Solid-state yet flexible supercapacitors made by inkjet-printing hybrid ink of carbon quantum dots/graphene oxide platelets on paper

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ABSTRACT Paper-based flexible supercapacitors (SCs) show advantages due to the improved adhesion between paper and active materials, the simplified printing process and the lower cost, compared to other substrates such as plastics. Here we report the fabrication of solid-state yet flexible SCs by inkjet-printing a hybrid ink consisting of carbon quantum dots (CQDs) and graphene oxide (GO) platelets, followed by casting of polyvinyl alcohol (PVA)/sulfuric acid (H₂SO₄) gel electrolyte. The SC obtained from 100-time-printing of the hybrid ink shows a specific capacitance of ~1.0 mF cm⁻² at a scan rate of 100 mV s⁻¹, which is enhanced by nearly 150%; the whole device including paper substrate, gel electrolyte and active material demonstrates an energy density of 0.078 mW h cm⁻³ at a power density of 0.28 mW cm⁻³. In addition, the excellent mechanical strength of GO platelets ensures the good flexibility and mechanical robustness of the printed SCs, which show a retention of 98% in capacitance after being bended for 1,000 cycles at a bending radius of 7.6 mm. This study demonstrates a promising strategy for the large-scale preparation of low-cost, lightweight, and flexible/wearable energy storage devices based on carbon-based ink and paper substrate.

Keywords: inkjet printing, paper, carbon-based hybrid ink, flexible supercapacitors

INTRODUCTION

Lightweight yet flexible energy storage devices are desired, as the development of wearable and miniaturized electronic devices [1–3]. Supercapacitors (SCs), which store ions on large-area surfaces through various electrochemical processes, have been considered as a promising

candidate due to the fast charging rate, high power output, and long cycle life [4–6]. Electrode materials for conventional SCs are typically coated on current collectors or rolled into membranes with thickness ranged from several tens to more than one hundred micrometers. Neither conventional ‘doctor-blade’ coating nor rolling is suitable for the preparation of ultrathin electrodes, restricting the development of flexible and wearable SCs [7]. Solution-based deposition has been utilized to fabricate solid-state yet flexible electrodes. For example, a spray method was used to prepare a thin film of single-walled carbon nanotubes (SWNTs) on a polyethylene-terephthalate (PET) substrate [8,9], and a Meyer-rod-coating was developed to spread ink of double-walled carbon nanotubes (DWNTs) on a paper substrate for flexible electrodes [5]. A dipping and drying of SWNTs ink on cotton fibers has been utilized to create three-dimensional (3D) porous structures [10]; the deposition of carbon nanotubes (CNTs) was also performed onto a bacterial cellulose substrate through a vacuum filtering process [11]. Drawing on a standard printing paper with a graphite rod has been reported to fabricate flexible SCs as well [12]. The above-mentioned methods, however, typically produce films with less control over thickness, geometry, position or uniformity. Shadow masking, on the other hand, has been used to provide a supplement for small-area electrodes [13]. For instance, a micro-SC (MSC) was obtained by spray-coating a hybrid ink of electrochemically-exfoliated graphite and poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) through a shadow mask with a custom-designed geometry (finger and channel widths of ~1,000 μm) on a PET

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substrate [14]. But the complicated process, high cost and pre-determined geometry may limit the further applications of shadow masking for the preparation of electrodes for flexible SCs.

