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ARTICLE TYPE

Facile Fabrication of Three-dimensional Hierarchical CuO Nanostructures with Enhanced Lithium Storage Capability

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Three-dimensional hierarchical CuO nanostructures with uniform flower-like and urchin-like morphologies have been successfully prepared by a facile, cheap and environmental friendly solvothermal method. The as-prepared flower-like 10 CuO is constructed by nanopetals, which is composed of nanoparticles, and the urchin-like CuO with hollow structure is composed of tightly ranged nanorods. As anode materials for lithium-ion batteries, the flower-like CuO material exhibits high initial discharge capacitance (1457.2 mAh g⁻¹ at 15 100 mA g⁻¹), good rate capability and excellent cycling stability. The superior electrochemical performance is mainly attributed to the hierarchical structure and the nanosize of the nanoparticles composed of the nanopetals, which benefit electrons and Li ions transportation, provide large electrode-20 electrolyte contact area. The extra capacity of the samples may due to the partial reversible formation and decomposition of the gel-like SEI film on the surface of the electrode and pseudocapacitance.

Introduction

- ²⁵ Transitional metal oxides (MOx, such as Co₃O₄, NiO, CuO, Fe₃O₄, etc.) have been regarded as promising anode materials for rechargeable lithium-ion batteries (LIBs) due to their high theoretical capacities and high energy densities. Their remarkably high capacity is based on the redox mechanism ³⁰ (MO_X+2xLi+2xe⁻↔M+xLi₂O) by delivering multiple electrons.¹⁻ ³ Among these materials, copper oxide (CuO) is a potential substitute for conventional graphite anode for its high theoretical capacity (674 mAh g⁻¹), environmental friendly nature, high safety and low cost. ⁴⁻⁸ However, its huge and uneven volume ³⁵ expansion during Li⁺ insertion/extraction processes (about 174%) leads to the pulverization and deterioration of CuO structures, resulting in rapid capacity decay and poor rate capabilities.⁹, ¹⁰Constructing novel nanostructures with different morphologies
- has been demonstrated to be an effective approach to overcome ⁴⁰ these problems. In this regard, CuO nanowires,¹¹ nanoribbons,^{12,} ¹³nanosheets,^{14, 15} nanofibers,¹⁶ bundle-like nanostructure,¹⁷coglike structures,¹⁸ leaf like structures¹⁹ and hierarchical nanostructures²⁰⁻²² have been fabricated via different methods. Three-dimensional (3D) hierarchical nanostructures assembled of ⁴⁵ nanosheets or nanorods have attracted great interest because the

3D structure favorably prevent the agglomeration of nanosheets and effectively avoid the reduction of discharge capacities. Moreover, the nanosheet and nanorod structures provide large contact surface area for active materials and electrolyte and allow ⁵⁰ the insertion of external ions efficiently^{23, 24}. Jin et al. synthesized 3D macroporous CuO structure composed of ultrathin nanosheets which could retain the exposed surface during reactions and significantly enhance the cycling performance.²⁵ Yuan et al. prepared flower-like CuO microspheres and obtained high initial ⁵⁵ discharge capacity of 1220 mAh g⁻¹ and a reversible capacity of 800 mAh g⁻¹ at a current density of 50 mA g⁻¹.²⁰ However, the fabrication of 3D hierarchical CuO morphologies usually involves multiple complicated processes or high temperature operation. It is still a challenge to use 3D hierarchical CuO ⁶⁰ composed of nanosheets towards high-performance LIBs.

Herein, flower-like CuO composed of nanosheets and urchinlike CuO composed of nanorods were fabricated by a facile, cheap, and environmental friendly solution-based method without any template or surfactant. As anode materials for LIBs, the 65 flower-like CuO displays high initial discharge capacitance (1457.2 mAh g⁻¹ at 100 mA g⁻¹), good rate specific capacitance and excellent cycling stability (797.5 mAh g⁻¹ after 50 cycles).

