RAPID COMMUNICATION

Controlled synthesis of micro/nanostructured CuO anodes for lithium-ion batteries

Chen Wang\textsuperscript{a}, Drew Higgins\textsuperscript{b}, Fangfang Wang\textsuperscript{a}, Deyu Li\textsuperscript{a}, Ruiqing Liu\textsuperscript{a}, Guofeng Xia\textsuperscript{a}, Ning Li\textsuperscript{a,*}, Qing Li\textsuperscript{b,*}, Hui Xu\textsuperscript{b}, Gang Wu\textsuperscript{b,c,**}

\textsuperscript{a}School of Chemical Engineering and Technology, Harbin Institute of Technology, Harbin 150001, China
\textsuperscript{b}Materials Physics and Applications Division, Los Alamos National Laboratory, Los Alamos, NM 87545, United States
\textsuperscript{c}Department of Chemical and Biological Engineering, University at Buffalo, The State University of New York, Buffalo, NY 14260, United States

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Abstract

Three different morphology controlled copper oxide materials (porous microspheres, flower-like, and thorn-like CuO) were prepared by facile and environmentally friendly processes, which were further investigated for their electrochemical properties and performance at lithium-ion battery anodes. CuO microspheres were prepared by simply solution chemistry, whereas flower-like and thorn-like CuO structures were prepared hydrothermally, with the structural transformations arising due to selection of chloride or sulfate counter ions in the precursor salts, respectively. After a 400 °C heat treatment in air, the morphology controlled materials demonstrated excellent phase purity as indicated by X-ray diffraction (XRD), and we propose a growth mechanism for the various materials based on systematic investigation of the structure and properties of the intermediate species. The electrochemical and lithium-ion battery performance employing the shape controlled CuO materials was investigated, allowing for elucidation of the synthesis-structure-performance correlations of CuO-based anodes. The performance of lithium-ion batteries was found to be highly dependent on the CuO morphology. The CuO microspheres exhibit a superior electrochemical performance to the other two CuO samples in terms of cycle capacity and rate performance, indicating a viable strategy to prepare next-generation lithium-ion battery systems with improved storage capacities.

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Corresponding authors.
**Corresponding author at: Department of Chemical and Biological Engineering, University at Buffalo, SUNY, Buffalo, NY 14260, United States.
E-mail addresses: ninglihit@263.net (N. Li), qinglianlg@gmail.com (Q. Li), gangwu@buffalo.edu (G. Wu).

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Introduction

Recently, considerable efforts have been aimed at developing high performance lithium-ion batteries (LiBs) for applications ranging from rapidly expanding portable electronics markets, electric vehicles (EVs) and hybrid electric vehicles (HEVs), along with stationary power storage devices [1-4]. The performance and economic feasibility of these technologies however depends largely on the properties and technological capabilities of the commercially available batteries they rely on. At the current state of LiBs technology, it is well accepted that commercial graphite anodes will not be capable of meeting rapidly increasing energy demands in the near feature [5]. As highly promising candidates for next generation LiBs devices, 3d transition oxides (such as CuO, Fe2O3, Co3O4, NiO, MnO2, etc.) anodes can provide much better electrochemical performance, inspiring many recent studies that investigate their potential replacement of conventional graphite anodes in high performance LiBs [6-9]. Among these transition metal oxides, CuO provides attractive properties, such as a high specific energy storage capacity of 674 mAh g⁻¹, abundant global reserves, economical affordability, environmental compatibility and ease of production [8,10]. Despite the many advantages, CuO electrodes suffer from low electrical conductivity, which is unfavorable for charge transfer during LiBs operation, thereby resulting in poor electrochemical performance. Additionally, CuO electrodes suffer from rapid capacity decay due to the large volume variations and significant structural changes occurring during charge and discharge processes. This in turn leads to mechanical pulverization and makes it difficult for CuO electrodes to achieve long cycling lifetimes and high rate capabilities [2,11,12].

