

The sonochemical preparation of tungsten oxide nanoparticles†

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Received 9th July 2001, Accepted 3rd January 2002

First published as an Advance Article on the web 21st February 2002

Amorphous tungsten oxide has been prepared by ultrasound irradiation of a solution of tungsten hexacarbonyl $W(CO)_6$ in diphenylmethane (DPhM) in the presence of an Ar (80%)–O₂ (20%) gaseous mixture at 90 °C. Heating this amorphous powder at 550 °C under Ar yields snowflake-like dendritic particles consisting of a mixture of monoclinic and orthorhombic WO₂ crystals. Annealing of the as-prepared product in Ar at 1000 °C causes the formation of a WO₂–WO₃ mixture containing nanorods (around 50 nm in diameter) and packs of these nanorods. Heating the product in air for 3 hours leads to triclinic WO₃ crystal formation, with a basic size of 50–70 nm. The prepared oxides have been characterized by elemental analysis, X-ray powder diffraction measurements, FTIR spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and energy dispersive X-ray analysis (EDX).

1. Introduction

Tungsten oxides have been intensively studied for a long period of time because of their promising physical properties and applications in chemistry. WO₃ is a good electrochromic,^{1–7} optochromic,^{8–10} and gasochromic^{11,12} material. It has been used to construct electrochromic windows,^{1,13–15} infrared switching devices,^{2,16} writing–reading–erasing optical devices,^{8,17} gas sensors for the determination of NO₂,¹² hydrogen sulfide,¹¹ hydrogen,¹⁸ ammonia,¹⁹ and O₃,^{20,21} and to produce humidity and temperature sensors.²¹ WO₃ and the sub-stoichiometric tungsten oxide WO₂ are good catalysts^{22–25} and photocatalysts.²⁶ Some non-stoichiometric oxides WO₂/WO₃ exhibit interesting electronic properties, such as superconductivity²⁷ and charge carrying.²⁸

Of special interest is a preparation of nanostructured tungsten oxide since nanometric particles exhibit novel properties due to the larger number of surface atoms and/or three-dimensional confinement of electrons. It has been shown that WO₃ nanoparticles demonstrate a very strong photochromic effect: the color change is one order of magnitude faster than that observed for the correspondent bulk material.¹⁰ Nanopowders of supported WO₃ catalysts have enhanced photocatalytic behavior when compared with regular submicron powders.²⁶

Numerous methods for the preparation of fine powders and thin layers of tungsten oxides include: cathodic arc deposition,²⁹ gas-phase adsorption in a fluidized-bed reactor,²⁵ laser vaporization,^{4,9,10} chemical vapor deposition from metalorganic precursors,^{30,31} magnetron sputtering,³² electrochemical deposition,^{33,34} wet chemical deposition,⁶ sol–gel process,^{3,9,26,35,36} hydrothermal reactions, *etc.*^{1,5,37} Methods related to tungsten oxides deposition from the gaseous phase are technically complex. Sol–gel and hydrothermal methods

are the multistage processes and proceed with a low yield. For these reasons, the development of simple and effective methods for tungsten oxide nanoparticles preparation is of practical interest.

Sonochemical decomposition of volatile metal carbonyls has been recently proposed as a means of obtaining nanosized materials.^{38–40} The chemical effects of ultrasound irradiation arise from acoustic cavitation. That is, the formation, growth and collapse of bubbles in a liquid. The extremely high temperatures (~5000 °C), pressures (>20 Mpa), and cooling rates (>10⁹ degrees s⁻¹) attained during cavitation collapse lead to many unique properties in the irradiated solution, and these extreme conditions have been exploited to decompose the metal–carbonyl bonds and generate nanoscale metals,^{41–44} metal carbides,⁴⁵ metal oxides and sulfides,^{46–49} and nanocomposites.^{42,50–53}

The most common solvents for the metal carbonyl sonolysis are alkanes.^{42–53} Unfortunately, the solubility of tungsten hexacarbonyl in these solvents is very low. On the other hand, it is well known that W(CO)₆ is soluble in aromatic solvents. In the present work, we report a simple and effective method of preparing tungsten oxide by the sonochemical decomposition of tungsten hexacarbonyl in diphenylmethane (DPhM). This aromatic solvent has physico-chemical properties suitable for sonochemistry (mp 25 °C, bp 265 °C, vapor pressure of 1 hPa at 77 °C), and the solubility of W(CO)₆ in this solvent is reasonable.

