# Replacing a Battery by a Nanogenerator with 20 V Output

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We have been working on "self-powered nanotechnology" since 2005 with the aim to build self-powered systems that operate independently, sustainably, and wirelessly without the use of a battery.[1,2] One of the great applications for such a self-powered system is that it can be used for driving portable/wearable personal electronics in our daily life. Nanogenerators (NG) are one of the technologies that are developed to harvest irregular mechanical energy with variable frequency and amplitude in our environment by way of the piezoelectric effect.[3–12] It is designed to have a tolerance for variable environments without relying on the traditional approach of cantilever-based resonators. Irregular mechanical energy can manifest itself in the form of gentle airflows, ambient noise, and activity of the human body, such as walking, typing, etc. Such energy forms are abundant in the working environment for personal consumer electronics. In fact, after sustainable development the NG has been demonstrated to power small electronic devices, such as the lighting of a small LCD screen of a calculator[13] and flashing a single LED.[7,8] But the low output current limits the application of the NG to drive commercial consumer electronics, which usually have a higher power consumption and require a power source with a regulated voltage and maintaining a constant current supply. To solve this problem, the optimization of the NG's performance and in particular the output current is desperately needed. And a convertor is required to obtain a sustainable regulated power source from the stored energy harvested by the NGs.

In this work, we have systematically investigated various approaches for improving the intrinsic properties of ZnO in order to achieve a high performance. The NGs' performance was greatly improved by pretreatment of the ZnO nanowire (NW) arrays in the device with oxygen plasma, annealing in air and surface passivation with certain polymers. The maximum output voltage reached from a single layer of nanowire reached 20 V, and the maximum output current exceeded 6 μA, in corresponding to a power density of 0.2 W cm$^{-3}$, which is 20 times larger than the former best NG we have achieved.[12] The NG's performance is good enough to drive a commercial buck convertor board, and a regulated voltage of 1.8 V with constant current load was achieved to drive an electrical watch for more than 1 minute after the board was charged by the NG with 1000 cycles of deformation. This is the first time that a NG works as a battery part for real commercial consumer electronics.

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Based on our former experimental and calculation results,[14,15] the carrier density in ZnO NWs plays an important role on the NG's output performance. Our experimentally observed output voltage is much lower than the theoretically calculated piezopotential present in the material if doping occurs. This is because the positive side of the piezopotential introduced by mechanical deformation will be partially screened by free electrons, which are the dominant charge carriers in n-type ZnO NWs. While the negative side of the piezoelectric potential preserves as long as the donor concentration is not too high, which is the case for the unintentionally doped, as-grown n-type ZnO. The calculation results show that the piezopotential is reduced by almost a factor of 10 at the positive side comparing to the negative side when the n-type doping is 1 × 10$^{17}$ cm$^{-3}$. Thus we can expect that the strain induced piezopotential can be remarkable increased if the carrier density in ZnO could be greatly depressed. The NG used in this investigation has the same structure as our prior study,[12] which achieved the best performance of ZnO NW based NG with a power density of 10 mW cm$^{-3}$. As shown in the insert of **Figure 1**a, NG with this design has a five-layer structure. First, ZnO NW arrays with a high packaging density were grown on the top and bottom surfaces of a flexible polyester (PS) substrate by hydrothermal method (See Supporting Information). After spin-coating with polymethyl methacrylate (PMMA), a thin layer of Cr/Au was deposited on the NW arrays to work as the electrodes. The size of the effective working area of the NG was about 1 cm × 1 cm. When the NG was mechanically bent, the deformation in the nanowire film will introduce a piezopotential distribution in the ZnO NWs. Thus induced charges in the electrodes are created by flowing electrons through the external load from one electrode to the other for balancing the electrostatic field. The dynamic potential drop across the top and bottom electrodes is the driving force for the transient flow of electrons in the external load in responding to repeated mechanical deformation. According to this working mechanism, we can expect that, reducing carrier density will lead to an increased piezopential and thus an increased amount of induced charges in the electrodes. Thus the output current and voltage of the NG will be greatly enhanced.

