Growth of carbon sausages filled with *in situ* formed tungsten oxide nanorods: thermal dissociation of tungsten(VI) isopropoxide in isopropanol

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In this article, we report a simple, one-stage, efficient synthetic method for the growth of **c**arbon **s**ausages filled with *in situ* formed **t**ungsten **o**xide **n**anorods (CSTON), without any external catalyst. The thermal dissociation of tungsten(VI) isopropoxide, 5% w/v in isopropanol at 700 °C in a closed Swagelok cell in an inert atmosphere yielded a CSTON product. The product is characterized by SEM, TEM, EDAX, C, H, N, S analysis, TGA, Raman spectroscopy, and HR-TEM. The assignment of the structure of the sausages as a carbon shell, with the central part being the WO_x, is based on SAEDS spectra. The same reaction was also conducted at a lower temperature closer to the temperatures of solvothermal reactions, at 350 °C. The reaction yielded WO_x nanorods with a diameter ranging from 10 nm to 50 nm and a length of up to 6 μm.

1. Introduction

Due to their novel properties, recent years have seen the development of technologies for fabricating interesting nanostructures by a variety of methods, as compared to the corresponding bulk materials. WO_3 and its sub-oxides have been intensively studied for a long time due to their promising physical and chemical properties.[1] For instance, their excellent photo- and electro-chromic properties are commonly used in devices for smart windows[2] and information storage.[3] In addition, WO_{3-x} showed sheet superconductivity; this is closely related to its substructures and defects.[4] A variety of methods have been developed to prepare tungsten oxide nanoparticles,[5] nanotubes,[6] nanorods or nanowires.[7] In most of this work, the products of tungsten oxides are a mixture of WO_3 and its sub-oxides with complex crystallographic defects. It is well known that certain significant properties of the materials are not governed only by the structure of material itself, but by faults or defects in the materials.

The synthesis and characterization of carbon-supported[8] Pt-Ru-WO_x catalysts by spectroscopic and diffraction methods was carried out by Roth *et al*. The electro-oxidation of methanol has been studied[9] in sulfuric acid electrolytes at 60 °C on carbon-supported Pt-WO_{3-x} electrodes employing varying amounts of WO_{3-x}. An interesting micrometer scale, tree-like structure of tungsten oxide has been generated by heating a W foil, partly covered by a SiO_2 plate, in an Ar atmosphere at *ca*. 1600 °C.[10] TiO_2/WO_x-supported metal oxide materials were prepared by grafting a tungsten(V) ethoxide precursor onto a titania support.[11] The improvement of electrochromic coloration efficiency (ten fold) by oxygen deficiency in sputtering WO_x films is described by an intervalence charge-transfer transition mechanism between localized W^{5+} and W^{6+} states.[12] The WO_3/polyvinylimidazole core-shell structures have chemical and thermal stabilities higher than those of pure WO_3 nanoparticles.[13] Carbon coated CdS core-shell nanowires were reported by using a room-temperature chemical reduction method.[14] In addition, Bando *et al*. published a series of articles on the core-shell morphologies for cable like[15a–f] structures. For example, silica-shielded Ga-ZnS metal-semiconductor nanowires, liquid gallium columns sheathed with carbon, FeCo nanowires inside carbon, SiC-shelled ZnS nanoribbons, SiC nanowires encapsulated in BN nanotubes, and Fe nanowires encapsulated in BN nanotubes with intermediate C layers.

The simple, one-stage, efficient synthesis technique for the growth of carbon sausages filled with *in situ* formed tungsten oxide nanorods, without using any external catalyst, is reported in this article. The thermal decomposition of tungsten (VI) isopropoxide, 5% w/v in isopropanol at 700 °C in a closed Swagelok cell in an inert atmosphere, yielded a CSTON product. In our group, similar reactions were recently carried out for a variety of alkoxides (without the isopropanol) and the reactions were termed RAPET[16–19] (Reactions under Autogenic Pressure at Elevated Temperature). The present paper is focused on the thermal dissociation of tungsten(VI) isopropoxide in an isopropanol solution (Alfa Aesar Nr.41843) at 700 °C. In addition, since the current reaction is not a typical RAPET reaction because of the presence of a solvent, and since this reaction can be considered a solvothermal reaction, it was also carried out at 350 °C. This reaction yielded WO_x nanorods with a diameter ranging from 10 nm to 50 nm, and a length up to 6 μm. The present report concentrates on the fact that morphologically different, fascinating nanostructures, could be obtained from the same reaction at various temperatures.