2. Experimental

Diphenylmethane (>99%, Fluka) and W(CO)₆ (97%, Aldrich) were used without additional purification. 80 mmol of a slurry of W(CO)₆ in DPhM was sonicated for 3 h in a spherical glass reactor with a volume ~80 cm³ under a gas mixture of 20% O₂–80% Ar. Ultrasonic irradiation was accomplished with a high-intensity ultrasonic probe (Sonics & Materials VCX 600 Sonifier, 1/2" diameter titanium horn, 20 kHz, 100 W cm⁻¹). Temperature during sonication was kept at 90 °C. At the end of the sonication, a residual black solid was removed by

†Electronic supplementary information (ESI) available: Table S1; elemental analysis values of the product of W(CO)₆ sonication in diphenylmethane and of samples heated at 550 °C in Ar and 1000 °C in Ar or air. Fig. S1: TEM image of the product heated at 1000 °C. See <http://www.rsc.org/suppdata/jm/b1/b106036h>

centrifugation under open air, was washed three times with dry pentane, and then dried under vacuum at room temperature. Elemental analysis of the prepared material was carried out on an Eager 200 CHNS Analyzer. XRD diffractograms were collected by employing a Bruker AXS D* Advance Powder X-Ray Diffractometer (Cu-K α radiation, $\lambda = 1.5418 \text{ \AA}$). EDX measurements were conducted using an X-ray microanalyzer (Oxford Scientific) built on a JSM-840 Scanning Electron Microscope (JEOL). The transmission electron micrographs were obtained on a JEOL-JEM 100SX microscope, working at 80 kV acceleration voltage. Samples for TEM were prepared by placing a drop of the sample suspension on a copper grid coated with a carbon film and allowing it to dry in air. The TGA and DSC analysis were performed by using Mettler Toledo TGA/SDTA 851 and DSC-25/TC-15 devices, respectively. FTIR spectra were recorded in KBr pellets, using an Impact 410 Nicolet spectrometer.

3. Results and discussion

The results of CNH elemental analysis for the as-prepared material, for the material heated at 550 °C for 3 h in Ar atmosphere, and for the material heated at 1000 °C for 3 h under Ar and air, are presented in the Table S1 of the ESI.† The as-prepared material contains >18% carbon, ~4% hydrogen, and ~1.8% nitrogen. It is clear that this material contains not only products of the sonochemical decomposition of tungsten carbonyl, but also products of decomposed diphenylmethane. In fact, the sonolysis of pure DPhM yields a polymeric black solid. After heating at 550 °C in Ar atmosphere, the major part of N, C and H impurities disappear, but ~4% of carbon is still present in the product. On the other hand, heating at 1000 °C under Ar or, especially, under air leads to a dramatic reduction of the carbon, nitrogen and hydrogen contaminants. After this annealing procedure, only traces of C are found. EDX measurements show the presence of tungsten and oxygen for the as-prepared material, as well as for all of the heated samples.

The FTIR spectrum of the as-prepared product exhibits absorption bands at 3060–3020, 2900–2850, and 1100–1000 cm^{-1} and is related to the presence of DPhM sonication products. These peaks disappear upon heating due to removal of the organic admixtures. The broad peaks at wavelengths less than 1000 cm^{-1} in the FTIR spectra of as-prepared and heated products can most probably be assigned to W–O bonds vibrations.

The TGA measurement, performed in nitrogen atmosphere, shows a mass loss at about 17% in a wide temperature range from 150 to 450 °C. This mass loss can be attributed to the degradation of the organic product of the DPhM decomposition during the heating and accords with the results of elemental analysis. The DSC curve exhibits a sharp exothermic peak, centered at 380 °C. This peak, most likely, corresponds to crystallization of the product of sonication. A second DSC run for the measured sample (after it is cooled to room temperature) shows no peaks whatsoever.

