Coaxial Co₃O₄@polypyrrole core-shell nanowire arrays for high performance lithium ion batteries

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ABSTRACT

Coaxial Co₃O₄@polypyrrole (Co₃O₄@PPy) nanowire arrays have been successfully synthesized via a simple hydrothermal method and further a polymerization process. According to the composition and morphology characterization, it is found that a thin layer of amorphous PPy is uniformly coated on the surface of the Co₃O₄ nanowire. When directly used as an anode material for lithium-ion batteries, the Co₃O₄@PPy nanowire arrays exhibit high reversible capacity, good rate capability, and improved cycling stability. A reversible capacity of 700 mAh g⁻¹ is sustained at the current of 3 A g⁻¹ after 500 cycles, showing better cycling stability than the bare Co₃O₄ nanowire arrays (only 150 mAh g⁻¹ at the current of 3 A g⁻¹ after 100 cycles). Even at a high current of 20 A g⁻¹, the Co₃O₄@PPy nanowire arrays can still maintain a capacity of 470 mAh g⁻¹, which is much higher than that of the bare Co₃O₄ nanowire arrays (158 mAh g⁻¹). The synergetic effect of the arrays structure and the PPy buffer layer contributes to the enhanced electrochemical performance of the Co₃O₄@PPy nanoarrays. As a result, the introduction of conductive polymer coating layer is an effective strategy to enhance the electrochemical performance of nanoarrays structure for advanced energy storage.

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1. Introduction

Driving by the urgent desire to alleviate environmental pollution, great research efforts have been devoted to develop clear and renewable energy sources, such as wind, tide, and solar energy. Therefore, efficient energy storage devices especially lithium-ion batteries (LIBs) have attracted a lot of researchers attention [1–3]. However, as a commercial anode material, graphite is limited by low theoretical capacity (372 mAh g⁻¹, LiC₆). To meet the ever-growing demand for high energy LIBs, anode materials with high capacity, rate capability and cycling stability are required.

Transition metal oxides (Co₃O₄ [4,5], Fe₂O₄ [6], NiO [7], MnO [8], SnO₂ [9], etc.) have attracted much attentions due to their high capacities (two or three times higher than that of graphite) [10]. Among them, Co₃O₄ with the theoretical capacity of 890 mAh g⁻¹ has been considered as one of the most promising candidates [11]. However, due to the poor electrical conductivity and volume changes during cycling, the Co₃O₄ anode usually suffers from poor rate capability and rapid capacity fading, resulting in unsatisfactory cycling performance [12–14]. To solve these problems, tailoring Co₃O₄ material into nanoscale is a popular approach to shorten both the electron and Li⁺ diffusion pathways [15]. Up to now, various Co₃O₄ nanostructures such as nanorod [16], nanotube [17], nanobelt [18], nanocage [19], and nanofiber [20] have been reported as anode materials for LIBs. It has been demonstrated that the nanostructured Co₃O₄ electrode can significantly improve the electrochemical performance. But traditional electrode preparation is usually accompanied by the use of insulating organic binders, which might suppress the electron and ion transportation, affecting the electrochemical performance at high current density [21]. Hence, for the purpose of practical application, rational structure design of Co₃O₄ nanomaterials is essential.

Recently, designing nanoarray structure without the use of binder has been regarded as an effective strategy to improve the cycle stability and rate performance of anode materials [22–27]. Nanoarray materials have been grown directly on the current collector, which reduces the resistance of the integral electrode.