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2. Experimental

2.1. Synthesis of carbon sausages filled with *in situ* formed tungsten oxide nanorods (CSTON product)

The growth of carbon sausages filled with *in situ* formed tungsten oxide nanorods, took place from the thermal dissociation of tungsten(VI) isopropoxide, 5% w/v in isopropanol. The 4 ml closed vessel cell was assembled from stainless steel Swagelok parts. A 1/2″ union part was plugged from both sides by standard caps. For this synthesis, 2 ml [1.5 g] of tungsten(VI) isopropoxide, 5% w/v in isopropanol (later called precursor solution) was introduced into the cell at room temperature under nitrogen (glove box). The filled cell was closed tightly the temperature was raised at a heating rate of 10 °C per minute. The closed vessel reactor (Swagelok) was heated at 700 °C for 1 h. The reaction took place at an autogenic pressure of the precursor. The Swagelok reactor heated at 700 °C was gradually cooled (∼5 hours) to room temperature, opened with the release of a little pressure, and 0.841 g of black powder was obtained. The product is termed as CSTON (carbon sausages filled with *in situ* formed tungsten oxide) and the obtained yield is 56%. In addition, three control experiments were carried out. In the first experiment, we changed the reaction time, *i.e.*, instead of 1 h, thermal dissociation was carried out for 3 h. In the second experiment, the precursor solution was heated at ∼90 °C for 20 minutes to evaporate isopropanol (5% w/v), and the residue was used for thermal dissociation, keeping the same experimental conditions for the other parameters. As the tungsten(VI) isopropoxide is in a solution of isopropanol, it can be considered as a solvothermal reaction. The third reaction was carried out at 350 °C, which is closer to temperatures of solvothermal reaction. This reaction yielded WO_x nanorods with a diameter ranging from 10 nm to 50 nm and a length up to 6 μm and the product was termed as **t**ungsten **o**xide **n**ano**r**ods (TONR).

2.2. Characterizations

The X-ray diffraction pattern of the products were measured with a Bruker AXS D* Advance Powder X-ray diffractometer (using Cu Kα = 1.5418 radiation). Two methods were used for the determination of the carbon content; they are: C, H, N, S, and EDAX analysis. Elemental analysis of the CSTON sample was carried out on an Eager 200 C, H, N, S analyzer. The elemental composition of the materials and the SEM image were analyzed by an energy-dispersive X-ray analysis technique attached to a JEOL-JSM 840 scanning electron microscope. The particle morphology and structure was studied with a JEOL-2010 HRTEM instrument, using an accelerating voltage of 200 kV. Samples for TEM and HR-TEM were prepared by ultrasonically dispersing the CSTON product into absolute ethanol, then placing a drop of this suspension onto a copper grid coated with an amorphous carbon film, and then drying in air. The thermogravimetric analysis of the CSTON product was carried out under a stream of air, at a heating rate of 3 °C per minute using a Mettler TGA 851 instrument. The Olympus BX41 (Jobin Yvon Horiba) Raman spectrometer was employed, using the 514.5 nm line of an Ar laser as the excitation source to analyze the nature of the carbon present in the CSTON product.

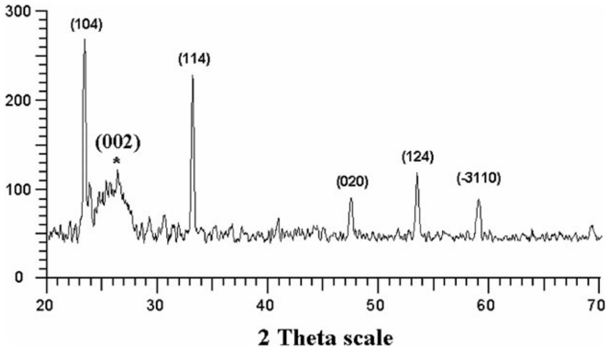


Fig. 1 The powder XRD pattern of the carbon sausages filled with an *in situ* formed tungsten oxide (CSTON) product.

