Urchin-like Co$_3$O$_4$ Nanostructure and Their Electrochemical Behavior in Rechargeable Lithium Ion Battery

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3D urchin-like Co$_3$O$_4$ have been successfully prepared by calcination of the urchin-like precursors, which were synthesized through a facile hydrothermal route. The morphology and structure of the 3D urchin-like Co$_3$O$_4$ have been characterized by field emission scanning electron microscopy, transmission electron microscopy, high resolution transmission electron microscopy, and X-ray powder diffraction. The as-synthesized Co$_3$O$_4$ products are of urchin-like structures with approximated 5−7 µm in diameter, and are composed of numerous nanoparticles chains with the particles diameter of about 15 nm. This kind of urchin-like Co$_3$O$_4$ exhibits superior energy storage properties with the high capacity of 1.369 Ah/g and its good cyclic stability shows great potential in the rechargeable Li-ion battery.

Key words: Co$_3$O$_4$, Urchin-like structure, Hydrothermal, Lithium ion battery, Discharge capacity

I. INTRODUCTION

Rechargeable lithium ion batteries have been considered as the dominant power source for the next-generation energy storage devices resulting from its high energy density and environmentally-friendly characteristics [1, 2]. However, the current used graphite-based electrode of material lithium ion batteries is still far from perfect in accordance with the ever-increasing need for high capacity devices due to the limited theoretical Li-storage capacity of 0.372 Ah/g [3, 4]. Recently, the transition metal oxides, especially the CoO and Co$_3$O$_4$, have drawn increasing attention in lithium ion battery devices since the discovery of their highly reversible capacities of almost three-time larger than those using graphite as the electrode materials [3, 5−7]. It is also reported that the electrochemical properties of the cobalt oxides are strongly dependent on their morphology and microstructure [1, 5, 8].

Over the few years, various methods, such as hydrothermal oxidation [9−12], chemical vapor deposition (CVD) [13−16], melt infiltration method [17], molten salt synthesis [18], etc. have been used to fabricate the Co$_3$O$_4$ with varied morphologies of different dimensions, including nanoparticles [19], nanotubes [20], nanocubes [21], and flower-like [22]. Among these morphologies, urchin-like morphology of 3D divergent structure with many nanowires emanating from the center, may present a superior performance as it combines the properties of high specific surface and large porosity together [23]. The nanowires of high specific surface could provide more active centers and short path length for Li$^+$ transport, while the 3D urchin-like structure with large porosity may resist larger volume expansion during the redox action of the electrodes, which is advantageous to the application in lithium ion batteries, especially for the alleviation of the poor capacity retention. However, there has been no report on the fabrication and application of urchin-like Co$_3$O$_4$ products for rechargeable lithium-ion batteries as far as we know.

In this work, we prepared the 3D urchin-like precursor through the facile and environmentally benign hydrothermal process and then convert them to Co$_3$O$_4$ by calcination without the change of the morphologies. The as-synthesized Co$_3$O$_4$ exhibits superior energy storage properties with the high capacity of 1.369 Ah/g in the first cycle and retain capacity of ca. 1.204 Ah/g after 20 cycles.

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II. EXPERIMENTS

A. Synthesis of Co$_3$O$_4$ nanocrystals

In our experiment, all chemicals were analytical grade and used without further purification. 1.50 g (25 mmol) of urea and 0.05 g of cetyltrimethylammonium bromide (CTAB) were dissolved in 30 mL deionized water under stirring. After the solution was transparent, 10 mL 0.5 mol/L of CoSO$_4$·7H$_2$O were added and stirred for another 10 min. The whole mixture was transferred into a Teflon-lined autoclave maintained at 120 °C for 12 h. After the autoclave was cooled to room temperature naturally, the rosy products were collected by filtration, washed several times with deionized water and absolute ethyl alcohol, and dried at 60 °C in an oven for 10 h. Finally, the rosy precursor was annealed at 350 °C for 2 h in air, and black powders were obtained.

B. Characterization

The samples were characterized by X-ray powder diffraction (XRD, Philips X'pert PRO diffractometer, Cu Kα radiation), field emission scanning electron microscopy (FESEM, Hitachi S-4800, Japan), and high-resolution transmission electron microscopy (HRTEM, JEOL, 2010, 200 kV).

