Selective Crystal Facets Exposing of Dumbbell-like Co_3O_4 towards High Performances Anode Materials in Lithium-Ion Batteries

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Abstract:

In this study, dumbbell-like Co_3O_4 is obtained via calcination of the prepared spindle-like CoCO_3 precursor. The Co_3O_4 displays high specific surface area of $162.7 \text{ m}^2 \text{ g}^{-1}$ and narrow pore-size-distribution of 3.54 nm. When applied as anode material, Co_3O_4 delivers a specific capacity as high as 1719 mA h/g for initial discharge, and retains low discharge capacity loss over 200 cycles at 0.1 C conditions. The improved lithium storage capability of the Co_3O_4 anode can be attributed to high specific surface area and the shortened transport path for Li^+ that resulted from specific facet effects.

Keywords: Co_3O_4 ; Dumbbell-like; Crystal Facets; Anode; Capacity.

1 Introduction

Rechargeable lithium-ion batteries (LIBs) have become one of the most prominent power sources due to their excellent electrochemical performance and high energy density compared to other energy carriers [1-5]. However, current LIB technologies primarily use graphite as the anode material; with a low theoretical specific capacity of 372 mA h/g, and unsatisfactory high-rate performances, these graphite-based materials are far from satisfied with the ever-increasing technical demands of high power applications such as electric vehicles [6]. Hence, exploring novel anode materials with excellent lithium storage capabilities has become highly urgent for many researchers.

In past decades, numerous efforts have been devoted to the development of advanced anode materials with higher capacity, better cyclic stability, and high rate capability [7, 8]. Various materials including nanostructured transition metal oxides (TMOs) like SnOx [9], FeOx [10], TiO₂ [11], and CoOx [12] have been extensively investigated as anodes in LIBs due to their higher theoretical capacities. Among them, Co₃O₄ has attracted tremendous attention due to its high specific capacity of approximately 890 mA h/g [13, 14]. However, Co₃O₄ generally suffers from poor conductivity and huge volume expansion during the charging–discharging process, as well as severe particle aggregation associated with the Li⁺-insertion and extraction process, which leads to electrode pulverization and the loss of interparticle connectivity, and ultimately causes a large irreversible capacity decaying and poor cycling durability [15]. These problems greatly hamper the practical application of

Co_3O_4 in LIBs. It was believed that these problems are associated with long transport pathways for electrons and Li^+ as well as poor strain accommodation [16]. Therefore, to improve the cycling stability of Co_3O_4 electrodes, nanostructured Co_3O_4 with various morphologies has been fabricated, with the aim to buffer the volume changes and shorten the diffusion path for lithium ions; these morphologies include nanotubes, spheres, nanorods, and nanoneedles. Compared with bulk Co_3O_4 materials, these nanostructured Co_3O_4 anodes indeed exhibit improved discharge specific capacity, cycling durability, and rate capability [17-23].

In addition, to further enhance the conductivity of Co_3O_4 anode materials, other conductive species, including carbon nanotubes, graphene, and polypyrrole, are commonly introduced into Co_3O_4 [24-26]. Results have demonstrated that these Co_3O_4 -based composite anodes can exhibit improved lithium-ion storage performances in LIBs. Nevertheless, the synthetic processes involved in making Co_3O_4 -based composites are always time-consuming, complicated, high-cost, and even pollute the environment, which limit their practical applications in LIBs. It should be noted that many studies have proven the crystal plane structure of electrode material has a significant influence on the electrochemical properties. For example, previous computational analyses and experimental results demonstrated that the exposed (111) plane of Co_3O_4 promotes faster Li^+ transport than the (100) and (110) planes and then enhance the specific capacity and rate capability of Co_3O_4 anodes [27, 28]. However, to our knowledge, seldom studies of the effect of specific crystal facets on lithium storage capability, specifically on the cycling stability of Co_3O_4 anode

materials in LIBs, have been reported until now.

