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Fabrication of lithium manganese oxide nanoribbons by electrospinning: A general strategy and formation mechanism

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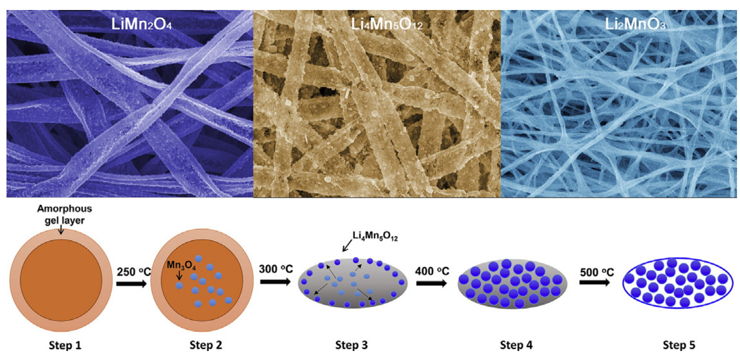
HIGHLIGHTS

- Lithium manganese oxide nanoribbons with high purity were fabricated under low temperature.
- The nanoribbons possess higher surface areas compared with the nanoparticles.
- A general mechanism for the synthesis of Li-Mn-O nanoribbons was proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

Various lithium manganese oxides (LMOs), including $LiMn_2O_4$, $Li_4Mn_5O_{12}$ and Li_2MnO_3, nanoribbons with excellent continuities have been fabricated by the electrospinning method, as $Li_4Mn_5O_{12}$ was chosen as a model to illustrate this topic in detail. Both scanning electron microscopy and transmission electron microscopy observations showed that $Li_4Mn_5O_{12}$ structures were well-defined one-dimensional nanoribbons. The X-ray diffraction results exhibited that the regular ribbon-like nanostructures possessed highly crystalline structures without any detectable impurities, while their nanoparticle counterparts prepared by a sol-gel route were introduced several foreign impurities. Moreover, such nanoribbons also demonstrate larger surface areas compared with the nanoparticles. The temperature-dependent experiment has been adopted in an attempt to trail the growth process of the nanoribbons, and a possible formation mechanism was proposed based on it.

1. Introduction

Since the discovery of carbon nanotubes in 1991 [1], considerable efforts have been devoted to fabricating one-dimensional (1D) nanostructures with tailoring morphologies as well as desired components for their exceptionally electronic, optical, magnetic and thermal properties [2,3]. Such intriguing features are believed to be primarily originated from 1D nanomaterials' instinct advantages including the large surface-to-volume ratio, the directional mobility of charge carriers and the quantum confinement effects [4]. Therefore, remarkable research recently focused on the preparation of various types of 1D nanostructures, such as nanorods, nanotubes, nanoribbons, nanofibers and so forth [5–8]. Among these, the nanoribbons have especially attracted extensive attention, because its unique flat geometries are capable of prompting positive changes in terms of the pore shape and size

