Ultrasmall MnO Nanoparticles Supported on Nitrogen-Doped Carbon Nanotubes as Efficient Anode Materials for Sodium Ion Batteries

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Supporting Information

ABSTRACT: Sodium ion batteries (SIBs) have attracted increasing attentions as promising alternatives to lithium ion batteries (LIBs). Herein, we design and synthesize ultrasmall MnO nanoparticles (~4 nm) supported on nitrogen-doped carbon nanotubes (NDCT@MnO) as promising anode materials of SIBs. It is revealed that the carbonization temperature can greatly influence the structural features and thus the Na-storage behavior of the NDCT@MnO nanocomposites. The synergetic interaction between MnO and NDCT in the NDCT@MnO nanocomposites provides high rate capability and long-term cycling life due to high surface area, electrical conductivity, enhanced diffusion rate of Na+ ions, and prevented agglomeration and high stability of MnO nanoparticles. The resulting SIBs provide a high reversible specific capacity of 709 mAh g\(^{-1}\) at a current density of 0.1 A g\(^{-1}\) and a high capacity of 536 mAh g\(^{-1}\) almost without loss after 250 cycles at 0.2 A g\(^{-1}\). Even at a high current density of 5 A g\(^{-1}\), a capacity of 273 mAh g\(^{-1}\) can be maintained after 3000 cycles.

KEYWORDS: Sodium ion battery, anode, electrode reactions, MnO nanoparticle, nitrogen-doped carbon nanotube

1. INTRODUCTION

Sodium ion batteries (SIBs) have attracted great attentions as a promising alternative to lithium-ion batteries (LIBs) due to the abundance and low cost of sodium resources.\(^4\) However, further development of SIBs relies on great improvement of the electrode materials, as current electrode materials suffer from unstable rate capability, short cycle life, and large volume change during cycling in view of the larger ionic radius of Na\(^+\) ion as compared to that of Li\(^+\) ion.\(^5\) Consequently, it remains challenging while becomes urgent to prepare high-activity electrode materials with desired excellent electrochemical performances.\(^6\)

Recently, transition metal oxides have received growing attentions due to the increasing demand of green anodes for SIBs.\(^7\) MnO, because of its natural abundance, environmental benignity, low conversion potential, and voltage hysteresis, is promising as electrode materials of LIBs and supercapacitors, as well as attractive electrocatalysts for oxygen reduction reaction (ORR) and oxygen evolution reaction (OER).\(^8\) For example, reduced graphene oxide (RGO)–MnO–RGO sandwich nanostructures prepared through layer-by-layer electrodeposition method showed unprecedented rate capability and outstanding cyclic stability as anodes for LIBs.\(^9\)

Impregnation of MnO@N-doped carbon nanoparticles into a conductive graphene matrix presented high electrochemical performance for both LIBs and ORR.\(^10\) In addition, other MnO-based materials have also been prepared in recent years, such as three-dimensional arrays of MnO in carbon nanosheets,\(^11\) carbon-anchored MnO nanosheets,\(^12\) and MnO/carbon hybrid materials.\(^13\) However, little attention has been paid to the Na-storage behavior of MnO-related materials. What’s more, the electrochemical performances of MnO are currently impeded by the inherent poor electrical conductivity and rigorous volume change during the charge/discharge process.\(^14\)

To date, one of the effective strategies to overcome the above bottlenecks is to construct nanocomposites through combining MnO nanoparticles within conductive scaffolds such as N-doped carbon materials, since the N-doped carbon materials possess the capability of accelerating electron transport, increasing the binding sites, and improving Na\(^+\) ion adsorbability in the charging process due to the presence of...
N element. Along with the intensive studies, N-doped carbon materials derived from conjugated polymers, especially polyaniline (PANI), are regarded as new but significant members with promising applications in energy devices. The key point of choosing PANI as precursor is that through high-temperature treatment, the pivotal N element in its backbones can not only be introduced into the carbon framework at a relatively high content, but also stay stable under harsh working conditions. Furthermore, using conjugated polymers as carbon precursors can lead to homogeneous distribution of nitrogen sites. Meanwhile, one-dimensional N-doped carbon nanotubes (NDCT) with higher surface area and expanded interlayer distance can offer more active sites and short transport pathway for both electrons and Na+ ions.

