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Lignin-derived hierarchical mesoporous carbon and NiO hybrid nanospheres with exceptional Li-ion battery and pseudocapacitive properties

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ABSTRACT

Most high capacity anode materials expand significantly during charging, such anodes must contain sufficient porosity or tough protective layer in the discharged state to enable the expansion, yet not excess porosity or low mobility of mass, which lowers the overall energy density. Here, we present a high capacity anode consisting of hierarchical mesoporous carbon nanospheres without any additives, which are derived from lignosulfonate and can be used as an excellent support for *in-situ* embedding NiO nanoparticles of 11 wt%. The as-prepared hybrid nanospheres have an integrated architecture with micropore-to-mesopore distribution and a surface area of 852 $m^2 g^{-1}$. As a result, the hybrid nanosphere anode exhibit a high discharging capacity of 863 $mAh \cdot g^{-1}$ at 0.1 $A g^{-1}$ is retained after 100 cycles for a Li-ion battery. When evaluated as an electrode material for supercapacitors, the as-prepared hybrid nanospheres manifest exceptional performance with a high pseudocapacitance of 508 $F g^{-1}$. Remarkably, about 92% of the initial capacitance can be retained after 2000 charge/discharge cycles. This approach generates a strategy to combine metal oxide nanoparticles with nanostructured carbon derived from biomass, which is expected for a broad set of possible electrode chemistries.

1. Introduction

Due to the increase of energy consumption, energy storage system with high energy storage and energy saving receives great attention. The current electrochemical energy storage system can be divided into three different systems based on its performance and energy storage mechanism: batteries, supercapacitors and capacitors [1]. The development of environmental benign materials for lithium-ion battery (LIBs) with high energy density and cyclic stability is of great significance for large-scale applications [2–4]. Because the commercialized graphite, which has been used conventionally as the anode material for LIBs, has a low theoretical capacity (372 $mAh \cdot g^{-1}$ in the form of LiC_6) [5–8], much effort has been paid to yield new anode materials capable of having practical applications in the electric vehicles (EVs) [9–11].

In recent years, transition metal oxides (NiO [12–17], Fe_2O_3 [18,19], Co_3O_4 [20,21], etc.), which can go fast and reversible faradic redox reaction, have attracted extensive attention as the alternative anode materials with superior electrochemical performance [22]. Therein, NiO has been considered as one of the most promising anode materials for LIBs due to its high theoretical capacity (718 $mAh \cdot g^{-1}$), low cost, low toxicity, low environmental impact and improved safety [13,22–24,43]. However, its low conductivity and poor cycling stability still hinder its further commercial applications [25]. The usage of the combination of NiO and carbon materials is an effective way to solve the problem. Carbon materials, such as activated carbon [26], porous carbon [13], carbon nanotubes [27], nanofibers [28], carbon aerogels [29], graphene [30] and other carbon materials [31], especially mesoporous carbon (MPC) [32], can improve the dispersibility and conductivity of

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metal nanoparticles (NPs), effectively alleviate the infiltration volume expansion, accelerate the change of electrolyte ions of the active substance that can fully contact electrolyte, thus to improve the electrochemical performance. In numerous transition metal oxides, NiO has been considered as one of the most promising anode materials for LIBs due to its high theoretical capacity (718 $mAh \cdot g^{-1}$), low cost and improved safety. Fan et al. demonstrated a simple precipitation method to obtain ultrathin NiO nanosheets on the highly ordered CMK-3. The final electrode composite displays a novel nanosheets-mesoporous structure [12]. The composites show an excellent rate capability with enhanced cycling performance (879 $mAh \cdot g^{-1}$ in average from the second cycle and only 9.8% capacity loss after 50 cycles at a rate of 100 $mA\,g^{-1}$). Jiang et al. studied the nanowires of the Ni@MPC nuclear shell structure, which can be used to oxidize nanoscale nickel into the corresponding nickel oxide [33]. The composite electrode shows higher specific capacitance with increasing discharge capacity and cycling stability in 1 M KOH aqueous solution, but expensive dopamine is needed as a carbon precursor.