Compared to direct coating or shadow masking, inkjet printing has advantages of low cost, large area and high throughput for the preparation of thin film electrodes, yet with readily-controlled geometry, thickness and micrometer resolution of patterns [15–17]. Micro-electrodes of SWNTs have been successfully fabricated by printing inks of aqueous sodium dodecyl sulfate (SDS)-functionalized SWNTs on flexible PET substrates, with controllable patterns in the areas of 0.4–6 cm² and electrode thicknesses of 20–200 nm [18]. However, the rheology of inks challenges the uniformity of the printed patterns on PET. In fact, the poor wetting of most solvents (e.g., deionized water and ethanol) on plastic substrates leads to the difficulty in controlling the electrode patterns [19]. In contrast, papers, which are typically obtained from cellulose fibers with superior hydrophilicity and have been used for writing in last thousand years, are beneficial to the efficient adhesion of many solvents. Paper-based planar MSCs have been successfully prepared by inkjet printing of PEDOT:PSS-CNT/Ag ink [17]. For the efficient inkjet printing of active materials on papers, the preparation of the ink is critical and needs to meet specific requirements (including but not limited to particle size, ink viscosity, surface tension and so on) for the jetting through the micro-nozzles [20]. To improve the solubility of CNTs in ink (the typical solubility of intrinsic SWCNTs in water is 5 ppm due to the hydrophobic nature [21]), surfactants or surface functionalization are used [5,10,22–23], although the use of surfactants is generally undesirable because they may significantly deteriorate the capacitance [21]. Graphene oxide (GO) has an excellent solubility in water and alcohol [24], but suffers from the problems of aggregation and restacking during the solvent evaporation after printing and/or in the following reduction processes [25–27]. It has been proved that a commercial pen ink consisting of carbon black could reduce the agglomeration of GO during solvent evaporation [28], leading to an enhancement of nearly 780% in the areal capacitance (19.18 $\mu\text{F cm}^{-2}$, measured at 0.12 $\mu\text{A cm}^{-2}$) compared to that of bare GO ink. On the other hand, carbon quantum dots (CQDs) have excellent aqueous solubility and contain more functional groups and open edges, probably providing more active sites for pseudocapacitance when being properly utilized [29,30]. Thus, it is expected that CQDs are suitable nano-spacers for GO based ink for inkjet-printing of SC electrodes. Although an inter-

connected 3D network of reduced GO (rGO) decorated with CQDs was prepared through a hydrothermal method [31], a stable hybrid ink and the fabrication of SCs by inkjet-printing such an ink are highly desired.

In this work, we report the fabrication of solid-state SCs based on inkjet-printing of CQDs/GO hybrid ink on paper substrates. Because of numerous oxygen-containing groups in CQDs and GO platelets, the aqueous ink remains stable in ambient conditions for several months. By printing the hybrid ink through a commercial inkjet printer, the areal capacitance of CQDs/GO hybrid electrodes obtained with the designed geometry is far greater than the simple summary of CQDs electrodes and GO electrodes. In addition, a proper tuning of the functional groups by using the thermal processing has further optimized the electrochemical performance of the hybrid ink, leading to an areal capacitance of 4.2 mF cm^{-2} and an energy density of 0.078 mW h cm^{-3} when normalized to the whole volume (including the paper substrate) of the solid-state SCs. Favorable cycling stability (83% capacitance retention after 10,000 cycles at 100 mV s^{-1}) has been achieved as well. The solid-state SCs show high flexibility, and a capacitance retention of 98.8% is obtained at a bending radius of 7.6 mm.

EXPERIMENTAL

Fabrication of CQDs and CQDs/GO hybrid ink

CQDs prepared by KOH activation of fullerenes (C_{60}) were described in our previous study [32]. Briefly, the mixture of C_{60} powder (200 mg, XF NANO, Inc.) and KOH (4 g) was heated at 600°C for 4–5 min in Ar. Then, the product dissolved in de-ionized (DI) water was filtered and dialyzed in DI water for 7 days to obtain a clear suspension. Finally, CQDs powder was obtained by freeze-drying in a yield of about 20%. Aqueous suspension of GO platelets (D50: 2–3 μm , 10 mg mL^{-1}) was purchased from the Sixth Element (Changzhou) Materials Technology Co., Ltd. To prepare the hybrid ink, DI water (30 mL) and ethanol (15 mL) were mixed with the GO aqueous solution (5 mL). Then CQDs power (100 mg) was slowly added into the mixed solution and bath-sonicated for 1 h at room temperature to form a suspension. The resultant suspension was further agitated with a probe sonication for 1 h (400 W, 24 kHz) at 0°C to obtain the final hybrid ink with a concentration of 3 mg mL^{-1} . For comparison, CQDs ink or GO ink was prepared by solely dispersing CQDs (100 mg) or GO (5 mL) in 35 mL (for CQDs) or 30 mL (for GO) mixture of DI water and 15 mL ethanol following the similar processing.

