Flower-like ZnCo$_2$O$_4$ nanowires: toward a high-performance anode material for Li-ion batteries

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Rising interest in lightweight, thin, and flexible energy storage devices has led to numerous studies that aim to fulfill the special needs of next-generation, high-performance flexible electronics. In this study, flower-like ZnCo$_2$O$_4$ nanowires are fabricated by a facile hydrothermal method followed by heat treatment in air at 400 °C. The structures and morphologies of as-prepared ZnCo$_2$O$_4$ nanowires are characterized by X-ray diffraction, scanning electron microscopy, and transmission electron microscopy. The data indicate that the as-synthesized flower-like ZnCo$_2$O$_4$ nanowires are approximately 2.5 μm in length and range from 50 nm to 150 nm in diameter. The as-prepared flower-like ZnCo$_2$O$_4$ nanowire products are evaluated as anode materials for lithium-ion battery application. The special structural features of ZnCo$_2$O$_4$ nanowires, including high coating uniformity, high coating density, and porous architecture, exert a significant effect on the electrochemical performance of the nanowires. The discharge capacity of ZnCo$_2$O$_4$ flower-like nanowires can reach first discharge capacity at 1430 mA h g$^{-1}$ to ~900 mA h g$^{-1}$ after 50 charge–discharge cycles at a current density of 200 mA g$^{-1}$, indicating its potential applications for next-generation, high-performance flexible electronics. High battery performance is mainly attributed to the dense and porous nanowire structures composed of interconnected ZnCo$_2$O$_4$ nanoparticles, which provide good electrolyte diffusion and large electrode-electrolyte contact area while reducing volume change during the charge–discharge process. The fabricated electrode can be used to light up commercial light emitting diodes.

1. Introduction

Development of high-capacity lithium-ion (Li-ion) microbatteries is of great importance to meet increasing power requirements that result from the rapid advances in integrated microsystems. The increasing demand for high-energy-density, long-cycle-life, and low-environmental-impact power sources in the fields of portable electronic devices, electric vehicles, implantable medical devices, and so forth, has stimulated an intensive search for new electrode materials in rechargeable Li-ion batteries. Similar to conventional energy storage devices, flexible power sources with high capacity and rate performance are very important for applications of high-performance flexible electronics because they enable the long, continuous use of electronic devices and fully charge in a very short time. Li-ion batteries have a high capacity, but usually suffer from a low charge–discharge rate compared with another important electrochemical storage device, supercapacitors. Therefore, the manufacture of a flexible electrochemical energy storage system with supercapacitor-fast charge–discharge rate and battery-like high capacity is essential.

One of the most promising routes toward the development of flexible batteries is the use of nanoscale materials to prepare electrodes. Transition metal oxides (TMOs) with nanostructural characteristics have attracted broad attention because of their higher surface-to-volume ratio and shorter path length for Li-ion diffusion in comparison with their bulk counterparts. Among these TMOs, cobalt oxide, iron oxide nickel oxide, and manganese oxide exhibit high reversible capacities (500 mA h g$^{-1}$ to 1000 mA h g$^{-1}$ compared with 372 mA h g$^{-1}$ for conventional graphite) at relatively low potential.

