

Research Article

Twist-Shaped CuO Nanowires as Anode Materials for Lithium Ion Batteries

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Received 21 April 2016; Accepted 8 May 2016

Academic Editor: Gongming Wang

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Twist-shaped CuO nanowires were synthesized by two-step method consisting of solution reaction and then heat treatment. The as-synthesized samples were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). When evaluated as anode materials for lithium ion batteries, twist-shaped CuO nanowires showed a high initial discharge capacity of 983 mAh g^{-1} and maintained a reversible capacity of 320 mAh g^{-1} over 50 cycles at the current density of 100 mA g^{-1} . Thus, 1D twist-shaped CuO nanowires provide a new insight into the development of anode materials for next-generation high performance lithium ion batteries.

1. Introduction

Rechargeable lithium ion batteries have been considered as the most promising energy storage device for portable electronic devices and electrical vehicles due to their high electromotive force and high energy density [1–4]. Graphite is commonly used as the anode material for commercial lithium ion batteries owing to its natural abundance and low cost [5, 6]. However, graphite with low capacity of 372 mAh g^{-1} can not meet the increasing demand for high energy density [7, 8]. Therefore, it is urgent to explore a novel anode material with high theoretical capacity, such as silicon based materials [9], lithium alloy materials, and transition metal oxides [10].

As one of the transition metal oxides, CuO has attracted extensive attention because of its natural abundance, low cost, and ecofriendliness [11, 12], and it has a high theoretical capacity of 674 mAh g^{-1} , which is almost two times that of graphite. Same as the other transition metal oxides, it suffers from the large volume expansion and agglomeration during the discharge-charge process, which results in poor conductivity, rapid capacity fading, and poor cycle performance [13]. Some strategies have been made to resolve these issues significantly [14, 15]. It is reported that the CuO with various nanostructures can effectively alleviate these drawbacks, such as 0D nanoparticles [16], 1D nanowires [17],

2D nanoplates [18], and 3D nanoflowers [19]. Recently, 1D nanowires have shown great potential application in lithium ion batteries due to their large specific surface area and the porous nanostructures. It can provide short diffusion path lengths for lithium ion transport to improve the electrical conductivity and relieve the volume expansion [20, 21].

Herein, twist-shaped CuO nanowires were synthesized by two-step method consisting of solution reaction and then heat treatment for the $\text{Cu}(\text{OH})_2$ precursor at different temperatures (300°C , 400°C , and 500°C) in air. The as-prepared CuO nanowires exhibited enhanced lithium storage capacity and good cyclic performance as anode materials for lithium ion batteries.

2. Experimental

2.1. Preparation of Materials. All reagents were of analytical grade and directly used without further purification. In the typical synthesis process, 0.302 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and 5 mL of H_2O_2 were dissolved in 50 mL of deionized water under stirring constantly at room temperature for 15 min . Then, 50 mL of NaOH (0.15 M) aqueous solution was added to the above solution under mild mechanical stirring and kept for another 30 min . Next, the resulting samples were collected and washed and centrifuged with deionized water

and ethanol for several times and then dried at 60°C for a night in air. Finally, the CuO nanowires were obtained by annealing at 300°C, 400°C, and 500°C in air for 20 min and named as CuO-300°C, CuO-400°C, and CuO-500°C, respectively.

2.2. Structure and Morphology Characterization. X-ray powder diffraction patterns were collected with a TD-3500 X-ray diffractometer equipped with Cu/K α radiation ($\lambda = 0.154056$ nm); the collection angles were set to 10° to 80° with a scanning rate of 0.07° s⁻¹. The morphology and microstructure of the samples were investigated by scanning transmission electron microscopy (TEM-2100).

2.3. Electrochemical Measurements. Electrochemical experiments were carried out in 2032 coin-type cells. The working electrodes were prepared by mixing the active material (CuO nanowires), acetylene black, and polyvinylidene fluoride (PVDF) with a weight ratio of 80:10:10 in 1-methyl-2-pyrrolidinone (NMP) to form homogeneous slurry and the slurries were uniformly coated on the copper foil and finally dried at 100°C under vacuum for 12 hours; the total mass loading of the electrode is about 3 mg. The pure lithium sheet was as the counter and reference electrode. The electrolyte was 1 M LiPF₆ in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume). All the cells were assembled in an argon-filled glovebox with the content of moisture and oxygen below 0.1 ppm.