Inkjet printing preparation of solid-state SCs

For inkjet printing, the CQDs/GO hybrid ink (denoted as H-ink) was slowly injected into a clean ink cartridge using a syringe. A commercial printer (Deskjet 1110, HP) was used for printing on printing paper (A4, TANGO) or weighing paper (100×100 mm², SCRC) for various cycles (20, 30, 50, 100 times). To modify the functional groups, printed electrodes were thermally annealed at various temperatures (100, 200, 250 or 300°C) under Ar for 180 min. The typical size of the electrode was 1 cm×1.5 cm. The electrodes with bare CQDs or GO ink were also obtained in the same way. For better electrical connection, 30-nm-thick gold (Au) was sputtered on the four edges of each square-shaped electrode with a current of 10 mA and chamber pressure of $\sim 5 \times 10^{-6}$ Torr (Magnetron Sputter, SBC-12). Polyvinyl alcohol (PVA)/sulfuric acid (H₂SO₄) gel electrolyte was drop-casted onto the surface of electrodes and solidified for overnight. The gel electrolyte was prepared by mixing 6 g of PVA and 6 g of H₂SO₄ (98%) into 60 mL of DI water, and heated at 80°C for 180 min under stirring. Finally, two electrodes were assembled face-to-face for an overlapping area of 1 cm² in the sandwich device.

Characterizations

Morphology of as-prepared samples was characterized by scanning electron microscopy (SEM) performed on JEOL-6700F (JEOL, Japan). Transmission electron microscopy (TEM) images of dried CQDs ink, GO ink, and H-ink were taken with a JEM-2100F (JEOL, Japan). Atomic force microscopy (AFM, Park, Korea) images were obtained for the CQDs ink. Raman spectra of blank A4 paper, CQDs printed paper, GO printed paper, and H-ink printed paper were obtained using an inVia Raman microscope (Renishaw, 532 nm laser, UK). UV-vis-NIR absorption spectra of CQDs suspension were obtained using a DUV-3700 (Shimadzu, Japan). Photoluminescence (PL) spectra of CQDs and modified CQDs with amide (called as NH-CQDs) suspension were recorded using a Fluorolog-3-TAU (Jobin Yvon, France). X-ray photoemission spectroscopy (XPS) was carried out on a Thermo ESCALAB 250 (Thermo Scientific, US) with Al K α radiation ($h\nu=1,486.6$ eV). Fourier transform infrared spectroscopy (FTIR) spectrum of H-ink printed or annealed at 100, 200, 250, and 300°C was measured using a Nicolet 8700 (Thermo Scientific Instrument, USA).

Electrochemical measurements

All cyclic voltammetry (CV), galvanostatic charge and discharge (GCD) and electrochemical impedance spec-

troscopy (EIS) were carried out on inkjet-printed SCs using a PARSTAT MC (AMETEK, US) electrochemical workstation. Areal capacitance (C_A) and volumetric capacitance (C_V) of the device in the two-electrode configuration were calculated based on the CV curves by using the following equations:

$$C_A = \frac{1}{\nu(V_f - V_i)A_{\text{device}}} \int_{V_i}^{V_f} I(V) dV, \quad (1)$$

$$C_V = \frac{1}{\nu(V_f - V_i)V_{\text{device}}} \int_{V_i}^{V_f} I(V) dV, \quad (2)$$

where ν is the scan rate (V s⁻¹), V_f and V_i are the integration limits of the potential, $I(V)$ is the response current (A), A_{device} and V_{device} are the total area (cm²) and volume (cm³) of the device, respectively.

The energy density E_{device} (W h cm⁻³) and power density P_{device} (W cm⁻³) of the device were obtained based on the following equations:

$$E_{\text{device}} = \frac{C_V \times (\Delta V)^2}{2 \times 3600}, \quad (3)$$

$$P_{\text{device}} = \frac{E_{\text{device}} \times 3600}{\Delta t}, \quad (4)$$

where C_V is the volumetric capacitance of the device obtained from Equation (2), ΔV is the discharge voltage range (V), and Δt is the discharge time (s).