Of all the oxides studied so far, comparative studies of the several binary and ternary TMOs reveal that Co$_3$O$_4$ exhibits the best anodic performance. Poizot et al. have reported capacity values as high as ~900 mA h g$^{-1}$ and stable up to 25 cycles for Co$_3$O$_4$, which possesses a cubic spinel structure. Wang et al. have reported that as-grown Co$_3$O$_4$ hexapods on copper foil exhibit very high reversible capacity of 800 mA h g$^{-1}$ at 100 mA g$^{-1}$ and
440 mA h g\textsuperscript{-1} at 500 mA g\textsuperscript{-1} even after 40 cycles. Moreover, Kang et al.\textsuperscript{14} have reported a capacity of 700 mA h g\textsuperscript{-1} and stability up to 100 cycles for Co\textsubscript{3}O\textsubscript{4}. However, cobalt is toxic and expensive, and thus serious efforts are being made to partially replace Co\textsubscript{3}O\textsubscript{4} with eco-friendly and cheaper alternative metals such as Ni,\textsuperscript{4,19} Zn,\textsuperscript{11} Mn,\textsuperscript{3,11} and Cu,\textsuperscript{44} which are also electrochemically active for Li insertion and extraction. In particular, Zn\textsuperscript{2+} ions can partially substitute the metal ions of binary TMOs to form their ternary isostructures, leading to enhanced electrochemical lithium-storage properties. Considering that Zn\textsuperscript{2+} replaces Co\textsuperscript{3+} at the tetrahedral site in spinel Co\textsubscript{3}O\textsubscript{4}, ZnCo\textsubscript{2}O\textsubscript{4} has strong potential as an electrode material for lithium storage because both Zn and Co are electrochemically active with respect to lithium.\textsuperscript{11} Furthermore, ZnCo\textsubscript{2}O\textsubscript{4} is considered as an attractive candidate to substitute for conventional graphite anode in Li-ion battery due to its superiorities such as improved reversible capacities, enhanced cycling stability, and good environmental benignity.\textsuperscript{16} Thus far, different-shaped ZnCo\textsubscript{2}O\textsubscript{4} nanomaterials, such as nanoparticles\textsuperscript{11,15} (≈500 and ~900 mA h g\textsuperscript{-1} at 100 and 60 mA g\textsuperscript{-1} up to 50 and 60 cycles respectively), nanoflakes\textsuperscript{16} (~750 mA h g\textsuperscript{-1} at 80 mA g\textsuperscript{-1} up to 50 cycles), nanotubes\textsuperscript{15} (~1454 mA h g\textsuperscript{-1} at 100 mA g\textsuperscript{-1} up to 30 cycles), nanowires\textsuperscript{16,18} (~1200 and ~1197 mA h g\textsuperscript{-1} at 200 mA g\textsuperscript{-1} and 100 mA g\textsuperscript{-1} up to 160 and 20 cycles respectively), and nanorods\textsuperscript{19} (~767 mA h g\textsuperscript{-1} at 0.2 mA cm\textsuperscript{-2} up to 50 cycles) have been prepared by different methods, and their electrochemical performances have been improved to an extent.

Generally, according to the abovementioned studies, one-dimensional (1D) nanowires show promising results in enhancing the electrochemical performance of Li-ion batteries because of their high surface-to-volume ratio and excellent electronic transport properties. In this paper, we report the synthesis of flower-like ZnCo\textsubscript{2}O\textsubscript{4} nanowires onto carbon fiber, which exhibits high capacity and excellent cycling performance, via simple hydrothermal synthesis followed by heat treatment at 400 °C. The flower-shaped nanowires completely cover the carbon fiber surface with very high density, which facilitates Li ion insertion and electrolyte penetration. By using the flower-like ZnCo\textsubscript{2}O\textsubscript{4} nanowires over carbon fibers as current collectors (copper and aluminum current collector replacements), a new class of highly flexible and binder-free anodes can be obtained for lithium rechargeable batteries with excellent electrochemical performance and greater mechanical strength. The fabricated anodes can also be used to light up commercial light emitting diodes (LEDs).

2. Experimental section

Hydrothermal synthesis of flower-like ZnCo\textsubscript{2}O\textsubscript{4} nanowires

0.1 M zinc nitrate hexahydrate [Zn(NO\textsubscript{3})\textsubscript{2}:6H\textsubscript{2}O, 99.9%, J. T. Baker], 0.2 M cobalt nitrate hexahydrate [Co(NO\textsubscript{3})\textsubscript{2}:6H\textsubscript{2}O, 99%, ACROS], 0.5 M urea [CO(NH\textsubscript{2})\textsubscript{2}, 99%, Sigma-Aldrich], and 0.2 M ammonium fluoride (NH\textsubscript{4}F, 98%, Merck) were prepared by dissolving an appropriate weight in 50 mL deionized water (DIW). A 2 cm × 3 cm piece of cleaned (30 min of successive sonication cleaning using acetone, DIW, and ethanol, respectively) carbon fiber (CeTech Co., Ltd., Taiwan) was pleased in the top of precursor’s solution. The solution was then transferred into a 100 mL Teflon-lined stainless autoclave where the carbon fiber piece was kept on top. The autoclave was sealed and maintained at 140 °C for 7 h. After the autoclave cooled down to room temperature, the product was collected, washed, dried, and then thermal-treated at 400 °C for 2 h.