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Moreover, the abundant inner space of the array structure can provide large contact area with electrolyte to improve the accessibility of Li ion and accommodate the volume changes during cycling. Based on this idea, the grass-like Co3O4 nanowire arrays have been synthesized in our previous works, showing excellent electrochemical performance [28]. Notably, due to the poor conductivity of Co3O4, the rate performance of as-prepared grass-like Co3O4 nanowire arrays at ultrahigh current density (≥ 5 A g⁻¹) was still unsatisfactory. On the other hand, the introduction of conductive coating layer on the surface of anode materials has been proved as another effective strategy to improve cycle performance and rate capability of transition metal oxides [34,35]. The coating layer must have good electronic conductivity and stable structure during Li⁺ extraction and insertion. Polypyrrole (PPy), a conducting polymer with high electrical conductivity (10–100 S cm⁻¹), has been considered as an effective coating layer to improve the electrochemical performance[36,37]. SnO2–PPy [35], CuO–PPy [38], and CoCO₃–PPy [39] composites have been investigated with improved cycle stability and rate capability. In those core-shell structure, the PPy coating layer not only acts as a conductive agent to reduce the charge transfer resistance, but also serves as a protective layer to relieve the structure destruction caused by volume changes during cycling, which finally improves the battery performance of anode materials. Therefore, there is reason to believe that the introduction of PPy into the grass-like Co3O4 array can improve the electrical conductivity of Co3O4 nanowire and enhance the structure stability of the Co3O4 arrays during cycling.

In this work, Co3O4@PPy core-shell nanowire arrays (NWAs) are synthesized by a two-step solution method with the assistance of hydrothermal method and oxidative cationic polymerization process (Fig. 1). In such unique architecture, a high stable structure with high electronic conductivity is constructed, which is beneficial to the electrochemical performance. The Co3O4@PPy NWAs electrode as an anode material exhibits many merits. Firstly, the hybrid NWAs electrode remains the advantages deriving from array structure, which includes reduced charge transfer resistance, improved Li ion accessibility, and stable structure during cycling. Secondly, the outside conductive PPy layer can increase the conductivity of Co3O4 nanowire and serve as a buffer to accommodate the volume change during lithium insertion/extraction. Based on above merits, the as-prepared Co3O4@PPy NWAs achieve high reversibly capacity and good cycle stability at high current density.

2. Experiment

2.1. Synthesis of Co3O4 nanowire arrays on Ti foil

Grass-like Co3O4 nanowire arrays were directly grown on Ti foil via a simple hydrothermal method. In detail, 1 mmol Co(NO₃)₂, 2 mmol NH₄F, and 5 mmol urea were dissolved in 70 mL deionized water. The homogeneous solution was then transferred into a 100 mL Teflon-lined stainless steel autoclave, and a piece of Ti foil (1 × 1 cm²) was immersed in it. The autoclave was maintained at 110 °C for 5 h in an electron oven. The precursor was annealed at 350 °C for 2 h to obtain Co3O4 nanowire arrays.

2.2. Synthesis of polypyrrole coated Co3O4 nanowire arrays

The polypyrrole was self-assembled on the surface of Co3O4 nanowire arrays by an oxidative cationic polymerization process. In a typical procedure, 0.208 g p-toluenesulfonic acid (p-TSA) was dissolved in 30 mL anhydrous alcohol. After vigorous stirring for 5 min, 0.05 mL pyrrole monomer was added into the above solution (solution A). In the meantime, 0.06 g ammonium persulfate (APS) was dissolved in 20 mL deionized water (solution B). Subsequently, 50 μL solution A was dropped into a piece of Co3O4 nanowire arrays on Ti foil (1 × 1 cm²). After 1 minute, 50 μL solution B was dropped into the same sample. The polymerization was conducted in the dark for 7 h, and repeating above polymerization operation for one more time. Afterwards, the sample was rinsed with ethanol and deionized water for several times, and then dried at 60 °C for 24 h under vacuum, which was named as Co3O4@PPy. For comparison, the Co3O4@PPy hybrid composites with different PPy coating thickness were also synthesized through changing the polymerization times. The Co3O4 NWAs with one and three polymerization times were donated as Co3O4@PPy-1 and Co3O4@PPy-3, respectively. Pure PPy was prepared by mixing equal volume of solution A and solution B, and then stirred for 7 h in dark. The product was washed with ethanol and water, dried at 60 °C for 24 h under vacuum.