3. Results and discussion

3.1. Powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), energy-dispersive X-ray analysis (EDAX), and elemental (C, H, N, S) analysis

The XRD patterns of the CSTON product presents (Fig. 1) the full assignment of the diffraction peaks. The peaks correspond to the reflection lines of the monoclinic phase of tungsten oxide $WO_{2.83}$ or $W_{24}O_{68}$ (PDF No. 36–103). Of all the known carbon diffraction lines only an underlying diffraction peak of carbon at 26.3° (marked by *) is detected, with no other characteristic carbon peaks. This might be due to the amorphous/disordered nature of carbon. XRD measurements for the CSTON product after a month at ambient conditions did not detect any changes in the diffraction peaks, thus confirming the stability of the $W_{24}O_{68}$ phase inside the *in situ* formed carbon layer.

The morphology of the carbon sausages filled with an *in situ* formed tungsten oxide (CSTON) sample was primarily investigated by SEM measurements. The sample has a morphology composed of elongated (∼90%) and spherical particles (∼10%) (Fig. 2a). The elongated particles (sausages) have an average diameter of ∼200 nm and a length of a few micrometers. A few spherical bodies having a diameter around 3 μm are identified by EDAX as carbon spherules. The distinction between the elongated and spherical bodies is made by using EDAX analysis attached to the SEM instrument. EDAX measurements of the CSTON sausages reveal the presence of W, O, and C (Fig. 3). On the other hand, for the spherical particles, only the presence of C is detected. The carbon peak is more intense for the sausages/spherical carbon than for the peak measured for the bare, carbon-coated copper support. The CSTON sausages are shown at high resolution in Fig. 2b. The sausages possess diameters of ∼100 nm and a length of more than 3 micrometers. This result led us to attribute the presence of W and O, or WO_x, as the consequence of the catalyzed growth of the carbon around the WO_x, leading to the formation of a CSTON product. A more detailed understanding of the core-shell structures is developed

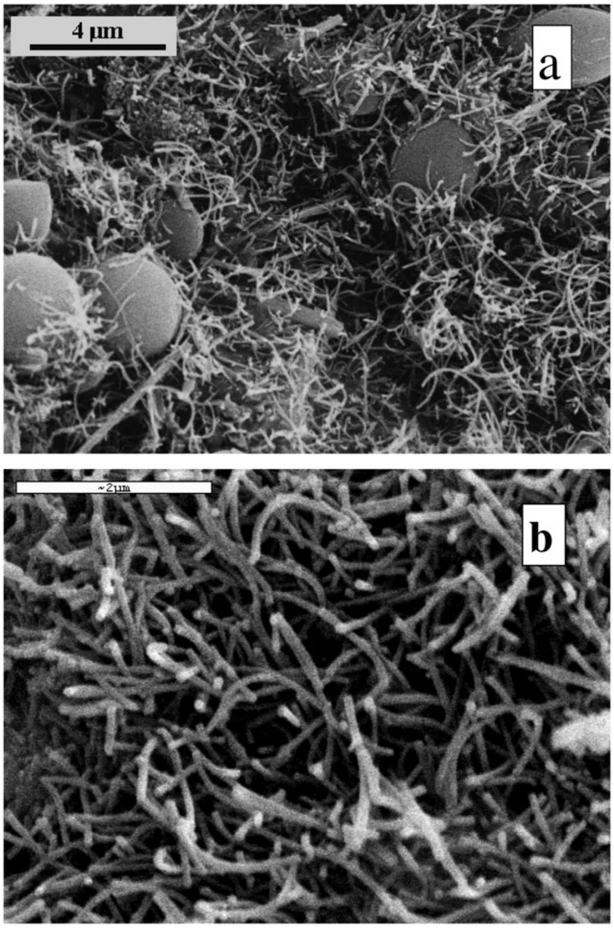


Fig. 2 Scanning electron micrograph of (a) carbon sausages filled with WO_x and (b) carbon sausages filled with WO_x shown at higher resolution.

by characterizing the CSTON sample using TEM, HR-TEM and the SAEDS measurements that are discussed in the following section.