It should be noted that the specific capacities of Co_3O_4 reported in previous studies were usually obtained at relatively low current densities and/or with a limited cycle numbers (50 ~100 cycles) [28, 29]. The criteria for evaluating Co_3O_4 electrode materials are much more stringent in terms of practical application requirements. As a result, to maintain Co_3O_4 -based anode materials with high reversible capacity and long cycling stability required by future practical applications still poses an urgent problem.

Herein, it was reported that dumbbell-like Co_3O_4 superstructures can be produced via facile hydrothermal synthetic strategy followed by a simple calcination process. The unique CoCO_3 superstructures were generated through a template-directed growth mechanism [30], in which, an initial biomolecule-directed assembly step forms aggregates that then act as intermediates for growing the final dumbbell-like superstructures. After this, simple calcination of solid CoCO_3 precursor results in the spontaneous formation of porous dumbbell-like Co_3O_4 superstructures, wherein the primary Co_3O_4 nanoparticles are interspersed throughout the dumbbell-like superstructure. The whole preparation process is described in Scheme 1. These porous dumbbell-like superstructures, with well-defined channel features, are able to buffer volume expansion upon prolonged cycling and greatly shorten the transport path for lithium ions. Furthermore, the obtained Co_3O_4 displays a high specific surface area of $162.7 \text{ m}^2 \text{ g}^{-1}$ and excellent lithium-ion storage performances. When applied as the anode in LIBs, Co_3O_4 can deliver a specific capacity as high as 1036 mA h/g after 200

cycles at 0.1 C. The improved cycling stability of the Co_3O_4 anode is associated with the presence of the specific (111) and (311) crystal facets on the superstructure. This synthetic process maybe provides a novel design strategy for developing advanced anode materials for use in LIBs.

2. Experiment Section

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, Na_2CO_3 , and ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$) were analytical grade and used without further purification.

2.1 Synthesis of dumbbell-like Co_3O_4 .

First, CoCO_3 was synthesized via a facile hydrothermal method. In a typical synthesis, 1.08 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 50 mL of distilled water, after stirred for 0.5 h, then 24 ml 0.5 M of Na_2CO_3 aqueous solution was added drop by drop. And then the mixture was stirred for another 0.5 h, and then 1.0 g of ascorbic acid was added to the above solution under continuous agitation. After stirred for 0.5 h, the resultant homogeneous solution was transferred to a Teflon-lined stainless autoclave with 100 mL capacity, which was sealed and maintained at 160 °C oven for 16 h. The mixture was cooled to room temperature naturally. The obtained product was collected via centrifugation and washing with distilled water and ethanol for several times and then dried at 60 °C in an oven for 12 h. Finally, Co_3O_4 sample can be obtained after calcination of the prepared CoCO_3 precursor at 450 °C oven for 3 h in air at a heating rate of 2 °C min⁻¹.

2.2 Characterization

Powder X-ray diffraction (XRD) patterns were obtained in a Bruker AXS-D8 powder diffractometer in use of Cu-K α ($\lambda = 0.15405$ nm) radiation. Fourier Transform infrared spectroscopy (FTIR) was recorded with Bruker EQUINOX-55 infrared spectrophotometer on KBr pellet. Samples morphology was observed by field emission scan electron microscope (FE-SEM; Hitachi, S-4800) with accelerating voltage of 15 KV. The structural and composition analysis were taken via using high-resolution transmission electron microscopy (HRTEM) (Philips Tecnai G2 F30) at 200 kV that equipped with energy-dispersive spectroscopy (EDS). The specific porous structures of the prepared cobalt based samples were determined by Brunaur-Emmett-Teller (BET) surface analyser (Tri Star-3020, Micromeritics, USA). Thermogravimetric analysis (TGA) was conducted (TGA, Entzsch-Sta 449) in N₂ atmosphere over a temperature range of 25-1000 °C at a heating rate of 10 °C min⁻¹.