Because of H adsorption there are always several monolayers of hydroxide (OH) at the surface of the as-grown ZnO film, which introduces an electron accumulation layer at the surface.[16,17] This phenomenon is also observed in the ZnO nanowire system.[18] Oxygen plasma contains various oxygen ions and radicals such as O$^+$, O$_2^+$, and the main species O∗. These oxygen radical atoms, O∗, can combine with the surface-adsorbed H atoms and diffuse through the ZnO bulk to fill oxygen vacancies,[19] which are doubly charged electron donors for ZnO. Thus, the use of oxygen plasma treatment can efficiently suppress such a surface accumulation layer as well as oxygen vacancies in ZnO,[20,21] by which a one order of
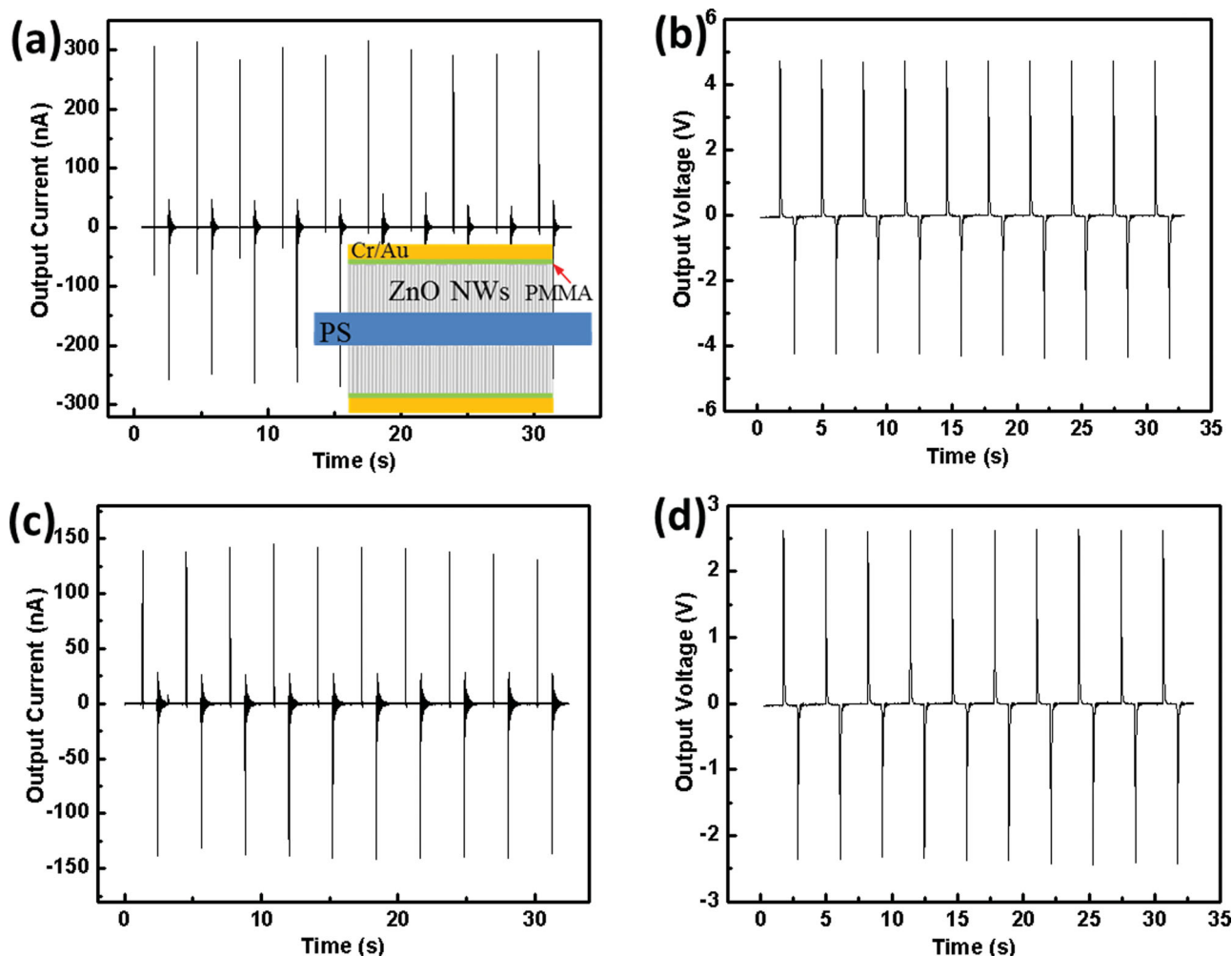
**Figure 1.** (a,b) The measured output performance of the NG with oxygen plasma pre-treatment for 30 min on the as-grown ZnO NW arrays. (c,d) The NG's performance after exposure to air for 2 weeks; both panels clearly show that the NG's performance has decreased over time.

