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# A low ion-transfer resistance and high volumetric supercapacitor using hydrophilic surface modified carbon electrodes<sup>†</sup>

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A hydrophilic surface modified carbon electrode shows a good electrolyte affinity with homogeneous dispersibility in water, resulting in low ion-transfer resistance and a uniform and dense electrode to give a high volumetric capacitor. The hydrophilic carbon electrode exhibits a superior capacitance (58 F  $\rm cm^{-3}$ , 99.3 mF cm<sup>-2</sup>) and is stable up to 5000 cycles.

# Introduction

Recent increase in the use of various portable and flexible electronic devices has generated a growing demand for advanced energy storage devices that are lightweight, flexible, highly efficient, and require a short charging time.<sup>1</sup> Supercapacitors have received a great deal of attention as next generation energy storage systems due to their outstanding characteristics such as high power density, long cycle life, safety, fast charge–discharge rate, and high efficiency.<sup>2–10</sup> Supercapacitors undergo a simple charge storage and release mechanism based on an electrostatic interaction between the electrolyte and the electrode surface called electrical double layer capacitance (EDLC).<sup>2–6</sup> The simplicity of this mechanism of energy storage allows a number of advantages.

For the supercapacitors based on EDLC, low resistance of the electrode material and its high accessibility with the electrolyte are the most decisive factors. To achieve high accessibility and penetration of ions from the electrolyte into the electrode, several composite designs have been adopted such as graphene–CNT<sup>7</sup> (carbon nanotube) and graphene–CDC<sup>8</sup> (carbon derived carbon). CNTs and CDCs can effectively exfoliate graphene sheets and prevent restacking, resulting in enhanced electrolyte accessibility.<sup>2,7,8</sup> Another interesting attempt to enhance ion accessibility is using in-plane or vertical structures, which successfully increase ion accessibility and penetration between two vertically aligned electrodes, resulting in high capacitance and low ion-transfer resistance compared to the common 2D-stacked normal supercapacitors.<sup>9</sup>

On the other hand, additional strong demands for the power sources for portable electronic devices require compactness and integration with other electronic components like solid chip type devices.9-13 In addition, miniaturizing power sources into solid-chip design devices can potentially increase the density of electronic devices with various functions and expand their applications.<sup>9,10</sup> Despite these advances, low energy density remains the biggest challenge and obstacle for the realization of carbon-based supercapacitors.14 Practically, the volumetric specific capacitance (F cm<sup>-3</sup>) and areal specific capacitance  $(F \text{ cm}^{-2})$  of supercapacitors based on carbon materials are very low due to their low density (g  $cm^{-3}$ ). Likewise, the thickness of electrodes on supercapacitors with common 2D stack structures is strongly restricted to a few micrometres and a very low loading amount due to their low ion diffusion and penetration properties into the electrodes, and thus they usually exhibit a very low volumetric specific capacitance (3–50 mF  $cm^{-2}$  or less) and restrict realization of supercapacitors.<sup>5,11,15</sup> According to a previous study, the laser-scribed graphene electrode shows 4.04 mF cm<sup>-2</sup> areal capacitance and less than 0.5 F cm<sup>-3</sup> volumetric capacitance with a H<sub>2</sub>SO<sub>4</sub>-PVA solid electrolyte.<sup>5</sup> The all-solid-state micro-SC based on graphene and H<sub>3</sub>PO<sub>4</sub>-PVA shows 0.462 mF cm<sup>-2</sup>.<sup>13</sup> The micro-SC using a graphene and CNT composite electrode exhibits 6.1 mF cm<sup>-2</sup> at 10 mV s<sup>-1,<sup>23</sup></sup> Actually, there are many studies concerning the RGO-CNT composite with superior capacitance performance. Most of them checked capacitance properties under solution electrolytes and 3 electro-measurement systems. Still, the study of solid-state supercapacitors is rare and shows a very low volumetric capacitance even though RGO-CNT composite electrodes are used (see the comparison tables in Table S1<sup>+</sup> for RGO-CNT supercapacitors and Table S2<sup>†</sup> for solid-state supercapacitors).

