Tungsten Oxide Nanowires Grown on Carbon Cloth as a Flexible Cold Cathode

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Nanowire arrays for field emission have attracted a lot of interest in the last few years because of numerous applications such as flat-panel displays, X-ray radiotherapy, microwave amplifiers, and vacuum microelectronic devices.[1,2] The growth of field emitters on flexible substrates may open up numerous fields of applications such as roll-up field emission displays (FEDs),[3] and flexible and stretchable electronics. Carbon nanotube (CNT) field emitters on polymer films are the typical choice.[4–8] Despite the demonstration of good field emission performance, there are several outstanding problems about the polymer substrates for such devices, such as poor thermal and chemical stability, low electrical conductivity, low melting point, and week bonding between CNTs.

Among various transition metal oxides, tungsten oxides (WO_{3-x}) are of great interest for their promising physical and chemical properties for applications such as electrochromic devices,[9,10] semiconductor gas sensors,[11,12] and photocatalysts.[13] In the past few years, the growth and field emission properties of 1D tungsten oxide nanostructures have been intensively studied.[14–21] Various reports show that tungsten oxide nanostructures have uniform and stable field-emission properties with low threshold fields,[15–17,22] indicating their potential as cold cathodes.[23] In this communication, we report the growth and field emission properties of tungsten oxide nanowire (TONW) arrays on highly flexible carbon cloth by a thermal evaporation process. The TONWs on the carbon cloth substrate satisfy most requirements as an ideal flexible cold cathode, with high aspect ratio, excellent electrical conductivity, and thermal and chemical stability.

The TONWs were grown on carbon cloths by a high temperature, catalyst-free, physical evaporation deposition process, but with a slightly modified approach in reference to a previously reported method.[17,18] **Figure 1a** shows optical images of the carbon cloth after growing TONWs on its surface. It can be seen that the center area of the carbon cloth has been changed from dark grey to blue. The blue color distributes uniformly on the carbon cloth, implying that the TONWs are uniform. More importantly, the carbon cloth preserves the high flexibility after the growth of TONWs at high temperature and it can even be rolled up periodically (inset of Figure 1a). The inset in Figure 1b shows a low-magnification scanning electron microscopy (SEM) image of the carbon cloth, revealing that the carbon cloth is woven by carbon fibers. Figure 1b and 1c show the SEM images of the carbon fibers before and after growing TONWs, respectively. It can be observed that each of the carbon fibers was uniformly covered by TONWs, with a spiky structure. The average diameters of the TONWs range from 20 to 200 nm and their lengths are around 10 μm (Figure 1d).

The chemical compositions of the TONWs on carbon cloth were analyzed by using X-ray photoelectron spectroscopy (XPS), as shown in **Figure 2a**. The peaks, from left to right, correspond to W4f, W4d, C1s, W4p, O1s, W4s, and O Auger signals from low binding energy to high energy, respectively. The data indicates that there are three elements (W, O, and C) existing at

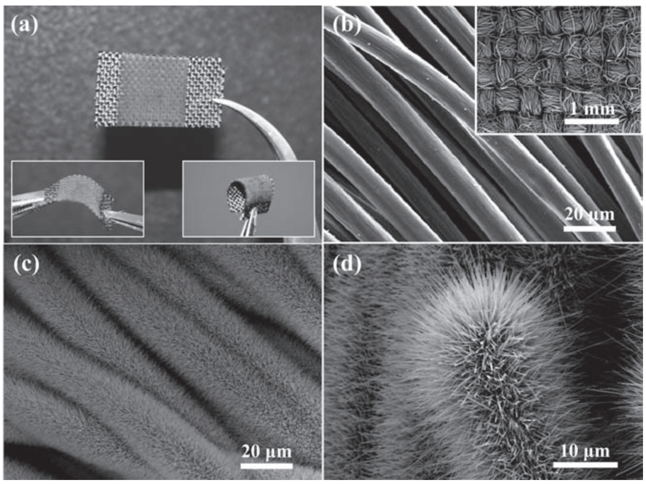

Figure 1. a) Optical images of the carbon cloth with TONWs, left-inset and right-inset show the optical images of a carbon cloth with TONWs under slight bending and severe bending, respectively. b,c) SEM images of the carbon cloth before and after growing TONWs, respectively. Inset in (b) is a low-magnification SEM image of the carbon cloth. d) High-magnification SEM image of the TONWs.