The content of carbon and hydrogen in the product/carbonaceous material was determined by an elemental analysis measurement. We have calculated the element (wt) percent of carbon and hydrogen in the precursor solution and compared it with elemental analysis data of the CSTON product. The calculated element percent of carbon in the precursor solution is 42.15% (in 1.5 grams of precursor), while the percentage of hydrogen is 8.42%. The measured element percentage of carbon in the CSTON product is 86.5% (in 0.841 grams of product), while the percentage of hydrogen is 1.2% and rest is WO_x. The percentage of conversion was determined by the balance of the tungsten weight. The weight of W in the reacting sample was 0.0256 grams. The amount of tungsten in the product is 0.023 grams as obtained by EDAX (2.74 wt%). Thus the reaction yield in terms of the amount of W is 90%.

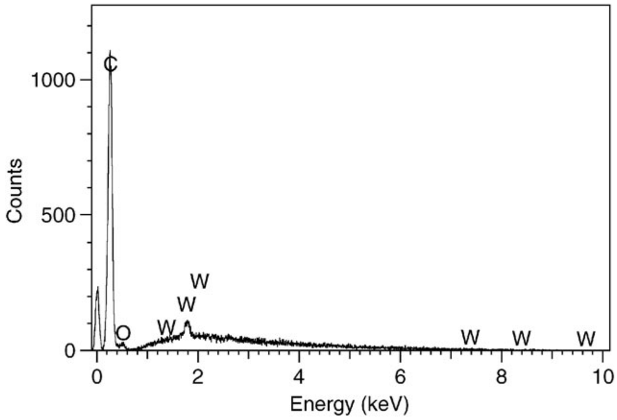


Fig. 3 EDAX analysis of a bulk CSTON (carbon sausages filled with an *in situ* formed tungsten oxide nanorods) sample.

The pure $W[OCH(CH_3)_2]_6$ is not delivered commercially, supposedly because of its poor stability. A control experiment was carried out where the precursor solution was heated at ~90 °C for 20 minutes to evaporate the isopropanol (5% w/v). The residue was used for the thermal dissociation reaction, keeping other experimental conditions identical to those described above. A mixture of WO_x nanorods, spherical carbon, and a few additional particles were observed in TEM measurements as the products of this control reaction.

3.2. TEM, SAEDS and HR-TEM measurements

The morphology and structure of the CSTON sample was further studied by TEM, SAEDS, and HR-TEM measurements. Fig. 4a presents the structure of the long sausages that are formed. The dark and light contrasts seen in these bodies indicate two different materials (Fig. 4b). The identification of the surface as carbon and the dark centre as the WO_x is based on SAEDS measurements. We have focused a 25 nm electron beam on the edge of several sausages to understand the composition. The SAEDS of the contrasting material (edge) shows the presence of O, C, and Cu. and is identified as a carbon, which covers the central part. (Spec. I). However, the typical SAEDS of the dark (center) part of the sausage shows the presence of W, O, C, and Cu (Spec. II), and is identified as the WO_x core. The presence of Cu is from the Cu grid that is used for the TEM sample preparation. From these observations, it is clear that the formed sausage is composed of carbon and the core is an *in situ* grown WO_x. These WO_x-filled sausages have a diameter of ~400 nm and a length of a few microns. The diameter of the central WO_x nanorod is ~50 nm and its length is almost equal to that of the carbon sausage, namely, of several microns. The thermal dissociation of the precursor solution in isopropanol for a long period (3 h), was expected to perhaps produce longer carbon sausages filled with WO_x nanorods. However, it yielded sausages of almost the same length and width. This means that the growth is dependent only on the availability of the WO_x catalyst and is a quick process, essentially completed in 1 h.

