Metal Oxide Nanotubes

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Formation of Metal Oxide Nanotubes in Neutral Aqueous Solution Based on a Photocatalytic Effect**

Dong Sik Kim, Yang Yang, Hyunbin Kim, Andreas Berger, Mato Knez, Ulrich Gösele, and Volker Schmidt*

In memory of Ulrich Gösele

Hollow nanotubes are of great interest for use as catalysts[1] and gene delivery vehicles,[2] and in terahertz electronic devices.[3] Diverse approaches to fabricating such hollow nanostructures have been discussed: catalytic growth,[4] transformation of core–shell nanowires into nanotubes by the Kirkendall effect,[5] the use of porous templates,[6] hydrothermal synthesis based on ion-exchange reactions,[7] self-assembly,[8] and gas-phase synthesis.[9] Alternative methods with simple and straightforward procedures may provide new insights into the design of nanomaterials.

Here, we present a new concept for forming nanotubes based on a photocatalytic effect. As examples, ZnO–TiO_2 and CuO–TiO_2 core–shell nanowires undergo a reaction in a neutral aqueous solution under UV light. The resulting oxide nanotubes show a uniform and tunable wall thickness. Mechanisms for the tube formation will be suggested and discussed.

The morphology of the ZnO–TiO_2 core–shell nanowires was investigated by transmission electron microscopy (TEM). For details on sample preparation see the Experimental Section. Figure 1 a shows typical ZnO nanowires coated with a TiO_2 shell. A uniform layer of amorphous TiO_2 with a thickness of 25 nm on a single-crystalline ZnO nanowire is visible in Figure 1 b. Energy-dispersive X-ray (EDX) analysis revealed a characteristic intensity profile of core–shell nanowires where the intensities of Zn and Ti are predominantly in the core and the shell part, respectively (Figure 1 e).

After exposure of the samples in neutral aqueous solution to UV light for 2 h, hollow TiO_2 nanotubes with uniform, smooth walls had formed (Figure 1 c; a magnified view of a single nanotube is shown in Figure 1 d). ZnO was completely eliminated from the core part of the nanowires, and the reaction resulted in a TiO_2 nanotube without any structural modification or damage. EDX line analysis across the nanotube revealed the distinct presence of Ti in the nanotube. The intensity of the Zn signal in the TiO_2 shell was below the detection limit (Figure 1 f).