2.3 Electrochemical measurements

The electrochemical experiments of the CoCO₃ and Co₃O₄ samples were performed using CR 2032 type coin cells. The working electrode slurry was made by mixing the active materials, acetylene black (super P) and polyvinylidene fluoride (PVDF) binder with a mass ratio of (7:2:1) in N-methyl-2-pyrrolidone (NMP). After magnetic stirring for 24 h, the slurry was casted on Cu foil and dried at 60 °C in an air-circulated oven. The anode electrodes were cut into discs of 12 mm. The electrolyte was 1 M LiPF₆ in ethylene carbonate (EC)/diethylcarbonate (DEC) (1: 1, v/v). The 2032 coin cells were assembled in an argon-filled glove box. A Celgard 2400 microporous polypropylene membrane was used as the separator, Li foil as the

anode. Electrochemical measurements were performed in a LAND-CT2001A battery test system. The cells were discharged and charged in the fixed voltage range of 0.005-3V with a current density of 0.1 C. cyclic voltammetry was performed on a CHI660D electrochemical workstation at a scan rate of 0.1 mV s^{-1} .

Scheme 1: Schematic illustration the synthesis of dumbbell-like Co_3O_4

3 Results and discussion:

Fig. 1a presents the XRD pattern of CoCO_3 ; in which all of the diffraction peaks can be assigned to CoCO_3 phase when compared to standard JCPDS card no. 78-0209. The main diffraction peaks of the product at 25.0° , 32.6° , 38.6° , 42.7° , 46.5° and 53.8° correspond to (012), (104), (110), (113), (202), and (116) facets, respectively. No impurity peaks were detected in the XRD pattern; additionally, the prepared sample is highly crystalline. The prepared cobalt carbonate displays a specific spindle-like morphology as observed with SEM technique; the mean length of CoCO_3 was measured to be approximately $15 \mu\text{m}$, as shown in Fig. 1b. The specific spindle-like structure clearly exhibits a hierarchical assembly feature; the spindle-like structure was formed via ordered stacking and aggregation of numerous similar triangular cone units along the radial direction, as shown in Fig. 1c and d. In addition, many obvious bulges at the ends of the spindle-like superstructure can be seen via TEM observation

Fig. 1: Typical spindle-like CoCO_3 sample, (a) XRD pattern; (b) low-magnification FESEM image; (c, d) High-magnification FESEM images; (e) TEM image; (f) electron diffraction (ED) pattern; (g) HRTEM image.

(Fig. 1e), and further electron diffraction testing showed that the spindle-like structure has a well-resolved diffraction pattern, indicating a single crystalline nature (Fig. 1f). We also performed high-resolution TEM (HRTEM) analysis on the spindle-like CoCO_3 sample; it was found that the sample exhibits well-defined crystal lattice stripes, and the average crystal facet spacing were measured to be 3.51 and 2.49 Å,

corresponding to the (012) and (006) planes, respectively. These results further confirm the single crystalline nature of the spindle-like CoCO_3 sample, as shown in Fig. 1g.

Fig. 2: The typical dumbbell-like Co_3O_4 sample, (a) XRD pattern; (b) FESEM images; (c) TEM image; (d) HRTEM image; (e) ED pattern.

After calcination of the spindle-like CoCO_3 precursor at 450 °C for 3 h, a black sample was obtained. XRD testing was performed to confirm the presence of pure cubic phase Co_3O_4 according to standard JCPDS card no. 78-1969. As shown in Fig. 2a, the diffraction peak at 36.8° corresponding to (311) crystal facets displays optimal growth orientation. No impurity diffraction peaks are detected in the XRD pattern. In addition, SEM characterization reveals the novel dumbbell-like morphology shown in