From SEM, EDAX, TEM and SAEDS analysis it is clear that the product, CSTON, after the thermal dissociation of tungsten(VI) isopropoxide, 5% w/v in isopropanol, is composed of WO_x nanorods surrounded by carbon. We assume that the dissociation of $W[OCH(CH_3)_2]_6$ at 700 °C leads to the immediate formation of WO_{3-x}, supposedly, directly the highly anisotropic $W_{24}O_{68}$ phase *via* the fast reactions of ether

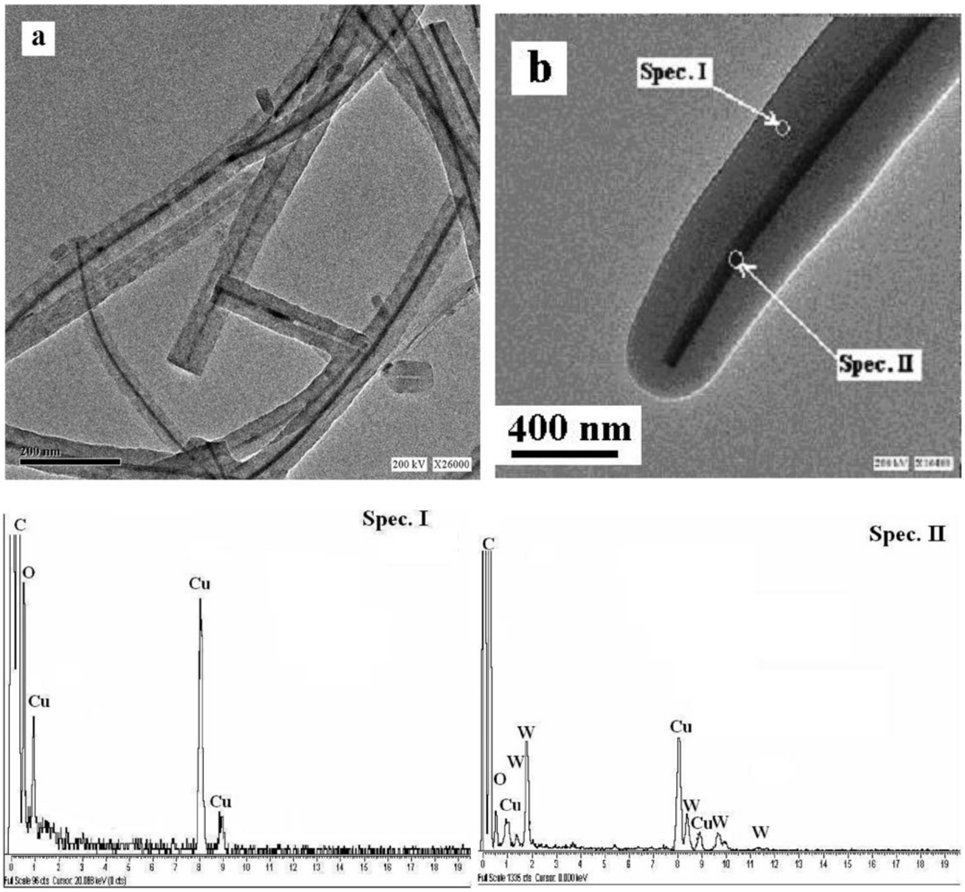
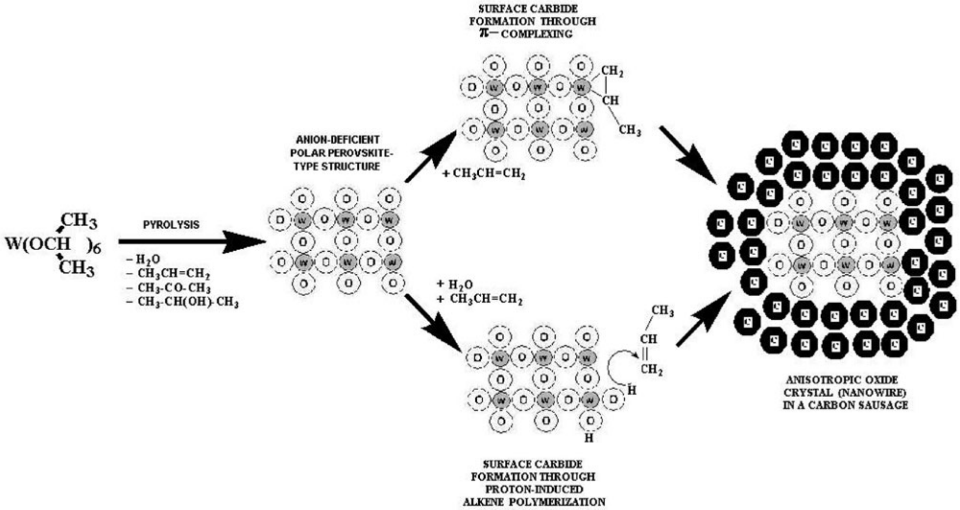


