

# Binder-Free LiCoO<sub>2</sub>/Carbon Nanotube Cathodes for High-Performance Lithium Ion Batteries

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There is an increasing interest in developing rechargeable lithium ion batteries (LIBs) with higher energy density and longer cycle life for applications such as portable electronic devices and electric vehicles. Traditional electrodes in LIBs are often composed of active materials, binders, and conductive carbon additives such as carbon black and graphite. Recently, carbon nanotubes (CNTs) have been evaluated as a promising material to improve the performance of electrodes, owing to their excellent electrical and mechanical properties, one-dimensional structure, and large aspect ratio.<sup>[1–3]</sup> In many previous studies of CNT composite electrodes, CNTs are incorporated with active particles by either mechanical mixing<sup>[4,5]</sup> or chemical bonding,<sup>[6–14]</sup> and they only serve as an electrical conductor. Binders, which are electrochemically inactive, are commonly required to provide mechanical connections between active materials and conductive additives. The insulating binders reduce the overall energy density by adding weight to the electrodes and lead to poor electron transfer on cycling. Thus, the elimination of binders will be a remarkable progress for high-performance LIBs.

Efforts have been made to obtain binder-free CNT composite electrodes. For example, Fe<sub>3</sub>O<sub>4</sub>-single walled carbon nanotube (SWCNT) electrodes were fabricated by dispersing SWCNT and FeOOH nanorods in sodium dodecyl sulfonate (SDS) solution followed by vacuum filtration and annealing process.<sup>[15]</sup> Binder-free CNT composite electrodes were also obtained by loading functional particles onto CNT sheets drawn from CNT arrays by spraying, filtration, electrophoresis, evaporation, sol-gel method and so on.<sup>[16,17]</sup> However, these methods require costly specific equipment and multi-step operations, and cannot be used for mass production of CNT composite electrodes.

In this work, we develop an ultrasonication and co-deposition (USCD) technique and fabricate binder-free electrodes using super-aligned CNTs (SACNTs). SACNTs form a three-dimensional conductive and flexible structural network

in which active particles (such as LiCoO<sub>2</sub>) can be embedded (Figure 1a). The electrodes contain 95 wt% LiCoO<sub>2</sub> and only 5 wt% SACNT as both conductive additive and structural framework (typical electrodes contain 80 wt% active material, 10 wt% conductive additive such as Super P, and 10 wt% binders such as PTFE (Figure 1b)). These binder-free LiCoO<sub>2</sub>-SACNT composite cathodes exhibit high electrical conductivity, great flexibility, high energy density, outstanding cycling stability (151.4 mA h g<sup>-1</sup> at 0.1 C with retention of 98.4% after 50 cycles), and rate capability (137.4 mA h g<sup>-1</sup> at 2 C, corresponding to capacity retention of 90.8% compared to 0.1 C). The advantages of this work are: 1) the procedure is very simple and fast (10 min of ultrasonication) using mass produced SACNTs and commercial LiCoO<sub>2</sub> particles as raw materials; 2) as there is no binder in the cathodes, compact LIBs with less weight and higher energy density can be achieved; 3) with LiCoO<sub>2</sub> particles uniformly distributed in the highly conductive SACNT network, it is easy to achieve full utilization of the active material and to prevent polarization; 4) the continuous and three-dimensional SACNT network renders well-developed porous structures, high mechanical strength, and superior flexibility of the composites. Therefore, the LiCoO<sub>2</sub>-SACNT composites are capable of enduring the volume changes of the active particles on cycling and thus achieving longer cycle life; 5) both the porous and binder-free natures of the LiCoO<sub>2</sub>-SACNT composites facilitate more efficient electrolyte infiltration and faster Li ion transport throughout the electrodes, thus enabling better rate capability.