Fig. 2b, further high-magnification FESEM observation find that the dumbbell-like Co_3O_4 superstructure was formed via divergent aggregation of numerous bundle-like units that composed of smaller size of nanoparticles (inset in Fig. 2b). We can also confirm the presence of dumbbell-like morphology via TEM observation (Fig. 2c). Thus, we conducted HRTEM analysis of the dumbbell-like Co_3O_4 superstructure, and found that the Co_3O_4 exhibited well-defined crystal lattice stripes. The average spacing are measured to be 4.65 and 2.43 Å, which correspond to the (111) and (311) planes, respectively, indicating an oriented growth pattern, as shown in Fig. 2d. Moreover, the dumbbell-like sample displays obvious multiple-diffraction circles during electron diffraction (ED) analysis, indicating a polycrystalline character, which is very consistent with the HRTEM and FESEM results, as shown in Fig. 2e. Furthermore, EDS analysis further confirms the presence of Co and O elements in the sample, implying the formation of Co_3O_4 (Supporting Information Fig. S1).

Fig. 3: Isothermal N_2 adsorption-desorption curves (a); Pore-size-distribution curve of the prepared spindle-like CoCO_3 sample (b).

Isothermal N_2 adsorption-desorption analysis was performed to evaluate the porous features of the spindle-like CoCO_3 product. The N_2 adsorption-desorption isotherm acquired at 77 K and the Barrett-Joyner-Halenda (BJH) adsorption pore size

distribution plot of as-prepared CoCO_3 are shown in Fig. 3a. The nitrogen adsorption isotherm is a typical IV type curve. Additionally, the loop nature of the nitrogen adsorption isotherm reveals a uniform mesoporous structure. The specific BET surface area for the as-prepared CoCO_3 was measured to be $6.13 \text{ m}^2 \text{ g}^{-1}$. In addition, according to the corresponding Barrett-Joyner-Halenda (BJH) calculation, the pore size-distributions are measured to be 4.0 and 7.90 nm, respectively, as shown in Fig. 3b. It is believed that the bimodal pore size distribution primarily results from the oriented aggregation of the two building unit present triangle cones and nanoparticles. Meanwhile, we performed isothermal N_2 absorption/desorption analysis on the prepared Co_3O_4 sample, and the nitrogen adsorption isotherm was found to be a typical IV type curve. Additionally, judged from the BJH calculation model, the specific BET surface area and pore size for the as-prepared Co_3O_4 were measured to be $162.7 \text{ m}^2 \text{ g}^{-1}$ and 3.54 nm, respectively, as shown in Fig. 4.

Fig. 4: Isothermal N_2 adsorption/desorption curves (a); Pore-size-distribution curve of the prepared dumbbell-like Co_3O_4 sample (b).

Fig. 5: FTIR spectrum (a) and thermogravimetric analysis (TGA) curve (b) of the prepared CoCO_3 sample.

To investigate the structural features of the prepared cobalt carbonate sample, we performed Fourier transform infrared (FTIR) spectroscopy, as shown in Fig. 5a. Herein, the broad and strong peak at 3404 cm^{-1} was produced from the $\nu(\text{O-H})$ stretching vibration. The peaks at 2927 and 2504 cm^{-1} can be assigned to vibration modes of the $-\text{CH}$ group. The characteristic peak of the $\text{C}=\text{C}$ functional group was centered at approximately 1815 cm^{-1} . The strong bands present at approximately 1453 cm^{-1} were assigned to the symmetric stretching modes of $\text{O}-\text{C}=\text{O}$ group. The relatively strong peak at 857 cm^{-1} can be assigned to the out-of-plane bending vibrational modes of the $-\text{CH}$ group. The peak at 751 cm^{-1} can be assigned to the vibration mode of the $\text{Co}-\text{O}$ group. In addition, the thermal stability of the as-synthesized cobalt carbonate was investigated by thermogravimetric analysis (TGA) technique under N_2 atmosphere. The first part of the weight loss was measured to be 1.9 wt% when the temperature was increased from room temperature to $170\text{ }^\circ\text{C}$, corresponding to the elimination of bound water [31]. The second part of the weight loss was measured to be 36.3 wt% over the temperature range from 310 to $800\text{ }^\circ\text{C}$,

and which was ascribed to the decomposition of cobalt carbonate and the formation of the Co_3O_4 component, as shown in Fig. 5b. XPS analysis results, which reveal additional structural information on Co_3O_4 , are given in Fig. S2.

