



Full Length Article

Co₃O₄ nanocrystals with exposed low-surface-energy planes anchored on chemically integrated graphitic carbon nitride-modified nitrogen-doped graphene: A high-performance anode material for lithium-ion batteries

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ABSTRACT

A facile strategy to synthesize a composite composed of cubic Co₃O₄ nanocrystals anchored on chemically integrated g-C₃N₄-modified N-graphene (CN-NG) as an advanced anode material for high-performance lithium-ion batteries is reported. It is found that the morphology of the Co₃O₄ nanocrystals contains blunt-edge nanocubes with well-demarcated boundaries and numerous exposed low-index (1 1 1) crystallographic facets. These planes can be directly involved in the electrochemical reactions, providing rapid Li-ion transport channels for charging and discharging and thus enhancing the round-trip diffusion efficiency. On the other hand, the CN-NG support displays unusual textural features, such as superior structural stability, accessible active sites, and good electrical conductivity. The experimental results reveal that the chemical and electronic coupling of graphitic carbon nitride and nitrogen-doped graphene synergistically facilitate the anchoring of Co₃O₄ nanocrystals and prevents their migration. The resulting Co₃O₄/CN-NG composite exhibits a high specific reversible capacity of up to 1096 mAh g⁻¹ with excellent cycling stability and rate capability. We believe that such a hybrid carbon support could open a new path for applications in electrocatalysis, sensors, supercapacitors, etc., in the near future.

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1. Introduction

Lithium-ion batteries (LIBs) have long been considered as attractive rechargeable energy storage devices for a wide range of applications, such as portable electronic devices, electric vehicles, hybrid electric vehicles, and so on [1–3]. One of the main barriers to the development of LIBs lies in the low charge storage capability of anode [4]. Graphite has been used for a long time as a material in commercial LIBs anodes; however, its relatively low charge storage capability (theoretically 372 mAh g⁻¹) and confined rate capability limit its practical applications in electrical vehicles. On the other hand, transition metal oxides (TMOs) have been extensively studied as anode materials for high-performance LIBs due to their higher theoretical capacities (~500–1000 mAh g⁻¹) and environmental benignity [5,6]. Among the TMOs used for LIBs, Co₃O₄, a naturally abundant and nontoxic material, is by no means an especially promising candidate [7–9]. However, the main bot-

tleneck for its practical application is its large volume expansion during the Li⁺ insertion/extraction process [10]. This expansion may cause local stress and eventually result in pulverization and exfoliation of the active material from the current collector, consequently leading to fast capacity fading, poor life cycle, and low coulombic efficiency. It seems that a significant challenge still remains for the rational design and synthesis of Co₃O₄-based electrode materials with high reversible capacity, long cycling life and excellent rate capability.

In the past few decades, a variety of strategies have been investigated to enhance the overall electrochemical performance of Co₃O₄-based anodes, including the design of unique Co₃O₄ nano/micro-structures based on nanowires [7,11,12], nanotubes [8], nanoparticles [13,14], nanoplates [15], octahedral cages [16,17] and hollow nanospheres [18]. These nanostructures can remarkably improve contact between the active materials and electrolytes, shorten the Li-ion (Li⁺) diffusion length and promote volume strain relaxation during the electrochemical reaction. Another efficient strategy is to use carbon-based nanocomposites [2,19]. Graphene, a novel two-dimensional (2D) monolayer of sp²-hybridized carbon, is expected to be a promising substrate

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on which to load active nanomaterials for energy applications owing to its large surface area, superlative conductivity, high flexibility and chemical stability [20]. In particular, graphene can stably store lithium on both of its sides (LiC_3), giving rise to a higher theoretical capacity than any other carbon allotrope [21–25]. However, pristine graphene cannot strongly anchor the active nanoparticles due to its chemical inertness, which may result in aggregation or abscission of the active nanoparticles, thus deteriorating their electrochemical performance [26,27]. It has been found that chemical doping is an excellent strategy to overcome the inertness while altering the electronic and chemical properties [28], and to enhance the electrochemical properties for applications in LIBs as electrode materials or electrode supports [29–32]. To date, graphene sheets doped with various heteroatoms have been developed, such as nitrogen-[33,34], phosphorus-[35] and boron-doped graphene [36], as well as nitrogen and sulfur-codoped graphene [37], and nitrogen and boron-codoped graphene [38]. Recently, our group has succeeded in synthesizing a covalently coupled hybrid of graphitic carbon nitride and graphene [27,39], which possesses a stable structure, superior reactivity, and abundant anchoring sites. This unique carbon material can be further used as a support for loading metal nanoparticles to enhance the performance towards methanol or formic acid electrooxidation due to the strong interactions between the active materials and the support, which play important roles in improving the electrochemical activities and stabilities in energy storage devices [40,41]. Therefore, $g\text{-C}_3\text{N}_4$ can be regarded as one of the most promising dopants, that not only can optimize the physicochemical property of graphene, but also serve as a bridge to strengthen the interactions between the active materials and the graphene support. However, it should be noted that the study of carbon nitride-modified graphene-based materials for energy storage and conversion, including electrocatalysis, supercapacitors, and batteries, is just beginning and much more still remains to be done.

