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CoS_2 embedded graphitic structured N-doped carbon spheres interlinked by rGO as anode materials for high-performance sodium-ion batteries

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ABSTRACT

Much attention has been paid to the Cobalt-based sulfides in recent years due to their high specific capacity and strong catalytic activity in the field of sodium-ion batteries (SIBs). Nevertheless, the poor cycling stability and low rate capability have hindered their practical applications. Herein, an effective strategy for the rational design of CoS_2 nanoparticles embedded in the graphitic structured N-doped porous carbon spheres interlinked by the reduced graphene oxide (rGO) nanosheets (rGO-CoS_2-GNCSs) is proposed. The interconnected multidimensional nanostructure constructed by CoS_2 nanoparticles, graphitic structured N-doped porous carbon spheres and rGO nanosheets can provide a fast transfer pathway for electrons and electrolyte ions, which helps enhance the electric conductivity of the material and facilitate the reaction kinetics in SIBs. Moreover, benefiting from this unique microstructure, the change of the volume during sodiation/desodiation can be effectively alleviated and the stability of the architectural morphology can be enhanced. As a result, the rGO-CoS_2-GNCSs used as the anode of SIBs presents an impressive electrochemical performance at a cut-off voltage of 0.4–2.9 V in the electrolyte of 1.0 M $NaCF_3SO_3$ in diglyme, delivering a high reversible capacity of 523.9 mAh g^{-1} at 100 mA g^{-1} after 150 cycles, an excellent rate capability of 423.3 mAh g^{-1} at 2 A g^{-1} and extraordinary long-term cycling stability of 465.9 mAh g^{-1} at 500 mA g^{-1} after 600 cycles and 412.2 mAh g^{-1} at 1 A g^{-1} after 400 cycles. This study puts forward a promising strategy for the rational design of anode materials for high-efficiency sodium storage by interconnecting transition metal compounds, two-dimensional materials and nanocarbon to form multidimensional nanohybrids.

1. Introduction

With the fast development of smart power grids, electric vehicles (EVs) and soaring popularity of portable electronic devices, it is very necessary to develop energy materials with high performance and long cycling life [1–8]. Over the past two decades, rechargeable lithium-ion batteries (LIBs) have obtained tremendous success owing to their long lifespan, high energy density and environmentally friendly feature [9–14]. However, LIBs may not meet the increasing demand for large-scale energy storage devices because of the scarcity and uneven distribution of lithium resources and high production cost [15,16]. Therefore, it is imperative and critically significant to develop an innovative rechargeable battery as an alternative.

In recent years, sodium-ion batteries (SIBs) have attracted increasing investigations as a promising candidate to substitute LIBs due to their similar working mechanisms to the lithium-ion batteries and the lower price of sodium-salt resources than that of lithium resources [17–19]. However, it is still a challenge to find suitable anode materials of SIBs because of the larger ionic radius of Na^+ than that of Li^+ ($r_{Na+} = 1.02$ Å vs. $r_{Li+} = 0.76$ Å) [20–23]. Recently, much effort has been devoted to developing diverse types of anode materials for SIBs, such as carbon-based materials [24–26], phosphorus and phosphide nanomaterials [27–31], metal alloys [32–35], transition metal chalcogenides (TMCs) [36–38], etc. It is worth noting that increasing attention has been paid to the transition metal sulfides (TMSs) (e.g., VS_2, FeS_2, NiS_2, MoS_2, SnS_2, CoS_2 and so on) which act as potential anodes for Na^+ ion storage owing to their high theoretical specific capacity, rapid Na^+ ion

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diffusion and high electrochemical activity [39,40]. Among these TMSs materials, CoS_2 has been regarded as one of the most promising candidates for anode materials for SIBs due to its unique advantages of high theoretical specific capacity (871 mAh g^{-1}) and low cost [41,42]. For example, Han et al. reported CoS_2 nanoparticles encapsulated in N/S-doped carbon polyhedron, delivering a high initial discharge capacity of 776 mAh g^{-1} and remaining a reversible capacity of 510 mAh g^{-1} at 100 mAh g^{-1} after 100 cycles [43]; Li et al. prepared a fascinating flaky structure in which CoS_2 particles are uniformly anchored on rGO nanosheets, delivering a capacity of 250.8 mAh g^{-1} at 0.5 A g^{-1} after 150 cycles [41]; and Ma et al. synthesized a N-doped CoS_2/C/CNT electrode material, exhibiting excellent cycling performance of 402 mAh g^{-1} at 100 mA g^{-1} after 200 cycles and good rate capacity of 306 mAh g^{-1} at 2 A g^{-1} [3]. It can be seen in recent reports that the electrochemical performance of CoS_2-based materials has been improved to some extent when acting as the anode material for SIBs; Nevertheless, their relatively poor long cycling stability, low rate performance and large volume change during charging and discharging processes cannot still meet the practical applications as an anode in SIBs.

