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Simple synthesis of surface-modified hierarchical copper oxide spheres with needle-like morphology as anode for lithium ion batteries

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ABSTRACT

Hierarchical, nanostructured copper oxide spheres were synthesized in a stirred solution of cupric acetate and ammonium hydroxide. Cetyltrimethylammonium bromide (CTAB) was used as a surfactant to modify the surface morphology of CuO spheres. Ordered nano-needle arrays can be formed on the surface of the CuO spheres (instead of disordered nano-leaves) in the presence of CTAB. Each CuO sphere is about $2 \mu m$ in diameter and possesses a large number of nano-needles that are about 20-40 nm in width and more than 300 nm in length. The needle-like hierarchical structure can greatly increase the contact area between CuO and electrolyte, which provides more sites for Li⁺ accommodation, shortens the diffusion length of Li⁺ and enhances the reactivity of electrode reaction, especially at high rates. After 50 cycles, the reversible capacity of the prepared needle-like CuO can sustain 62.4% and 56.4% of the 2nd cycle at a rate of 0.1C and 1C, respectively.

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1. Introduction

Since Tarascon and co-workers [1] first reported the high capacity and excellent cycling capacity retention of CoO, many oxides of 3d transition metals (Fe, Co, Ni, and Cu) have been widely investigated as promising anodes for lithium ion batteries [2–5]. Among these transition metal oxides, CuO is proposed as an attractive anode because it is inexpensive, non-toxic, easily produced, readily stored and has a high theoretic capacity (670 mAh g⁻¹). The electrochemical reaction mechanism of CuO with Li⁺ is as follows:

$$CuO + 2Li^+ + 2e \Leftrightarrow Cu + Li_2O$$

Different morphologies and sizes of CuO can greatly influence its electrochemical properties [6]. Hence, in the past few years, many efforts have been devoted to synthesize CuO with various morphologies including hollow spheres, nanotubes, nanorods, nanoflowers and the like [7–13]. For instance, Gao et al. fabricated fine and polycrystalline CuO nanorods, which can deliver a reversible capacity of 550 mAh g⁻¹ for up to 100 cycles [8]. Chen et al. reported CuO nanowires can exhibit a reversible capacity of more than 600 mAh g⁻¹ even after 100 cycles [12]. Pan et al. demonstrated that sheaf-like CuO can sustain a reversible capacity of 580 mAh g⁻¹ after 40 cycles [14]. The improved electrochemical performances of CuO are due to the nanostructure, which increases the contact area between CuO and electrolyte and shortens the diffusion length of Li⁺ [15]. However, most nanostructured CuO is prepared within a relatively long time or under a complex preparation condition such as hydrothermal synthesis [12,14,16–18].

In the present work, we develop a very simple method to synthesize hierarchical, nanostructured CuO in a stirred solution of cupric acetate and ammonium hydroxide. Cetyltrimethylammonium bromide (CTAB) was used as surfactant to modify the surface morphology of the CuO spheres. The morphology modification mechanism under the effect of CTAB is discussed, and the improved electrochemical performance of CuO spheres obtained in the presence of CTAB is investigated.

2. Experimental

(1)

Hierarchical structured CuO particles were obtained from a stirred solution of $Cu(Ac)_2 \cdot H_2O$ and $NH_3 \cdot H_2O$. In a typical procedure, 0.4 g $Cu(Ac)_2 \cdot H_2O$ (0.01 M) was first dissolved in aqueous solution. Ammonia was used to adjust the pH of the solution to 11. Several minutes later, flocky precipitates appeared in the blue solution. Next, the solution was stirred at a temperature of 90 °C for 1 h. Subsequently, 0.1 g CTAB was added to the mixed solution as a surfactant. After stirring at 90 °C for 12 h, the blue solution became black and turbid. The precipitates were finally separated by centrifugation, washed with deionized water and ethanol for several times, and then dried in vacuum at 60 °C for 12 h.

The structure and morphology of the prepared precursor and CuO particles were characterized by X-ray diffraction (XRD, Philips PC-APD with Cu K α radiation), field emission scanning electron

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microscopy (FESEM, FEI SIRION) and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2010F), respectively.