Fig. 6: CV curves of the prepared dumbbell-like Co_3O_4 based anode.

Herein, it should be noted that, three factors simultaneously influence the overall reaction process. The formation of Co_3O_4 can be described with the following mechanistic steps [32]:

(1) Na_2CO_3 in the mixture solution is a source of CO_3^{2-} that can react with Co^{2+} to form CoCO_3 as a precursor.

(2) Ascorbic acid and Ostwald ripening play an essential role in the hydrothermal reaction, during which ascorbic acid directs the assembly of small CoCO_3 particles into the spindle-like CoCO_3 intermediate structure. If the same reaction process is carried out without ascorbic acid, thicker plates and numerous irregular particles are obtained, as shown in Fig. S3.

(3) The reaction temperature greatly affects the formation of the spindle-like CoCO_3 structure. When the reaction was carried out at low temperature of 100°C , irregular spherical aggregates and rod-like structures were formed, as shown in Fig. S4.

Fig. 7: Electrochemical performances of the prepared cobalt carbonate and cobalt oxide based anode materials, (a) charge/discharge curves of CoCO_3 ; (b) charge/discharge curves; (c) rate capability curves; (d) cycling performances testing curves of Co_3O_4 anode at different rates.

Next, we investigated the electrochemical performances of the cobalt-based samples as anodes in LIBs. The lithium storage performance of dumbbell-like Co_3O_4 as anode material for LIBs was first investigated using cyclic voltammetry (CV). As shown in Fig. 6, two pairs of well-defined redox peaks were observed on the CV curve, which correspond to the reversible conversions of cobalt oxide and lithium

species. The CV profiles of dumbbell-shaped Co_3O_4 show a difference between the first profile and those of subsequent cycles when acquired at a scanning rate of 0.1 mV s^{-1} in a Li/Li^+ voltage window from 0.01 to 3 V. In the first cycle, a small irreversible peak at approximately 1.09 V may be attributed to the formation of intermediate $\text{Li}_x\text{Co}_3\text{O}_4$ [33]. A sharp reduction peak located at 0.71 V can be ascribed to the further reduction of cobalt-based species to metallic cobalt, accompanied by the formation of amorphous Li_2O . This reduction reaction has a significant effect on the reversible capacity of Co_3O_4 [16]. For the anodic scan, a broad peak at approximately 2.15 V is associated with the oxidation of metallic cobalt into various cobalt oxides, in good agreement with peaks observed for other cobalt-based materials [34, 35]. It was found that the electrochemical behavior of Co_3O_4 in the subsequent cycles are similar to one another and can be characterized by two distinct sharp cathodic peaks at approximately 1.24 and 0.89 V and two anodic peaks at approximately 1.3 and 2.1 V. It was found that the reduction peak potential was shifted from 0.71 to 1.24 V, suggesting the existence of the polarization effect after the first cycle. The peak location and integration areas of the anodic oxidation reactions after the second cycle are almost identical, indicating the excellent reversibility and stability of the dumbbell-shaped Co_3O_4 anode.

Fig. 7a depicts the charge/discharge profiles of the spindle-like CoCO_3 anode undergoing different cycles at a current density of 0.1 C in the voltage range of 0.01 – 3.0 V (vs. Li^+/Li). The first discharge voltage profile of the CoCO_3 anode displays two distinct discharge plateaus at approximately 0.96 and 0.75 V, respectively. The initial

discharge specific capacity can deliver 1313 mA h/g at 0.1 C. It was seen that the discharge specific capacities after 5th, 10th and 50th cycles are 629, 551, and 379 mA h/g, respectively; the corresponding charge specific capacities are 592, 543, and 376 mA h/g, respectively, indicating good capacity reversibility. This observation can be attributed to the formation of a stable solid electrolyte interface (SEI) layer on the surface of active materials after the initial cycles.