2.3. Materials characterizations

The chemical composition of the products was characterized by X-ray diffraction (XRD, Bruker D8 Advance X-ray diffractometer, Cu Kα radiation) and Fourier transform infrared spectra (FT-IR, LabRAM Aramis). The X-ray photoelectron spectroscopy (XPS) analysis was performed on an ESCALAB 250 X-ray photoelectron spectrometer using a Al Kα X-ray source. All XPS spectra were calibrated with the C 1s peak at 284.6 eV. The detail content of PPy in Co3O4@PPy was determined by thermogravimetric analysis (TG, NETZSCH STA449C) with the heating rate of 5 °C min⁻¹ under an air atmosphere. The structure and morphology were characterized by scanning electron microscopy (SEM, Merlin, 5 kV) and transmission electron microscopy (TEM, JEM-2100F, 200 kV).

2.4. Electrochemical measurements

The electrochemical performances of Co3O4@PPy NWAs were measured using half coin cells (CR2025). Co3O4@PPy NWAs on Ti
foil was directly used as a working electrode without addition of any binder and carbon black. Pure Li foil was used as the counter electrode. Whatman GF/B glass fiber membrane was used as the separator. The electrolyte consisted of a solution of 1 mol L\(^{-1}\) LiPF\(_6\) in ethylene carbonate (EC)/diethylcarbonate (DEC) (1:1 by volume). The coin cells were assembled in an argon-filled glove box (Mikrouna, super 1220) where the oxygen and moisture contents are less than 1 ppm. Galvanostatic charge-discharge cycles were tested using a Battery Testing System (Neware Electronic Co., China) between 0.01-3.0 V. Cyclic voltammetry
(CV) measurements were carried out on an electrochemical workstation (CHI604D, Shanghai Chenhua Co., China) over the potential range of 0.01-3.0 V vs. Li/Li’ at a scanning rate of 0.2 mV s⁻¹. The impedances of the batteries were measured on the Zahner IM6ex electrochemical workstation. The frequency range was set from 0.01 Hz to 1 MHz with the potential amplitude of 5 mV. The specific capacity of the Co₃O₄@PPy NWAs was calculated based on the total weight of Co₃O₄ and PPy.

3. Results and discussion

The phase and composition of the Co₃O₄@PPy core-shell nanowire were determined by XRD in Fig. 2a. For pure PPy, a broad diffraction peak appears at around 25°, indicating that PPy exists in amorphous form. For the Co₃O₄ NWAs, all the diffraction peaks are well indexed to cubic Co₃O₄ phase (JCPDS 74-2120). After coating with PPy, the diffraction peaks of the Co₃O₄@PPy NWAs are similar to the Co₃O₄, which indicates the PPy coating process did not affect the crystal structure of the Co₃O₄. However, PPy cannot be detected in the XRD pattern due to the low content in the Co₃O₄@PPy NWAs and the amorphous form.

In order to identify the existence of PPy in the Co₃O₄@PPy NWAs, FT-IR spectra were recorded and shown in Fig. 2b. In the spectrum of the Co₃O₄, the peaks at about 562 and 662 cm⁻¹ are characteristic of the spinel Co₃O₄, the peaks at around 1630 and 3399 cm⁻¹ belong to the vibrational mode of absorbed H₂O [40]. In the spectrum of the Co₃O₄@PPy, except for characteristic peaks of the Co₃O₄, there are several typical peaks corresponding with pure PPy: the peaks located at 1050 can be ascribed to C-H deformation vibration [41]. The peak centered at 1198 cm⁻¹ is contributed to the N–C stretching vibration and bands at 809 and 936 cm⁻¹ verify the presence of polymerized pyrrole [42]. Moreover, the peak at about 1692 cm⁻¹ is assigned to the C–O stretching vibrations of doped PPy [43]. According to the FT-IR results, the presence of PPy in the as-prepared Co₃O₄@PPy NWAs is verified.