Herein, we report the synthesis of a ternary anode material by growing well-distributed Co_3O_4 nanocrystals on a covalently coupled hybrid of graphitic carbon nitride ($g\text{-C}_3\text{N}_4$; CN) and nitrogen-doped graphene (N-graphene; NG). The resulting $\text{Co}_3\text{O}_4/\text{CN-NG}$ nanocomposite possesses unique structural features for use in high-performance LIBs. By virtue of the concerted effects of the individual components, such as the exposed low-surface-energy plane on the highly dispensable Co_3O_4 nanocrystals, the large quantity of accessible active sites on CN for lithium-ion insertion, and the optimized topological defects and good electrical conductivity of N-graphene, this novel hybrid shows a remarkable lithium capacity and stable capacity retention up to 1096 mA h g^{-1} at current densities of 100 mA g^{-1} , as well as high coulombic efficiency and good rate capability. This work provides new insights into the fabrication of advanced supports for the maximum utilization of electrochemically active materials in energy storage applications.

2. Experimental section

2.1. Preparation of covalently functionalized $g\text{-C}_3\text{N}_4$ nanoflakelets with nitrogen-doped graphene (CN-NG)

All the chemical reagents used in this work were of analytical grade, and deionized water was employed in the corresponding experiments. First, graphite oxide (GO) was synthesized from commercial graphite powder by a modified Hummers' methods. The CN-NG sheets were typically fabricated as follows: the as-prepared GO (200 mg) was dispersed in an aqueous solution containing 400 mg melamine by sonication for 2 h. Then, the mixture

was stirred and heated at reflux for another 2 h. During the procedure, the epoxide groups of GO react with the amine groups of melamine and undergo a ring-opening reaction ($\text{S}_{\text{N}}2$ attack), while the remainder of the melamine deposits on the surface of GO due to electrostatic interactions and hydrogen bonding. After lyophilization, the GO-melamine samples were placed in a tube furnace and first heated at 550°C in N_2 to eliminate the oxygen-containing groups of GO and form $g\text{-C}_3\text{N}_4$ nanosheet layers on the graphene surface. Then, the temperature was increased from 550°C to 700°C to fully exfoliate the multilayered $g\text{-C}_3\text{N}_4$ nanosheets, while the large-sized $g\text{-C}_3\text{N}_4$ nanosheets were further broken into smaller nanoflakelets, forming the desired CN-NG nanosheets.

2.2. Preparation of $\text{Co}_3\text{O}_4/\text{CN-NG}$, $\text{Co}_3\text{O}_4/g\text{-C}_3\text{N}_4\text{-rGO}$, $\text{Co}_3\text{O}_4/\text{rGO}$ and Co_3O_4

In a typical synthesis of $\text{Co}_3\text{O}_4/\text{CN-NG}$, 33 mg of the as-obtained CN-NG was suspended in 100 mL of anhydrous ethanol by ultrasonication for 0.5 h, and then, 5 mL of 0.2 M $\text{Co}(\text{Ac})_2$ and 5 mL of deionized water were added to the above solution. The reaction mixture was kept at 80°C with stirring for 10 h. After that, the mixture was transferred to a 200 mL Teflon-lined stainless-steel autoclave and solvothermally treated at 150°C for 3 h. The final product (labelled $\text{Co}_3\text{O}_4/\text{CN-NG}$) was centrifuged, washed with ethanol and water, and then collected after lyophilization. For comparison, Co_3O_4 nanoparticles supported on carbon nitride modified graphene (labelled $\text{Co}_3\text{O}_4/g\text{-C}_3\text{N}_4\text{-rGO}$), graphene (labelled $\text{Co}_3\text{O}_4/\text{rGO}$) and pure Co_3O_4 nanoparticles were synthesized by the same procedure.

2.3. Characterization

Transmission electron microscopy (TEM) and elemental mapping were carried out on a JEOL JEM-2100 microscope. Powder X-ray diffraction (XRD) patterns were obtained using a Bruker D8 advance diffractometer with $\text{Cu K}\alpha$ radiation. The Brunauer-Emmett-Teller (BET) surface area was measured via nitrogen sorption experiments conducted at 77 K on a Micromeritics TriStar II 3020 automated gas adsorption analyser. Thermal gravimetric analysis (TGA) and DSC were performed on a simultaneous DSC-TGA analyser (SDT Q600, TA Instruments Co.). X-ray photoelectron spectroscopy (XPS) was performed on a PHI Quantera X-ray photoelectron spectrometer.

2.4. Electrochemical measurements

The working electrode was fabricated by mixing 80 wt% of the active material ($\text{Co}_3\text{O}_4/\text{CN-NG}$, $\text{Co}_3\text{O}_4/g\text{-C}_3\text{N}_4\text{-rGO}$, $\text{Co}_3\text{O}_4/\text{rGO}$ or Co_3O_4), 10 wt% acetylene black (Super P) and 10 wt% polyvinylidene fluoride (PVDF) binder dispersed in N-methyl-2-pyrrolidinone (NMP) [42]. The obtained slurry was coated on a copper foil substrate and dried under vacuum at 120°C for 2 h to remove the solvent. After pressing, the electrodes were cut into disks (10 mm in diameter) and dried at 80°C for 12 h before testing. The average loading density of active material on work electrodes was between 1.5 and 2.0 mg cm^{-2} . Electrochemical measurements were performed using lab-made Swagelok cells with Li foil as both the counter and reference electrode, a Celgard 2400 porous membrane separator, and a 1 M LiPF_6 electrolyte solution dissolved in ethylene carbonate and diethyl carbonate (EC-DEC, $v/v = 1:1$). The cells were assembled in an Ar-filled glovebox. Galvanostatic charge-discharge voltage profiles were measured using a LAND CT2001A electrochemical workstation at different current densities between 0.01 and 3 V vs Li^+/Li at room temperature. Cyclic voltammetry (CV) and electrochemical impedance

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