Here, we demonstrate a low resistance and high volumetric on-chip type solid-state supercapacitor (SSC) using hydrophilic surface modified multi-walled CNTs (MWCNTs) and reduced graphene oxide (RGO). The hydrophilic surface modified

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carbon electrode is expected to show good electrolyte affinity and homogeneous dispersibility in water, resulting in low resistance and a uniform and dense electrode to give high volumetric capacity. Especially, for the good accessibility of the electrolyte into the carbon-based electrode, we carefully design the surface modified MWCNTs with hydrophilic sulfonate groups ( $R-SO_3^-$ ), which leads to a hydrophilic surface of the outer carbon nanotube, while maintaining high electric conductivity through inner carbon nanotubes. Different from previous results, this hydrophilic carbon composite film electrode exhibits a much lower series resistance and simultaneously lower charge-transfer resistance despite its highly dense structure (over 0.9 g cm<sup>-3</sup>).

### Experimental

#### Preparation of diazonium salts

4-Benzenediazonium sulfonate was synthesized by diazotization of *p*-sulfonic acid (Aldrich). In a three-necked round bottom flask, 12.99 g (0.075 mol) of *p*-sulfonic acid was dispersed in 1 M HCl. To the well-stirred suspension in an icewater bath (3–5 °C), a 10% excess of 1 M aqueous solution of NaNO<sub>2</sub> (82.5 ml) was added. Solid *p*-sulfanilic acid was slowly dissolved during the addition of NaNO<sub>2</sub> and a clear solution was obtained after the NaNO<sub>2</sub> solution was added completely. The resulting mixture was then stirred for another 45 min at the same temperature. A white precipitate was formed and was collected by filtration, washed with cold water, and then dried under vacuum.

#### Preparation of SCNTs

200 mg of MWCNTs were added to a three-necked round bottom flask with 10 ml of distilled water and 10 ml of ethanol. The mixture was then sonicated for 30 min and cooled to 0–5 °C in an ice bath. Next, 10 ml of hypophosphorous acid (H<sub>3</sub>PO<sub>2</sub>, 50%, Aldrich) and the prepared 4-benzenediazonium sulfonate powder (1.2 g) were added to the MWCNT mixture under stirring. After stirring for 1 h, an additional 10 ml of H<sub>3</sub>PO<sub>2</sub> aqueous solution was added. The mixture was then stirred at 5 °C for another 6 h. The resulting product was filtered with a nylon membrane (0.45 µm, Whatman) and repeatedly washed with distilled water. Finally, the resulting powder was dispersed in D.I. water with 0.5 mg ml<sup>-1</sup> by sonication, and left to stand for 2–3 days. The resulting SC solution without sedimentation was collected and dried at R.T.

# Preparation of film-RGO-SCNT and spray-RGO-SCNT electrodes

Graphene oxide (GO) was prepared from natural flake graphite (Bay Carbon, SP-1) by an improved method that was previously described.<sup>20</sup> GO was dispersed into distilled water at a concentration of 1 mg ml<sup>-1</sup> and a SCNT dispersion was also prepared at a concentration of 0.5 mg ml<sup>-1</sup> in distilled water. The SCNT solution was then added to the GO solution under stirring. The resulting mixture was sonicated for 1 h, and filtered by vacuum filtration with an Anodisc (0.2  $\mu$ m, with a support ring,

Whatman). After drying in a vacuum oven (60 °C), the GO–SCNT composite films were reduced by HI vapor reduction with 0.2 ml of HI (57 wt%, Aldrich) and 0.5 ml of acetic acid (99.5 wt%, OCI Company Ltd) in a 300 ml chamber at 40 °C for 24 h.<sup>21</sup> For spray-RGO–SCNT electrodes, the dispersed mixture solution of GO and SCNTs was sprayed using a spray-gun with a specific pattern mask on a PET substrate, which was heated to 100 °C during the spraying process. After spray coating, the pattern electrode was dried under vacuum at 60 °C for 24 h. The dried electrode was then reduced by hydrazine (35%, 0.3 ml, Aldrich) vapour reduction in a 300 ml chamber at 90 °C for 24 h. After reduction, the electrode was repeatedly washed with D.I. water, and then dried under vacuum at 60 °C for 24 h.

