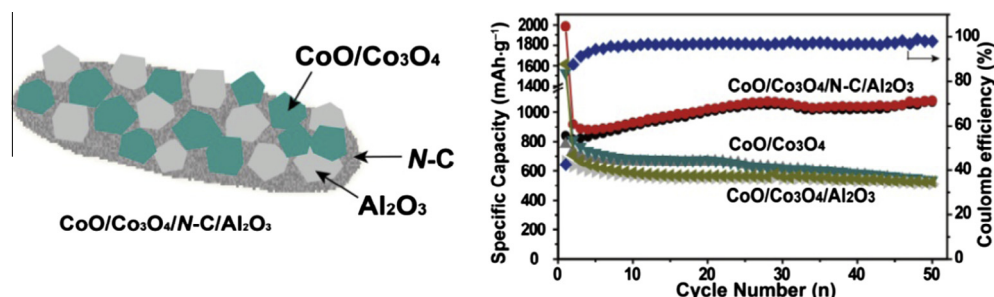# Nitrogen-doped carbon and high-content alumina containing bi-active cobalt oxides for efficient storage of lithium

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GRAPHICAL ABSTRACT

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ABSTRACT

Low-content ultrathin coating of non-active alumina (Al_2O_3) has been extensively utilized as one of the most effective strategies to improve electrochemical performances of electrodes for lithium-ion batteries (LIBs), however, typically by employing expensive atomic layer deposition equipment. We herein demonstrate a simple preparation of high-content and well-dispersed Al_2O_3 (24.33 wt.%)-containing multi-component composite ($CoO/Co_3O_4/N–C/Al_2O_3$) by calcination of melamine/CoAl-layered double hydroxide (CoAl-LDH) mixture. The resulting composite bundles the advantages expected to improve electrochemical performances: (i) bi-active CoO/Co_3O_4, (ii) highly conductive N-doped carbon, and (iii) N-doped carbon and high-content non-active Al_2O_3 as buffering reagents, as well as (iv) good distribution of bi- and non-active components resulted from the lattice orientation and confinement effect of the LDH layers. Electrochemical evaluation shows that the composite electrode delivers a highly enhanced reversible capacity of 1078 mA h g^{-1} after 50 cycles at 100 mA g^{-1}, compared with the bi-active CoO/Co_3O_4 mixtures with and without non-active Al_2O_3. Transmission electron microscopy/scanning electron microscopy observations and electrochemical impedance spectra experimentally provide the information on the good distributions of multiple components and the improved conductivity underlying the enhancements, respectively. Our LDH precursor-based preparation route may be extended to design and prepare various multi-component transition metal oxides for efficient lithium storage.

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1. Introduction

Lithium-ion batteries (LIBs) have been utilized widely in various applications such as portable electric devices, hybrid electric vehicle, and storage of renewable energy [1–4]. Increasing market demand requires designing and developing new electrode materials with long cycle life, high power and energy density, and improved safety. Transition metal oxides (TMOs, M = Fe, Co, Ni, and Cu) [5–8] have hitherto generated much attention as anode composites for LIBs, owing to the relatively higher theoretical capacities than that (372 mA h g^{-1}) of the commercially available

graphite. Cobalt-based oxides exhibit high theoretical reversible specific capacities of 715 and 890 mA h g^{-1} for CoO and Co$_3$O$_4$, respectively, however, still suffer from the common problems of large voltage hysteresis and irreversible capacity [9,10].

One typical improvement approach is to introduce carbonaceous composites. The advantages lie in alleviating the stress and volume changes of cobalt oxides during cycling by virtue of the carbonaceous structural stability, and especially enhancing the electronic conductivity. For instance, graphene/CoO composite [11], prepared via synthesis and calcination of graphene oxide/Co(OH)$_2$ ultrathin nanosheets, was able to deliver a reversible capacity of 640 mA h g^{-1} after 150 cycles at 100 mA g^{-1}. Co$_3$O$_4$ supported on the pre-designed onion-like carbon [12] obtained via a solvothermal method, exhibited a reversible capacity of 632 mA h g^{-1} after 100 cycles at 200 mA g^{-1}. Another feature improvement approach is to hybridize electrochemically bi-active TMO composites at the nanoscale. Most of the as-prepared TMO composites were capable of exhibiting greatly enhanced electrochemical performances compared with single TMO because of the well-recognized synergistic effect of bundling two-component advantages. Branched Co$_3$O$_4$/α-Fe$_2$O$_3$ nanowire [13] was synthesized by using hydrothermal synthesis and calcination, and delivered a reversible capacity of 980 mA h g^{-1} after 60 cycles at 100 mA g^{-1}. CoO/ZnO nanotube arrays [14] were prepared via hydrothermal treatment of cobalt nitrate grown on the pre-elaborated ZnO nanorod template. A reversible capacity reached 1000 mA h g^{-1} after 50 cycles at 50 mA g^{-1}. Alternatively, combining both supporting carbon and multi-active TMOs can effectively improve electrochemical properties. For example, core/shell Co$_3$O$_4$/NiO/C nanowire arrays [15] were synthesized via hydrothermal synthesis, chemical bath deposition, and annealing carbonation. A highly improved electrochemical performance was achieved up to 1053 mA h g^{-1} after 50 cycles at 0.5 C. However, it is necessary to build up elaborately pre-designed composite architectures using simple preparation methods.