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DOI: 10.1002/adma.201002526

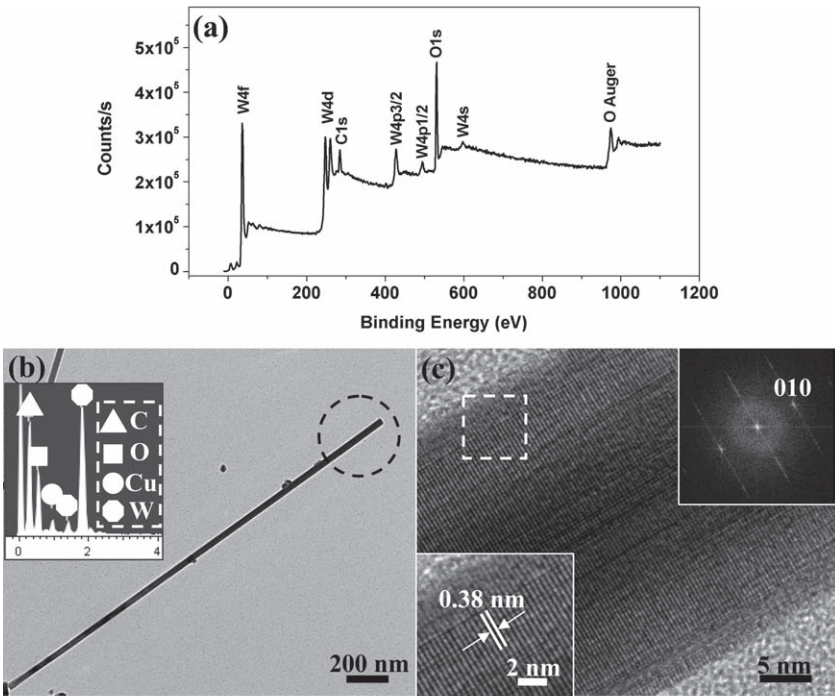

Figure 2. a) XPS survey of the TONWs. b) Low-magnification TEM image of a single TONW, inset shows the EDS from the dashed circle area. c) HRTEM image of the same TONW. Upper inset shows the corresponding FFT pattern. Lower inset is the enlarged image of the rectangle-enclosed area.

the sample surface. From the results of the curve fitting, two peaks of O1s and six peaks of W4f could be seen (see Supporting Information, Figure S1). According to the O1s peaks, the lower binding energy is related to the metal oxide, and the higher binding energy is related to the oxygen contamination. According to the W4f peaks, two strong peaks corresponding to W^{6+} and two medium peaks corresponding to W^{5+} were found as expected. However, two weak peaks corresponding to W^{4+} were also found, which belong to the impurity WO_2. The Raman characterization of the TONWs is in agreement with the nanosized nature of $W_{20}O_{58}$ (see Supporting Information, Figure S2).[24,25]

The detailed microstructures of the TONWs were characterized by using transmission electron microscopy (TEM). Figure 2b shows a typical TEM image of a TONW. The surface of the TONW is very smooth and the diameter of the TONW is around 35 nm and remains uniform along the growth axis. Energy dispersive X-ray spectroscopy (EDS) analysis was conducted from the dashed circle area of the TONW (inset in Figure 2b). Besides the Cu and the C signals coming from the TEM grid, only W and O are detected in the TONW. Figure 2c shows the high-resolution TEM (HRTEM) image and corresponding fast Fourier transformation (FFT) (upper inset in Figure 2c) of the same TONW, indicating that the TONW is single crystalline with a growth direction of [010]. No obvious amorphous layer was found on the surface of the TONW. The lower inset in Figure 2c is the enlarged TEM image from the rectangle-enclosed area of Figure 2c, the space fringe of ~0.38 nm is indexed to be the (010) plane of $W_{20}O_{58}$. It is noticeable that there are streaks in the FFT pattern which are normal to the growth direction of the TONW and are caused by the corresponding planar defects.[18]

The anisotropic formation of TONWs may be explained by the vapor–solid (VS) growth mechanism, as no additional metal catalyst was used in our experiments. In addition, no catalysts were found at the tips of the TONWs according to the SEM and TEM studies, hence the vapor–liquid–solid (VLS) growth mechanism is ruled out. During the heating process, the atoms on the surface of the tungsten powders reacted with the oxygen and formed tungsten oxides, and then the oxides were evaporated and redeposited onto the substrate surface, forming 1D TONWs. In our study, we found that the growth of the TONWs was very sensitive to the growth temperature and the oxygen gas flow. By adjusting the growth parameters, various tungsten oxide nanostructures including $W_{18}O_{49}$ and WO_3 nanowire networks were obtained (see Supporting Information, Figure S3).

