Patterned Growth of TiO$_2$ Nanowires on Titanium Substrates

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The vapor–liquid–solid (VLS) method in an inductively heated reactor to synthesize high-quality oxide NWs with extremely short growth mechanisms have been successfully realized to fabricate nanostructured TiO$_2$ NWs on Ti foil substrates patterned with Sn nano-islands. In this facile approach, the reactive Ti foil both as a substrate and as a metal supply, thus eliminating the need for a separate titanium source.

nanostructured TiO$_2$ has versatile chemical, electrical, optical, and mechanical properties that are important for application in catalysis,$^1$ optical devices,$^2$ gas and humidity sensors,$^3,4$ solar cells,$^5$ Li-ion batteries,$^6$ and biomedical materials.$^7$ TiO$_2$ nanowires (NWs) can be synthesized by a variety of wet chemistry and vapor transport methods. Adachi et al. have reported the synthesis of titania NWs using hydrothermal reactions in the presence of micelles.$^8$ The fabrication of TiO$_2$ NWs by the direct oxidation of titanium substrates$^9$ and chemical vapor deposition (CVD)$^{10,11}$ including metal–organic CVD$^{12}$ has also been reported. However, these methods typically require complex setups and processes, harsh environmental conditions, and extended processing times.

We have recently reported the fabrication of nanostructures such as carbon nanotubes,$^{13}$ zinc oxide NWs,$^{14}$ and TiO$_2$ nano-“swords”$^{15}$ in an inductively heated system. The vapor–liquid–solid (VLS)$^{14}$ and the vapor–solid (VS)$^{15}$ growth mechanisms have been successfully realized to fabricate high-quality oxide NWs with extremely short heating times. In this study, we utilized the metal-catalyst VLS method in an inductively heated reactor to synthesize TiO$_2$ NWs on a Ti foil substrate patterned with Sn nano-islands. In this facile approach, the reactive Ti- and O-containing species were supplied by the titanium substrate and residual oxygen from the carrier gas, respectively.

The growth process started with the deposition of a 200-nm-thick titanium layer by thermal evaporation onto a 0.5-mm-thick Ti foil, followed by thermal evaporation of a 50-nm-thick Sn film using a transmission electron microscopy (TEM) grid as a shadow mask to create a periodic array of $70 \times 70 \mu$m$^2$ square patterns. The Sn-patterned Ti substrate was placed on a susceptor inside the induction heating system described in ref. 15. After the quartz chamber was evacuated to 250 mTorr, Ar with 2% H$_2$ (99.99% purity) was introduced into the system through a mass-flow controller. Upon reaching 1 atm, the gas flow was terminated and the sample was subjected to inductive heating. After reaching 850°C within 10 s (as monitored by optical pyrometry), the process temperature was held for 10 min followed by a power-off cooling process.

The crystal structure of the fabricated TiO$_2$ NWs was analyzed by X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM). The shapes, composition, and microstructure of NWs were characterized by field-emission scanning electron microscopy (FESEM), equipped with X-ray energy dispersive spectroscopy (X-EDS) and electron backscatter diffraction (EBSD).

Figure 1 shows an array of TiO$_2$ NWs fabricated on titanium foil. NWs grew selectively within the Sn-patterned squares, clearly demonstrating the catalytic effect of Sn on the growth process. The lengths of the NWs varied from 3 to 8 μm, and their diameters varied from 50 to 500 nm. The high-magnification SEM (Fig. 1, inset) image shows a representative NW of rectangular prismatic shape with the solidified catalytic droplet atop. X-EDS elemental analysis confirmed that the droplets were tin-based, while the NWs were composed of titanium and oxygen (33 ± 2 at. % Ti and 67 ± 2 at. % O, which corresponds to the TiO$_2$ stoichiometry).

Microstructural EBSD analysis (Fig. 2) substantiated the X-EDS results: the catalytic caps had β-Sn structure and the NWs were single crystals with rutile structure. According to EBSD, the NW growth direction was along the [110] axis and the prismatic side facets were (001) and (110) planes. TEM analysis (not shown) verified the NW growth axis and facet identification and indicated that the NWs were virtually free of structural defects.