In this work, we designed and synthesized ultrasmall MnO nanoparticles (~4 nm) homogeneously distributed on N-doped carbon nanotubes (NDCT@MnO) as anode materials for high-performance SIBs. NDCT@MnO nanocomposites were converted from pyrolysis of hydrothermally prepared Mn3O4 nanosheets on PANI nanotubes in N2 atmosphere. Such NDCT@MnO nanocomposites, with a synergistic effect from each component, displayed many advantages including high surface area, increased diffusion rate of Na+ ions, enhanced electrical conductivity and high stability of the MnO nanoparticles. As anode materials in SIBs, NDCT@MnO-7 (carbonized at 700 °C) displayed high rate capacity (709 and 292 mAh g$^{-1}$ at the current density of 0.1 and 5 A g$^{-1}$, respectively) and superior long-term cycling life (capacity retention of 91% after 3000 cycles at a current density of 5 A g$^{-1}$).

2. EXPERIMENTAL SECTION

Reagents. Aniline monomers were distilled under reduced pressure and blanketed with nitrogen before use. Iron(III) chloride hexahydrate (FeCl3·6H2O), methyl orange (MO), concentrated sulfuric acid (H2SO4), ammonium persulfate (NH4)2S2O8, APS, potassium permanganate (KMnO4) and ethanol were all AR grade (National medicine group chemical reagent Co., LTD) and used as received without further purification. Ultrapure water was used for all experiments.

Preparation of Polyaniine (PANI) Nanotubes. PANI nanotubes were synthesized using a modified self-degraded template method. In a typical procedure, 0.2 mmol MO and 3 mmol FeCl3·6H2O were added to 50 mL ultrapure water under magnetic stirring. To the above mixture, appropriate amount of APS was gradually added after 30 min and kept in ambient condition. After successive addition of 3 mmol aniline and 30 mL 0.5 M H2SO4 aqueous solution, the reaction was allowed to continue for 24 h under magnetic stirring. The resultant product was collected and repeatedly washed with ethanol and water mixture until the filtrate became colorless. At last, the precipitate was dried in a vacuum drier at 60 °C for overnight.

Preparation of NDCT@MnO Nanocomposites. In a typical procedure, 0.2 g PANI nanotubes were dispersed in 70 mL 12 mM PANI nano-tubes were synthesized using a modified self-degraded template method. In a typical procedure, 0.2 mmol MO and 3 mmol FeCl3·6H2O were added to 50 mL ultrapure water under magnetic stirring. To the above mixture, appropriate amount of APS was gradually added after 30 min and kept in ambient condition. After successive addition of 3 mmol aniline and 30 mL 0.5 M H2SO4 aqueous solution, the reaction was allowed to continue for 24 h under magnetic stirring. The resultant product was collected and repeatedly washed with ethanol and water mixture until the filtrate became colorless. At last, the precipitate was dried in a vacuum drier at 60 °C for overnight.

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Conversion into NDCT@MnO Nanocomposites

High-Temperature Carbonization Process for the Preparation of PANI@Mn3O4 Nanocomposites and a Subsequent SIBs, Which Involves a Hydrothermal Procedure of Preparing PANI@Mn3O4 Nanocomposites and a Subsequent High-Temperature Carbonization Process for the Conversion into NDCT@MnO Nanocomposites

Scheme 1. Schematic Illustration of the Synthetic Process of NDCT@MnO Nanocomposites As Anode Materials for SIBs, Which Involves a Hydrothermal Procedure of Preparing PANI@Mn3O4 Nanocomposites and a Subsequent High-Temperature Carbonization Process for the Conversion into NDCT@MnO Nanocomposites

Figure 1. (a) XRD patterns and (b) Raman spectra of the as-prepared PANI@Mn3O4 and NDCT@MnO-7 nanocomposites. (c) Mn 2p and (d) N 1s high-resolution XPS spectra of NDCT@MnO-7 nanocomposites.