To overcome these drawbacks, significant research efforts have been devoted to improving the performance of CuO-based electrodes through micro/nanstructured design [13,14], morphology control techniques [11,15], and hybridization of composites materials [16,17]. This has resulted in the development of several materials with unique structures and encouraging electrochemical properties reported in recent years. Particularly, three-dimensional hierarchical architectures with tailored morphologies and patterns built from micro/nanosized building blocks have attracted considerable interest in battery electrode material research [2,18-20]. By careful control the active material morphology in the electrodes, the diffusion length of lithium-ions, contact areas between active materials and the electrolyte, and the properties of the SEI film can be modulated, providing a profound influence on the resulting electrochemical behavior and performance [21-23]. Recent studies have demonstrated that optimization of morphology of electrode materials was a critical factor in modulating the electrochemical properties and battery performance. For instance, ordered mesoporous carbons (OMCs) anodes with different channel lengths demonstrate different reversible discharge capacities, which is attributed to morphology governed changes to the lithium-ion diffusion path and thereby modifying the reversible capacity, cyclic and the rate performance [24]. A series of hematite (α-Fe2O3) hierarchical structures have been fabricated by hydrothermal procedures, and the electrochemical measurements of these structures have also shown that lithium storage properties are closely related to the crystallinity and morphology, once again indicating that the surface and morphological properties are of fundamental importance to electrochemical performances [25]. Several structural amorphous TiO2 film electrodes have also indicated the cyclability, rate capability, and Coulombic capacity of the electrodes depended on their morphology and porosity [26]. As for cathode materials in LiBs, several tailored morphologies of LiMnP04 also showed electrochemical properties are correlated with morphologies greatly, the optimization of morphology are beneficial to fast lithium-ion diffusion rate, short diffusion length as well as large contact area between the electrode and electrolyte [27]. While studies of this nature for a variety of different materials are prevalent in the literature, the influence of CuO-based material morphology remain largely uninvestigated, whereby the controllable synthesis of CuO materials with novel morphologies is crucial for understanding morphology-dependant electrochemical properties and performance. Not only will this generate fundamentally significant knowledge, critical insight will be provided into realizing performance gains through CuO morphology design for practical applications [28-30]. Herein, we design a simple method for the large-scale synthesis of CuO microspheres, flower-like CuO and thorn-like CuO, allowing us to explore the influence of CuO micro/nanostructure on the electrochemical properties and LiB performance.

Electrochemical properties

Materials synthesis

All reagents used in the present study were of analytical grade and used without further purification. In a typical CuO microsphere synthesis, 2.42 g of copper nitrate and 1.06 g of anhydrous sodium carbonate were dissolved in 50.0 mL of distilled water and mixed together. While stirring, the mixture was maintained at 70 °C in a water bath for 2 h. The resulting green precipitate was collected by centrifugation, washed several times with distilled water and dried in a blast drying oven. Finally, the powder was calcined in air at 400 °C for 2 h, and the resulting black powders were collected for testing. Flower-like CuO and thorn-like CuO were synthesized by a hydrothermal method using copper chloride, and copper sulfate as copper precursors, respectively. In a typical procedure, 0.81 g copper chloride (or 1.2 g copper sulfate) and 0.86 g urea were added into 320 mL of deionized water to form a transparent blue solution. The solution was then transferred to a 400 mL Teflon-lined stainless steel autoclave, which was allowed to react at 180 °C for 18 h, followed by cooling to room temperature under ambient conditions. The obtained powders were collected by centrifugation and washed several times with deionized water and ethanol. Finally, the as-synthesized powders were further calcined in air at 400 °C for 2 h to obtain the final product.

Physical characterization

Phase structures of the samples were characterized in the 2θ range of 20-70° by x-ray diffraction (XRD, D8, Bruker AXS) using a copper target. Sample morphologies were determined using field emission scanning electron microscopy.
(FESEM, Quanta 200F, FEI). The sample surface atomic concentrations and chemical bonding energies were obtained by x-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo Fisher Scientific) using microfocused monochromatized Al Kα radiation. Spectra were collected under the residual pressure of the analysis chamber which was $1 \times 10^{-9}$ mbar. All the XPS spectra data were corrected with respect to the C 1s peak (at a binding energy of 284.6 eV). The XPS peak software was used to fit the photoelectron spectra using a least squares algorithm with the background accommodated by a nonlinear Shirley function.

