Synthesis of Three-Dimensional Mn_3O_4 Nanowires

Chunsheng Du[*], Jondo Yun[**], Randy Dumas[***], Kai Liu[***], Nigel Browning[****] and Ning Pan[*]

[*]Nanomaterials in the Environment, Agriculture and Technology (NEAT)
University of California, Davis, CA 95616, USA, cdu@ucdavis.edu
[**]Nanostructure and Microstructure Research Laboratory
Kyungnam University, Masan, 631-701, Korea
[***]Department of Physics, University of California, Davis, CA 95616, USA
[****] Department of Chemical Engineering and Materials Science
University of California, Davis, CA 95616, USA

ABSTRACT

Mn_3O_4 nanostructures with three-dimensionally intercrossing nanowires have been synthesized by soft chemistry templating process using block copolymer as structure-directing agent. The nanowires were grown out of the bulk structure and with planar defects. The magnetic properties of such nanostructured film have been measured and this newly grown nanowire structures could be the foundation for developing Mn_3O_4 film with nanowires oriented in one direction, which is believed to show greater anisotropy in magnetic and catalytic properties.

Keywords: Mn_3O_4, nanowire, template synthesis, three-dimensional, magnetic properties

1 INTRODUCTION

Owing to the large specific surface area and other superior properties over their bulk counterparts arising from quantum size effect, nanoscaled and nanostructured materials have attracted considerate research interest and many novel nanoscale materials have been synthesized in the past 10 years[1-5]. It is well known that the behaviors of nanomaterials strongly depend on the sizes, shape, dimensionality and morphology, which are thus the key factors to their ultimate performance and applications. Therefore it is of great interest to synthesize nanomaterials with a controlled structure and morphology.

Mn_3O_4 is an important material due to its wide applications in the area of catalysis, magnetic material and electrode material for batteries. In this paper, we report the synthesis of three-dimensional Mn_3O_4 nanostructures by soft chemistry templating process using block copolymer as structure-directing agent. This 3-dimensioanl nanostructured material has a unique structure of inter-crossing nanowires grown from faceted Mn_3O_4 particles, and are aligned in each facet. The density and length of the nanowires can be varied by controlling the growth time. We anticipate that it may provide another kind of manganese oxide with different characteristics.

2 EXPERIMENTAL

The Mn_3O_4 nanostructures were prepared by a soft chemistry templating synthesis approach using block copolymer $EO_{20}PO_{70}EO_{20}$ (BASF, Pluronic P-123) as structure-directing agent[6-9]. $MnCl_2$ (Alfa Aesar, 97%) was used as precursor and dissolved in the ethanol, followed by filtration (Millipore filter membrane) to remove the insoluble impurities (Based on the induced coupled plasma mass spectrometry (ICP-MS) analysis, the major impurities in the solution after filtration include Na, Mg and K, at about 3ppm, 1.9ppm and 0.2ppm, respectively). Into this filtered solution, the block copolymer was added with vigorous stirring to form $MnCl_2$ sol. To prepare the Mn_3O_4 nanostructures, 5μl of the resultant sol were deposited on a 4mm×4mm silicon wafer (with a thin oxide layer) and dried at room temperature. The silicon wafer was then heated to 400°C in air, and held at that temperature for a few hours.

The as-synthesized products were then characterized by scanning electron microscopy (SEM: FEI XL30-SFEG) and high resolution transmission electron microscopy (HRTEM: JEOL JEM-2500SE). X-ray diffraction patterns were obtained on a Scintag XDS 2000 x-ray powder diffractometer using Cu Ka radiation.

Magnetic measurements were performed on a Quantum Design SQUID magnetometer on a film sample of Mn_3O_4 after it was removed from the silicon substrate. Measurement of magnetization versus temperature was carried by varying the temperature between 5K and 150 K according to zero-field-cooling (ZFC)/field-cooling (FC) procedure at 100 Oe. Specifically, sample was first cooled to 5K without any external magnetic field, then temperature was raised up to 150K then back to 5K during which a 100 Oe field was applied in-plane of the sample. The magnetization versus field was measured at 5 K in a magnetic field of up to ±7 T.