0.70 for NDCT@MnO-8, which demonstrates that with increase in carbonization temperature, the graphitization degree of carbon nanotubes gets increased and the amount of defects is decreased.30,44 The other small peak at 646 cm⁻¹ can be assigned to the Mn–O vibration in MnO.45 Here, the MnO content in NDCT@MnO-6, NDCT@MnO-7 and NDCT@MnO-8 nanocomposites was determined to be 33.99, 42.06, and 25.58 wt %, respectively, from the thermogravimetric analysis (SI Figure S2).

To further evaluate the surface area and porosity, N2 adsorption–desorption isotherm measurement was conducted. The absorbed volumes exhibited by PANI@Mn3O4, NDCT, and NDCT@MnO materials are remarkably larger than that of pure MnO nanoparticles with a tiny specific surface area of 7 m² g⁻¹ (SI Figure S1c,d and S3). The N2 adsorption–desorption isotherm of NDCT@MnO exhibits a typical type-IV behavior with a distinct hysteresis loop at relative pressure (P/P0) ranging from 0.45 to 1,35 implying that the NDCT@MnO nanocomposites contain a large number of mesopores (SI Figure S1c and S3a). According to the pore size distribution profile (SI Figure S1d and inset in SI Figure S3a), the pore size is mainly distributed at ~20 nm. From the Brunauer–Emmett–Teller (BET) method, NDCT@MnO-7 nanocomposites possess a relatively high surface area of 234 m² g⁻¹ (SI Figure S4), which however is lower than that of NDCT, possibly due to the filling of ultrasmall MnO nanoparticles into the mesopores of NDCT.17 X-ray photoelectron spectroscopy (XPS) measurement was also performed. Only Mn, O, C, and N elements are observed in the XPS survey spectrum (SI Figure S5a and S6a) with an atomic ratio of Mn:O = 1:1, directly indicating the formation of MnO and successful incorporation of N into carbon framework. The high-resolution XPS spectrum of Mn 2p for NDCT@MnO-7 nanocomposites (Figure 1c) exhibits two characteristic peaks at 641.8 eV (Mn 2p1/2) and 653.8 eV (Mn 2p3/2) with a spin-energy separation of 12.0 eV, which is another proof of the formation of MnO.16

The C 1s XPS spectrum of NDCT@MnO nanocomposites can be successfully transformed into NDCT@MnO by our pyrolysis technique, which is also confirmed by Raman study (Figure 1b and S1b). Minor peaks at 361 and 621 cm⁻¹ observed from PANI@Mn3O4 originate from crystalline Mn3O4,39 and the other Raman bands can be assigned to PANI.40 For NDCT@MnO materials, two emerged broad peaks at 1358 and 1587 cm⁻¹ can be distinguished due to its polymeric nature. After carbonization in N2 atmosphere (Figure 1a and SI Figure S1a), distinct peaks at 34.9, 40.5, 58.7, 70.2, and 73.8° from NDCT@MnO nanocomposites can be well indexed to the (111), (200), (220), (311), and (222) crystal planes of cubic MnO (JCPDS card No. 07-0734),37 where PANI can be barely distinguished by its polymeric nature. After carbonization in N2 atmosphere (Figure 1a and SI Figure S1a), distinct peaks at 34.9, 40.5, 58.7, 70.2, and 73.8° from NDCT@MnO nanocomposites can be well indexed to the (111), (200), (220), (311), and (222) crystal planes of cubic MnO (JCPDS card No. 07-0734),36 where PANI can be barely distinguished by its polymeric nature. After carbonization in N2 atmosphere (Figure 1a and SI Figure S1a), distinct peaks at 34.9, 40.5, 58.7, 70.2, and 73.8° from NDCT@MnO nanocomposites can be well indexed to the (111), (200), (220), (311), and (222) crystal planes of cubic MnO (JCPDS card No. 07-0734),37 where PANI can be barely distinguished by its polymeric nature.