**Electrochemical measurements**

Electrochemical testing was performed using coin type (CR-2025) testing cells, containing the CuO active material as the working electrode and metallic lithium foil as both the reference and counter electrodes. The CuO working electrodes were prepared by a slurry coating procedure. The slurry consisted of active material, acetylene black and polyvinylidene fluoride (PVDF) binder with a weight ratio of 80:10:10. All of these components were dispersed in N-methyl-2-pyrrolidone (NMP) solvent and stirred over night to form a uniform slurry. The mass of each working electrodes was precisely measured with an electronic analytical microbalance. Testing cells were assembled in an argon filled glovebox, where the moisture content and oxygen levels were controlled below 1 ppm (20°C). The electrolyte was 1 M LiPF$_6$ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with a 1:1 volumetric ratio, and polypropylene microporous membrane (Celgard 2300) was used as the separator. Cyclic voltammetry (CV) was conducted using an electrochemical workstation from 0.02 to 3.0 V (vs. Li$^+$/Li) at a scan rate of 0.2 mV s$^{-1}$. Electrochemical impedance spectroscopy (EIS) was also performed in the range from 100 kHz to 0.01 Hz at open circuit potential.

**Results and discussion**

**Morphology**

Morphologies and microstructures of the as-prepared samples were examined by SEM. Typical SEM images of the samples are shown in Figures 1 and S1, demonstrating uniform morphologies for all as-prepared materials. Among them, CuO solid spheres with a diameter of 5.5-7.0 μm composed of numerous nanorods were prepared when CO$_3^{2-}$ was used as the anion precursor species (Figure 1a). The surface of CuO microspheres is very rough, which could contribute to enhanced contact between the electrode and electrolyte. Furthermore, the spherical structure is stable from an architecture perspective and may absorb deformation energy during discharge/charge processes. When Cl$^-$ was used as the anion precursor species, CuO exhibiting a flower-like morphology resulted as shown in Figure 1b. This flower-like structure is composed of nanoplates (Figure S1f) a few nanometers in thickness and width, and about 1.5-2.0 μm long. In Figures 1c and S1g, the brawny thorn-like CuO skeletons with a size of about 10-25 μm and hierarchical construction prepared using SO$_4^{2-}$ as the anion precursor species are displayed. These structures consist of a large number of branches, whereby each branch is ca. 10 μm in length and 4 μm in width.

![Figure 1](image-url) SEM images of the (a,d) CuO microspheres, (b,e) flower-like CuO and (c,f) thorn-like CuO samples after calcination.
XRD patterns

The crystal structure of the as-prepared CuO samples (CuO microspheres, flower-like CuO and thorn-like CuO after calcination) was confirmed by XRD as shown in Figure 2. No obvious impurities (such as basic cupric carbonate or copper hydroxide) were detected, indicating the high phase purity of the prepared samples. All of the diffraction peaks can be well indexed to the monoclinic symmetry of CuO (JCPDS file no. 45-0937) with lattice constants \( a = 4.684 \text{ Å} \), \( b = 3.425 \text{ Å} \) and \( c = 5.129 \text{ Å} \). Furthermore, as calculated using the Scherrer equation, the average crystal size of the CuO microspheres, flower-like CuO and thorn-like CuO was estimated to be 14.3 nm, 23.1 nm and 26.1 nm, respectively.

