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Smart construction of polyaniline shell on cobalt oxides as integrated core-shell arrays for enhanced lithium ion batteries

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ABSTRACT

Smart construction of advanced anode materials is extremely critical to develop high-performance lithium ion batteries. In this work, we have reported a facile strategy for fabricating Co_3O_4/polyaniline (PANI) core–shell arrays (CSAs) by chemical bath deposition (CBD) + electrodeposition methods Electrodeposited PANI shell is intimately decorated on the CBD-Co_3O_4 nanorods forming composite CSAs. Highly conductive network and stress buffer layer are achieved with the aid of tailored PANI shell. Due to these advantages above, the designed Co_3O_4/PANI CSA_S exhibit good electrochemical performance with higher reversible capacity (787 mAh g^{-1}) and better cycle stability than the unmodified Co_3O_4 counterpart. Our results show a new way for preparing advanced inorganic-organic composite electrodes for electrochemical energy storage.

1. Introduction

Transition metal oxides (TMOs) (such as cobalt oxides, nickel oxides, copper oxides, iron oxides) have been thriving over the past decade as anode materials for lithium ion batteries (LIBs) with the purpose of achieving superior specific capacities to commercial graphite [1–7]. Typically, Co_3O_4 is a highly attractive anode candidate due to its high theoretical capacitance (890 mAh g^{-1}), low cost, environmentally friendly nature, and superior electrochemical reactivity [8–10]. Although Co_3O_4 holds tremendous potential, its commercial application is still hindered by some serious drawbacks such as poor cycle stability and rate performance resulting from slow kinetics of lithium ion/electron transport, large volume change associated with electrode pulverization [11–13]. Therefore, it remains great challenge to design/fabricate Co_3O_4 electrodes with good high-rate capability.

It has been reported that rational construction of nanostructure arrays on conductive substrate is an effective strategy to alleviate those disadvantages aforementioned. Compared with the powder form materials, the binder-free nanostructure arrays could provide fast electron transport path during the charge/discharge process. Additionally, the porous architecture of the arrays offers large channels for fast electron/ion transport, thus accelerating the electrochemical kinetics process [14–19]. For instance, Zhan et al. synthesized Grass-like Co_3O_4 nanowire arrays (NWAs) grown on Ti foil with good rate capability and long cycle life (662 mAh g^{-1} at 5 A g^{-1}) [20]. Qi et al. fabricated CoO/NiSix core–shell NW arrays through a combination of CVD and subsequent RF-sputtering approaches with good cycling performance (900 mAh g^{-1} after 200 cycles at 0.5C) [21]. Despite this progress, it is proven that single nanostructure arrays could not offer omnibearing conductive network for active materials, and just provide fast electron transfer path at the bottom of composite arrays, but absence of the top electron transfer path on the Co_3O_4 arrays. In this context, composite modification is indispensable to achieve boosted performance. Typically, among the conducting polymers, polyaniline (PANI) has been extensively utilized owing to high conductivity and easy processing [22–24]. PANI is demonstrated with good electrochemical enhancement for other materials such as PANI/$LiCoO_2$ [25], PANI/$ZnFe_2O_4$ [26,27] and PANI/V_2O_5 [28]. These examples have shown that the PANI layer could not only enhance the conductivity, but also preserve the structural and interfacial stabilization avoiding the aggregation. Recently, Padwal et al. synthesized layered composite PANI/Co_3O_4 electrode, and showed almost 50% enhancement in specific energy/power in comparison with the pure Co_3O_4 electrode [29]. Inspired by these successful

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samples, it provides us great impetus to explore the rational electrochemical combination between PANI and self-supported Co_3O_4 arrays.

The one-dimensional (1D) Co_3O_4 arrays have been prepared by different methods including thermal oxidation, hydrothermal and chemical bath deposition (CBD) [30]. But the preparation of 1D Co_3O_4 nanowires/nanorods via thermal oxidation and hydrothermal is tedious, requiring caustic chemical treatments, and long curing times. CBD can overcome these disadvantages and produce high-quality 1D Co_3O_4 arrays. To date, there is no report on the construction of PANI on CBD-1D Co_3O_4 arrays and their electrochemical application. In this work, we demonstrate a facile and controllable strategy to synthesize Co_3O_4/PANI core–shell arrays by integrating PANI shell on the free-stranding 1D Co_3O_4 core. In such a core-shell structure, the designed arrays are directly connected to the current-collector, leading to improved electron transfer of the electrodes. More importantly, compared to the pristine Co_3O_4 arrays, the as-prepared Co_3O_4/PANI core–shell arrays deliver higher reversible capacity as well as better cycling stability and high-rate performance.

2. Experimental

2.1. Material synthesis

The fabrication process of Co_3O_4/PANI core–shell nanorod arrays was schematically shown in Fig. 1. It could be clearly seen that the whole process involved two steps: (1) Co_3O_4 nanorods were grown vertically on nickel foam by a CBD and annealing process; (2) PANI layer was electrodeposited on the Co_3O_4 nanorod core forming Co_3O_4/PANI core–shell nanorod arrays as following.

