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Unexpected Long-Term Instability of ZnO Nanowires “Protected” by a TiO_2 Shell

Yang Yang,* Dong Sik Kim, Yong Qin, Andreas Berger, Roland Scholz, Hyunbin Kim, Mato Knez, and Ulrich Gösele

Max Planck Institute of Microstructure Physics, Weinberg 2, 06120 Halle, Germany

Received July 22, 2009; E-mail: yangyang@mpi-halle.de

ZnO nanowires (NWs) are probably among the most important one-dimensional (1-D) nanomaterials for future device applications.[1,2] The unique properties of ZnO make ZnO NWs great candidates for solar cells,[3] sensors,[4] UV lasers,[5] light emitting diodes,[6] energy generators,[7] and photocatalysts.[8] Typical nanodevices involving ZnO NWs are expected to work under ambient conditions. In a dry, low humidity environment, the long-term stability of ZnO NWs is usually considered unproblematic because ZnO is neither reactive to air nor sensitive to light.[9] Besides, ZnO is remarkably resistant to damage by energetic particles. The high mobility of interstitial pairs in ZnO allows for rapid defect annihilation even at low temperatures.[10] Therefore, the inherent reliability of these nanodevices generally profits from the stability of ZnO NWs when they operate under ambient conditions.

Furthermore, ZnO NW-based 1-D heterocomposites have been developed for improved or optimized performance in nanodevices as compared to pure ZnO NWs. One attractive core−shell concept was recently demonstrated in ZnO NW dye-sensitized solar cells.[11] It was found that a 10−25 nm conformal TiO_2 shell on ZnO NWs could lead to a dramatic increase in open-circuit voltage and fill factor with little current falloff. In addition, a substantial improvement in overall conversion efficiency was achieved. This superior performance was attributed to the high band edge energy of TiO_2, which suppressed interfacial recombination and built up a radial energy barrier that repels electrons from the ZnO NW surface. This functionalized coating makes TiO_2 more promising than other oxides such as Al_2O_3 which can only work as insulating barriers. However, in this communication we will demonstrate that ZnO NWs covered with a “protective” TiO_2 shell show an unexpected long-term instability under ambient conditions which should be taken into account for the application of such structures, e.g. in photoelectric devices.

Figure 1a shows a typical TEM image of *c*-(0001) oriented single-crystalline ZnO NWs freshly coated with a uniform 5-nm TiO_2 film by atomic layer deposition (ALD). The as-prepared coaxial NWs present a compact and intact core−shell interface structure. The TiO_2 shell is amorphous owing to the low deposition temperature (100 °C). Interestingly, a gradual loss of ZnO cores was observed during long-term storage under ambient conditions. As summarized in Figure 1b, visible voids appeared at the core−shell interfaces of the different-sized NWs after 1 month. The loss of ZnO was obviously aggravated after 9 months, given that discontinuous nanotubes and even totally hollow thin nanotubes were often encountered during our TEM observations (Figure 1c). To further clarify this morphology alteration, we deposited TiO_2 films of various thicknesses such as 12 and 42 nm, respectively, around the same ZnO NWs by ALD (Figure S1). It took more than 4 months to find the prevalent interfacial void formation when the thickness of the TiO_2 shell was increased to 12 nm (Figure 1d). In contrast, a much thicker TiO_2 shell of 42 nm again accelerated the loss of the ZnO cores. Figure 1e shows typical images of this sample aged for 2 months, where even some completely hollow 1-D nanostructures were observed. EDX analysis (Figure S2) confirms that these nanotubes are just composed of titania. We only detected very feeble Zn signals which are distributed over the surroundings. These findings also elucidate an unexpected phenomenon (Figure S3 and its note) during the fabrication of 1-D nanoscale zinc titanate from ZnO/TiO_2 core−shell coaxial NWs.[12]

