonable value compared to other values in the literature.[17] Due to the lightweight SWNT films are used as the current collectors to replace heavy metals, the capacitance of assembled device could be greatly improved when compared with traditional supercapacitors. SWNT is with mass of 0.3 mg/cm^2, paper is $\sim$3 mg/cm^2, and metal is $\sim$10 mg/cm^2. Therefore, the capacitance of assembled paper supercapacitor is $\sim$3 F/g. The specific capacitance decreases with the current density, which is due to the decreased accessible electrode surface area with increasing current density. When compared with our previous study on paper supercapacitors,[13] the specific capacitance is two to three times smaller, which may be due to the possible blocking of electrolyte to the SWNT surface by the PVDF coating on the paper. The supercapacitor consisting of the printed SWNTs on newspaper shows excellent cycling stability, as shown in Fig. 3(d). There is very little loss of capacitance

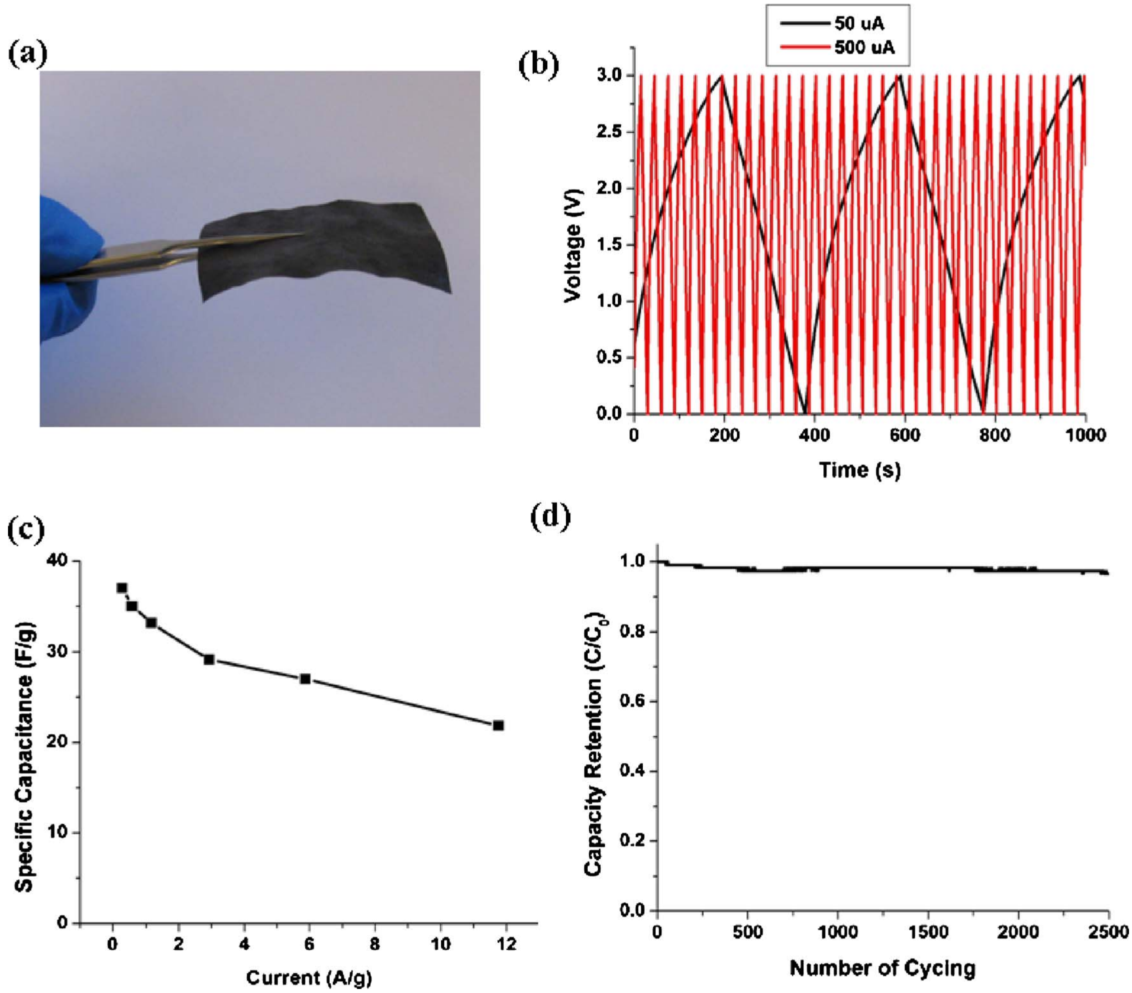

FIG. 3. (Color online) (a) A printed supercapacitor on a 30 μm thick newspaper substrate/separator membrane. (b) Charge-discharge performance of a printed paper supercapacitor with paper as both separator and substrate. (c) Specific capacitance at different current density. (d) Cycling performance of a printed paper supercapacitor with 1 mA/cm^2 current.

after 2500 cycles. The good cycling stability may be due to the excellent binding of SWNTs onto paper fibers.

In conclusion, we have successfully demonstrated a fully integrated printed supercapacitor on a paper substrate with SWNT ink and a paper surface pretreatment. The device structure is extremely simple, with SWNT films behaving as both the electrodes and the current collectors and paper as both the substrates and separator. In addition, the method for fabricating such a device is scalable and could be accomplished through roll-to-roll methods. Such a paper supercapacitor could be used to power other paper electronic devices and facilitate the development of fully paper-based electronics.

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