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Nanostructured $Ba_6Mn_{24}O_{48}$ whiskers

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A simple method of simultaneous nanostructuring and chemical modification providing proton conduction of $Ba_6Mn_{24}O_{48}$ whisker crystals is developed for tuning their catalytic, sensory and electrochemical properties.

A new method of $Ba_6Mn_{24}O_{48}$ whiskers growth and techniques for proton and lithium insertion into their structural tunnels[1,2] make this phase potentially attractive as a cathode material in batteries; manganese oxides are also known as prospective sensors and catalysts.[3,4] All these applications require a proper modification of the material surface to change its hydrophilicity/hydrophobicity, superficial adhesion, to protect the surface from corrosion and to achieve finally better functional properties. In this work, we present a robust and simple method of $Ba_6Mn_{24}O_{48}$ whiskers[5] nanostructuring, which would lead to more attractive catalytic, sensory and electrochemical applications[6,7] of this new material.

$Ba_6Mn_{24}O_{48}$ whiskers have been readily grown by isothermal evaporation of a KCl flux with an admixed charge material.[1] High-grade $BaCO_3$ and Mn_2O_3 reagents were mixed to prepare $BaMnO_3$. The precursor powder was milled in heptane for 30–60 min in agate bowls using a planetary micromill (Fritsch Pulverizette 7). The fine powder obtained was then pressed into pellets under uniaxial pressure of ~2–3 kbar and annealed at 1000 °C in air for ~24 h. Thus obtained pellets were vertically placed on their rim into alumina crucibles filled with KCl, then heated up to 950 °C (p_{O_2} = 0.21 atm, 5 K min^{-1}), kept at this temperature for ~50 h and quenched in air. 1–2 mm long $Ba_6Mn_{24}O_{48}$ whiskers grown on the surface of the $BaMnO_3$ pellet were cut off with a blade, washed thoroughly with distilled water to remove remaining non-evaporated flux and dried at 60 °C in a drying chamber for 1–2 h.

Proton insertion into $Ba_6Mn_{24}O_{48}$ whiskers (the whisker H-form formation) was carried out by immersion of the as-grown crystals into concentrated HNO_3[2,4] for three to nine days at room temperature or for 5–7 h under vigorous stirring at 65–75 °C. Then, whiskers were repeatedly washed with distilled water until neutral pH and dried at 60 °C in a drying chamber. To modify the crystals morphologically, powdered $BaMnO_3$ was added to hot nitric acid together with $Ba_6Mn_{24}O_{48}$ whiskers; in such a case, the treatment duration varied from 5 to 12 h. Alternatively, the whiskers placed in a glass vessel with concentrated HNO_3 were sonicated for 3–5 h in a standard ultrasound bath filled with preheated water (60–70 °C).

Phase identification and unit cell parameter determination were carried out by X-ray powder diffraction experiments using a focusing FR-552 Guinier camera ($Cu_{K\alpha 1}$) with germanium as an internal standard. To minimise a fluorescence effect and obtain a high quality XRD spectrum the data were collected at a KEK-PF BL-20B synchrotron source (Tsukuba, Japan) in the Debye–Sherrer geometry (λ = 1.102 Å). Morphology and chemical composition studies were performed using a Supra 50VP scanning electron microscope (LEO) with an INCA Energy+ EDX/WDX analyzer (Oxford).

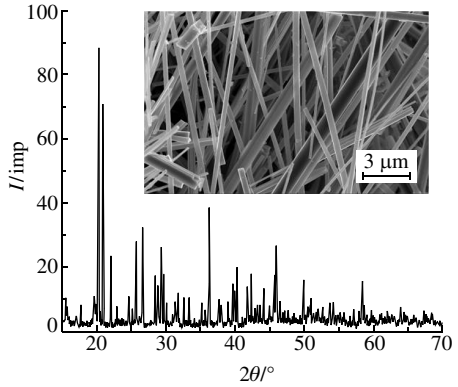

Figure 1 X-ray diffraction pattern (λ = 1.102 Å) of the $Ba_6Mn_{24}O_{48}$ phase. The inset shows a typical SEM micrograph of $Ba_6Mn_{24}O_{48}$ whiskers grown from the evaporating KCl flux.

Formation of $Ba_6Mn_{24}O_{48}$ whiskers was confirmed by XRD and EDX/WDX data (Figure 1).[5] A typical view of $Ba_6Mn_{24}O_{48}$ whiskers is shown in Figure 1. The whiskers grow as chaotically intersecting long fibers forming fluffy fabrics. Such a layer can be mechanically separated from the growth pellet after complete flux evaporation. The whiskers are ~100–500 nm thick and up to several millimeters long. Bushes or closely packed colonies of whiskers forming ~10 μm thick pseudo-single-crystalline needles were also observed. Previously, it was reported that $Ba_6Mn_{24}O_{48}$ whiskers grow preferentially in the [001] direction, while whiskers grown in the [112] direction were also found in a layer of solidified KCl melt.[1] According to the EDX analysis, whiskers are chemically homogeneous corresponding well to the expected ratio Mn:Ba = 4:1.

It was shown that the treatment with nitric acid is the best way to obtain the H-form of $Ba_6Mn_{24}O_{48}$ whiskers. This form is characterised by distinct changes in unit cell parameters (Table 1) while the crystal structure is kept undestroyed. The lattice parameters of $Ba_6Mn_{24}O_{48}$ whiskers three days after the treatment with concentrated nitric acid at room temperature were found to be a = 18.064(3) Å and c = 2.832(5) Å, *i.e.*, the parameter a changes by about 0.15 Å as compared to a = 18.195(1) Å for as-grown whiskers while the parameter c remains almost unchanged [2.838(1)–2.831(1) Å]. According to the EDX / WDX analysis, the barium content of protonated whiskers is 30% decreased down to Mn:Ba = 6:1.