XPS analysis

The surface composition and electronic structures for the nanostructure controlled CuO materials were examined by XPS, with the spectra obtained for CuO microspheres shown in Figure 3. The XPS spectrum of the Cu 2p 3/2 core-level spectra of calcined CuO microspheres was resolved using a Gaussian curve-fitting procedure, with results presented in Figure 3a. The Cu 2p 3/2 core level spectrum reveals a main peak at 934.2 eV and a series of shake-up satellites peaks (941.5 and 943.9 eV, respectively) with higher binding energy values. These features correspond to Cu\(^{2+}\) the state of copper characteristic of the CuO phase. Furthermore, the shake-up satellite peaks are evident of an open 3d\(^9\) shell which corresponds to Cu\(^{2+}\) in the ground state. The XPS O 1s core-level spectrum (Figure 3d) was also resolved using a curve-fitting procedure. The main peak of O 1s observed at 529.5 eV corresponds to the binding energy value of Cu-O, which is further evidence of the presence of CuO on the surface of the CuO microspheres. On the other hand, two peaks (531.2 and 533.4 eV, respectively) observed with higher binding energy values can be attributed to O-O and O-H bonds. These additional peaks may be due to the physically adsorbed O\(_2\) or H\(_2\)O on the surface of the CuO microspheres. The XPS spectra of flower-like CuO (Figure 3b, e) and thorn-like CuO (Figure 3c, f) also exhibit similar features. These features all suggest the predominant existence of CuO after the calcination step.

Formation mechanism

As illustrated in Figure 4, the probable steps for the formation and transformation mechanism of the nanostructured CuO materials are proposed.
For CuO microspheres, Na₂CO₃ hydrolyzes in the hot solution during the preparation process. Decomposition of OH⁻ and CO₃²⁻ deposit Cu²⁺ into Cu₂(OH)₂CO₃ solid, whereby the XRD patterns and FT-IR spectrum of the CuO microspheres before calcination correspond to Cu₂(OH)₂CO₃ (JCPDS file no. 41-1390) as shown in Figure S2, supporting information. The chemical reactions involved in the CuO microspheres formation are proposed as follows [41]:

\[
\text{CO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{HCO}_3^- + \text{OH}^- \\
2\text{Cu}^{2+} + 2\text{OH}^- + \text{CO}_3^{2-} \rightarrow \text{Cu}_2(\text{OH})_2\text{CO}_3 \downarrow
\]

The TG-DSC curve of the precursor Cu₂(OH)₂CO₃ is shown in Figure S3. Only a single weight-loss peak is observed at 331 °C, which can be ascribed to the decomposition of the Cu₂(OH)₂CO₃ precursor:

\[
\text{Cu}_2(\text{OH})_2\text{CO}_3 \rightarrow 2\text{CuO} + \text{CO}_2 \uparrow + \text{H}_2\text{O}
\]

From the reaction above, the estimated weight loss is 28.0%, which is in agreement with the experimental value of 28.1% at 400 °C observed by TG. It is concluded that the precursor is completely decomposed above 400 °C.

For flower-like CuO and thorn-like CuO, urea was used as a homogeneous precipitation agent during the hydrothermal process. Urea is usually stable in aqueous solutions without obvious hydrolyzation below 70 °C [42,43]. During the hydrothermal process, the decomposition of urea produce OH⁻ and CO₃²⁻ anions in an aqueous solution, and slowly deposit Cu²⁺ cations, and then form homogeneous precipitation gradually [44,45]. XRD patterns, FT-IR spectra and SEM imaging were also used to study the evolution of phase formation and morphologies for flower-like CuO and thorn-like CuO. The XRD patterns (Figure S4a, c, supporting information) of the flower-like CuO and thorn-like CuO samples (employing copper chloride and copper sulfate as copper source, respectively), correspond to Cu₂(OH)₃Cl (JCPDS file no. 50-1559) and Cu₄(OH)₆SO₄ (JCPDS file no. 43-1458), respectively [46–48]. The FT-IR spectra also confirm these results as shown in Figure S4b, d, supporting information. The copper chloride hydroxide shows an octahedral morphology, whereas copper sulfate hydroxide shows a ribbon like morphology.

