



# Hetero- and homogeneous three-dimensional hierarchical tungsten oxide nanostructures by hot-wire chemical vapor deposition



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## ABSTRACT

We present the synthesis of three-dimensional tungsten oxide ( $\text{WO}_3 - x$ ) nanostructures, called nanocacti, using hot-wire chemical vapor deposition. The growth of the nanocacti is controlled through a succession of oxidation, reduction and re-oxidation processes. By using only a resistively heated W filament, a flow of ambient air and hydrogen at subatmospheric pressure, and a substrate heated to about 700 °C, branched nanostructures are deposited. We report three varieties of simple synthesis approaches to obtain hierarchical homo- and heterogeneous nanocacti. Furthermore, by using catalyst nanoparticles site-selection for the growth is demonstrated. The atomic, morphological and crystallographic compositions of the nanocacti are determined using a combination of electron microscopy techniques, energy-dispersive X-ray spectroscopy and electron diffraction.

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## 1. Introduction

Since the 1950s surface science has seen a dramatic evolution through the synthesis of nanostructures of ever more complexity. The high surface-to-volume ratio of nanomaterials raises the surface energy and thus the chemical and physical reactivity. Additionally, crystalline semiconducting nanostructures of sizes below the Bohr exciton radius of the material exhibit quantum confinement effects, which significantly influence charge transport, electronic band structure and optical properties [1]. Presently there are many reports in the literature about high-surface area nanostructures of widely varying materials. However, the synthesis of *tungsten oxide* ( $\text{WO}_3 - x$ ) branched nanostructures is not so common.  $\text{WO}_3 - x$  is currently the leading electrochromic material [6] and has besides its excellent chromogenic properties a very wide applicability. Granqvist [7] and Deb [6] published important reviews of research on  $\text{WO}_3 - x$  in 2000 and 2008, respectively; followed more recently by Baetens et al. [8] in 2010 and Zheng et al. [1] in 2011. Interestingly, the physical properties of  $\text{WO}_3 - x$  depend mainly on the amount of surface defects, rather than on the intrinsic  $\text{WO}_3 - x$  material

[9,10]. Therefore, it is inviting to study also the synthesis of three-dimensionally (3D) nanostructured  $\text{WO}_3 - x$  of a high specific surface area. Such complex  $\text{WO}_3 - x$  structures have previously been synthesized by Zhou et al. [11] using a thermal evaporation method, by Zhu et al. [12] using a thermal oxidation procedure, by Shibuya and Miyauchi [2] using a sulfate-assisted hydrothermal reaction of tungsten metal, and finally by Baek et al. [13] using a two-step evaporation process. The hierarchical  $\text{WO}_3 - x$  structures are found to exhibit promising field-emission performance [13], much faster proton diffusion than for polycrystalline  $\text{WO}_3$  films [14] and remarkable electrochromic properties [15]. With catalysis, a significant improvement in efficiency can be achieved when catalytically active nanoparticles are supported on nanostructured materials [2–5]. For instance with the presence of Pd nanoparticles at the bottom of tree-like  $\text{WO}_3 - x$  structures, the photocatalytic activity of the nanotrees is enhanced, which consequently exhibit photoinduced superhydrophilicity [2].

Previously we reported the hot-wire chemical vapor deposition (HWCVD) of amorphous  $\text{WO}_3 - x$  thin films [16] and crystalline nanostructured depositions of a controllable morphology [17] and a  $\text{W}_{24}\text{O}_{68}$  composition [18]. In those studies only a resistively heated W filament (as source of W atoms), an oxidizing air flow at subatmospheric pressure and a substrate heated to  $700 \pm 100$  °C, were used. The authors also reported the subsequent reduction [19] to metallic  $\alpha$ -W of the deposited  $\text{W}_{24}\text{O}_{68}$ . Here, we extend the deposition process by additionally using a hydrogen ( $\text{H}_2$ ) flow, which allows an intermediate and essential reduction step during the synthesis procedure due to the catalytic generation of atomic H by the hot filaments. It will be shown that good control over the morphology is obtained as well as site-selection over the arrangement of the nanostructures on the substrate. Three different varieties of synthesis approaches are presented, with which

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hierarchical 3D homo- and heterogeneous nanostructures are readily deposited. These routes comprise *continuous* upscalable [21] CVD processes at relatively low temperatures.