X-Ray diffraction patterns are shown for the as-prepared material (Fig. 1(a)), the product heated at 550 °C for 3 hours in Ar atmosphere (Fig. 1(b)), the product heated at 1000 °C for 3 hours in Ar atmosphere (Fig. 1(c)), and the product heated at 1000 °C under air (Fig. 1(d)). Fig. 1(a) demonstrates the amorphous nature of the as-prepared product. Heating this product above its crystallization temperature of 380 °C should yield a crystalline material. The XRD pattern of the product, heated at 550 °C (Fig. 1(b)), reveals that the sample is crystalline and contains crystallites of WO_2 in two modifications: orthorhombic (PDF# 82–728) and monoclinic (PDF# 32–1393). Annealing the as-prepared sample at 1000 °C under Ar leads to the formation of monoclinic tungsten dioxide, as

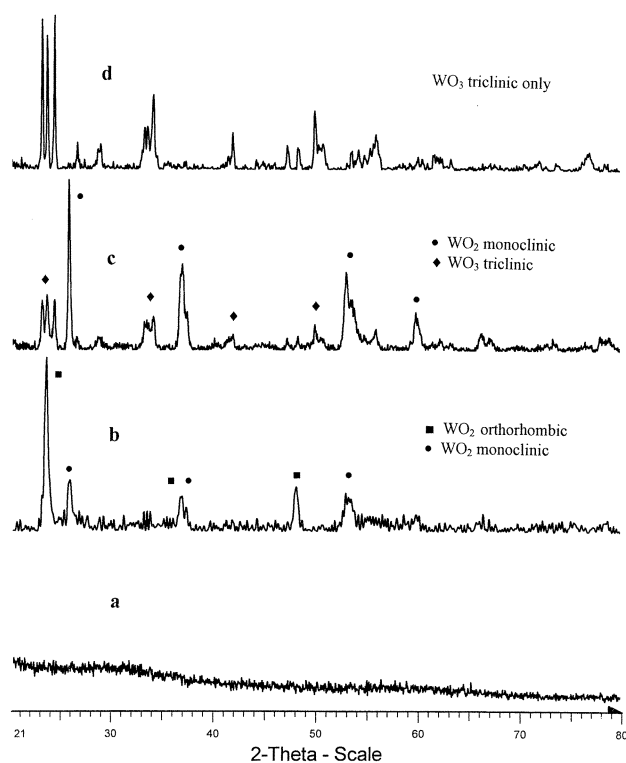


Fig. 1 XRD patterns of the product of $\text{W}(\text{CO})_6$ sonication in diphenylmethane: (a) as-prepared; (b) annealed at 550 °C for 3 hours in Ar; (c) annealed at 1000 °C for 3 hours in Ar; (d) annealed at 1000 °C for 3 hours in air.

well as triclinic WO_3 (PDF# 20–13230), Fig. 1(c). No traces of orthorhombic WO_2 are detected in this sample. Since our material does not contain an oxidizing agent, we suspect that the conversion of tungsten dioxide to tungsten trioxide has been carried out by traces of oxygen, present in Ar gas, and perhaps also because of a small leakage in our flow system. The XRD pattern for the material heated at 1000 °C under air (Fig. 1d) shows only triclinic WO_3 with no trace of tungsten dioxide being observable. The formation of pure tungsten trioxide by heating the as-prepared sample under air is also evidenced by the change of color for the annealed sample. The color of the as-prepared product and the product heated under Ar is black or dark gray–brown, while the product heated under air has a light yellow–green color.

