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Synthesis of self-assembled cobalt sulphide coated carbon nanotube and its superior electrochemical performance as anodes for Li-ion batteries

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ABSTRACT

In this work, cobalt sulphide/functionalised carbon nanotube (CoS_2/fCNT) nanocomposites were synthesized via solvothermal method followed by annealing sulphidation. The nanocomposites were composed of fine nanoparticles (2–10 nm) coated along the surfaces of fCNT as well as nanoclusters (30–60 nm) formed by the nanoparticles which intertwined with the fCNT network. The as-synthesized CoS_2/fCNT nanocomposites exhibited excellent electrochemical performance as an anode material in Lithium-ion batteries (LIBs), such as superior specific capacity, enhanced rate capability, outstanding cycling stability and near 100% Coulombic efficiency. CoS_2/fCNT hybrid nanocomposite electrodes were able to deliver high reversible capacities of 783.4 mAh g^{-1} and 337.8 mAh g^{-1} at the current densities of 50 and 1000 mA g^{-1}, respectively. Furthermore, the electrode sustained an impressive capacity retention of 84.1% after unprecedented 1000 discharge-charge cycles at a high current density of 1000 mAh g^{-1} The ultra-long cycle stability is much higher than all other reported cobalt sulphide anodes so far. The excellent electrochemical performance of CoS_2/fCNT nanocomposite is attributed to the synergistic effects of CoS_2 and fCNT. The outstanding stability of the CoS_2/fCNT nanocomposites makes it a highly promising anode material to instead of the conventional graphite for future generation LIBs.

1. Introduction

Lithium-ion battery (LIB) is one of the most successful electrochemical batteries so far due to the salient features such as high energy density, long life time and no memory effect [1]. However, the development of LIB is still unable to keep up with fast progress of personal electronic devices. Research efforts to improve LIB technology has led to the discovery of a new storage mechanism (conversion reaction) in transition metal oxides and sulphides which was firstly reported by Poizot et al. [2] The reaction mechanism of this group of material can be described as follows: [3]

$$M^{n+}(X) + ne^- + nLi^+ \leftrightarrow M^0 + nLi(X),$$

$$M = (Mn, Co, Fe, Mo, Cu, Ni, etc), X = (S, O) \quad (1)$$

Based on different oxidation states of the metal anions, these transition metal oxides/sulphides have been reported to achieve lithium storage of more than 2 times higher than that of graphite (~372 mAh/g) anode used in conventional LIBs [4–10]. Among various metal oxides/sulphides, cobalt sulphides with a broad range of stoichiometry, such as CoS, $Co_{1-x}S$, Co_9S_8, Co_3S_4 and CoS_2, have attracted much attention as a promising anode material for next generation LIB due to their high theoretical capacities [11–17]. However, the electrochemical performance of cobalt sulphides in LIB remain inferior due to the intrinsically low electronic conductivity and poor capacity retention caused by large volumetric changes [47.1%] that occurs during lithiation/delithiation process which causes pulverization of the active materials [18].

Tremendous research efforts have been devoted into improving the conductivity and lithium ion kinetics in cobalt sulphides mainly via two strategies. Firstly, the controlled synthesis of

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nanomaterials with unique morphology which is able to increase the surface area for Li-ion exchange and also reduce volume changes. For instance, hollow spheres of CoS_2 [12] and Co_9S_8 [19], 3D flower-like CoS [13] and $Co_{1-x}S$ [16] and rose-like Co_9S_8 [15] have all shown improved electrochemical performances compared to the bulk sample owing to the novel nanostructures. Another strategy is the incorporation of carbon materials to increase electronic conductivity and reduce the volume change during lithiation/delithiation process, leading to an enhanced performance. For example, amorphous carbon coating of Co_9S_8 [20] and CoS_2 [17], graphene composites with CoS [21], Co_3S_4 [14], and CoS_2 [22], as well as reduced graphene oxide (rGO) composites of CoS_2 [18,23] and Co_9S_8 [24] have shown much improved specific capacity and cycle life time of the active materials. Although cobalt sulphide with graphene hybrid nanostructures achieved amongst the highest electrochemical performance owing to graphene's unique properties such as high electron mobility and large surface area, graphene sheets are prone to restacking due to strong $\pi-\pi$ interaction and van der Waal forces between layers in these graphene-based hybrid. [25–32] One potential alternative is the use of single or multiwall carbon nanotubes (CNT), which can provide highly conductive 1D network channel that facilitates the rapid flow of ions and electron transfer. Furthermore, the large surfaces of these conductive CNTs is able to support growth and decoration of nanoparticles which can effectively cushion volume changes during the LIB operation. [6,33,34] Although CoS_2/CNT has been reported as an active material in supercapacitors, [35,36] there is no report of lithium kinetics behaviours yet.