RESULTS AND DISCUSSION

To obtain high-quality printed patterns, restricting the size of particles dispersed in the ink is critical. Fig. S1a shows the TEM image of the obtained CQDs casted on carbon film from an aqueous dispersion, with the size distribution of CQDs concentrated in the range of 6–12 nm (Fig. S1b). The similar estimation based on the AFM image (inset of Fig. S1c) indicates an average height of CQDs as ~ 2.9 nm. The UV-vis-NIR absorption result (Fig. S1d) shows that the CQDs have one absorption band centered at 260 nm, which is attributed to n- π^* transition of C=O bonds [33]. Fig. S1e shows that the CQDs suspension has a weak yet broad PL spectrum and it is invisible under UV irradiation (inset of Fig. S1f). However, the CQDs can be readily modified with amide and ring-opening amination of epoxide [34], resulting in stronger blue emission which can be seen with the naked eyes (Fig. S1f). Fig. S2a shows that the typical size of GO platelets is 2–3 μm . Fig. S2b, c show the obvious agglomeration and crumpled morphology of GO platelets after the solvent is volatilized. After being loaded in the GO ink, CQDs show a uniform distribution on GO platelets (Fig. S2d). After drying, the H-ink shows layered

Figure 1 (a) Schematic of the fabrication of solid-state SCs. SEM images of (b) blank A4 paper, H-ink printed paper with printing times of (c) 20, (d) 30, (e) 50 and (f) 100 times, respectively.

structures in which GO platelets are intercalated by CQDs (Fig. S2e). The as-prepared H-ink can be stored for several months without any visible aggregation or precipitation, which is related to numerous hydrophilic functional groups on CQDs or GO platelets (Fig. S2f). The as-obtained ink has been readily printed on flexible paper substrates to realize large-scale fabrication of electrodes for SCs (defined as CQDs-SCs, GO-SCs, or H-SCs based on CQDs-ink, GO-ink, or H-ink, respectively). Fig. 1a illustrates the fabrication of the paper-based flexible SCs using H-ink. The H-ink has been optimized to consist of 2 mg mL^{-1} CQDs and 1 mg mL^{-1} GO platelets to balance between the possible clogging of nozzle and the printing times for desired thickness. A personal computer is used to design different patterns such as the university logo and interdigital fingers which were then inkjet-printed using a home printer. For better conductivity of the devices, the four edges of each electrode has been sputtered with 30-nm-thick Au and assembled in a sandwich structure; the relatively simple geometry of the square electrode is beneficial to the multiple printing cycles for increasing the loading without considering the alignment in different printing cycles. From Fig. 1c–f, when the printing time is increased from 20 to 100 times, the fibers are covered by more and more CQDs/GO mixture. The mixture tends to penetrate and fill up the gap between fibers in the paper. Raman spectra (Fig. S3) have clearly indicated the successful loading of H-ink,

exhibiting two intense peaks centered at about $1,350 \text{ cm}^{-1}$ (D band) and $1,598 \text{ cm}^{-1}$ (G band), respectively.

The electrochemical performance of H-SCs in PVA/ H_2SO_4 gel electrolyte was evaluated by changing the printing time from 20, to 30, 50 and 100, respectively. Fig. 2a shows that the current density of H-SCs generally increases with the printing time. The CV curves display a little deviation from rectangular shape, which may be explained by the redox reaction of oxygen-containing functional groups in the printed electrodes from the H-ink [29,31,35]. The GCD curves in Fig. 2b show that the H-SCs with 100-time-printing possesses obviously longer charge/discharge time compared with those from 20, 30, and 50 times of printing for the same current. Fig. 2c shows that the capacitance is systematically improved when the printing time is increased. It is worth noting that a sudden increase in the performance is observed when the printing time is increased from 50 to 100, which may be explained by the significantly-improved conducting network from 100 times of printing (Fig. 1f).

To investigate the effect of hybridizing CQDs and GO, the electrochemical performance of H-SCs, CQDs-SCs, and GO-SCs all with 100 times is compared in Fig. 2d–f. As shown in Fig. 2d, e, the H-SCs show obviously increased performance compared to the GO-SCs, although the CQDs-SCs solely show negligible capacitance. Fig. 2f shows that the specific capacitance of the H-SCs (2.34 mF cm^{-2}) is higher than that of GO-SCs

Figure 2 (a) CV curves of the H-SCs with different printing times at a scan rate of 100 mV s^{-1} . (b) GCD curves of the H-SCs at a current density of $100 \mu\text{A cm}^{-2}$. (c) Areal capacitance with respect to the scan rate. (d) CV curves of H-SCs, GO-SCs, and CQDs-SCs with 100 times of printing at a scan rate of 100 mV s^{-1} . (e) GCD curves of H-SCs, GO-SCs, and CQDs-SCs at a current density of $100 \mu\text{A cm}^{-2}$. (f) Comparison of areal capacitances of H-SCs, GO-SCs, and CQDs-SCs with respect to the scan rate.