Based on the above experimental observations, it is believed that during the hydrothermal process, the formation of copper hydroxide salt compounds proceeds by the following reactions:

\[
\text{H}_2\text{NCONH}_2 + 3\text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{NH}_4^+ + 2\text{OH}^- \\
2\text{Cu}^{2+} + \text{Cl}^- + 3\text{OH}^- \rightarrow \text{Cu}_2(\text{OH})_3\text{Cl} \downarrow \\
4\text{Cu}^{2+} + 2\text{SO}_4^{2-} + 6\text{OH}^- \rightarrow \text{Cu}_4(\text{OH})_6\text{SO}_4 \downarrow
\]

The formation of the copper hydroxide salt compounds is due to the nature of the layered crystal structure as shown in Figure S6, supporting information [49,50]. The structure can be viewed as layers of octahedral copper stacked on top of each other. The anions (Cl⁻ and SO₄^{2-}) are situated in the interlayer, which are linked by hydrogen bonds to the hydroxyl groups belonging to the octahedral copper layers. With prolongation of the hydrothermal reaction time, the decomposition of urea could produce more ammonium hydroxide, and hence the anions would be replaced by OH⁻ resulting in the rapid collapsing and destruction of the layer structure under the high hydrothermal treatment temperatures [51]. The resulting copper hydroxide species can then be easily converted to copper oxide under the hydrothermal reaction conditions. This process can be described by the following reactions:

**Figure 4** Scheme of formation mechanism of CuO anodes with controlled morphologies.
\[
\text{Cu}_2(\text{OH})_3\text{Cl} + \text{OH}^- \rightarrow 2\text{Cu}((\text{OH})_2 + \text{Cl}^-
\]
\[
\text{Cu}_4(\text{OH})_6\text{SO}_4 + 2\text{OH}^- \rightarrow 4\text{Cu}((\text{OH})_2 + \text{SO}_4^{2-}
\]
\[
\text{Cu}((\text{OH})_2 \rightarrow \text{CuO} + \text{H}_2\text{O}
\]

**CV measurements**

CV curves were obtained at a scan rate of 0.2 mV s\(^{-1}\) to identify the electrochemical reactions of as-prepared CuO samples occurring at room temperature. All of the CuO electrodes exhibit similar features in the CV curves, as shown in Figure 5. Using CuO microspheres as the example, there are three cathodic peaks (at about 1.55 V, 0.89 V and 0.68 V) found in the first cathodic scan process as shown in Figure 5a. These cathodic peaks are related to the multi-step electrochemical reactions, which are attributed to the formation of an intermediate phase, the reductive reaction from CuO to Cu\(_2\)O, and finally the further reduction to Cu and Li\(_2\)O, respectively [7,52,53]:

\[
\text{CuO} + x\text{Li}^+ \rightarrow \text{Cu}_1\text{O} - x/2 + x/2\text{Li}_2\text{O} - xe^-
\]
\[
\text{Cu}_{1-x}\text{O} - x/2 + (1-x)\text{Li}^+ \rightarrow (1-x)/2\text{Cu}_2\text{O} + (1-x)/2\text{Li}_2\text{O} - (1-x)e^-
\]
\[
1/2\text{Cu}_2\text{O} + \text{Li}^+ \rightarrow \text{Cu} + 1/2\text{Li}_2\text{O} - e^-
\]

The reduction of the electrolyte solvent and growth of a solid electrolyte interface (SEI) film proceeding between 0 and 0.3 V on the first discharge process cannot be ruled out and result in an observed first cycle capacity loss [52].

In the first anodic scan process, there are two oxidation peaks found at 2.45 and 2.76 V, which are ascribed to the formation of Cu\(_2\)O and CuO. These electrochemical processes are expressed as follows [18,54]:

\[
\text{Cu} + 1/2\text{Li}_2\text{O} \rightarrow 1/2\text{Cu}_2\text{O} + \text{Li}^+ + e^-
\]
\[
1/2\text{Cu}_2\text{O} + 1/2\text{Li}_2\text{O} \rightarrow \text{CuO} + \text{Li}^+ + e^-
\]

Different from the flower-like and thorn-like CuO samples, the weak oxidation peak at 2.76 V of CuO microspheres likely corresponds to the process the partial oxidation of Cu\(_2\)O into CuO. This may be due to the rough and permeable surface of microsphere CuO electrodes as shown in Figure S1d and e, which helps facilitate the partial oxidation of Cu\(_2\)O into CuO, and result in this minor oxidation peak being observed.

