

Direct growth of tungsten oxide nanorods from heated tungsten foils

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Tungsten oxide ($\text{W}_{18}\text{O}_{49}$) nanorods were grown by directly heating tungsten foils covered with potassium bromide (KBr) in low-pressure wet oxygen. The approach featured such advantages as convenient manipulation, low cost and rapid accessibility to high temperatures. A solid-liquid-solid (SLS) mechanism is believed to have dominated the growth process, in which the $\text{W}_{18}\text{O}_{49}$ nanorods segregated from eutectic droplets of potassium tungstate and tungsten oxide. The ultraviolet photoelectron spectroscopy (UPS) analysis disclosed that the valence band maximum (VBM) of these nanorods was approximately 9 eV below the vacuum level. The feasibility of using the such-fabricated nanorods as field emitters was tested and the related mechanism was also discussed.

$\text{W}_{18}\text{O}_{49}$, fast heating CVD, field emission

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1 Introduction

Tungsten oxides nanostructures have exhibited application perspectives in such fields as electrochromic (EC) devices [1], photocatalysis [2], gas sensing [3], adsorption of organic dyes [4], etc. So far, in most high-temperature-reaction fabrications of the tungsten oxide nanostructures, the reactant sources and the substrates are separated. Occasionally, tungsten oxide nanostructures are grown directly from the metallic tungsten, which serves as both the reactant source and the substrate. Liu et al. [5] obtained tungsten trioxide (WO_3) nanowires by heating a thin W filament in vacuum with some air leakage. Quan et al. [6] developed a single-step route for the direct growth of monoclinic WO_3 nanobelt arrays by heating a W sheet without additional catalysts or reactants. The advantages of this direct heating

method include short fabrication time, convenient manipulation, less expensive instrumentation and easy access to high reaction temperatures. Most importantly, tungsten oxide nanostructures can grow directly from, instead of depositing on, the substrates. Therefore, a number of desired properties, such as good adhesion and low contact interface resistance, can be expected.

As previously reported, in this laboratory a fast heating chemical vapor deposition (CVD) system was developed, in which the temperature of the carbon substrate could be raised to 1800°C in 15 seconds with the passage of large electric current. Combined structures of conical carbon fiber and carbon nanotube (CCF/CNT), which had large length, good straightness and perfect crystallinity, were fabricated using this system [7, 8]. Recently, tungsten oxide nanostructures were also attained with similar instrumentation. This paper describes the fabrication process, characterization and field emission properties of these tungsten oxide

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nanostructures. In terms of heating uniformity, a W filament is apparently more controllable than a W foil when used as the directly heated substrate. However, since some applications, e.g., field emission and dye adsorption, require relatively large-area arrays of tungsten oxide nanostructures, W foils were deliberately used in this work.

2 Experimental

In each fabrication, a W foil of high purity, 1 cm×0.5 cm in area and 0.2 mm in thickness, was used as the substrate. It was first submitted to such routine treatments as electrochemical polishing in potassium hydroxide (KOH) solution, cleansing in deionized water and drying in air. Then, solution of potassium bromide (KBr) was applied onto the W foil. After the evaporation of water, the W foil was tightly clamped between two graphitic electrodes in the fabrication chamber. The chamber was subsequently evacuated by a mechanical pump and a rotary molecular pump. When the pressure was lowered to 1×10^{-2} Pa, the molecular pump was switched off and oxygen was introduced into the chamber with a flux of 5 sccm after passing through deionized water, so that the oxygen was accompanied by a certain amount of water vapor when entering the chamber. When the pressure rose to approximately 10 Pa, a several-ten-volt voltage was applied to the two electrodes so that a 1.5 A current passed through the W substrate. Due to the direct heating by this current, the temperature of the W foil rose to $6.0\text{--}7.5 \times 10^2$ °C in about 10 seconds. The heating was allowed to last 5 minutes before the power supply was turned off. The oxygen was kept flowing until the W foil finally cooled down to room temperature naturally.

The morphologies and the crystalline structures of the as-grown samples were observed using a scanning electron microscope (SEM) and characterized by x-ray diffraction (XRD). With a view to knowing something about the energy band structure of the samples, ultraviolet photoelectron spectroscopy (UPS) analysis of the samples was also performed. The ultraviolet light used in the analysis was generated by the He I radiation, whose photon energy was 21.21 eV. The sample was negatively biased by a voltage $V_b=30.2$ V with respect to the detector probe, so that the complete collection of all the photoelectrons emitting from the sample by the detector could be guaranteed.