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be deconvoluted into four peaks at 284.7, 285.5, 286.5, and 289.1 eV (SI Figure S5b,c,d), attributed to sp$^2$-C–sp$^2$-C, N–sp$^2$-C, N–sp$^3$-C, and C = O bonds, respectively. 46,47 Similarly, the surface nitrogen functional groups (Figure 1d and SI Figure S6b,c) can be deconvoluted into four bands centered at 398.4, 400.6, 402.0, and 403.2 eV, corresponding to the Pyridinic-N, Pyrrolic-N, Graphitic-N, and Oxidized-N, respectively. 48 Remarkably, with increase in the carbonization temperature, Graphitic-N and Oxidized-N become dominant, accompanied by the reduced content of Pyridinic-N and Pyrrolic-N due to their low thermal stability (SI Figure S6d and Table S1). The presence of N element in carbon nanotubes can enhance the electronic conductivity of the as-prepared nanocomposites. 23 Furthermore, Pyridinic-N and Pyrrolic-N can not only create some defects in carbon nanotubes, but also provide more transport channels and active sites for Na$^+$ ion insertion. 49 Meanwhile, high content of Graphitic-N can also enhance the reactivity, electrical conductivity and the transfer of Na$^+$ ions, which is beneficial to improving the rate capability of the anode materials for SIBs. 50 These can be proved by electrical conductivity and electrochemical impedance spectrum (EIS) studies. Electrical conductivity measurement was conducted by a four-point probe method (SI Table S2). It is found that PANI@MnO$\textsubscript{4}$ has very limited conductivity ($<10^{-6}$ S m$^{-1}$), while NDCT@MnO nanocomposites show greatly improved conductivity (0.20–0.37 S m$^{-1}$). Electrochemical impedance spectra were collected based on the assembled cells (SI Figure S7 and Table S3). According the reported method, 40 the charge transfer resistance ($R_{\text{ct}}$) and diffusion coefficient of Na$^+$ ions ($D_{\text{Na}}$) were calculated. It can be seen that $R_{\text{Na}}$ values of NDCT@MnO nanocomposites are substantially smaller than those of PANI@MnO$\textsubscript{4}$ NDCT, and MnO, while $D_{\text{Na}}$ values of NDCT@MnO nanocomposites are obviously larger. As compared to the individual NDCT and MnO, a synergistic effect between MnO and NDCT can enhance the $D_{\text{Na}}$ by at least 3 orders of magnitude. Here, NDCT@MnO$\textsubscript{7}$ shows the smallest charge transfer resistance and largest diffusion coefficient of Na$^+$ ions. Above results reveal that the electrical conductivity, charge transfer and Na$^+$ diffusion can be highly enhanced in the NDCT@MnO nanocomposites.