For a flexible and stable cold cathode, a robust and highly conductive substrate is desired. The conductance of the carbon cloth substrate with different bending curvatures was studied as shown in **Figure 3a**. The black and gray curves are the corresponding *I–V* characteristics of the carbon cloth substrate without stress (upper inset in Figure 3a) and with severe bending stress (lower inset in Figure 3a), respectively. The linear behavior of the *I–V* curves indicates that the Cu plates and carbon cloth have a very good Ohmic contact. No remarkable changes in the conductance can be observed under different bending curvatures and over 100 bending cycles (see

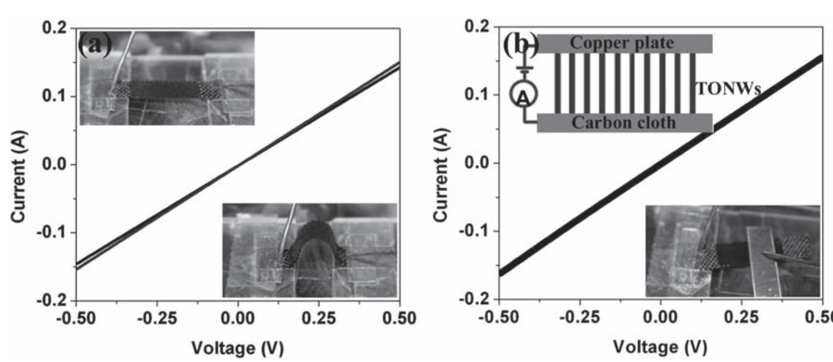

Figure 3. a) *I–V* characterizations of the carbon cloth substrate with TONWs free of stress (black curve) and with severe bending (gray curve). The upper and lower insets show the digital camera images of the carbon cloth substrate free of stress and with severe bending, respectively. b) *I–V* characterization of the TONWs. The upper and lower insets show schematic and digital camera images of the carbon cloth–TONW–Cu plate sandwich structure, respectively.

Supporting Information, Figure S4). These facts imply that stresses do not have significant effects on the conductance of the carbon cloth substrate with TONWs on it. These findings suggest that the carbon cloth substrate is robust and tough, suitable for use in a practical flexible cold cathode device.

She et. al. indicated that the conductivity of the cold cathode is a very important factor affecting field emission properties.[26] The conductance of the TONWs was roughly studied through a carbon cloth–TONW–Cu plate sandwich structure which is shown in the upper inset of Figure 3b. From the *I–V* curve shown in Figure 3b, we can calculate the resistance of the carbon cloth–TONW–Cu plate sandwich structure which is only 3.22 Ω. The high conductance of the TONWs may be attributed to the high density of the planar defects along the growth axis of the TONWs.

The thermal properties of the carbon cloth sample after growing TONWs were characterized by using a transient electrical heating method. The sample was heated using a step-rise electrical power starting from time zero (t = 0). The temperature rise was recorded by monitoring the change of the electrical resistance. This temperature rise can be analytically calculated as:[27]

$$T^* = \frac{96}{\pi^4} \sum_{n=1}^{\infty} \frac{1 - \exp\left[-(2n-1)^2 \pi^2 \alpha t / L^2\right]}{(2n-1)^4} \quad (1)$$

where $T^* = \left[T(t) - T(0)\right] / \left[T(\infty) - T(0)\right]$ is the normalized temperature, α is the thermal diffusivity, t is time, and L is the length of the sample. By fitting the temperature rise data with Equation (1), the thermal diffusivity of the sample was found to be 8.7×10^{-7} m^2 s^{-1}, as can be seen in **Figure 4**. The thermal conductivity of the sample then can be estimated as about 1.6 W m^{-1} K^{-1} by using the density and specific heat of graphite, roughly about one order of magnitude higher than that of most polymer substrates.[4–8]

The field emission measurement of the TONWs was carried out in a vacuum chamber at a pressure of ~2.0×10^{-7} torr at room temperature. A typical plot of emission current versus electric field (J–E) at a vacuum gap of ~200 μm is shown in **Figure 5a**. The electron field-emission threshold field (E_{thr}), defined as the macroscopic field required to produce a current density of 10 mA cm^{-2}, is about 4.30 MV m^{-1}, which is comparable to that of tungsten oxide nanotip arrays.[17] The highest current density obtained in our experiments is ~12 mA cm^{-2}, which is one to two orders of magnitude higher than that of most polymer substrate-based flexible CNT field emitters.[3,4,6–8] For comparison, the field emission characterization of a bare carbon cloth without TONWs was also studied, no field emission data were achieved under an electric field in the range of 2.0–5.0 MV m^{-1} (see Supporting Information, Figure S5).