**Battery and electrochemical measurements**

In order to test the morphology influence on the electrochemical properties, the as-prepared CuO samples were investigated and compared for their performance in LIBs. First, the galvanostatic discharge-charge curves of as-prepared CuO samples for the 1st, 2nd, 3rd and 15th cycles recorded in the voltage range of 0.02–3.0 V (vs. Li\(^+/\)Li) are provided in Figure 6. In the first discharge curve for CuO microspheres (Figure 6a), there are three plateaus (2.5-1.5 V, 2.5-1.0 V and 1.0-0.2 V) which involve formation of a Cu\(_{1-x}\text{O} - x/2\) solid and the Cu\(_2\)O phase, as well as decomposition of Cu\(_2\)O into Cu and Li\(_2\)O, respectively [7].

Similar behavior also observed for flower-like CuO and thorn-like CuO electrodes (Figure 6b and c, respectively), which are consistent with the results of CV discussed previously. The initial charge and discharge capacities of the CuO microspheres are measured to be 1063.9 and 664.1 mAh g\(^{-1}\), respectively. This represents an initial Coulombic efficiency of 62.4% in the first discharge-charge cycle, which is significantly higher than that of the other as-prepared samples (the initial Coulombic efficiencies of flower-like CuO and thorn-like CuO are 36.8% and 28.8%, respectively). The irreversible capacity can most likely be attributed to interfacial lithium storage, the formation of a SEI layer and electrolyte decomposition.

As shown in Figure 7a-c, the cycle performances of the CuO microspheres, flower-like CuO and thorn-like CuO cycled at a current density of 0.1 C were also compared.
Generally, the CuO microspheres electrode exhibited excellent cyclic retention capacity (669.7 mAh g\(^{-1}\)) and a high Coulombic efficiency (nearly 98%) from the third cycle onward. After 50 cycles, the reversible capacity of the CuO microspheres was still as high as 429.0 mAh g\(^{-1}\), indicating good cycle performance. In contrast, the flower-like CuO and thorn-like CuO show relatively stable albeit low cycle performance. As for the flower-like CuO and the thorn-like CuO, the electrode exhibits a reversible discharge capacity of 392.4 and 193.0 mAh g\(^{-1}\) after 50 cycles respectively.

Figure 7d exhibits the rate capability of the three different CuO electrodes at varying current densities. Overall, the CuO microsphere based electrode showed improved rate capability performance than the other as-prepared CuO electrodes. After 5 C rate test and upon decreasing the rate to 0.1 C, the reversible capacities of the CuO microsphere electrode reached 589.6 mAh g\(^{-1}\), likely due to better mass/charge exchange between the electrode and electrolyte. In contrast, the rate tests of flower-like CuO and thorn-like CuO show mediocre performance.

Electrochemical impedance spectroscopy (EIS) is useful widely used in studying rechargeable LIBs, which has led to a better understanding of many aspects such as SEI film properties, property of SEI film, failure mechanisms, self-discharge, lithium-cycling efficiency, interfacial phenomenon between the electrode and the electrolyte, and lithium-ion diffusion in the electrode and electrolyte [55,56]. The influence between morphology and conductivity of the as-prepared CuO electrodes was further compared by EIS measurements as shown in Figure 8a, with the corresponding equivalent circuit shown in Figure 8b. Generally, the plots consist of two semicircles, including a high-frequency semicircle and a medium-frequency semicircle overlapping each other, and a gradient line at a slope of about 45° in the low frequency region [57]. In the typical EIS equivalent circuit, the parameters \(R_e\), \(R_f\), \(R_{ct}\) and \(Z_w\) in the circuit correspond to the Ohmic resistance of the electrolyte and electrode in the test cells, the Ohmic resistances of lithium-ion migration through the SEI film, the charge-transfer resistance of corresponding electrochemical reactions and the Warburg impedance related to lithium-ion diffusion, respectively [21,58,59]. Moreover, \(C_t\) and the \(Q\) constant phase element (CPE) are related to SEI film capacitance and the double-layer capacitance of the working electrode, respectively [60].

