

# Highly conductive paper for energy-storage devices

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Paper, invented more than 2,000 years ago and widely used today in our everyday lives, is explored in this study as a platform for energy-storage devices by integration with 1D nanomaterials. Here, we show that commercially available paper can be made highly conductive with a sheet resistance as low as 1 ohm per square ( $\Omega/\text{sq}$ ) by using simple solution processes to achieve conformal coating of single-walled carbon nanotube (CNT) and silver nanowire films. Compared with plastics, paper substrates can dramatically improve film adhesion, greatly simplify the coating process, and significantly lower the cost. Supercapacitors based on CNT-conductive paper show excellent performance. When only CNT mass is considered, a specific capacitance of 200 F/g, a specific energy of 30–47 Watt-hour/kilogram (Wh/kg), a specific power of 200,000 W/kg, and a stable cycling life over 40,000 cycles are achieved. These values are much better than those of devices on other flat substrates, such as plastics. Even in a case in which the weight of all of the dead components is considered, a specific energy of 7.5 Wh/kg is achieved. In addition, this conductive paper can be used as an excellent lightweight current collector in lithium-ion batteries to replace the existing metallic counterparts. This work suggests that our conductive paper can be a highly scalable and low-cost solution for high-performance energy storage devices.

conformal coating | carbon nanotubes | nanomaterial | solution process

Printable solution processing has been exploited to deposit various nanomaterials, such as fullerene, carbon nanotubes (CNTs), nanocrystals, and nanowires for large-scale applications, including thin-film transistors (1–3), solar cells (4, 5), and energy-storage devices (6, 7), because the process is low-cost while maintaining the unique properties of the nanomaterials. In these processes, flat substrates, such as glass, metallic films, Si wafers, and plastics, have been used to hold nanostructure films. Nanostructured materials are usually first capped with surfactant molecules so that they can be well-dispersed as separated particles in a solvent to form “ink.” The ink is then deposited onto the flat substrates, followed by surfactant removal and solvent evaporation. To produce high-quality films, significant efforts have been spent on ink formulation and rheology adjustment. Moreover, because the surfactants are normally insulating, and thus limit the charge transfer between the nanomaterials, their removal is particularly critical. However, this step involves extensive washing and chemical displacement, which often cause mechanical detachment of the film from the flat substrate. Polymer binders or adhesives have been used to improve the binding of nanomaterials to substrates, but these can also cause an undesirable decrease in the film conductivity. These additional procedures increase the complexity of solution processing and result in high cost and low throughput. Here, we exploit paper substrates used in daily life to solve these issues and develop a simple, low-cost, high-throughput, and printable process for achieving superior device performance.

Throughout human history, paper has been the most important medium to express and propagate information and knowledge. The Prisse Papyrus, the oldest existing piece of writing on paper, dates back to 2,000 B.C. (8). The critical feature that enables paper to record information in such an enduring manner is the strong adhesion of ink onto paper, resulting from the 3D

hierarchical porous fiber structures, surface charges, and functional groups in paper, which are under fine control today (9). Paper has continued to expand its applications beyond information recording, and recently, novel applications such as microfluidic and electronic devices have been demonstrated. Whitesides and colleagues fabricated 3D microfluidic devices by stacking paper and adhesive tape (10) and, in a separate study, portable bioassays on patterned paper substrates (11). Researchers in the flexible electronics community have also explored paper as substrates for organic photodiodes (12), organic thin-film transistors (13, 14), circuits (15), and active matrix displays (16). In this study, we demonstrated that the application of paper can be expanded even further to important energy-storage devices by integrating with single-walled CNTs and metal nanowires by solution-based processes. The coated 1D nanomaterial films show high conductivity, high porosity, and robust chemical and mechanical stability, which lead to high-performance supercapacitors (SCs) and lithium-ion (Li-ion) batteries.

## Results and Discussion

Aqueous CNT ink with sodium dodecylbenzenesulfonate (SDBS) as a surfactant was used in this study (17), where SDBS and CNT were 10 and 1–5 mg/mL in concentration, respectively. Once CNT ink was applied onto paper by the simple Meyer rod coating method (Fig. 1A), the paper was transformed into highly conductive paper with a low sheet resistance around 10  $\Omega/\text{sq}$  (Fig. 1B), which is lower than previous reports by several orders of magnitude because of the ink formulation and the choice of substrates (18, 19). Fig. 1C and D shows the conformal coating of CNTs on the fiber structure of the paper, which contributes to high film conductivity (see Figs. S1 and S2 for more details). One important reason for this conformal coating might be the porous structure of paper, which leads to large capillary force for the ink. The strong capillary force enables high contacting surface area between flexible nanotubes and paper after the solvent is absorbed and dried out. We also applied the same method to produce conductive paper based on ink of other nanoscale materials, by using Ag NWs as an example (Fig. 1E and Table S1; see *Materials and Methods* for detailed procedures). The sheet resistances at different effective film thicknesses for CNTs and Ag NWs are plotted in Fig. 1F. Benefitting from the conformal coating, the sheet resistances reached a low level of 1  $\Omega/\text{sq}$  for Ag NWs at the effective film thickness of 500 nm. As film thickness increased, the scaling of the resistance changed from percolation-like to linear behavior, which is similar to CNT networks on flat substrates. The cross-over from percolation to linear region was found to be  $\approx 20$ –30 nm on other flat substrates, which is close to our value,  $\approx 10$  nm (Fig. 1F), and the difference is likely due to the length differences of CNTs (20, 21).