The morphology characterization of as-prepared materials was performed by transmission electron microscopy (TEM). The as-prepared PANI samples are nanotubes with roughened surface and an inner diameter of $\sim$70 nm (SI Figure S8). Through the hydrothermal technique, nanosheet-like MnO$\textsubscript{4}$ nanosheets from the decomposition of KMnO$\textsubscript{4}$ are homogeneously anchored to the PANI nanotubes (Figure 2a). A closer look from the high resolution TEM (HRTEM) image (inset in Figure 2a) reveals an interplanar spacing of 0.26 nm, corresponding to the $\{211\}$ planes of Mn$\textsubscript{3}$O$\textsubscript{4}$ crystals. 51 Interestingly, ultrasmall MnO nanoparticles are evolved from MnO$\textsubscript{4}$ nanosheets by the calcination treatment, and the inner diameter of NDCT is shrunk to $\sim$50 nm (Figure 2b and SI Figure S9). Of note is that the MnO nanoparticles are firmly anchored on the NDCT. Figure 2c shows clear lattice fringes of single MnO nanoparticles for NDCT@MnO$\textsubscript{7}$ with interplanar distances of 0.22 nm, attributed to the $\{200\}$ plane of cubic MnO. 52 The average size of the obtained ultrasmall MnO nanoparticles for NDCT@MnO$\textsubscript{7}$ is $\sim$4 nm (SI Figure S8b). However, the size of MnO nanoparticles is obviously larger after calcination at 800 °C than that of NDCT@MnO-6 and NDCT@MnO-7 due to the Ostwald ripening effect (SI Figure S9). 53 Scanning transmission electron microscopy (STEM)
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The cyclic performance of the NDCT@MnO-7 nanocomposites at 0.2 A g\(^{-1}\) shown in Figure 3c displays that CE reaches almost 100\% after 20 cycles, and the reversible capacity retains stable at 536 mAh g\(^{-1}\) without obvious fading after 250 cycles. To further study the long-term cycling performance of the as-fabricated NDCT@MnO-7 nanocomposites, the durability at 5 A g\(^{-1}\) was recorded (Figure 3e). The reversible capacity can reach 301 mAh g\(^{-1}\) and be kept at 273 mAh g\(^{-1}\) (91\% retention) after 3000 cycles with nearly \(\sim\)100\% CE, indicating good cycling stability. Through a careful comparison, the electrochemical Na-storage properties of the NDCT@MnO-7 nanocomposites can outperform most of transition metal oxide anodes for SIBs (SI Table S5).\(^{1,23,54,55,61-69}\)

In order to better understand the electrochemical processes, with NDCT@MnO-7 as a typical sample, the cells were disassembled and characterized by ex situ XRD and HRTEM techniques at selected sodiation (discharge to 0.01 V) and desodiation (charge to 3.0 V) states after the first full process. As shown in Figure 4a, diffraction peaks of MnO are replaced by metallic Mn when the electrode is fully discharged to 0.01 V.\(^{69}\) Na\(_2\)O phase cannot be observed in the XRD pattern by metallic Mn when the electrode is fully discharged to 0.01 V.\(^{69}\) Na\(_2\)O phase cannot be observed in the XRD pattern possibly due to its poor crystallization or limited content.\(^{65}\)

After fully charged to 3.0 V, peaks of MnO reappear, demonstrating the reversal of the discharge process for a return to the initial form of the material. TEM images of the NDCT@MnO-7 display no obvious change in the size and morphology at selected discharge and charge states, confirming the robustness of the MnO nanoparticles supported on NDCT (SI Figure S14). HRTEM images of NDCT@MnO-7 electrodes at the same discharge and charge states were also collected (Figure 4b and 4c). After the discharge process, an observed interplanar spacing of 0.21 nm can be indexed to the (221) planes of Mn (JCPDS card No. 33–0887).\(^{18}\) Notably, the particle size of Mn is similar to that of MnO, indicating that MnO nanoparticles anchored on the carbon framework can effectively mitigate volume change during sodiation. When charged to 3.0 V (Figure 4c), the interplanar spacing of 0.22 nm is consistent with the (200) plane of MnO, an indication of successful reversible conversion from Mn to MnO. These results confirm the proposed electrochemical reactions and significant role of MnO during charge and discharge process using NDCT@MnO-7 as the anode materials for SIBs.

The long-term cycling stability of NDCT@MnO-7 can also be reflected from the structure characterization after charge–discharge tests (SI Figure S15). NDCT@MnO-7 nano-

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**Figure 3.** Na\(^+\) ion storage performance of NDCT@MnO-7 nanocomposites. (a) Cyclic voltammetry curves scanned at a rate of 0.2 mV s\(^{-1}\) in the voltage window of 0.01–3.0 V vs. Na/Na\(^+\). (b) Discharge/charge profiles of NDCT@MnO-7 for the first three cycles at 0.2 A g\(^{-1}\). (c) Cycling performance of NDCT@MnO-7 nanocomposites at 0.2 A g\(^{-1}\). (d) Rate capability in the potential window of 0.01–3.0 V vs. Na/Na\(^+\). (e) Long-term cycling stability of NDCT@MnO-7 nanocomposites at a current density of 5 A g\(^{-1}\).

