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Hierarchical mesoporous flower-like $ZnCo_2O_4$@NiO nanoflakes grown on nickel foam as high-performance electrodes for supercapacitors

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ABSTRACT

Herein, mesoporous $ZnCo_2O_4$@NiO nanoflakes grown on a nickel foam conductive substrate are prepared through a simple hydrothermal method combined with environmentally friendly chemical bath deposition method. The as-synthesized three-dimensional nanoflakes used as a binder-free supercapacitor electrode possess high specific surface area and shorten the ions and electron diffusion path. Electrochemical measurements indicate that $ZnCo_2O_4$@NiO (M3) nanoflakes deliver an ultrahigh specific capacitance of 2797 F g^{-1} at a current density of 1 A g^{-1}, and 2287.2 F g^{-1} at 10 A g^{-1}, even 1079.2 F g^{-1} at 40 A g^{-1}, respectively, revealing a remarkably improved rate performance. Moreover, the $ZnCo_2O_4$@NiO (M3) composite electrode exhibits superior cycling stability with ~100% initial capacitance retention at the current density of 30 A g^{-1} after 3000 cycles, and the coulombic efficiency remains over 97%. The first principle calculation shows that strong chemical bonds are formed between Ni (Co) and O species at the interface, which is favorable for the stabilization of the composite, resulting in a smaller interfacial polarization. The results indicate that $ZnCo_2O_4$@NiO with excellent electrochemical properties can be considered as a promising candidate for high-performance supercapacitors, and the facile architectural design strategy offers new insights in opportunities to exhibit promising potential in the field of the energy storage conversion applications.

1. Introduction

Nowadays, lithium-ion batteries (LIBs) and supercapacitors (SCs) are the promising alternatives for energy storage devices [1,2]. Especially, electrochemical capacitors have attracted widely interest because of their high-power density, long durability, excellent portability and strong security highly, which compensates for the shortages of the LIBs and conventional dielectric capacitors in numerous regards [3–6]. To date, single metal oxides (MOs) and hydroxides with redox reaction ability (e.g. MnO_2, Co_3O_4, NiO, $Ni(OH)_2$, $Co(OH)_2$, etc.) were vital components of electrode materials for SCs and have been investigated for ages [7–11]. Compared with binary MOs, ternary metal oxides with rich redox reactions usually have higher electrical conductivity and more excellent electrochemical activity [12,13]. Hence, ternary transition metal oxides (TMOs) as electrode materials have been widely applied to SCs [14,15]. Typically, cobalt-based TMOs like Co_3O_4 have attracted extensive attention due to the high theoretical capacitance, high electrochemical activity and remarkable cycling stability [16,17]. However, the low electronic conductivity, large volume changes during cycling, high cost and poor cycling stability at high current densities hinder the practical application. Hence, it is necessary to develop environment-friendly and low-cost alternative ternary TMOs used base metals (such as Zn [18], Cu [19], Ni [20], Mn [21], and Fe [22]) substituted partially Co in Co_3O_4, without affecting its excellent electrochemical properties. Ternary TMOs manifest excellent performance because of the synergistic effects: one metal oxide exhibits a feasible oxidation state and displays large specific capacity, and one exhibits good conductivity [23].

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Among the above mentioned ternary oxides, $ZnCo_2O_4$ has been considered as a promising multifunctional material for these considerations. Up to now $ZnCo_2O_4$ has been widely applied to LIBs [24], electrocatalyst [25], Li-air batteries [26], and SCs [27]. In the cubic spinel structure, bivalent Zn ion occupies the tetrahedral position, and Co^{3+} ion occupies the octahedral position. Zinc compounds with good electrical conductivity and higher electrochemical activity [28]. $ZnCo_2O_4$ also has an acceptable theoretical capacitance of $2604\,F\,g^{-1}$ [27]. Lately, direct growth of three-dimension (3D) hierarchical materials on the high conductive substrate as binder-free electrode has attracted broad attention for potential commercial application in SCs. For example, in Liu's report [29], a $ZnCo_2O_4$/nickel foam film electrode delivered a specific capacitance of $1400\,F\,g^{-1}$ at $1\,A\,g^{-1}$ and a superior cyclic stability with 3% decrease capacity after 1000 cycles. Nevertheless, the simple structures, low surface area and intrinsic poor electric conductivity of the $ZnCo_2O_4$ structures caused rapid capacity fade and large volume change charge-discharged at large current density. Hence, construction of different structures materials with different merits has been proved as a promising strategy to improve the electrochemical performance. In addition, NiO has been considered as one of the remedial measures because of high theoretical capacitance ($3750\,F\,g^{-1}$) [30], low-cost, excellent thermal stability, and eco-friendly [31,32]. The effective approach of fabricating composites materials not only possess the advantages of all the constituents, but also overcome the disadvantages of individual components. Therefore, combining $ZnCo_2O_4$ with NiO can easily acquire superior electrical conductivity and larger specific surface [33]. Especially, NiO can relieve the internal stress and restrain the rapid capacity decay during charge-discharge cycle process [34] compared with other metal oxides. Finally, a fascinating method to enhance the performance of electrode material is promotion of the ion/electron transfer rate by direct growth of electroactive species on the conductive substrate. The binder-free design can improve the interfacial contact between the current collector (including carbon fiber paper, carbon cloth, copper substrates, titanium foil, stainless-steel foil and nickel foam [35–38]) and active materials. This design can expose most electroactive sites of electrode to electrolyte, and then promote electrochemical reaction and active material utilization. To our knowledge, only ternary $ZnCo_2O_4$/reduced graphene oxide/NiO nanowire arrays grown directly on a piece of Ni foam has been used to supercapacitor electrode, and it delivered a low specific capacitance of $1256\,F\,g^{-1}$ at a current density of $3\,A\,g^{-1}$ [27], which made it difficult to meet the demands of practical application. As far as we know, no investigation was reported on capacitive performance of mesoporous $ZnCo_2O_4$/NiO nanoflake composites. Though the synergistic effect between different TMOs has been used to improve the electrochemical performance of supercapacitor, the mechanisms improving performance are difficult to be clarified only used experimental method. Fortunately, first principles computation methods have showed superiority in developing and optimizing new energy storage and conversion materials, and the predictions of the material performances are also possible thanks to the density functional theory (DFT). To our knowledge, no investigation was reported on mechanisms improving electrochemical performance of NiO modification used by DFT calculation.