magnitude reduction of the carrier concentration is obtained.[22] In our investigation, the device was treated with oxygen plasma for 30 min after the ZnO NW arrays had been grown on the substrates. Then, as usual, the PMMA spin-coating and electrode deposition procedures followed to finish the device fabrication. The performance of the NG was then tested; the results are shown in Figures 1a and 1b. The measured output voltage reached 5 V and the measured output current exceeded 300 nA. One thing that should be mentioned here is that we tested over 20 NGs, and 80% of them achieved such a performance. A high reproducibility in the performance of NGs is an important step toward large-scale production and technological applications. Another very interesting observation is that after 2 weeks since the first measurement of the device, we found that the performance of all the devices was lowered, as shown in Figure 1c and 1d. It indicated that the effect of plasma treatment on ZnO is likely not very stable under atmospheric conditions. The H atom may re-adsorb on the ZnO surface or the plasma-induced O∗ injection may effuse. Therefore, a better packaging technology to isolate the device from the atmosphere is essential.
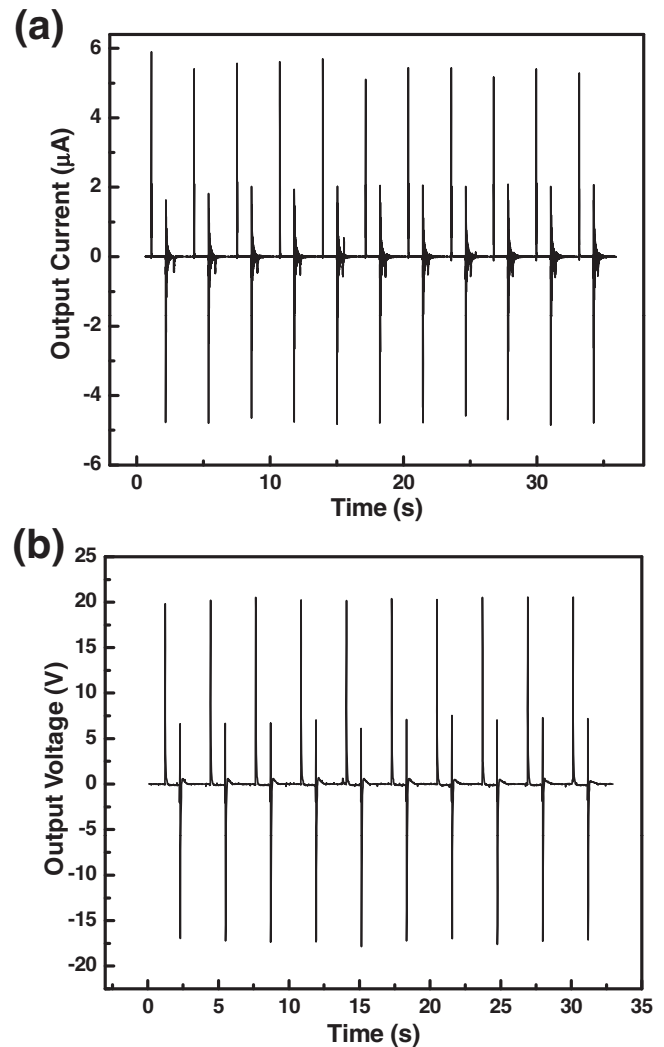
Normally, ZnO NWs grown with the hydrothermal method show a large defect concentration, but is still one of the best choices to accommodate flexible substrates because of benefits of the low growth temperature. Different post-growth methods have been investigated to improve the crystal quality. One of them is annealing the ZnO NWs in different environments. Prior research showed that the oxygen-vacancy-related defects could be significantly reduced by annealing in air above 200 °C.[23,24] Also, the presence of the OH groups at the surface of ZnO will be desorbed after annealing at temperatures of 150 °C and above.[24,25] All of these facts indicate that we can anneal our device in ambient conditions to reduce the carrier density and improve the output performance. In order to meet the requirement of high temperature annealing, we changed the NG's substrate from PS to Kapton polyimide film (DuPont), which can be subjected to a temperature as high as 400 °C. After the growth of ZnO NW arrays on the Kapton film, the device was put in a furnace at 350 °C for 30 min. There was no significant morphology change of the NWs after this treatment, which was confirmed by scanning electron microscopy