SACNTs are distinguished from ordinary CNTs in terms of their “super-aligned” nature, large aspect ratio (~10<sup>4</sup>), clean surface, and as a result, strong van der Waals force among tubes and bundles.<sup>[18–22]</sup> Continuous and aligned sheets can be directly drawn from SACNT arrays and further twisted into yarns,<sup>[18,21,22]</sup> which have been presented in various applications.<sup>[22–28]</sup> As shown in Figure 2a, parallel SACNTs connect tightly into bundles, and a continuous string can be extracted with a pair of tweezers due to the end-to-end joining mechanism<sup>[21]</sup> of SACNTs. After being dispersed in ethanol by ultrasonication, SACNT bundles were entangled into a continuous and robust three-dimensional network, leaving the surrounding ethanol solution very transparent (Figure 2b). The volume of the SACNT network expanded by about one hundred times, indicating the large porosity inside.

When active particles (such as LiCoO<sub>2</sub>) and SACNTs were dispersed together in ethanol, LiCoO<sub>2</sub> particles were trapped and uniformly distributed in the porous SACNT network. As the density of the composite network was much higher than the solvent, the LiCoO<sub>2</sub>-SACNT composite would co-deposit to the bottom of the container as soon as the ultrasonication process terminated, with no visible particles left in the transparent supernate (Figure 2b).

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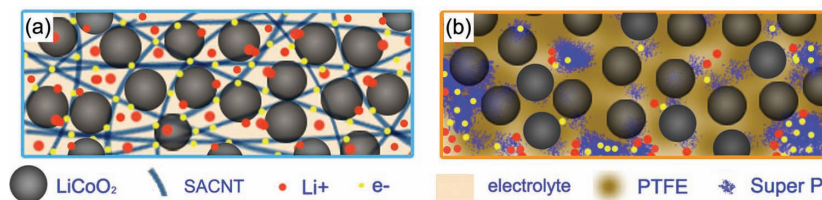


**Figure 1.** Schematic of the structures of a) the binder-free  $\text{LiCoO}_2$ -SACNT cathode and b) the classical  $\text{LiCoO}_2$ -Super P cathode. In the binder-free  $\text{LiCoO}_2$ -SACNT cathode,  $\text{LiCoO}_2$  particles are uniformly distributed in the continuous SACNT network. Without the hinder of insulating binder, both electron and ion transfer are greatly improved. While for the  $\text{LiCoO}_2$ -Super P cathode, Super P powders agglomerate heavily and are separated from  $\text{LiCoO}_2$  particles by the binder (PTFE).