C. Electrochemical measurements

The electrochemical properties were carried out using two-electrode cells with lithium metal as the counter and reference electrodes. The working electrode was fabricated by spreading the mixture of the as-prepared products, acetylene black (ATB) and polyvinylidene fluoride (PVDF) in a weight ratio of 7:2:1 onto the copper foil. The electrode was then dried at 120 °C for 1 h. After the solution was transparent, 10 mL of 0.5 mol/L of CoSO$_4$·7H$_2$O were added and stirred for another 10 min. The whole mixture was transferred into a Teflon-lined autoclave maintained at 120 °C for 12 h. After the autoclave was cooled to room temperature naturally, the rosy products were collected by filtration, washed several times with deionized water and absolute ethyl alcohol, and dried at 60 °C in an oven for 10 h. Finally, the rosy precursor was annealed at 350 °C for 2 h in air, and black powders were obtained.

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III. RESULTS AND DISCUSSION

A. Structural characterization

Figure 1 shows the XRD pattern of the as-prepared products. As shown in the figure, all the diffractions peaks can be indexed as cubic Co$_3$O$_4$ (JCPDS 76-1802, a=8.072 Å). No other peaks appear indicating that the product is of high purity. According to Scherrer’s formula, the size of the crystallite, determined from the strongest peak located at about 37°, is calculated to be about 13.8 nm.

The morphology of the as-prepared Co$_3$O$_4$ products is shown in Fig.2. Figure 2(a) is the low magnification FESEM image of typical products. It can be seen from Fig.2(a), that the as-prepared Co$_3$O$_4$ products are of urchin-like structures with approximate 5–7 μm in diameter. The inset displays the enlarged view of the urchin-like products. The detailed morphology shown in Fig.2(b) reveals that the entire structures consisted of many nanowires, which were of several nanometers in diameter and connected to each other making the formation of nanowire bundles. To clearly characterize the microstructure of the urchin-like products, transmission electron microscopy (TEM) observation was performed. Figure 2 (c) and (d) show the TEM image of as-prepared Co$_3$O$_4$ products. Figure 2(c) demonstrates the typical morphology of the as-prepared Co$_3$O$_4$ from which it can be seen that the microstructures of the 3D Co$_3$O$_4$ are of urchin-like with many nanowires emanated from the center loosely, exhibiting the large porosity. Upon the closer inspection of Fig.2(d), each nanowire was composed of numerous nanoparticles with the diameter of about 15 nm, which shows a good conformance to the XRD results. Furthermore, the selected area electron diffraction (SAED) analysis (Fig.2(e)) exhibits the high poly-crystalline nature of the as-prepared Co$_3$O$_4$ products. A HRTEM taken from individual Co$_3$O$_4$ nanoparticles is shown in Fig.2(f). The measured lattice spacing of 0.47 nm is found to be in good agreement with the (111) planes separation of Co$_3$O$_4$.

B. Electrochemical characterization

Figure 3 shows the first three CV curves of the electrodes made from the urchin-like Co$_3$O$_4$ at a scan rate of
FIG. 2 Characterization of urchin-like Co$_3$O$_4$ nanostructures. (a) Low-magnification FESEM image, inset is the higher magnification. (b) High-magnification FESEM image. (c) and (d) TEM images. (e) SAED pattern of the as-obtained Co$_3$O$_4$ products. (f) HRTEM image.

0.2 mV/s and temperature of 26 °C. In the first cycle, an irreversible reduction peak with a maximum at 0.735 V was observed, representing the reduction (electrochemical lithiation) of Co$_3$O$_4$ to metallic cobalt. While in the oxidation scan, a broad anodic peak appears at 2.196 V corresponding to the oxidation (delithiation) of metallic cobalt. As Poizot et al. have proposed that the electrochemical reaction mechanism of Li with the transition metal oxides [1, 24], such as cobalt oxides, mostly involves the formation and the decomposition of Li$_2$O, accompanying with the reduction and oxidation of the metal oxides. The total displacement redox reactions are as follows:

$$\text{Co}_3\text{O}_4 + 8\text{Li}^+ + 8e^- \leftrightarrow 4\text{Li}_2\text{O} + 3\text{Co}$$  \hspace{1cm} (1)

$$8\text{Li} \leftrightarrow 8\text{Li}^+ + 8e^-$$  \hspace{1cm} (2)

$$\text{Co}_3\text{O}_4 + 8\text{Li} \leftrightarrow 4\text{Li}_2\text{O} + 3\text{Co}$$  \hspace{1cm} (3)