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**Fig. 1.** Plan-view SEM image of periodic array of TiO$_2$ NWs fabricated on Ti foil. The Sn-based cap is clearly visible atop the NW (marked with arrow) in the inset, indicating the VLS growth mechanism.
The third phase was identified as titanium (P42/mnm; a = 0.4584 ± 0.0002 nm, c = 0.2955 ± 0.0001 nm) and tin (I41/amd; a = 0.5830 ± 0.0003 nm, c = 0.3179 ± 0.0002 nm), was expected because of the EBSD and TEM analyses of the NWs and agreed well with the reference XRD data.\textsuperscript{16,17} The third phase was identified as Ti-based hcp P63/mmc and was thought to come from the titanium substrate. However, its experimental lattice parameters (a = 0.2958 ± 0.0005 nm, c = 0.4756 ± 0.0006 nm) were significantly larger than those of pure titanium (a = 0.2950 nm, c = 0.4686 nm\textsuperscript{18}), suggesting the formation of a Ti\textsubscript{1−x}O\textsubscript{x} phase due to the dissolution of oxygen in the titanium foil. Based on the known compositional dependence of lattice parameters for the Ti\textsubscript{1−x}O\textsubscript{x} solid solution,\textsuperscript{18} the x value was calculated to be 0.19 ± 0.03 (i.e., 81 ± 3 at.% Ti and 19 ± 3 at.% O). The dissolution of oxygen in the substrate during growth was verified by point-to-point microstructural EBSD and compositional X-EDS analyses on a cross-sectional sample from Fig. 1. The perspective SEM view of such a sample in Fig. 4(a) revealed two distinct layers underneath the NWs. It can be seen that the top 1-μm-thick “layer A” was partially delaminated from the adjacent thick substrate “layer B”. Cross-sectional X-EDS line scan (not shown) identified “layer A” as having 34 ± 2 at.% Ti and 66 ± 2 at.% O (i.e., close to TiO\textsubscript{2} stoichiometry), while the adjacent ca. 250-μm-thick “layer B” had an average composition of 82 ± 2 at.% Ti and 18 ± 2 at.% O. EBSD analysis of the top surfaces of both layers identified “layer A” as the TiO\textsubscript{2} rutile phase [Fig. 4(b)] and the adjacent substrate “layer B” as the hcp P63/mmc phase [Fig. 4(c)]. The SEM/EBSD results explain the XRD results in Fig. 3: the TiO\textsubscript{2} peaks (filled squares in Fig. 3) are reflections from both NWs and “layer A”, while the Ti\textsubscript{1−x}O\textsubscript{x} peaks (open circles in Fig. 3) are from the partially oxidized “layer B”. Thus, SEM, EBSD, and XRD consistently describe the final product microstructure, which consisted of single-crystalline TiO\textsubscript{2} NWs that grew on top of a 1-μm-thick TiO\textsubscript{2} polycrystalline layer, which in turn resided on the Ti\textsubscript{1−x}O\textsubscript{x} (x = 0.19 ± 0.03) substrate layer.

A schematic diagram of the growth process is given in Fig. 5, and can be summarized as follows: the Sn-coated Ti substrate reacts at elevated temperatures with O\textsubscript{2} and forms three distinct products: (i) TiO\textsubscript{2} NWs, (ii) TiO\textsubscript{2} polycrystalline thin film (“layer A”), and (iii) Ti\textsubscript{1−x}O\textsubscript{x}, partially oxidized titanium substrate (“layer B”). For (i),
NWs apparently grow via the VLS mechanism: molten tin islands, which form upon dewetting from titanium substrate, act as catalytic nucleation sites by absorbing O- and Ti-containing gas species with subsequent precipitation of TiO\textsubscript{2} phases. The formation of both layers is in good agreement with previously reported titanium oxidation experiments, in which two distinct processes take place: oxygen dissolution and "rutile-scale" formation\textsuperscript{21-23}. While there were no in-situ growth and observation experiments here, it is reasonable to assume that the NW growth (i) proceeds in parallel with the substrate oxidation processes (ii) and (iii).

In conclusion, single-crystalline rutile TiO\textsubscript{2} NWs were fabricated by the tin-catalyst assisted VLS method in an inductively heated CVD reactor. Patterned titanium substrates served as a source of Ti-containing reactive species, while residual oxygen was supplied from the ambient gas in the reactor. Sn-capped TiO\textsubscript{2} NWs were 3 to 8\,\mu m in length and 50 to 500\,nm in diameter. The NWs had a rectangular cross section with (110) and (001) side facets and grew along the [110] axis. This facile approach, with fast induction heating and a short processing time, in which the metal foil serves both as a substrate and as a material source for the oxide growth, could be readily applied for a variety of metal oxide NW fabrications.

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