A widely used equivalent circuit model (shown in Figure 8b) was constructed to analyze the impedance spectra [24,56,59]. The values of as-prepared CuO samples for \(R_e\), \(R_f\), \(R_{ct}\), and \(R_{total}\) are simulated from EIS data by using the equivalent circuit were listed in Table 1. Generally, the values of \(R_e\) for the three as-prepared CuO samples are not obviously different. However, it can be seen the value the \(R_e\) of as-prepared CuO (934.4 Ω) is significantly larger than the other samples (21.6 Ω for CuO microspheres and 11.9 Ω for flower-like CuO, respectively), which may due to the smooth surface of thorn-like CuO, which favors the formation of a dense SEI film. Meanwhile, \(R_{ct}\) values for CuO microspheres, flower-like CuO and thorn-like CuO are 162.46 Ω, 254.4 Ω and 153.9 Ω respectively. The difference of the value of \(R_{ct}\) between each sample may due to the different influence of morphology on the electrochemical performance. Furthermore, the value of total resistance of the thorn-like CuO (1092.6 Ω) is the largest. The results of impedance are in good agreement with the electrochemical performance discussed above. The thorn-like CuO sample suffered the largest initial performance loss accompanied by a higher \(R_e\) value determined by EIS. This is likely due to more dense SEI formation on the relatively smooth surface of the thorn-like structure.

Overall, in conjunction with the battery performance, the resistance of the SEI film is the main factor governing the observed electrochemical capacities.

The diffusion coefficient of LIBs is one of the most important parameters used to evaluate electrode materials [60]. The diffusion coefficient of lithium ions (\(D_0^{+}\)) in the CuO electrode can be calculated from a linear relationship between \(Z'\) and \(ω^{-1/2}\) from the EIS, with the model
Described by [6, 61, 62]:

\[
D_{Li^+} = \frac{R^2T^2}{2A^2n^4F^4C^2\sigma^2}
\]

\[
Z_w = R_0 + R_L + \sigma \omega^{-1/2}
\]

where \( R \) is the gas constant, \( T \) is the test absolute temperature in test environment, \( A \) is the surface area of the working electrode, \( n \) is the number of electrons per molecule attending the electronic transfer reaction, \( F \) is Faraday constant, \( C \) is the concentration of lithium ion in the working electrode, and \( \omega \) is the angular frequency, \( \omega = 2\pi f \) [28, 60]. Furthermore, the \( \sigma \) is the slope of the plots of \( Z' \) against \( \omega^{-1/2} \) which is shown in Figure 9. The diffusion coefficients of lithium-ions were calculated using the above equation, and the working electrode discharge to 1.5, 1.0 and 0.2 V, respectively. When the electrode is at different voltages, the \( n \) in the equation varies correspondingly, thus the lithium-ion diffusion is directly affected. Furthermore, the lithium-ion diffusion in the electrode is also strongly affected by the neighboring atoms, which change according to the electrode voltage [63].

The results presented in Table 2 show that \( D_{Li^+} \) of the CuO microspheres are \( 9.17 \times 10^{-11} \), \( 7.66 \times 10^{-9} \) and \( 3.93 \times 10^{-10} \) cm\(^2\) s\(^{-1}\) at 1.5, 1.0 and 0.2 V respectively, which is a significant improvement over the results of the other as-prepared CuO electrodes. It can be concluded that the CuO microspheres nanostructure is considerably more stable during the discharge-charge process.