The field emission measurements were carried out in a lab-built ultrahigh vacuum system with a base pressure of 10^{-7} Pa. In each measurement, the sample was fixed on a Mo holder and used as the cathode. Two kinds of anodes were respectively used in the measurement. One was a glass screen coated with tin oxide (SnO_2) for observing the two-dimensional distribution of the emission sites on the cathode. The other was a stainless steel anode, which could bear long-term bombardment of relatively high current density. It was used in the measurement of the dependence of

the emission current on the anode-cathode voltage (I - V behavior). The cathode surface was separated from the anode by 0.3 mm.

3 Results and discussion

Figure 1 gives the SEM images of the respective nanostructures on three samples. Figures 1(a) and (b) are from one sample. Nanorods spread uniformly over the whole field of view in Figure 1(a), indicating the potential of producing large-area tungsten oxide nanorod arrays using this direct-heating method. As disclosed in Figure 1(b), most of these nanorods were of 10^1 to 10^2 nm orders of magnitude in diameter and 1 to 3 μm in length. They either discretely distributed or agglomerated into nanorod clusters. Though their alignment was still unsatisfactory, they were all more or less upward oriented instead of lying on the substrate. This feature is believed to be conducive to field emission application. Figure 1(c) shows the morphology of another sample also fabricated under the conditions described in the preceding section. The similarity between Figures 1(a) and (c) suggests the good reproducibility of this direct-heating method. In order to confirm the role of KBr in the growth of the nanorods, synthesis with similar conditions except for the absence of KBr were also performed for comparison. As shown in Figure 1(d), when a W rod was used as the directly heated substrate with no KBr applied on it beforehand, nanostructures similar to those shown in Figures 1(a) to (c) were no longer obtainable. Figure 1(e) presents the energy-dispersive x-ray spectroscopy (EDS) of the sample whose SEM image is shown in Figure 1(c). Tungsten and oxygen are the two dominant elements in the EDS and trace amount of potassium also exists. Another element involved in the synthesis, bromine, is not detectable. The major W peak is much higher than the O peak, apparently because both the nanorods and the substrate contributed to the W peaks.

The XRD result of a sample is given in Figure 2. All the peaks in it can be well indexed to either the metallic tungsten from the substrate or monoclinic $\text{W}_{18}\text{O}_{49}$, which is an oxygen-deficient nonstoichiometric tungsten oxide. In a $\text{W}_{18}\text{O}_{49}$ crystal, an ordered 2-D lattice of edge-sharing WO_6 octahedra constitutes a network of pentagonal columns interspersed with hexagonal channels [9, 10].

Obtainment of nanostructures of alkali metal tungstates, e.g., $\text{Na}_{0.65}\text{WO}_3$ [11] and $\text{K}_2\text{W}_4\text{O}_{13}$ [12], are often reported in the literature on similar works. It is essential to know whether the nanorods in this work also contained potassium tungstates for clarifying the actual role of KBr. A comparison between the peaks in Figure 2 and those of $\text{K}_2\text{O} \cdot n\text{WO}_3$ ($n=1, 2, 3, 4$) given in ref. [13] has arrived at the safe conclusion that potassium tungstates can be considered as non-existent in the nanorods shown in Figure 1. Thus, the K peak in the EDS result shown in Figure 1(e) is believed to have arisen from the residual potassium-containing inter-