Cyclic voltammetry (CV) and electrochemical impedance spectra (EIS) measurements were performed using CHI 760E electrochemistry workstation. The CV curves were obtained at a scan rate of 0.2 mV/s and the EIS plots were conducted in the frequency range from 100 kHz to 0.01 Hz. The galvanostatic charge-discharge tests were recorded on a Battery Testing System (Neware BTS-610) at the current density of 100 mA g⁻¹ in the voltage range of 0.01 to 3.0 V.

3. Results and Discussion

The schematic growth progress for the formation of twist-shaped CuO nanowires via a typical solution reaction and then heat treatment method is shown in Figure 1. When Cu(NO₃)₂·3H₂O and H₂O₂ solution were mixed under stirring constantly at room temperature, a blue solution was obtained. After 15 min, NaOH was added to the above solution, immediately resulting in a black turbid solution and forming numerous black Cu(OH)₂ precipitates. With increasing reaction time, the Cu(OH)₂ further aged and finally formed individual nanowire structures. Lastly, the twist-shaped CuO nanowires were obtained by annealing at temperature of 300–500°C.

The morphology and structure of twist-shaped CuO nanowires (500°C) were characterized by TEM. Figure 2(a) confirmed that the samples were a uniform nanowires' structure with a length of 0.75–2.7 μm. From the enlarged TEM image of samples in Figure 2(b), we could further see that the porous structure-like Chinese hemp flowers rope consisted of several twist-shaped nanowires with a width of

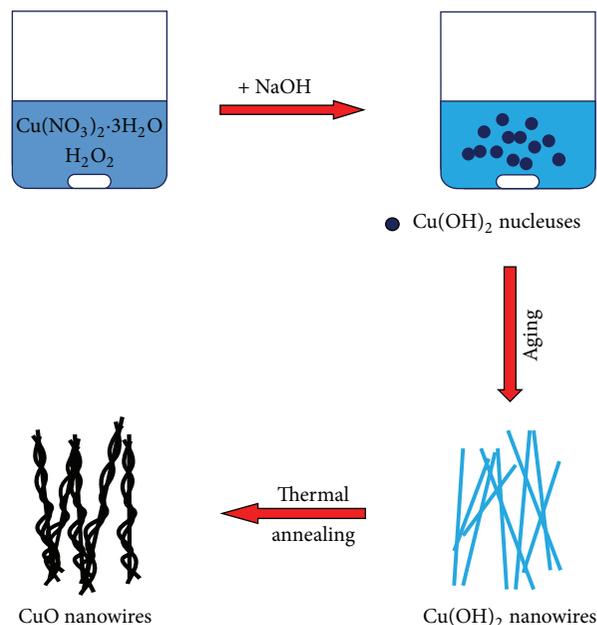


FIGURE 1: Schematic illustration of twist-shaped CuO nanowires.

about 20–75 nm and pores ranging from a few to a few tens of nanometers in diameter, which was beneficial to the intercalation of extra lithium and shortened the path of lithium ion transport during the charge-discharge process. The electron diffraction pattern of twist-shaped CuO nanowires (500°C) was shown in inset of Figure 2(b).

The crystal structures of the samples were further studied by powder X-ray diffraction in Figure 3. Apparently, the diffraction peaks of Cu(OH)₂ nanowires at different angles were like high pure crystal without other peaks compared with the standard card of Cu(OH)₂ (JCPDS 13-0420). Meanwhile, CuO-300°C, CuO-400°C, and CuO-500°C nanowires were also consistent with the standard card of CuO (JCPDS 48-1548), indicating that Cu(OH)₂ nanowires had transformed to monoclinic crystal CuO nanowires. Besides, the order of the full-width-at-half-maximum (FWHM) of XRD peaks for three CuO samples was 0.484° (CuO-500°C) < 0.593° (CuO-400°C) < 0.851° (CuO-300°C), which confirmed that the CuO-500°C nanowires had better pure crystallinity than others.