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3 RESULTS AND DISSCUSSION

Fig.1 shows the typical morphologies of the products prepared at 400°C for different times. As can be seen in Fig.1a, the products consist of unique structures in which aligned nanowires grown from facet particles and remained spatially perpendicular in three dimensions.

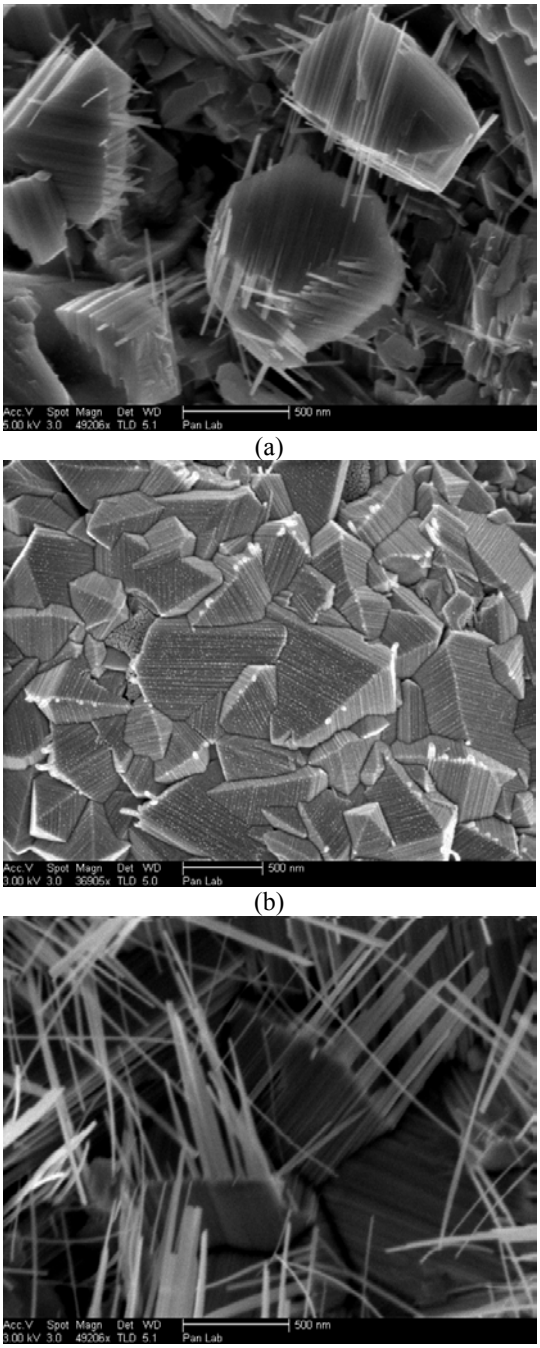


Fig.1 SEM images of Mn3O4 nanostructures prepared at 400°C for different times: (a) 5h, (b) 2h, (c) 7.5h

The nanowires were actually grown from the bulk particles, evidenced by the fact that both the density and the length of the nanowires increased when the growth time was extended. Shown in Fig.1b is the SEM image of the product prepared at 400°C for 2h. As can be seen, very short nanowires just grew out of the particles. However, when the growth time was prolonged to 7.5h, many long nanowires were grown, as shown in Fig.1c. X-ray diffraction pattern (Fig.2) reveals that the product is consistent with the spinel structure of tetragonal Mn_3O_4 (t-Mn_3O_4, hausmannite). All diffraction peaks can be perfectly indexed to the hausmannite structure (JCPDS card 24-0734).