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(AgCl) was ground finely and added to the flask for initial nucleation. After 3 minutes, 0.22 g of silver nitrate (AgNO<sub>3</sub>) was titrated for 10 minutes. Then, the flask was kept at the same temperature for another 30 minutes. After the reaction was completed, the solution was cooled down and centrifuged three times to remove solvent, PVP, and other impurities.

**Cell Preparation and Measurements of SCs.** For aqueous electrolyte devices, two pieces of CNT conductive paper were first attached on glass slides. CNT films were used as both electrodes and current collectors. At the end of the CNT paper, a small piece of platinum was clipped onto the CNT conductive paper by a toothless alligator clip to connect to a battery analyzer (Maccor 4300). Both glass slides were assembled with a separator (Whatman 8- $\mu$ m filter paper) sandwiched in between. The paper assembly was wrapped with parafilm and then dipped in the electrolyte solution. The active area overlapped by both CNT conductive papers was 1 cm<sup>2</sup>. For organic electrolyte devices, cells were assembled by inserting the same separator soaked with the standard battery electrolyte (1 M LiPF<sub>6</sub> in ethylene carbonate:diethylene carbonate = 1:1 vol/vol; Ferro) between two CNT conductive paper substrates. The active area overlapped by both CNT conductive paper substrates was also 1 cm<sup>2</sup>. Then, the entire assembly was sealed in a polybag (Sigma-Aldrich). As in the aqueous cells, small pieces of platinum were attached to the end of CNT conductive paper for a good electrical contact. The current collectors came out through the sealed edges of polybags and then were connected to the battery analyzer. All steps in the cell preparation were done in an argon-filled glove box (oxygen and water contents below 1 and 0.1 ppm, respectively). Typical mass loadings for data shown in the main text Fig. 3 C and D are 72  $\approx$  270  $\mu$ g/cm<sup>2</sup>. Larger mass loadings up to 1.7 mg/cm<sup>2</sup> were also tested (Fig. 3 D and E, and Fig. S6C), and the capacitances are plotted in Fig. S6. Capacitance, energy density, and power density are all characterized by galvanostatic measurements. A total of 0.02  $\approx$  20 mA/cm<sup>2</sup> were applied to cells while potentials between both electrodes swept between cutoff values (0  $\leq$  V  $\leq$  0.85  $\approx$  1 V in aqueous phase, 0  $\leq$  V  $\leq$  2.3  $\approx$  3 V in organic phase). Voltages were recorded every 0.01  $\approx$  0.2 seconds. For the cycling test in both phases of electrolyte,  $\approx$  5 A/g was applied. The cutoff potentials for the sulfuric acid and organic electrolyte were 0.85 and 2.3 V, respectively.

**Battery Fabrication and Test.** The cathode materials LiMn<sub>2</sub>O<sub>4</sub> nanorods were synthesized according to our previous work, with modification (38). Typically,

8 mmol MnSO<sub>4</sub>·H<sub>2</sub>O and 8 mmol (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> were dissolved in 20 mL of deionized water, and the solution was transferred to a 45-mL, Teflon-lined stainless steel vessel (Parr). The vessel was sealed and heated at 150 °C for 12 h to obtain  $\beta$ -MnO<sub>2</sub> nanorods. The as-synthesized MnO<sub>2</sub> nanorods were mixed and ground with lithium acetate (Aldrich) at a molar ratio of 2:1. A total of 1 mL of methanol was added to make a uniform slurry mixture. Then, the mixture was sintered at 700 °C for 10 h under air to obtain LiMn<sub>2</sub>O<sub>4</sub> nanorods. The carbon/silicon core/shell nanowires were synthesized by CVD method. Carbon nanofibers (Sigma-Aldrich) were loaded into a tube furnace and heated to 500 °C. Then, silane gas was introduced and decomposed onto carbon nanofibers. The weight ratio of silicon shell to carbon core was typically  $\approx$  2:1. Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> powder was used as received from Süd Chemie.

Electrodes for electrochemical studies of LiMn<sub>2</sub>O<sub>4</sub> and Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> were prepared by making slurry of 70 wt % active materials, 20 wt % Super P Carbon, and 10 wt % PVDF binder in *N*-methyl-2-pyrrolidone (NMP) as the solvent. The slurry was coated onto a piece of conductive CNT paper by an applicator and then dried at 100 °C in a vacuum oven overnight. For C/Si core/shell nanowires, the as-synthesized nanowires were dropped onto a CNT paper and dried to form the anode.

The half-cell tests of both cathode (LiMn<sub>2</sub>O<sub>4</sub>) and anode (Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>) were carried out inside a coffee bag (pouch) cell assembled in an argon-filled glovebox (oxygen and water contents below 1 and 0.1 ppm, respectively). Lithium metal foil (Alfa Aesar) was used as the counter electrode in each case. A 1 M solution of LiPF<sub>6</sub> in EC/DEC (1:1 vol/vol; Ferro) was used as the electrolyte, with separators from Asahi Kasei. The charge/discharge cycles were performed at different rates at room temperature, where 1C was 148 mA/g for LiMn<sub>2</sub>O<sub>4</sub> and 175 mA/g for Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>, respectively. The voltage range was 3.5–4.3 V for LiMn<sub>2</sub>O<sub>4</sub> and 1.3–1.7 V for Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>. Tests were performed by either Bio-Logic VMP3 battery testers or MTI battery analyzers. To fabricate a full cell with high voltage to light a blue LED, silicon/carbon core/shell nanowires and LiMn<sub>2</sub>O<sub>4</sub> nanorods were used as anode and cathode, respectively. Then, the two electrodes were assembled to make a 5 cm<sup>2</sup> pouch cell as described above, and it was used to repeatedly light the blue LED.

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