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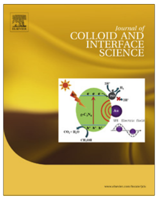

Regular Article

Graphene oxide assisted template-free synthesis of nanoscale splode-like $NiCo_2O_4$ hollow microsphere with superior lithium storage properties

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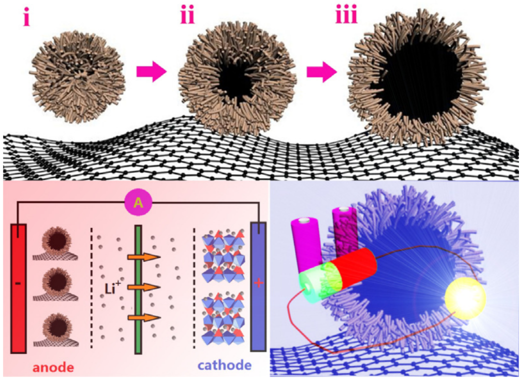
GRAPHICAL ABSTRACT

Reduced graphene oxide (GO) supported splode-like $NiCo_2O_4$ hollow microsphere (SNHM/rGO) has been synthesized by a facile template-free Ostwald ripening method. Due to its specific structure, the SNHM/rGO shows advanced performance and can deliver a stable reversible capacity of 1048.1 mA h g^{-1} at the current density of 100 mA g^{-1} when used as anode for lithium-ion batteries.



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ABSTRACT

A facile template-free Ostwald ripening method is developed for the preparation of the reduced graphene oxide supported splode-like $NiCo_2O_4$ hollow microsphere (SNHM/rGO). The graphene oxide used in the reaction mixture is found to play a crucial role in the formation of the SNHM/rGO. It promotes the formation of the NiCo-glycerol microspheres suitable for the Ostwald ripening to form the reduced graphene oxide supported hollow NiCo-glycerol microspheres, which is important for the subsequent calcination to form the SNHM/rGO. The obtained SNHM/rGO shows a great promise as the anode for lithium-ion batteries and can deliver a stable reversible capacity of 1048.1 mA h g^{-1} at the current density of 100 mA g^{-1}. The performance of the SNHM/rGO is much higher than that of most $NiCo_2O_4$-based materials reported previously, strongly suggesting that the SNHM/rGO could be used as the anode for practical

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Lithium ion battery
Improved performance

applications. This is well supported by the higher performance of the $LiCoO_2$//SNHM−rGO full cell. The excellent electrochemical performance can be attributed to the specific structure of the SNHM/rGO, which comprises the splode-like hollow $NiCo_2O_4$ microspheres with the reduced graphene oxide integrated.

1. Introduction

Lithium-ion batteries (LIBs) have been utilized in a wide variety of portable electronics and are considered as potential power sources of electric vehicles (EVs) and hybrid EVs [1–3]. To meet the growing appetite for the applications in EVs and HEVs, the energy density of the LIBs must be further improved [4,5]. However, the relatively low storage capacity (372 mA h g^{-1}) of the commercial graphite is apparently far from the ever-increasing needs for high-energy density applications [6–10].

In this regard, a variety of transition metal oxides (TMOs) have been widely investigated as potential anode materials for high energy density LIBs, due to their high theoretical capacities and widespread availability [11–13]. In the reported candidates, spinel nickel cobaltite ($NiCo_2O_4$, NCO) is of particular interest because of its environmental friendliness, low cost, earth abundance and high Li^+ storage capacity arising from both redox and alloying reactions [14–16]. However, NCO is confronted with a common problem of the TMO based anodes, i.e. the huge volumetric changes resulting from the Li^+ insertion/extraction processes. This could induce a large strain, resulting in the pulverization and detachment of the active materials from the current collectors and thereby a rapid capacity degradation upon cycling [17,18]. The nanostructured NCO materials, including nanoneedles, nanoflakes, nanobelts, nanosheet, nanoribbons, and nanorod, etc. [16–24], have therefore been developed to improve its cycling performance, since nanostructuring could effectively reduce the overall strain induced by the volumetric changes and the path length of the Li^+ diffusion in the active materials.

