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Rectangular structure of manganese oxide nanowires

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Abstract

A new form of 1D nanomaterials is reported. Solid-state synthesis of manganese oxide nanowires is accompanied by bunching of individual nanowires. It was found that a peculiar structure of individual nanowires is formed in the course of this synthesis. In this case, nanowires have rectangular shape instead of conventional cylindrical shape. In fact, each individual nanowire consists of smaller ingredients, which are sheet-like nanoribbons. Of course, these nanoribbons are closely packed and can only be distinguished on broken heads of nanowires. Both SEM and TEM results confirm this novel structure. High resolution AFM with scanning area of about one individual nanowire was also employed to visualize rectangular structure of these nanowires with high resolution.

Keywords: Manganese oxide; Nanowires; Low-density channels; Nanostructure; Electron microscopy; AFM

1. Introduction

More recently, we reported a simple method based on solid-state reaction for synthesis of manganese oxide nanowires [1,2]. In addition to excellent efficiency of this procedure for nanowire synthesis, it is also accompanied by an interesting phenomenon, i.e. alignment of individual nanowires in specified directions [1]. The individual nanowires tend to be formed close together. Formation of bunches of nanowires via a simple solid-state synthesis is of interest from both fundamental and applied research points of view. In the present study, we wish to communicate some interesting features about structure of individual nanowires. Indeed, they have a peculiar structure in comparison with known 1D nanostructures. Of course, the important point is the formation of such complicated structure as a result of simple solid-state reaction.

2. Experimental

The manganese oxide nanowires were synthesized in accordance with conventional solid-state syntheses as described previously [1]. Briefly, stoichiometric ratios of the reactants (sodium carbonate and MnO_2) were mechanically mixed. The heating process was a 5 h heating at 600 °C followed by 40 h heating at 800 °C. Then, the sample was slowly cooled to room temperature. Sodium can be easily extracted from the manganese oxide nanowires via a chemical extraction process [3].

SEM images were recorded using a Cambridge scanning electron microscope model Stereoscan 360, and TEM studies were performed using a Phillips transmission electron microscope with field emission gun (FEG). AFM investigations were carried out using a Park Scientific atomic force microscope. Commercial sharpened tips of Si_3N_4 with tips smaller than 10 nm were employed. The AFM images were recorded under contact mode to obtain high resolution. Since the samples are powders, there is a severe difficulty for AFM studies. Two types of samples were prepared for AFM studies: (i) individual particles (bunches of nanowires, not individual nanowires) were attached to a substrate under optical microscope, (ii) a small amount of powder was mechanically pressed with a slight force. In the latter case, as mechanical force may affect the nanowire structures, scanning areas were selected from cavities on the sample surface. However, there was no significant difference between these two methods, and we just examined both of them to assure about accuracy of experimental data, though there was an excellent repro-

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ducibility for both experiments. To avoid tip contaminations, the sample was thoroughly washed with deionized water and AFM tips were changed several times for different experiments.

3. Results and discussion

After report of the phenomenon of formation of bunches of manganese oxide nanowires (Fig. 1), which is of particular interest for applied purposes [1], we attempted to investigate individual nanowires. In this direction, we employed the most appropriate technique in this context, i.e. TEM. The results were surprising, as an extraordinary structure was detected (Fig. 2A and B). It seems that the so-called nanowires are multi-channel nanotubes. This suggests that not only the bunching of individual nanowires in the course of this simple solid-state synthesis is an extraordinary phenomenon, but also these individual nanowires have peculiar structure. Wang and Li [4] have reported transformation of manganese oxide nanowires to manganese oxide nanotubes under hydrothermal condition. However, the latter process produces conventional nanotubes with a single channel in the center. High resolution TEM image of the individual nanowires (Fig. 2C) was also suggested a similar molecular structure in comparison with other cases [5–11].

It should be emphasized that the channels quoted above do not necessarily refer to common empty voids through the tube. Instead, this novel structure indicates periodic change of the material density across the nanowire width. Of course, this density difference is not due to chemical composition of the nanowire, as EDX studies suggested similar elemental composition at different regions. Probably, structural construction of individual nanowires is responsible for such shape.