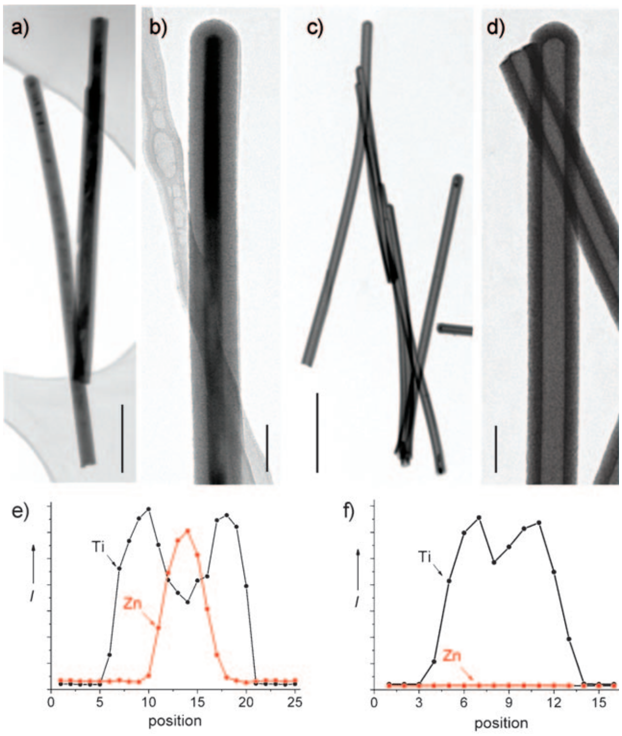

Figure 1. a) Typical TEM image of single-crystalline ZnO nanowires coated with a TiO_2 layer 25 nm thick by atomic layer deposition; scale bar: 250 nm. b) Magnified view of a ZnO–TiO_2 core–shell nanowire; scale bar: 80 nm. c) Typical TEM image of TiO_2 nanotubes formed under UV irradiation for 2 h in aqueous solution; scale bar: 650 nm. d) Magnified view of a TiO_2 nanotube; scale bar: 100 nm. e) EDX line analysis across a single ZnO–TiO_2 core–shell nanowire. f) EDX line analysis across a single TiO_2 nanotube.

We evoke a photocatalytic effect as part of the etching mechanism that leads to the formation of the hollow nanotubes. It is known that the photocatalytic reaction of water with TiO_2 produces H^+ ions.[12,13] Once the aqueous solution in the vicinity of the TiO_2 surface under UV irradiation is saturated with H^+ ions, the ions might diffuse partly to the ZnO core through the nanoshell. The diffusion length of H^+ ions through a TiO_2 shell is apparently more than 50 nm since TiO_2 nanotubes with a thickness of 50 nm were formed in controlled experiments. Eventually, a chemical reaction can take place continuously at the ZnO–TiO_2 interface. To verify the diffusion of H^+ ions through the oxide shell, a controlled

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[*] Dr. D. S. Kim, Dr. Y. Yang, Dr. H. Kim, Dr. A. Berger, Dr. M. Knez, Prof. U. Gösele, Dr. V. Schmidt
Max Planck Institute of Microstructure Physics
Weinberg 2, 06120 Halle (Germany)
Fax: (+49) 345-551-1223
E-mail: dskim@mpi-halle.de

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experiment was carried out. ZnO nanowires with a TiO_2 coating 32 nm thick were prepared on a Si substrate and immersed in a strongly acidic solution (0.1M HCl, pH 1) for 2 h without UV light at room temperature. In this case, too, TiO_2 nanotubes formed as a result of the chemical reaction of ZnO with H^+ ions diffusing through the TiO_2 wall (a typical TEM image of TiO_2 nanotubes is shown in Figure S1 in the Supporting Information).

The reactions at the photocatalytically active TiO_2 surface and the interface under UV light might be described by Equations (1; h^+ = photoexcited 'hole') and (2). Also, ZnO with adsorbed H^+ ions produced by the Equation (1) can be decomposed under UV light according to Equation (3; h^+ = photoexcited 'hole').[14] Note that the pH of the neutral aqueous solution does not change during the reaction.

$$H_2O + 2\,h^+ \rightarrow 2\,H^+ + {}^1\!/_2\,O_2 \qquad (1)$$

$$ZnO + 2\,H^+ \rightarrow Zn^{2+} + H_2O \qquad (2)$$

$$ZnO\text{-}H^+ + h^+ \rightarrow Zn^{2+} + {\cdot}OH \qquad (3)$$

The evolution of the hollow nanotubes was analyzed by a series of TEM investigations (Figure 2). Initially, small voids form at the interface between the core and the shell of the nanowire. Over time the voids (Figure 2c) enlarge and finally merge (Figure 2d). After exposure of the samples to UV irradiation for 2 h most of the nanowires are hollow (Figure 2e).

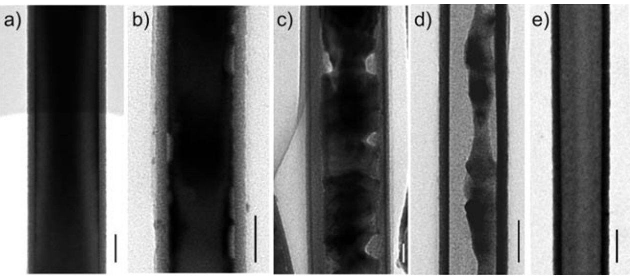

Figure 2. TEM images of ZnO–TiO_2 core–shell nanowires after irradiation with UV light for a) 0 min, b) 10 min, c) 30 min, d) 60 min, and e) 120 min; scale bar: 50 nm.

