Excellent cycling stabilities of a novel calliandra-like Co_3O_4 acted as anode materials for the lithium-ion battery

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ABSTRACT

Herein, a hierarchical calliandra-like Co_3O_4 is successfully synthesized via a simple carbon sphere and hydroxypropyl cellulose assisted hydrothermal process. X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) characteristics results indicate that the hierarchical Co_3O_4 spheres are 3–6 μm in diameter and belong to spinel structure. Each Co_3O_4 sphere is consisted of radially oriented nanocystals accumulated nanorods building blocks. The formation mechanism for this structure maybe ascribed to the collaboration effect of carbon sphere and hydroxypropyl cellulose, which act as hard template and dispersion stabilizer respectively. The calliandra-like Co_3O_4 particles exhibit satisfied electrochemical performance with high specific capacities and good rate capabilities, especially superior cycling stability when used as anode active materials in the lithium-ion batteries, which release an initial discharge capacity of $1139.42\,mA\,h\,g^{-1}$ at $200\,mA\,g^{-1}$, and maintain a reversible capacity of $734.64\,mA\,h\,g^{-1}$ after 500 cycles.

1. Introduction

The depletion of fossil fuel resources and increasing energy consumption in electronics, transportation and electric vehicles have inspired intensive researches on lithium ion batteries (LIBs) with high specific capacity, good cycling performances and superior stability [1–5]. Therefore, it is crucial to synthesis well-designed substitute electrode materials with special structure to improve electrode transportation and alleviate large volume expansion. Transition metal oxides are one of the promising anode materials due to the high theoretical capacity which is compared with that of the commercial graphite [5]. As one of the transition metal oxides, cobalt oxide has attracted great attention in the recent years due to its good chemical or thermal stability, and relative high theoretical capacity (about $890\,mA\,h\,g^{-1}$) which is almost two times larger than that of the graphite [6–9]. However, this material suffers from problems of relatively low ionic, electronic conductivities and large volume expansion during Li^+ insertion and extraction, which results in capacity reduction and poor cycling performance.

One effective method is to fabricate nano-size-structured materials including hollow structures, nanowires [10–12], polyhedron structures [9,13–15] and hierarchical Co_3O_4 nanosheets [16,17] or nanoflakes [18,19]. Co_3O_4 hollow structured materials like single or multi-layer hollow spheres [9,17,20–24], hollow nanofibers [23,25,26] have been fabricated. For example, Lou and his collaborators [22] synthesized multi-shelled hollow spheres with good cycling stability and rate capacity. These hollow structures can shorten diffusion lengths and provide sufficient void space to buffer the volume expansion. The hybrid anode materials are prepared, which are composed of nano-structured Co_3O_4 and carbon matrix such as porous carbon [10,27–29], carbon nanotubes [8,13,30] and graphene [18,26,31–33]. Interestingly, some researchers synthesized C&N co-doped Co_3O_4 hybrid materials [25,27]. Nitrogen-doping way can provide more active sites for enhancing the lithium ion storage and increase the reactivity and electric conductivity of the carbon materials, thus benefit for the improvement of electrochemical performance.

In this paper, the hierarchical nanoscale-sized calliandra-like Co_3O_4 was synthesized by employing carbon sphere as hard template and hydroxypropyl cellulose (HPC) as dispersion stabilizer. The electrochemical measurements of Co_3O_4 calliandras showed high specific capacities and good cycling performance, which can last for 500 cycles with few capacity fading, demonstrating its superior electrochemical performance. The growth mechanism of calliandra-like Co_3O_4 is as follows. Bivalent Co^{2+} ions are disperse uniformly in the solution and then combined with OH^- anion to form a nucleus on the surface of carbon sphere due to the effect of HPC, which acts as dispersion

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stabilizer and surfactant in the process. Then short nanorods grown radially on the surface and uniform calliandra-like Co_3O_4 spheres formed with the further proceeding of reaction.

2. Experimental

2.1. Materials synthesis

Carbon spheres were prepared by a reported method [34]. As a typical synthesis, glucose (55 mg) was dissolved in 60 mL ultrapure water, the solution was stirred to clear and transferred to a 100 mL Teflon autoclave. The autoclave was sealed and maintained at 453 K for 4 h, and cooled naturally to the room temperature. The brown products were washed by ethanol and ultrapure water repeatedly and vacuum dried at 353 K overnight. 50 mg of hydroxypropyl cellulose (average MW of ~80000, Sigma-Aldrich) was dispersed in 15 mL ultra-pure water, then 45 mg $Co(NO_3)_2$, 90 mg urea $(CO(NH_2)_2)$ and 50 mg carbon spheres were added. After hydrothermal reaction at 453 K for 8 h, the precipitation was washed, dried and sintered at 773 K for 2 h at a heating rate of $2 K min^{-1}$. The obtained powder was denoted as sample C. For comparison, the product, which was synthesized without addition of carbon spheres while keeping other conditions unchanged, was marked as sample A. Similarly, sample B was prepared without participation of hydroxypropyl cellulose in reaction.

2.2. Materials characterization

XRD patterns were recorded on a Bruker AXS D8 advance X-ray diffractometer equipped with Cu Kα radiation. XPS spectrums were measured on ESCALAB XPS by referencing the C 1 s peak to 284.6 eV. The morphologies were characterized by field-emission SEM, Gemini SEM 500 and the nanostructure was recorded on a JEM-2010 system.