Electrochemical performance of the CuO particles was investigated with two-electrode coin-type cells (CR 2025). The working electrodes were prepared using a slurry coating procedure. The slurry consisted of 80 wt.% CuO particles, 10 wt.% acetylene black and 10 wt.% polyvinylidene fluoride (PVDF) dissolved in N-methyl pyrrolidinone (NMP). The slurry was incorporated on a piece of nickel foam with diameter of 12 mm. After drying at 90 °C for 24 h in vacuum, the foam was pressed under a pressure of 20 MPa. Test cells were assembled in an argon-filled glove box with the metallic lithium foil as both the reference and counter electrodes, 1 M LiPF₆ in ethylene carbonate (EC)–dimethyl carbonate (DME) (1:1 in volume) as the electrolyte and a polypropylene (PP) micro-porous film (Cellgard 2300) as the separator.

The galvanostatic charge–discharge tests were conducted on a LAND battery program-control test system at rate of 0.1*C* and 1*C* (1*C* = 670 mA g⁻¹) in the voltage range of 0.02–3.0 V (versus Li/Li⁺) at room temperature (25 ± 1 °C). Cyclic voltammetry (CV) was performed on a CHI660C electrochemical workstation at a scan rate of 0.1 mV s⁻¹ from 0 to 3.0 V.

3. Results and discussion

Fig. 1a shows the XRD pattern of the precursor precipitated in the blue solution before heat treatment. All the diffraction



Fig. 1. XRD patterns of (a) $Cu(OH)_2$ precursor precipitated in the solution before heat treatment and (b) CuO particles obtained after heat treatment at 90 °C for 12 h.



Fig. 2. TEM images of $Cu(OH)_2$ precursor precipitated in the solution before heat treatment.

peaks correspond well with orthorhombic Cu(OH)₂ (Space group Cmcm(63), JCPDS 35-0505). Broadening in the peaks of Cu(OH)₂ indicates the formation of a Cu(OH)₂ nanostructure. The XRD patterns of the powders obtained from the solutions after stirring at 90 °C for 12 h are shown in Fig. 1b. In samples prepared with and without CTAB, the samples exhibit similar diffraction peaks that can be perfectly indexed to monoclinic CuO (Space group C2/c, JCPDS 48-1548) with lattice constants *a* = 4.68 Å, *b* = 3.42 Å, and *c* = 5.13 Å. The reactions for CuO precipitation can be summarized as follows:

$$Cu^{2+} + 2NH_3 \cdot H_2O \rightarrow Cu(OH)_2 \downarrow + 2NH_4^+$$
(2)

$$Cu(OH)_2 \xrightarrow{90 \ \circ} CuO + H_2O \tag{3}$$

Fig. 2 shows the TEM images of Cu(OH)₂ precursor appearing in the mixed solution before heat treatment. It is noticed that Cu(OH)₂ precursor exhibits a highly dispersed nanowire morphology. The nanowires are 10 nm in diameter and 300-400 nm in length. The SEM images of CuO particles prepared without CTAB in the solution are shown in Fig. 3a and b. The CuO spheres has a "bird nest" appearance and exhibits a hierarchical system, in which the skeleton is made up of spheres with diameters of 2-4 µm and possessing thousands of 2D leaves. The nano-leaves are about 200 nm in width and 20 nm in thickness. For the CuO particles obtained in the existence of CTAB, the diameter of each sphere is also about $2-4 \,\mu\text{m}$, and when viewed under low magnification, the morphology is similar to that synthesized without CTAB, as shown in Fig. 3c. However, the nanostructure on the surface of the hierarchical CuO sphere is quite different. As shown in Fig. 3d, ordered nano-needle arrays appear on the surface of CuO spheres instead of disordered nano-leaves. Each needle is about 20-40 nm in width and more than 300 nm in length.



Fig. 3. SEM images of the prepared CuO particles: (a, b) in the absence of CTAB and (c, d) in the presence of CTAB.