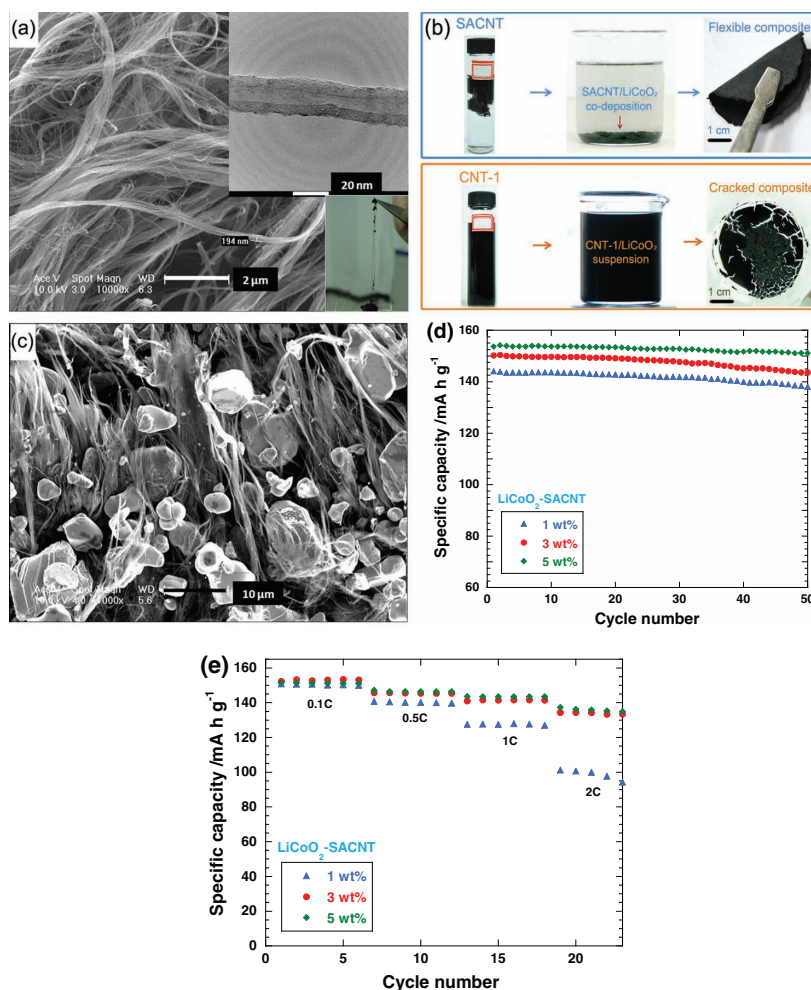


**Figure 2.** a) SEM and transmission electron microscopy (TEM) images of SACNTs. The inset photograph shows that a CNT string was extracted out by a pair of tweezers. b) Different features of SACNT and CNT-1: SACNT network vs. CNT-1 suspension;  $\text{LiCoO}_2$ -SACNT co-deposition vs.  $\text{LiCoO}_2$ -CNT-1 suspension; flexible  $\text{LiCoO}_2$ -SACNT composite vs. cracked  $\text{LiCoO}_2$ -CNT-1 composite. c) Cross-sectional SEM image of a  $\text{LiCoO}_2$ -1 wt% SACNT composite. d) Cycling (0.1 C) and e) Rate performance of the binder-free  $\text{LiCoO}_2$ -SACNT composite cathodes.

Due to the high intrinsic strength and flexibility of the SACNT bundles, the obtained LiCoO<sub>2</sub>-SACNT composites after removal of ethanol and drying were highly flexible and strong for further processes such as folding, pressing, and punching without cracking. The ultrasonication and co-deposition (USCD) procedure for making binder-free composite electrodes is very simple and fast, which includes only 10 min of ultrasonication. It is notable that the quality of CNTs is very essential for the USCD procedure. CNTs with smaller aspect ratios, more defects, and weaker interaction among tubes could not form a network by ultrasonication (as shown in Figure 2b, CNT-1 as an example, whose detailed features are provided in Supporting Information). When such CNTs were mixed with LiCoO<sub>2</sub> particles by ultrasonication, they could not co-deposit, and the obtained LiCoO<sub>2</sub>-CNT-1 composite after evaporation of ethanol was brittle and cracked into pieces, with non-uniform distribution of CNTs indicated by the uneven color on the top surface.