Furthermore, the surface chemical compositions of the Co₃O₄@PPy NWAs were analyzed by XPS, as shown in Fig. 3. A full survey scan spectrum in Fig. 3a indicates the presence of Co, O, C and N element at the surface of the Co₃O₄@PPy NWAs. For the Co 2p XPS spectrum in Fig. 3b, two peaks at 780.1 and 795.5 eV are

![Fig. 4. TG curves of pure PPy, the Co₃O₄ NWAs and the Co₃O₄@PPy NWAs.](image)

![Fig. 5. SEM images of the bare Co₃O₄ NWAs viewed from the top view (a, b) and the cross-section view (c). SEM images of the Co₃O₄@PPy NWAs from the top view (d, e) and the cross-section view (f).](image)
observed, corresponding to Co 2p\(3/2\) and Co 2p\(1/2\), respectively [44]. After deconvolution of Co 2p\(3/2\) branch, two peaks at 779.9 and 781.5 eV are obtained, which belongs to Co\(^{3+}\) and Co\(^{2+}\), respectively [45]. The O 1s in Fig. 3c can be fitted into two peaks: one at 530.1 eV is well matched with lattice oxygen in the Co\(_3\)O\(_4\) and the other at 532.7 eV is related to the H-O bonds of the surface hydroxyl groups [46,47]. The N 1s spectrum in Fig. 3d shows that the N 1s peak can be decomposed into two peaks. The peak located at 399.9 eV is attributed to positively charged amine nitrogen in polypyrrole (N\(^+\)), and the peak at 401.7 eV can be assigned to neutral amine nitrogen in the pyrrole ring (N-N) [48].

The accurate amount of PPy in the Co\(_3\)O\(_4\)@PPy composite was estimated by TG analysis and the result are shown in Fig. 4. For the Co\(_3\)O\(_4\) NWAs, there is no weight loss except for the removal of moisture in the Co\(_3\)O\(_4\). While for Co\(_3\)O\(_4\)@PPy, the weight loss (7%) below 120 °C is attributed to the dehydration of the adsorbed water or moisture, the weight loss (15%) between 120 °C and 450 °C is associated to the decomposition of PPy. So the weight content of PPy in the Co\(_3\)O\(_4\)@PPy is calculated to be about 15%.

The morphological characteristics of the Co\(_3\)O\(_4\) and the Co\(_3\)O\(_4\)@PPy NWAs were observed by SEM, as shown in Fig. 5. Fig. 5a clearly indicates that the Co\(_3\)O\(_4\) NWAs completely cover the Ti foil. The diameter of each nanowire is about 100 nm and the length is about 5 \(\mu\)m, the surface of each nanowire is smooth (Fig. 5b). From the cross section view in Fig. 5c, the Co\(_3\)O\(_4\) NWAs show a robust adhesion on Ti foil. After polymerization, the Co\(_3\)O\(_4\)@PPy NWAs keep the array structure with enough space between nanowires (Fig. 5d), implying that no structure change appears during PPy coating. In an enlarged image as shown in Fig. 5e, it is clear that the surface of nanowires becomes rough and the diameter of nanowires increases to 150–200 nm, indicating the uniform coating of PPy. From the cross-section view, it can be seen that the Co\(_3\)O\(_4\)@PPy NWAs still keep good contact with the Ti foil which ensures the good electrical contact of the electrode.

TEM was performed to further characterize the morphology and core-shell structure of the Co\(_3\)O\(_4\)@PPy NWAs, as shown in Fig. 6. The low-magnification TEM image in Fig. 6a shows that the diameter of the Co\(_3\)O\(_4\)@PPy nanowire is about 200 nm. From the enlarged TEM images in Fig. 6b and Fig. 6c, it can be found that the Co\(_3\)O\(_4\) nanowire is wrapped by a thin layer of amorphous PPy, the thickness of PPy is about 10 nm. The HR-TEM image in Fig. 6d displays clear lattice fringes with an interplanar spacing of 0.28 nm corresponds to the (220) crystal plane of cubic Co\(_3\)O\(_4\).