Experimental

2.1. Materials synthesis

⁷⁰ In a typical synthesis, 0.21 g of CuCl₂·7H₂O was dissolved in 30 mL of deionized water to form a blue solution. Then 2 mL of ammonia was added into the above solution under vigorous stirring and flocky precipitates appeared. After stirring for 10 min, the suspension was transferred into a 50 mL Teflon-lined ⁷⁵ stainless steel autoclave and maintained at 130 °C for 8 h. The resulting samples were centrifuged, washed with de-ionized water and ethanol for three times, respectively. Finally, the flower-like CuO was obtained after dried at 80 °C in a vacuum. When the amount of ammonia was changed into 3 mL, urchin-like CuO ⁸⁰ was obtained with other conditions unchanged.

2.2 Materials characterization

The crystal structure and morphologies of the as-prepared CuO samples were characterized by powder X-ray diffraction (XRD, Rigaku D/Max-2500 powder diffractometer, Cu K α radiation, ss λ =0.15418 nm), field emission scanning electron microscopy

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(FESEM; JEOL JSM-6700F), transmission electron microscope (TEM) and high-resolution TEM (HRTEM; Tecnai G2 F20). The elemental composition of the products was detected by energy dispersive spectroscopy (EDS, ISIS300, Oxford Instrument). The 5 specific surface areas of the as-prepared samples were investigated by nitrogen adsorption/desorption measurements (ASAP 2020/Tristar 3000).

2.3 Materials characterization

For electrochemical measurements,80 wt% active materials, 10 ¹⁰ wt% carbon black and 10 wt% poly(vinylidene fluoride) (PVDF) binder were mixed to form viscous slurry. Then the slurry was pasted onto Cu foils and dried at 100°C in a vacuum to form working electrodes. The testing cells were assembled with the working electrode, metallic lithium cathode, Celgard 2300 film ¹⁵ separator and 1 M LiPF₆ in 1:1 ethylene carbonate (EC)/dimethyl carbonate (DMC) electrolyte in an argon-filled glove box (a home-made). The discharge-charge cycle tests by Land battery test instrument (CT2001A). Cyclic voltammetry (CV) was conducted with a CHI600E electrochemical workstation with a ²⁰ voltage scan rate of 0.1 mV s⁻¹. All the tests were performed at room temperature.

Results and discussion

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Fig. 1 shows the XRD patterns of the as-synthesized CuO samples. All diffraction peaks in the patterns can be indexed to a ²⁵ monoclinic phase of CuO (space group C2/c; lattice constant a=4.68 Å, b=3.42 Å and c=5.13 Å; JCPDS file no. 48-1548), confirming the high purity phase of the products. The formation of CuO samples can be interpreted as follows:

(2)

$$Cu^{2*} + 2NH_3 \cdot H_2O \longrightarrow Cu(OH)_2 \downarrow + 2NH_4^+$$
(1)
³⁰
$$Cu(OH)_2 \longrightarrow CuO + H_2O$$
(2)



Fig.1 XRD patterns of the as-prepared CuO samples.

The morphologies of the as-obtained CuO samples were characterized by SEM and TEM. As shown in Fig. 2a, under low ³⁵ ammonia concentration, the CuO product presents well-defined 3D flower-like microstructures with the average size of 2 µm in



Fig.2 SEM images of the as-prepared flower-like CuO (a, b) and urchinlike CuO (e, f), and TEM images of flower-like CuO (c, d) and urchin-⁴⁰ like CuO (g, h).

2b reveals that individual flower-like diameter. Fig. microstructure is assembled with many densely and randomly arranged nanopetals with the thickness of about 40 nm, which grow from the centre of the flower. The TEM image in Fig. 2c 45 further confirms the flower-like structure of CuO. From the corner of nanopetals, it can be seen that each petal is assembled by nanoparticles. The lattice fringes on a representative HRTEM image (Fig. 2d) are clearly visible with a spacing of 0.254 nm, corresponding to the spacing of the (-111) planes of monoclinic ⁵⁰ CuO.²⁶ The SAED pattern shown in inset of Fig. 2d reveals the polycrystalline nature of the nanopetal. The morphologies of the CuO product obtained under high ammonia concentration is shown in Fig. 2e-h. From Fig. 2e, it can be seen that the CuO sample is composed of uniform urchin-like microspheres with the 55 diameter of about 5 µm. Interestingly, it is observed that the urchin-like spheres are of hollow structure. High-resolution SEM image (Fig.2f) shows that the shell of the hollow urchin-like sphere is composed of nanorods with the length of about 1 μ m, which range regularly and tightly with each other. TEM image 60 shown in Fig. 2g confirms the urchin-like architecture composed of CuO nanorods. A typical HRTEM image of an individual CuO nanorod shown in Fig. 2h demonstrates that the measured lattice spacing is 0.275 nm, which corresponds to the (110) lattice plane