Obviously, the varying morphology of CuO sphere should be attributed to the surfactant effect of CTAB. Fig. 4 presents a schematic of the formation of CuO without and with CTAB. Several minutes after the Cu(Ac)₂·H₂O solution is mixed with a proper amount of NH₃·H₂O, Cu(OH)₂ nanowires are first formed (Step A) and then assemble closely parallel to their length and become leaf-shaped sheets (Step B). Subsequently, these nano-leaves are prone to building up a hierarchical structure (Step C). In the absence of CTAB, the CuO grains then grow disorderly on the surface, and a bird nest-like sphere is finally formed after dehydration (Step E₁). However, the growth of CuO on the surface of the sphere changes

significantly upon addition of CTAB into the solution. CTAB is a typical ionic compound that can ionize completely in aqueous solution. The resulting cation is a positively charged tetrahedron with a long hydrophobic tail, which can be absorbed onto the surface of some nanocrystals [19]. In this work, as CTAB is added into the stirring solution, the cations are absorbed to the Cu(OH)₂ nanowires at the outer surface of the assembled spheres. Under the electrostatic and stereochemical effects, the Cu(II) ions are dispersed in an orderly way at the outward end of the sphere (Step D). After dehydration, CuO grains grow perpendicularly to the surface of the sphere rather than growing out of order. In addition, the existence of CTAB can



Fig. 4. Schematic illustration of the formation of CuO with and without CTAB.



Fig. 5. Cycling performance of the CuO electrodes at different rates (from the 2nd cycle to the 50th cycle).

also reduce the Gibbs free energy of the surface of the hierarchical CuO sphere [20]. Thus, the hierarchical sphere with nano-needle arrays on the surface is formed by using CTAB as surfactant (Step E_2).

The cycling performance of the obtained CuO particles at different rates is shown in Fig. 5. After 50 cycles, the bird nest-like CuO and needle-like CuO spheres can sustain 59.6% (392 mAh g⁻¹) and 62.4% (441 mAh g⁻¹) capacity of the 2nd cycle at a rate of 0.1C, respectively. The high reversible capacity of both the CuO electrodes at 0.1C can be attributed to their hierarchical nanostructure. A large number of nano-leaves and nano-needles, which make up the CuO spheres, can provide sufficient contact between CuO and the electrolyte, and offer a great deal of sites to accommodate Li⁺, leading to high-discharge capacity. As the discharge-charge rate increases to 1C, the discharge capacity of the CuO electrode synthesized without CTAB maintains only 39.5% (183 mAh g^{-1}) capacity of the 2nd cycle, while the CuO obtained by using CTAB maintains 56.4% (303 mAh g^{-1}) capacity of the 2nd cycle after 50 cycles. The capacity fade of both electrodes is a little faster than cycling at 0.1C. There are two causes for the relatively fast capacity fade. One is that CuO is a typical semiconductor with poor conductivity, and the charge transfer between each CuO sphere is not as sufficient when discharged at a lower rate. The other is that the indirect contact of the CuO/current collector and supplementary inactive interfaces via the traditional slurry coating procedure will also limit the electron transfer between the CuO and the current collector, especially at high rates. Even though, the capacity fade of the pure needle-like CuO spheres is much less influenced by the discharging rate when compared with the bird nest-like CuO sphere. The good capacity retention can be attributed to the needle-like surface morphology of CuO formed under the effect of CTAB, which provides more contact area between the CuO and the electrolyte and greatly enhances the reactivity of electrode reaction, especially at higher rate.

The SEM images of the CuO electrodes after cycling are shown in Fig. 6. The CuO spheres prepared without CTAB adhere to each other, and the bird nest morphology can hardly be identified (Fig. 6a). However, for the CuO spheres obtained by using CTAB, the needle-like morphology is still sustained, though the needles on the surface become a little shorter after cycling (Fig. 6b). The relatively stable structure and morphology also indicates better capacity retention of the needle-like CuO.

Fig. 7 displays the first three discharge-charge curves for bird nest-like and needle-like CuO electrodes between 0.02 V and 3.0 V at rate of 0.1*C*. Both electrodes exhibit similar discharge behaviors. Three plateaus at the potential of 1.6-1.8 V, 1.0-1.2 V and



Fig. 6. SEM images of the CuO electrodes prepared (a) in the absence of CTAB and (b) in the presence of CTAB after 20 cycles at 0.1*C*.