Therefore, it can be concluded that the as-prepared CuO samples exhibit considerable morphology-dependent electrochemical properties. In particular, the CuO microspheres
exhibit a superior electrochemical performance over the other two CuO samples (flower-like CuO and thorn-like CuO) in terms of cycle capacity and rate performance. The excellent electrochemical performance achieved on CuO microspheres can be attributed to its morphology advantages. Durable spherical structures and rough surfaces, which are beneficial to faster lithium-ion diffusion rates and better battery performance, result in the fast interfacial charge transfer and low electrode polarization. The synthesis-structure-property correlations were well established so as to provide valuable insights for the development of nanostructured oxide anodes, which may lead to important implications in designing new high-performance lithium ion batteries materials.

**Conclusion**

Micro/nanostructure controlled CuO materials were prepared by simple, environmentally friendly procedures. CuO microspheres resulted from a simplistic aqueous based reaction, whereas flower-like and thorn-like CuO materials resulted from a hydrothermal reaction employing chloride and sulfate counter ions, respectively. The influence of CuO morphology on the electrochemical properties and performance as lithium-ion batteries was investigated in detail in terms of specific capacity, cyclability, rate performance, EIS spectra and diffusion coefficient of lithium ions. The electrode performance of CuO microspheres electrode perform an excellent cycle capacity with a reversible capacity from 664.1 to 429.0 mAh g\(^{-1}\) after 50 cycles, as well as good Coulombic efficiency and rate performance between as-prepared CuO electrodes. The role of CuO morphology was demonstrated to play an important role in tuning the lithium-ion battery performance, representing an ideal strategy to further improve the performance of unique electrode chemistries.

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**Appendix A. Supporting information**

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2014.08.009.

**References**

Fangfang Wang received her Ph.D. on synthesis and electrochemical characteristics of fullerenol at Harbin Institute of Technology in 2011. Now she is doing her postdoctoral research at State Key Laboratory of Physical Chemistry of Solid Surfaces at Xiamen University. Her research mainly focuses on localized surface plasmon resonance biosensor, and tip-enhanced optical spectroscopies.

Deyu Li is a lecturer in School of Chemical Engineering and Technology at Harbin Institute of Technology in China. He received his Ph.D. in the Applied Chemistry from Harbin Institute of Technology in 2014. His research mainly covers electronic electroplating and Li-ion batteries.

Guofeng Xia is a postdoctoral research associate at Shanghai Jiaotong University. He received his Ph.D. from Harbin Institute of Technology in 2013. His research interests are in the field of Li-ions and Li-air batteries.

Ning Li is a professor of Chemical Engineering at Harbin Institute of Technology. She received her Ph.D. in Environmental Engineering in 2000 from Harbin Institute of Technology. Her major research interests are batteries, metal materials corrosion mechanism and control, and principles and applications of electrodeposition and electroless deposition.

Qing Li is a postdoctoral research associate at Los Alamos National Laboratory. He received his B.Sc. from Wuhan University in 2005 and his Ph.D. from Peking University in 2010, both in chemistry. His research interests include functional nanomaterials and their applications in PEM fuel cells, metal-air batteries, and biosensors.

Hui Xu now is a senior scientist at Giner Inc. He obtained his Ph.D. in Chemical Engineering from the University of Connecticut in 2005. He was a postdoc at Los Alamos National Laboratory. His researches focus on the development of high-performance energy materials for electrochemical energy conversion and storage.

Gang Wu is an Assistant Professor in the Department of Chemical and Biological Engineering at the University at Buffalo (UB), the State University of New York. Prior to joining UB, He was a permanent staff Scientist at Los Alamos National Laboratory (LANL) from 2010 to 2014. He obtained his Ph.D. in Electrochemical Engineering at the Harbin Institute of Technology in 2004, followed by extensive postdoctoral trainings at Tsinghua University, the University of South Carolina, and LANL. His research focuses on functional materials and catalysts for electrochemical energy storage and conversion technologies.