Fig. 4 Transmission electron micrographs of (a) carbon sausages filled with tungsten oxide nanorods (CSTON), (b) tip of the CSTON shown at high resolution. The SAEDS taken from the coated carbon of the marked area (depicted in Fig. 4b) is presented in Spec. I and that from the WO_x central part is presented in Spec. II.

elimination and β-hydrogen transfer. Occurrence of these reactions providing oxide nanoparticles on both solution and gas phase thermolysis of metal alkoxides has earlier been demonstrated by us in a series of mechanistic studies.[20,21] This WO_{3-x} core acted as a catalyst to the subsequent growth of smooth carbon surfaces around it under further heating. The partially reduced surface of a transition metal oxide nanocrystal acts as a highly reactive adsorbent for alkene molecules formed on high temperature thermolysis of isopropanol and di-isopropyl ether—primary products of the thermal decomposition. Two types of interaction are commonly discussed in the literature on organic catalysis:[22] (1) protonation of the double bond with subsequent initiation of alkene polymerization on the surface, which, in combination with thermal dehydrogenation can offer a carbon core as observed in the present experiments, and (2) formation of surface π-complexes and subsequently alkylidene complexes, associated with further polymerization and dehydrogenation, leading to a carbon shell (See Scheme 1). Realization of this mechanism requires elevated temperatures for the formation of a core-shell structure, which has been supported by the difference in the nature of materials obtained at different temperature conditions. It is important to note that in the absence of an anisotropic metal oxide crystal the polymerization and carbonization can occur to a minor extent and these processes result quite logically in isotropic amorphous carbon spheres. The mechanism for the formation of a similar core-shell structure was discussed in earlier reports.[17b,18b] Similar reactions, under the same conditions, were conducted for $VO(OC_2H_5)_3$ and $MoO(OMe)_4$. In both cases, the process is kinetically controlled, and V_2O_3 nanoparticles[17b] or MoO_2 nanoparticles[18b] showed a higher solidification rate than carbon to form the core of the composite. Carbon, having a slower solidification rate, forms the shell layer.

The typical TEM image (Fig. 5a, bottom right) was taken from the edge of the starting point of the sausage growth. It was intricate to get well-resolved electron diffraction patterns and the interlayer spacing for the globular WO_x particle. This difficulty arises from covering the bare WO_x with carbon under the electron beam. In other words, the electron beam during the measurement stimulates the movement of the carbon. After prolonged efforts, we could achieve the HR-TEM image of the underlying globular part of the CSTON sample (Fig. 5a) at the edge of the rod. The spacings of the lattice fringes are 0.375 nm, which is very close to the distance between the planes reported in the literature, *i.e.*, 0.378 nm for the reflecting plane ⟨104⟩ of the monoclinic $W_{24}O_{68}$ structure [International Centre for Diffracton Data's powder diffraction profile PDF: 36–103]. It is well known that the sub-stoichiometric WO_3 nanorods,[1] prepared at about 830 °C under an



Scheme 1 Schematic diagram of the growth mechanism.

atmosphere of an H_2 and Ar mixture, could grow along either the ⟨0 0 1⟩ or the ⟨1 1 0⟩ direction with evident stacking faults and textural structure. For the intermediate oxides of tungsten, WO_x ($x = 2$–3), when the value of x does not satisfy 3, the growth direction is limited by a planar defect of oxygen layers in the crystal, resulting in the spontaneous formation of a rod-shaped structure.[1] In the present case, $W_{24}O_{68}$ is initially formed as a spherical core of the carbon sausage which has grown along the ⟨104⟩ plane.