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**Figure 4.** (a) XRD patterns of the NDCT@MnO-7 electrodes in the states of sodiated (after the 1st discharge) and desodiated (after the 1st charge), HRTEM images of (b) sodiated (after the 1st discharge) electrode and (c) desodiated (after the 1st charge) electrode of NDCT@MnO-7 nanocomposites.
composites are almost unchanged after 3000 cycles at 5 A g\(^{-1}\), where MnO nanoparticles are still homogeneously distributed on NDCT without obvious aggregation. Well-resolved periodic lattice fringes with interplanar spacing of 0.22 nm corresponding to the (200) plane of cubic MnO phase can be clearly observed, an indication that the crystallinity of MnO is also not influenced. We think the defect sites and roughened surface of the NDCT can account for the size and morphology stability of these MnO nanoparticles during the charge–discharge process. Also, from the HR-TEM images shown in Figure 4b and c, the very slight difference in the dominant lattice fringes between MnO and Mn may be another reason for the almost unchanged size and morphology of the MnO nanoparticles. Based on above results, the improved electrochemical performance of NDCT@MnO nanocomposites can be understood from a synergistic effect between MnO nanoparticles and NDCT: NDCT provides nucleation sites for MnO during the synthesis, maintains the stability of the MnO nanoparticles during the charge–discharge process, affords the improved surface area and electrical conductivity, and ultrafine MnO nanoparticles supported on the NDCT can greatly enhance diffusion rate of Na\(^+\) ions and thus the electrochemical performances (rate capability and cycling life) as anode materials for SIBs.

4. CONCLUSIONS

In summary, we demonstrate the promising Na-storage behavior of ultrasmall and stable MnO nanoparticles uniformly supported on N-doped carbon nanotubes (NDCT@MnO). The electrochemical reactions using NDCT@MnO-7 (carbonized at 700 °C in N\(_2\) atmosphere) as anode materials for SIBs have been revealed by ex situ XRD and HRTEM studies at selected sodiation and desodiation states. The as-prepared NDCT@MnO nanocomposites display exceptional rate capability (709 and 292 mAh g\(^{-1}\) at the current density of 0.1 and 5 A g\(^{-1}\), respectively) and ultralong cycling life (capacity retention of 91% after 3000 cycles at a current density of 5 A g\(^{-1}\)). The enhanced rate performances and durable long-term cycling stability of NDCT@MnO-7 nanocomposites can be attributed to the improved surface area, higher diffusion rate of Na\(^+\) ions, and enhanced electrical conductivity due to the distinctive structure and compositional characteristics. This work recognizes MnO as a promising anode material for SIBs, and reveals that distinct structure features of ultrasmall MnO nanoparticles supported on highly conductive N-doped carbon nanotubes are significant for high-performance SIBs.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b09559.

Figure S1–S15, and Table S1–S5 (PDF)

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Notes

The authors declare no competing financial interest.

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Free Electrocatalysts for Oxygen Reduction: Polyaniline-Derived N-Carbon Nanofiber Webs as Anodes for Lithium Ion Batteries with a High Surface Area.


This page contains a collection of research articles focusing on the development and properties of various materials for energy storage applications, primarily lithium and sodium-ion batteries. The articles discuss the synthesis and performance of materials such as graphene, metal-organic frameworks, and nanocomposites. Specific topics include the use of metal-organic frameworks for battery materials, the synthesis of nitrogen-doped graphene, and the incorporation of nanoparticles and hollow structures to enhance battery performance. The research papers span a range of years, indicating ongoing advancements in the field of energy storage technologies.