Instrumentation and sample analysis

The crystallographic information of the prepared samples was established by powder X-ray diffraction [XRD, Bruker D2 PHASE XRD Analyzer with Cu K\textalpha\textsubscript{2} radiation (\textlambda = 1.54178 Å)]. Field-emission scanning electronic microscopy (FESEM, JEOL JSM-6700F) was employed to examine the morphologies of the products. Structural and compositional investigations were carried through transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) using JEM-2100F (JEOL) and energy dispersive spectrometer (EDS) instruments. Surface analysis of samples was carried out with X-ray photoelectron spectroscopy (PHI Quantera) under Al K\textalpha\textsubscript{2} radiation (\textlambda = 8.3406 Å).

Electrochemical measurements

Electrochemical tests were performed under ambient temperature using two-electrode coin cells (CR 2032) with lithium serving as both counter electrode and reference electrode. A piece of the carbon fiber mounted by flower-like ZnCo\textsubscript{2}O\textsubscript{4} nanowire (the weight of grown ZnCo\textsubscript{2}O\textsubscript{4} is 3.7 ± 0.3 mg per each disk, area of 1.33 cm\textsuperscript{2}, which was cut for coin cell fabrication) was directly used as the working electrode without any polymeric binder or carbon black conductive additives involved. Celgard 2400 polymer separators were also employed. Afterward, 1 M LiPF\textsubscript{6} in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1 : 1 by volume) was used as the electrolyte. The cell assembly was carried out in an argon-filled glovebox with both moisture and oxygen content below 1 ppm. Testing of pristine ZnCo\textsubscript{2}O\textsubscript{4} powder was done by preparing of a slurry containing 70 wt% ZnCo\textsubscript{2}O\textsubscript{4} powder prepared by the same hydrothermal method without inserting a carbon fiber piece, 15 wt% carbon black (super P) and 15 wt% polyvinylidene fluoride (PVDF) as the binder and then the slurry was casted on a copper foil. Galvanostatic charge–discharge was conducted using a battery tester (AcuTech Systems Co., Ltd., Taiwan) with a voltage window of 0.005 V to 3.0 V at a constant density 200 mA g\textsuperscript{-1}. Cyclic voltammetry (CV) test was carried out in the potential window of 0.005 V to 3.0 V at a scan rate of 0.5 mV s\textsuperscript{-1} by an electrochemical workstation (AUTOLAB PGST30, Eco Chemie).

The full battery was assembled by using the as-fabricated ZnCo\textsubscript{2}O\textsubscript{4} nanowires/carbon fibers as the anode, commercial LiCo\textsubscript{2}O\textsubscript{4} as a cathode (SYNergy ScienTech Corp., Taiwan), 1 M LiPF\textsubscript{6} in EC and DMC (1 : 1 by volume) as the electrolyte, and a Celgard 2320 polymer separator. The electrochemical tests were performed between 2.2 and 3.7 V for a full battery at a constant current density of 200 mA g\textsuperscript{-1} with respect to the anode weight. To fabricate a soft packaging battery, aluminum and nickel strip used as the current collectors were jointed to the side of the LiCo\textsubscript{2}O\textsubscript{4} cathode and flower-like ZnCo\textsubscript{2}O\textsubscript{4} nanowire anode electrodes respectively. Next, 1 M LiPF\textsubscript{6} in EC and DMC (1 : 1 by volume) was used the electrolyte and a Celgard 2320 polymer separator.
3. Results and discussion