Binder-free LiCoO<sub>2</sub>-SACNT cathodes with 1–5 wt% SACNTs were prepared by the USCD method. The cross sectional scanning electron microscopy (SEM) image (Figure 2c) shows the uniform distribution of LiCoO<sub>2</sub> particles in the continuous SACNT network and the well-developed porous structure of the composite cathode. The LiCoO<sub>2</sub>-SACNT composite displayed a high conductivity of  $3.8 \times 10^2 \text{ S m}^{-1}$  with only 1 wt% of SACNTs, which is attributed to the great intrinsic conductivity ( $3 \times 10^4 \text{ S m}^{-1}$  for the SACNT film<sup>[28]</sup>), large aspect ratio ( $\sim 10^4$ ), and uniform distribution of SACNTs in the composite. As the amount of SACNTs increased to 5 wt%, the conductivity of the composite rose dramatically to  $2 \times 10^3 \text{ S m}^{-1}$ , with an improvement of almost one order of magnitude. All of these composite cathodes showed high specific capacities (144.1–151.4 mA h g<sup>-1</sup> at 0.1 C) and excellent cycling performance with capacity retention more than 95% after 50 cycles (Figure 2d and table S1). The LiCoO<sub>2</sub>-5 wt% SACNT composite cathode presented the best cycling stability (151.4 mA h g<sup>-1</sup> at 0.1 C with retention of 98.4% after 50 cycles) and rate capability (137.4 mA h g<sup>-1</sup> at 2 C, corresponding to capacity retention of 90.8% compared to 0.1 C), as shown in Figures 2d and 2e. To our knowledge, the LiCoO<sub>2</sub>-5 wt% SACNT cathode performed the best rate capability among micrometer sized LiCoO<sub>2</sub> cathodes so far. For example, carbon coated LiCoO<sub>2</sub> cathodes displayed a specific capacity of only 123 mA h g<sup>-1</sup> at 1 C.<sup>[29]</sup> The LiCoO<sub>2</sub>-5 wt% SACNT cathode even showed better rate capability (capacity retention at higher rate compared to 0.1 C) than nanometer sized LiCoO<sub>2</sub> cathodes reported in literature. LiCoO<sub>2</sub> nanoparticles (300 nm),<sup>[30]</sup> thin films (30 nm coated on Al nanotubes),<sup>[31]</sup> and nanotubes<sup>[32]</sup> exhibited a rate capability of 82.3% at 2 C, 87% at 2 C, and 90.5% at 0.25 C respectively, which are inferior to the LiCoO<sub>2</sub>-5 wt% SACNT cathode (90.8% at 2 C) in this work.

One reason for the excellent cycling and rate performance of the binder-free LiCoO<sub>2</sub>-SACNT cathodes is the well-developed porous structures of the composites. According to the rule of mixture, the volume fraction of pores was estimated to be 60%, given the actual density of the LiCoO<sub>2</sub>-1 wt% SACNT at 1.94 g cm<sup>-3</sup>, and the theoretical specific densities of LiCoO<sub>2</sub> and SACNT at 5.1 g cm<sup>-3</sup> and 1.2 g cm<sup>-3</sup>, respectively.<sup>[33]</sup> The pores in the composites are favorable for electrolyte infiltration and accommodation with the volume changes of the cathodes on

cycling. In addition, due to the absence of binder in the LiCoO<sub>2</sub>-SACNT cathodes, the liquid electrolyte can access LiCoO<sub>2</sub> particles more easily, which facilitates faster Li ion transfer among LiCoO<sub>2</sub> particles and significantly reduces polarization.

Different LiCoO<sub>2</sub>-carbon composites as control samples were prepared by mixing active particles, carbon materials (including CNT-1, Super P, and KS6), and 10 wt% polytetrafluoroethylene (PTFE) as binder together, and then cold rolling the mixtures. The conductivities of these composites with 1 wt% carbon additive are shown in Figure 3a. Obviously, the binder-free LiCoO<sub>2</sub>-SACNT composite possessed much higher conductivity ( $3.8 \times 10^2 \text{ S m}^{-1}$ ) than all the other LiCoO<sub>2</sub>-carbon composites ( $5.7 \times 10^{-2} \text{ S m}^{-1}$ – $5.8 \text{ S m}^{-1}$ ). Stress-strain curves of the binder-free LiCoO<sub>2</sub>-SACNT composites and the LiCoO<sub>2</sub>-Super P composite are shown in Figure 3b. The strength of the binder-free LiCoO<sub>2</sub>-SACNT composites increased linearly with the amount of SACNTs (inset of Figure 3b), indicating the strengthening effect of SACNTs. The strength and Young modulus of the classical LiCoO<sub>2</sub>-Super P composite were much lower, with only 3% the strength and 10% the Young modulus of the binder-free LiCoO<sub>2</sub>-SACNT composites, respectively. For the binder-free LiCoO<sub>2</sub>-SACNT composites, the strain at fracture was around 3–3.5%, which is twice that of the LiCoO<sub>2</sub>-Super P composite. Both the high strength and high flexibility of the binder-free LiCoO<sub>2</sub>-SACNT composites are beneficial for enduring the volume changes of the cathodes on cycling and achieving better cycling stability.

