Template-free preparation of bunches of aligned manganese oxide nanowires

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Abstract
A simple method based on a conventional solid-state process is proposed for synthesis of manganese oxide nanowires. This method provides an opportunity for bunching the nanowires synthesized, since the nanowires form in one direction. Thus, aligned bunches (e.g. $>100\,\mu$m long and about $50\,\mu$m in diameter) consisting of individual nanowires (diameters ranging between 50 and 200 nm) can be prepared simply. The phenomenon of simultaneous alignment of the nanowires in one direction to form ordered bunches is indeed an interesting development in the realm of nanotechnology. It can be considered as an alternative to conventional template-based methods.

1. Introduction

The fabrication of one-dimensional nanomaterials (such as nanowires, nanotubes, nanofibres, etc) is an active area of research in nanotechnology. However, the task of nanotechnology is not restricted to such syntheses; the main mission is to control the growth of such one-dimensional nanomaterials. Towards this end, the preparation of highly ordered and well-aligned one-dimensional nanomaterials is of particular interest since this provides easier transport processes through nanostructured materials. This action is mainly based on template-based synthesis of one-dimensional nanomaterials. However, this approach is not always applicable due to the difficulties of working with nanostructured templates. In addition, the fabrication of such templates is time-consuming and complicated. Separation of the nanowires synthesized from the base template is not a simple task. Thus, the design of a template-free procedure for the preparation of highly ordered one-dimensional nanomaterials is of great importance for commercial purposes, though it is difficult to achieve.

Here, we report a simple procedure based on a conventional solid-state synthesis leading to the formation of bunches of aligned manganese oxide nanowires. As diffusion of Na ions through the MnO_2 structure leads to the formation of a nanostructured material [1], the application of a high temperature may coordinate the diffusion direction. This is

indeed an extraordinary phenomenon, and generation of such bunches consisting of individual nanowires is even simpler than synthesis of random nanowires.

There are few reports on the synthesis of template-free MnO_2 nanowires [1–4]. Since these procedures are based on hydrothermal routes (i.e. a template-free method), it is improbable that well-aligned nanowires will be produced as the nanowires generated are dispersed through the bulk solution, whereas, the solid-state synthesis proposed in the present report can produce nanowires side-by-side to form a bunch of well-aligned nanowires. This is of particular interest for lithium battery applications, since it has been reported that diffusion of an intercalating ion through a highly ordered nanostructure is more effective than the use of conventional microstructured cathodes, leading to better battery performance [5, 6]. This increases the efficiency of the electrochemical reactions, leading to the attainment of the theoretical capacity of the cathode material [5]. Martin and co-workers [6] have reported better battery performance of nanostructured $LiMn_2O_4$ cathodes prepared using a template-based method upon decreasing the template (pore) size.

2. Experimental

Solid-state synthesis is the most common method widely reported in the literature for preparation of this class of cathode materials (e.g. metal oxides such as manganese oxide) for lithium batteries. To this aim, stoichiometric amounts of the

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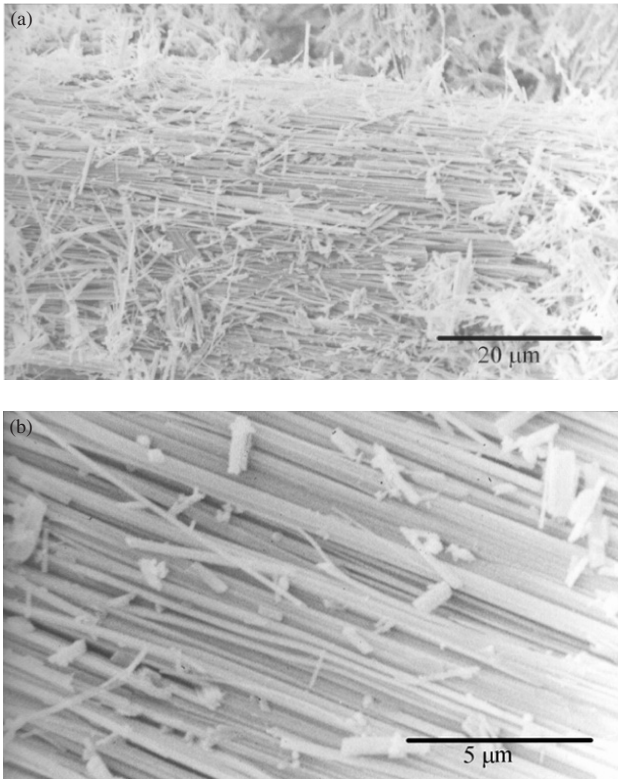[1] Author to whom any correspondence should be addressed.