The coated carbon is mostly found to be disordered since the thermal decomposition of the precursor solution was carried out at low temperature (Fig. 5a, bottom left). To understand the nature of coated carbon in the CSTON sample, Raman spectroscopy measurements were performed. The micro-Raman spectrum of CSTON is shown in Fig. 5b. The two characteristic bands[23] of carbon were detected at 1339 cm^{-1} (D-band), and at 1595 cm^{-1} (G-band). The intensity of the G-band, associated with graphitic carbon, is larger for the CSTON sample than the intensity of the D-band. The intensity ratio of the D- and G-bands is $I_D/I_G = 0.74$ for the CSTON product. It is suggested that the existence of the non-graphitic layers is due to the execution of the present reaction at 700 °C, which is not high enough to permit an enhancement in the local order of the deposited carbon around the WO_x core.

After characterizing the CSTON sample by XRD, SEM, TEM, EDAX, CHNS analysis, SAEDS, HR-TEM and Raman spectroscopy measurements, it was unambiguously proved that the growth of carbon sausages took place with the core of the *in situ* formed tungsten oxide nanorods upon the thermal dissociation of tungsten(VI) isopropoxide, 5% w/v in isopropanol *via* a RAPET reaction. The CSTON sample that possesses ~70% (wt) C, 1.2% (wt) H (the rest is WO_x), was heated in air atmosphere to burn off the surrounding carbon. The TGA analysis of the CSTON sample was carried out with a flow of air and has shown an expected weight loss of about 70% due to the burning of carbon in a temperature range between 500 °C to 600 °C (data not shown). The CSTON sample annealed at 600 °C for 2 h in air is identified by XRD measurements as $W_{18}O_{49}$(PDF: 5–392). The nanorods are found to be a typical $W_{18}O_{49}$ phase, which is a stable,[1] layered,[6] structure at the high temperature range. A typical $W_{18}O_{49}$ nanorod is shown (Fig. 5c, bottom left) having a diameter of ~60 nm and possessing a length of more than a micron. The HR-TEM of a bare $W_{18}O_{49}$ nanorod (Fig. 5c) illustrates the perfect arrangement of the atomic layers. The measured distance between these (010) lattice planes is 0.38, which is very close to the distance between the planes reported in the literature, *i.e.*, 0.378 nm for the monoclinic phase of the $W_{18}O_{49}$ (PDF: 5–392). A selected area electron diffraction (Fig. 5c, top left) was measured for the $W_{18}O_{49}$ particle and the identified planes are highlighted.

Since the tungsten(VI) isopropoxide is in a solution of isopropanol, which makes the decomposition a solvothermal reaction, we have carried out the same reaction at a lower temperature, 350 °C, closer to the temperatures of common solvothermal reactions. This reaction yielded $W_{18}O_{49}$ nanorods, without a carbon cover, and with a diameter ranging from 10 nm to 50 nm and a length of up to 6 μm (Fig. 5d). The HR-TEM of $W_{18}O_{49}$ nanorod (Fig. 5d, bottom right image) has perfect arrangement of the atomic layers with measured distance of 0.381 nm between these (010) lattice planes is very close to the distance 0.378 nm between the planes reported in literature for the monoclinic phase of $W_{18}O_{49}$ (PDF: 5–392). The selected area electron diffraction (Fig. 5d, top right image) was measured. This fact also serves to confirm the reality that the initial formation of WO_x occurs *via* lower-temperature reaction mechanisms and not *via* the simultaneous atomization of the samples.