Recently, numerous studies have been employed for producing MPC by the biomass materials due to their natural reproduction, excellent reactivity and versatile applications. In nature, lignin is second only to cellulose as the most abundant and important macromolecules in organic matter [34]. Lignosulfonate comes from the traditional sulfite pulping process, which has high sulfur content and good water solubility [35]. Due to the complex composition (containing phenolic hydroxyl groups, methoxyl groups, carboxyl groups and other functional groups in side chains) and the relative wide molecular mass distribution (ranging from hundreds to millions of molecules), it has many attractive properties such as high carbon content, high thermal stability, biodegradability and antioxidant ability [36]. These advantages have inspired researcher's interest in developing lignin into a variety of value-added products [37]. Wang et al. used the electrospun carbon fiber felt derived from lignin as a high performance anode material for lithium ion batteries. The results show that the nitrogen free fused carbon fiber has a high specific capacity up to 445 $mAh \cdot g^{-1}$ at a current density of 30 $mA\,g^{-1}$ and a good cyclic stability at different current rates [32]. Li et al. prepared low cost amorphous carbon (AC) bituminous with a suitable morphology which exhibited good performances with a high reversible capacity of 254 $mAh \cdot g^{-1}$, a high initial coulombic efficiency of 82% and excellent cycling stability [38]. Our group reported the successful synthesis of hierarchical mesoporous carbon (HMPC) material from lignosulfonate [13,31]. This low-cost HMPC has high conductivity, high porosity and larger specific surface area, which could provide more reactive interface and electrons/ions transfer channels. The unique pore size distribution is beneficial to the conduction and the rapid transport of electrons/ions. In addition, at high temperature, the sulfonate groups are almost reduced to inorganic sulfur, which is trapped in the porous carbon framework, could highly improve the electrochemical properties [31]. Moreover, we also demonstrated that lignin can function as a matrix for the self-assembly of metal oxide NPs, and can form highly graphitized MPC framework with improved conductivity and capacity for the electrode material [37].

All of the above studies show that lignin/derivative materials can be applied to energy storage and its performance is better than that of raw materials. Since lignin is derived from biomass and usually discarded as waste, it is prominent to use lignin as a cheap alternative material in woody materials. On the other hand, few studies have investigated the fabrication of lignin-derived NPs and their potential usage in high-performance electrode materials [12]. In this work, we firstly synthesized uniform HMPC nanospheres (NSs) from lignosulfonate in a simple one-step process. To overcome the unstable capacity of common NiO anode material, we designed and synthesized $Ni(OH)_2$/HMPC NSs using HMPC NSs as both the carbon source and the matrix. The final NiO/HMPC NSs [39] was obtained by the subsequent thermal treatment in a nitrogen atmosphere. Owing to the unique hierarchical structure, NiO/HMPC NSs not only reserved all advantages of the spherical structure, but also increased the reversible capacity and the cycling performance. Besides, the graphitized carbon skeleton among the HMPC NSs worked as a cushion to alleviate the phenomenon of volume expansion by NiO NPs during the charging-discharging process. Meanwhile, it would also increase the electrical conductivity and act as the passage of electron transfer.

2. Experimental details

2.1. Preparation of HMPC nanospheres

In this work, 0.5 g of sodium lignosulfonate was dissolved in water and slowly dripped into isopropyl alcohol. After 2 h, the LS (lignin-derived nanospheres) were centrifuged and dried in an oven at 60 °C for 12 h. The HMPC NSs were obtained by thermal treatment at 800 °C under a nitrogen atmosphere. NiO/HMPC NSs were synthesized by the in-situ carbonization of Ni(OH)2/HMPC NSs in an argon atmosphere [12]. The major process steps employed in this work are illustrated in Scheme 1. $Ni(OH)_2$ was deposited on the carbon sphere to form a nano-scale shell. The composites were then carbonized at 450 °C in a nitrogen atmosphere to forme the final NiO/HMPC NSs.

2.2. Characterization

Fourier Transform Infrared Spectroscopy (FTIR) analysis was performed on a Nicolet 6700 type spectrometer. The sample spectra were recored from 400 cm^{-1} to 4000 cm^{-1} with a resolution of 0.4 cm^{-1}. Scanning electron microscopy (SEM, Hitachi SU-1510) was taken to analyze the morphologies of the materials. The accelerate voltage was 10 kV and the working distance was 8 mm. Transmission electron microscopy (TEM) was performed on a JEOL JEM-100CX II microscope operated at an accelerate voltage of 300 kV. Thermogravimetry (TG) test was performed using a TA Instrument SDT Q600 under a N_2 atmosphere with 10 °C/min ramp rate from room temperature to 1000 °C ASAP2020 automatic physical adsorption instrument from Micromeritics was used for Brunauer-Emmentt-Teller (BET) test. X-ray photoelectron spectroscopy (XPS) measurement was performed on a Kratos AXIS Ultra DLD system (Shimadzu-Kratos) employing a monochromatic Al K_α X-Ray. Raman spectrum was taken with a Lab RAM HR UV800 Raman spectrometer (JOBIN YVON) using an excitation wavelength of 632.81 nm at room temperature.

2.3. Electrochemical test

The electrodes for LIBs were prepared according to the following steps. Poly(vinylidene fluoride) and N-Methyl pyrrolidone (mass ratio, 1:10) were configured as a conductive gel. A small amount of N-Methyl pyrrolidone was added to evenly mixed carbon spheres, acetylene black and conductive gel (mass ratio 8:1:1), stirred for 3 h to form a uniform slurry. The slurry was applied on copper and then dried in a vacuum oven at 60 °C for 3 h. The dried electrodes were then pressed (15 MPa) and placed in a vacuum oven for an overnight dry at 60 °C. Finally, the electrodes were assembled into a CR 2025 button battery. The KOH 6 M solution electrolyte was used to test the charging and discharging performance.

The electrodes for supercapacitors were prepared according to the following steps. Polytetrafluoroethylene and deionized water