To inspect this apparent structure of multi-channel nanotubes, we once again employed SEM. If these are truly multi-channel nanotubes, such channels will be detectable on heads of individual nanowires in SEM images. Fig. 3A and B illustrate heads of individual nanowires. Contrary to quick judgment from TEM images, no empty channel is observed on the nanowire head. As stated above, apparent channels in TEM images are representative of low-density channels (not empty voids). Instead, it is obvious that the individual nanowires include some tinier sheet-like nanoribbons, and the apparent channels detected in TEM image (Fig. 2A and B) are

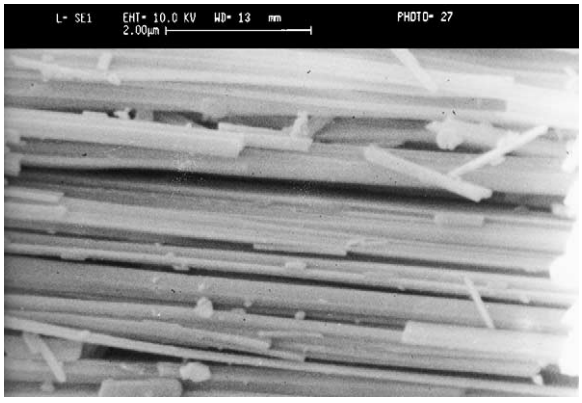

Fig. 1. Typical SEM image of a bunch of manganese oxide nanowires. This is the sample prepared for AFM studies.

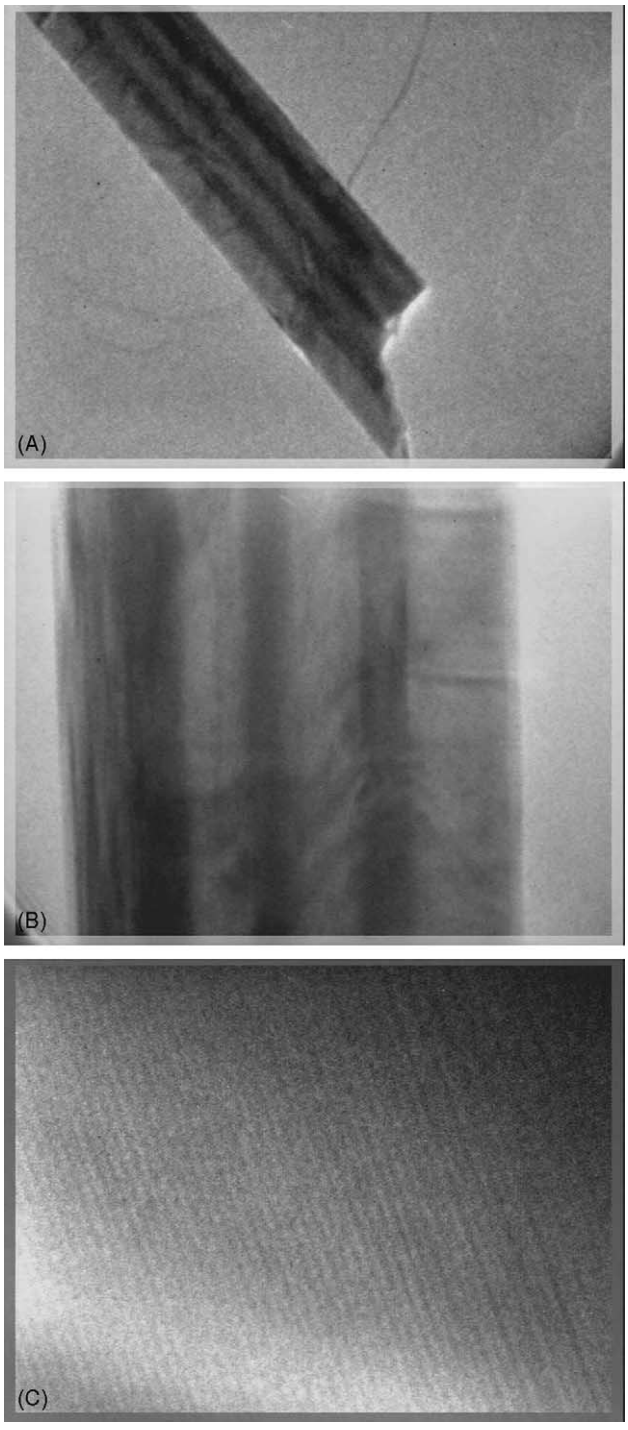

Fig. 2. (A and B) Conventional TEM images of an individual nanowire displaying multi-channel structure (the width of the nanowire illustrated is 84 nm). (C) High-resolution TEM displaying the lattice structure of the manganese oxide lattice (the distance between the lines is 0.23 nm).