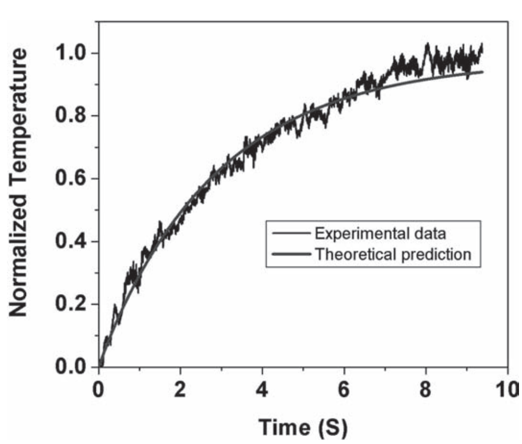

Figure 4. Normalized temperature rise of the carbon cloth sample after growing TONWs and subjected to a step-rise electrical power. The black curve is the experimental data, and the gray curve is the theoretical prediction with the best fitted $\alpha = 8.7 \times 10^{-7}$ m^2 s^{-1}.

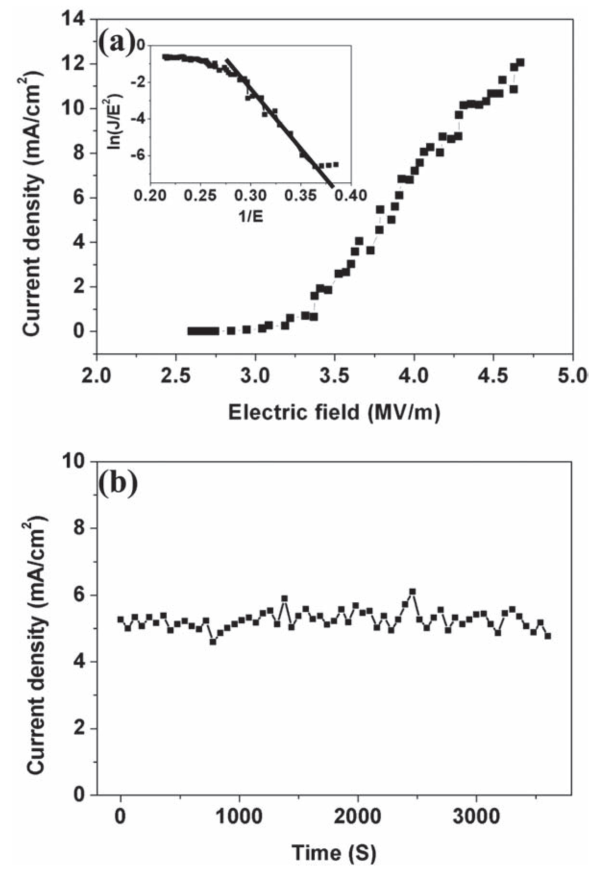

Figure 5. a) Field emission current density versus electric field (J–E) plot of TONWs. The inset is the corresponding Fowler–Nordheim (FN) plot. b) The field emission current stability of the TONWs over time.

The obtained J–E curves were further analyzed on the basis of the classical Fowler–Nordheim (FN) theory,[28] $J = (A\beta^2 E^2/\varphi) \exp[-B\varphi^{3/2}/(\beta E)]$, where J is the emission current density, E is the applied field, φ is the work function, A and B are constants, and β is the field enhancement factor, respectively. The corresponding FN plot, obtained by plotting $\ln(J/E^2)$ versus $1/E$, is exhibited in the inset of Figure 5a. The slope of the FN plot shows approximately a linear relationship under low electric field and non-linear behavior under a high electric field. This non-linear behavior of the FN plot under high electric field can be explained by the emission of thermal electrons at high temperature caused by the high current, which enhances the field electron emission under high electric field. The work function of TONWs was assumed to be ~5.6 eV.[29] The field enhancement factor β, estimated from the slope of the FN plot under low electric field is about 1657.

The emission stability of TONWs was examined at a fixed voltage (direct current, dc, mode) by automatically recording the emission current every minute. An average emission current density of 5.25 mA cm^{-2} was adjusted and its fluctuation was recorded for 1 h. As shown in Figure 5b, no obvious emission degradation was observed and the fluctuation is ~5%.