## 2. Experimental details

### 2.1. Conditions for synthesis route #1: $W_{24}O_{68}/W_{24}O_{68}$ nanocacti

As substrates  $1 \times 1 \text{ cm}^2$  c-Si (100) wafers, with a  $TiN_{0.5}O_{0.9}$  barrier film of a thickness of  $120 \pm 10 \text{ nm}$  are prepared. On a selection of samples a monolayer mask of colloidal spheres (of  $1400 \pm 20 \text{ nm}$  diameter) is applied; consequently on all the samples a Ni top-film of a thickness of  $2.4 \pm 0.2 \text{ nm}$  is deposited. The deposition through a colloidal mask results in an array of prism-like particles in a honeycomb lattice; the method is called nanosphere lithography. This approach is similar to that reported by Micheletto et al. [41] and has been used and described by the authors previously [29]. After removal of the colloids through sonication, Ni prisms of a lateral size of  $a = 335 \pm 20 \text{ nm}$  and a height of  $2.4 \pm 0.2 \text{ nm}$  reside. Thus the result of this procedure is that the first selection of samples comprises Si/ $TiN_{0.5}O_{0.9}$ /Ni (film) and the second selection of samples comprises Si/ $TiN_{0.5}O_{0.9}$ /Ni (array of prisms). The details of the physical vapor depositions (PVD) and characterizations of the barrier and catalyst films are provided elsewhere [18]. The barrier film is employed to prevent the formation of nickel silicides at temperatures above  $300 \text{ }^\circ\text{C}$  [37–40]. Next, the samples are annealed in an atmosphere of atomic hydrogen to dewet the Ni top-film and Ni prisms such that rounded nanoparticles are formed [29,30] that can act as catalyst sites for growth of tungsten oxides. Hereto the samples are loaded onto a sample holder in a  $13.5 \text{ dm}^3$  vacuum chamber [18], which is evacuated to  $1.0 \times 10^{-7}$  mbar. Two parallel straight tungsten filaments (GoodFellow, 10.5 cm in length and 0.3 mm in diameter, 99.95% purity), situated 1 cm directly above the samples, are resistively heated by a constant direct current of 8.0 A, which thus constitutes a filament temperature of  $2160 \pm 30 \text{ }^\circ\text{C}$  [17]. Then a flow of 100 standard cubic centimeter per minute (sccm)  $H_2$  of 1.0 mbar is introduced. The  $H_2$  is dissociated to atomic hydrogen [19,24,22,23], which proceeds at about  $1370 \text{ }^\circ\text{C}$  [22,23]. The substrate surface temperature ( $T_{\text{surface}}$ ) is ramped to about  $750 \text{ }^\circ\text{C}$  in a period of 15 min by heating the sample holder. In the second subsequent stage the  $WO_3 - x$  deposition is performed, which is started by adding a flow of 18 sccm ambient air, while maintaining the total pressure at 1.0 mbar. The deposition is stopped after 15 min; when the filament current is stopped, then all flows *except the air flow* are stopped and the sample cools to room temperature.

### 2.2. Conditions for synthesis route #2: $W_{24}O_{68}/W_{24}O_{68}$ nanocacti

As substrates single-side diamond-polished  $1.0 \times 1.0 \text{ cm}^2$  Sigradur G vitreous glassy carbon wafers of a thickness of 1.0 mm are used. After positioning the substrates on the sample holder, the system is evacuated to  $1.0 \times 10^{-7}$  mbar. Then  $T_{\text{surface}}$  is ramped to  $700 \pm 100 \text{ }^\circ\text{C}$  and the filaments are heated to a temperature of  $2160 \pm 30 \text{ }^\circ\text{C}$ . Next, an air flow of 25 sccm of a pressure  $P_{\text{air}} = 0.039 \text{ mbar}$  is introduced for 30 min, defining the duration of deposition. These conditions result in  $W_{24}O_{68}$  nanostructured crystallite films [17]. After 30 min the air flow is terminated and a  $H_2$  flow of 100 sccm of a pressure of 0.14 mbar is introduced for a period of 1 min. This is performed to reduce the surface of the  $W_{24}O_{68}$  crystallites and thus to form centers for nucleation of new tungsten oxide. Next, the  $H_2$  flow is terminated and an air flow of 25 sccm of a pressure  $P_{\text{air}} = 2.0 \times 10^{-3} \text{ mbar}$  is introduced, for a period of 15 min, which is a recipe for the growth of  $W_{24}O_{68}$  nanowires [17].

