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Chemical integration of reduced graphene oxide sheets encapsulated $ZnCo_2O_4$ quantum dots achieving excellent capacity storage for lithium-ion batteries

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ABSTRACT

Chemically integrated hybrid quantum dots $ZnCo_2O_4$/reduced graphene oxide (QDs ZCO/rGO) sheets nanocomposites are synthesized through polyol processes. rGO sheets grow and interweave to form basic skeletons. Ultrafine ZCO particles with a size of around 3.66 nm grow and embed on both sides of the rGO sheets, and the rGO sheets restrain the reunion of ZCO nanoparticles. The existence of rGO sheets and ZCO nanoparticles can engender the mutual synergistic effects so that hybrid QDs ZCO/rGO electrodes exhibit the excellent electrochemical properties. Owing to this special nanoparticles-on-sheets structure, the hybrid QDs ZCO/rGO electrodes exhibit an excellent initial discharge capacity for rechargeable lithium-ion batteries (1325.9 mAh g^{-1} at the current density of 200 mA g^{-1}), high rate stability (532.3/566.1 mAh g^{-1} at 4000 mA g^{-1}) and outstanding electrochemical cyclic stability (657.6/668.2 mAh g^{-1} at 2000 mA g^{-1} after 2000 cycles with a capacity retention of 68.6%). For full-cells, high initial reversible discharging capacity (646 mAh g^{-1} at 200 mA g^{-1}) and good cyclic stability (514 mAh g^{-1} at 200 mA g^{-1} after 100 cycles) are obtained. The superior performance of the as-prepared electrodes is ascribed to the advantage of nano-sized particles. With the successful synthesis of hybrid QDs ZCO/rGO nanocomposites, the facile synthetic route and unique growth of nanostructuring method can be extended to high electrochemical performance electrodes for commercial lithium-ion batteries.

1. Introduction

With the imminent of the global energy crisis and the deteriorated greenhouse effects, large energy density, high rate capability and prolonged lifetime of lithium-ion batteries (LIBs) have received broad attention [1–3]. However, the current commercial graphite anode has a limited theoretical specific capacity (372 mAh g^{-1}), hindering its further application in electric vehicles (EVs) [4]. Great efforts have been undertaken to search alternative anode materials for high performance LIBs.

Currently, owing to their high theoretical capacities and high abundance, the binary and ternary transition metal oxides (TMOs) have been widely studied as the next generation anode materials for rechargeable LIBs [5], such as $ZnMn_2O_4$ [6,7], $MnCo_2O_4$ [8–10], $ZnFeO_4$ [11,12] and $CaCrO_4$, [13] et al. Meanwhile, polynary TMOs display an excellent cyclic performance because of their complementary and synergistic effect of different metal elements. However, TMOs electrodes also have some fatal flaws, such as large volume, poor cycling stability and detrimental structural collapse during the charge/discharge process [14,15].Besides, the intrinsically poor electronic/ionic conductivities of TMOs have yet to be well resolved.

Tremendous efforts have been adopted to solve these intractable issues, such as carbon based nanocomposites [16,17], nanostructure construction [18] and element doping [19,20]. Designing hybrid carbon based TMOs nanocomposites is one of the promising ways to overcome the above challenges to improve the reaction flaws and promote the superior energy storage performance. Among various carbon materials, two-dimensional structural

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layers of graphene sheets are found to exhibit much more outstanding properties since they have been discovered in 2004 [21–24]. Until now, graphene is still one of the greatest excellent electronic conductors, exhibiting good mechanical properties and high theoretical specific surface area of 2630 $m^2 g^{-1}$ [25]. Besides, two-dimensional structure of reduced graphene oxide (rGO) also provides an excellent building block and an ideal conductive platform for anode materials [26,27]. There are much more oxygen-containing groups anchored on the surface of the rGO so that these functional groups are very reactive to oxidize the electrolyte and subsequently minimize the electrochemical instabilities. Furthermore, rGO sheets have a relatively low volumetric change during the electrochemical process [28]. Thus, a controlled synthesis strategy of TMOs/rGO nanocomposites with integrated nanoparticles anchored on the surface of rGO sheets is extremely desirable. It is expected that intimate interactions between TMOs and rGO sheets can not only promote Li^+/electrons transfer, but also inhibit the volume expansion and aggregation during the electrochemical cyclic process [29,30].