#### Fabrication of supercapacitor cells

To prepare film electrode supercapacitors, the as-prepared electrode films were cut into 10 mm  $\times$  5 mm square pieces. Two pieces of electrode films were placed on opposite sides of the PET substrate with a 0.2–0.3 mm gap and attached with ketone tape. Pt foil (thickness; 0.1 mm) was used as a current collector, and was also attached using ketone tape covering the electrode films with a width of 0.2 mm. A PVA (10 wt% with H<sub>2</sub>O) solution containing 10 wt% of H<sub>2</sub>SO<sub>4</sub> was then cast on the electrodes. After drying on a clean bench for 1 day to remove excess H<sub>2</sub>O, electrochemical measurements were carried out. Spray pattern electrodes were fabricated by the same procedure using Pt foil and an H<sub>2</sub>SO<sub>4</sub>/PVA electrolyte.

#### Characterization

Microstructural characterization was performed using a JEOL JSM-7404F field emission scanning electron microscope operating at 15 kV. XPS measurements were conducted using a Thermo VG Microtech ESCA 2000 with a monochromatic Al-K $\alpha$ X-ray source at 100 W. Water contact angle FT-IR spectra were collected using a Thermo Nicolet AVATAR 320 instrument. Contact angles were measured using a SEO Phoenix 300 microscope.

#### **Electrochemical characterization**

Cyclic voltammograms of SSCs were measured at various scan rates. The volumetric capacitance derived from CV curves was calculated according to the following equation:  $C = 2(\lceil IdV \rceil)/2$  $(sv\Delta V)$ , where I is the voltammetry current, s is the potential scan rate, V is the potential for one sweep segment, and v is the volume of one electrode. The galvanostatic charge-discharge curves of SSCs were obtained at 2 mA cm<sup>-2</sup>. The volumetric capacitance derived from galvanostatic discharge curves was calculated based on the following equation:  $C = 2(I\Delta t)/(v\Delta V)$ , where I is the discharge current,  $\Delta t$  is the time taken for full discharge, v is the volume of one electrode, and  $\Delta V$  is the change in potential during discharge. The effective series resistance (ESR) was estimated using the voltage drop at the beginning of the discharge,  $V_{drop}$ , at a certain constant current  $I_{\rm cons}$ , with the formula  $R_{\rm ESR} = V_{\rm drop}(2I_{\rm cons})$ . Energy density (E) and power density (P) were calculated from galvanostatic discharge curves by the equations  $E = (1/8)C\Delta V^2$  and  $P = E/\Delta t$ ,

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where *C* is the volumetric capacitance,  $\Delta V$  is the change in potential during discharge, and  $\Delta t$  is the time taken for full discharge. The electrochemical impedance spectroscopy measurements were performed over a frequency range from 10<sup>6</sup> to 10<sup>-2</sup> Hz using a CHI660D electrochemical workstation. Based on a RC model, the capacitance was also calculated using the frequency response analysis, by  $C = -1/(2\pi f Z'')$ , where *f* is the frequency in Hz and Z'' is the imaginary part of the impedance, to show the trend of changes in capacitance with frequency.<sup>4</sup>

