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Synthesis of Mn_3O_4 Microflowers Anode Material for Lithium-ion Batteries with Enhanced Performance

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Authors' contributions

This work was carried out in collaboration between both authors. Author HLF designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors HLF and CY managed the analyses of the study. Author CY managed the literature searches. Both authors read and approved the final manuscript.

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ABSTRACT

It is important to prepare novel micro-nanostructures of Mn-based oxides for energy storage. In this study, a simple and versatile method for preparation of Mn_3O_4 microflowers associated with super-thin nanosheets has been developed via a solvo-thermal approach in the presence of a surfactant hexadecyl trimethyl ammonium bromide (CTABr). Mn_3O_4 nanoparticles can be selectively prepared without organic solvents and surfactants. When tested as a new high-capacity anode material for lithium-ion batteries, Mn_3O_4 microflowers showed better cycling performance than Mn_3O_4 nanoparticles. The Mn_3O_4 microflowers-based composite electrode delivered a second discharge capacity of 870.2 mA h g^{-1} at a current density of 240 mA g^{-1}. While the Mn_3O_4 nanoparticle- based composite electrode delivered a second discharge capacity of 332.8 mA h g^{-1}. The improved discharge capacity and cycling performance occurred as the Mn_3O_4 microflower did not undergo reduction from Mn(III) to Mn(II) in the discharge process and it also reduced polarisation. Research on this topic mainly shed some light on the preparation of three-dimensional flower-like oxide hierarchical architectures with an improved electrochemical performance for energy storage.

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1. INTRODUCTION

Rechargeable batteries with reversible and efficient electrochemical energy storage and conversion are urgent in various applications, such as portable electronic consumer devices, electric vehicles, and large-scale electricity storage in smart and intelligent grids as renewable and clean energy [1,2]. Lithium-ion battery is one of the fascinating rechargeable batteries for high energy density, coupled with a long life cycle and charge-discharge rate capability [3]. Studies have been conducted to develop low-cost, sustainable, renewable, safe, and high-energy density electrode materials for lithium-ion batteries. Considering environmental safety, researchers should prepare potential electrode materials for lithium-ion batteries through green chemistry based on inexpensive and straightforward procedures.