(1.85 mF cm^{-2}) or CQDs-SCs (0.32 mF cm^{-2}) at 1 mV s^{-1} . The synergistic effect is more obvious at higher scan rates, as indicated by the specific capacitance of 1.04 mF cm^{-2} for the H-SCs, much higher than that of the GO-SCs (0.69 mF cm^{-2}) and the CQDs-SCs (0.045 mF cm^{-2}) at 100 mV s^{-1} . At a scan rate of 500 mV s^{-1} (CV in Fig. S4a), the H-SCs still maintain an areal capacitance of 0.70 mF cm^{-2} , while that of GO-SCs and CQDs-SCs has decayed to 0.32 and 0.025 mF cm^{-2} , respectively. The EIS data in Fig. S4b show that the vertical spike of the H-SCs is steeper than that of GO-SCs or CQDs-SCs in the low-frequency region, indicating more ideal capacitive performance and largely reduced diffusive resistance. In the high-frequency region, the H-SCs show a smaller intrinsic resistance (40Ω) than GO-SCs (50Ω) or CQDs-SCs (144Ω). Clearly, the H-SCs demonstrate more efficient electron-transfer pathways and faster electrolyte-ion diffusion. In the printed H-ink, the CQDs may serve as nano-spacers which can separate GO platelets and effectively inhibit the agglomeration during solvent evaporation after printing, thus providing more accessible surface area for the electrodes [36].

Tailoring the type and amount of oxygen functional groups is essential to obtain higher capacitance [29–31,37]. The rich oxygen-containing functional groups in CQDs or GO platelets, such as carbonyl, hydroxyl, or carboxyl groups, are expected to afford active redox sites

to provide pseudocapacitance [38–41]. The electrodes obtained by printing H-ink for 100 times have been annealed at various temperatures (100 , 200 , 250 or 300°C) and the H-SCs (noted as H-SCs- x , where x is the annealing temperature) assembled with the annealed electrodes were evaluated. As shown in Fig. 3a, the area enclosed by the CV curve of H-SCs-200 is larger than those of other annealed electrodes (at 100 , 250 or 300°C) or original H-SCs measured at 100 mV s^{-1} . The GCD curves in Fig. 3b also show the significantly longer charge/discharge time for H-SCs-200 compared with the other annealed electrodes. The comparison of areal capacitances in Fig. 3c shows that the areal specific capacitance of 3.67 mF cm^{-2} for the H-SCs-200 is obtained at a scan rate of 1 mV s^{-1} , higher than that of H-SCs-100 (2.03 mF cm^{-2}), H-SCs-250 (2.69 mF cm^{-2}), or H-SCs-300 (3.48 mF cm^{-2}). Correspondingly, the Nyquist plot (Fig. 3d) of H-SCs-200 shows much lower equivalent series resistance (ESR, 6Ω) than H-SCs-100 (56Ω), H-SCs-250 (30Ω), or H-SCs-300 (25Ω).

To investigate the mechanisms for the relatively high electrochemical performance from H-SCs-200, FTIR, XPS, and Raman were utilized to trace the changes in oxygen-containing functional groups and defects in H-inks during the annealing. The FTIR spectra in Fig. 3e shows that the peak intensity of the epoxy (C–O–C, at $\sim 1,086 \text{ cm}^{-1}$) is generally reduced with the annealing

Figure 3 Electrochemical characterizations of H-SCs after the printed electrodes were annealed at 100, 200, 250 and 300°C, respectively. (a) CV curves measured at 100 mV s⁻¹. (b) GCD curves measured at 100 μA cm⁻². (c) Comparison of areal capacitances and (d) Nyquist plots of H-SCs with details in the high-frequency region in the inset. (e) FTIR spectra of H-ink printed and annealed at different annealing temperatures. (f) Fraction of peak area for various oxygen groups and the O/C atomic ratio estimated XPS as a function of annealing temperature.