In comparison with the initial cycle, decreasing peak intensity can be observed with a shift of the potential to the positive direction in the subsequent cycles. Such an irreversible phenomenon could be ascribed to the decomposition of the electrolyte and the formation of solid electrolyte interface film (SEI layer) that leads to extra lithium consumption irreversibly during the lithiating process [3, 7]. There is also another reduction peak at about 2.124 V for the second and third discharge process, corresponding to the multistep redox actions of Co$_3$O$_4$ in the cycles. The well-overlapping trend of the 2nd and 3th cycles indicates the excellent cyclic stability of the as-synthesized Co$_3$O$_4$.

The 1st, 2nd, 15th, and 20th galvanostatic charge-discharge curves of lithium cells cycle between 0.01 and 3.0 V at a constant current density of 0.1 A/g are shown in Fig.4. The initial discharge curve shows a long potential plateau at about 1.06 V, followed by a sloping curve down to the cutoff voltage of 0.01 V. The first specific lithiation capacity was found to be as high as 1.369 Ah/g, which is much higher than its theoretical value of 0.89 Ah/g. The extra capacity could be contributed to the formation of polymer-gel like film in the reduction process of Co$_3$O$_4$ to Co, corresponding to the irreversible reduction peak of the first cycle shown in Fig.3. Furthermore, the excessive irreversible capacity still occurs in the sloped regime, associated with the formation of the Co/Li$_2$O interface in the course of heterogeneous solid-state reaction, which can be explained by the heterogeneous interfacial mechanism [5, 25].

FIG. 3 First three cyclic CV curves of the urchin-like Co$_3$O$_4$ at a scan rate of 0.2 mV/s and temperature of 26 °C.

FIG. 4 The charge-discharge behavior of the Co$_3$O$_4$ electrode at a current density of 0.1 A/g between 0.01 and 3.0 V.
25, 26]. In the second discharge process, two obvious sloping potential ranges appeared at about 2.7−2.0 and 1.75−0.0 V, respectively, corresponding to the two complete multistep reduction processes. Compared to the initial discharge curve, the capacity decreased to ca. 1.115 Ah/g. During the extended cycles, the redox reaction is similar to the second discharge process. However, the discharge capacity has gone through a complex change, as will be discussed later.

The cycle behavior of the Co$_3$O$_4$/Li cell was presented in Fig. 5. There is an ultrahigh initial capacity followed by degradation. In the sequential 2−15 cycles, the discharge capacity undergoes escalation instead of a continuous decline, afterward it resumed falling down. It is reported that such an interesting feature resulted from the particles morphology effect and the formation of the SEI layer between the electrolyte and the nonconductive Co$_3$O$_4$ electrode [1, 27]. The reversible capacity after 20 cycles remained about 1.204 Ah/g, which exhibits high capacity retention properties.

Compared to the reported data of the other Co$_3$O$_4$ structures [5−7, 14], the discharge capacity of this structure behaved pretty good, which is believed to benefit from nanowires consisting of numerous nanoparticles and the unique urchin-like structure. As is known, with decrease of the particle size, the specific surface increasing, makes more active centers, which will favor increasing the electrolyte/Co$_3$O$_4$ contact area and shorts path length for Li$^+$ transport during the electrochemical reaction, and thus improves the discharge capacity. With the formation of the urchin-like structure, it reserved the full advantages of the nanowires, i.e. high surface-to-volume ratio, short transport length. Furthermore, the large porosity of the urchin-like structure could resist the larger volume expansion during the charge-discharge cycles, which makes an improvement of the capacity retention [5, 27, 28].

**IV. CONCLUSION**

3D urchin-like Co$_3$O$_4$ products have been fabricated through a simple hydrothermal process followed by calcination in air. Electrochemical measurement of the Li-ion batteries demonstrated that the as-synthesized Co$_3$O$_4$ urchin-like products exhibited a high discharge capacity of 1.369 Ah/g and excellent cycle life. The experimental research results will hopefully serve as useful feedback information for improvements for the properties of lithium ion battery.

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