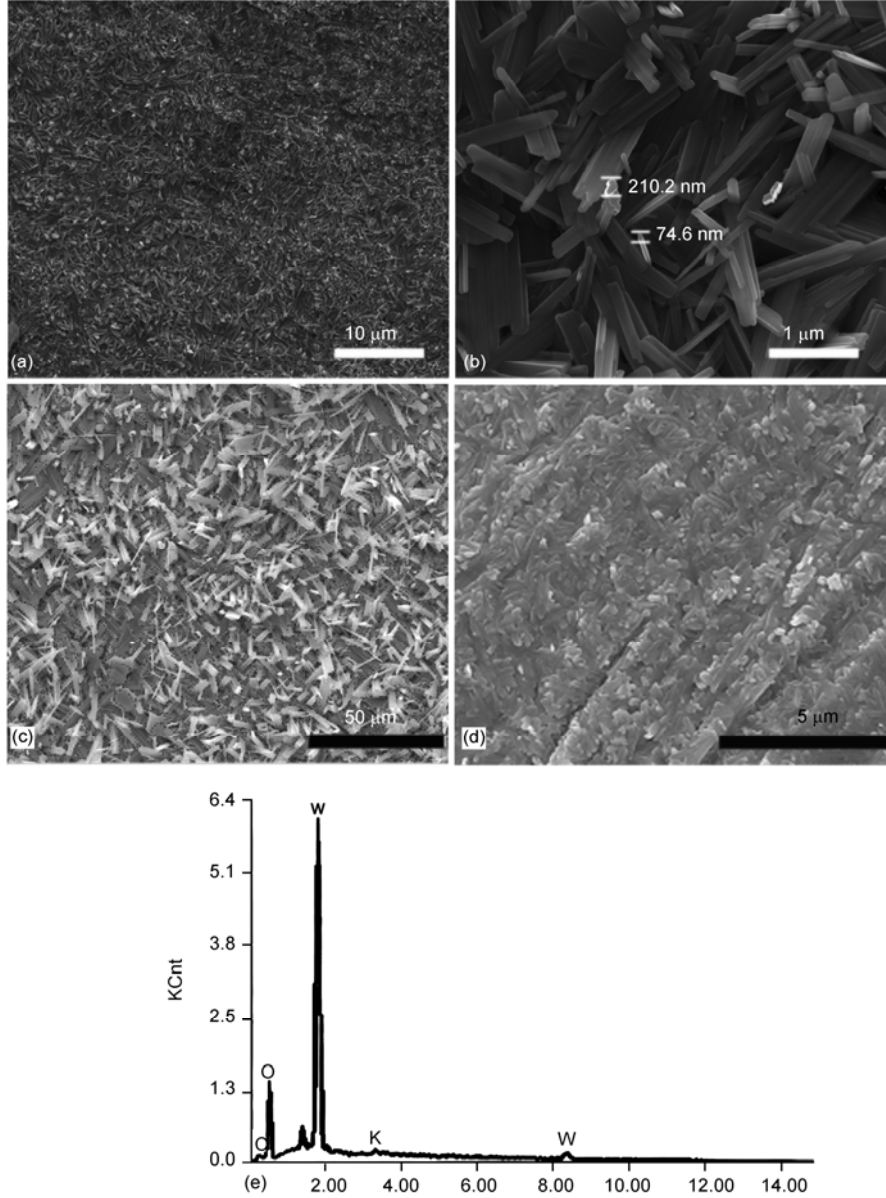


Figure 1 SEM images of the nanostructures grown on the directly heated W substrates. (a)–(c) were fabricated on the W substrates covered by KBr; (d) was fabricated on a W rod free from KBr; (e) is the EDS of (c).

mediate products. That is, elemental potassium played the role of a catalyst and did not enter the nanorods, at least in large amount.

The result of the UPS analysis of the nanorods is given in Figure 3. UPS is an effective approach to determining the work function [14–16]. For metallic samples, the existence of electrons with energies higher than the Fermi level, which is actually the chemical potential and usually denoted by μ , is generally neglected. That is, the sample is assumed to be at the absolute zero temperature and the Fermi level and the Fermi energy E_F , which is the highest electron energy at the absolute zero temperature, are considered to be equal. Under an ultraviolet radiation of a specific wavelength, the upper cutoff E_U and the lower cutoff E_L of the

photoelectron energy distribution are determined by the Fermi energy and the vacuum level E_V , respectively. Thus the work function can be obtained by the difference between the ultraviolet photon energy and the width of the photoelectron energy distribution, i.e., the difference between the two cutoffs:

$$\Phi = E_V - E_F = h\nu - \Delta E, \quad (1)$$

$$\Delta E = E_U - E_L. \quad (2)$$

The distinguishing advantage of this method is that the work function can be directly known from the photoelectron spectrum without a calibration process.