Figure 1. SEM images of (*a*) a bunch of (Na-intercalated) manganese oxide nanowires formed among randomly generated nanowires and (*b*) a close view of individual nanowires.

reactants, Na_2CO_3 and MnO_2, were mechanically mixed and heated for 5 h at 600˚C, followed by 40 h heating at 800˚C. No special procedure was used to control the heating rate, and the temperature was fixed at the values specified. All thermal treatments were performed in an air atmosphere. In fact, this process is just simple intercalation of Na into MnO_2 to form $Na_{0.5}MnO_2$. Li-intercalated manganese oxide nanowires were prepared by ion-exchanging the Na-intercalated manganese oxide nanowires (i.e. $Na_{0.5}MnO_2$) via a thermal process within a molten salt mixture of $LiNO_3/KNO_3$ (68/32% mol) at 250˚C. A four-fold excess of the Li salt was employed, compared with the amount of the Na-intercalated manganese oxide sample. This process was repeated twice each time with a duration of 6 h. The efficiency of extraction of Na ions from the manganese oxide nanowires was examined by means of EDX in the course of scanning electron microscopy (SEM) investigations.

SEM investigations were carried out using a Cambridge electron microscope, model Steroscan 360. Energy dispersive x-ray (EDX) analysis was performed using a DDAX Leica-exL2. Powder x-ray diffraction (XRD) patterns were recorded using a Philips PW 1371 diffractometer with Cu Kα radiation.

3. Results and discussion

Figure 1 shows SEM images of the (Na-intercalated) MnO_2 nanowires synthesized. It is obvious that the MnO_2 raw material has been successfully transformed to the manganese oxide nanowires, with diameters ranging between 50 and 200 nm. Not only were the nanowires generated, they are also aligned unidirectionally. In other words, some bunches of

nanowires form through individual nanowires settling beside each other in one direction. The sizes of these bunches are significantly large (e.g. >100 μm long and about 50 μm in diameter), and they can be separated easily from the randomly formed nanowires by simple mechanical separation (e.g. sifting or selective separation under microscopic devices). This phenomenon occurs locally as such bunches of aligned nanowires are partly formed among randomly generated nanowires. Thus, this synthesis procedure can be considered as an efficient method for the preparation of bunches of well-aligned MnO_2 nanowires.

According to the model proposed by Wang and Li [1], the space between layers of the MnO_2 structure is spacious enough for diffusion of Na ions (e.g. 7 Å). Thus, this provides an opportunity for the formation of nanowires as a result of longitudinal diffusion of Na ions across the channel. This phenomenon has also been observed in the case of the hydrothermal process [1–4]. However, the case of solid-state synthesis is different from hydrothermal synthesis, in which the nanowires are dispersed in a fluid medium.

It was found that the amount and structure of these nanowires strongly depend on the Na concentration employed for the solid-state synthesis [7]. Although increasing the Na concentration (up to 0.5 in Na_xMnO_2) strengthens the tendency of nanowire formation, no nanowire forms upon a further increase ($x > 0.5$ in Na_xMnO_2). This is exactly what is expected in accordance with the structural change of Na_xMnO_2 due to the concentration of intercalated sodium [8]. In the case under investigation, where x is close to 0.44, it tends to form a double-tunnel compound containing both MnO_6 octahedra and MnO_5 square pyramids [9, 10].