Herein, CoS_2/fCNT nanocomposites were synthesized via a simple two-step approach of solvothermal followed by sulphidation process. The resulting hybrid nanocomposites composed of CoS_2 nanoclusters intertwined with the interconnected fCNT network and ultra-fine CoS_2 nanoparticles uniformly coated on the surfaces of the fCNTs. This unique morphology gave rise to the synergistic effect between CoS_2 and fCNT, which lead to an enhance electrochemical performance in terms of improved specific capacity, high rate capability, as well as outstanding cycle stability up to 1000 cycles.

2. Experimental

2.1. Synthesis of CoS_2/fCNT nanocomposites

All materials and reagents used in the synthesis were purchased from Sigma Aldrich and used without further treatment. CoS_2/fCNT nanocomposites were synthesized via a two-step process comprising of the synthesis of CoS_x/fCNT followed by sulphidation. Firstly, CoS_x/fCNT nanocomposites were grown by a solvothermal method [35]. In a typical process, 50 mg fCNT was added into 50 mL of ethylene glycol (EG) and dispersed by a probe sonicator for 1 h. Thereafter, $CoCl_2{\cdot}6H_2O$ (0.08 mol L^{-1}) was dissolved into 10 mL of EG and added dropwise to the above dispersion under stirring. The mixture was stirred in an oil bath at 80 °C for 12 h followed by the addition of thioacetamide (TAA) (0.2 mol L^{-1}), dissolved in 10 mL EG, with continuous stirring for another 4 h in the oil bath. The mixed dispersion was then transferred to a 100 mL Teflon-lined stainless steel autoclave and heated to 180 °C for 12 h. The resulting black precipitates were washed several times under deionized (DI) water and absolute ethanol by centrifugation and dried at 60 °C for 8 h. In the second step of sulphidation, 100 mg of CoS_x/fCNT loaded into a ceramic boat and 1 g sulphur were transferred into a quartz tube. Thereafter, sulphidation proceeded at 500 °C for 1 h in Ar gas environment.

2.2. Characterization

The morphology and structure of the products were examined by field-emission scanning electron microscopy (FESEM, JEOL JSM-7600F), transmission electron microscopy (TEM) and high resolution TEM (HRTEM, JEOL JEM 2100F). Powder X-ray diffraction (XRD) patterns were performed by an X-ray diffractometer (Bruker, D8 Advance Eco) equipped with a Cu Kα radiation ($\lambda \approx 1.54$ Å). Raman spectroscopy was carried out using WITec Confocal Raman Microscope alpha 300 R. Thermal gravimetric analysis (TGA) was tested by Shimadzu DTG-60. Energy dispersive X-ray (EDX) was carried out using the Oxford Silicon Drift Detector (SDD) - X-Max^N.

2.3. Electrochemical measurements

A typical two-electrode half-cell configuration composed of lithium metal as the counter electrode and active material as the working electrode was used to evaluate the electrochemical performance of the CoS_2/fCNT nanocomposites. The as-synthesized product was mixed with conductive carbon black and polyvinylidene fluoride (PVDF) binder in a weight ratio of 80:10:10 and added with several drops of N-Methylpyrrolidone (NMP) solution to form a slurry. The slurry was then coated onto Ni foam current collector and dried in a vacuum oven at 120 °C for 12 h to form CoS_2/fCNT working electrodes. The working electrodes were then assembled into standard CR2032 coin cell in an argon-filled glove box. Celgard 2400 membranes and 1 M $LiPF_6$ solution in a mixture ethylene-carbonate/dimethyl-carbonate (EC/DMC, 1:1 v/v) were used as separators and electrolyte, respectively. Galvanostatic cycling of all the assembled half-cells were carried out in the potential range of 0.01–3.0 V by the Neware battery tester. Cyclic voltammetry (CV) was measured at a scan rate of 0.05 mV s^{-1} and electrochemical impedance spectra (EIS) was measured in a range of 0.01 Hz to 1 MHz on an electrochemical workstation (VMP3, Bio-Logic).

3. Results and Discussions

Fig. 1 illustrates the two-step approach to synthesize CoS_2/fCNT. Prior to the solvothermal process, the precursors were stirred in an oil bath at 80 °C to allow CoS_x seeds to uniformly grow on the surfaces of fCNT. After the solvothermal process, the obtained product was a mixed phase of CoS and CoS_2 which is confirmed by the multiple peaks obtained from the XRD patterns (Fig. S1). Although several authors have previously reported the use of this

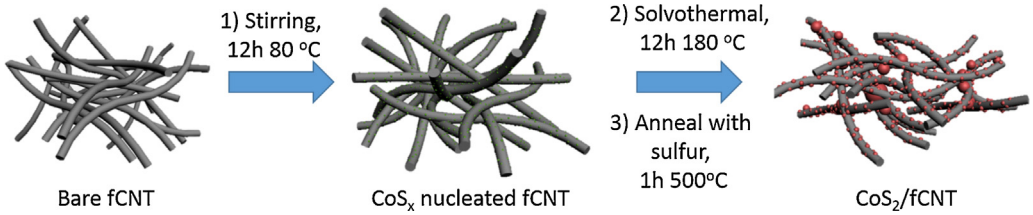

Fig. 1. Schematic diagram of the two-step process to synthesize CoS_2/fCNT nanocomposites.