LiCoO<sub>2</sub> cathodes mixed with Super P (more than 2 wt%) had comparable initial specific capacity with the binder-free LiCoO<sub>2</sub>-SACNT composites, but their cycling stability was much worse. Compared to the high capacity retention of 95.6%–98.4% for the binder-free LiCoO<sub>2</sub>-SACNT composites, the capacity retention of LiCoO<sub>2</sub>-2 wt% Super P and LiCoO<sub>2</sub>-5 wt% Super P composites were only 49.6% and 87.3% after 50 cycles (Figure 3c). The rate capability of the Super P composites was also poorer, with a capacity of 62.7 mA h g<sup>-1</sup> at 2 C for the LiCoO<sub>2</sub>-5 wt% Super P composites (Figure 3d), which is less than half the capacity of the binder-free LiCoO<sub>2</sub>-5 wt% SACNT composites (137.4 mA h g<sup>-1</sup> at 2 C). Even with the amount of Super P increased to 10 wt%, the rate performance was still inferior, with a capacity of only 126.6 mA h g<sup>-1</sup> at 2 C. The distinct performance of the SACNT and Super P composite cathodes is attributed to the different distribution of the conductive additive. Since it is difficult to obtain uniform distribution of the nanometer-sized Super P powders among LiCoO<sub>2</sub> particles,<sup>[34,35]</sup> serious polarization and capacity loss was inevitable in classical LiCoO<sub>2</sub>-carbon composites. However, in the binder-free LiCoO<sub>2</sub>-SACNT composites, LiCoO<sub>2</sub> particles were uniformly distributed in the SACNT conductive network. The direct conductive bridges formed by CNTs among LiCoO<sub>2</sub> particles would enable quick electron transfer and full usage of the active material, resulting in larger capacity and excellent cycling and rate performance.

As the LiCoO<sub>2</sub>-SACNT composites were binder free, the improvement in the specific capacity based on the total mass or volume of the cathode compared to the control samples should be even more significant. The capacities of the binder-free LiCoO<sub>2</sub>-3 wt% SACNT composites were 145.7 mA h g<sup>-1</sup> at 0.1 C and 130.4 mA h g<sup>-1</sup> at 2 C (based on the total mass of the cathode), showing remarkable improvements of 20.6% at