## Results and discussion

As expected, the sulfonate functionalized MWCNTs (SCNTs, Fig. 1a) are well-dispersed in water and freely mixed with graphene oxide (GO) to give a uniform GO-SCNT film, followed by reduction of GO-SCNT to finally give reduced graphene oxide (RGO-SCNT) films (Fig. 1b). Flexible and uniform film electrodes (Fig. 1c) are fabricated by vacuum filtration using an Anodisc, and the specific patterned electrodes on the PET substrate (Fig. 1d) are prepared through a simple spray coating process with a patterned mask. The density of RGO-SCNT is approximately 40 vol% less than that of the normal RGO-CNT. The resulting high density of the RGO-SCNT film is attributed to the homogeneously mixed SCNTs without aggregation into the graphene sheets, which result in a better packing structure (Fig. S2<sup>†</sup>). For the hydrophilic-surface modified SCNTs, the aryl diazonium salts of sulfanilic acid are prepared as previously described and confirmed by <sup>1</sup>H NMR (Fig. S1<sup>†</sup>).<sup>16</sup> Surface functionalization of CNTs with aryl diazonium salts is performed by a chemical diazotization reaction using hypophosphorous acid (H<sub>3</sub>PO<sub>2</sub>, 50%, Aldrich)<sup>17</sup> and the CNTs are repeatedly washed with a large amount of D.I. water after the reaction. The as-prepared SCNTs are then characterized by Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS) and compared with CNTs. FT-IR spectra of SCNTs (Fig. S3b<sup>†</sup>) reveal differential adsorption features such as sharp peaks at 1036 cm<sup>-1</sup> and a broad peak around 1190 cm<sup>-1</sup>, which corresponded to the symmetrical and asymmetrical vibrational adsorptions of the  $SO_3$  group, respectively. The peak observed at 1120 cm<sup>-1</sup> is assigned to the in-plane bending vibration of the benzene ring.<sup>18</sup>

The XPS spectra from SCNTs exhibited peaks at 168.03 eV and 532.12 eV, which originated from SO<sub>3</sub> groups. The S and O contents of SCNTs are 2.8 and 13.8 at.%, respectively. Hydrophilic-surface treated SCNTs are completely different from normal CNTs, in that they are freely dispersed in water through simple sonication (Fig. S3a†). The SCNT solution (1 mg ml<sup>-1</sup> and 0.01 mg ml<sup>-1</sup> in H<sub>2</sub>O) can be uniformly mixed with a GO solution, and homogeneous and flexible RGO–SCNT films are subsequently prepared.

After HI vapor reduction, reference RGO films have a bright grey color and flat surface morphology according to field emission scanning electron microscopy (FE-SEM) images on both the up and down sides of the film (Fig. 2a). An RGO-SCNT50 composite film is prepared by mixing 50 wt% SCNTs and 50 wt% GO, followed by reduction of the mixed films. The RGO-SCNT50 film shows almost the same black color on both sides of the film and exhibits uniformly dispersed CNTs with a bundled microstructure and less aggregation (Fig. 2b). The black colored down-side morphology of the RGO-CNT50 films is attributed to aggregation of CNT bundles while the grey colored up side is attributed to exposure of RGO sheets, indicating that the CNT bundles are sparsely mixed with RGO sheets (Fig. 2c). On the other hand, according to the water contact angle, RGO films exhibit hydrophobic surface properties typical of chemically reduced graphene films.<sup>21</sup> As expected, the surface of the RGO-SCNT50 films is highly hydrophilic (water contact angle; 66.7° and 56.3° on the up and down sides of films, respectively) due to the presence of SO<sub>3</sub>H functional groups of SCNTs, and is significantly different from those of the RGO and RGO-CNT50 films. On the other hand, the down side of RGO-SCNT50 in comparison with the up side is more hydrophilic due to higher sedimentation of SCNTs at down-side during the vacuum filtration process. RGO-CNT50 films exhibit a more



Fig. 1 Schematic fabrication process of RGO–SCNT electrodes and images of (a) SCNTs and (b) RGO–SCNT electrodes. Optical images of the (c) film-RGO–SCNT electrode and (d) spray-RGO–SCNT electrode on the PET substrate.



Fig. 2 Optical images, SEM images (up and down sides), and water contact angles (up and down sides) of (a) RGO electrode films, (b) RGO-SCNT50 electrode films, and (c) RGO-CNT50 electrode films.

hydrophobic surface ( $82.4^{\circ}$  and  $89.8^{\circ}$  on the up and down sides of the film, respectively), which is due to the strong hydrophobic properties of CNTs. The bottom-side of RGO–CNT50 in comparison with up-side is more hydrophobic due to the existence of more CNTs at the bottom side.