In this work, 3D porous Ni foam is utilized as a support for the uniform growth of $ZnCo_2O_4$@NiO electroactive materials and is also conducted as current collector. We firstly adopt a facile hydrothermal growth and chemical bath deposition synthesis method to prepare 3D nanoflower-like structure with rich mesoporous, and then the mechanisms improving performance of NiO modification were studied by DFT calculation. Owing to the desired structure, the hybrid $ZnCo_2O_4$@NiO electrode shows a high specific discharge capacity over long cycle, as well as excellent cycle stability and prominent rate capability. These research results shed new light on how to improve the electrochemical performance of $ZnCo_2O_4$ material by simple and reproducible NiO modification.

2. Experimental

All the chemical reagents are analytically grade, commercially available and used without any purification. The preparation process of nickel foam (NF) substrate is given in Supporting Information (SI). The synthesis schematic illustrations of $ZnCo_2O_4$@NiO/NF composite are given in Fig. 1 a, and the preparation process of NiO/NF, $ZnCo_2O_4$/NF and $ZnCo_2O_4$@NiO/NF is given in SI. According to the deposition time of NiO (0, 20, 40 and 60 min), the corresponding $ZnCo_2O_4$@NiO samples are named M1, M2, M3, M4. The crystal structure, particle size, morphology, microstructures and distribution of element of $ZnCo_2O_4$ and $ZnCo_2O_4$@NiO powders were characterized by XRD, SEM, TEM, HRTEM and EDS mapping, respectively. The Brunauer–Emmett–Teller specific surface area (S_{BET}) was investigated by a specific surface and pore size analysis apparatus, and the detailed process is given in SI. The three-electrode system was used to test electrochemical performances of all samples, and the detailed prepared process is given in SI. The CV (cyclic voltammetry) and EIS (electrochemical impedance spectroscopy) tests are performed on a Princeton P4000 workstation, and the Galvanostatic charge and discharge (GCD) performance tests are performed on a LAND CT2001A system. The detailed test process is given in SI.

3. Results and discussion

3.1. Structure characterization

The growth mechanism of mesoporous $ZnCo_2O_4$/NiO nanoflake composites on NF is plotted in Fig. 1(b). Briefly, the preparation process contains two steps. Firstly, the raw materials reacted under hydrothermal conditions and formed nanometer scale layered precursor aligned on the NF. The color changes from amaranth to black after calcined process, and it reveals that the precursor nanosheets are successfully transformed to $ZnCo_2O_4$ nanosphere. As $ZnCo_2O_4$ nanospheres directly contact on NF, an effect combination between electroactive material and current collector is highly possible to reduce the interface resistance, leading to superior capacitive performances. In addition, the NiO coated layer can be deposited onto $ZnCo_2O_4$ nanosphere to form $ZnCo_2O_4$/NiO nanoflower with larger specific surface.

XRD pattern was further employed to identify crystal structure and phase composition information of both compound $ZnCo_2O_4$@NiO and pristine $ZnCo_2O_4$ samples. To avoid the strong diffraction peak of NF substrate, the $ZnCo_2O_4$ sample was peeled from the NF via long periods of ultrasonication. As shown in Fig. 1(c), the primary diffraction peaks at $2\theta = 31.24°$, $36.8°$, $59.28°$ and $65.1°$correspond to the lattice planes of (220), (311), (511) and (440) of $ZnCo_2O_4$. The diffraction peaks at $2\theta = 43.3°$ and $62.9°$ correspond to the reflection planes of (200) and (220) of NiO. All the peaks can be accordingly indicated the cubic $ZnCo_2O_4$ with spinel structure (JCPDS no. 23-1390) and face-centered cubic structure phase NiO (JCPDS no. 36-1451). The result confirms the coexistence phases of $ZnCo_2O_4$ and NiO after deposition process without any impurities and contaminants.

The morphology and structures of the 3D flower-like $ZnCo_2O_4$@NiO nanocomposites are mainly characterized through SEM, TEM, HR-TEM and selected-area electron diffraction (SAED). Fig. 2(a) and b depict SEM images of the pure $ZnCo_2O_4$ composed of nanosheets, forming orderly microsphere with particle size of