Manganese-based anode materials are less toxic, abundant in natural resources [4]. Though Mn_3O_4 is isostructural with Co_3O_4, it has poor lithiation activity and electrically insulating, resulting in fast capacity decay as anode materials for lithium-ion batteries. Recently significantprogress has been achieved for Mn_3O_4 anode materials. The improved electrochemical properties turned true via the following methods. Mesoporous carbon, graphene, carbon nanotube and various carbon nanostructures were introduced to prepare carbon based Mn_3O_4 nano-composites. These composites showed better cycling stability and higher discharge capacity than bulk Mn_3O_4 for fast ion diffusion, good electronic conductivity, and skeleton supporting function [5-35]. People also designed various Mn_3O_4 nanostructures to improve the cycling performance of Mn_3O_4. In these Mn_3O_4 nanostructures, well-shaped nanostructure, pore, hollow structure and 3D array played an important role in the long cycling performance. Novel spongelike nanosized Mn_3O_4 exhibits a high initial reversible capacity of 869 mA h g^{-1} and significantly enhanced first coulomb efficiency with a stabilised reversible capacity of around 800 mA h g^{-1} after more than 40 charge/discharge cycles [4]. Mn_3O_4 hollow microspheres demonstrate a good electrochemical performance, with a high reversible capacity of 646.9 mA h g^{-1} after 240 cycles at a current density of 200 mA h g^{-1} [36], while pluorinated Mn_3O_4 nanospheres for lithium-ion batteries show poor cycling performances [37]. 3D porous Mn_3O_4 nanosheet arrays could be directly used as a binder-free and conductive-agent-free electrode to deliver ultrahigh electrochemical performance [38]. It has been reported that the 3D pores and voids between the nanosheet arrays could provide rapid ion transfer channels, as well as accommodating the volumetric changes of Mn_3O_4 during the electrochemical cycling [38]. The ultrathin Mn_3O_4 nanosheets exhibit a high reversible capacity and stronger cycling stability for the high surface area [39]. The well-shaped Mn_3O_4 tetragonal bipyramids with high-energy facets show a high initial discharge capacity. Besides, the anode displays a fast performance and delivers a reversible capacity of 822.3 mA h g^{-1} (the theoretical capacity: 937 mA h g^{-1} at a current density of 0.2 C after 50 cycles [40]. The porous Mn_3O_4 nano rods can improve electrochemical reaction kinetics and favour the formation of Mn_3O_4 [41]. Mn_3O_4 nano-octahedra has a discharge capacity of 667.9 mA h g^{-1} after 1000 cycles at 1.0 A g^{-1} ascribed to the lower charge transfer resistance due to the exposed highly active {011} facets. This can facilitate the conversion reaction of Mn_3O_4 and Li owing to the alternating Mn and O atom layers, resulting in easy formation and decomposition of the amorphous Li_2O and the multi-electron reaction [42]. The hollow Mn_3O_4 spheres deliver a highly stable cycle performance with capacity retention of similar to 980 mA h g^{-1} for over 140 cycles at 200 mA g^{-1} and an excellent rate capability [43]. It can be seen that Mn_3O_4 with nanosheets, pore, high surface area and interconnected voids are suitable to show high discharge capacity and long cycling stability. The 3D Mn_3O_4 microflowers assembling with nanosheets are expected to show favourable electrochemical performances for the presence of voids among the nanosheet arrays. There are few reports on the research of Mn_3O_4 microflowers except Mn_3O_4-Fe_3O_4 and MnO-Mn_3O_4 nanoflowers. Mn_3O_4-Fe_3O_4 nanoflowers are simply fabricated through one step etching $Mn_5Fe_5Al_{90}$ ternary alloy, which exhibits higher performance as anode material for lithium-ion batteries than that of pure Mn_3O_4 and Mn_3O_4 anodes for unique hierarchical flower-like structure and the synergistic effects between Mn_3O_4 and Mn_3O_4 [44]. A hierarchically porous MnO-Mn_3O_4 nano-flowers can be fabricated by dealloying Mn/Al alloys in aqueous NaOH solution in the presence of H_2O_2, and upon annealing, which has a capacity of 1018, 901 and 757 mA h g^{-1} with nearly 100% retention capacity after 100 cycles at 100, 200 and 500 mA g^{-1} [45]. Mn_3O_4 nanosheets associated with nanorods can be assembled to 3D flower-like Mn_3O_4 with hexadecyl trimethyl ammonium bromide (CTABr), urea and $MnSO_4$ as reagents, while they did not test any properties, e.g. batteries [46].

In this study, a simple method was developed to prepare Mn_3O_4 microsflowers associated with nanosheets. These microflowers were synthesised in a N,N-dimethylformamide (DMF)–water solution with the aid of CTABr. When tested as an anode material for lithium-ion batteries, the Mn_3O_4 microflowers exhibited enhanced cycling stability than Mn_3O_4 nanoparticles.

2. MATERIALS AND METHODS

All commercially available chemicals were used for the study. The preparation was performed via a solvothermal method in a DMF-water mixed solvent. In a typical procedure, 1 mmol manganese acetate tetrahydrate and 0.5 g hexadecyl trimethyl ammonium bromide (CTABr) were added to a 5 ml DMF- 25 ml water solution and stirred at room temperature for 2 hours. After that, the mixture was transferred to a 50-ml Teflon-lined stainless autoclave, sealed, kept at 200°C for 24 hours and then cooled to room temperature. It was then washed with absolute alcohol and dried at 70°C for 12 hours (marked with DT-1). Sample DT-2 was prepared without CTABr under the identical condition, while sample DT-3 was prepared with 30 ml water in the absence of CTABr.

The morphological characteristics of the as-synthesised materials were observed with a Hitachi S-4800 field emission scanning electron microscope (SEM). X-ray diffraction (XRD) patterns were recorded on a diffract meter (Co Kα, Analytical, and Pert). Cyclic voltammetry (CV) experiments were performed with a Chi660c electrochemical work station at a scan rate of 1 mV S^{-1}. A Land CT2001A battery tester was used to measure the electrode activities at room temperature.

The as-synthesised samples were tested as anode materials for lithium-ion batteries. The composite of the negative electrode material was consisted of the active material, a conductive material (super-pure carbon) and binder polyvinylidene difluoride (PVDF) in a weight ratio of 7/2/1. The Li metal was used as the counter electrode. The cells were charged and discharged between a 0.05 - 3.0 V voltage limit.