TEM images of as-prepared product are presented in Fig. 2(a) and (b). These images show that the product consists of small globular agglomerates (100–200 nm in diameter)

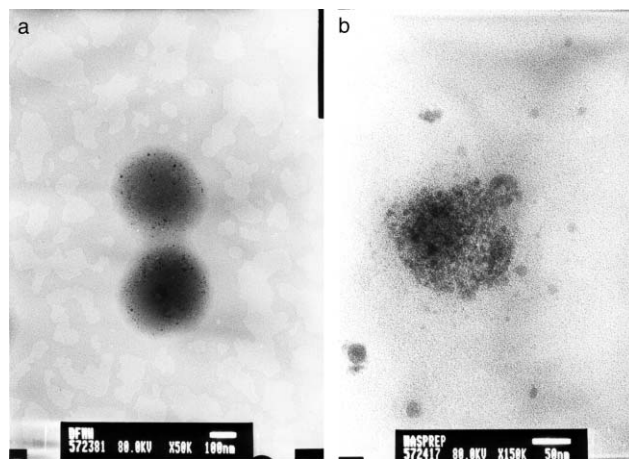


Fig. 2 TEM images of the as-prepared product of $\text{W}(\text{CO})_6$ sonication in diphenylmethane.

composed of very small (<5 nm) dense particles dispersed inside the globules. The polymeric residue mentioned above provides the cohesive force leading to the globular shape. This product is XRD amorphous. Heating the as-prepared material at 550 °C (above the crystallization temperature) leads to the appearance of snowflake-like dendritic crystals (Fig. 3(a) and (b)). The formation of this structure may be understood from the fact that two types of tungsten dioxide crystals, monoclinic and orthorhombic, exist in the heated material. A similar dendrite structure of tungsten oxide had been obtained by Zhu *et al.*,⁵⁴ in which a W foil, partly covered with a SiO₂ plate, was heated in Ar atmosphere at 1600 °C, and by Hu *et al.*,⁵⁵ in which WS₂ powder was heated in oxygen. It should be mentioned that in Fig. 3(b) one can see not only snowflake-like crystalline structures, but also a crystalline rod with a diameter of