To evaluate the role of PPy in the as-obtained Co\(_3\)O\(_4\)@PPy NWAs, Co\(_3\)O\(_4\) and Co\(_3\)O\(_4\)@PPy NWAs are investigated as anode materials for LIBs. Fig. 7a shows the CV curve of the Co\(_3\)O\(_4\)@PPy NWAs in the potential range of 0.01-3.0 V at the scanning rate of 0.2 mV s\(^{-1}\). One cathodic peak at 0.78 V in the first cathodic scan, which is attributed to the formation of a solid electrolyte interface (SEI) film and the reduction of Co\(_3\)O\(_4\) to Co [16]. Two anodic peaks located at

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Fig. 6. (a) Low-magnification TEM image of a single Co\(_3\)O\(_4\)@PPy nanowire. (b–c) Enlarged TEM images of the Co\(_3\)O\(_4\)@PPy nanowire. (d) HRTEM image of the Co\(_3\)O\(_4\)@PPy nanowire.
1.47 and 2.10 V are observed, the peak at 1.47 V can be assigned to the partial decomposition of the SEI layer, the peak at 2.10 V corresponds to the oxidation of metal Co to Co$_3$O$_4$ [49]. In subsequent cycles, two cathodic peaks at 0.94 and 1.13 V can be clearly observed, which can be regarded as the reduction of Co$_3$O$_4$ to Co. The overlapping CV curves after the first cycle exhibit good electrochemical reversibility. The CV curves of bare Co$_3$O$_4$ NWAs and pure PPy are shown in Fig. 7b. For pure PPy, only one weak cathodic peak at 0.5 V can be observed in the first cycle, which is in accord with the result in Fig. 7a. By comparing with the curves of the Co$_3$O$_4$ NWAs, no peak belong to PPy can be observed in the CV curves of the Co$_3$O$_4$@PPy NWAs in the second and third cycles.

The charge and discharge curves of the Co$_3$O$_4$@PPy NWAs at 0.2 A g$^{-1}$ for the first four cycles are shown in Fig. 7c. In the first cycle, a voltage platform at about 1 V is observed, which is consistent with the above CV measurement. The initial discharge and charge capacities of the Co$_3$O$_4$@PPy NWAs are 1293 and 927 mAh g$^{-1}$, respectively. The capacity loss (28.3%) in the first cycle is likely to be attributed to the electrolyte decomposition and SEI formation [20]. The charge-discharge curve from the 2nd cycle shows good reproducibility, indicating the excellent cycle stability of the Co$_3$O$_4$@PPy NWAs.

Fig. 7d shows the rate capabilities of the Co$_3$O$_4$@PPy and the Co$_3$O$_4$ NWAs electrode from 0.2 A g$^{-1}$ to 20 A g$^{-1}$. The specific capacities of the Co$_3$O$_4$@PPy NWAs at the rate of 2, 5, and 10 A g$^{-1}$ are 790, 682, and 582 mAh g$^{-1}$, respectively. Even at the high rate of 20 A g$^{-1}$, the Co$_3$O$_4$@PPy NWAs electrode still delivers a capacity of 470 mAh g$^{-1}$. For comparison, the specific capacities of the Co$_3$O$_4$ NWAs at 5, 10, and 20 A g$^{-1}$ are 535, 320, and 158 mAh g$^{-1}$, respectively, which are lower than those of the Co$_3$O$_4$@PPy NWAs at the same rate. The cycle performances of the Co$_3$O$_4$@PPy and the Co$_3$O$_4$ NWAs at 3 A g$^{-1}$ are shown in Fig. 7e. Obviously, the Co$_3$O$_4$@PPy NWAs exhibit much better cycle stability compared to bare Co$_3$O$_4$ NWAs. After 500 cycles, the Co$_3$O$_4$@PPy NWAs can still maintain a high capacity of 700 mAh g$^{-1}$ without any capacity fading. For the Co$_3$O$_4$ NWAs, a low capacity of 153 mAh g$^{-1}$ is obtained only after 100 cycles, displaying a poor cycle stability. Such distinct differences of rate and cycle performance are related to the conductivity of the Co$_3$O$_4$@PPy coating layer. In the Co$_3$O$_4$@PPy core-shell structure, PPy coating layer not only offers a pathway to accelerate electron transfer which is beneficial to the rate capability of the electrode, but also acts as a cushion to protect the array structure from disintegration caused by large volume change, ensuring the cycling stability of the Co$_3$O$_4$@PPy NWAs. While in the bare Co$_3$O$_4$ NWAs, electron cannot be transferred timely to the current collector, the Co$_3$O$_4$ nanowire is easy to pulverize and fall off from the current collector at ultra-high current density, resulting in an unsatisfactory rate capability and cycling stability.