Notably, introduction of non-active coating of active materials has been demonstrated both experimentally and theoretically to be an effective strategy to mitigate undesirable side reactions and thereby improve the overall battery performance. Non-active aluminum oxide (Al$_2$O$_3$) is one of the most attractive coating materials utilized widely for anode and cathode materials. The non-active coating layer has the potential to reduce the amount of the solid electrolyte interphase (SEI) formed on anodes [16,17], and thus to achieve long-term durability and high rate capability of the resulting electrode materials. The artificial several-nanometer-thick ultra-thin coatings were created controllably, however, by the aid of expensive atomic layer deposition (ALD) equipment [18], by using time-consuming high-energy mechanical milling [19], or by controlling pH value of buffer solution exquisitely [20]. Especially, in the case of multi-component TMO composites, using simple and economic preparation methods to guarantee multi-component homogeneous distribution is really important to manifest a synergistic effect between the active and non-active components and thereby to improve the electrochemical performances [21,22].

Layered double hydroxides (LDHs) are such a type of precursor materials to prepare multi-component TMOs as anode composites for LIBs. LDHs are well-known as one large family of anionic clays with brucite-like layers. LDHs have the general formula [M$^{2+}_{1-x}$M$^{3+}_x$(OH)$_2$]$^{x+}$[A^{n-}]$_{x/n}$·yH$_2$O, where M^{2+} and M^{3+} are arranged as divalent and trivalent metal cations in the LDH layers, respectively, and A^{n-} is intercalated as an anion between the LDH interlayer galleries [23], as well as the M^{II}/M^{III} molar ratio is tunable typically between 2 and 4. Various studies have demonstrated that the unique feature of flexibly tuning LDH metal cations, M^{2+}/M^{3+} molar ratios, and interlayer anions within wide ranges, has made
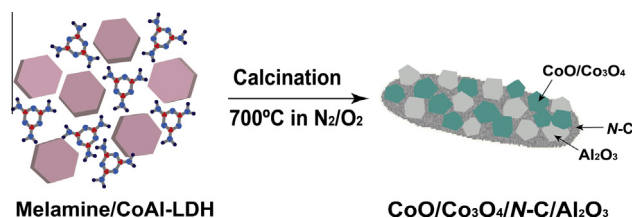
Scheme 1. Schematic illustration of the formation of CoO/Co$_3$O$_4$/N–C/Al$_2$O$_3$ composite.

the LDH-based materials attractive in extensive promising applications, including superconductive/magnetic devices [24], and photocatalysts [25], as well as clinical application [26]. Especially, thermal decomposition of LDH precursors is an intriguing alternative to traditional preparation methods to design and prepare various multi-component TMO composites consisting of both single and binary TMOs. ZnO/ZnAl$_2$O$_4$ film, derived from ZnAl-LDH film precursor [27], exhibited the improved electrochemical performances which were ascribed to the buffering effect of the inactive ZnAl$_2$O$_4$ matrix on chemically active ZnO by relieving the stress of the volume change during charge/discharge cycling. In our previous study [21], well-dispersed bi-active CoO/CoFe$_2$O$_4$ composite was prepared via high-temperature decomposition of CoFe-LDH single-source precursor, and exhibited tunable electrochemical performances by varying Co/Fe molar ratio of the precursors, but with a rapid decay in cycling stability.

In the present study, we describe a simple preparation of multi-component CoO/Co$_3$O$_4$/N–C/Al$_2$O$_3$ nanoplatelets via calcination the precursor of melamine/CoAl-LDH mixture (Scheme 1). Despite a high content of non-active Al$_2$O$_3$ contained, the integrated features of the multi-component composite are expected to facilitate high electrochemical performances: (i) synergism of bi-active CoO/Co$_3$O$_4$, (ii) improved conductivity of N-doped carbon, (iii) buffering effect of N-doped carbon and non-active Al$_2$O$_3$, as well as (iv) good distribution of bi- and non-active components. Electrochemical tests were performed between the CoO/Co$_3$O$_4$/N–C/Al$_2$O$_3$ composite and the CoO/Co$_3$O$_4$ mixtures with or without non-active Al$_2$O$_3$. The enhanced electrochemical performances were illustrated experimentally in terms of TEM/SEM observations and electrochemical impedance spectra.

2. Experimental

2.1. Preparation of CoO/Co$_3$O$_4$/N–C/Al$_2$O$_3$ composite

Nanosized CoAl-LDH precursor was prepared by a scalable method reported in our previous study [28]. In brief, a 80 mL of salt solution of Co(NO$_3$)$_2$·6H$_2$O and Al(NO$_3$)$_3$·9H$_2$O with a Co^{2+}/Al^{3+} ratio of 2.0 was prepared in deionized water, and a 80 mL of mixed basic solution was prepared by mixing a certain amount of NaOH and Na$_2$CO$_3$. Equal volume of the above two solutions were mixed for 2 min after simultaneously adding to a colloid reactor at a rotor speed of 3000 rpm. The slurry was collected and then transferred into a stainless steel autoclave for hydrothermal treatment at a temperature of 120 °C for 24 h. The as-prepared suspension was centrifuged and washed with deionized water for several times. The CoAl-LDH was obtained after drying the precipitate at 80 °C for 24 h.

CoAl-LDH/melamine mixture was mixed by fully grinding the individuals with a well-determined mass ratio of 1:3 for 30 min. The CoO/Co$_3$O$_4$/N–C/Al$_2$O$_3$ composite was prepared by calcining the mixture under an N$_2$/O$_2$ (50 ppm) atmosphere at temperature 700 °C for 2 h with a temperature ramping rate of 2 °C/min.

For comparison, two types of mixtures were prepared with and without the non-active Al$_2$O$_3$. The physical mixture of mCoO/Co$_3$O$_4$