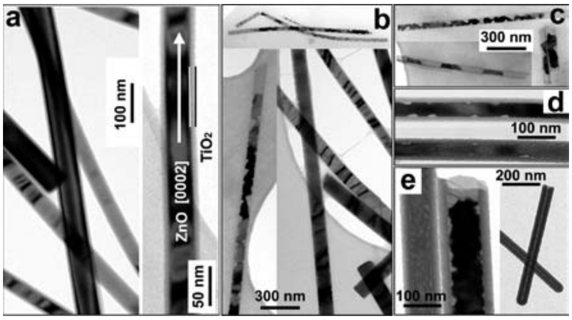

Figure 1. (a) TEM image of as-deposited ZnO NWs with a 5-nm TiO_2 shell by ALD. The ZnO NWs are *c*-(0001) oriented. TEM images of ZnO NWs covered by a 5-nm TiO_2 film stored under ambient conditions for (b) 1 and (c) 9 months; (d) by a 12-nm TiO_2 film stored for 4 months; (e) by a 42-nm TiO_2 film stored for 2 months.

It is known that ZnO undergoes photolysis in the presence of moisture under strong UV irradiation.[13−15] When ZnO NWs are aged under ambient conditions, electron and hole (e^-/h^+) pairs are supposed to be generated by absorption of trace UV photons from the daylight. Some unrecombined h^+ will then migrate to their surfaces. Usually the fresh surface of oxides can quickly become saturated with moisture from the air.[16] The encounter of the h^+ and water might lead to a sluggish corrosion of the ZnO NWs. However, the side faces of uncoated ZnO NWs never became rugged even after storage for 2 years. Moreover, we coated a 10-nm Al_2O_3 film on the ZnO NWs by ALD. It was found that partial ZnO NW cores only became slightly shortened from their open ends during 2 years (Figure S4a). This minor end-initiated corrosion might also occur to our uncoated ZnO NWs. However it is more difficult to detect this change when there was no Al_2O_3 shell as a reference. The above results indicate that the photocorrosion of uncoated and Al_2O_3-coated ZnO NWs under ambient conditions is generally negligible.

The uncoated ZnO NWs were seriously photoetched (Figure S4b) when they were put into neutral aqueous solutions under direct UV irradiation (254 nm; 15 W). From the residual fragments of some ZnO NWs, we confirm that the self-induced photocorrosion of *c*-(0001) oriented ZnO NWs preferentially started from the NW ends (Figure S4c). We further investigated the evolution of the

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Al_2O_3-shelled and TiO_2-shelled ZnO NWs during exposure to UV light in aqueous solution (Figure S4d, e). The photoetching of the ZnO/Al_2O_3 coaxial NWs only processed from the ends, showing the same behavior as that of uncoated ZnO NWs. However, the etching of the ZnO/TiO_2 coaxial NWs occurred at the ends as well as the core−shell interfaces,[17] comparable to their behavior in air. In addition, this etching mode is unaffected when the amorphous TiO_2 was transformed into anatase (Figure S4f).

Water-assisted photolysis has been found to be face-dependent for bulk ZnO single crystals.[15] The polar ZnO(0001)-O surface exhibits the most pronounced photolysis compared with nonpolar sides like ZnO(1010). This selectivity indicates that the nonpolar surfaces of ZnO are rather inert to photolysis. The side faces of *c*-(0001) oriented ZnO NWs are usually enclosed by (1010) and (1120) nonpolar surfaces. This structure explains why the photocorrosion of *c*-oriented ZnO NWs generally processes along the NW ends. The preferentially etched surfaces are either (0001)-O or (0111)-O polar faces (see panels (1) and (2) in Figure 2c), which was confirmed by our observations (Figure S4c).

