Journal of Ceramic Processing Research. Vol. 9, No. 6, pp. 678~682 (2008)

J O U R N A L O F
Ceramic Processing Research

Characterization of manganese oxide nanowhiskers

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Manganese oxide is used for a catalyst in organic chemistry, as electrodes for lithium ion batteries, and as a magnetic material. When manganese oxide is in a form of nano-size whiskers, it shows higher activity and efficiency. In this study, nano-size whiskers of manganese oxide prepared by the soft chemistry templating synthesis method, were characterized by electron microscopy and spectroscopy. It was found that nanowhiskers grew three dimensionally from nanoparticles of Mn_3O_4. The structure and chemistry of whiskers were analyzed using transmission electron microscopy, electron energy loss spectroscopy, and energy dispersive x-ray spectrometry. It was found that whiskers contained point defects and atomic ratio of oxygen to manganese varied in a range of 0.7-1.6.

Keywords: Nanowhiskers, Scanning, Transmission, And high resolution electron microscopy, X-ray spectrometry.

Introduction

Nanomaterials have been focused on by many research scientists due to their quantum effect, large surface area, and high chemical activity, which arise from their size being on the nanoscale [1, 2]. Many nanomaterials, such as nanotubes, nanowires, nanowhiskers, nanopowders, and even nanosprings, or nanocoils, have been synthesized and prepared [3-4]. It is well known that the properties of nanomaterials are a strong function of their structure and morphology which should be characterized and controlled.

Manganese oxide is used as a catalyst for the oxidation of methane, the selective reduction of nitrobenzene, or NOx and CO removal in waste gases. It can be also used as a raw material for magnetic devices in the form of manganese zinc ferrite, or as electrodes for batteries as lithium manganese oxides or rechargeable lithium batteries [5-6].

The nanoscale form of manganese oxide, such as nanowhiskers, is expected to have better or novel properties due to increased surface area and activity. When manganese oxide is on a nanoscale, its structure and composition may be unstable and this may affect its properties. The oxidation state, defects, crystal structure or nanostructure need to be characterized. Recently, various techniques have been developed for the characterization of nanomaterials. In this study, manganese oxide nanowhiskers with a three dimensional structure were examined using various techniques of nanocharacterization.

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Experimental Procedures

Nanowhiskers were prepared by a soft chemistry templating synthesis method. $MnCl_2$ in ethanol was used as source materials. A block copolymer was added as a structure-directing agent. The sol on a silicon wafer was heated at 400 degree C for five hours in air. The details of preparation procedures have been reported elsewhere [7]. The morphology and growing pattern of nanowhiskers were examined by scanning electron microscopy using either an independent or a TEM-attached instrument. The structure and defects were examined by transmission electron microscopy, selected area diffraction pattern analysis, and high resolution electron microscopy. The chemical composition and oxidation state were examined by energy dispersive x-ray spectrometry, and electron energy loss spectroscopy in a scanning transmission electron microscopy mode using a JEM-2500SE (JEOL, Japan). Quantitative analysis was performed using a standard specimen of a hausmannite single crystal mineral, which was collected from the N'Chwaning mine in South Africa. The Cliff-Lorimer method was used and the k factor was measured with no absorption correction. Spectrometric conditions such as dead time, time constant, and energy range were set constant.

Results and Discussion

Manganese oxide nanowhiskers grown by a soft chemistry templating synthesis method were found to have a three-dimensional structure as shown in the SEM micrograph of Fig. 1, resembling a straw house for crickets. This structure did not look like a piece of a solid grain but rather consisted of many pieces of thin and long

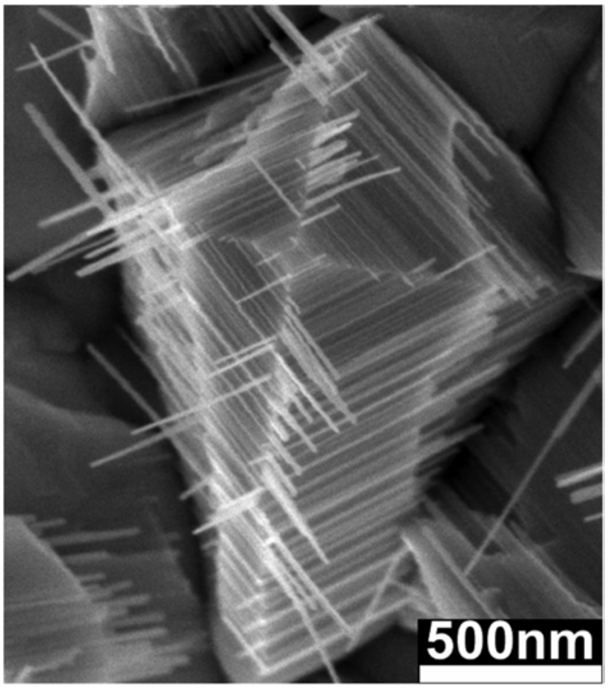
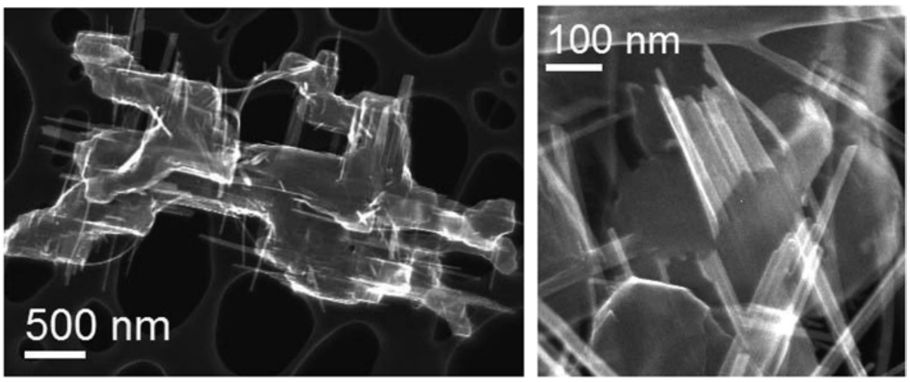


Fig. 1. Three dimensionally grown nanowhiskers of manganese oxide [7].

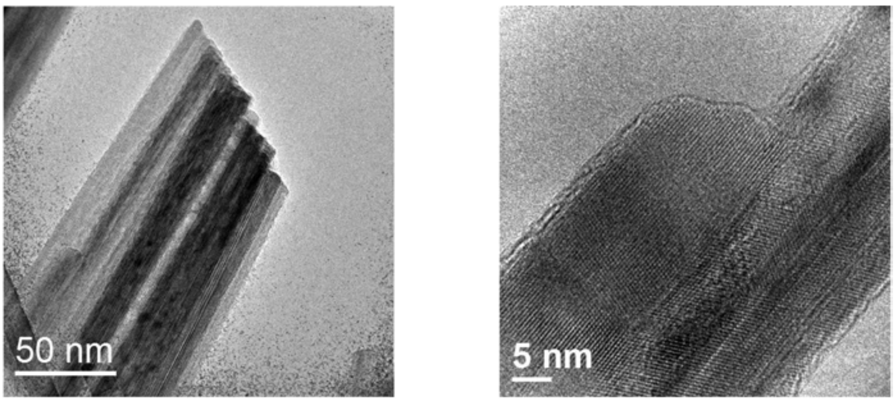
whiskers in the same but three different perpendicular directions. Since a bundle of whiskers having the same direction, one may assume that these whiskers were grown from the same source material such as a single grain. To investigate this assumption, whiskers were investigated morphologically and crystallographically by scanning electron microscopy and transmission electron microscopy. It turned out that the whiskers have the same orientation as the other whiskers in the neighbor and matrix. The large faceted particle is not a single crystal, but a composite of nanowhiskers in two orthogonal directions. Most nanowhiskers were found to form bundle in three-dimension as shown in Fig. 1 and Fig. 2. It was suggested that the whiskers were grown from a particle in three dimensional directions, consuming their mother particle.

The orientation relationship of nanowhiskers in a bundle was examined by transmission electron microscopy. Figs. 3(a) shows a bundle of nanowhiskers. Fig. 3(b) shows lattice fringes of two whiskers in a bundle. The lattice directions of the two whiskers were 50.1 ± 1.0, and 49.9 ± 0.9 degrees away from the horizontal line, respectively, showing that they have the same crystallographic orientation with less than one degree error.



(a) (b)

Fig. 2. Nanowhiskers grown from a particle at (a) low and (b) high magnification.



(a) (b)

Fig. 3. (a) Transmission electron micrograph of a bundle of nanowhiskers and (b) high resolution image of two nanowhiskers in a bundle.

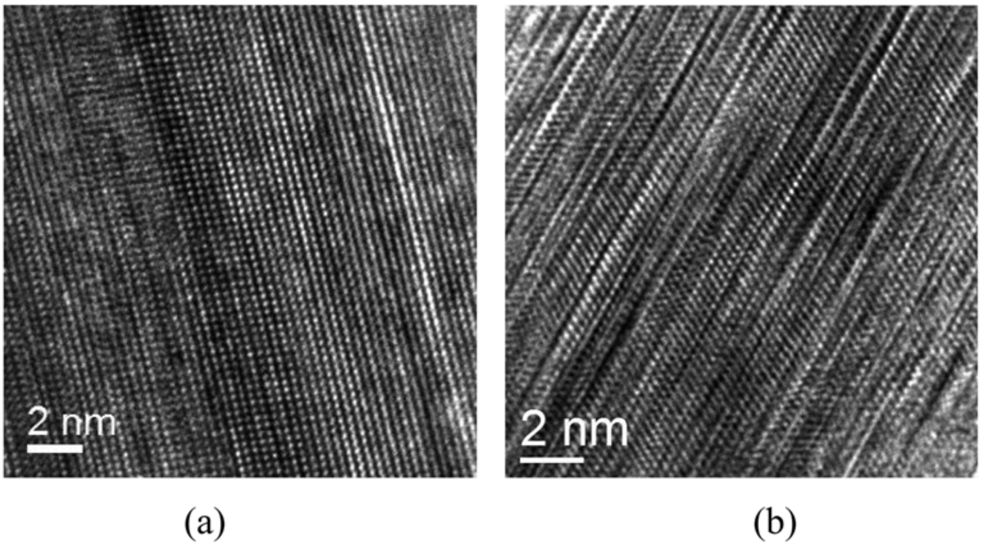


Fig. 4. High resolution electron microscopy (HREM) images of nanowhiskers (a) without and (b) with defects.

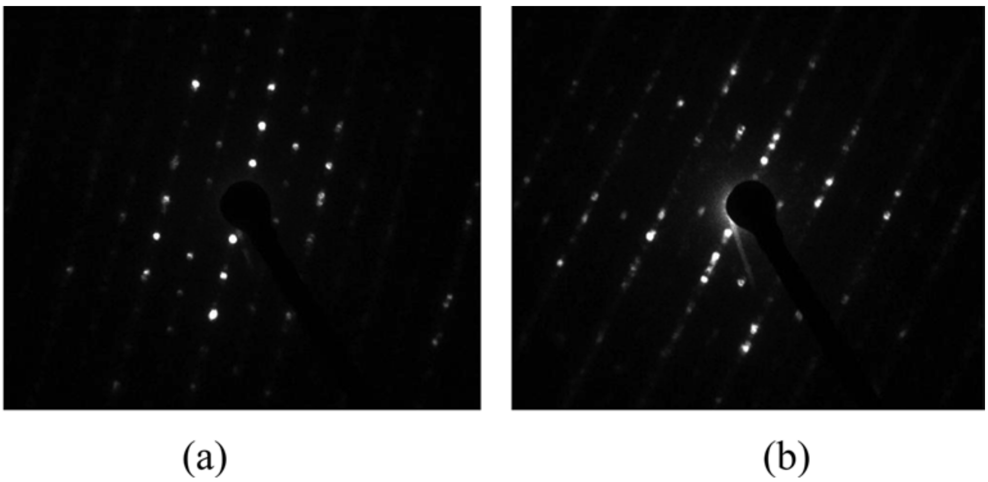


Fig. 5. Nanodiffraction patterns (NDP) of nanowhiskers (a) without and (b) with defects.

The electron diffraction analysis also showed that they have the same pattern and orientation. The TEM specimen holder was intentionally tilted by various angles to see whether the cross-sectional shape of the whisker was isotropic. It was found that the thickness of the whisker changed with the tilt angle, showing that the cross-section was not isotropic but rather anisotropic with a rectangular shape.

High resolution transmission electron microscopy (HREM) images were obtained from a couple of whiskers. Fig. 4(a) and (b) show HREM images from whiskers without and with defects, respectively. The atomic arrangement of Fig. 4(a) looks more perfect than that of Fig. 4(b). The nanodiffraction pattern of nanowhisker with defects (Fig. 5(a)) shows more streaks and extra spots than that of whiskers without defects (Fig. 5(b)). The HREM images were filtered using image analysis technique of fast Fourier transformation (FFT) with a spot pass mask (Fig. 6). In the nanowhisker with defects as the one in Fig. 6(b), the lattice line was deflected as in a case of interplanar defects, and there were domain-like defects with a size of several nanometers. The defects in the nanowhiskers may be either nano-size domains of short-range ordered (SRO) point-type defects which Wang and other scientists pointed out, or interplanar distance modulation defects [8-10].

Manganese oxides have various forms depending on the oxygen content: MnO, Mn_3O_4, Mn_2O_3, Mn_5O_8, and MnO_2. The oxygen content was examined by measuring the atomic ratio of oxygen to manganese by energy dispersive x-ray spectrometry. Quantitative analysis was performed using single crystals of an hausmannite standard. Fig. 7 and 8 respectively show EDS patterns and measured values of metal to oxygen ratio. It turned out that the ratios of the nanowhiskers were not uniform, but varied in a range from 0.7 to 1.6. Artifact effects such as beam damage, or area-to-area variation was examined. The manganese to oxygen ratio did not change

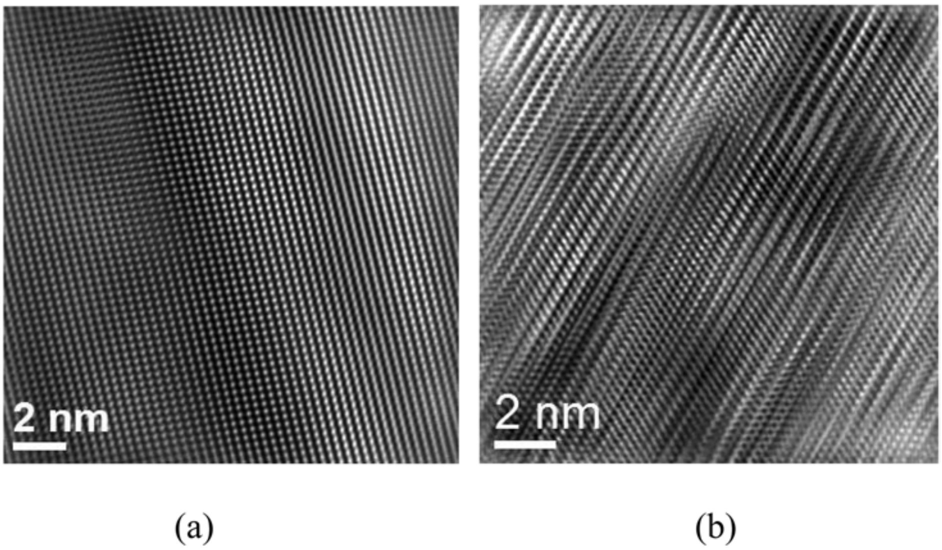


Fig. 6. Filtered images of nanowhiskers (a) without defects, and (b) with defects using fast Fourier transformation filter with spot pass mask.

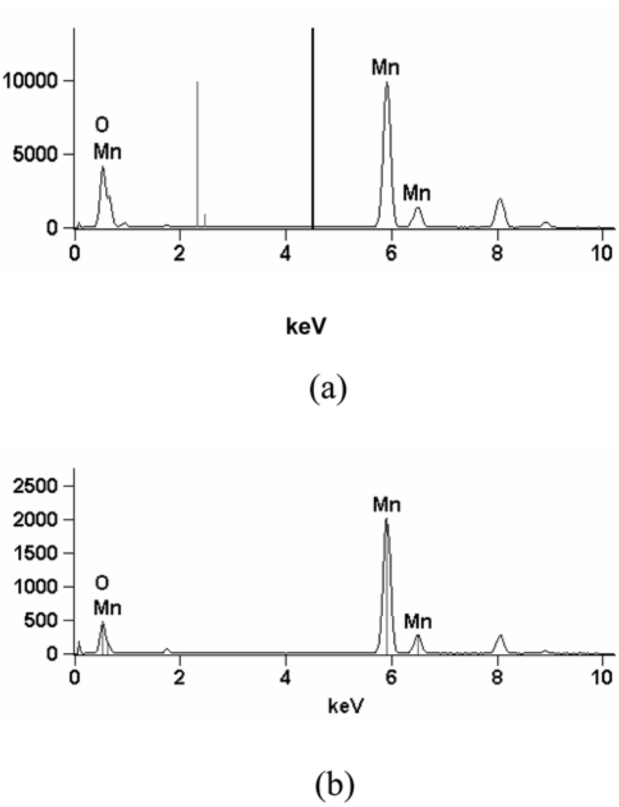


Fig. 7. Energy dispersive x-ray spectrometry pattern from (a) a hausmannite standard and (b) a manganese oxide nanowhisker.

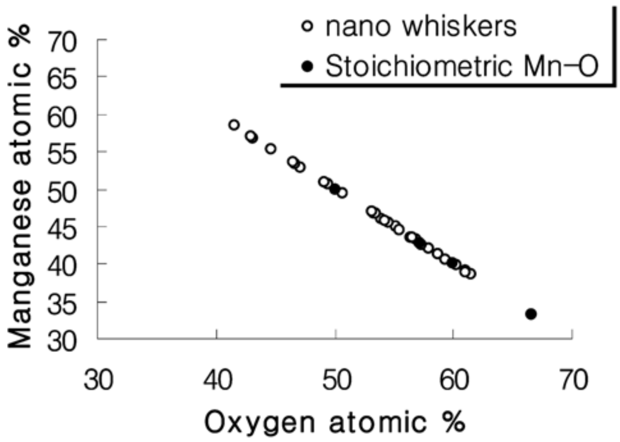


Fig. 8. Result of EDS analysis for nanowhiskers showing the ratio of oxygen to manganese contents. Solid circular points indicate stoichiometric manganese oxides: MnO, Mn_3O_4, Mn_2O_3, and MnO_2, from left to right.

under the stational e-beam up to 600 seconds. The ratio obtained from area analysis was found the same as that from point analysis. The artifact may not have contributed to the variation of the ratio. The variation must have been due to the difference of ratios from whisker to whisker. The result may show that different types of nanowhiskers with various oxygen contents were made by this method. Electron energy loss spectroscopy was also performed for the quantitative analysis of nanowhiskers. But since the background signals for the standard and specimen were not uniform, background modeling did not work, and no consistent results were obtained.

Conclusions

Manganese oxide nanowhiskers were characterized using SEM, TEM, STEM, EDS, and EELS techniques. They were found to show a three dimensional structure, forming bundles with individual nanowhiskers of the same crystallographic direction. Nanowhiskers had many defects possibly of a short range ordered point type. Nanowhiskers also had variations of the oxygen to manganese ratio in the range from 0.7 to 1.6, showing that various types of nanowhiskers were made.

Acknowledgement

Authors are grateful to Dr. C. Mittelbauer for his technical help. This work was supported by Kyungnam University Research Fund.

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