Fig. 1 shows the XRD pattern of ZnCo$_2$O$_4$ nanoparticles. All the peaks at 2θ values of 18.97°, 31.22°, 36.79°, 38.49°, 44.74°, 55.57°, 59.36°, and 65.13° [corresponding respectively to the diffraction planes (111), (220), (311), (220), (400), (422), (511), and (440)] match well with the cubic spinel structure [JCPDS card no. 23-1390, space group (Fd$_3$m)], where the bivalent Zn ions occupy the tetrahedral sites and the trivalent Co ions occupy the octahedral sites. The low intense peak at around 2θ was also observed coming from the carbon fiber. Moreover, no other peaks from carbon were detected, such as the (100) reflection plane at 2θ around 43°, which reveals the dense nanowires coating compared to the report by Liu et al., and no other peaks were observed indicating the pure ZnCo$_2$O$_4$ phase.

The morphology and microstructure of the as-synthesized ZnCo$_2$O$_4$ flower-like nanowires were examined with scanning electron microscopy (SEM). The SEM images in Fig. 2a and b show that the ZnCo$_2$O$_4$ coating uniformly, completely, and densely covers the carbon fiber. The SEM images in Fig. 2c–f provide clearer information about the final products. The SEM images in Fig. 2c–f illustrate the floriated structure of ZnCo$_2$O$_4$ arrays with relatively high flowery nanowire density grown on a carbon fiber. Fig. 2f shows that each ZnCo$_2$O$_4$ nanowire consists of a large number of 1D flower-like nanowires. The diameters range from 70 nm to 150 nm, from flower center to the nanowire end tips with different lengths. This structure helps in fast electron transfer and lithium diffusion.

Further information on the ZnCo$_2$O$_4$ nanowires microstructure was obtained from the transmission electron microscopy (TEM) image in Fig. 3. Fig. 3a and b show the low-magnification TEM image, where nanowires ~2.5 μm in length (Fig. 3a) and about 70 nm to 100 nm in diameter (Fig. 3b) can be clearly seen having good agreement with the SEM images in Fig. 2e. A higher-magnification TEM image depicted in Fig. 3b reveals that a typical ZnCo$_2$O$_4$ nanowire composed of infinitesimal nano-ZnCo$_2$O$_4$ particulates form a porous nanowire instead of a conventional single-crystalline nanowire. The porosity in the nanowires can enhance Li-ion intercalation and diffusion into the spinel lattice and electrolyte facile penetration into the anode material, thus enhancing the electrolyte/ZnCo$_2$O$_4$ contact areas and shortening the Li-ion diffusion length in the nanowires.

The HRTEM image shown in Fig. 3c reveals two sets of lattice fringes with interplane spacings of 0.244 and 0.467 nm respectively, corresponding to the (311) and (111) planes of the spinel ZnCo$_2$O$_4$ phase. The HRTEM image in Fig. 3c reveals two sets of lattice fringes with interplane spacings of 0.244 and 0.467 nm respectively, corresponding to the (311) and (111) planes of the spinel ZnCo$_2$O$_4$ phase. Fig. 3d shows the corresponding selected area electron diffraction (SAED) pattern of the ZnCo$_2$O$_4$ flower-like structure. Reflections corresponding to the (111), (220), (311) planes confirm that the porous ZnCo$_2$O$_4$ flower-like nanowire is single crystalline with a cubic structure, which is in accordance with the XRD results. The EDS microanalysis of the ZnCo$_2$O$_4$ nanowires (Fig. 3e) shows that the nanostructure contains only Zn, Co, and O elements, indicating the formation of pure ZnCo$_2$O$_4$. The EDS mapping shown in Fig. 3f provides clearer...
information about the element distribution within the nanowires, further confirming the formation of pure ZnCo$_2$O$_4$ products.

Important information about the purity and chemical composition of the sample can be further provided via X-ray photoelectron spectroscopy (XPS). Fig. 4a shows a full wide-scan spectrum of the ZnCo$_2$O$_4$ nanowires. There exist characteristic peaks for Zn, Co, and O elements. Fig. 4b shows the high-resolution Zn 2p spectrum. It indicates two peaks with binding energy values of 1022.6 and 1045.6 eV, which are ascribed to Zn 2P$_{3/2}$ and Zn 2P$_{1/2}$, indicating the Zn(II) oxidation state of ZnCo$_2$O$_4$. Fig. 4c shows the deconvoluted Co 2p spectrum. Two strong peaks at 794.5 eV for Co 2P$_{3/2}$ and 779.8 eV for Co 2P$_{1/2}$. 