The situation is drastically different when the ZnO NWs are enclosed by a conformal TiO_2 shell. Similar to ZnO, wide band gap TiO_2 is also an efficient photocatalyst that can provide photogenerated holes with higher oxidizing power.[18] Therefore, when the ZnO/TiO_2 core−shell NWs were exposed to daylight under ambient conditions, more e^-/h^+ pairs could be excited as compared to the ZnO or ZnO/Al_2O_3 NWs. It is expected that partial dissociative h^+ generated by the TiO_2 will gradually migrate to the core−shell interface and accordingly augment the local density of the h^+ in certain restricted spots. The interfacial TiO_2 is hardly affected because of its high light stability even in water. Consequently, the concentrated h^+ in conjunction with the absorbed moisture will sufficiently attack both the polar end faces and the nonpolar side faces of the ZnO NWs via a possible pitting corrosion. This TiO_2 enhanced photocorrosion process can persist during storage. With the gradual loss of ZnO, interfacial voids will be created and enlarged along the whole surface of the ZnO NW core, and finally a tubular structure will develop.

Figure 2a, b show representative TEM images of the ZnO NWs coated by a 5-nm TiO_2 shell after storage under ambient conditions for 9 months. It can be seen that most ZnO cores have been etched and only several residual fragments with unusual morphologies are encapsulated by an integral TiO_2 shell. A close view reveals that the voids developed from the core−shell interface have a given crystallographic shape. All the individual voids (marked by the arrows in Figure 2a) show a combination of a polar ZnO(0111) surface and a nonpolar one, which is (0112), (0113), or (0114) of ZnO (panel (3) in Figure 2c). Obviously, the photoetching in these voids is still face-dependent, which most probably developed along the polar ZnO(0111)-O surface from one direction and terminated by some nonpolar surface from the other side. This result also demonstrates that once the nonpolar surfaces were breached, plentiful fresh polar facets could be exposed along the ZnO NW surface. Formation of so many photocorrosion-sensitive facets might also accelerate the loss of the ZnO NWs during storage. Based on our current TEM observations, there is no linear relationship between the photocorrosion rate of ZnO and the thickness of TiO_2. Although a thicker TiO_2 shell can provide more photogenerated e^-/h^+ pairs, it widens the migration distance of the free h^+ to the core−shell interface, which will accordingly increase their recombination probability in transit. The photolysis rate will very likely also depend on the amount of the absorbed moisture at the core−shell interface.

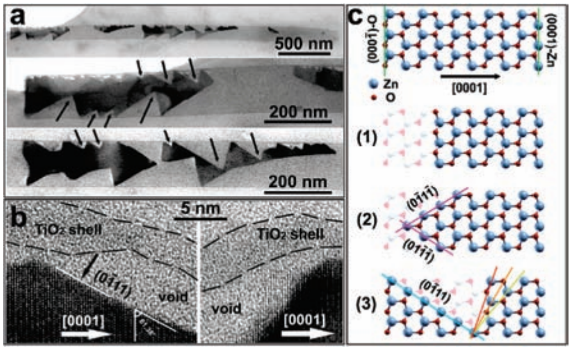

Figure 2. Low (a) and high (b) resolution TEM images of ZnO NWs covered by a 5-nm TiO_2 film stored under ambient conditions for 9 months. (c) Three photoetching modes suggested for *c*-oriented ZnO NWs. The yellow, orange, and red line in panel (3) refers to ZnO(0112), (0113), and (0114) surface, respectively.

In summary, we have shown an unexpected long-term instability of ZnO NWs when they are covered by a conformal TiO_2 shell even under ambient conditions. Although TiO_2 coatings have been widely used as a stable protective barrier for corrosion,[19] as well as a passivation layer for suppressing carrier recombination in ZnO NWs, it appears that such a coating with high band gap semiconductors is actually two-edged, especially for photocorrosion sensitive materials such as CdS, PbS, and ZnO.[13] This shell-enhanced photocorrosion effect should be taken into account in the design of novel 1-D nanoscale core−shell heterocomposites because a potentially unstable structure will directly influence the useful lifespan and performance of the nanodevices involved.

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Supporting Information Available: Materials and Experimental details, Analysis data: TEM and EDS. This material is available free of charge via the Internet at http://pubs.acs.org.

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