Fig.3 EDS patterns of the as-prepared flower-like CuO (a) and urchin-like CuO (b)

⁵ of monoclinic CuO.¹⁷ The corresponding SAED pattern (insert of Fig. 2h) illustrates that the CuO nanorods are single crystalline.EDS analysis (Fig. 3) reveals that the both body of the as-prepared CuO samples are composed of Cu and O with the atomic ratio of about 1:1, further confirming the high purity of

¹⁰ the CuO samples, which is in good agreement with the XRD results. The specific surface areas of the CuO samples were further investigated. The BET specific surface areas of the asprepared flower-like CuO and urchin-like CuO are 30.17 and 19.25 m² g⁻¹, respectively. The improved BET specific surface ¹⁵ area is mainly due to the small size of flower-like CuO, which

may provide more active sites to take part in electrochemical activity. It is inferred that flower-like CuO electrode may display better electrochemical properties.

The electrochemical performance of the as-prepared CuO ²⁰ anodes was evaluated by cyclic voltammetry (CV) and galvanostatic charge-discharge cycling. The CV curves collected between 0.01 and 3.0 V at a scan rate of 0.1 mV s⁻¹ are shown in Fig. 4. It is confirmed that the overall reversible electrochemical reaction of CuO anode electrode during the charge-discharge ²⁵ process is as follows:²⁷

$$CuO + 2Li^+ + 2e^- \longleftrightarrow Cu^0 + Li_2O$$
 (3)

It clearly shows in the CV curves that three main electrochemical steps occur during the above conversion reaction. In the first cathodic sweep, a broad and weak reduction peak presents at

 $_{30}$ 1.55~1.95 V, which is corresponding to the formation of Li_xCuO. Then two sharp peaks are observed at around 1.0 and 0.65 V in succession, which can be attributed to the phase transformation from Li_xCuO to Cu₂O and further to Cu(0), respectively.



Fig.4 The charge-discharge curves of the as-prepared flower-like CuO (a) and urchin-like CuO (b) electrodes.

Additionally, a solid electrolyte interphase (SEI) layer generates on the electrode surface at lower voltage (below 0.5 V).28, 29 40 During the anodic polarization process, the two peaks appearing at 2.55 and 2.70 V mainly correspond to the oxidation of Cu(0) to Cu₂O and further oxidation to CuO,³⁰ and the broad peak appearing at 1.0~2.0 V could be attributed to partial decomposition of the SEI layer.¹⁶ In the following cycles, the 45 lithiation voltages (about 0.75, 1.35 and 2.25 V) are higher than those in the first cycle, which may due to the improved kinetics of the CuO electrode after the first lithiation.³¹ The CV curves in the subsequent cycles display good reproducibility, indicating good reversibility of the electrochemical reactions. It is observed 50 that the area of closed CV curves of flower-like CuO electrode (Fig. 4a) is much larger than that of urchin-like CuO electrode (Fig. 4b), indicating higher discharge capacities of flower-like CuO.

Fig. 5 shows the discharge-charge curves of the as-prepared ⁵⁵ CuO samples for the selected cycles at a current density of 100 mA g⁻¹, in which the voltage plateaus are in good agreement with the peaks of the CV curves in Fig. 4, even after quite long cycling. It is obvious that the flower-like CuO electrode displays much higher charge and discharge capacities than the urchin-like CuO, ⁶⁰ which is also in good accordance with the CV curves. As shown in Fig. 5a, it exhibits high initial discharge capacity of 1457.2 mAh g⁻¹ and charge capacity of 917.3 mAh g⁻¹, resulting in a limited initial Coulombic efficiency of 62.9%. In the second cycle, the discharge capacity abruptly decreases to 943.8 mAh g⁻¹, ⁶⁵ however, the Coulombic efficiency increased to over 97% in subsequent cycles. It is observed that the shapes of the curves do not change significantly in the following cycles, indicating good

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Fig.5 The charge-discharge curves of the as-prepared flower-like CuO (a) and urchin-like CuO (b) electrodes.