However, as understood by the authors, the validity of using eq. (1) to the non-metal samples here is still doubtful,

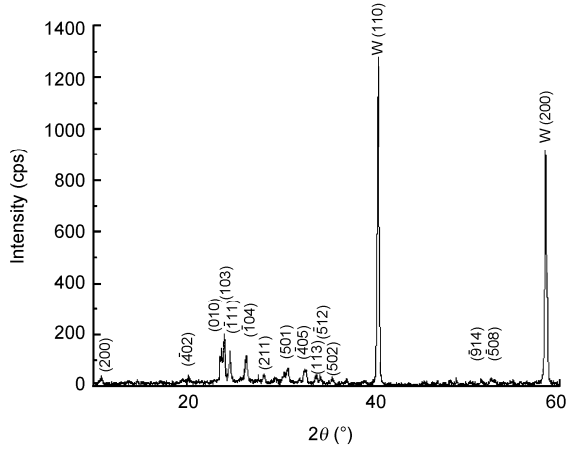


Figure 2 XRD of a sample.

especially if the Fermi level was in the vicinity of neither the conduction band minimum (CBM) nor the valence band maximum (VBM), because the Fermi level of a semiconductor or an insulator was empty and could no longer determine the upper cutoff of the photoelectron spectrum. Provided that the electrons in the conduction band, impurity levels and/or surface states were not sufficient to make a considerable contribution to the spectrum, what can be obtained from the spectrum is then the difference between the vacuum level and the VBM, as shown in Figure 3(a). Similar to a metallic sample, the low-energy part of the spectrum, which often falls rather sharply near the cutoff, still arose

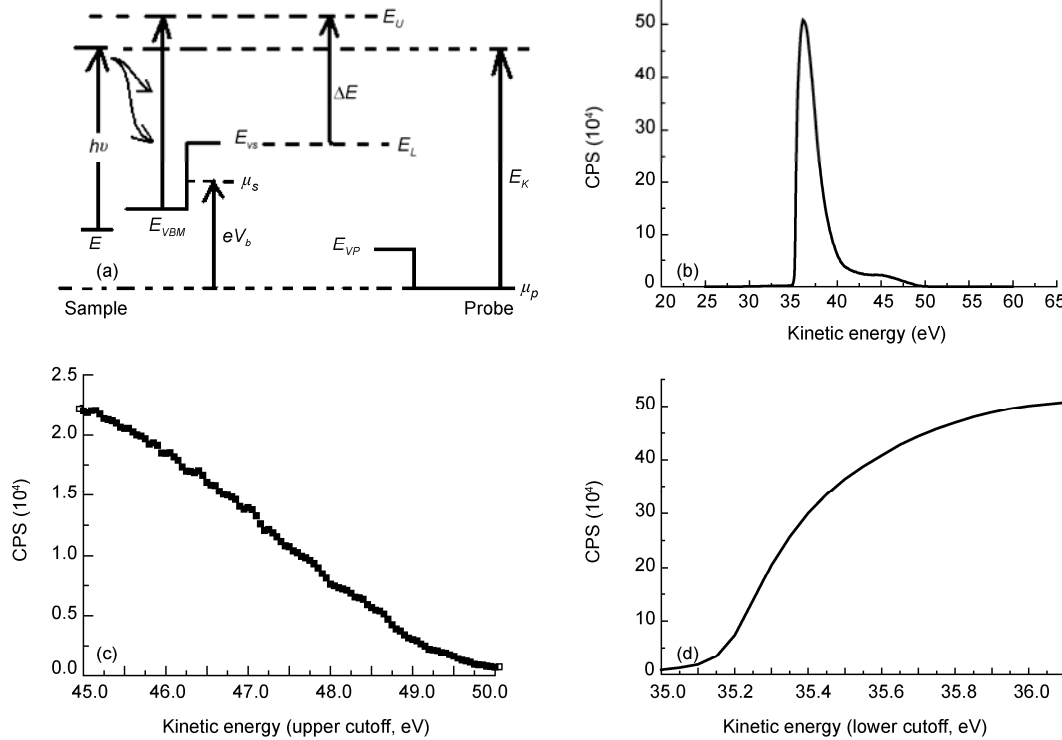


Figure 3 UPS of the nanorods. (a) The energy levels involved in the UPS result; (E_{vs} , E_{vp} , μ_s , and μ_p denote the vacuum levels and the Fermi levels of the sample and the probe, respectively. E_K denotes the kinetic energy of the photoelectron as measured against μ_p); (b) the UPS; (c) the region near the upper cutoff; (d) the region near the lower cutoff region.