Among the aforementioned polynary TMOs, cubic spinel crystallize $ZnCo_2O_4$ has drawn considerable attention because of its unique crystalline structure and electrochemical reaction mechanism: Co^{3+} holds octahedral sites while Zn^{2+} occupies tetrahedral sites, possessing better electrical conductivity and electrochemical properties compared to the single metal oxide M_xO_y (ZnO, CoO and Co_3O_4, x = 1, 2, 3; y = 1, 2, 3,4) [31–33]. So far, various shapes of $ZnCo_2O_4$ have been widely studied, such as nano-flakes [34,35], nano-tubes [36], nano-sheets [37,38] and nano-rods [39] as well as nano-particles [40,41]. The preparation methods are different and the resultant materials exhibit specific electrochemical performance. Liu et al. synthesized $ZnCo_2O_4$ nanorods through a hydrothermal method [42]. The prepared $ZnCo_2O_4$ electrodes displayed a high initial capacity (1509 mAh g^{-1}) and outstanding cyclic performance (767.15 mAh g^{-1} after 50 cycles). Xu et al. fabricated 3D hierarchical porous $ZnO/ZnCo_2O_4$ nano-sheets via a reflux method [43]. As an anode material for LIBs, the as-prepared electrodes show a high reversible capacity (1016 mAh g^{-1} at 2A g^{-1} after 250 cycles) and excellent rate capacity (630 mAh g^{-1} under the current of 10 A g^{-1}). Wu et al. synthesized a highly symmetric $Zn_xCo_{3-x}O_4$ hollow polyhedral with an excellent reversible capacity (990 mA h g^{-1} after 50 cycles) [44]. Nevertheless, these special morphologies of $ZnCo_2O_4$ electrodes are still needed to further improve to meet the needs of high power EVs and LIBs.

Herein, we report a facile two-steps synthesis method that involves a polyol process and a thermal annealing process to prepare quantum dots $ZnCo_2O_4$ (QDs ZCO) with homogeneous size range from 2–6 nm, subsequently anchoring on the surface of rGO sheets through a facile polyol process (Fig. 1). Owing to the exceptional structure, the hybrid QDs ZCO/rGO electrodes exhibit an excellent specific discharge capacity over long cycles, as well as outstanding cyclic stabilities and high rate capabilities.

2. Experimental section

All the reagents are analytically grade, commercially available and used without further purification.

2.1. Preparation of hybrid QDs ZCO/rGO nanocomposites

The graphene oxide (GO) was synthesized from natural flake graphite by a novel modified Hummers method, in accordance with our previous publications [10,33]. In the typical synthesis, 1.0 mmol $Zn(AC)_2{\cdot}2H_2O$ (Aladdin, 99%) and 2.0 mmol $Co(AC)_2{\cdot}4H_2O$ (Aladdin, 99%) were dissolved in 45 mL ethylene glycol (Aladdin, 99%) under vigorous stirring for 20 min. Meanwhile, 60 mg GO was added into 55 ml ethylene glycol with ultrasonic agitation for 40 min to form a uniform solution, subsequently 5 ml $NH_3{\cdot}H_2O$ (Aladdin, 98%) was added dropwise. Then, the resultant solution was mixed together and stirred for another 30 min. Subsequently, the obtained solution was transferred into a round bottom flask and heated to 180 °C in an oil bath. Meanwhile, the heating process was controlled at 5 °C per minute and the stirring speed was controlled between 500 and 600 rpm. After refluxed for 10 h, the solution was cooled down to room temperature naturally. Ultimately, the precipitate was collected by centrifugation and cleaned with ethanol and deionized water at least three times alternately. The as-precipitate was then annealed at 200 °C under the air atmosphere for 3 h at a heating rate of 1 °C min^{-1} to obtain hybrid QDs ZCO/rGO nanocomposites. As a comparison, a bare ZCO material and rGO material were synthesized via the same procedures except adding the GO material, $Zn(AC)_2{\cdot}2H_2O$ and $Co(AC)_2{\cdot}2H_2O$, respectively.

2.2. Material characterizations

The crystal structures and morphology of hybrid QDs ZCO/rGO nanocomposites were checked by X-ray diffraction (XRD)

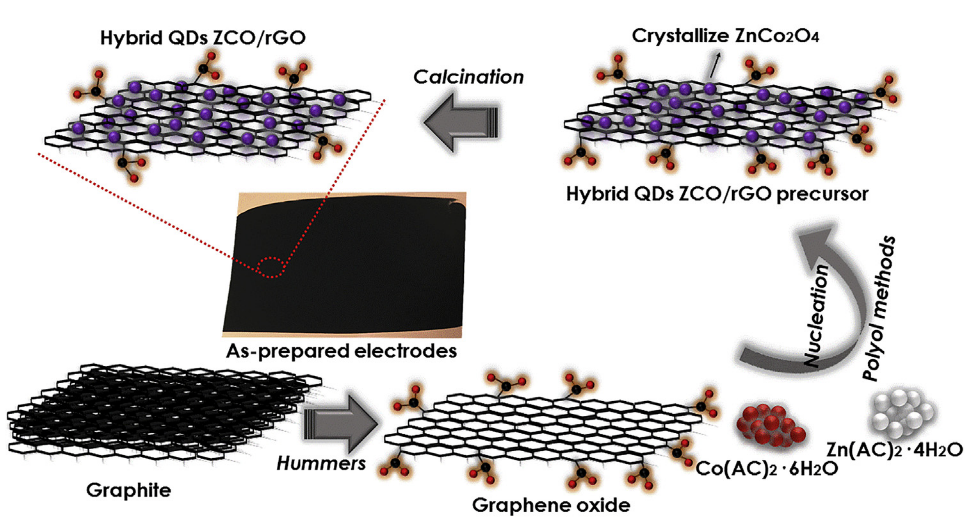

Fig. 1. Schematic diagram for the preparation process of hybrid QDs ZCO/rGO nanocomposites.