To address the above-mentioned issues, an effective method to improve the sodium storage capacity of CoS_2-based anode materials should include the two following aspects: (i) the nanocrystallization of active materials can shorten the transmission distance of Na^+ during sodiation and desodiation processes and enhance the electrochemical activity of the materials [44]; and (ii) the combination of CoS_2 with various nanocarbon materials (such as CNTs, heteroatom-doped porous carbon, rGO, and so on) can strengthen the structural skeleton of the electrodes, prevent the agglomeration of active materials, enhance the electron conductivity and buffer the volume stress [45,46]. Based on this idea, an interconnected multidimensional nanohybrid of CoS_2 nanoparticles embedded in the graphitic structured N-doped porous carbon spheres interlinked by rGO nanosheets was designed as the electrode material for Na^+ ion storage. This unique design of rGO-CoS_2-GNCSs anode material has excellent sodium storage performance: (i) nanocrystallization of CoS_2 can shorten the transmission distance of electrons and ions, increase the contact area between CoS_2 and the electrolyte, and improve the utilization rate of CoS_2; (ii) N-doped nano-carbon is beneficial to generate more active sites and optimize the surface wettability, which is a superior method to improve the cycling performance of the electrode; (iii) the porous architecture of rGO-CoS_2-GNCSs can effectively alleviate the large volume change caused by repeated sodiation/desodiation; and (iv) the graphitized carbon spheres catalyzed by cobalt are interconnected by rGO to form a high-efficiency conductive network, which can greatly enhance the transfer rate of the electrons and reaction kinetics. As expected, rGO-CoS_2-GNCSs presents an outstanding electrochemical performance when used as the electrode material for SIBs, delivering a superior reversible specific capacity of 523.9 mAh g^{-1} at 100 mA g^{-1} after 150 cycles and exhibiting a prominent rate capability of 423.3 mAh g^{-1} at 2 A g^{-1} and extraordinary long-term cycling stability at high discharge rates (465.9 mAh g^{-1} at 500 mA g^{-1} after 600 cycles and 412.2 mAh g^{-1} at 1 A g^{-1} after 400 cycles).

2. Experimental

2.1. Materials

1,3-Dihydroxybenzene ($C_6H_6O_2$, RG), formaldehyde (CH_2O, RG), Sulfur (S, 6N) and absolute ethyl alcohol (C_2H_6O, AR) were purchased from Shanghai Titan. Scientific Co., Ltd. Melamine was obtained from Aladdin Chemical Co., Ltd, China. Cobalt-nitrate hexahydrate ($Co(NO_3)_2.6H_2O$, AR) and ammonium hydroxide ($NH_3.H_2O$, GR) were provided by Sinopharm chemical Reagent Co., Ltd. Graphene oxide was purchased from Nanjing XFNANO Materials Tech Co., Ltd. All the chemicals were used without further purification. Deionized (DI) water was used throughout the study.

2.2. Synthesis of materials

2.2.1. Synthesis of the phenolic resin nanospheres containing Co^{2+}/nitrogen (Co^{2+}/N-PRNSs) and the phenolic resin nanospheres containing nitrogen atoms (N-PRNSs)

In a typical synthetic process, 1 mL ammonium hydroxide, 0.01 mol resorcinol and 1.48 mL formaldehyde (37 wt %) were successively added to the solution of 200 mL DI water and 80 mL anhydrous ethanol under vigorous agitation, and then refluxed at 70 °C for 0.5 h. After that, 0.005 mol melamine, 1.1 mL formaldehyde and 1.72 mmol cobalt-nitrate hexahydrate ($Co(NO_3)_2.6H_2O$) were added to the above-mentioned mixture and refluxed for 24 h continually. Next, the mixed solution was transferred into a 100 mL Teflon-lined stainless-steel autoclave and maintained at 120 °C for 24 h. Finally, the yellowish-brown powder (Co^{2+}/N-PRNSs) was obtained by centrifugating and washing with absolute ethyl ethanol several times and dried at 60 °C in a vacuum oven overnight. As a reference, the N-PRNSs can be obtained under the same conditions with the absence of cobalt-nitrate hexahydrate.

2.2.2. Synthesis of Co-embedded graphitic structured N-doped porous carbon spheres (Co-GNCSs) and N-doped carbon spheres (NCSs)

The Co-GNCSs were synthesized by carbonizing Co^{2+}/N-PRNSs at high temperature. Typically, the obtained yellowish-brown powder (Co^{2+}/N-PRNSs) was heated at 800 °C for 3 h at a heating rate of 2 °C min^{-1} in argon atmosphere. After cooling down to room temperature, the metallic Co nanoparticle embedded graphitic structured N-doped porous carbon spheres (Co-GNCSs) were obtained. The N-doped carbon spheres (NCSs) were also produced via the carbonization of N-PRNSs under the same reaction conditions.

2.2.3. Synthesis of CoS_2 embedded graphitic structured N-doped porous carbon spheres (CoS_2-GNCSs)

The CoS_2-GNCSs were fabricated by the sulfurization of Co-GNCSs. In a typical procedure, the Co-GNCSs and sulfur powders were placed at two separate positions in a closed porcelain boat, in which Co-GNCSs and sulfur powders were at the downstream and upstream of the furnace, respectively. The mass ratio of the Co-GNCSs powder to sulfur was 1:2. Subsequently, the samples were heated at 300 °C for 2 h at a heating rate of 5 °C min^{-1} in argon atmosphere. Finally, the black CoS_2-GNCSs powder was obtained after cooling down to room temperature.

2.2.4. Synthesis of CoS_2 embedded graphitic structured N-doped porous carbon spheres interlinked by reduced graphene oxide nanosheets composites (rGO-CoS_2-GNCSs)

The rGO-CoS_2-GNCSs nanocomposite was prepared through direct carbonization and sulfurization of the mixture of Co^{2+}/N-PRNSs and graphene oxide (GO) sheets. Simply speaking, 1.2 g Co^{2+}/N-PRNSs nanospheres were first dispersed into 300 mL absolute ethyl alcohol and ultrasonically treated for 3 h to form a suspension solution. Then, 40 mL homogeneous GO (7.5 mg mL^{-1}) aqueous suspension was added into the suspension of Co^{2+}/N-PRNSs nanospheres under vigorous agitation. After stirring for 5 h, the mixture of Co^{2+}/N-PRNSs and GO sheets was collected by centrifugating and dried at 60 °C for 12 h. The obtained powers were annealed at 800 °C for 3 h at a heating rate of 2 °C min^{-1} in argon atmosphere to obtain the rGO-Co-GNCSs nanocomposites. After