Synthesis of Co_3O_4 nanorod arrays on nickel foam. Firstly, the nickel foam with thickness was ultrasonically cleaned with acetone and ethanol, and then was blow-dried with compressed air. Secondly, 3 g cobalt nitrate was dissolved in 40 mL distilled water. Third, the nickel foam was immersed in the above solution and kept for 8 h to 10 h at 90 °C, and then cooled to room temperature. Finally, the Co_3O_4 nanorod arrays were obtained by annealing at 300 °C in air for 1 h.

Synthesis of Co_3O_4/PANI core–shell nanorod arrays. The self-supported Co_3O_4/PANI nanorod arrays were synthesized via a simple ED method. The ED electrolyte consisted of 1 ml aniline and 1 ml sulfuric acid dissolving in 100 ml distilled water. The ED was performed in a standard two-electrode glass cell at 25 °C, the above Co_3O_4 nanorod arrays as the working electrode, and a Pt foil as the counter electrode. The ED was conducted at a constant anodic current density of 2.5 mA cm^{-2} for 10 min to form the final Co_3O_4/PANI nanorod arrays.

2.2. Material characterizations

The Raman spectra were measured by the Renishawin Via Raman microscope using 532 nm laser excitation. The X-ray diffraction (XRD) measurements were collected on a Rigaku D/Max–2550 pc X-Ray diffractometer. The samples were characterized by Raman spectroscopy (LABRAMHR-800). The morphology and microstructure were conducted on scanning electron microscopy (SEM, Hitachi S4800 microscopy) and transmission electron microscopy (TEM, JEOL 2100F) at an acceleration voltage of 200 kV.

2.3. Electrochemical measurements

The Co_3O_4/PANI core–shell arrays were cut into a circular pellet with a diameter of 12 mm and directly used as the working electrode. The electrochemical measurements were carried out by two-electrode coin cells (CR2025). The test CR2025 coin cells were assembled in an argon-filled glove box with the metallic lithium foil as the counter electrode, 1 M $LiPF_6$ in ethylene carbonate (EC)-dimethyl carbonate (DME) (1: 1 in volume) as the electrolyte, and a polypropylene (PP) microporous film (Cellgard 2300) as the separator. Cyclic voltammetry (CV) tests were carried out on a CHI 600C electrochemistry workstation from 0.01 to 3.0 V (vs. Li/Li^+) at a scan rate of 0.1 mV s^{-1}. The galvanostatic charge-discharge measurements were conducted on LAND battery test system at different current densities between cut-off voltages of 0.01–3 V at room temperature (25 ± 1 °C). The capacities of Co_3O_4/PANI electrode were calculated based on the total mass of Co_3O_4 and PANI in the composite. The load weight of Co_3O_4 is about 6.8 mg cm^{-2}.

3. Results and discussion

The crystallographic structures of Co_3O_4 and Co_3O_4/PANI nanorod arrays are confirmed by X-ray diffraction (XRD) spectroscopy (Fig. 2a). Both in patterns of Co_3O_4 and Co_3O_4/PANI nanorod arrays, the diffraction peaks of Co_3O_4 at 19.1°, 31.1°, 36.8°, 38.8°, 45.1°, 55.2°, 59.8°, 65.1° and 77.8° can be clearly observed, which can be attributed to the (111), (220), (311), (222), (400), (422), (511), (440) and (533) planes of cubic spinel phase Co_3O_4 (JCPDS No. 42-1467). As for Co_3O_4/PANI nanorod arrays, no diffraction peaks of PANI are detected, indicating that the electrodeposited PANI is amorphous in nature [31,32].

Raman measurement is used to verify the formation of Co_3O_4 and Co_3O_4/PANI nanorod arrays (Fig. 2b). Indeed, the Raman spectra of the PANI and core Co_3O_4 crystals are different. The Raman spectrum of the Co_3O_4/PANI arrays shows the superimposition of the spectrum of PANI (broad bands between 1400 and 1600 cm^{-1}) and weak signals between 400 and 800 cm^{-1}

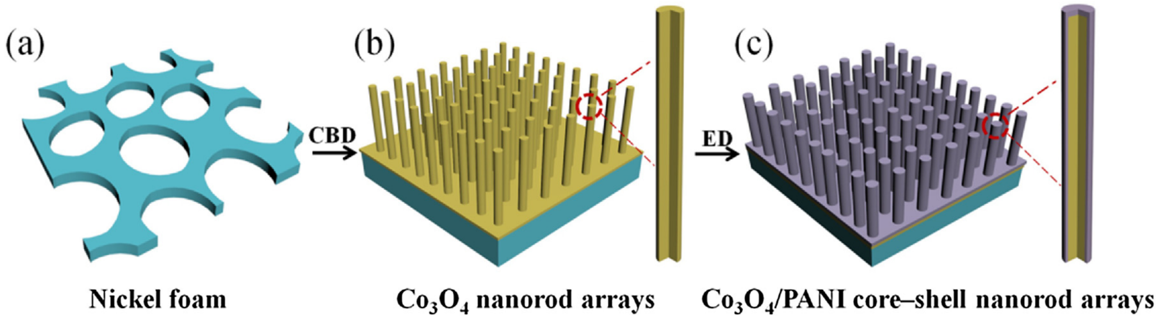

Fig. 1. Fabrication process of Co_3O_4/PANI core–shell nanorod arrays on nickel foam.