3. RESULTS AND DISCUSSION

Three samples were obtained by adjusting synthesis parameters. Both DMF and CTABr play an important role in the formation of different morphologies. When water was used as the solvent in the absence of CTABr, the sample appeared as monodispersed nanoparticles between 30 and 150 nm in Fig. 1a, b. As shown in Fig. 1c, d, when DMF was added, thin microplatelets were obtained,. The length and width of microplatelets can be up to several µm. There are also some thin nanobelts. Some microflowers composed of superimposed thin and wide nanosheets were prepared with CTABr in the DMF-H_2O mixed solvent in Fig. 1e, f. Certain microflower is several µm in size.

XRD was performed to identify the structure of the three samples. It can be seen that CTABr played an important role in the crystallisation of products. The diffraction peaks of the sample prepared with DMF, water and CTABr had the highest intensity than samples prepared with water, CTABr and DMF (Fig. 2). The diffraction peaks can be ascribed to Mn_3O_4 in Fig. 2a (JCPDS 89-4837). The other samples can also be ascribed to Mn_3O_4 as can be seen in Fig. 2b, c,. All the Mn_3O_4 showed lack of the peak of (101), which means that it was not the high-energy {101} plane.

The electrochemical performance of Mn_3O_4 nanoparticles and microflowers was evaluated as anode materials for lithium-ion batteries (Fig. 3). Fig. 3a shows the 1st and 2nd charge–discharge profiles of Mn_3O_4 microflowers at a current density of 240 mA g^{-1} (Sample T-72). A long discharge platform is observed at 0.5 V in the first discharge curve, but this platform disappears in the succeeding discharge curves. The Mn_3O_4 microflowers-based composite electrode delivers an initial discharge capacity of 1496 mA h g^{-1}. However, the 1st discharge profiles of Mn_3O_4 nanoparticles showed four discharge platforms at 0.33, 0.44, 0.92 and 1.3 V, implying the occurrence of a multi-step conversion reaction. A new platform at 0.7 V appeared in the succeeding discharge curves. The Mn_3O_4 nanoparticles-based composite electrode delivered an initial discharge capacity of 1280 mA h g^{-1}. It can be seen that Mn_3O_4 without high-energy {101} plane can also have a very high initial discharge capacity. It can also be found that Mn_3O_4 nanoparticles have a steeper charge curve than Mn_3O_4 microflowers between 1.4 and 3.0 V implying that a severe polarisation takes place in the Mn_3O_4 nanoparticles-based composite electrode.

Figs. 4 and 5 display the dQ/dV~V curves obtained from the 1st and 2nd charge-discharge curves of Mn_3O_4 nanoparticles and microflowers . In the first charge-discharge cycle of Mn_3O_4 nanoparticles, four reduction peaks are centered at 0.33, 0.45, 0.90 and 1.3 V, and the oxidation peak is at 1.24 V as shown in Fig. 4a. In the first charge-discharge cycle of Mn_3O_4 microflowers, the reduction and oxidation peaks were centered at 0.33 and 1.28 V (Fig. 4b), respectively. In the second charge-discharge cycle of Mn_3O_4 nanoparticles, two reduction peaks were centered at 0.45 and 0.52 V, and the oxidation peak was at 1.24 V (Fig. 5b). In the second charge-discharge cycle of Mn_3O_4 microflowers, the reduction and oxidation peaks were centered at 0.54 and 1.25 V (Fig. 5a), respectively. The reduction peaks in the range of 1.3-0.4 V was ascribed to reduction from Mn(III) to Mn(II), and the 0.4-0.1 V range reflected the reduction from Mn(II) to Mn(0) [47,48]. The difference of first discharge curve between Mn_3O_4 microflowers and nanoparticles is because Mn_3O_4 microflowers only undergoes the reduction from Mn(II) to Mn(0). While Mn_3O_4 nanoparticles undergo reductions from Mn(III) to Mn(II) to Mn(0). In the second discharge, the contribution to discharge capacity is mainly ascribed to the reduction around 0.5 V. The Li+ charge reaction: is Mn_3O_4 + 8Li+ + 8e- to 3Mn(0) + $8Li_2O$ [49]. Compared to Mn_3O_4 nanoparticles, Mn_3O_4 microflowers does not undergo reduction from Mn(III) to Mn(II) and reduce polarisation.