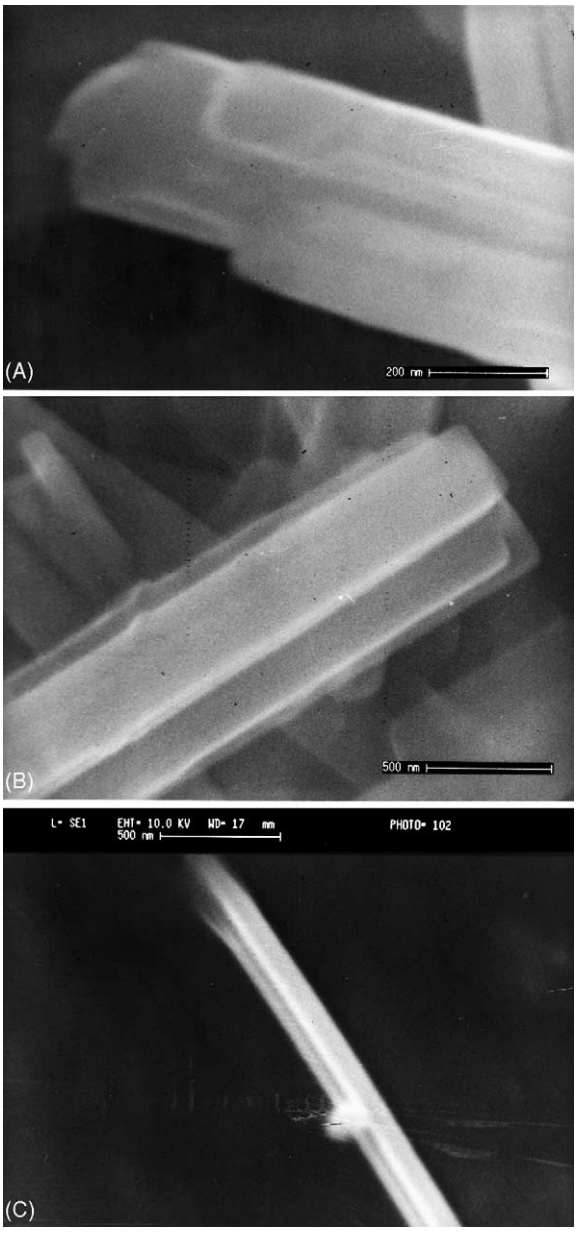

Fig. 3. SEM images of (A) and (B) heads of manganese oxide nanowires, and (C) body of a rectangular nanowire.

due to structural construction of an individual nanowire from tinnier nanoribbons. Incomplete attachment of such nanoribbons can also lead to the formation of empty channel through an individual nanowire. Distinguishing between empty channels or low-density channels within such nanowires is a difficult task and needs deep investigation; however, it falls out of the scope of this preliminary report aiming to reveal external structure of such manganese oxide nanowires.

Of course, SEM technique has a serious limitation for such investigation at higher resolution, as manganese oxide is not sufficiently conductive and it is needed to coat the sample with Au–Pd alloy, according to the conventional method for SEM imaging of insulating materials. We tried to minimize the thickness of this coating layer, but this restricts SEM imaging at high resolution. To overcome this problem, larger individual nanowires were chosen for this study as the nanowires synthesized by this method have a broad range of sizes varying from 50 to 200 nm in diameter (and rarely larger) [1]. In any case, the results reported are satisfactorily convincing.

In addition to the peculiar internal structure of these nanowires, this peculiarity can also be detected on the external structure of them. As the nanowires have been fabricated from attachment of tinier nanoribbons, the conventional cylindrical shape of nanowires is no longer expected for these nanowires. Thus, the nanowires will have rectangular shape. For detecting this structure, it is not needed to inspect the nanowire heads, since it can be seen across the nanowire body (Fig. 3C). The typical nanowire illustrated in Fig. 3C has a complete rectangular shape, as it was checked by looking at different angles. It is worth noting that all of the individual nanowires do not have ordered rectangular-shape like the typical one illustrated in Fig. 3 (though most of them have this structure). This does not means that individual nanowires have not ordered structure, but they are not necessarily rectangular as they can be pentagonal, hexagonal, etc., depending on attachment of tinier nanoribbons.

In general, these results suggest that the multi-channel structure detected here is completely different from that reported by Wang and Li [4], as they prepared manganese oxide nanotubes based on the well-known phenomenon that 1D nanostructured materials with layered structure may transform to nanotubes under appropriate conditions [12–14]. Whereas, the multi-channel structure of the present case and generation of nano-channel across the nanowire is due to the existence of tinier nanoribbons constructing the individual nanowires.

Since the TEM results just suggest the existence of multi-channel structure, and not the rectangular structure of these nanowires, it is useful to inspect this issue by means of another nanotechnological technique to confirm the rectangular structure detected by SEM (Fig. 3C). To investigate the structure of these rectangular nanowires and particularly smaller nanowires (which were not investigated in SEM studies), AFM provides an excellent opportunity, though, it is a difficult task and time-consuming since it is required to find individual nanowires with appropriate direction (it should be exactly horizontal in respect with the substrate surface). In Fig. 4, AFM image of an individual nanowire is presented. The rectangular structure of the nanowire is completely obvious. As stated above, it is truly difficult to find a nanowire appropriately positioned on one base of the rectangular structure, but it is not impossible. Interestingly, in some places, grooves generated as a result of incomplete attachment of nanoribbons are also observable. Of course, in this scale, we encounter the resolution limitation of AFM, but we were successful to monitor an individual nanowire (Fig. 4).