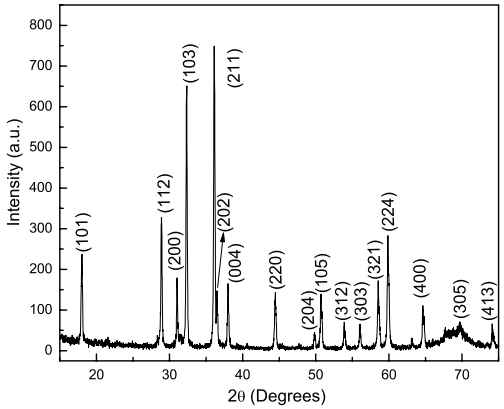


Fig.2 XRD pattern of the Mn_3O_4 nanostructures

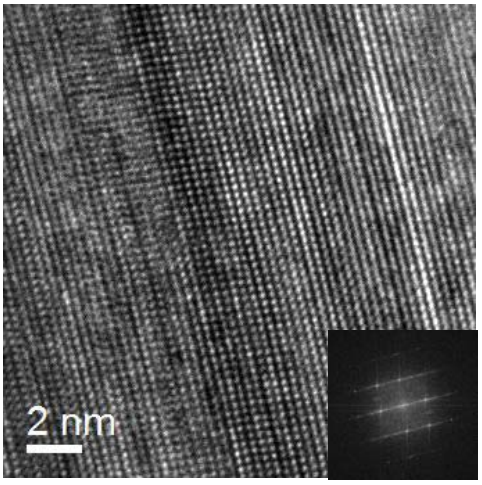
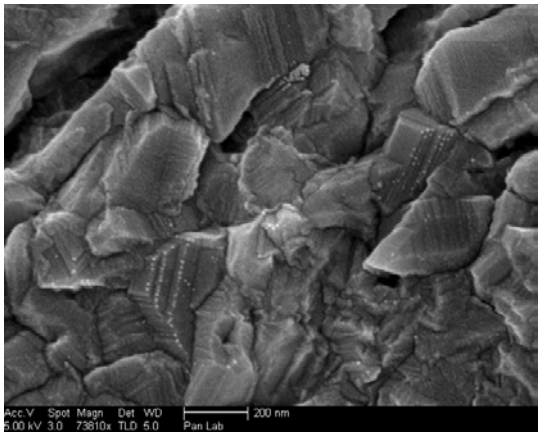


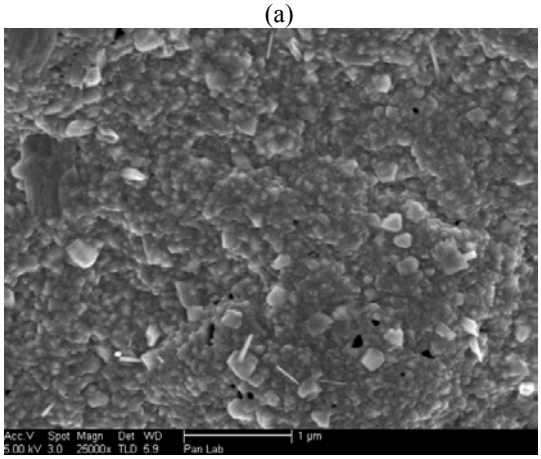
Fig.3 HRTEM image of a single Mn_3O_4 nanowire. Fast Fourier transformation (FFT) image was placed in the inset.

Fig.3 shows the HRTEM image of a single Mn_3O_4 nanowire with seemingly some defects. When the image was treated with fast Fourier transformation (FFT) filter using mask located between the spots in the FFT image in the inset of Fig.3, irregularities are seen more clearly. Atomic planes are distorted changing direction slightly. They are identified as nano-size domains of short-range

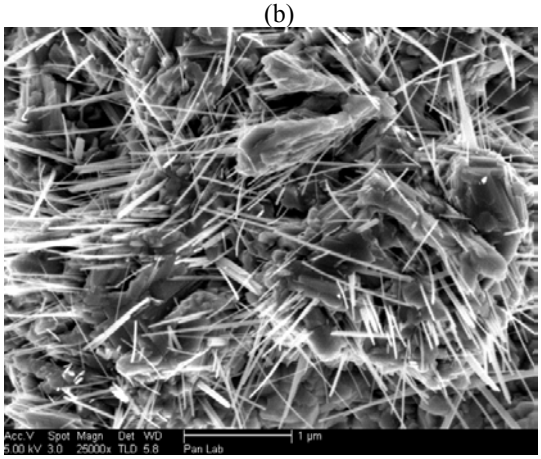
ordered point-type defects, interplanar distance modulation defects, or even planar-type defects.