In order to investigate the performance of twist-shaped CuO nanowires, electrochemical characterization was conducted based on 2032 coin-type cells with pure lithium sheet as the counter electrode. The cyclic voltammetry curves of the CuO-500°C nanowires anode for the 1st, 2nd, and 3rd cycles in the potential range from 0 V to 3 V (versus Li⁺/Li) at a scan rate of 0.2 mV s⁻¹ were shown in Figure 4(a). In the first cathodic process, there were two peaks located at around 0.69 V and 0.93 V, which might be ascribed to the formation of a solid electrolyte interface (SEI) layer and the reduction of CuO to Cu, respectively [22]. In the first anodic process, two oxidation peaks at 0.81 V and 2.48 V were attributed to the oxidation of metallic Cu to Cu₂O and the oxidation of Cu₂O to CuO, respectively [23]. In subsequent cycles, the cathodic peaks shifted to 1.09 V and 0.61 V due

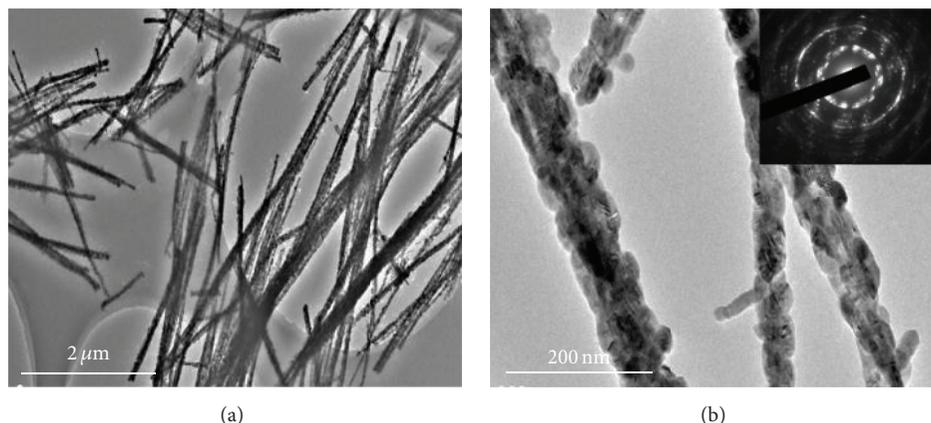


FIGURE 2: (a) Low-resolution TEM of twist-shaped CuO nanowires (500°C) and (b) high-resolution TEM of twist-shaped CuO nanowires (500°C). The inset presents SAED pattern of CuO nanowires (500°C).

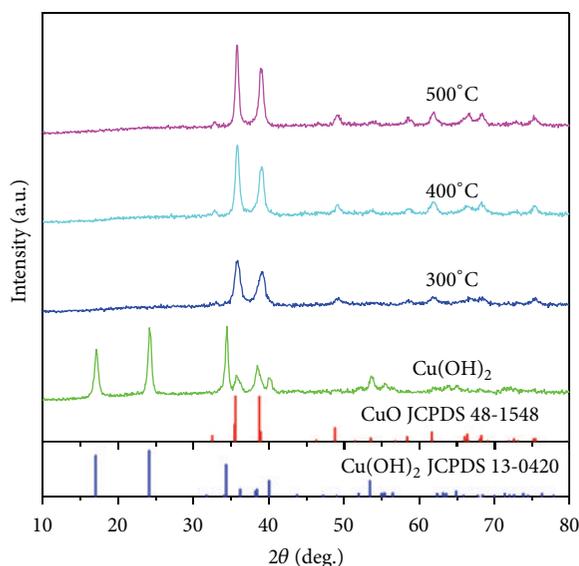


FIGURE 3: XRD patterns of the as-prepared Cu(OH)₂ nanowires and CuO-300°C, CuO-400°C, and CuO-500°C nanowires.

to the structure modification after the first cycle [18], and the anodic peaks overlapped very well, suggesting that the electrochemical reversibility of CuO tended to be more stable.

Figure 4(b) presented the galvanostatic discharge-charge profiles of CuO-500°C nanowires at the current density of 100 mA g⁻¹ in the voltage of 0~3.0 V. In the first discharge profile, two obvious sloping potential plateaus located at 1.6–1.15 V and 1.0–1.25 V were observed. The first long voltage plateau (1.6–1.15 V) implied that the lithium insertion to CuO was to form Cu and the second voltage plateau at 1.0–1.25 V was ascribed to the formation of a solid electrolyte interface (SEI) layer [16, 24]. In the following charge profile, an unobvious voltage plateau at around 2.41 V represented the oxidation of metallic Cu to CuO [23], which was in good agreement with the CV results. In the first cycle, the discharge capacity of CuO-500°C nanowires was about 983 mAh g⁻¹; however, the first charge capacity dramatically decreased to 496 mAh g⁻¹ corresponding to low coulombic efficiency

of 50%. The high capacity loss was believed to originate from the decomposition of electrolyte and the formation of solid electrolyte interface (SEI) layer on the electrode surface [25, 26]. At the second cycle, the discharge capacity was 495 mAh g⁻¹, with coulombic efficiency of 95.2%, and 482 mAh g⁻¹ and 96.5% at the third cycle, which indicated that the reversible performance increased.