**(a)**



**(b)**
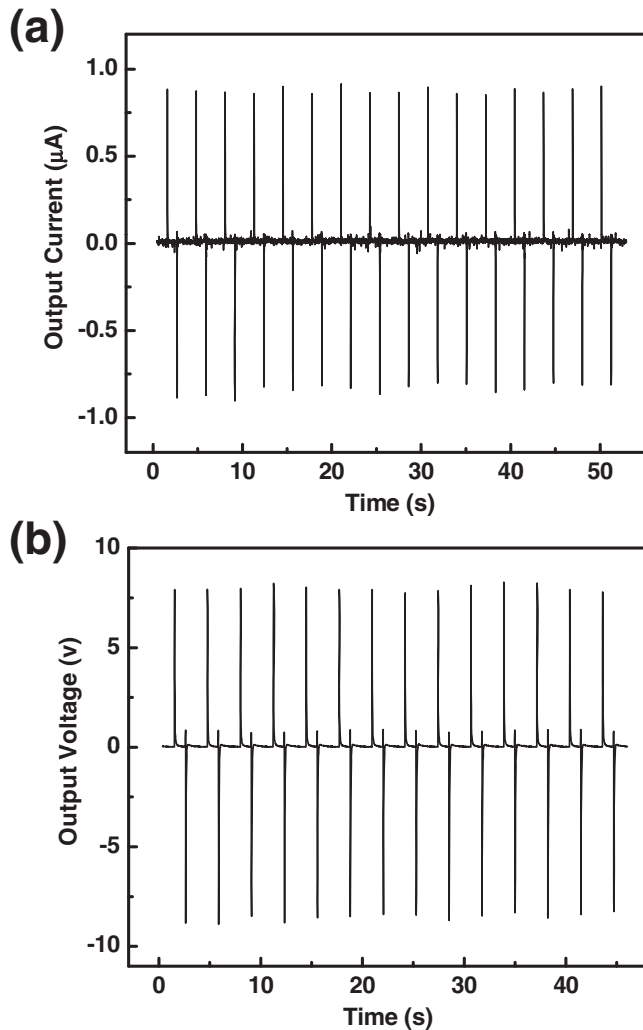


**Figure 2.** The NG's performance with ZnO NW arrays annealed at 350 °C for 30 min in air. This pre-treatment can reduce the oxygen-vacancy-related defects, and also desorb the hydroxide on NW's surface.