(a)



(b)



(c)

Fig.4 SEM images of products using high purity $MnCl_2$ precursor: (a) no NaOH addition, (b) with 0.06wt% of NaOH addition, and (c) with 0.18wt% of NaOH addition in the $MnCl_2$ sol.

It is interesting to note that no nanowires were grown when using the high purity $MnCl_2$ (Alfa Aesar, 99.99%) as the precursor, as shown in Fig.4a. The difference between the high purity $MnCl_2$ sol and the filtered 97% $MnCl_2$ sol is the small amount of impurity (about 3ppm Na and 1.9ppm Mg after filtration, based on the ICP-MS analysis), as mentioned earlier. We speculated that the elements of Na and Mg were present in the form of NaOH and $Mg(OH)_2$ in the precursor. The small amount of NaOH and/or $Mg(OH)_2$ might then act as a catalyst for hydrolysis of $MnCl_2$ in a controlled manner (without precipitation) in the nonaqueous media. It may also act as a promoting agent during the assembly of wire shaped $Mn(OH)_2$-blocked copolymer micelles, followed by a progressive conversion into Mn_3O_4 nanowires during calcination by removing the copolymer and reacting of $Mn(OH)_2$ with oxygen in the air.

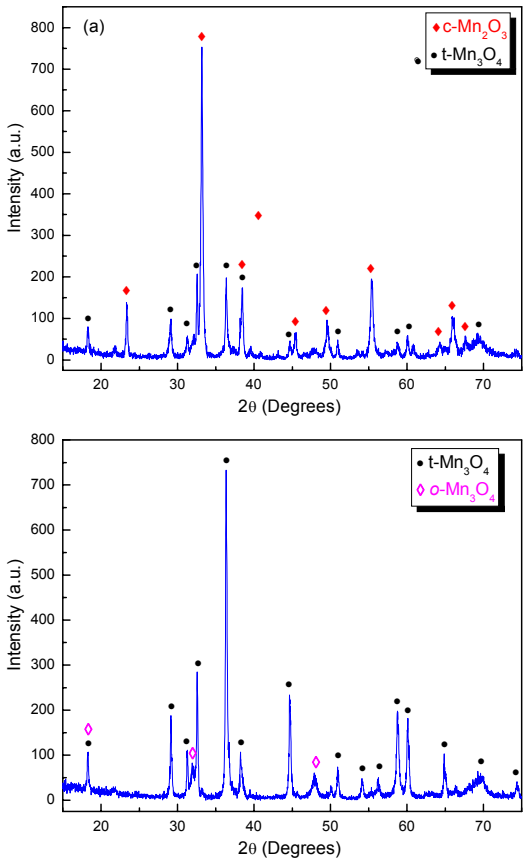


Fig.5. XRD patterns of the products using high purity $MnCl_2$ precursor: (a) no NaOH addition, and (b) with 0.18wt% of NaOH addition in the $MnCl_2$ sol.