The cycling performances of twist-shaped CuO nanowires of different temperature and their corresponding coulombic efficiencies at the current density of 100 mA g⁻¹ were shown in Figure 4(c). It can be seen that the CuO-500°C nanowires showed the highest capacity of 983 mAh g⁻¹ for the first cycle, the CuO-400°C presented lower capacity of 956 mAh g⁻¹, and the CuO-300°C presented the lowest capacity of 948 mAh g⁻¹. Although all samples had a higher capacity than the theoretical capacity of CuO (670 mAh g⁻¹) for the first cycle, they have a low coulombic efficiency, which is attributed to the formation of SEI layer on the electrode surface, large volume expansion, and electrode decomposition during the charge-discharge process [12, 27]. Even after 50 cycles, the discharge capacity of 320 mAh g⁻¹ of CuO-500°C was much higher than 203 mAh g⁻¹ of CuO-400°C and 133 mAh g⁻¹ of CuO-300°C. It is also better than that of spherical CuO nanoparticles reported by Zhang et al., 300 mAh g⁻¹ after 30 charge/discharge cycles [28]. Therefore, CuO-500°C nanowires exhibited the most excellent performance, which indicated that high temperature calcination was beneficial to the lithium storage. In addition, all samples possessed a high coulombic efficiency of 98% except the first several cycles.

In order to verify the remarkable cycle performance of CuO nanowires electrodes, electrochemical impedance spectrum (EIS) was performed on the cell. Electrochemical impedance spectrum (EIS), in Figure 4(d), consisted of a small semicircle at the high-medium frequency region and a long line at the low-medium frequency region. In the high-medium frequency, semicircle represented the electric contact and charge-transfer resistance and, in the low-medium frequency, the slope of line associated with lithium ion diffusion activity. Obviously, we could observe that the diameter