Fig. 8: SEM images of the Co_3O_4 anode, (a) before cycling; (b) after 200th cycles

The charge/discharge profiles of the dumbbell-like Co_3O_4 anode undergoing cycling at a current density of 0.1 C in the voltage range of 0.01 – 3.0 V (vs. Li^+/Li) are shown in Fig. 7b. It was observed that the first discharge voltage profile of Co_3O_4 anode exhibited two apparent discharge plateaus at approximately 1.07 and 0.89 V. In addition, the voltage rapidly decreased from the open-circuit voltage (about 2.5 V) to approximately 1.07 V, which corresponds to the insertion of lithium ions into the Co_3O_4 structure [36]. For the first discharge process, lithium interaction with oxygen species in Co_3O_4 , the reduction of cobalt ions to cobalt metal, and the formation of Li_2O are the three major electrochemical reactions, as shown in Fig. S5. The initial charge and discharge specific capacities are 1105 and 1719 mA h/g, respectively. The

difference between the first discharge capacity and charge capacity is ascribed to the inevitable formation of an unstable SEI film on the surface of the electro-active materials and decomposition of the electrolyte during the first cycle. After the first cycle, the charge/discharge voltage profiles are very similar to one another, indicating comparable electrochemical pathways. The discharge capacities of Co_3O_4 in the 5th, 10th and 50th cycles are 981, 949 and 915 mA h/g, respectively. Thus, the charge/discharge curves clearly demonstrate that the dumbbell-shaped Co_3O_4 anode materials possess reversible lithium storage capability.

Rate capability is regarded as one of the important assessment criteria for practical application in LIBs. The dumbbell-shaped Co_3O_4 and spindle-like CoCO_3 anode materials were evaluated at various rates that ranged from 0.1 to 5 C, as shown in Fig. 7c. At applied current densities of 0.1, 0.2, 0.5, 1, 2 and 5 C, the delivered charge/discharge capacities of the dumbbell-shaped Co_3O_4 anode after 10 cycles are 948, 843, 641, 575, 463 and 242 mA h/g, respectively. When the current density was returned to 0.1 C after 70 cycles, an average charge/discharge capacity of 762 mA h/g was maintained, suggesting partial decay in battery capacity. In contrast, the spindle-like CoCO_3 anode exhibits a lower rate capability than the Co_3O_4 anode. When evaluated at 0.1, 0.2, 0.5, 1, 2 and 5 C, the delivered average discharge capacities of the CoCO_3 anode after 10 cycles are approximately 554, 415, 262, 148, 110 and 47 mA h/g, respectively. When the current density is returned to 0.1 C after 70 cycles, however, an average discharge capacity of 542 mA h/g is maintained, implying good storage lithium reversibility. Thus, it was considered that the formation

of a stable SEI film and the porosity of the electrode material have a significant influence on its electrochemical performances.