From Figure 2b,c it can be derived that the etching behavior is facet-dependent; this is more evident under specific etching conditions.[15] H^+ ions in Equation (3) will be predominantly adsorbed on the O polar surface of ZnO, and the reaction results in rugged ZnO nanowires while the etching proceeds. As the reaction continues, the Zn^{2+} ions resulting from the decomposition diffuse out through the amorphous TiO_2 shell, and the resulting H_2O molecules undergo the photocatalytic reaction on the TiO_2 surface.

The efficiency of the etching reaction may depend on the crystallinity of TiO_2, but the ZnO nanowires were etched under the conditions described above even with an amorphous TiO_2 shell. In addition, it is worth noting that the dissolution of core nanowires also takes place at the exposed open ends of the photocatalytically active ZnO nanowires through reactions (1)–(3) since the H^+ ions produced by the direct splitting of water on the ZnO surface under UV light will initiate the etching.[16] To confirm this hypothesis, ZnO nanowires grown on a substrate were coated with an alumina shell, which has no photocatalytic activity. After these core–shell nanowires had been prepared on a TEM grid, the samples were placed in neutral aqueous solution and irradiated with UV light. An EDX spectrum of a ZnO–Al_2O_3 core–shell nanowire is shown in Figure S2 in the Supporting Information. As shown in Figure 3, ZnO nanowires started to decompose from the open end of the nanowires, not from the interface. After UV irradiation for 4 h most of the core–shell nanowires changed into alumina tubes.

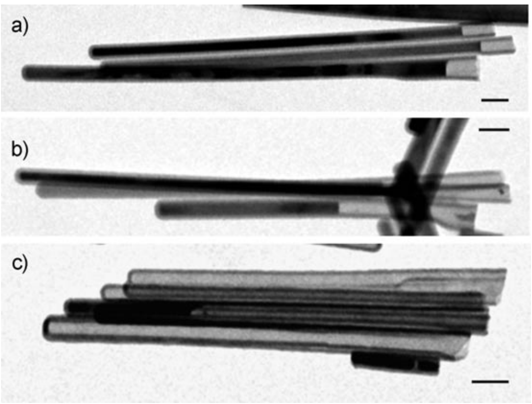

Figure 3. TEM image of ZnO–Al_2O_3 core–shell nanowires exposed to UV light for a) 10 min, b) 30 min, c) 4 h; scale bar: 100 nm.

To demonstrate that this method for nanotube formation is generally applicable, we also applied the concept to another metal oxide material, CuO. CuO nanowires, which had been grown on a TEM grid, were coated with an amorphous TiO_2 layer 25 nm thick. Figure 4a shows a typical TEM image of

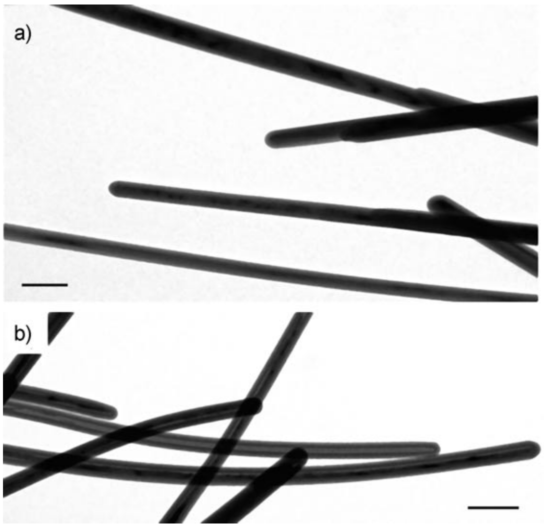

Figure 4. a) Typical TEM images of CuO nanowires grown on a TEM grid and coated by atomic layer deposition with a TiO_2 layer 25 nm thick. b) Typical TEM images of TiO_2 nanotubes after UV irradiation in aqueous solution for 2 h; scale bar: 200 nm.