We investigate the capacitance performance through the inplanar symmetrical two-electrode system. Prototype solid-state supercapacitor cells (Fig. 3a) are fabricated using as-prepared RGO-SCNT50 film electrodes (5 mm  $\times$  10 mm) and Pt foil (5 mm  $\times$  30 mm  $\times$  0.1 mm) as the current collector and then attached on a PET substrate. The as-prepared solid-state supercapacitors are evaluated by cyclic voltammetry (CV), galvanostatic charge-discharge, and Nyquist impedance plots. Fig. 3b shows the CV curves of RGO, RGO-CNT50, and RGO-SCNT50 at 20 mV s<sup>-1</sup>. RGO exhibits a narrow curve shape, whereas RGO-CNT50 and RGO-SCNT50 exhibit a rectangular curve shape. RGO-SCNT50 has the largest specific capacitance  $(33.2 \text{ F cm}^{-3})$ , while RGO-CNT50 and RGO exhibit capacitance values of 14 F cm<sup>-3</sup> and 3.3 F cm<sup>-3</sup> at the same scan rate, respectively. The specific capacitance and ESR calculated from galvanostatic charge-discharge curves (Fig. 3c and S4,† detailed voltage drop) for RGO-SCNT50 are 29.4 F cm<sup>-3</sup> and 29.7  $\Omega$ , while those of RGO-CNT50 are 12.9 F cm<sup>-3</sup> and 43.3  $\Omega$ , respectively. The RGO-SCNT50 exhibits superior capacitance



Fig. 3 (a) Photo image of proto type solid-state supercapacitor cells, (b) CV curves of RGO, RGO–CNT50 and RGO–SCNT50 at a scan rate of 20 mV s<sup>-1</sup>, (c) galvano charge–discharge at constant 2 mA cm<sup>-2</sup>, (d) volumetric capacitance with different scan rates from 2 to 100 mV s<sup>-1</sup>, (e) Nyquist impedance plots, and (f) frequency response *versus* capacitance.

properties and lower ESR than those of RGO-CNT50 and RGO. Fig. 3d shows the specific capacitance *versus* scan rate from 2 to 100 mV s<sup>-1</sup>. The specific capacitance of RGO-SCNT50 is 44.5 F  $\rm cm^{-3}$  at 2 mV  $\rm s^{-1}$  and decreases to 20 F  $\rm cm^{-3}$  as the scan rate increases to 100 mV s<sup>-1</sup>. Similarly, the capacitances of RGO-CNT50 and RGO decrease from 21.4 F cm<sup>-3</sup> to 8.4 F cm<sup>-3</sup> and from 8.2 F cm<sup>-3</sup> to 1.2 F cm<sup>-3</sup>, respectively (Fig. 3d). Frequency response analysis (FRA) over a frequency range from  $10^6$  to  $10^{-2}$ Hz yielded the Nyquist plots of RGO-SCNT50, RGO-CNT50 and RGO, as shown in Fig. 3e. Plots of RGO-SCNT50 and RGO-CNT50 featured vertical curves, which are different from RGO, indicating nearly ideal capacitive behaviour. The typical Nyquist plot of the supercapacitor can be classified into three regions following the frequency range. At high frequency, the intersection point on the real axis (Z') represents the ohmic resistance of the electrolyte and the internal resistance of the electrode, which is described as the series resistance  $(R_s)$ . The semicircular plot in the high to middle frequency range corresponds to the parallel connection of the ion transfer resistance  $(R_{\rm TT})$  and the EDLC. The transition from the semicircle to the long tail is attributed to the ion diffusion to the inside electrode.<sup>22</sup> Based on the magnified curve in the high-frequency range (Fig. 3e, inset), the  $R_{\rm S}$  and  $R_{\rm IT}$  are 20.2  $\Omega$  and 19.2  $\Omega$  for RGO–SCNT50, 15.5  $\Omega$  and 53  $\Omega$  for RGO–CNT50, and 60  $\Omega$  and over 380  $\Omega$  for RGO, respectively. The Rs of RGO-CNT50 and RGO-SCNT50 are lower than that of RGO, suggesting that the enhanced electric conductivity of the electrode is due to the presence of CNTs and SCNTs. As expected, the  $R_{\rm S}$  of RGO–SCNT50 is slightly higher than that of RGO-CNT50, which can be explained by the aromatic SP3 defects of SCNTs resulting from outer carbon surface functionalization. Furthermore, the R<sub>IT</sub> values of RGO-SCNT50 and RGO-CNT50 are much lower than that of RGO and the slope of the linear plot after semicircle transition is steeper, suggesting better accessibility and low ion-transfer resistance of the electrolyte. In contrast, RGO exhibits a non-ideal capacitive curve and high RIT, suggesting very poor accessibility of the polymer electrolyte and high resistance. Our results indicate that the CNTs are able to function as spacers between RGO sheets, thereby preventing strong restacking of RGO and enhancing electrolyte accessibility. Furthermore, the  $R_{\rm IT}$  of RGO-SCNT50 is lower and its curve is steeper than that of RGO-CNT50, since SCNTs have hydrophilic SO<sub>3</sub>H functional groups on their outer layer that provides easy access of protons from the electrolyte. Simultaneously, the inner layers of SCNTs maintained high electric conductivity, and thus  $R_s$  is also effectively decreased. The capacitance from FRA data versus frequency based on a series RC model is shown in Fig. 3f. The capacitance of RGO-SCNT50 is the highest among all the films tested in the entire frequency range, while RGO exhibits a very small capacitance even in a low frequency range. These results confirm that the superior electrochemical performance of RGO-SCNT50 composite electrodes is due to the enhanced electric conductivity and high accessibility of the electrolyte.