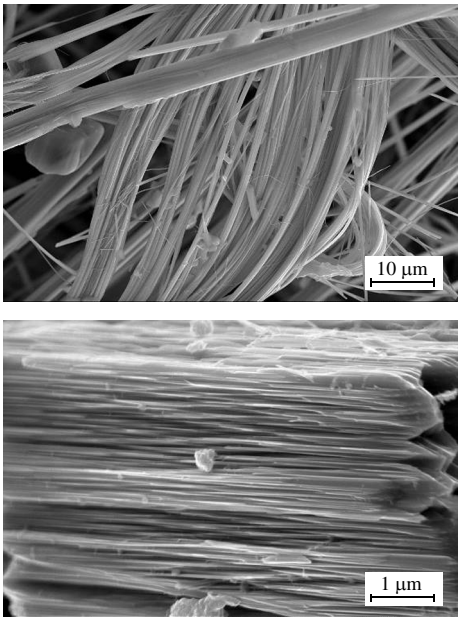

Figure 2 $Ba_6Mn_{24}O_{48}$ whiskers morphology modification upon the H-form formation in concentrated HNO_3. (*a*) Delamination of pseudosingle crystals into separate fibers (seven days of acidic treatment at 25 °C). (*b*) Whisker morphology after acidic treatment for 5 h at 65 °C.

It was also found for the first time that the acid treatment results in dramatic whisker morphology changes (Figure 2). Most of the needles being the colonies of initially intergrown elementary whiskers become delaminated into 20–40 nm thick nanofibers [Figure 2(*b*)] demonstrating surprising flexibility and bending angles up to 90° [Figure 2(*a*)]. This splitting of the whiskers seems to be caused by either internal tension forces resulting from lattice parameters contraction during proton insertion into the structural tunnels or whiskers partial etching [Figure 2(*b*)] in the regions of intergrowth boundaries of the elementary whiskers constituting pseudosingle crystals. The X-ray analysis of protonated whiskers reveals that the crystal structure shrinks anisotropically (Table 1), perpendicular to the tunnel direction and consequently to the whisker growth direction [001], which results in longitudinal splitting. The etching effect might appear due to partial disproportionation of Mn^{III} into Mn^{IV} and Mn^{II}, the latter easily transferring into the solution.[3] Thus, the acid treatment leads to the formation of chemically modified nanowhiskers.

Further effects of surface modification have been achieved by sonication of $Ba_6Mn_{24}O_{48}$ whiskers in the hot nitric acid (Figure 3). These conditions allow us to achieve surface coverage with a submicron layer consisting of nanometer crystals of hydrated MnO_2. Such a small size of the particles in the decorating layer seems to be connected with a known effect of nucleus formation enhancement in an ultrasonic field.[8] Component diffusion enhancement under ultrasonic treatment can

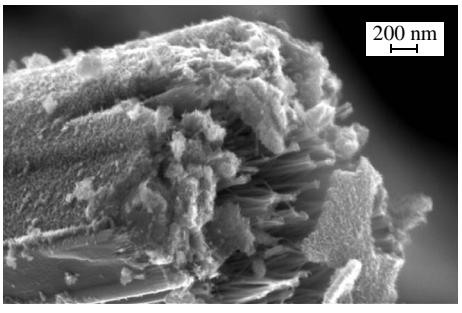

Figure 3 Nanowhisker formation after the sonication of whiskers in nitric acid at 65 °C for 2 h.

Table 1 Lattice parameters of $Ba_6Mn_{24}O_{48}$ whiskers before and after their treatment with concentrated HNO_3 at room temperature.

Parameter	Original whiskers	3 days	6 days	9 days
a/Å	18.195(1)	18.064(3)	18.047(2)	18.030(1)
c/Å	2.831(1)	2.832(5)	2.831(5)	2.831(5)

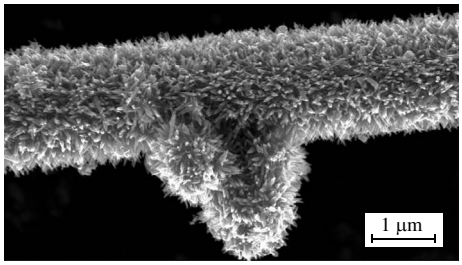

Figure 4 $Ba_6Mn_{24}O_{48}$ whisker morphology change as a result of treatment of original whiskers together with a $BaMnO_3$ admixture with concentrated HNO_3 for 7 h at 65 °C. Thus processed whiskers are decorated with the nanocrystals of hydrated MnO_2 grown on their surface.

also cause a deeper etching of the pseudocrystals leading to the observed complex architecture of such acid-treated whiskers. Another decoration effect was observed for $Ba_6Mn_{24}O_{48}$ whiskers treated with hot concentrated HNO_3 in the presence of powdered $BaMnO_3$ giving 3–10 nm nanoparticles of plate-like hydrous MnO_2 grown on the surface of whiskers (Figure 4). They most probably start to grow on the whisker joints in a pseudosingle crystal or on the etching groove of the H-form. The dissolution and degradation of $BaMnO_3$ particles resulted in the sedimentation of hydrated manganese(IV) oxide on the whiskers. In contrast, ultrasound speeds up the diffusion and facilitates nucleation; thus, supersaturation is released due to the formation of a continuous layer of nanocrystals on the surface of the whisker (Figure 3).

In conclusion, a set of simple techniques is suggested allowing the morphological control of manganite whiskers with a tunnel crystal structure. These experimental results could be important for achieving new functional performance of the whiskers.

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