**(a)**



**(b)**



**Figure 3.** The NG's performance after the surface of ZnO nanowire arrays was coated with PDAMAC and PSS through a layer-by-layer self-assembling method. NGs gave the maximum optimization of the output performance in this case.

(see Supporting Information). Then, the device was fabricated following the normal procedure. The performance of the NG was shown in **Figure 2**. The output voltage was around 8 V, and the output current approached 900 nA. Also the devices' performance was reproducible for different batches. There was no obvious drop in performance after one month for the NGs that were pre-treated using this method. It seems that this approach is very suitable for practical applications.

The third pre-treatment method we chose is passivation of ZnO NWs' surface using certain polymers. It is well known that metal oxides surfaces are rich in defects, predominantly oxygen vacancies, which are electron donors and also serving as the binding sites for chemical adsorption processes. Surface passivation can eliminate these defects and also render the surface to be more chemically inert, for example, to be more resistive to H atom adsorption. Research on ZnO NW FETs showed that the on/off ratio of the device can be greatly enhanced by reducing the off-status current by surface passivation.[25,26] In our experiment, the surface of the ZnO nanowire arrays were sequentially

coated with positive charged poly (diallydimethylammonium chloride) (PDADMAC) and negative charged poly (sodium 4-styrenesulfonate) (PSS) through a layer-by-layer self-assembly method. Prior research has shown that this coating can reduce the dark current for the ZnO UV sensors.[27] **Figure 3** shows the output performance of the NG after this pre-treatment. For this method, the NG reached the maximum optimization of the output performance. The measured output voltage reached 20 V, and the output current exceeded 6 μA. The corresponding power density is 0.2 W/cm$^3$ which is 20 times larger than the previous best ZnO NW based NG. In addition to the elimination of the surface oxygen vacancies, this dramatic improvement of the output performance may result from the introduction of a depletion layer at the ZnO NWs' surface by further transfer of electrons from the NWs to the positively charged polymer PDADMAC. We have tested NGs passivated only with PDADMAC or PSS. There was no obvious performance
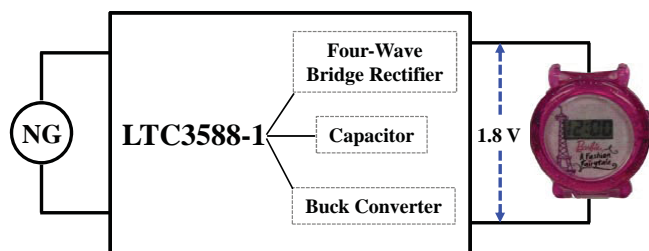
**Figure 4.** The NG was connected to a commercialized buck convertor board, which include a low loss bridge rectifier, capacitors, and a high-efficiency buck convertor to get a regulated voltage of 1.8 V. A digital watch was turned on, and kept working for more than 1 minute after the board was powered by a NG for 20 min.

improvement with such treatment. The underlying mechanism that is responsible for the enhanced NG performance remains to be investigated systematically.

To replace a battery with NGs for driving commercial consumer electronics, one of the problems that must be solved is to convert the NG's AC signal into a regulated voltage with a constant current supply. To address this issue, a commercial buck convertor board (LTC3588-1, Linear Technology) was used, as shown in **Figure 4**. This board integrates a low-loss full-wave bridge rectifier, capacitors for energy storage, and a high-efficiency buck converter. The minimal input current and voltage for such a board is 960 nA and 2.7 V. The voltage output after regulation is 1.8 V. The AC signals is first rectified by the full-wave bridge and the charges are stored in the capacitor. The buck converter can only start to work until the voltage on the capacitor reaches a threshold point and the control circuits wake up. The NG now is powerful enough to drive such a commercial board to realize voltage regulation. After the energy harvested for 1000 strain cycles of the NG (around 20 min), an electronic watch that is normally driven by a button battery was powered to work for more than 1 minute (see Video in the Supporting Information). This is the first time we demonstrate that a nanogenerator replaces a battery part in real commercial consumer electronics.