Aside from the huge volumetric change, NCO also suffers from low electric conductivity, which decreases the reaction kinetics of the intercalation/deintercalation process. Attempts have been devoted to developing the materials with integration of NCO and electric conducting materials, because the electric conducting materials could effectually improve the transfer of charges, allowing for a fast reaction kinetics. Among various electric conducting materials, graphene is of particular interest, because of its appealing characteristics of large specific area, superior electric conductivity and excellent mechanical strength. Additionally, graphene is also an excellent anode for LIBs and could deliver a reversible capacity much higher than graphite [25–27]. This makes the graphene integrated NCO materials particularly attractive as the anode for LIBs.

Recently, materials with a hollow structure are capturing tremendous attraction, especially those with porous walls in nanoscales or/and consisting of nanoscaled sub-particles. That is because the hollow structure could increase the contact area between electrolyte and active materials and reduce the path length for the Li^+ diffusion, allowing for a better access of the electrolyte and utilization of the active material. Additionally, the nanoscaled porous wall and hollow interior reduces the overall strains caused by volumetric changes and provides additional spaces for the accommodation of large volume changes during the repeated cycling processes, allowing for a ready diffusion of the Li^+ ions and the alleviation of the active material pulverization and detachment from the current collectors [28,29]. The template-sacrificing method is a most frequently used technique for the preparation of the hollow structured materials. This method, however, involves a complex process of the template synthesis, the material coating, and the template removal, which is tedious and not time-saving, making it unfavorable for the large-scale applications [30,31]. The development of template-free methods is therefore of great significance for practical uses of the hollow materials in LIBs. Up to now, although much work has reported on the fabrication of nanostructured NCO materials, the preparation of those with a hollow structure, especially those from the template-free method, still remains a great challenge.

Here, we report a novel template-free method, i.e. the Owstald ripening approach, for the preparation of the reduced graphene oxide supported splode-like NCO hollow microsphere (SNHM/rGO). Specifically, the GO are used as a support for the nucleation and growth of the NiCo-glycerol microspheres, whose Ostwald ripening leads to the formation of hollow NiCo-glycerol microspheres. The formation of the SNHM/rGO is achieved through the calcination of the rGO supported hollow NiCo-glycerol micro spheres(NiCo-glycerol/rGO). To our knowledge, it is the first time to report on the preparation of this unique hollow NCO microspheres using the template-free Owstald ripening approach. More interestingly, the obtained SNHM/rGO is highly active for the Li^+ ion storage and could deliver a stable reversible capacity of 1048. 1 mA h g^{-1} at the current density of 100 mA g^{-1}. The full cell tests show a great possibility of the practical use of the SNHM/rGO as the anode for LIBs.

2. Experimental section

2.1. Synthesis of the SNHM/rGO

Briefly, 0.5 mmol $Co(NO_3)_2$, 0.25 mmol $Ni(NO_3)_2$, 5 mL of glycerol (all obtained from Guangzhou Chemical Reagents Co.) were dissolved into 25 mL of isopropanol to form a homogeneous solution A. 3 mL GO (7 mg/mL, prepared from the modified Hummers method) was dispersed into 5 mL isopropanol with ultrasonic treating for 1 h to obtain a solution B. This solution was then added into solution A with constant stirring for 1 h at room temperature. The obtained mixture was transferred to a Teflon-lined stainless steel autoclave (50 mL) and hydrothermally reacted at 180 °C for 12 h. The black precipitates (NiCo-glycerol/rGO) were collected after cooling through centrifugation, washing with ethanol and deionized water (Mill-Q®, $R = \sim 18.0\ M\Omega\ cm^{-1}$) several times, and freeze-drying. For the synthesis of the SNHM/rGO, the obtained NiCo-glycerol/rGO was heated at 350 °C and calcined in air for 2 h. Control experiment showed the formation of the solid NCO microspheres, when the same synthetic route was employed while in the absence of GO.

2.2. Materials characterization

An X-ray diffractometer (XRD, Bruker D8 ADVANCE, Germany) was employed for the collection of the XRD patterns. The SEM images were obtained on a scanning electron microscopy (Merlin, Germany). The structure of the samples was analysed by a transmission electron microscope (TEM, JEM-2100HR, Japan). The Brunauer-Emmett-Teller (BET) specific surface area of the samples