temperature. The peak of carboxyl/carbonyl (C=O, at ~1,624 cm⁻¹) seems unchanged relative to that of hydroxyl (-OH, at ~3,443 cm⁻¹, sensitive to H₂O content) till 200°C then decreases at higher annealing temperatures. The reduction of H-inks by annealing is consistent to the decrease in intensity ratio of D to G bands (I_D/I_G), as shown in the Raman spectra and analysis (Fig. S5a and Table S1). At the same time, the O/C ratio estimated from XPS gradually reduces from 0.44 to 0.28 with the increase in the annealing temperature (Fig. 3f). The deconvolution of O 1s peaks (Fig. S5b-f) generates three sub-peaks at around 531.6, 532.5 and 533.5 eV, corresponding to C=O, C-O-C, and O=C-O groups, respectively [42]. As seen from Fig. 3f, the fractions of C-O-C and O=C-O peak areas decrease with the thermal annealing, while that of C=O increases till 200°C and then reduces at higher

temperatures. It was reported that the labile epoxy and hydroxyl groups can transform to more stable C=O group by heat treatment at 200°C [43–45], which may be further reduced at higher temperatures. The high fraction of the C=O groups in annealed H-ink at 200°C may explain the excellent electrochemical performance of H-SCs-200, as it has been reported that the existence of stable oxygen-containing functional groups (C=O) is beneficial to the pseudocapacitance and rate capability [29–31].

To evaluate the potential of the solid-state paper-based SCs for flexible energy storage, the H-SCs-200 device was subject to different bending radius during electrochemical measurement. Fig. 4a shows that the bending till a radius of 7.6 mm (optical image in the inset of Fig. 4b) has almost no influence on the capacitive behavior. After the device was bent for 1,000 cycles at the radius of 7.6 mm,

Figure 4 (a) CV curves of the H-SCs-200 under normal and bending conditions at a scan rate of 10 mV s^{-1} . (b) Capacitance retention after 1,000 cycles performed at a bending radius of 7.6 mm at 100 mV s^{-1} , and the inset shows a photograph of the bent device. (c) CV curves of the H-SCs-200 printed on weighing paper at different scan rates. (d) Ragone plots of solid-state H-SCs-200 printed on weighing paper compared with reported values for other solid-state symmetric SCs.

$\sim 98\%$ of capacitance remained (Fig. 4b), showing great stability and robustness of the flexible SCs. This durability may be attributed to the high mechanical flexibility of the electrodes along with the interpenetrating network structure between the H-ink and the paper substrate, which has largely benefited from the hygroscopic nature of the paper. Fig. S6 shows that the flat H-SCs-200 exhibits an excellent cycling stability, maintaining 83% of capacitance with respect to the first cycle after 10,000 cycles measured at 100 mV s^{-1} .

In addition to the standard A4 paper, other paper substrates such as weighing paper has also been used for inkjet-printing, as the weighing paper ($30\text{ }\mu\text{m}$) is thinner and lighter than A4 paper ($90\text{ }\mu\text{m}$), providing opportunities to further optimize the gravimetric and volumetric performance. The CV and GCD measurements (Fig. S7a–c) show that the electrochemical performance is not changed by the different paper substrates. Fig. S7d and the inset show that the H-SCs-200 on weighing paper has a slightly lower resistance ($5.7\text{ }\Omega$) in high frequency region than the H-SCs-200 on A4 paper ($6\text{ }\Omega$). Fig. 4c shows the CV curves of H-SCs-200 on weighing paper keep rectangular at a scan rate of up to $1,000\text{ mV s}^{-1}$, and an areal specific capacitance of 4.2 mF cm^{-2} is obtained at a scan