In summary, NG performance has been improved significantly by using various pretreatment methods, such as oxygen plasma, annealing in air, and surface passivation with certain polymers on the as-grown ZnO nanowire films. The maximum measured output voltage of an NG reached 20 V, and the output current exceeded 6 $\mu$A, which corresponds to a power density of 0.2 W cm$^{-3}$. A regulated voltage of 1.8 V with constant current load was achieved through a commercial buck convertor board connected to a NG, and an electronic watch was powered to working for more than 1 minute using the power generated for 1000 cycles of deformation of the NG. This is the first demonstration that a NG is powerful enough to replace a battery for driving commercial consumer electronics.

## Experimental Section

For the nanogenerator fabrication, first, a 50-nm thick ZnO seed layer on the top of a 5 nm thick Cr adhesion layer was deposited on the top and bottom surface of a flexible polyster (PS) film or Kapton polyimide film (DuPont). An equal molar aqueous solution (0.12 M)

of Zn(NO$_3$)$_2$·6H$_2$O and hexamethylenetetramine (HMTA) was used in the hydrothermal growth process. ZnO densely packed nanowires textured films were grown at the top and bottom surfaces sequentially by placing the substrate floating at the top of the nutrient solution with one face down. The growth process was carried out in a mechanical convection oven (model Yamato DKN400, Santa Clara, CA) at 95 °C for 5 hours. The dimension of the as-grown ZnO nanowire was 150 nm in diameter and 2 $\mu$m in length. The effective working area of the NG was about 1 cm × 1 cm. Plasma treatment using oxygen gas was performed on a plasma cleaning system (South Bay Technology, Inc., PC-150). The chamber pressure was maintained at 170 mTorr with 30-Watt forward power during the process. The duration time of plasma treatment was 30 min. For annealing pretreatment, the as-grown nanowires on the Kapton substrate were put into a furnace (Type 6000 Furnace, Barstead|Thermolyne Company) at 350 °C for 30 min under ambient conditions. For passivation of the ZnO nanowire's surface with polymers, the substrate with the as-grown nanowires was first immersed into poly (diallydimethylammonium chloride) (PDADMAC) solution for 90 s. After rinsing with DI water to remove the excess of unreacted molecules the substrate was immersed into poly (sodium 4-styrenesulfonate) (PSS) for another 90 s. Then, the device was rinsed again with DI water and dried in air. After different pre-treatments, a 2-$\mu$m thick poly(methyl methacrylate) (PMMA) layer was spin-coated on the device and subsequently a Cr/Au layer serving as the electrode of the NG was deposited on top. Finally, after two leads were connected to the top and bottom electrodes, the whole device was fully packaged with poly(dimethylsiloxane) (PDMS) to enhance the mechanical robustness and flexibility. The output signal of the nanogenerator was recorded by using a low-noise voltage preamplifier (Stanford Research System Model SR560) and a low-noise current preamplifier (Stanford Research System Model SR570). For comparison, all the NG's performance tests were carried out under the same experimental conditions, in which the applied strain was 0.12% at a strain rate of 3.56% S$^{-1}$.

## Supporting Information

Supporting information is available from the Wiley Online Library or from the author.

[1] Z. L. Wang, J. H. Song, *Science* **2006**, *312*, 242.

[2] Z. L. Wang, *Sci. Am.* **2008**, *298*, 82.

[3] X. D. Wang, J. H. Song, J. Liu, Z. L. Wang, *Science* **2007**, *316*, 102.

[4] Y. Qin, X. D. Wang, Z. L. Wang, *Nature* **2008**, *451*, 809.

[5] M.-Y. Choi, D. Choi, M.-J. Jin, I. Kim, S.-H. Kim, J. Y. Choi, S. Y. Lee, J. M. Kim, S.-W. Kim, *Adv. Mater.* **2009**, *21*, 2185.