This is an excellent candidate for lithium battery applications, since this double-tunnel compound is stable and does not undergo rearrangement to a spinel, which is a common problem for layered manganese oxide [10]. On the other hand, the best condition for the preparation of manganese oxide nanowires is using $x \approx 0.44$, which is excellent for lithium batteries. In fact, the best Na concentration for efficient synthesis of uniform manganese nanowires is 0.44. In this case, the raw MnO_2 mainly transforms to (Na-intercalated) manganese oxide nanowires, and the sizes of the nanowires synthesized are close (in a narrow range). The double-tunnel structure of Li_xMnO_2 prepared from $Na_{0.44}MnO_2$ has been extensively described in the literature (cf figure 1 of [11]). Doeff *et al* [11] have shown using TEM images that the spacing in this structure is as large as 2.97 Å. This is a suitable tunnel for diffusion of counter-ions as needed for battery performance. Since this structure has been arranged in an orderly fashion in nanowires, Li ions diffuse longitudinal through the nanowires in the course of battery performance.

Figure 2 shows the head of a bunch of manganese oxide nanowires. This indeed confirms that the internal structures of these bunches are similar to those of their crusts as shown in figure 1(*a*). It is indicative of the fact that the nanowires synthesized are placed across the bunches. The cross-section of the bunch shown in figure 2(*b*) displays an important advantage of the method proposed here in comparison with the template-based ones available. It is obvious that the nanowires are closely packed together in this typical bunch. Thus, no empty pores exist within the bunch, as this is an essential
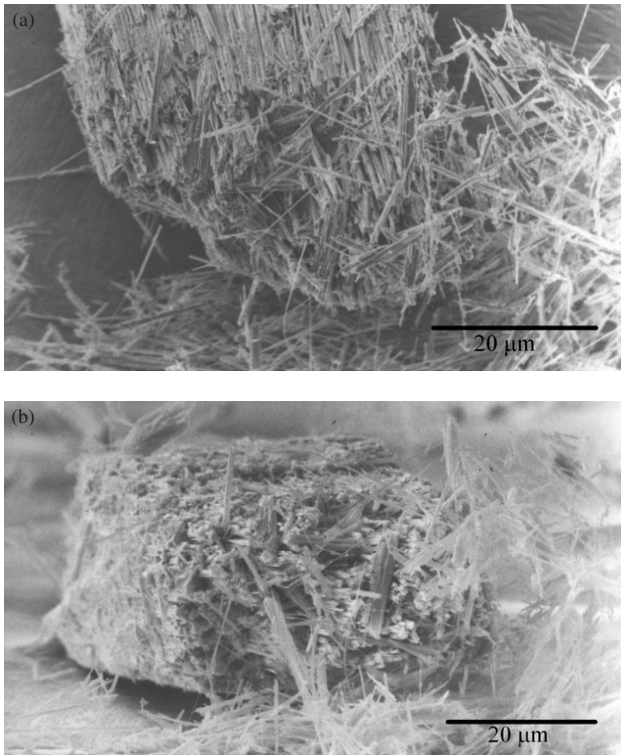
Figure 2. SEM images of (*a*) head of a single bunch formed by close packing of individual (Na-intercalated) manganese oxide nanowires and (*b*) its cross-section.

Figure 3. A typical bunch of (Na-intercalated) manganese oxide nanowires vertically placed focused on (*a*) its whole and (*b*) its head.

consequence of template-based methods (empty spaces created upon template removal). This is very important for the battery industry, as it needs high-density materials to increase battery energy. In other words, such a large porosity of the scale of hundreds of nanometres is not needed for effective diffusion of Li ions in the course of battery performance and is just a waste of volume in a commercial battery.