rate of 1 mV s^{-1} (1.6 mF cm^{-2} at 100 mV s^{-1}). Such a value is higher than those reported for N-doped graphite (2.3 mF cm^{-2}) [12], SCs based on laser-writing GO film (0.51 mF cm^{-2}) [25], cellulose nanofiber (CNF) paper-based rGO (1.73 mF cm^{-2}) [46], graphene film (0.47 mF cm^{-2}) [47], photoresist-derived porous carbon (0.75 mF cm^{-2}) [48], and nitrogen-doped rGO (3.4 mF cm^{-2}) [49]. A comparison based on the areal performance is shown in Table S2. The Ragone plot in Fig. 4d also compares the energy density and power density of H-SCs-200 to other reported solid-state symmetric SCs, based on the estimation of the whole device volume including substrate, gel electrolyte, and active material. The maximum volumetric energy density of $\sim 0.078\text{ mW h cm}^{-3}$ for the H-SCs-200 on weighing paper is much higher than those reported from MWNTs-based SCs ($0.008\text{ mW h cm}^{-3}$, by a drop-dry on office papers and in PVA/ H_2SO_4 gel electrolyte) [5], SWNTs-based SCs (0.02 mW h cm^{-3} , sprayed on PET substrate and in PVA/ H_3PO_4 gel electrolyte) [50], $\text{TiO}_2@\text{C}$ nanowires-based SCs ($0.011\text{ mW h cm}^{-3}$, by a two-step hydrothermal on carbon fabrics substrate and in PVA/ H_2SO_4 gel electrolyte) [51], and $\text{ZnO}@\text{MnO}_2$ core-shell-based SCs ($0.038\text{ mW h cm}^{-3}$, by a wet chemical and self-limiting deposition on carbon

cloth substrate in PVA/LiCl gel electrolyte) [52]. While the performance of H-SCs-200 is slightly lower than TiN nanowire-based SCs ($0.05 \text{ mW h cm}^{-3}$, by a seed-assisted hydrothermal method and annealing in ammonia on carbon cloth substrate in PVA/ H_2SO_4 gel electrolyte) [53], the inkjet printing provides advantages for the scalable and controllable preparations of SCs devices based on H-ink.

CONCLUSIONS

In summary, a simple inkjet-printing method has been taken to prepare flexible yet solid-state SCs on paper substrates based on a hybrid ink of CQDs and GO platelets. The SCs made from the H-ink exhibit high specific capacitance, good rate capability and high stability when being bent. Printing time and annealing temperature have been optimized to enhance the conductivity and electrochemical activity, leading to a specific capacitance of up to 4.2 mF cm^{-2} at a scan rate of 1 mV s^{-1} in PVA/ H_2SO_4 gel electrolyte, which is superior to those of typical carbon-based sandwich SCs ($0.5\text{--}2 \text{ mF cm}^{-2}$). The relatively high energy density ($0.078 \text{ mW h cm}^{-3}$ at a power density of 0.28 mW cm^{-3}), the excellent mechanical robustness, coupled with the low-cost, scalable yet controllable inkjet printing may allow more potential applications of H-inks for portable/wearable electronics, integrated circuits and flexible energy storage systems.

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喷墨打印碳量子点/氧化石墨烯混合墨水制备纸基全固态柔性超级电容器

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摘要 与其他柔性基底材料如塑料相比, 纸基柔性超级电容器具有印刷工艺简单、制造价格低廉以及基底和活性材料之间具有更好的粘合力等优势. 在这里, 我们通过喷墨打印碳量子点(CQDs)和氧化石墨烯(GO)组成的混合墨水、采用PVA/H₂SO₄为凝胶电解质制备了固态柔性超级电容器, 并对其性能进行了系统研究. 打印100次混合墨水获得的超级电容器在100 mV s⁻¹的扫描速率下显示出~1.0 mF cm⁻²的比电容, 相比于纯GO墨水制备的超级电容器其比电容增加了150%; 通过进一步优化, 基于超级电容器整个装置(包括纸基、凝胶电解质和活性材料)在0.28 mW cm⁻³的功率密度下表现出0.078 mW h cm⁻³的能量密度. 此外, GO薄片具有出色的机械强度, 确保超级电容器具有良好的柔韧性和机械强度, 在弯曲半径为7.6 mm的条件下弯曲1000次后, 仍保留98%的电容. 基于碳基墨水和纸张基材的喷墨打印的技术为低成本、轻便、灵活/可穿戴式储能装置的大规模制备提供了可能.