Fig. 6 shows the cycling performance tested at current densities of 240 and 480 mA g^{-1}. The Mn_3O_4 microflowers-based composite electrode delivered a second discharge capacity of 870.2 and 714.8 mA h g^{-1} as shown in Fig. 6a, b, respectively. A reversible capacity of 392.8 and 358.5 mA h g^{-1} was retained after 20 cycles. The Mn_3O_4 nanoparticles-based composite electrode showed lower discharge capacity and worse cycling stability at current densities of 240 and

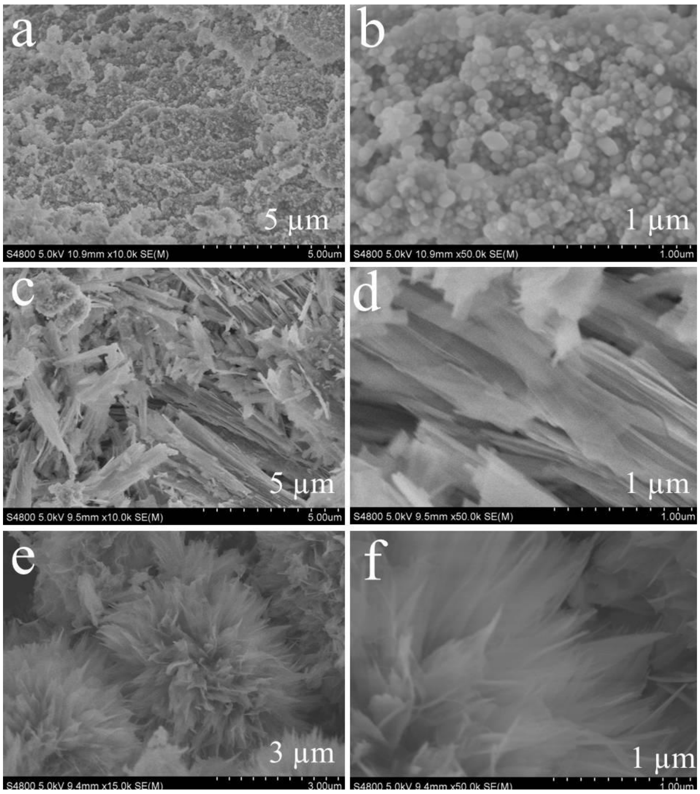

Fig. 1. SEM images of samples with (a, b) water, (c, d) water and DMF, and (e, f) water, DMF and CTABr

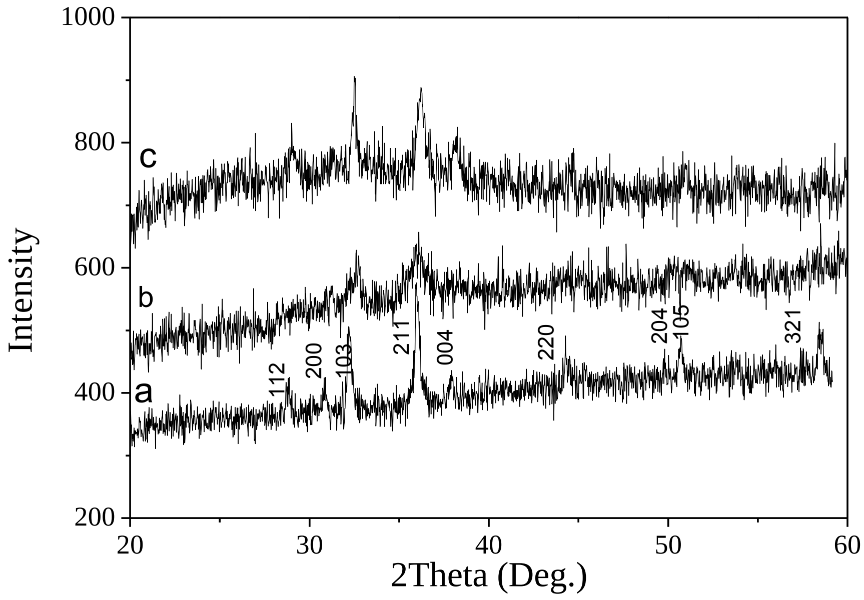

Fig. 2. Wide angle XRD patterns of samples with (a) water, DMF and CTABr, (b) water and DMF, and (c) water