The close packing of nanowires in a bunch, which is an important feature of this novel method, may cause difficulty in distinguishing individual nanowires. For instance, by looking at the image of an entire bunch (figure 3(*a*)), one may conclude that they are microwires. However, a closer look reveals the existence of nanowires (figure 3(*b*)). Through statistical analysis of the whole sample via numerous SEM images, we found that the nanowires are mainly in the range of 50–200 nm. This feature can also be observed in figure 1(*b*). Although, nanowires as large as 500–700 nm can apparently be detected, lines indicating smaller individual nanowires can be distinguished from a quick look.

The manganese oxide nanowires synthesized by this method are of Na-intercalated MnO_2 (i.e. $Na_{0.5}MnO_2$). This is of particular interest for lithium battery applications, since it is known that the almost ideal layered arrangement of the lithium and manganese ions in $LiMnO_2$ cathode materials is obtained from Li-ion exchange from α-$NaMnO_2$ [12–16]. The intercalated Na ions can be simply extracted via a simple process. Na extraction does not change the structure of the nanowires (as checked by SEM evidence).

Since the Li-intercalated form of manganese oxide nanowires is of particular interest (for lithium battery applications), we investigate it by means of powder XRD. In
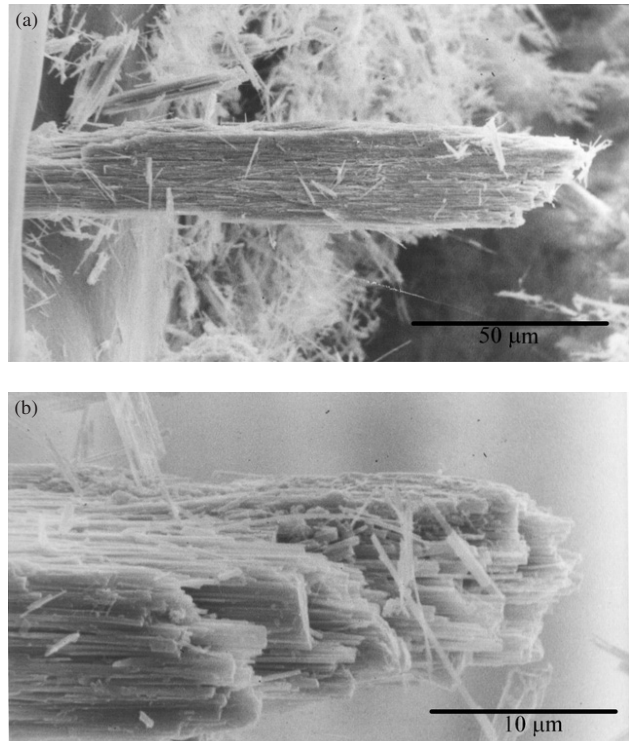
fact, we aim to compare the lattice structure of $Li_{0.5}MnO_2$ cathode materials prepared from Na-intercalated nanowires (as synthesized in the present research) with the conventional $Li_{0.5}MnO_2$ prepared directly by Li incorporation into the MnO_2 lattice. A typical XRD pattern of (Li-intercalated) manganese oxide nanowires is illustrated in figure 4. The XRD pattern is an analogue to orthorhombic $LiMnO_2$ with space group Cmcm. Of course, due to the poor fit obtained without structural constrains, performing exact Rietveld refinement is not possible. Probably, as with the case of $Li_{0.82}Mn_{0.85}Co_{0.15}O_2$ reported by Paulsen *et al* [15], the present case is possibly composed of random stacking of O_2 and O_4. However, this falls out of the scope of the present work, and needs extensive crystallographic investigation. Fortunately, the results obtained indicate a well-known structure. In other words, the battery performance of $LiMnO_2$ cathode materials with this lattice structure is known, and our task was to control its morphology, which may improve battery performance.