### 2.3. Conditions for synthesis route #3: $W/W_{24}O_{68}$ nanocacti

As substrates again glassy carbon wafers are used. A  $W_{24}O_{68}$  crystallite film is deposited as described in Section 2.2. Then a  $H_2$  flow of

100 sccm of 1.0 mbar is introduced for 30 min to completely reduce the  $W_{24}O_{68}$  to  $\alpha$ -W, as shown in earlier work [19]. To subsequently re-oxidize the surface of the  $\alpha$ -W an air flow of 25 sccm of  $P_{\text{air}} = 0.039 \text{ mbar}$  is introduced for 30 min, with the current through the filaments turned off, thus without new deposition of  $WO_3 - x$ .

### 2.4. Structural and chemical characterization

All depositions are characterized *ex situ*. High-resolution scanning electron microscopy (HRSEM) and energy-dispersive X-ray spectroscopy (EDS) are performed with a Philips XL30 SEM, equipped with a field emission gun, using 5 kV and 30 kV, respectively. High-resolution scanning transmission electron microscopy (HRSTEM), STEM imaging with a high-angle annular dark-field (HAADF) detector and selected-area electron diffraction (SAED) images are taken using a FEI Tecnai 20F TEM at 200 kV. The crystallographic structure of the species deposited is determined by XRD with a powder diffraction setup equipped with a Philips PW 1729 X-ray generator using monochromatic  $Cu K\alpha$  radiation at a voltage of 40 kV with a current of 20 mA.

## 3. Results and discussion

### 3.1. Synthesis route #1—homogeneous $W_{24}O_{68}/W_{24}O_{68}$ nanocacti using Ni

HWCVD is employed for the deposition of  $WO_x$  on a thin Ni film in a reducing environment. After deposition HRSEM is used to image the external surface of the substrate. Fig. 1(a),c),e) shows secondary electron (SE) images revealing a 3D nanostructured deposition.

Numerous high-surface area branched cactus-like structures with an orientation perpendicular to the substrate are observed. The SE images in Fig. 1(a),c) have been taken with a through-lens detector (TLD) for very high resolution; the nanorod superstructures appear brighter than the stem due to charging by the incident electrons. Fig. 1(e) shows a SE image taken without the TLD. Fig. 1(b),d) shows BSE images that are complementary to the SE images of Fig. 1(a),c). In the BSE images the stems display little variation in brightness indicating a homogeneous composition and thickness, since the brightness of a BSE signal strongly depends on the atomic number ( $Z$ ). The superstructures are clearly visible in the BSE image, but appear less bright; they are thus either of a reduced mass density or are just very thin and thus backscatter few electrons. The nanocacti consist of a stem that measures  $120 \pm 40 \text{ nm}$  in width and up to about  $1.5 \mu\text{m}$  in length, and of nanorod superstructures that measure about 5–15 nm in width and about 5–250 nm in length. The aspect ratios of the stems amount to 9–19 and of the superstructures to 17–50; this illustrates the sharp features of the very thin superstructures.

To determine the atomic composition of these nanocacti and to inspect the detailed morphology of the stems and branches, a number of complementary HRSEM and scanning (S)TEM techniques are utilized. Fig. 2(a) shows a TEM bright field image of a nanocactus that was collected on a copper TEM grid with a thin silicon nitride (SiN) film.

In the bright field image of Fig. 2(a) the stem appears dark due to its relatively large thickness, which attenuates the signal of transmitted electrons. The stem of the cactus reveals a nanogranular morphology. The nanorod superstructures appear to be monocrystalline. Fig. 2(b) shows a STEM image taken with a high-angle annular dark-field (HAADF) detector, which is only sensitive for electrons scattered over large angles allowing to indicate the local regions where heavier elements are present. As in the BSE SEM images shown earlier, the superstructures are also visible in the HAADF STEM image, confirming a composition containing a heavy element, but appear with a lower brightness due to either a reduced mass density or a small diameter. Fig. 2(c) and d) represents TEM images of a larger cactus collected on a copper TEM grid with a thin holey carbon film. Fig. 2(c) shows a bright field image. Some of the superstructures are broken off from the stem due to a sonication treatment to collect the material on the TEM grid.

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