Fig. 3 (a and b) TEM images, (c) HRTEM image ZnCo$_2$O$_4$ floriated nanowires, and (d) SAED pattern. (e and f) The EDS microanalysis on selected areas and EDX elemental mappings of Zn, Co, and O for the ZnCo$_2$O$_4$ flower-like nanowire. Scale bars, (a) 0.2 μm, (b), 50 nm and (c) 5 nm.

Fig. 4 XPS spectra for the ZnCo$_2$O$_4$ floriated nanowires: (a) survey spectrum and high-resolution (b) Zn 2p, (c) Co 2p, (d) O 1s spectra.
are observed, confirming the Co(III) oxidation state of ZnCo$_2$O$_4$, respectively. The O 1s peaks at 530.1 and 532.0 eV correspond to the oxygen species in ZnCo$_2$O$_4$ (Fig. 4d).\textsuperscript{15,22}

With the combined properties of porous inside architecture and high surface area, the as-prepared ZnCo$_2$O$_4$ flower-like nanowire may display promising applications in a variety of fields. The as-fabricated ZnCo$_2$O$_4$ flower-like nanowires exhibit porous 1D nanostructures and large surface areas, and can, therefore, be applied as high-performance anode materials of a Li-ion battery. According to previous papers,\textsuperscript{8,9,16-19} the entire electrochemical process can be clarified as follows:

\begin{align}
ZnCo$_2$O$_4$ + 8Li$^+$ + 8e$^-$ &\rightarrow Zn + 2Co + 4Li$_2$O & (1) \\
Zn + Li$^+$ + e$^-$ &\leftrightarrow LiZn & (2) \\
Zn + Li$_2$O &\leftrightarrow ZnO + 2Li$^+$ + 2e$^-$ & (3) \\
2Co + 2Li$_2$O &\leftrightarrow 2CoO + 4Li$^+$ + 4e$^-$ & (4) \\
2CoO + 2/3Li$_2$O &\leftrightarrow 2/3Co$_3$O$_4$ + 4/3Li$^+$ + 4/3e$^-$ & (5)
\end{align}

When the ZnCo$_2$O$_4$ nanowires are electrochemically discharged with lithium metal, crystal structure destruction occurs, followed by the formation of Li$_2$O and of nanosized Zn and Co, as shown in eqn (1). Then, the consequent electrochemical process may be the combined reaction based on the ZnO (eqn (3)) and Co$_3$O$_4$ (eqn (3) and (4)) respectively. Individual ZnO and Co$_3$O$_4$ components, as the anode materials of Li-ion batteries, have been clearly detailed in many papers.\textsuperscript{8,23-25}

Fig. 5a shows the first three CV curves of the electrodes made from ZnCo$_2$O$_4$ flower-like nanowires at a scan rate of 0.5 mV s$^{-1}$ and at room temperature. The first discharge for the ZnCo$_2$O$_4$ nanowires shows a large, irreversible reduction peak, broad with a maximum at 0.35 V, because of the decomposition of ZnCo$_2$O$_4$ to Zn and Co by lithium insertion and the formation of Li$_2$O, accompanied by the decomposition of organic electrolyte to form a solid electrolyte interphase (SEI) layer (eqn (1)), similar to the findings in previous reports.\textsuperscript{5} Compared with the first cycle, the discharge of the second and third cycles shows a peak at $\sim$0.8 V, indicative of the different electrochemical reactions that govern the two processes. However, in the anodic polarization process, two peaks are recorded at $\sim$1.7 and

![Figure 5](https://example.com/fig5.png)