from the inelastically scattered photoelectrons. The precise determination of the values of the two cutoffs in Figure 3(b) requires laborious consideration of a variety of factors, e.g., analyzer broadening. In this work, nonetheless, an approximate assessment would suffice. The two cutoffs shown in Figures 3(c) and (d), determined by the position of the VBM and the vacuum level, were respectively estimated to be 47.2 and 35.3 eV. Using eq. (2), ΔE is calculated to be 11.9 eV. Eq. (1) is revised as

$$E_V - E_{VBM} = h\nu - \Delta E = 9 \text{ eV}. \quad (3)$$

So far, most interpretations to the growth of the tungsten oxide nanostructures at high temperatures are based on either the vapor-solid (VS) mechanism [5, 6, 17–20] or the vapor-liquid-solid (VLS) mechanism [11, 12]. The growth mechanism of the $W_{18}O_{49}$ nanorods in this work was found to be more or less different from these two standard models. Oxygen has a larger electronegativity than bromine. Therefore, it is reasonable to believe that KBr would be oxidized at high substrate temperature by the O_2 introduced into the chamber, i.e., the elemental bromine in the KBr powder was replaced by elemental oxygen and certain kind of potassium oxide, e.g., K_2O , was generated. This belief is indirectly supported by the EDS result shown in Figure 1(e), in which no elemental bromine can be found. The absence of bromine in the product can be attributed to its low boiling point, which led to its immediate evaporation after the replacement by oxygen. The existence of eutectics between the potassium tungstates and tungsten oxides, e.g., $K_2O \cdot WO_3$

and WO_3 , have been reported in some old literatures and an example was given in Figure 4 from ref. [13]. The mixture of a potassium tungstate and a tungsten oxide can start to liquefy at a temperature, namely the eutectic point, lower than the respective melting points of the two constituents. Therefore, the growth probably resembled a VLS process, in which nanostructures grew out from a eutectic droplet due to supersaturation. However, in contrast to the feature of rounded terminations of the nanostructures grown in a typical VLS process [21], the nanorods shown in Figure 1 had flat ends. This difference is believed to have arisen from the spatial locations of the source materials for the nanostructure growth. A nanostructure growth dominated by a VLS process entails incessant feeding of source materials to the eutectic droplets from the vacuum space, e.g., SiCl_4 in the growth of the Si nanowires [21] and C_2H_2 in the growth of the carbon nanofibers [22]. In the work described here, the source materials, tungsten and oxygen, were in the substrate instead of in the vacuum space. Therefore, the growth of the $\text{W}_{18}\text{O}_{49}$ nanorods should be referred to as a solid-liquid-solid (SLS) process [23].

With the substrate temperature rising rapidly to above 600°C , the O_2 introduced into the chamber oxidized both the W substrate and the KBr powders on it. Then the generated $\text{K}_2\text{O} \cdot \text{WO}_3$ and WO_3 , or other kinds of potassium tungstates and tungsten oxides, mixed and eutectic droplets resulted. Because the heating was realized by the direct passage of electricity through the substrate, the temperature rising was fast and a thermal equilibrium was difficult to establish. Therefore, the temperature dropped considerably even in the space of the very near vicinity of the substrate. Tungsten oxide in the eutectic then continuously segregated at the droplet-vacuum interfaces and resulted in the growth of the $\text{W}_{18}\text{O}_{49}$ nanorods. Since the source materials were in the substrate, tungsten and oxygen entered the eutectic droplets from below. Consequently, the eutectic droplets remained at the nanorod-substrate interfaces instead of being propped up and no rounded terminations emerged.

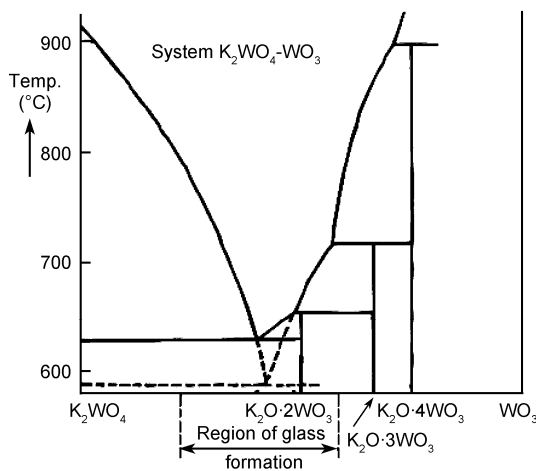
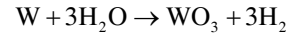


Figure 4 Phase diagram of K-W-O system [13].