0.7–0.9 V appear in the first discharge curves, which corresponds to the reductive reaction from CuO to the intermediate composite copper oxide phase, to Cu₂O and further decomposition into Cu and Li₂O, respectively [21]. In the first charge curves, only two inclined plateaus near 2.5 V and 1.5 V can be observed, corresponding to the process $2Cu + Li_2O \rightarrow Cu_2O + 2Li$ and the partial oxidation of Cu₂O to CuO, respectively. However, there are still some differences in the discharge–charge curves. For instance, the needle-like CuO exhibits higher first discharge capacity (1047 mAh g⁻¹) than the bird nest-like CuO (958 mAh g⁻¹). The extra capacity compared with the theoretic capacity (670 mAh g⁻¹) results from the formation of SEI during the first discharging process [21]. Hence, it is also indicated that a larger area of SEI is formed in the needle-like CuO during the initial cycle due to larger specific surface of the sphere.

The SEI film is known as a gel-like layer, which contains ethylene oxide based oligomers, LiF, Li₂CO₃, and lithium alkyl carbonate (ROCO₂Li) [22]. The incomplete decomposition of SEI is always the main reason for the low coulombic efficiency and large capacity loss during the initial cycle, which happens for all 3d transition metal oxides, including CuO, NiO, Co₃O₄ [23–26]. However, as seen from Fig. 5, the needle-like CuO exhibits a higher initial coulombic efficiency (65%) than the bird nest-like CuO (60%) though a larger area of SEI is formed on the surface of the needle-like CuO. This may also be due to the better contact between the CuO nano-needles and the electrolyte, making the Li ions transfer quickly and efficiently at the CuO/electrolyte interface, which greatly enhances the reactivity of electrode reaction. Therefore, the decomposition of SEI is relatively efficient of needle-like CuO during the initial cycle.

The first cyclic voltammogram curves of CuO electrodes at a scan rate of 0.1 mV s^{-1} are shown in Fig. 8. The electrochemical



Fig. 7. The discharge–charge curves for CuO electrodes prepared (a) in the absence of CTAB and (b) in the presence of CTAB.



Fig. 8. The first cyclic voltammogram curves of CuO electrodes prepared (a) in the absence of CTAB and (b) in the presence of CTAB at a scan rate of 0.1 mV s^{-1} from 0 to 3.0 V.

peaks correspond well with the discharge–charge plateaus in Fig. 7. Compared to the bird nest-like CuO, the cathodic peaks of the needle-like CuO are located at relatively high potentials. The anodic peaks of both electrodes are almost at the same locations. The interval between the cathodic and anodic peaks can be suggested as the polarization of the electrode. Therefore, it is considered that the needle-like CuO electrode exhibits a smaller polarization than the bird nest-like CuO. As is well known, the transferring delay of electrons and lithium ions on the active material/electrolyte interface is one of the main causes for the polarization in lithium ion batteries [27]. Therefore, the results of the CV curves show that the electrons and lithium ions can transfer more actively in needle-like CuO due to the better contact between the CuO needles and electrolyte.

4. Conclusions

Hierarchical, nanostructured CuO spheres with needle-like morphology were successfully prepared in a stirred solution of $Cu(Ac)_2 \cdot H_2O$ and $NH_3 \cdot H_2O$ by using CTAB as a surfactant. The hierarchical nanostructure of CuO has some influence on the electrochemical performance. The needle-like CuO obtained in the presence of CTAB shows better high rate properties than that of bird nest-like CuO prepared without CTAB. It is attributed to the larger specific surface area of needle-like CuO, leading to sufficient contact area for CuO/electrolyte, shortened the diffusion length of Li⁺, and enhanced reactivity of electrode reaction during cycling. In addition, the needle-like morphology can be sustained well after cycling. Therefore, the hierarchical structured CuO sphere with needle-like morphology synthesized through this simple and low-cost method is an extremely promising anode for lithium ion batteries.

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