In the typical case investigated in this paper, raw β-MnO_2 was transformed to Na-intercalated MnO_2 with a nanostructured morphology. The Na-intercalated manganese oxide nanowires had a lattice structure similar to that of β-$Na_{0.52}MnO_2$, which is itself an analogue to the known structure of $K_{0.51}Mn_{0.93}O_2$ with the space group Cmcm [8]. Upon ion-exchanging, to incorporate Li instead of Na into the manganese oxide structure, neither the morphology of the nanowires nor the lattice structure changes; there is only a slight change in the lattice constant. In fact, the latter process leads to the formation of conventional orthorhombic $LiMnO_2$, which is a well-known cathode material of lithium batteries.

The sizes of such bunches are sufficiently large for simple handling and positioning on specified devices for various
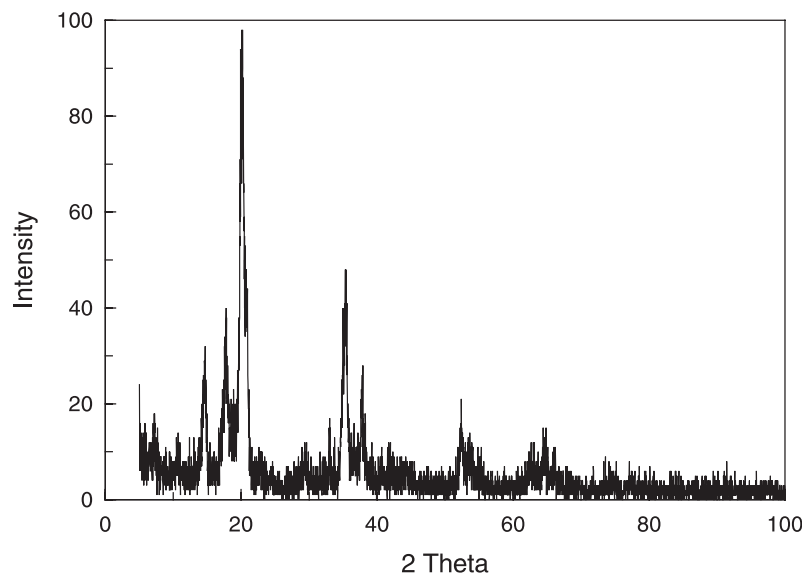
Figure 4. XRD pattern of the (Li-intercalated) manganese oxide nanowires.

applications. For instance, by positioning them vertically on a substrate electrode (like the situation illustrated in figure 3(*a*)), it is possible to fabricate a cathode for lithium batteries with an electroactive material thickness of about $100\,\mu$m. This cathode will show a superior battery performance since Li^+ ions can easily diffuse through individual nanowires which are aligned in one direction [5].

As stated above, an important advantage of the method proposed, in comparison with template-based methods, is that no empty pores exist within such bunches of aligned nanowires. In other words, the nanowires are closely packed to form dense bunches. This is an important requirement for fundamental studies of solid-state diffusion, as diffusion through a fluid medium should be neglected [17]. On the other hand, it is an interesting feature for applications, e.g. preparation of all-solid-state cells where such empty pores are undesirable, and this feature will reduce capacity fading [18]. A dense material has some valuable advantages, like reducing the interfacial resistance which can improve the material properties such as the conductivity, which is very important for electroactive materials [19, 20].

4. Conclusion

The simple solid-state procedure proposed is suitable for fabricating manganese oxide nanowires just by a high-temperature process. This is indeed an important achievement in the realm of nanotechnology. With a general interest, we have communicated this interesting phenomenon. It has been shown that the nanowires synthesized using this simple approach are significantly stable upon ion-exchange and the morphology and lattice structure remain unchanged. However, this is just the beginning that we have aimed to report of this interesting

phenomenon, and further investigations are needed to reveal its exact mechanism. Upon achieving this, it is possible to design similar processes for different cases. On the other hand, it deserves the particular attention of the applied physics community, since it may be of interest for various applications, which should be practically examined.

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