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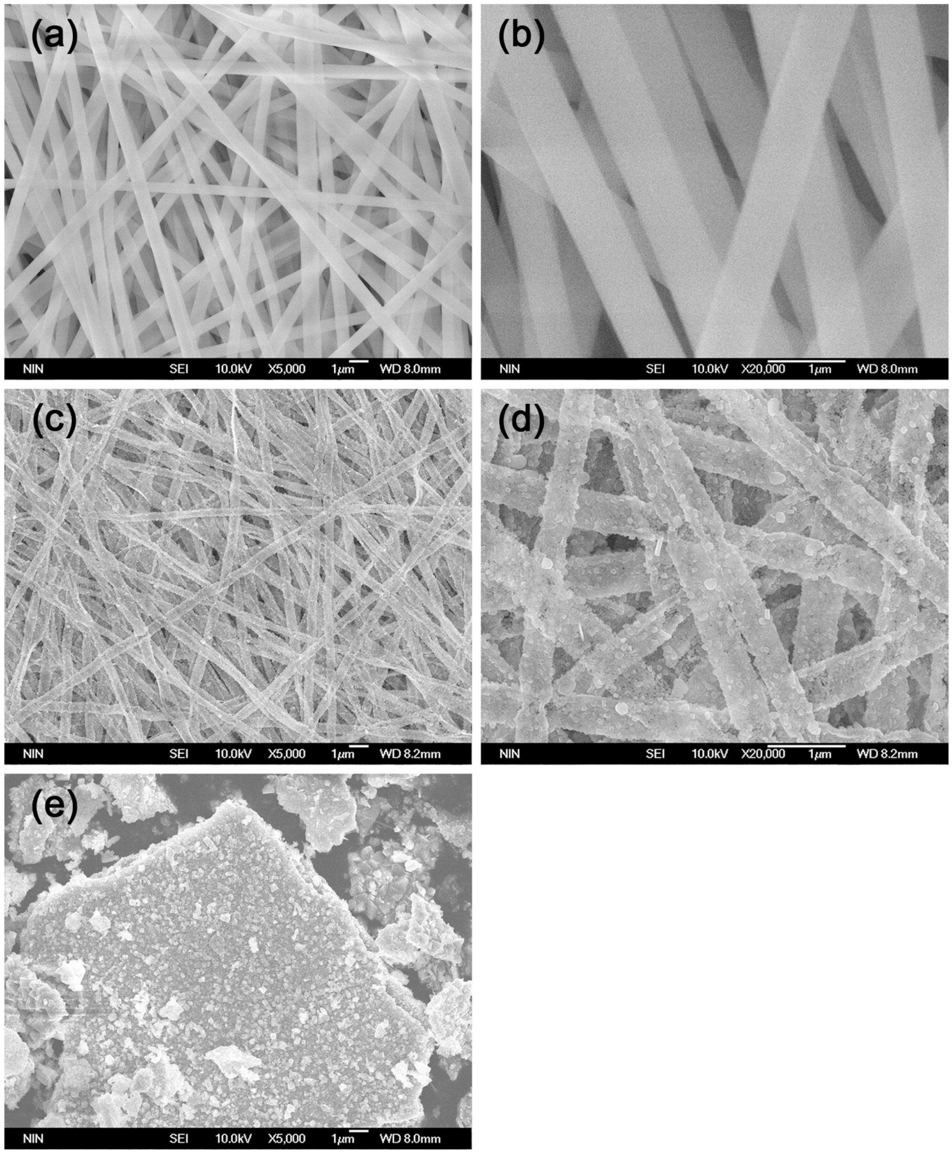

Fig. 1. SEM images of $Li_4Mn_5O_{12}$ precursor nanofibers with different magnifications (a, b); sample E-5 with different magnifications (c, d); sample S-5 (e).

distribution, improving the anisotropic mass and heat transport and strengthening mechanical properties [9]. As a result, 1D nanoribbons are readily to be endued with better gas selectivity, multiferroic and optical properties [10].

LMOs, have been regarded as ideal alternative materials to $LiCoO_2$ in the realm of cathode for Li-ion batteries, in view of their numerous virtues associated with low-cost, environmental benignity, abundant resources, and outstanding safety [3,11]. For instance, $Li_4Mn_5O_{12}$ firstly reported by Thackeray et al. [12], as an important member among this renowned family, has acquired intensive interest as a potential cathode candidate for Li-ion batteries, originating from its distinctive three-dimension interstitial channel for the cation' s transport [13], which presents a theoretical storage capacity of 163 $mAhg^{-1}$ [14]. In addition, it was also used as electrodes for hybrid supercapacitor, sodium-ion batteries and modules in 3D battery structures, besides the precursor of Li-ion sieve [15–18]. Through reducing minor number of Mn^{4+} ions, it even could be utilized as promising heavy-fermion materials [19].

So far, many different methods have been recruited to produce LMOs in order to meet the increasing requirements. Unfortunately, the conventional strategies either need long time or merely generate simple nanoparticles. To make matter worse, the high covalent values of the manganese atoms even strand the preparation of pure $Li_4Mn_5O_{12}$ with tailoring as well as regular morphologies [13,20]. The physical/chemical properties as well as the performance of the nanomaterials are intimately correlated with their morphologies, dimensions, crystallinity, and purity degree [21,22]. Tian and co-workers has prepared $Li_4Mn_5O_{12}$ nanowires [23], as it exhibited a high-degree stable discharge plateau at 2.8 V deriving from the elegant 1D nanostructure. This exciting work shone light on that the 1D LMOs that, especially nanoribbons, are expected to exhibit particular and enhanced electrical properties in comparison with the nanoparticle or bulk counterparts [24].

Electrospinning has been regarded as a straightford, versatile and economic technique to fabricate 1D nanostructures with continuous geometry and tunable compositions. To date, numerous types of 1D metal oxides have been obtained by this method [25,26]. Nevertheless, to the best of our knowledge, reports covering the acquisition of pure LMOs with 1D nanoribbon structures are yet comparatively scarce. Hence, it is not only meaningful work but also a huge challenge to prepare $Li_5Mn_4O_{12}$ 1D nanoribbons by electrospinning. Herein, we proposed for the first time electrospinning technique followed by pyrolysis treatment to prepare LMOs 1D nanoribbons, motivated by above concerns.