For obtaining high resolution in such small scanning area, commercial 5 μm scanner was employed, which has the limitation of 1.0 μm for height difference. Thus, some regions of

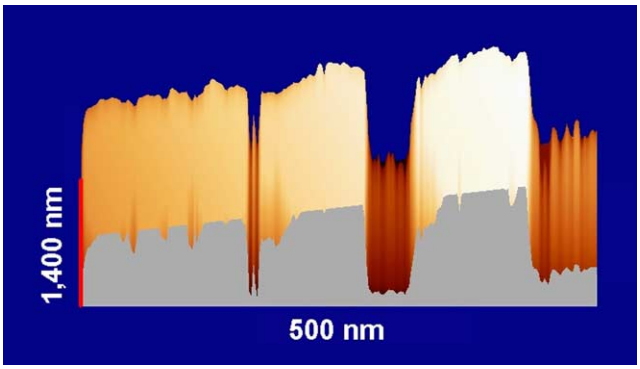

Fig. 4. AFM monitoring of individual nanowires available on the sample surface. The scales are (x, y, z) 500 nm, 500 nm, and 1.4 μm, respectively.

the scanning area may seem to be flat. However, AFM study (Fig. 4) satisfactorily confirmed the rectangular structure of the individual nanowires and existence of tinier nanoribbons. Moreover, it indicates overall structure of the bunch. Similar to SEM images (e.g. Fig. 1), deep grooves between individual nanowires packed together are observable, but the size of the nanowire visualized by AFM (Fig. 4) is significantly smaller than that monitored by SEM (Fig. 3C). This also detects the nanowires placed within these grooves.

Partial existence of such grooves is of interest for applied purpose, as these channels improve diffusion processes [15]. This is of double interest, as this novel structure also have internal channel within the individual nanowires as revealed by TEM (Fig. 2). This provides a superior behavior for this nanostructured material for using in systems involving diffusion processes, such as electrochemical systems [16]. Manganese oxide is a potential candidate for cathodes of lithium batteries, and because of this application, a considerable attention has been paid to synthesize manganese nanowires, as they exhibit better battery performance [17–19]. It should be emphasized that two types of channels exist within this nanostructured material: low-density channels within individual nanowires, and empty channels within the bunch of nanowires. Both of them can improve diffusion process in an electrochemical system.

On the other hand, fabrication of such rectangular nanowires is of great interest for applied purposes, as it provides a great opportunity for better packing of individual nanowires. This increases the material density (free of waste voids within the material), which is of great importance and improves the material properties for specified applications [20,21]. Further investigations in this context may lead to a solid approach for controlling the size of these nanowires for fabricating an ordered package of rectangular nanowires. For instance, reducing surface area of manganese oxide improves its battery performance, as decreases Mn dissolution in the course of charge/discharge process. High surface area is also accompanied by severe structural changes upon insertion/extraction process [22]. It should be taken into account, better diffusion process requires nano-channel as it is mainly in the form of solid-state diffusion in such systems. In fact, low-density channels within the manganese oxide nanowires are possible paths for diffusion processes.

4. Conclusion

The present study by means of different techniques revealed complicated structure of manganese oxide nanowires synthesized by simple solid-state reaction. The nanowires prepared have a novel structure in comparison with available 1D nanostructured materials. The most peculiar feature of these nanowires is that they have been generated as a result of attachment of tinier nanoribbons, and this is the reason for the formation of such multi-channel structure. Different microscopic techniques (SEM, TEM, and AFM) confirmed this peculiar structure through visual evidences.

As the final words, it should be emphasized that in the light of results discussed above, these manganese oxide nanowires are not similar to conventional nanowires. Thus, the term of nanowire seems to be inappropriate for them, but the term of multi-channel nanotubes is also falls out of the definition of nanotubes. In any case, we use this term following the literature. However, this makes an important question that whether this simple synthesis procedure leads to the formation of such peculiar nanowires, which are not similar to other known nanowires? We believe that many synthetic nanowires may have similar complicated structures, but less attention has been paid to this issue and possibility of the existence of such peculiar structures. In other words, the present report wishes to attract attention of materials scientists to study of internal structure of nanowires (and generally 1D nanomaterials) beyond current examinations.

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