4. Conclusions

To summarize, we report a simple, efficient, one-stage synthesis technique for the growth of carbon sausages filled with an *in situ* formed monoclinic phase of crystalline $W_{24}O_{68}$ nanorods, from the thermal dissociation of tungsten(VI) isopropoxide, 5% w/v isopropanol at 700 °C in a closed cell under an inert atmosphere. The reaction is carried out without using

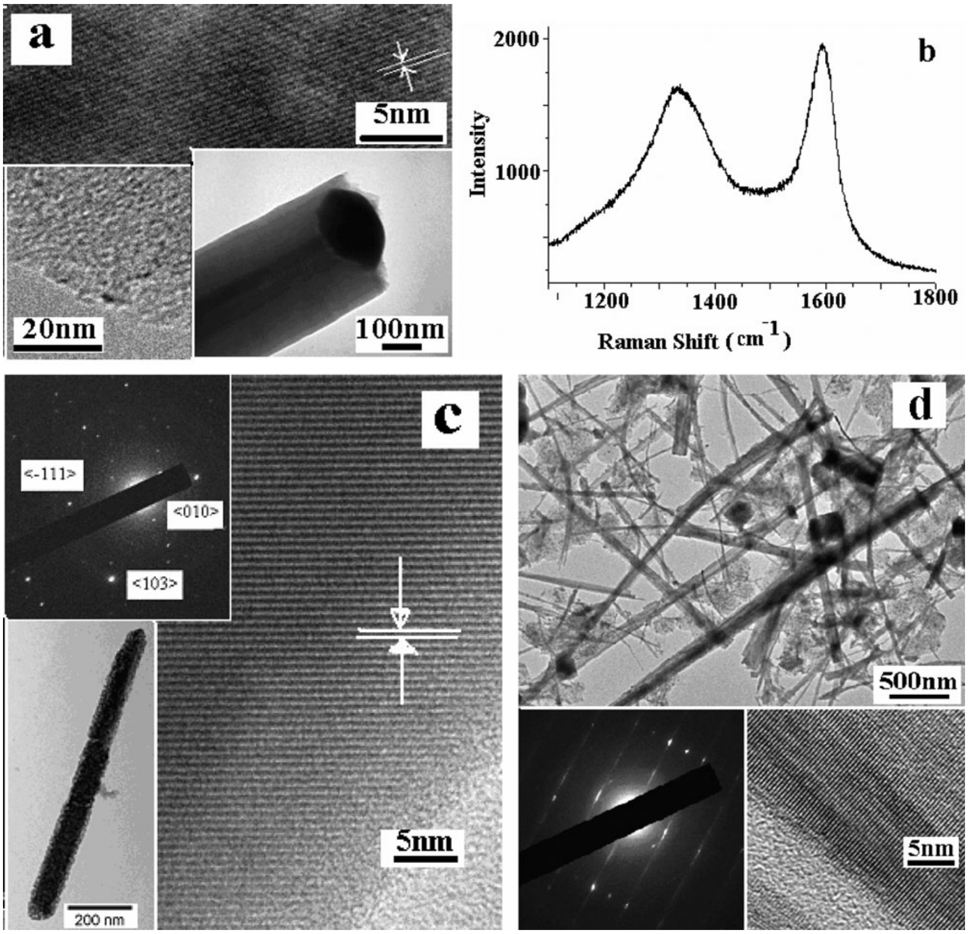


Fig. 5 (a) Highlighted interlayer spacing of a $WO_{2.83}$ nanorod—the TEM image (bottom right) was taken from the edge of the starting point of the sausage growth—and the coated disordered carbon (bottom left) (b) Raman spectrum of a CSTON sample. (c) Interlayer spacing of $W_{18}O_{49}$ nanorods, the WO_x nanorod obtained by heating the CSTON sample at 600 °C (bottom left) and the electron diffraction pattern of a $W_{18}O_{49}$ particle and highlighted identified planes (top left). (d) TEM of TONR sample and its HR-TEM image (bottom right), the obtained electron diffraction pattern (bottom left).

any external catalyst. SEM, TEM, EDAX, CHNS analysis, TGA, Raman spectroscopy, HR-TEM and SAEDS measurements systematically characterize the product. The probable reaction mechanism is discussed and the assignments of the surfaces as a carbon and centre to the WO_x are based on obtained SAEDS spectra for the CSTON product. A solvothermal reaction, carried out at 350 °C yielded WO_x nanorods with a diameter ranging from 10 nm to 50 nm and a length of up to 6 μm.

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