To further evaluate RGO–SCNT electrodes as solid-state supercapacitors, we test RGO–SCNT electrodes with different ratios of SCNTs. As the ratio of SCNTs increased, CV curves (Fig. 4a) became more rectangular. The CV curves of



**Fig. 4** The supercapacitor performance of the RGO–SCNT electrodes with different contents of SCNTs from 25 to 75 wt%; (a) CV curves at a scan rate of 20 mV s<sup>-1</sup>, (b) volumetric capacitance with different scan rates from 2 to 100 mV s<sup>-1</sup>, (c) Nyquist impedance plots, and (d) frequency response *versus* capacitance.

RGO–SCNT25 show a moderate current increase and decreased shape, while RGO–SCNT75 exhibits a more rectangular curve shape. However, the CV curve area of RGO–SCNT75 is smaller than those of both RGO–SCNT25 and RGO–SCNT50, which is attributed to the active surface area of RGO–SCNT75, which decreased as the amount of CNTs increased. Specific capacitance *versus* scan rate is presented in Fig. 4b. RGO–SCNT25 shows the highest capacitance value at a low scan rate, but its capacitance sharply decreased from 58.4 F cm<sup>-3</sup> to 13 F cm<sup>-3</sup> as the scan rate increased from 2 to 100 mV s<sup>-1</sup>, ultimately decreasing with 77.7%. Likewise, the capacitance of RGO–SCNT75 decreased from 17.2 F cm<sup>-3</sup> to 12.9 F cm<sup>-3</sup>, eventually decreasing by 25%. RGO–SCNT75 has a lower capacitance than the other RGO–SCNT5; however, it exhibited a superior rate-capacitance.

RGO-SCNT50 exhibits a rather modest capacitance decay curve compared with RGO-SCNT25, exhibiting the highest capacitance at scan rates greater than 20 mV s<sup>-1</sup>. Fig. 4c shows Nyquist plots of RGO, RGO-SCNT25, RGO-SCNT50 and RGO-SCNT75. All RGO-SCNT samples exhibit vertical and steeper curves. Based on magnified curves in the high-frequency range (Fig. 4c and inset), RGO-SCNT25 is determined to have a relatively larger semi-circle and a high  $R_{\rm CT}$  of over 60  $\Omega$ , while RGO-SCNT75 exhibits a smaller semi-circle and an  $R_{\rm CT}$  of 12.3  $\Omega$ . In addition, the plot after semi-circle transition is steeper as the amount of SCNTs increases, which suggests better accessibility to the electrolyte. Interestingly, the  $R_{\rm S}$  of RGO–SCNT75 (24.6  $\Omega$ ) is higher than that of RGO-SCNT25 (20.8  $\Omega$ ) and RGO-SCNT50 (20.2  $\Omega$ ). This result is possibly due to a low packing density between RGO sheets and CNT bundles. The electric conductivity of electrodes is strongly affected by the packing density.<sup>19</sup> Indeed, the bulk-density of RGO-SCNT75  $(0.64 \text{ g cm}^{-3})$  is much lower than that of RGO-SCNT25 (0.94 g  $\text{cm}^{-3}$ ) and RGO-SCNT50 (0.9 g cm<sup>-3</sup>). With respect to hydrophilicity, the water