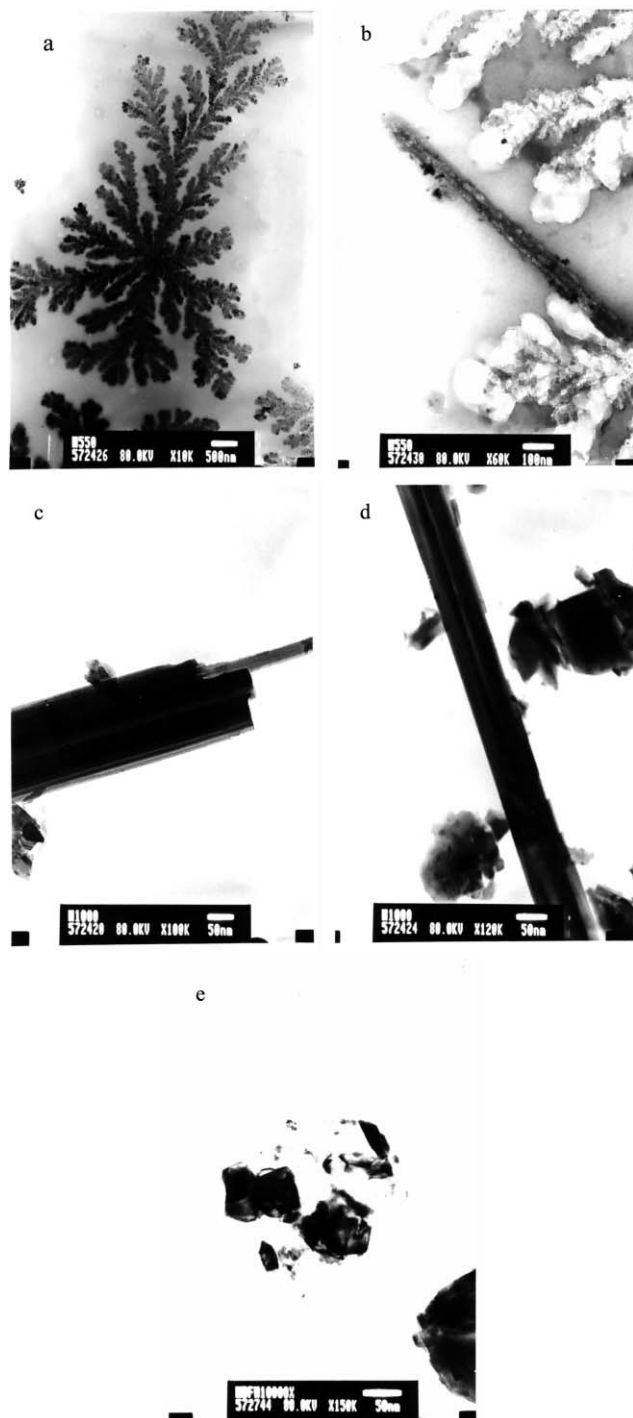


Fig. 3 TEM images of the product, annealed for 3 hours: ((a), (b)) at 550 °C in Ar; ((c), (d)) at 1000 °C in Ar; (e) at 1000 °C in air.

~50 nm. Fig. 3(c) and (d) show TEM images of the sonication product heated at 1000 °C under Ar. This crystalline material consists of nanorods (20–50 nm in diameter), packs of these rods, and some non-elongated crystallites. According to XRD measurements (Fig. 1(c)), the material under consideration consists of two types of crystallites: monoclinic WO₂ and triclinic WO₃. Taking into account the TEM image of pure crystalline tungsten dioxide (Fig. 3(b)), for which rod-like particles are observed, we can suppose that all the rod-like structures in Fig. 3(c) and (d) consist of WO₂. The non-elongated crystallites, on the other hand, are assigned to tungsten trioxide. The TEM images of the sonication product, heated at 1000 °C under air, are shown in Fig. 3(e) and Fig. S1 of the ESI.† In these images, one can see non-elongated crystallites with a particle size distribution in the range 20–100 nm. As can be seen from the XRD measurements (Fig. 1(d)), these crystallites are triclinic WO₃.

According to the published data,^{39,40} sonochemical decomposition of metal carbonyls occurs with the release of carbon monoxide. Thus, sonolysis of W(CO)₆ in the presence of an O₂–Ar gaseous mixture allows us to obtain tungsten oxide nanoparticles in DPhM solutions. Diphenylmethane sonolysis occurs simultaneously with W(CO)₆ sonochemical oxidation, followed by formation of the nanocomposite consisting of an organic matrix and highly dispersed WO₂ nanoparticles. Heating the as-prepared product causes thermal destruction of the organic components and the growth of WO₂ crystals. It can be assumed that the formation of snowflake-like dendritic structures involves the spontaneous self-organization of the mixture of orthorhombic and monoclinic WO₂ crystals. It is well known that dendrites are formed usually under slow crystallization conditions in the presence of admixtures.⁵⁶ In our system such conditions are provided by the presence of the organic matrix. Annealing of the dendritic structure causes the transformation of the less stable orthorhombic modification of WO₂ into the more stable monoclinic WO₂ crystals. Monoclinic WO₂ crystals have an elongated shape, which may be the reason why WO₂ nanorods are formed as a result of dendritic structure transformation.

4. Conclusion

1. Ultrasonic irradiation of W(CO)₆ in diphenylmethane (DPhM) in the presence of an Ar–O₂ mixture yields an X-ray amorphous deposit, containing tungsten oxide nanoparticles and the products of diphenylmethane sonolysis.
2. Heating of the amorphous solid at 550 °C for 3 hours in Ar atmosphere causes the formation of snowflake-like dendritic structures consisting of a mixture of orthorhombic and monoclinic WO₂ crystals.
3. Heating of the as-prepared product at 1000 °C for 3 hours under Ar leads to nanorods (ca. 20–50 nm wide and 50–500 nm long), consisting of monoclinic WO₂. Partial WO₂ oxidation by traces of O₂ causes formation of triclinic WO₃ nanoparticles.
4. Annealing the material at 1000 °C in the presence of air leads to the complete oxidation to WO₃. The average WO₃ particle size is about 50–70 nm.

Acknowledgements

S. I. N. thanks the Bar-Ilan Research Authority for his fellowship. A. G. is grateful for the support of the German Ministry of Science through the Deutsche–Israeli DIP program. Yu. K. thanks the Ministry of Absorption, the Center for Absorption in Science, for financial support. The authors also thank Dr Shifra Hochberg for editorial assistance.

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