Many previous works, either by other groups or in this laboratory, have shown the vital importance of water in the generation of tungsten oxide nanostructures [24–26]. So far, the exact function of water is still an open issue. In terms of chemical reaction, the water vapor possibly served directly as one of the oxidants to the W substrate for the generation of WO_3 [27]:



Furthermore, the water vapor probably also promoted the spread of the precursors for the growth of the $\text{W}_{18}\text{O}_{49}$ nanorods [24].

The field emission properties of the as-fabricated $\text{W}_{18}\text{O}_{49}$ nanorod arrays were measured and the results obtained from the sample shown in Figures 1(a) to (b) are given in Figure 5. The approximate linearity of the $\ln(I/I^2) - 1/V$ relation (FN plot) confirms that the measured current originated from the electron tunneling from the sample. Figure 5 also demonstrates the emission site distribution on the cathode. It should be noted that each bright spot on the transparent anode might have been the result of the bombardment by the electrons from a number of neighboring sites on the cathode. That is, the resolution of the transparent anode was not high enough for distinguishing the luminescence stimulated by the field emission from each nanorod. The “turn-on” field and “threshold” field are two important criteria for the field emission capability of the cold cathode. They are the fields that respectively extract current densities of $10 \mu\text{A}/\text{cm}^2$ and $1 \text{ mA}/\text{cm}^2$ from a field emitter array [28, 29]. It is worth emphasizing that the “electric field” here does not mean the actual field around an emission site, which was not directly measurable. Instead, it means the average field between the anode and the cathode. This average field can be obtained by simply dividing the voltage by the spacing between the anode and the cathode. From the data shown in Figure 5, the turn-on and threshold fields can be calculated to be 9.5 and $16 \text{ V}/\mu\text{m}$, respectively.

So far, neither the emission uniformity nor the emission

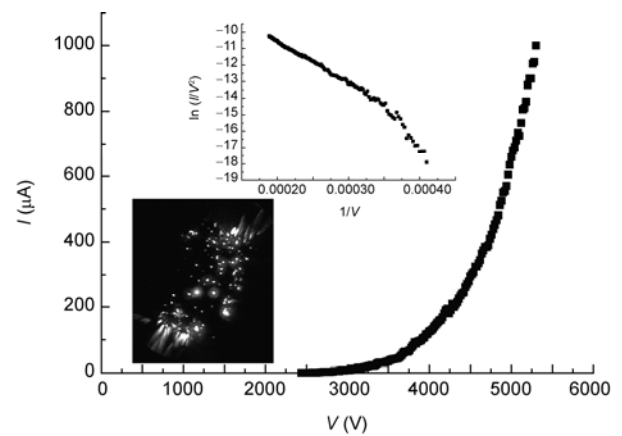


Figure 5 Field emission properties of a $\text{W}_{18}\text{O}_{49}$ nanorod array: I - V behavior, FN plot and the emission site distribution.

capability can directly meet the demands for practical applications, such as the cold electron sources in field emission displays (FEDs), traveling microwave tubes (TWTs), etc. As disclosed by eq. (3), the VBM of the sample was as large as 9 eV below the vacuum level, thus it is impossible for the electrons in the valence band to tunnel into the vacuum. Therefore, it is believed that the emitted electrons came from the conduction band, impurity levels and/or surface states. Due to the relative smallness in number, these electrons with energies above the VBM were not obviously detected in the UPS analysis. In the future work, efforts will be devoted to further increasing the number of these electrons by doping and other measures.

4 Summary

Nanorods of $W_{18}O_{49}$, an oxygen-deficient nonstoichiometric tungsten oxide, were fabricated by directly heating W foils. In the fabrication, the W foils functioned as both the substrates and the reactant sources. Other necessary conditions included the coverage of the substrates with KBr and the introduction of low pressure wet oxygen. The oxidized W surface and the KBr on it combined into eutectic droplets and tungsten oxide segregated from them due to supersaturation. This growth is referred to as an SLS process. Field emission was obtained from the such-fabricated $W_{18}O_{49}$ nanorods and the UPS analysis suggested that the emitted electrons were likely to have come from the conduction band, impurity levels and/or surface states of these nanorods.

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