these CuO–TiO_2 core–shell nanowires; an EDX line analysis is shown in Figure S3 in the Supporting Information. Figure 4b shows TiO_2 nanotubes formed after UV irradiation for 2 h. In this case, the CuO nanowires might chemically react with H^+ ions produced locally at the TiO_2 outer shell according to Equation (4). Subsequently, Cu ions might diffuse out through the TiO_2 wall.

$$CuO + 2\,H^+ \rightarrow Cu^{2+} + H_2O \qquad (4)$$

The approach presented here is highly selective and controllable and works in a neutral aqueous solution. The shape and morphology of hollow nanostructures can be fine-tuned. For instance, hollow spheres as well as multiple-wall metal oxide nanotubes can be fabricated based on this simple method. TiO_2 nanotube arrays fabricated by use of ZnO nanowires grown on substrates epitaxially or non-epitaxially[17] may be suitable for applications in energy-harvesting devices.[18]

In summary, we have developed a facile and efficient method for the fabrication of hollow oxide nanotubes based on a photocatalytic effect. H^+ ions, which are produced locally at TiO_2 nanotubes by the splitting of water under UV irradiation, diffuse to the ZnO or CuO cores and result in the formation of oxide nanotubes. This approach can be used to prepare TiO_2 nanostructures with various shapes. Furthermore, different material such as MgO, CdS, and ZnS may be used as reactive nanotemplates. Since MgO nanowires are frequently grown with a square cross-section, square-shaped tubes of TiO_2 could be produced.

Experimental Section

Preparation of the core–shell nanowires: Single-crystalline ZnO nanowires were prepared on Si substrates by using a vapor transport deposition method. Typically, the ZnO nanowires had a diameter of 20–100 nm and a length of several μm. Details on the experimental methods are given in Ref. [10]. For the growth of CuO nanowires, bare TEM Cu grids used as both source material and substrates were loaded in a quartz boat and placed inside a tube furnace in air at 475 °C for 2 h.[11] The diameter and the length of CuO nanowires varied in the range of 30–100 nm and tens of μm, respectively. The as-prepared nanowires were conformally coated with TiO_2 or Al_2O_3 by atomic layer deposition (ALD). Titanium isopropoxide (TIP) and deionized water for the TiO_2 deposition, while trimethylaluminum (TMA) and deionized water were used for the Al_2O_3 deposition. For TiO_2 coating, depositions were performed at 70 °C under N_2 atmosphere. The shell thickness in the core–shell structures was mainly controlled by the number of reaction cycles. For example, 350 reaction cycles were performed for TiO_2 coatings 12.5 nm thick, and 650 cycles were used for TiO_2 coatings 25 nm thick. For Al_2O_3 coating, 75 cycles under N_2 atmosphere were used for the deposition of an Al_2O_3 layer 12 nm thick.

For the etching experiment, the core–shell nanowires were prepared by the following procedure: First, the samples of core–shell nanowires were scratched with a sharp knife, put into a small bottle filled with methanol, and sonicated in an ultrasonic bath for 10 s. Then a TEM grid was placed in the bottle for a short time and then was dried in air. The final step was repeated twice. Finally, the TEM grid sample was placed in an aqueous solution in a small glass beaker and was irradiated at room temperature with a UV lamp (UVP Inc.) at a distance of 10 cm. The UV light used has a wavelength of 254 nm and a power of 15 W. In the case of TiO_2–CuO core–shell nanowires, the TEM grid samples were directly subjected to UV irradiation in water without further treatment.

The surface microstructure and morphological changes in the core–shell nanowires were investigated by transmission electron microscopy (TEM), and the elemental line scan profiles were determined by energy dispersive X-ray (EDX) in the scanning TEM mode.

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