Fig. 5  Electrochemical performance of flower-like nanowires ZnCo$_2$O$_4$/carbon fiber electrode. (a) First three cycles of CVs at a scan rate of 0.5 mV s$^{-1}$ in the voltage of 0.005 V to 3.0 V, (b) voltage vs. capacity profile for the first, second, fifth, and fiftieth discharge–charge cycle (under 200 mA g$^{-1}$), (c) cycle performance at a current of 200 mA g$^{-1}$, (d) rate capability at various current densities, (e) voltage vs. capacity profile for the first and second discharge–charge cycle of pristine ZnCo$_2$O$_4$ powder (under 200 mA g$^{-1}$) and (f) cycle performance of pristine carbon fiber at a current density of 200 mA g$^{-1}$.
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~2.1 V, which can be attributed to the oxidation of Zn$^0$ to Zn$^{2+}$ and Co$^0$ to Co$^{3+}$ respectively.

Fig. 5b shows the first, second, fifth, and fifth discharge curves of the electrodes made from the ZnCo$_2$O$_4$ flower-like nanowires onto carbon fiber at a current density of 200 mA h g$^{-1}$ and in the voltage window of 0.005 V to 3 V. The first discharge curve at ~0.9 V is larger with a capacity of about 500 mA h g$^{-1}$. The second at ~0.78 V, which extends up, shows about 170 mA h g$^{-1}$. This plateau disappears in the later cycle, which means that irreversible reactions took place, such as electrolyte decomposition or the formation of a solid electrolyte interphase (SEI) layer on the surface of the particles. The third minor shoulder plateau at ~0.45 V shows about 150 mA h g$^{-1}$. This result can be attributed to the formation of Li$_2$Zn alloys.$^8$ Finally, the first discharge capacity reaches about 1430 mA h g$^{-1}$, which is higher than the theoretical value (900 mA h g$^{-1}$).$^{16}$ The high initial capacity may be related to the dense nanowire shape, whose porous structure, and large surface area can shorten the Li$^+$ diffusion distance and increase the number of diffusion ions. These effects are in addition to the contribution of partially reversible formation/decomposition of the SEI and organic polymeric/gel-like layer by electrolyte decomposition, which are formed at very low cycling voltage (0.005 V) and will lead to extra cell capacity,$^{17}$ while the plateaus of the second and third discharge curves are slightly higher than that of the first discharge curve, which is similar to previous reports.$^5,8,16-19$ The discharge capacities of the electrode in the first, second, fifth, and fifth cycles are 1430.8, 1193.7, 1039.2, and 895.8 mA h g$^{-1}$, respectively. Irreversible capacity loss for the first cycle (about 16.5%) may be attributed to the formation of a SEI and the reduction of metal oxide to metal with Li$_2$O formation, which is commonly observed in various electrode materials.$^{16,26}$ However, the reversible capacity of the ZnCo$_2$O$_4$ flower-like nanowires is much higher than that of ZnCo$_2$O$_4$ nanoparticles, nanoflakes,$^3$ porous nanowires,$^18$ nanotubes,$^15$ and recently reported nanorods.$^{19}$ This reversible capacity also agrees with nanowires/carbon cloth, as reported by Liu et al.$^{16}$