[6] D. Choi, M. -Y. Choi, W. M. Choi, H.-J. Shin, H. K. Park, J.-S. Seo, J. Park, S. M. Yoon, S. J. Chae, Y. H. Lee, S.-W. Kim, J.-Y. Choi, S. Y. Lee, J. M. Kim, *Adv. Mater.* **2010**, *22*, 2187.

[7] S. Xu, Y. Qin, X. Xu, Y. G. Wei, R. S. Yang, Z. L. Wang, *Nat. Nanotechnol.* **2010**, *5*, 366.

[8] G. Zhu, R. S. Yang, S. H. Wang, Z. L. Wang, *Nano Lett.* **2010**, *10*, 3151.

[9] C. Chang, V. H. Tran, J. B. Wang, Y.-K. Fuh, L. W. Lin, *Nano Lett.* **2010**, *10*, 726.

[10] Y. Qi, N. T. Jafferis, K. Lyons Jr., C. M. Lee, H. Ahmad, M. C. McAlpine, *Nano Lett.* **2010**, *10*, 524.

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[11] X. Chen, S. Xu, N. Yao, Y. Shi, *Nano Lett.* **2010**, *10*, 2133.

[12] Y. F. Hu, Y. Zhang, C. Xu, L. Lin, R. L. Snyder, Z. L. Wang, *Nano Lett.* **2011**, *11*, 2572.

[13] Y. F. Hu, Y. Zhang, C. Xu, G. Zhu, Z. L. Wang, *Nano Lett.* **2010**, *10*, 5025.

[14] J. Liu, P. Fei, J. H. Song, X. D. Wang, C. S. Lao, R. Tummala, Z. L. Wang, *Nano Lett.* **2008**, *8*, 328.

[15] Y. F. Gao, Z. L. Wang, *Nano Lett.* **2009**, *9*, 1103.

[16] W. Gopel, *Progr. Surf. Sci.* **1985**, *20*, 9.

[17] V. E. Henrich, P. A. Cox, *The Surface Science of Metal Oxides* (Cambridge Univ., Cambridge, **1994**).

[18] Y. F. Hu, Y. Liu, W. L. Li, M. Gao, X. L. Liang, Q. Li, L.-M. Peng, *Adv. Funct. Mater.* **2009**, *19*, 2380.

[19] D. A. Gulino, L. A. Kren, *Thin Solid Films* **1990**, *188*, 237.

[20] B. J. Coppa, R. F. Davis, R. J. Nemanich, *Appl. Phys. Lett.* **2003**, *82*, 400.

[21] M. J. Liu, H. K. Kim, *Appl. Phys. Lett.* **2004**, *84*, 173.

[22] S. Lee, S. Bang, J. Park, S. Park, W. Jeong, H. Jeon, *Phys. Status Solidi (a)*, **2010**, *207*, 1845.

[23] U. Pal, P. Santiago, *J. Phys. Chem. B* **2005**, *109*, 15317.

[24] K. H. Tam, C. K. Cheung, Y. H. Leung, A. B. Djurisic, C. C. Ling, C. D. Beling, S. Fung, W. M. Kwok, W. K. Chan, D. L. Phillips, L Ding, W. K. Ge, *J. Phys. Chem. B* **2006**, *110*, 20865.

[25] W. I. Park, J. K. Kim, G.-C. Yia, M. H. Bae, H.-J. Lee, *Appl. Phys. Lett.* **2004**, *85*, 5052.

[26] W.-K. Hong, B.-J. Kim, T.-W. Kim, G. Jo, S. Song, S.-S. Kwon, A. Yoon, E. A. Stach, T. Lee, *Colloids Surf. A: Physicochem. Eng. Aspects* **2008**, *313–314*, 378.

[27] J. Zhou, Y. D. Gu, Y. F. Hu, W. J. Mai, P.-H. Yeh, G. Bao, A. K. Sood, D. L. Polla, Z. L. Wang, *Appl. Phys. Lett.* **2009**, *94*, 191103.