To prove the improved conductivity derived from the conductive PPy coating layer, electrochemical impedance spectroscopy (EIS) of the Co$_3$O$_4$@PPy and the Co$_3$O$_4$ NWAs electrodes were performed at the full charge state. Before the EIS testing, the batteries were cycled for three cycles to obtain the stable SEI layer. Both Nyquist plots contain a semicircle in the high frequency region and a sloped line in the low frequency region (Fig. 7f). The impedance data were fitted using an equivalent electrical circuit, where $R_s$ is the total resistance of the electrochemical system, $R_{ct}$ is the charge transfer resistance, $W_0$ is the Warburg impedance, and $CPE$ is the constant phase element which involves the double layer capacitance [50]. After fitting, it is clear that the charge transfer resistance ($R_{ct}$) of the Co$_3$O$_4$@PPy NWAs is 28 $\Omega$, which is much lower than that of the Co$_3$O$_4$ NWAs (201 $\Omega$). The EIS results suggest that the PPy layer can offer a fast charge transfer channel and effectively improve the conductivity of the array electrode.

To consider the thickness effect of the PPy layer, we have also synthesized the arrays with 1 and 3 polymerization times which are corresponding to different thickness of PPy layers compared with Co$_3$O$_4$@PPy, and tested their electrochemical performances.
For comparison (Fig. 8). When the arrays with only one polymerization time (Co₃O₄@PPy-1), the Co₃O₄ nanowires cannot be entirely coated by PPy (Fig. 8a), and a sharp capacity fading can be observed which might attribute to the destruction of the array structure during cycling. When the polymerization times is increased to three times (Co₃O₄@PPy-3), the thickness of the coating PPy is about 20 nm (Fig. 8b), and the sample showed excellent cycling stability. However, due to the specific capacity is calculated based on the whole arrays, too many inactive PPy in the arrays lower the specific capacity. The Co₃O₄@PPy-3 NWAs only displays a capacity of 620 mAh g⁻¹ after 500 cycles. As a result, the PPy coating layer with moderate thickness on the Co₃O₄ nanowire beneficial for the electrochemical performance of Co₃O₄ nanowire arrays.

To further certify the contribution of PPy coating to the structure stability, the morphology of the spent Co₃O₄@PPy and Co₃O₄ NWAs was investigated by SEM. Fig. 9 shows the SEM images of the Co₃O₄ and Co₃O₄@PPy NWAs after 100 cycles at 3 A g⁻¹. Visible cracks can be observed on the Co₃O₄ NWAs electrode, suggesting serious structure degeneration caused by volume change during charge-discharge cycling. On the other hand, no crack can be observed on the Co₃O₄@PPy NWAs electrode after 100 cycles, showing good structure stability. The results indicate the PPy coating can effectively alleviate the volume expansion of the Co₃O₄ nanowire and ensure the integrity of the electrode. As known, high conductivity and structural stability are critical characteristics of anode materials for LIBs, thus the introduction of PPy layer is a significant strategy to improve battery performance of the Co₃O₄ arrays.

4. Conclusion

In summary, the novel Co₃O₄@PPy NWAs hybrid composites were successfully synthesized. The thin PPy coating layer on the
CoO\textsubscript{2} nanowires not only improves the intrinsic conductivity of the CoO\textsubscript{2} arrays, but also acts as a buffer layer to relief the strain induced by volume change during cycling. The CoO\textsubscript{2}/PPy NWAs electrode exhibits remarkable improved cycle performance and outstanding rate capability compared with the bare CoO\textsubscript{2} nanowires arrays. These outstanding properties suggest the promising application of the CoO\textsubscript{2}/PPy NWAs anode material in next-generation high-energy LIBs.

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