contact angles (WCAs) of RGO–SCNT film electrodes (Fig. S5<sup>†</sup>) are slightly different between the up and down sides. Specifically, the down side of RGO–SCNT films is slightly more hydrophilic (with lower WCA) than that of the up side, which is possibly due to accumulation of vacuum force during production of the film electrode by the vacuum filter method. In addition, the WCA decreased as the ratio of SCNTs increased, which resulted in increased hydrophilicity. These results are consistent with our observation of a low ion-transfer resistance as the ratio of SCNTs increased. Fig. 4d shows the capacitances from FRA data *versus* frequency of the RGO–SCNT sample series; RGO–SCNT50 exhibits the highest capacitance among all the other samples in the entire frequency range.

We evaluate RGO–SCNT50 for electrochemical stability by CV at 100 mV s<sup>-1</sup>. RGO–SCNT50 maintains a specific capacitance of approximately 93% of the initial value after 5000 cycles (Fig. S5†), indicating good electrochemical stability. Table S1† summarizes the specifications of electrodes such as volumetric specific capacitance value, water contact angles, and resistance properties obtained from Nyquist plots.

To demonstrate on-chip solid-state supercapacitors with specific patterns, we fabricate RGO–SCNT50 capacitor cells on a PET substrate using a spray coating method with patterned mask (Fig. 1d and Movie clip S1†). FE-SEM images of spray-RGO–SCNT50 are shown in Fig. S7b† and compared with film-RGO–SCNT50 up side (Fig. S7a†). Spray-RGO–SCNT50 has a coarser surface morphology. In addition, the spray-RGO–SCNT50 has a lower density (0.7 g cm<sup>-3</sup>) than that of the RGO–SCNT50 film (0.9 g cm<sup>-3</sup>). The WCA of the spray-RGO–SCNT50 was 64°, which is similar to that of the spray-RGO–SCNT50 evaluated by CV curves at different scan rates and is similar to that of the RGO–SCNT50 film, suggesting that there is no difference in electrochemical properties for spray coating and vacuum filter processes (Fig. S6c and S6d†).

# Conclusions

In summary, we demonstrate low ion-transfer resistance and high volumetric on-chip solid-state supercapacitors consisting of hydrophilic MWCNTs and graphene flakes, and an H<sub>2</sub>SO<sub>4</sub>/ PVA electrolyte. The specially designed hydrophilic MWCNTs are prepared by chemical attachment on the outer surface of MWCNTs by reduction of para-sulfonic phenyl diazonium salt with hypophosphorous acid, and are freely dispersed in water and can be mixed well with GO solution, ultimately leading to a uniform RGO-SCNT film through reduction of a GO-RGO film. Hydrophilic treated SCNTs on the outer surface of MWCNTs exhibit a high electric conductivity throughout the inner layers of MWCNTs. Therefore, RGO-SCNT composite electrodes exhibit a low wetting angle as well as low ion-transfer resistance. In addition, the homogeneously dispersed RGO-SCNT solution in water gave a high volumetric capacitance with high packing density and it is easily applied for fabrication of specific patterned electrodes by a spray coating technique, allowing integration onto one flexible chip with specific patterns. RGO-SCNT films exhibit the highest capacity and rate-capacitance

properties and they are stable, maintaining a capacitance of 93% of the initial value after 5000 cycles. In addition, the solidstate spray-RGO–SCNT electrodes can be connected in series or in parallel to improve the overall output potential and/or current. In addition, they may also be integrated onto various substrates for energy storage devices, including portable, stretchable, and wearable electronic devices.

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