Next, we performed cycling performance testing for the prepared cobalt oxide anodes at different rate conditions, as shown in Fig. 7d. For the dumbbell-like Co_3O_4 anode, the discharge specific capacity was stable at 913 mA h/g after 60 cycles; after that, the discharge capacity gradually increased and then stabilized at 100 cycles. Remarkable, the discharge specific capacity was still 1036 mA h/g after 200 cycles at 0.1 C; thus, the specific capacity retention is as high as 91.3 %, which is much higher than previously reported results for similar materials [24, 26, 28, 32, 33, and 35]. We also performed cycling lifetime testing at higher rates such as 1 C and 5 C. The resultant discharge capacity at 1 C after 200 cycles was remained to be 543 mA h/g, the value is very close to the initial discharge capacity of about 566 mA h/g at 1 C (see Fig. 7c). Even at 5 C after 200 cycles, a similar case was observed, as shown in Fig. 7d. These results demonstrate that the dumbbell-like Co_3O_4 anode possesses a low discharge capacity loss even at high rate conditions. Additionally, the cycling performance of a spindle-like CoCO_3 anode was conducted, and the cycling performance of CoCO_3 displays similar behavior with the dumbbell-like Co_3O_4 . The specific discharge capacity of CoCO_3 was 565 mA h/g after 200 cycles at 0.1 C, and thus the specific capacity retention was measured to be as high as 76%, as shown in Fig. S6. Note that, the discharge specific capacity of Co_3O_4 can deliver 1036 mA h/g at 0.1 C after the 200 charge/discharge cycles, which is higher than its theoretical value (890 mA h/g). The extra discharge capacity may result from the electrolytic

decomposition process, interfacial lithium storage mechanisms and reversible reactions between intermediates such as LiOH and Li [37]. Previously reported studies have suggested that porous nanostructured materials can improve the number of Li^+ storage sites [38].

Fig. 9: the surface atomic configuration of the (111) and (311) planes of Co_3O_4 that binding with lithium ions.

Based on the above results, we found that the cycling performances of dumbbell-shaped Co_3O_4 achieved in this study are highly superior to previously reported results in the literatures. For example, Wang et al. reported that the charge capacity of carbon coated Co_3O_4 electrodes was 664 mA h/g at 500 mA g^{-1} after 50 cycles [39]. Yan et al. also found that the average discharge capacity of Co_3O_4 nanocages was approximately 487 mA h/g at a current density of 1000 mA g^{-1} after 50 cycles [40]. Ball-in-dodecahedron Co_3O_4 derived from metal organic frameworks (MOFs) deliver a reversible capacity of 650 mA h/g at 1000 mA g^{-1} after 100 cycles [41]. Moreover, the discharge capacity of Co_3O_4 anodes with different morphologies

including nanotubes, nanorods, and nanoparticles were found to be approximately 50 mA h/g at 0.1 C after 100 cycles, and have capacity retentions of only 58.8%, 57.8%, and 55.2%, respectively [42]. Note that, the specific discharge capacities of the dumbbell-shaped and spindle cobalt based anodes are much higher than that of commercial graphite (372 mA h/g) even at high current densities. Additionally, the prepared Co₃O₄ anode displays irregular particle shape and bulk structures before cycling, but exhibiting a larger particle-like structure after 200 cycles. This demonstrates that the Co₃O₄ anode underwent a slight volume expansion after 200 cycles and found that its particle-like morphology is almost completely preserved, indicating good structural stability upon cycling, as shown in Fig. 8. It was observed that the Co₃O₄ electrode obtained after thermal treatment had a higher Li-ion storage capability than the prepared CoCO₃ electrode. During the discharge cycle process, Co₃O₄ is converted to Co, which provides up to 8 Li storage sites per Co₃O₄ molecule, as described by the following chemical equation [43]:

Taken together, the excellent battery performances of dumbbell-shaped Co₃O₄ may be attributed to its unique structural properties. The enhanced storage lithium capability of dumbbell-shaped Co₃O₄ can be explained by the above electrochemical conversion reaction (3), in which, 8 lithium ions and 8 electrons are simultaneously involved in the electrochemical conversion of Co₃O₄ to a lithium storage site during the charge/discharge process [44].