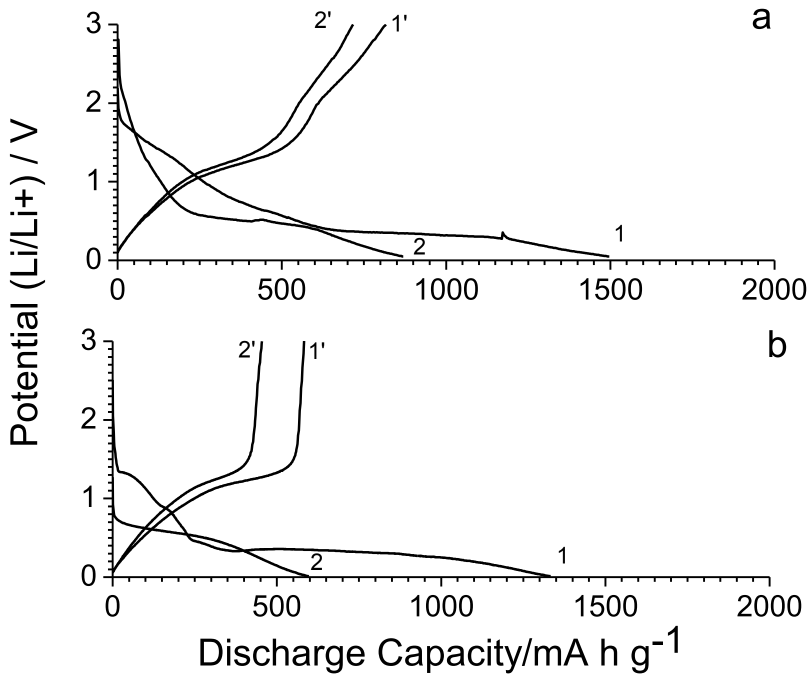

Fig. 3. The first and second charge-discharge profiles at a current density of 240 mA g^{-1} of (a) Mn_3O_4 microflowers and (b) Mn_3O_4 nanoparticles

480 mA g^{-1} as can be seen from Fig. 6c, d. It delivered a second discharge capacity of 332.8 and 156.5 mA h g^{-1}, respectively. The final discharge capacity was even low to 131.3 and 53.8 mA h g^{-1}. The fast capacity decay of Mn_3O_4 nanoparticles is due to the reduction from Mn(III) to Mn(II). The improved electrochemical performance of Mn_3O_4 microflowers is due to the reduced activity of Mn_3O_4, avoiding the complicated reduction from Mn(III) to Mn(II) and reduced polarisation. The present study focused on the research of flower-like rutile TiO_2 and

ammonium vanadium bronze. It was found that the effect of flower-like nanostructures on the reaction kinetics of the electrode are ascribed to the changes the total impedance and electron transfer resistance [50,51]. The improved performance of Mn_3O_4 micro-flowers is also ascribed to improve the transferring of electron.

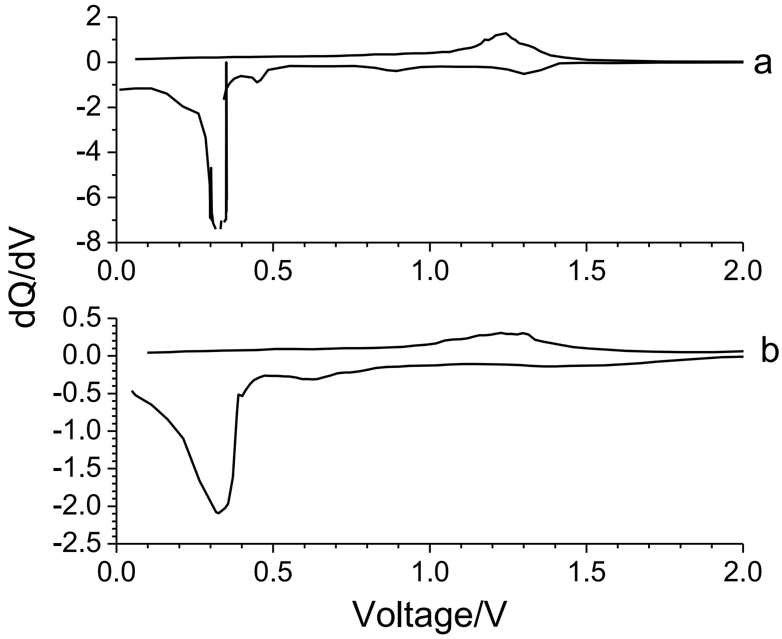

Fig. 4. The dQ/dV~cueve derived the first charge-discharge profiles of (a) Mn_3O_4 nanoparticles (b) Mn_3O_4microflowers