- ⁵ capacity retention. After 30 cycles, CuO exhibits a high discharge capacity of 873.3 mAh g⁻¹, which is much higher than the theoretical capacity and that of previously reported CuO nanostructures.^{17-19, 32} The extra initial discharge capacity could be mainly ascribed to the formation of the SEI layer during the ¹⁰ first discharge process at a low voltage (0.02~1.0 V). The SEI layer is a poly-meric gel-like film including organic layer and inorganic layer. In the following cycles, reversible formation and decomposition of the gel-like film on the surface of the electrode
- become partial reversible, resulting in extra capacity. Moreover, 15 the pseudocapacitance may also contribute to the high discharge capacity. ³³⁻³⁸

The rate capability is an important property of electrode materials. Fig. 6a presents the rate capability performance of the as-prepared CuO electrodes. It is observed that the flower-like

- ²⁰ CuO electrode displays much higher discharge capacity and better rate capability than the urchin-like CuO electrode. The capacities of the flower-like CuO electrode are about 820, 730, 620 and 480 mAh g^{-1} at the current densities of 100, 200, 500 and 1000 mA g^{-1} , respectively. The cycling performances of the CuO
- ²⁵ electrodes at the current density of 100 mA g⁻¹ are shown in Fig. 6b. The flower-like CuO electrode shows high initial discharge capacity (1457.2 mAh g⁻¹) and good cycle stability. After 50 cycles, the discharge capacity still remains 797.5 mAh g⁻¹, which is much higher than the urchin-like CuO electrode.
- In order to investigate the effect of structure durability on the electrochemical properties, the morphologies of cycled CuO electrodes are compared in Fig. 7. It is interesting to see that the flower-like CuO electrode could maintain its 3D hierarchical structure after 5 discharge-charge cycles (Fig. 7a and 7b). In





Fig.6 Rate capability (a) and cycling performance of the as-prepared flower-like CuO and urchin-like CuO electrodes.



⁴⁰ Fig. 7 SEM images of the cycled flower-like CuO electrode (a, b) and the cycled urchin-like CuO electrode (c, d). The cycled electrodes were detected after 5 discharge-charge cycles at 100 mA g⁻¹.

contrast, urchin-like CuO electrode has broken into aggregated microspheres and the urchin-like shape could not be maintained ⁴⁵ (Fig. 7c and 7d), resulting in a poor cycling performance and inferior rate capability of the urchin-like CuO electrode.

The higher discharge capacity and the better cycle stability of the flower-like CuO electrode may due to its higher surface area, which may bring larger contact area between CuO and the electrolyte. Moreover, the 3D hierarchical CuO nanostructure constructed by nanopetals, which is composed of nanoparticles may provide a fast and efficient transport of Li ions and effectively buffer the stress induced during the charge-discharge

s process. Moreover, the better structure durability of the flowerlike CuO is responsible for its excellent cycling stability. The good electrochemical performance makes the flower-like CuO a promising anode material for LIBs.

Conclusions

- ¹⁰ In conclusion, flower-like CuO and urchin-like CuO have been successfully prepared via a facile solvothermal method without any template or surfactant. Owing to the 3D hierarchical nanostructures and large specific surface area, the as-prepared flower-like CuO electrode shows enhanced electrochemical ¹⁵ performance as an anode material for LIBs. The flower-like CuO
- electrode delivers a high initial discharge capacitance of 1457.2 mAh g⁻¹ at 100 mA g⁻¹, desirable rate specific capacitance (480 mAh g⁻¹ at 1000 mA g⁻¹) and excellent cycling stability (797.5 mAh g⁻¹ after 50 cycles). The excellent electrochemical ²⁰ performance enables such flower-like CuO electrode to stand out as a promising electrode material for LIBs..

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Graphical Abstract



Three-dimensional hierarchical CuO nanostructures with uniform flower-like and urchin-like morphologies have been prepared by a facile solvothermal method. The CuO materials display high initial discharge capacitance, good rate capability and excellent cycling stability as anode materials for rechargeable lithium-ion batteries.