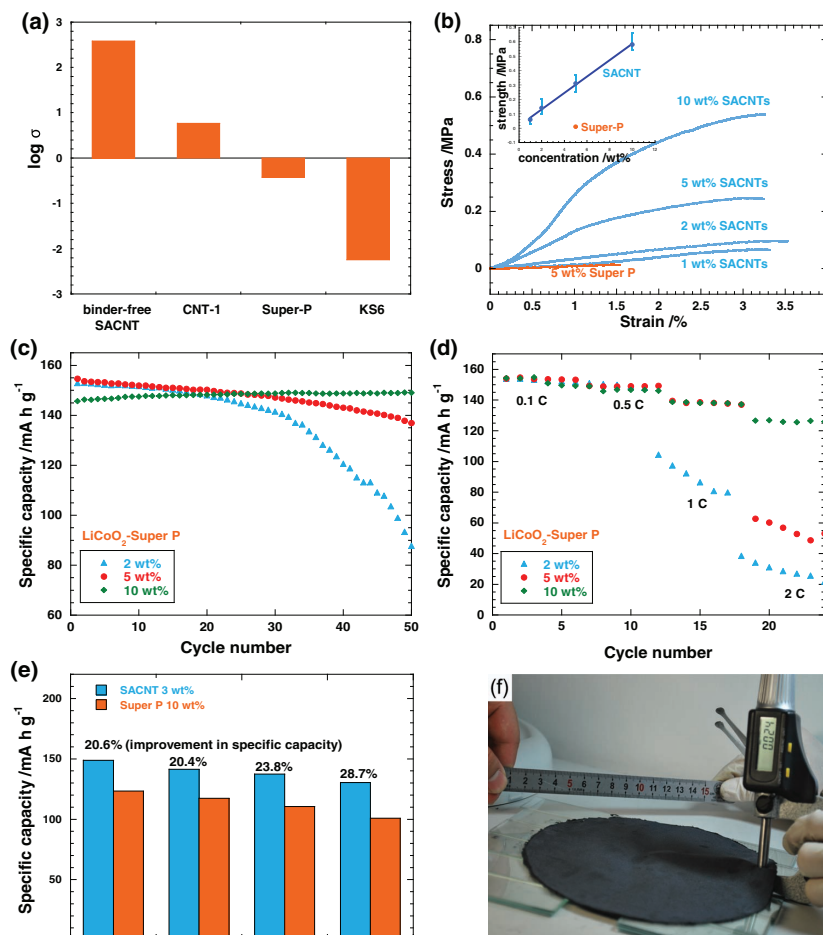


**Figure 3.** Comparisons among the binder-free LiCoO<sub>2</sub>-SACNT cathodes and the classical LiCoO<sub>2</sub>-carbon cathodes with 10 wt% PTFE as binder. a)  $\log \sigma$  ( $\sigma$ : conductivity, unit: S m<sup>-1</sup>). The amount of carbon conductive agent is 1 wt%. b) Mechanical properties of the binder-free LiCoO<sub>2</sub>-SACNT composites and the LiCoO<sub>2</sub>-Super P composite. c) Cycling (0.1 C) and d) Rate performance of the LiCoO<sub>2</sub>-Super P cathodes. e) Specific capacities of the binder-free LiCoO<sub>2</sub>-3 wt% SACNT cathode and the classical LiCoO<sub>2</sub>-10 wt% Super P cathode at different rates, based on the total mass of the cathodes. f) Thin (24  $\mu$ m) and free-standing LiCoO<sub>2</sub>-5 wt% SACNT composite can be made in a large scale.

0.1 C and 28.7% at 2 C (Figure 3e) than the classical LiCoO<sub>2</sub>-10 wt% Super P composites. The specific volume capacities of the LiCoO<sub>2</sub>-3 wt% SACNT composite and LiCoO<sub>2</sub>-10 wt% Super P composite were 289.9 mA h cm<sup>-3</sup> and 176.6 mA h cm<sup>-3</sup> respectively, revealing a significant improvement of 64% in the LiCoO<sub>2</sub>-3 wt% SACNT composite due to the removal of the 10 wt% inactive binder. Therefore, compact LIBs with less weight and volume can be developed using such binder-free LiCoO<sub>2</sub>-SACNT composites.

The USCD method described in this paper is extremely simple and easy for mass production. Both SACNTs and commercial LiCoO<sub>2</sub> can be mass-produced to meet industrial requirements. The co-deposited LiCoO<sub>2</sub>-SACNT composite is gel-like before drying, and can spread out on a large surface. Therefore,

continuous and large-scale production of binder-free LiCoO<sub>2</sub>-SACNT composites is possible using casting equipment. By controlling the process parameters, thin cathodes with a thickness of about 20  $\mu$ m were successfully prepared (Figure 3f). Binder-free LiMnO<sub>4</sub>-SACNT composite cathodes have also been made by the USCD method, and showed good cycling stability (107 mA h g<sup>-1</sup> at 0.1 C with capacity retention of 90.4% after 90 cycles) and rate performance (89.6 mA h g<sup>-1</sup> at 2 C) (Figure S2). As expected, this USCD method can be used to prepare other functional SACNT composites as well and extensive applications can be explored for SACNT composites.

