

# 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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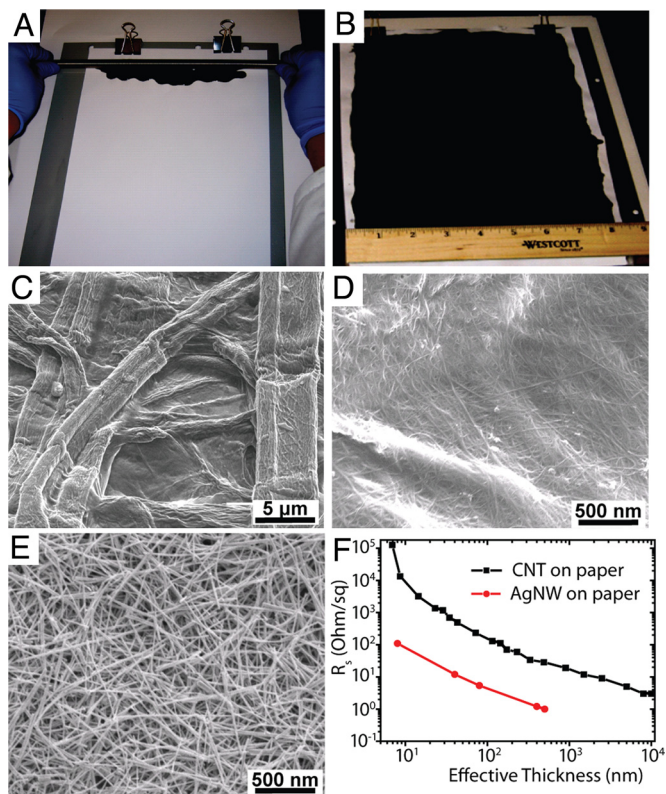
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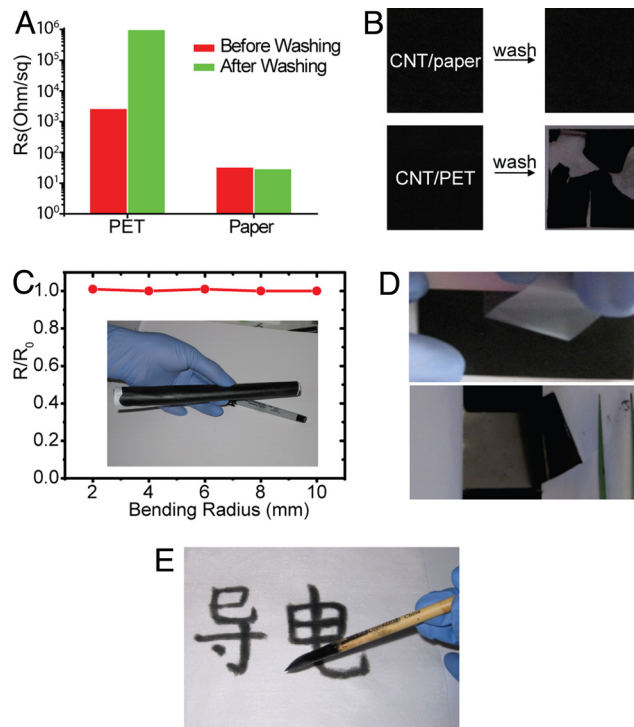
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**Fig. 1.** Conformal coating of CNTs or Ag NWs on commercial paper. (A) Meyer rod coating of CNT or Ag NW ink on commercial Xerox paper. (B) Conductive Xerox paper after CNT coating with sheet resistance of  $\approx 10 \Omega/\text{sq}$ . SEM images of (C) surface morphology of Xerox paper, (D) conformal CNT coating along fibers in Xerox paper, and (E) conformal Ag NW coating on Xerox paper. (F) Sheet resistances of conductive paper based on CNTs and Ag NWs with various thicknesses.

Because paper absorbs solvents easily and binds with CNTs strongly, the fabrication process for the conductive paper is much simpler than that for other flat substrates, such as glass or plastics. First, contrary to other substrates, ink rheology for paper is not strict at all. In glass and plastics, the ink surface energy needs to match with that of substrates, and the viscosity must be high enough to avoid surface tension-driven defects, such as rings and dewetting in the coating and drying processes (22). Therefore, various additives are incorporated in the ink to tune the rheology properties. These insulating additives decrease the conductivity of the final film. In contrast, our CNT ink does not need any additives to adjust the rheology, which simplifies the process and leads to high film conductivity. Second, the paper does not require surfactant washing processes to achieve high film conductivity, which is necessary for other substrates. As shown in Fig. 2A and B, the sheet resistance of the CNT paper was already as low as  $30 \Omega/\text{sq}$  before washing, and there was no film delamination and sheet resistance change after washing. In contrast, washing of CNTs on Polyethylene terephthalate (PET) substrates resulted in significant film cracking and peel-off (Fig. 2B). The local resistance of CNT film on PET decreased significantly (Fig. S3A); however, the global resistance became  $\approx 1,000$  times higher (Fig. 2A). Although the detailed mechanism behind this unusual phenomenon is unclear, it is likely that while solvent is sucked into paper by capillary force, surfactants become rearranged, perhaps toward porous fiber networks, such that surfactants do not hinder charge transport within CNT films as much as they do with flat substrates. This unusual property of paper renders the typical surfactant washing requirement un-



**Fig. 2.** Various performance tests of conductive paper. (A) Sheet resistance change of CNTs on paper and PET before and after the process of washing to remove surfactants. (B) The comparison of film peeling after washing surfactants. CNT films on PET are easily peeled off, whereas CNTs on paper still stick well. (C) Sheet resistance changes after bending conductive paper into different radii. (D) Film adhesion test with Scotch tape: CNTs on paper remain bound, whereas CNTs on PET are peeled off. (E) Direct writing of CNT ink on the paper with Chinese calligraphy.

necessary in the case of conductive paper, and thus its fabrication process becomes greatly simplified.

The conductive paper also has excellent mechanical properties. The conductive paper with CNT thicknesses from  $100 \text{ nm}$  to  $5 \mu\text{m}$  can be bent down to a  $2\text{-mm}$  radius (Fig. 2C) or folded without any measurable change in electrical conductivity. Fatigue tests show that the conductive paper can be bent to a  $2\text{-mm}$  radius for 100 times with resistance increase less than 5%. These mechanical behaviors are likely due to the combined effect of the flexibility of individual CNTs, the strong binding of the CNTs with the paper fibers, and the porous morphology of the paper, which can relax the bending strain. Such flexibility could satisfy the requirement in SCs and batteries. In comparison, conductive paper with a  $50\text{-nm}$  gold layer evaporated on Xerox paper showed  $R_s$  of  $7 \Omega/\text{sq}$ . The sheet resistance increased by 50% after folding the conductive gold paper three times. Moreover, the strong adhesion of the CNTs to paper lead to high film stability against damage, such as scratching and peeling-off. This is demonstrated via a Scotch tape test showing the clear superiority of using paper over the PET substrate (Fig. 2D). The Scotch tape did not peel off any CNTs on paper, and the sheet resistance remained the same,  $\approx 10 \Omega/\text{sq}$ . As in the conformal coating, the exceptionally strong binding is attributed to the large capillary force and maximized contact area and, subsequently, Van der Waals force between the CNTs and paper (23). The superior flexibility and high stability make conductive paper promising for various rolled-up devices. It is noteworthy that the conductive paper described here is completely distinct from previously reported bulky papers (24) or other conductive paper (25) in several perspectives. (i) We used widely available commercial paper, not paper-like films produced by more complicated processes. Therefore, we could





(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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- Ahn JH, et al. (2006) Heterogeneous three-dimensional electronics by use of printed semiconductor nanomaterials. *Science* 314:1754–1757.
- Talapan DV, Murray CB (2005) PbSe nanocrystal solids for n- and p-channel thin film field-effect transistors. *Science* 310:86–89.
- Duan XF, et al. (2003) High-performance thin-film transistors using semiconductor nanowires and nanoribbons. *Nature* 425:274–278.
- Kim JY, et al. (2007) Efficient tandem polymer solar cells fabricated by all-solution processing. *Science* 317:222–225.
- Bach U, et al. (1998) Solid-state dye-sensitized mesoporous TiO<sub>2</sub> solar cells with high photon-to-electron conversion efficiencies. *Nature* 395:583–585.
- An KH, et al. (2001) Supercapacitors using single-walled carbon nanotube electrodes. *Adv Mater* 13:497–500.
- Poizot P, et al. (2000) Nano-sized transition-metal oxides as negative-electrode materials for lithium-ion batteries. *Nature* 407:496–499.
- Edwards IES, Hammond NGL, Gadd CJ (1975) *The Cambridge Ancient History* (Cambridge Univ Press, Cambridge, UK).
- Roberts JC (1996) *Paper Chemistry* (Springer, New York).
- Martinez AW, Phillips ST, Whitesides GM (2008) Three-dimensional microfluidic devices fabricated in layered paper and tape. *Proc Natl Acad Sci USA* 105:19606–19611.
- Carrilho E, Martinez AW, Whitesides GM (2009) Understanding wax printing: A simple micropatterning process for paper-based microfluidics. *Anal Chem* 81:7091–7095.
- Lamprecht B, et al. (2005) Organic photodiodes on newspaper. *Physica Status Solidi A* 202:R50–R52.
- Kaihovirta NWC, Makela T, Wilen C, Osterbacka R (2009) Self-supported ion-conductive membrane-based transistors. *Adv Mater* 21:2520–2523.
- Eder F, et al. (2004) Organic electronics on paper. *Appl Phys Lett* 84:2673–2675.
- Kim DHK, et al. (2009) Ultrathin silicon circuits with strain-isolation layers and mesh layouts for high-performance electronics on fabric, vinyl, leather, and paper. *Adv Mater* 21:3703–3707.
- Anderson P, et al. (2002) Active matrix displays based on all-organic electrochemical smart printed on paper. *Adv Mater* 14:1460–1464.
- Islam MF, et al. (2003) High weight fraction surfactant solubilization of single-wall carbon nanotubes in water. *Nano Lett* 3:269–273.
- Kordas K, et al. (2006) Inkjet printing of electrically conductive patterns of carbon nanotubes. *Small* 2:1021–1025.
- Hecht DS, Hu L, Gruner G (2007) Electronic properties of carbon nanotube/fabric composites. *Curr Appl Phys* 7:60–63.
- Doherty EDS, et al. (2009) The spatial uniformity and electromechanical stability of transparent, conductive films of single walled nanotubes. *Carbon* 47:2466–2473.
- Hu L, Hecht DS, Gruner G (2004) Percolation in transparent and conducting carbon nanotube networks. *Nano Lett* 4:2513–2517.
- Gutof EB, Cohen ED (2006) *Coating and Drying Defects: Troubleshooting Operating Problems (Society of Plastics Engineers Monographs)*, (John Wiley & Sons, Hoboken, NJ).
- Hertel T, Walkup REAP (1998) Deformation of carbon nanotubes by surface van der Waals forces. *Phys Rev B* 58:13870–13873.
- Endo M, et al. (2005) 'Buckypaper' from coaxial nanotubes. *Nature* 433:476–476.
- Pushparaj VL, et al. (2007) Flexible energy storage devices based on nanocomposite paper. *Proc Natl Acad Sci USA* 104:13574–13577.
- Kaempgen M, et al. (2009) Printable thin film supercapacitors using single-walled carbon nanotubes. *Nano Lett* 9:1872–1876.
- Kimizuka O, et al. (2008) Electrochemical doping of pure single-walled carbon nanotubes used as supercapacitor electrodes. *Carbon* 46:1999–2001.
- Futaba DN, et al. (2006) Shape-engineerable and highly densely packed single-walled carbon nanotubes and their application as super-capacitor electrodes. *Nat Mater* 5:987–994.
- Du CS, Pan N (2006) Supercapacitors using carbon nanotubes films by electrophoretic deposition. *J Power Sources* 160:1487–1494.
- Ma RZ, et al. (1999) Processing and performance of electric double-layer capacitors with block-type carbon nanotube electrodes. *Bull Chem Soc Jpn* 72:2563–2566.
- Zhou CF, Kumar S, Doyle CD, Tour JM (2005) Functionalized single wall carbon nanotubes treated with pyrrole for electrochemical supercapacitor membranes. *Chem Mater* 17:1997–2002.
- Ahn HJ, et al. (2006) Electrochemical capacitors fabricated with carbon nanotubes grown within the pores of anodized aluminum oxide templates. *Electrochem Comm* 8:513–516.
- Niu CM, et al. (1997) High power electrochemical capacitors based on carbon nanotube electrodes. *Appl Phys Lett* 70:1480–1482.
- Malinauskas A, Malinauskiene J, Ramanavicius A (2005) Conducting polymer-based nanostructured materials: Electrochemical aspects. *Nanotechnology* 16:R51–R62.
- An KH, et al. (2002) High-capacitance supercapacitor using a nanocomposite electrode of single-walled carbon nanotube and polypyrrole. *J Electrochem Soc* 149:A1058–A1062.
- Pandolfo AG, Hollenkamp AF (2006) Carbon properties and their role in supercapacitors. *J Power Sources* 157:11–27.
- Landi BJ, et al. (2008) Lithium ion capacity of single wall carbon nanotube paper electrodes. *J Phys Chem C* 112:7509–7515.
- Yang Y, et al. (2009) Single nanorod devices for battery diagnostics: A case study of LiMn<sub>2</sub>O<sub>4</sub>. *Nano Lett*, in press.
- Cui LF, Yang Y, Hsu CM, Cui Y (2009) Carbon-silicon core-shell nanowires as high capacity electrode for lithium ion batteries. *Nano Lett* 9:3370–3376.
- Kavan L, Gratzel M (2002) Facile synthesis of nanocrystalline Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> (spinel) exhibiting fast Li insertion. *Electrochem Solid State Lett* 5:A39–A42.
- Zaghbi K, Simoneau M, Armand M, Gauthier M (1999) Electrochemical study of Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> as negative electrode for Li-ion polymer rechargeable batteries. *J Power Sources* 81:300–305.
- Thackeray MM, et al. (1984) Electrochemical extraction of lithium from LiMn<sub>2</sub>O<sub>4</sub>. *Mater Res Bull* 19:179–187.
- Muriset G (1952) Influence of the impurities in the foil, electrolyte and paper in the electrolytic capacitor. *J Power Source* 99:285–288.
- Zhou WVJ, et al. (2005) Charge transfer and Fermi level shift in p-doped single-walled carbon nanotubes. *Phys Rev B* 71:205423.
- Sun YG, Mayers B, Herricks T, Xia YN (2003) Polyol synthesis of uniform silver nanowires: A plausible growth mechanism and the supporting evidence. *Nano Lett* 3:955–960.