First, well-defined porous channel structures are favorable for improving the

diffusion rate for lithium ions, due to the shortened diffusion length. For dumbbell-like Co_3O_4 , these porous channels formed *via* the divergent aggregation of numerous bundle-like units composed of nanoparticles with a mean size of approximately 10 nm. The primary nanoparticles and highly porous character not only effectively shorten the diffusion path for lithium ions but also partially buffer the volume change during the charge/discharge process. Second, the exposed reactive facets of the material are beneficial for reducing the diffusion length and enhancing cycling stability. Theoretical studies have suggested that the (111) and (311) planes of Co_3O_4 samples possess more Co^{2+} in their crystal facet structures than other planes (for example, (001) or (110)), as shown in Fig. 9. The high concentration of Co^{2+} on the (111) and (311) planes can greatly facilitate the chemical reactions between the oxygen species of Co_3O_4 and lithium ions during the charge/discharge processes. This phenomenon has been extensively verified in previous literatures [27, 28, 45]. For example, various works have proved that the exposed (111) planes of Co_3O_4 promote faster lithium ion transportation than the (001) plane [28, 46, 47]. As a consequence, the exposed (111) active crystal facets in dumbbell-shaped Co_3O_4 are an important contributor to its enhanced lithium storage ability. In addition, according to the results of our DFT-based first-principles calculation, we find that the surface energy of (311) planes is approximately $0.114 \text{ eV}/\text{\AA}^2$, which is higher than that of the (100) plane $\sim$ about $0.057 \text{ eV}/\text{\AA}^2$ and the (110) plane $\sim 0.102 \text{ eV}/\text{\AA}^2$, as shown in Supporting Information Table 1. As a result, the exposed (311) plane possesses an exceptionally high reaction activity for binding with lithium ion. Once Li_2O forms on the planes of

Co_3O_4 , then, it must bind to the plane; thus, we also calculated the binding energy of Li_2O on different planes according to DFT-based first-principles analysis. The calculation results reveal that the binding energy of Li_2O on the (311) plane is -4.942 eV, which is higher compared with the (110) plane $\sim$ -3.987 eV and (111) plane $\sim$ -2.337 eV, as shown in Supporting Information Table 2. As a result, it was concluded that the high binding energy of Li_2O on the (311) plane can favor the structural integrity of the Co_3O_4 during prolonged charge/discharge cycling.

It should be noted that the microstructure of the Co_3O_4 electrode material is advantageous for maintaining an excellent electron transport pathway (i.e., providing a larger electron diffusion coefficient D , this case can be further evidenced according to the performed Nyquist plot result, as shown in Fig. S7. As is well known, electrode materials are usually semiconductors and hence suffer from poor conductivity. As a consequence, electron transport can potentially become the rate-determining step in lithium storage. In our study, the presence of the microstructure in the dumbbell-shaped Co_3O_4 is actually beneficial for faster electron transport. For one, the high surface area and easily accessible channel of the dumbbell-like structure results in a large contact area between Co_3O_4 and the lithium ions that in turn is capable of building up “highways” for fast electron transportation and diffusion, enhancing electron mobility. More importantly, the dense microstructures can offer boundaries to limit the diffusion of active atoms, leading to spatially confined lithiation-delithiation reactions and maintaining electrode integrity [48]. Meanwhile, the pores formed by the aligned stacking of the many rod-like bundles within the

Co₃O₄ structure, as well as the presence of the highly developed channels can provide greater lithium-ion storage capability and effectively buffer the material stress and volume change caused by the charge/discharge process, preserving the structural integrity of Co₃O₄ anode. All of these features effectively improve the specific capacity and cycling durability of the Co₃O₄ anode.

4 Conclusions

In summary, a dumbbell-like Co₃O₄ superstructure was derived from the thermal decomposition of the as-prepared spindle-shaped CaCO₃ precursor. The two cobalt-based materials were used as anode electrodes for LIBs; in particular, the Co₃O₄ anode exhibited high specific capacity and excellent cycling stability. Our results demonstrated that the exposed (311) crystal facets and the microstructure of the dumbbell-like Co₃O₄ improve the cycling stability of the Co₃O₄-based anode in LIBs. It is believed that the synthetic strategy can be extended to develop promising electrode materials for other transition metal oxides as energy storage devices.

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Graphical Abstract: