

SOLUTION-BASED SYNTHESIS OF MAGNESIUM OXIDE NANORODS

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ABSTRACT

A solution-based synthesis route was developed to produce large quantities of MgO nanorods. Hydrated basic magnesium chloride, which has needle-like crystal structure, was used as a precursor. A subsequent two-step transformation process with magnesium hydroxide as an intermediate product was used to preserve the morphology of the precursor to yield magnesium oxide nanorods. Scanning electron microscopy, powder X-ray diffraction and energy dispersive X-ray spectroscopy show that the products are very pure (>95%) crystalline MgO nanorods with diameters from 40 nm to 200 nm and lengths 10 microns or longer. High-resolution transmission electron microscopy and electron diffraction further reveal that these MgO nanorods are single crystals and that the rod axis is along the $\langle 110 \rangle$ crystal direction. A model for the structural transformation from hydrated basic magnesium chloride to magnesium oxide has been developed and compared to our experimental results. This solution-based process can be easily scaled-up, and is a low-cost source of pure magnesium oxide nanorods needed in many industrial applications, for example, as reinforcing agents in matrix composites and as flux-pinning centers in high- T_C superconductors.

INTRODUCTION

Magnesium oxide is an inorganic compound having very good heat resistance, thermal conductivity and alkali resistance [1]. Magnesium oxide whiskers have been produced and utilized as filling agents in composite materials to achieve better mechanical strength, thermal shock resistance and thermal conductivity [2]. For example, MgO whiskers were shown to be effective reinforcing agents for improved thermomechanical properties of BSCCO high- T_C superconductors [3,4]. More interestingly, MgO whiskers with diameters in the nanometer range, that is, MgO nanorods, can act as effective flux-pinning centers when incorporated into high- T_C superconductors and lead to enhanced critical current densities [5-7], which are crucial to most large-scale applications of the high- T_C superconductors. It is also expected that MgO nanorods are better reinforcing agents compared to their micron-sized cousins because the toughness and strength of single-crystalline whiskers increase with decreasing whisker diameters [8].

Currently most magnesium oxide nanorods are synthesized via vapor phase process. For example, carbothermal reduction of MgO at at least 1200 °C and subsequent re-oxidization of Mg vapor and condensation of MgO nanorods has been reported [5-7]. However, it is difficult to scale up this process without the formation of thick whiskers and round particles. In addition, this method is not cost-effective because of the high processing temperatures. In this paper, we report a simple solution-based procedure capable of producing large quantities of very pure (>95%) magnesium oxide nanorods.

EXPERIMENTAL METHODS

Basic magnesium chloride was chosen as a precursor because of its needle-like crystal morphology [9,10]. Precursor nanorods were prepared by the reaction between magnesium chloride solution and magnesium oxide supersaturated in the solution. After 48 hours of reaction

at room temperature the precipitate was collected and washed with isopropanol. Basic magnesium chloride nanorods were then transformed into magnesium hydroxide nanorods by base (NaOH) treatment at 60 °C in a mixed solvent of ethanol and water (3:1). Lastly the dried magnesium hydroxide nanorods were heated in flowing oxygen slowly to 900 °C and calcined at 900 °C for one hour to finish the conversion to crystalline magnesium oxide nanorods.

The morphology and structure of the products were examined by field-emission scanning electron microscopy (SEM) (LEO 982) and transmission electron microscopy (TEM) (Philips EM420 and JEOL 2010) equipped with energy dispersive X-ray (EDX) spectroscopy to evaluate the chemical composition. The phase analysis was performed using powder X-ray diffraction (XRD) (Scintag XDS2000).

RESULTS AND DISCUSSION

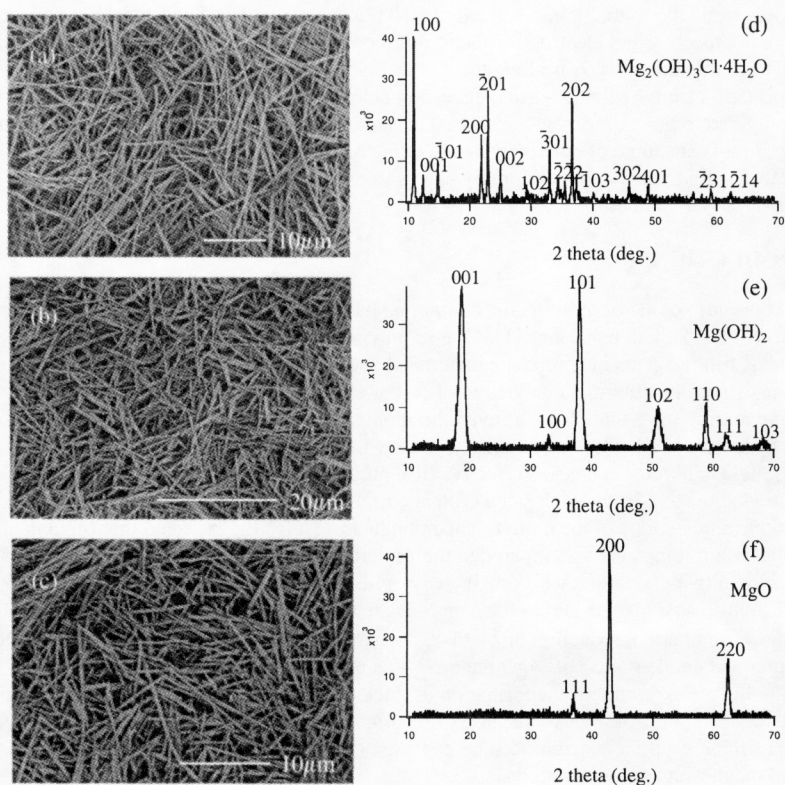


Figure 1. (a) - (c) SEM images of the precursor, the intermediate product after base treatment, and the final product after calcination, respectively. (d) - (f) Corresponding powder XRD patterns of products from each of the step in (a) - (c).

Figure 1 shows typical SEM images of the products from each step and their corresponding powder XRD patterns. The SEM data show clearly that they all have similar rod-like morphology with aspect ratios of at least 50 and relatively good uniformity. XRD patterns show that they are $\text{Mg}_2(\text{OH})_3\text{Cl}\cdot 4\text{H}_2\text{O}$, $\text{Mg}(\text{OH})_2$ and MgO , respectively, and that no second phase is present. This demonstrates a successful transformation from hydrated basic magnesium chloride nanorods to magnesium oxide nanorods via intermediate magnesium hydroxide nanorods. In general, the diameters of MgO nanorods range from 40 nm to 200 nm with an average of 120 nm and the lengths usually are 10 μm or longer. The nanorods have rectangular cross section and are straight and uniform in diameter along the axis. EDX spectroscopy measurements of these rods show no other heavy elements, such as Cl, other than Mg. Powder XRD pattern (figure 1(f)) can be indexed as cubic MgO structure. Together with the EDX measurement, it shows very high phase purity of these nanorods. In addition, from the SEM images it can be seen that particulate impurities are rarely found. Therefore the products are very pure (>95%) crystalline MgO nanorods.

Figure 2 shows a TEM image of a single MgO nanorod. The rod surface looks rough at this magnification. To determine whether the rods are single-crystalline or polycrystalline, electron diffraction patterns were recorded on a number of nanorods. Figure 3 shows three most commonly seen electron diffraction patterns. The arrows in the patterns indicate the direction of the rod axes. Clearly they are single crystalline patterns and can be indexed to the FCC MgO lattice with electron beam directions along $[\bar{1}11]$, $[001]$ and $[\bar{1}12]$ zone axes, respectively. It can be seen that in all three cases the rod axis goes along the $\langle 110 \rangle$ crystal direction. The fact that diffraction patterns of different zone axes can be found in the nanorods is a supplemental evidence of their rod-like morphology. When a rod is rotated around its axis which is the $\langle 110 \rangle$ direction of an FCC lattice, it is expected that electron beam will be coincident with $[\bar{1}11]$, $[001]$

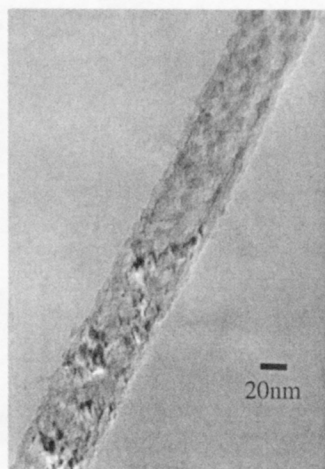


Figure 2. TEM micrograph of a MgO nanorod.

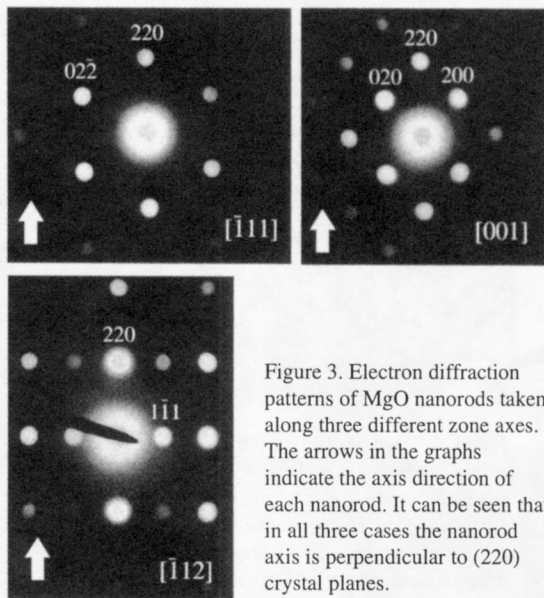


Figure 3. Electron diffraction patterns of MgO nanorods taken along three different zone axes. The arrows in the graphs indicate the axis direction of each nanorod. It can be seen that in all three cases the nanorod axis is perpendicular to (220) crystal planes.

and $[112]$ zone axes. The single crystal nature of these nanorods was further confirmed by high-resolution TEM (HRTEM) studies. Figure 4 shows a HRTEM micrograph of the nanorod. The HRTEM image agrees well with the electron diffraction patterns. The lattice fringe shown is from (220) planes with an inter-plane distance of 1.50\AA . These data confirm that the rod axis is along the $\langle 110 \rangle$ direction, and that the lattice is nearly perfect across the rod.

The $\langle 110 \rangle$ axis direction is also expected in the structural transformation from $\text{Mg}_2(\text{OH})_3\text{Cl}\cdot 4\text{H}_2\text{O}$ to MgO . $\text{Mg}_2(\text{OH})_3\text{Cl}\cdot 4\text{H}_2\text{O}$ has a triclinic structure [11]. The backbone of the structure is formed by puckered layers parallel to (100), consisting of infinite double chains of MgO_6 octahedra extending in the b direction. Figure 5(a) is the schematic plan and elevation view of the backbone structure. The Cl anions, alternating with an equal number of water molecules so as to form rows parallel to b , are situated between the layers. The forces between double chains within one layer or from neighboring layers are relatively weak hydrogen bonds formed by adjacent water molecules, hydroxyl and chloride anions. This explains the needle-like crystal habit of $\text{Mg}_2(\text{OH})_3\text{Cl}\cdot 4\text{H}_2\text{O}$. In the transformation to hexagonal $\text{Mg}(\text{OH})_2$, which has a layered CdI_2 structure, double chains within one layer move to each other to form a continuous layer by removing one half of the oxygen atoms (in the form of water) situated at the MgO_6

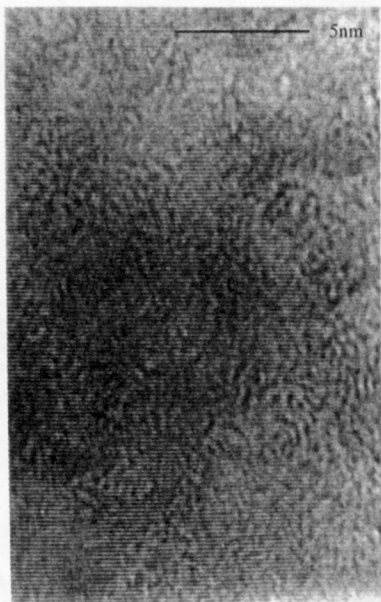


Figure 4. High-resolution TEM micrograph of the MgO nanorod. The edge of the nanorod is along the right edge of the micrograph. The lattice fringes shown are (220) planes with an inter-plane distance of 1.50\AA .

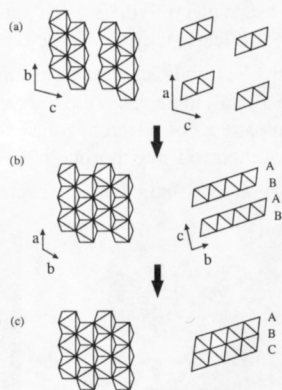


Figure 5. Schematic view of the backbone structures of

- (a) $\text{Mg}_2(\text{OH})_3\text{Cl}\cdot 4\text{H}_2\text{O}$ from a direction in the (001) plane perpendicular to the b axis (left), and from parallel to the b axis (right),
- (b) $\text{Mg}(\text{OH})_2$ from parallel to the c axis (left), and perpendicular to the c axis (right),
- (c) MgO from parallel to the $\langle 111 \rangle$ direction (left), and perpendicular to the $\langle 111 \rangle$ direction (right).

$\text{Mg}_2(\text{OH})_3\text{Cl}\cdot 4\text{H}_2\text{O}$ has a triclinic needle-like structure. $\text{Mg}(\text{OH})_2$ has a hexagonal layered structure. MgO has a face-center cubic (FCC) structure.

Octahedra in the graph stand for MgO_6 octahedra.

octahedron corners between two neighboring double chains. Upon release of the chloride anions and water molecules sitting between the layers, hexagonal $\text{Mg}(\text{OH})_2$ is formed (figure 5(b)). The axis of $\text{Mg}(\text{OH})_2$ nanorods formed in this way will be the a (or b) direction of the hexagonal lattice. Lastly, in the transformation from $\text{Mg}(\text{OH})_2$ to MgO , layers of MgO_6 octahedra in $\text{Mg}(\text{OH})_2$ move to each other to form the continuous three dimensional FCC structure by removing one half of the oxygen atoms (in the form of water) between neighboring layers and changing the stacking sequence from ABABAB... to ABCABC...(figure 5(c)). Therefore the axis of the MgO nanorods should be the $\langle 110 \rangle$ direction of the FCC structure, as we find in our experiments.

The analysis of the structural transformation also helps us understand the importance of using $\text{Mg}(\text{OH})_2$ as an intermediate product in the conversion from $\text{Mg}_2(\text{OH})_3\text{Cl}\cdot 4\text{H}_2\text{O}$ nanorods to MgO nanorods. Experiments show that direct conversion of $\text{Mg}_2(\text{OH})_3\text{Cl}\cdot 4\text{H}_2\text{O}$ to MgO by heat invariably breaks the nanorods into nanoparticles. In removing all the oxygen atoms required in one step, double chains are cut into from at least two faces. This likely promotes the collapse of the double chains and thus the nanorods. Pressure built up at elevated temperature by large amount of side products (three $\text{H}_2\text{O}/\text{HCl}$ molecules per one MgO unit) not released promptly is likely to break the nanorods too. However, in the two-step transformation two thirds of the side products are easily released through the channels between the layers in $\text{Mg}(\text{OH})_2$ by anion exchange reaction operated at close to room temperature. Moreover the structural change is less drastic in the two-step transformation, which also helps to maintain the crystal morphology.

CONCLUSIONS

In summary, a three-step solution-based process using hydrated basic magnesium chloride as a precursor and magnesium hydroxide as an intermediate product has been employed to make very pure single crystalline magnesium oxide nanorods with diameters from 40 nm to 200 nm and an average aspect ratio of 80. This process can be easily scaled-up, and should provide a low-cost source of pure magnesium oxide nanorods needed in many industrial applications.

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