To prove this assumption, we added small amount of diluted NaOH/ethanol solution to the high purity $MnCl_2$ sol. Fig.4b shows the SEM image of the product from the high purity $MnCl_2$ sol with a small amount of NaOH addition (0.06wt %). It can be seen that short nanowires formed in the product, though there were only few. When more NaOH was added to the sol (0.18wt %), more nanowires were grown, as shown in Fig.4c. Crystal phases of the products also changed remarkably. Fig.5 shows the XRD patterns of the products from high purity $MnCl_2$ precursor. When there

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was no NaOH addition, the product was a mixture of cubic Mn_2O_3 (c-Mn_2O_3) and tetragonal Mn_3O_4 (t-Mn_3O_4), with the former being the main phase. When NaOH was added to the sol (0.18wt %), the product was mainly t-Mn_3O_4, with only a small amount of orthorhombic Mn_3O_4 (o-Mn_3O_4) being the minor phase. No c-Mn_2O_3 phase was detected. Obviously, the small amount of NaOH addition in the sol played a very important role in the growth of Mn_3O_4 nanowires.

It should be noted that, although Mn_3O_4 nanowires were grown when small amount of NaOH was added to the high purity $MnCl_2$ sol, no facet structures as those shown in Fig.1a were obtained. This is likely due to the difference of how NaOH impurities were introduced. In the case of 97% $MnCl_2$, the impurity was released slowly and uniformly during the dissolving process of the precursor in the ethanol solvent. While when NaOH was added to the high purity $MnCl_2$ sol, no matter how careful to control the way it was added, there was always a sudden increase of the NaOH concentration locally in the sol. This difference may affect the hydrolysis of $MnCl_2$, and the growth of the nanowires.

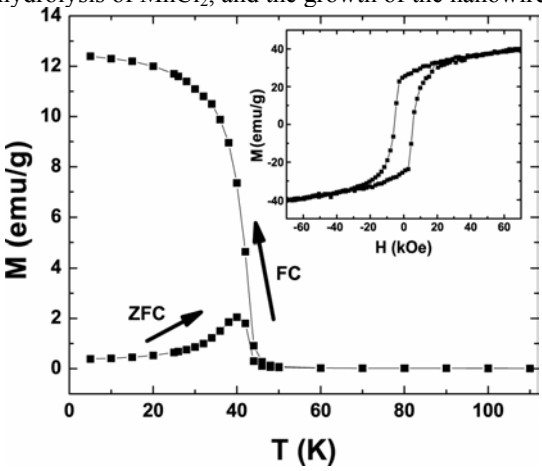

Fig. 6. Zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves of Mn_3O_4 nanostructures under an applied field of 100 Oe. Inset is a hysteresis loop at 5 K.

Magnetic measurements were carried out on the Mn_3O_4 nanowire sheet sample after it was removed from the silicon substrate. The temperature dependence of the magnetization in a 100 Oe field is shown in Fig. 6 after zero field cooling (ZFC) and field cooling (FC). The magnetization versus field was measured at 5 K in a magnetic field of up to ±70 kOe as shown in Fig. 6 inset. As expected, the Mn_3O_4 nanowire sample showed a ferromagnetic response at low temperatures. After removing the linear background of the M - H loop, a saturation magnetization of 30 emu/g was found at 5 K, consistent with previously reported results. A blocking temperature T_B of 40 K was observed, comparable to that reported by Seo *et. al.* for 10nm Mn_3O_4 spherical nanoparticles [10]. The Curie temperature is consistent with the bulk single-crystal Mn_3O_4 value of 41.9 K. Since the nanowires are aligned in one direction (as shown in Fig.1), it may be possible to synthesize such nanostructured film in which the Mn_3O_4 nanowires are all oriented in the planes vertical or parallel to the film. Such a film is expected to have more anisotropic magnetic and catalytic properties.

4 CONCLUSION

In summary, Mn_3O_4 nanostructures with three-dimensionally intercrossing nanowires have been synthesized using block copolymer as the structure-directing agent. The nanowires were grown out of the bulk structure and with planar defects. The presence of small amount of NaOH and/or $Mg(OH)_2$ in the precursor were suggested as the facilitating agent during the formation of wire shaped $Mn(OH)_2$-blocked copolymer micelles. The magnetic properties of such nanostructured film have been measured and this newly grown nanowire structures could be the foundation for developing Mn_3O_4 film with nanowires oriented in one direction, which is believed to show greater anisotropy in magnetic and catalytic properties.

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