2.3. Electrochemical measurements

A CR-2025-coin type cell configuration was utilized to conduct electrochemical measurement. For working electrode fabrication, active material, acetylene black (AB) and polyvinylidene fluoride (PVDF) were dispersed in N-methylpyrrolidone at a weight ratio of 80:10:10 to form slurry. The black slurry was ground adequately and pasted on copper foil uniformly and dried at 353 K in vacuum for 12 h. The test cells were assembled in an argon-filled glove box with pure lithium foil as counter electrode, Celgard 2400 membrane as separator and 1 M $LiPF_6$ in a mixture of ethylene carbonate (EC), diethyl carbonate (DEC) and dimethyl carbonate (DMC; 1:1:1, v/v/v) as electrolyte. The galvanostatical charge-discharge measurement and rate capability test from 100 to $2000 mA g^{-1}$ were conducted on Arbin BT-2000 battery testing system. The cycle voltammetry (CV) profiles was performed on Ametek VMC-4 instrument in the range of 0.01–3 V at a scanning rate of $0.5 mV s^{-1}$.

3. Results and discussion

The as-prepared calliandra-like sample was characterized as shown in Fig. 1. It can be observed that this material has well-defined diffraction peaks, and the diffraction peaks located at (220), (311), (400), (422), (511), (440) planes can be readily indexed to spinel Co_3O_4, indicating the formation of Co_3O_4 crystal. In order to further identify the phases of the sample, the XRD pattern was refined by the Rietveld refinement software GSAS [35,36], as shown in Fig. 1a. The experimental, calculated and difference X-ray diffraction patterns of Co_3O_4 powder were black, red and blue in color respectively. It can be seen from Fig. 1a that the calculated pattern matches well with the experimental data with the value of R_{wp} to be 13.49% and R_p to be 9.55%, which indicates the high purity of the Co_3O_4 powder. Fig. 1b presents the refined crystal structure of Co_3O_4, which adopts the spinel structure

with an Fd3 m space group. The unit-cell is composed of $[CoO_4]$ and $[CoO_6]$ clusters, with cations distributed among tetrahedral or octahedral sites. The lattice parameters are calculated to be $a = b = c = 8.0835$ Å, $\alpha = \beta = \gamma = 90°$. XPS measurements have been employed to verify the surface elemental composition valence with corresponding figures illustrated in Fig. 1c and d. The binding energies located at 779.8 and 780.5 eV correspond to Co $2p_{3/2}$, while the peaks at 794.8 and 796.2 eV correspond to Co $2p_{1/2}$, characteristic of Co_3O_4 phase [25,37]. This also indicates the coexistence of Co^{2+} and Co^{3+} in Co_3O_4 phase.

For the template-based fabrication of nano-sized Co_3O_4 spheres, carbon spheres were prepared by a typical hydrothermal method and the surface morphology of carbon spheres were displayed in Fig. S1(detailed in supporting materials) [34]. For the preparation of sample A, the reactants of cobalt sources, urea and carbon spheres were added and stirred to form a homogeneous solution firstly, followed by hydrothermal reaction and calcinations treatment. The surface morphology of sample A is composed of irregular arranged nano-plates and nano-spheres, which is demonstrated in Fig. 2a and b. When cobalt sources, urea and HPC were poured into autoclave as reactants without addition of carbon spheres, sample B was formed with cluster shape. This may be due to HPC, which acts as dispersion stabilizer during reaction process, and it can keep cobalt ions in the homogeneous state during reaction thanks to the weak chemical adsorption between HPC and cobalt salt [38]. What's more, it can also provide steric stabilization during precipitation of particles and promote the formation of well-dispersed cluster shaped sample B. These clusters are assembled from needle-like nanorods with 20–100 nm in width and 3–5 um in length, as shown in Fig. 2c and d. Calliandra-like sample C was fabricated when cobalt sources, urea, HPC and carbon spheres were used as reactants. The corresponding surface morphology of sample C was revealed by the low- and high- magnification FESEM images of Fig. 2e and f. An image of nature calliandra was shown in the inset of Fig. 2e. As can be seen from inset of Fig. 2f, the hierarchical calliandra-like sample A spheres show 3–6 μm in diameter, which are consisted of radially oriented nano-rods with typically diameter of 20 nm. In comparison, the hierarchical calliandra-like building blocks possess larger surface area and more void space, which is crucial for enhancement of the electrochemical performance in lithium ion battery field. The synthesis process for three types of Co_3O_4 samples are schematically summarized in Scheme 1.

Fig. 3a and b present the TEM images of fabricated calliandra-like Co_3O_4, which reveals that every building block (Co_3O_4 nanorod) is accumulated by Co_3O_4 nanocystals with grain size of 10–50 nm. The morphologies of these calliandras keep the same even under sonication for half an hour as illustrated by the TEM observation, suggesting their mechanically robust. The selected-area electron diffraction (SAED) pattern in Fig. 3c produces a pattern of well-ordered concentric rings, demonstrating good crystallinity and polycrystalline structure of calliandra-like Co_3O_4. The corresponding reflections of (111), (220), (311), (400), (511) and (440) are also noted in SAED, which is almost in line with the XRD results. The observed clear lattice fringe with a spacing of 0.46 nm corresponds to the (111) plane of Co_3O_4 crystal (Fig. 3d), which indicates that this particle grows along [111] crystal orientation.

Taking the above results together, a plausible mechanism for the growth of calliandra-like Co_3O_4 is proposed. In the initial stages, bivalent Co^{2+} are dispersed uniformly in the solution because of the existence of dispersion stabilizer HPC [38]. Hydroxypropyl cellulose can promote the mixing homogeneity of cobalt ions in the solution and make the growth of particles evenly. As the reactant temperature increases in the oven, the hydrolysis-precipitation process of urea occurred and OH^- anion was formed gradually. Afterwards, a number of OH^- anion will combine with Co^{2+} and lead to the formation of nucleus on the surface of carbon sphere under the effect of surfactant (HPC) [39]. Then short nanorods are grown radially on the surface of