Fig. 5c shows the charge and discharge capacity versus the number of cycles for the electrodes made from ZnCo$_2$O$_4$ flower-like nanowires at a current density of 200 mA h g$^{-1}$. The coulombic efficiency is obviously improved. As clearly shown in the cycling performance of 50 cycles (Fig. 5c), the capacity loss can be observed in the first several cycles. The specific discharge capacity is 912 mA h g$^{-1}$ after 10 cycles, which matches well with the theoretical value (~905 mA h g$^{-1}$) based on the reaction: ZnCo$_2$O$_4$ $+ 8$Li$^+$ $+ 8e^-$ $\rightarrow$ Zn $+ 2$Co $+ 4$Li$_2$O. The capacity loss is about 518 mA h g$^{-1}$. However, the reversible capacities gradually increase upon cycling. The coulombic efficiency shown in Fig. 5c indicates that the charge-discharge process gradually stabilizes. From the 1$^{st}$ cycle to the 50$^{th}$ cycle, the following charge-discharge capacities in the measured range tended to be stable, and the value almost remains constant in the range of about 912 mA h g$^{-1}$ to 890 mA h g$^{-1}$ with ~99.35% capacity retention. To further investigate the high rate performance of the ZnCo$_2$O$_4$ flower-like nanowires, the rate capability was evaluated by multiple-step charging-discharging at different current densities ranging from 200 to 800 mA g$^{-1}$ and the results were shown in Fig. 5d. It can be seen from Fig. 5d that the discharge capacity was slightly reduced from 1027 at current density 200 mA g$^{-1}$ (5$^{th}$ cycle) to 823, 639, 435, 374 and 347 mA h g$^{-1}$ at current densities of 300, 400, 500, 600, 700 and 800 mA g$^{-1}$, respectively. The current density was returned to the initial value of 200 mA g$^{-1}$, the capacity recovered to 849 mA h g$^{-1}$ after 10 cycles. This shows that ZnCo$_2$O$_4$ flower-like nanowires is of capacity retention capability and good rate performance. To further demonstrate the advantages of flower-like ZnCo$_2$O$_4$ nanowires/carbon fiber array electrode, anode composed of pristine ZnCo$_2$O$_4$ powder, which prepared by the same methodology without carbon fiber, was prepared and tested separately (at 200 mA g$^{-1}$). Fig. 5e shows that the pristine ZnCo$_2$O$_4$ powder exhibits worse cycling performance and shows rapid capacity fading as compared to flower structure ZnCo$_2$O$_4$ nanowires grown on carbon fiber, revealing that the poor electronic conductivity and large volume change of the ZnCo$_2$O$_4$ powder during the electrochemical reaction led to fast capacity decrease. Therefore, flower-like ZnCo$_2$O$_4$ nanowires architecture enhances the fast Li-ion transport, and accommodates volume expansion/contraction during Li insertion/extraction processes in addition to the presence of carbon fiber which improves the conductivity of binder-free ZnCo$_2$O$_4$ nanowires anode. Fig. 5f shows the capacity of pure carbon fiber to figure out the contribution of carbon fiber in anode total capacity (at 200 mA g$^{-1}$). The figure reveals that pure carbon cloth exhibited low capacity (only about 20 mA h g$^{-1}$ for 50 cycles), indicating that the capacity of carbon cloth has almost no effect on the overall capacity of ZnCo$_2$O$_4$ electrodes.

Fig. 6a shows the voltage–capacity profiles of an as-prepared full coin cell battery that uses LiCoO$_2$ as cathode and flower-like ZnCo$_2$O$_4$ nanowires/carbon fiber as anode for the first, second

![Image](310x99 to 546x303)

Fig. 6a shows the first three cycles of a full battery using LiCoO$_2$ cathode and ZnCo$_2$O$_4$ flower-like nanowire anodes. (b and c) The optical image of as-fabricated and bended flexible full battery based on ZnCo$_2$O$_4$/liquid electrolyte/LiCoO$_2$ show (LED) lighting, respectively.
and third charge–discharge cycles at a current rate of 200 mA g$^{-1}$ in the voltage window of 2.2 V to 3.7 V. The corresponding charge–discharge curves present two plateaus, with an average discharge voltage of ~3.4 V. The initial discharge capacity of the hybrid electrodes is about 1225 mA g$^{-1}$, and the discharge capacity remains stable in the following cycling, indicating good reversibility. Fig. 6b and c show that the commercial LED is easily lightened even when the battery was completely bent (Fig. 6c). This result indicates the ability of our fabricated flexible battery device to meet the special needs of next-generation, high-performance flexible electronics.

4. Conclusions

In summary, we have successfully fabricated flower-like ZnCo$_2$O$_4$ nanowires onto carbon fiber by using the hydrothermal synthesis method followed by a thermal procedure in air. The flower-like ZnCo$_2$O$_4$ nanowires are mainly composed of porous nanowires that converge to form a fluffy shape over carbon fiber. This architecture not only favors fast Li-ion transport, but also accommodates volume expansion/contraction during Li insertion/extraction processes. The flower-like ZnCo$_2$O$_4$ nanowires exhibit high capacity and excellent cycling stability when used as an anode material for Li-ion batteries, and can also be used to light up commercial LEDs.

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