In conclusion, binder-free LiCoO<sub>2</sub>-SACNT composite cathodes with superior properties such as high conductivity, great flexibility, and outstanding cycling stability (151.4 mA h g<sup>-1</sup> at 0.1 C with a

retention of 98.4% over 50 cycles) and rate capability (137.4 mA h g<sup>-1</sup> at 2 C) were obtained by constructing a continuous three-dimensional SACNT framework and embedding LiCoO<sub>2</sub> particles inside. These binder-free LiCoO<sub>2</sub>-SACNT composite cathodes perform much better than the classical composite cathodes with binder. Furthermore, the absence of binder is remarkable for high energy density batteries. The binder-free LiCoO<sub>2</sub>-3 wt% SACNT composite shows an impressive 20.6% increase in specific mass capacity and 64% increase in specific volume capacity than the optimized classical LiCoO<sub>2</sub>-10 wt% Super P cathode with binder. The USCD procedure developed in this work is very fast (10 min of ultrasonication) and easy for large-scale production. It is also possible for a wide variety of applications of SACNT composites depending on the selection of functional materials.

## Experimental Section

**Materials:** The matrix particles include LiCoO<sub>2</sub> (10 μm, Reshine, China) and LiMn<sub>2</sub>O<sub>4</sub> (10 μm, Reshine, China). The carbon materials include CNT-1 (5–20 nm in diameter and 1–10 μm in length, Chengdu Organic Chemicals Ltd., China), Super-P (carbon black, 50 nm in diameter, Timcal Ltd., Switzerland) and KS6 (graphite, 5–10 μm in planar size, Timcal Ltd. Switzerland). SACNT arrays with a diameter of 20–30 nm and a height of 300 μm were synthesized on 4 inch silicon wafers in a low pressure chemical vapor deposition (LP-CVD) system with iron as the catalyst and acetylene as the precursor. Details of the synthesis procedure can be found in previous papers.<sup>[19–21]</sup> It is notable that the growth of SACNT arrays on silicon wafers has been successfully scaled up with wafer diameter up to 8 inch to meet the industrial requirements.<sup>[22]</sup>

**Fabrication of binder-free composite electrodes by the USCD method:** SACNTs and LiCoO<sub>2</sub> (or other matrix particles) were simultaneously dispersed in an organic solvent (such as ethanol, isopropanol, acetone and so on) using an intensive ultrasonication probe (power: 300–600 W) for 10 min. As the density of the composite network is higher than the solvent, the LiCoO<sub>2</sub>-SACNT composite will co-deposit to the bottom of the container immediately after ultrasonication. The transparent supernate was removed and recycled. The LiCoO<sub>2</sub>-SACNT mixture was detached from the container, dried at 60 °C for 1 h, and pressed with a pressure of 100 kPa.

**Characterization:** Coin-type (CR 2016) half-cells were assembled in an argon-filled glove box (M. Braun inert gas systems Co. Ltd.) with the composites mentioned in this paper as the positive electrode and Li metal as the negative electrode. A porous polymer film (Celgard 2400, USA) was used as the separator and 1 M LiPF<sub>6</sub> solution in ethylene carbonate (EC) and diethyl carbonate (DEC) mixed at weight ratio of 1:1 was used as electrolyte. The cells were tested using a Land battery test system (Wuhan Land Electronic Co., China) with cut-off voltages of 3–4.3 V at room temperature. Tensile tests were performed using an Instron 5848 microtester with a strain rate of 1% min<sup>-1</sup> and a 1 cm gauge length. The conductivities of the composites were tested by a four-point method using a ResMap system. TGA tests were conducted using a Pyris 1 TGA (Perkin Elmer, USA) at a heating rate of 10 °C min<sup>-1</sup> between 50 and 800 °C in air.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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