In summary, uniform single crystalline TONWs were synthesized on highly flexible, highly conductive, and highly robust carbon cloth. The resistance of the carbon cloth with TONWs is as low as several ohms, and the thermal conductivity of the carbon cloth with TONWs is about 1.6 W m^{-1} K^{-1}. Field emission with a low threshold field of ~4.30 MV m^{-1} was observed from the TONWs. The threshold field of the TONWs can be further improved by adjusting the growth parameters. This finding opens up great opportunities to make light-weight and rollable field emission displays.

Experimental Section

Synthesis: The TONWs were prepared by a high temperature, catalyst-free, physical evaporation deposition process. The experimental setup consisted of a vacuum chamber (Φ 300 mm × 400 mm), two copper electrodes, a rotary pump system, and a gas controlling system. A tungsten (W) boat (120 mm × 20 mm × 0.3 mm) containing W powders (0.5 g, purity: 99.8%) was placed and fixed on the copper electrodes. Carbon cloth substrates were mounted above the boat with one side facing the tungsten boat. Ceramic strips were used as spacers between the carbon cloth substrates and the tungsten boat. After the vacuum chamber was first evacuated down to ~0.1 Pa, mixed gases of high purity argon gas (99.999%) with a constant flow rate of 100 standard cubic centimeters per minute (sccm) and high purity oxygen gas (99.999%) with a constant flow rate of 0.5 sccm were introduced into the chamber, and the chamber pressure was kept at ~100 Pa during the whole evaporation process. The tungsten boat was then heated to ~1100 °C and held at the peak temperature for 10 min. During the evaporation, the TONWs were grown on the carbon cloth substrates.

Characterization: The prepared products were characterized by high-resolution field emission SEM (FEI Sirion 200), Raman spectroscopy (Renishaw-inVia), field emission transmission electron microscopy (JEM-2010HR), EDS (OXFORD) attached to the SEM, and XPS (Thermofisher-ESCALab 250).

Conductance Measurement: The conductance of the carbon cloth after growing TONWs was studied by using a home-made probe station. First, the two ends of the carbon cloth were fixed to two separated and movable glasses (one glass was fixed to the stage, and the other was free) by two polished Cu plates, and then two probes were attached to the Cu plates. The *I–V* characteristic of the carbon cloth with TONWs under different bending curvatures was measured by sweeping the voltage from –0.5 to 0.5 V by using an electrochemical workstation (CHI660D). The conductance of the TONWs was measured by studying the *I–V* characteristic through a carbon cloth–TONW–Cu plate sandwich structure.

Field Emission Measurement: The field emission studies were carried out in a chamber with a vacuum of ~2.0×10^{-7} torr at room temperature. A stainless-steel probe with a diameter (2*R*) of 0.35 mm was used as the anode and TONWs on a carbon cloth were used as the cathode. The cathode was connected with a 10 MΩ resistor. A tunable high voltage source with voltage up to 10 kV was applied to the anode. The separation (*d*) between the anode and the grounded cathode sample was maintained at a certain distance (~200 μm) during the measurements.

Supporting Information

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

Acknowledgements

XHZ and LG contributed equally to this work. This work was financially supported by the startup fund from HUST (01-24-187051), the Program for New Century Excellent Talents in University (NCET-10–0397), the National Natural Science Foundation of China (10774053, 50572123, 50906064), and the Department of Science and Technology of Guangdong Province (8151027501000076).

Received: July 14, 2010
Revised: August 22, 2010
Published online:

[1] W. B. Choi, D. S. Chng, J. H. Kang, H. Y. Kim, Y. W. Jin, I. T. Han, Y. H. Lee, J. E. Jung, N. S. Lee, G. S. Park, J. M. Kim, *Appl. Phys.Lett.* **1999**, *75*, 3129.
[2] N. S. Xu, S. E. Huq, *Mater. Sci. Eng. R* **2005**, *48*, 47.
[3] K. Suzuki, H. Matsumoto, M. Minagawa, A. Tanioka, Y. Hayashi, K. Fukuzono, G. A. Amaratunga, *Appl. Phys. Lett.* **2008**, *93*, 053 107.
[4] O. J. Lee, K. H. Lee, *Appl. Phys. Lett.* **2003**, *82*, 3770.
[5] C. Y. Wang, T. H. Chen, S. C. Chang, T. S. Chin, S. Y. Cheng, *Appl. Phys. Lett.* **2007**, *90*, 103 111.
[6] B. J. Yoon, E. H. Hong, S. E. Jee, D. M. Yoon, D. S. Shim, G. Y. Son, Y. J. Lee, K. H. Lee, H. S. Kim, C. G. park, *J. Am. Chem. Soc.* **2005**, *127*, 8234.
[7] H. S. Sim, S. P. Lau, H. Y. Yang, L. K. Ang, M. Tanemura, K. Yamaguchi, *Appl. Phys. Lett.* **2007**, *90*, 143 103.
[8] P. Ghosh, M. Z. Yusop, S. Satoh, M. Subramanian, A. Hayashi, Y. Hayashi, M. Tanemura, *J. Am. Chem. Soc.* **2010**, *132*, 4034.
[9] C. Santato, M. Odziemkowski, M. Ulmann, J. Augustynski, *J. Am. Chem. Soc.* **2001**, *123*, 10 639.
[10] H. J. Chen, N. S. Xu, S. Z. Deng, J. Zhou, Z. L. Li, H. Ren, J. Chen, J. C. She, *J. Appl. Phys.* **2007**, *101*, 114 303.
[11] A. Ponzoni, E. Comini, G. Sbervglieri, J. Zhou, S. Z. Deng, N. S. Xu, Y. Ding, Z. L. Wang, *Appl. Phys. Lett.* **2006**, *88*, 203 101.
[12] J. Polleux, A. Gurlo, N. Barsan, U. Weimar, M. Antonietti, M. Niederberger, *Angew. Chem. Int. Ed.* **2006**, *45*, 261.
[13] K. Sayama, K. Mukasa, R. Abe, Y. Abe, H. Arakawa, *Chem. Commun.* **2001**, *23*, 2416.
[14] G. Gu, B. Zheng, W. Q. Han, S. Roth, J. Liu, *Nano Lett.* **2002**, 2, 849.
[15] Y. B. Li, Y. Bando, D. Golberg, *Adv. Mater.* **2003**, *15*, 1294.
[16] J. G. Liu, Z. J. Zhang, Y. Zhao, X. Su, S. Liu, E. G. Wang, *Small* **2005**, *1*, 310.
[17] J. Zhou, L. Gong, S. Z. Deng, J. Chen, J. C. She, N. S. Xu, R. S. Yang, Z. L. Wang, *Appl. Phys. Lett.* **2005**, *87*, 223 108.
[18] J. Zhou, Y. Ding, S. Z. Deng, L. Gong, N. S. Xu, Z. L. Wang, *Adv. Mater.* **2005**, *17*, 2107.
[19] M. T. Chang, L. J. Chou, Y. L. Chueh, Y. C. Lee, C. H. Hsieh, C. D. Chen, Y. W. Lan, L. J. Chen, *Small* **2007**, *3*, 658.
[20] J. C. She, S. An, S. Z. Deng, J. Chen, Z. M. Xiao, J. Zhou, N. S. Xu, *Appl. Phys. Lett.* **2007**, *90*, 073 103.
[21] K. Huang, Q. T. Pan, F. Yang, S. B. Ni, D. Y. He, *Mater. Res. Bull.* **2008**, *43*, 919.
[22] D. Lu, B. Liang, A. Ogino, M. Nagatsu, *J. Vac. Sci. Technol. B* **2010**, *28*, C2A98.

[23] J. Chen, Y. Y. Dai, J. Luo, Z. L. Li, S. Z. Deng, J. C. She, N. S. Xu, *Appl. Phys. Lett.* **2007**, *90*, 253 105.
[24] G. L. Frey, A. Rothschild, J. Sloan, R. Rosentsveig, R. Popovitz-Biro, R. Tenne, *J. Solid State Chem.* **2001**, *162*, 300.
[25] J. Chen, D. Y. Lu, W. H. Zhang, F. Y. Xie, J. Zhou, L. Gong, X. Liu, S. Z. Deng, N. S. Xu, *J. Phys. D: Appl. Phys.* **2008**, *41*, 115 305.
[26] J. C. She, Z. M. Xiao, Y. H. Yang, S. Z. Deng, J. Chen, G. W. Yang, N. S. Xu, *ACS Nano* **2008**, *2*, 2015.
[27] J. Guo, X. Wang, T. Wang, *J. Appl. Phys.* **2007**, *101*, 063 537.
[28] R. H. Fowler, L. Nordheim, *Proc. R. Soc. London, Ser. A* **1928**, *119*, 173.
[29] G. Vida, V. K. Josepovitsm, M. GyŐr, P. Déak, *Microsc. Microanal* **2003**, *9*, 337.