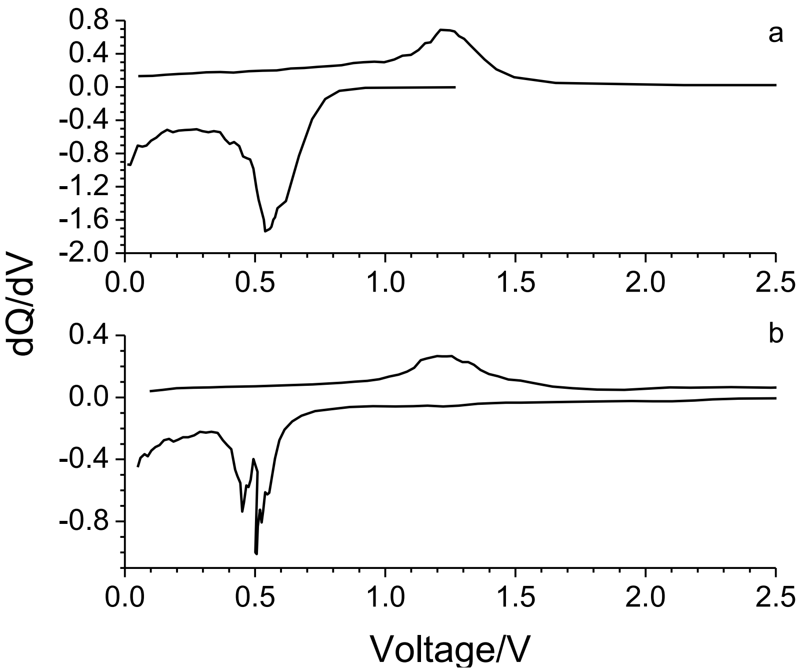

Fig. 5. The dQ/dV~cueve derived the second charge-discharge profiles of (a) Mn_3O_4 microflowers (b) Mn_3O_4 nanoparticles

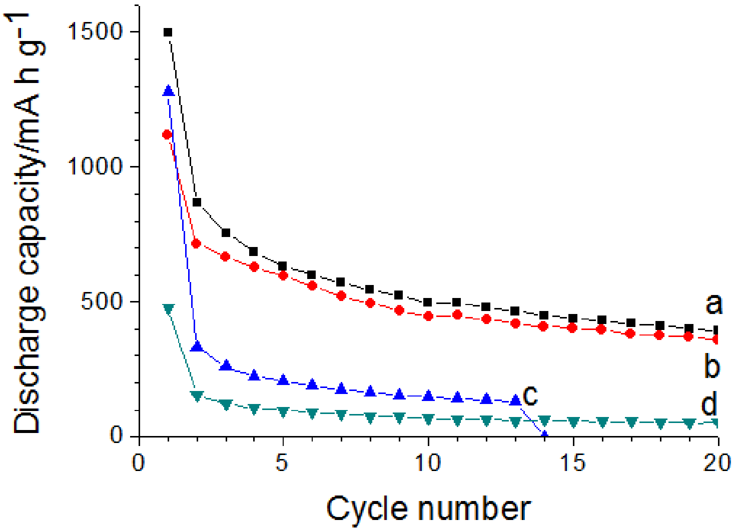

Fig. 6. The cyclic performance tested at current densities of 240 and 480 mA g^{-1} of (a, b) Mn_3O_4 microflowers, and (c, d) Mn_3O_4 nanoparticles

4. CONCLUSION

In summary, the controlled synthesis of Mn_3O_4 microflowers associated with super-thin nanosheets was achieved via using a solvo-thermal method with the aid of surfactant CTABr. The solvent plays an important role in the morphology of Mn_3O_4. Mn_3O_4 nanoparticles were prepared with water as a solvent, while Mn_3O_4 microplatelets were obtained with DMF via affecting nucleation. The surfactant CTABr directed the formation of Mn_3O_4 microflowers from platelet-like precursors. The Mn_3O_4 microflowers exhibited better cycling stability and higher discharge capacity than Mn_3O_4 nanoparticles as anode materials for lithium-ion batteries. It is due to the reduced activity of Mn_3O_4, avoiding the complicated reduction from Mn(III) to Mn(II) and reduced polarisation. It can be said that this simple method may also be used to fabricate other anode materials for lithium-ion batteries with improved electro-chemical performance.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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