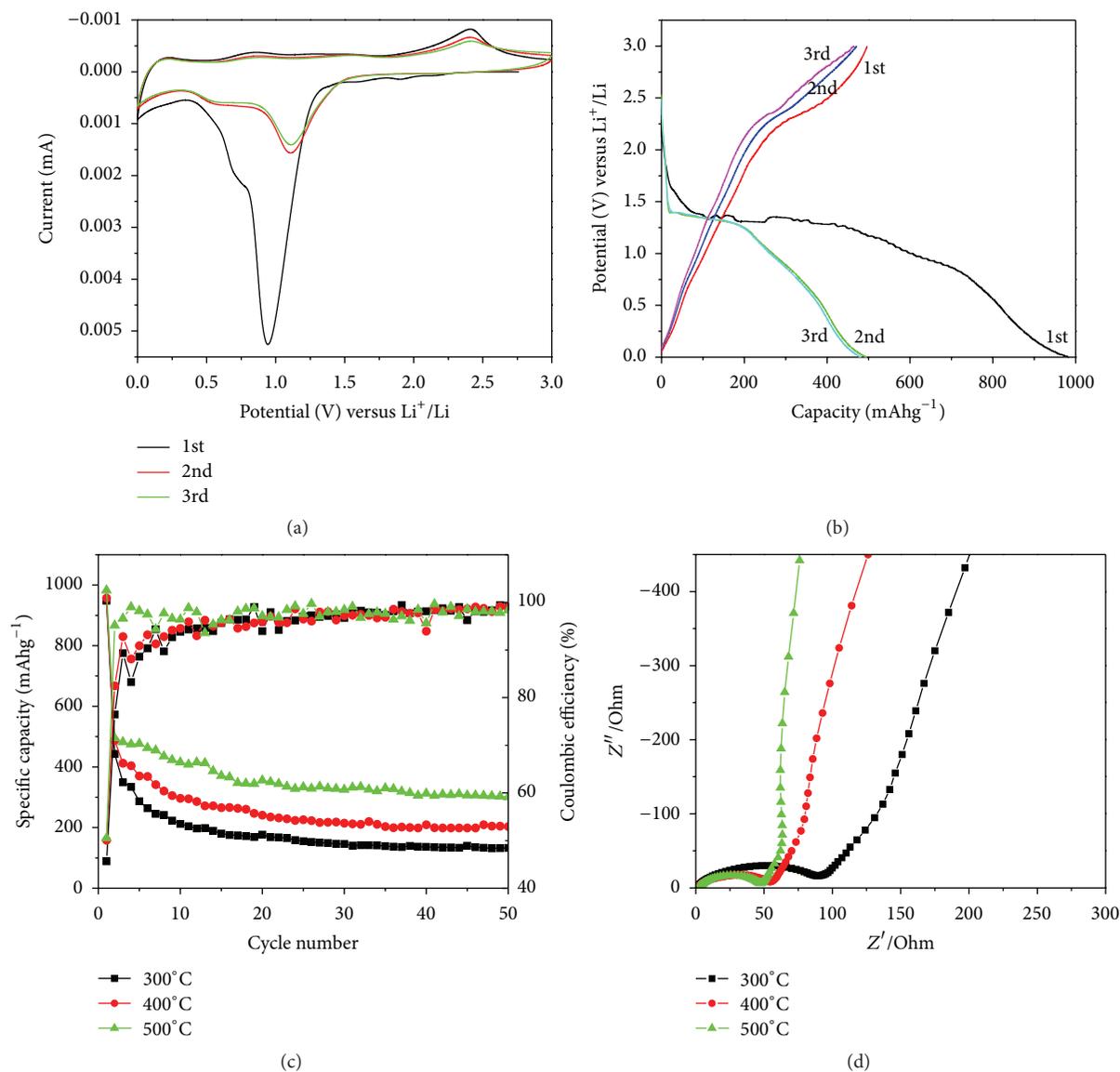


FIGURE 4: (a) Cyclic voltammograms of CuO-500°C nanowires in the 1st, 2nd, and 3rd cycles. (b) Galvanostatic discharge-charge profiles in the 1st, 2nd, and 3rd cycles of CuO-500°C nanowires at the current density of 100 mA g⁻¹. (c) Cycling performances of CuO-300°C, CuO-400°C, and CuO-500°C at the current density of 100 mA g⁻¹. (d) Electrochemical impedance spectra plots of CuO nanowires electrodes over the frequency range of 100 kHz and 0.01 Hz.

of the semicircle of CuO-500°C was smaller than that of CuO-400°C and CuO-300°C, suggesting that CuO-500°C had the lowest electric contact and charge-transfer resistance. What was more, the slope of line of CuO-500°C was bigger compared to others, which also verified the front result. Because of better crystallinity at 500°C, CuO at 500°C showed more superior electrochemical performance to the other temperatures.

4. Conclusion

In this work, twist-shaped CuO nanowires were successfully synthesized by two-step method consisting of solution reaction and then heat treatment for the Cu(OH)₂ precursor at different temperature in air. This method is simple, rapid,

green, and of low cost. When evaluated as anode materials for lithium ion batteries, CuO-500°C nanowires showed a great electrochemical performance, including high discharge capacity and high capacity retention, delivered a high initial discharge capacity of 983 mAh g⁻¹ in the first cycle, and maintained a reversible capacity of 320 mAh g⁻¹ over 50 cycles at a current density of 100 mA g⁻¹. Thus, 1D twist-shaped CuO nanowires provided a new insight into the development of anode materials for next-generation high performance lithium ion batteries.

Competing Interests

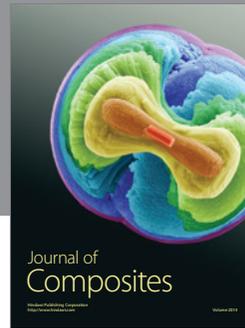
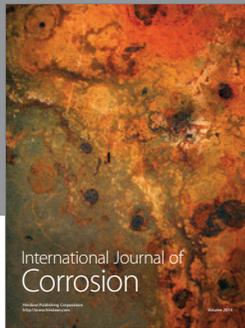
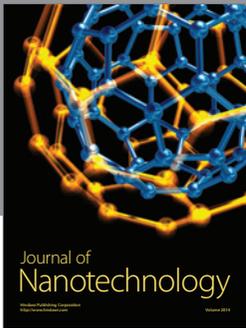
The authors declare that they have no competing interests.

Acknowledgments

This work was financially supported by Basic and Frontier Research Program of Chongqing Municipality (cstc2015jcyjA90020 and cstc2014jcyjA10063), Scientific and Technological Research Program of Chongqing Municipal Education Commission (KJ1501101, KJ1500323, and KJ1501116), Introduction of Talent Project of Chongqing University of Arts and Sciences (R2013CJ06), China Postdoctoral Science Foundation (2015M582499), Postdoctoral Special Foundation of Chongqing (Xm2015064), Project of Chongqing Normal University (14XY025 and 14XLB004), and National Natural Science Foundation of China (51502030).

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