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Synthesis of WO_3 nanorods by the oxidation of bulk tungsten samples with supercritical water

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Nanosized WO_3 possesses unique properties that provide a wide range of its application. It is used, for example, as an electrode in rechargeable lithium batteries,[1] gas and vapor sensors,[2] and for the production of electrochromic devices[3] and photocatalysts.[4] Nanoparticles of WO_3 are prepared by the methods of W oxidation in the gas medium,[5] chemical vapor deposition,[3] and hydrothermal synthesis.[4]

We have previously shown the possibility of preparing nanoparticles of zinc,[6] aluminum,[7] and zirconium[8] oxides by the oxidation of bulk metallic samples with sub- and supercritical water (SCW) and proposed the cluster mechanism for this process. In this work, we discovered the formation of nanorods of monoclinic WO_3 by the oxidation of bulk samples of metallic tungsten ⟨W⟩ using SCW.

Experiments were carried out on a pilot plant developed to study the interaction of SCW with various materials.[6] The ⟨W⟩ samples were prepared from rods 5 mm in diameter with a tungsten content of 99.98%. The rods were split into semicylinders or milled to form 2 mm thick plates. The semicylinders or plates were washed with alcohol and dried in an N_2 flow. The milled surface area was 68% of the total sample surface S and the chip surface area was 42%. The ⟨W⟩ samples were stored, weighed, and loaded into the reactor in nitrogen atmosphere.

The order of experiments was as follows. Entry *1* was carried out heating the reactor to 1015 K at a rate $dT/dt = 2$ K min^{-1}. A cell with a specified amount of water and a cell with the ⟨W⟩ sample were loaded in the reactor. In entries *2—4*, only a cell with the ⟨W⟩ sample was loaded in the reactor and water at the supercritical parameters ($T > 647$ K, $P > 22.1$ MPa) was sprayed in the preheated reactor through a high-performance gate from a pre-reactor. After water was sprayed, the temperature of the reactor was maintained constant. The volume of the pre-reactor is ~20 times of the volume (V_R) of the reactor occupied with water. The pressure (P) was measured by membrane tensiosensors, whose accuracy in the range from 1 to 40 MPa was 0.25%. The temperature regime of the reactor was established by a thermoregulator using ohmic heaters and chromel—alumel thermocouples. The temperature dependence of the hydrogen pressure was measured in entry *1*, and the time dependence of the hydrogen pressure was measured in entries *2—4*. At the end of experiments the reactor was rapidly cooled. Water and H_2, which was formed upon oxidation, were collected in a collector cooled with liquid nitrogen. The amount of hydrogen N_{H_2} was determined from the results of measurements of the H_2 pressure in a volumetric cylinder of a known volume, and the gas composition in the cylinder was measured on a quadrupole mass spectrometer.[6] In addition, the weights m_0 of the ⟨W⟩ samples were measured before and after oxidation, and the difference indicated the weight increase Δm. The values of the above parameters are given in Table 1

Table 1. Conditions and results of tungsten oxidation with supercritical water

Entry	T/K	m_0/g	V_R/cm^3	S /cm^2	t_{ox}	t_L	P_0 /MPa	ρ_0	ρ_f	Δm /mg	N_{H_2} /mmol	$k \cdot 10^{11}$	Sample shape
					min			mmol cm^{-3}					
1	524—1015	24.1584	16.00[a]	16.09[a]	194	—	24.91[b]	7.667[b]	7.289	28.4	1.77	1.78/2.29[c]	Semicylinder
2	917	15.1138	16.77	12.61	118	3.8	33.19	5.011	4.883	33.2	2.07	4.50	Plate
3[d]	917	18.9904	16.57	13.61	122	11.7	33.28	5.020	4.899	32.1	2.01	3.87	Plate
4	967	16.7692	18.15	11.79	180	2.5	32.66	4.511	4.450	19.2	1.20	1.96	Semicylinder

[a] At ~20 °C.
[b] At the moment of reaction beginning (687 K).
[c] For 917/967 K.
[d] In a mixture H_2O + Kr.

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along with the data on the pressure (P_0) and density of water at the moments of beginning (ρ_0) and end (ρ_f) of experiments, the surface areas of the samples (S), the duration of the period from the onset to completion of oxidation (t_{ox}), induction period encountered before the oxidation onset t_L, and the reaction rate constants.

Oxidized tungsten can be separated from the starting tungsten sample by easy percussion. Samples of oxidized tungsten were analyzed on a ThermoARL X-ray diffractometer (Fig. 1) and scanning (JCM-6700F) and transmission (JEM-2010) electron microscopes (Fig. 2) equipped with EDX energy dispersive spectrometers. The data in Fig. 1 show that monoclinic WO_3 (JCPDS 43-1035) was obtained in experiments. The increased intensity of the peaks corresponding to the interplanar spacings $d = 3.785$ and 1.893 Å can be a result of texturing the needle-like structure along the direction [010] when the sample was pressed for analysis. The elemental analysis results for oxidized tungsten samples on an EDX spectrometer also correspond to the ratio W/O = 1/3.

The oxidation of ⟨W⟩ with water can be described by the equation

$$\langle W\rangle + 3i\,H_2O = [\langle W\rangle a(WO_3)_n] + 3i\,H_2 + \Delta H(n), \qquad (1)$$

where n is the number of molecules in the cluster, a is the number of clusters $(WO_3)_n$ on the surface ⟨W⟩, and $an = i$. Since the enthalpy of formation of clusters of the new phase decreases sharply at $n < 30$,[9] the formation of new phase nuclei n^* in size is evidently the rate-determining step of nanostructuring. Ignoring the energy of detachment of the cluster $(WO_3)_n$ from the ⟨W⟩ surface at $n > 30$, $\Delta H(n > 30) = -117$ kJ mol^{-1} according to the reference data.[10] From the condition $\Delta H(n = n^*) = 0$ it is easy to estimate[6] that $n^* \approx 8$. The presence of large (8—45 nm in diameter and up to 1 μm long) nanorods (see Fig. 2) indicates that the nucleation rate is substantially lower than the rate of their further growth. It is most likely that the nanoparticle growth is favored by a high contact potential difference at the W/WO_3 interface (1.6 eV),[11] which facilitates orientation of the dipole H_2O molecules (1.85 D) by oxygen to the metal and also retains the H_2O molecules at the contact boundary W/WO_3.

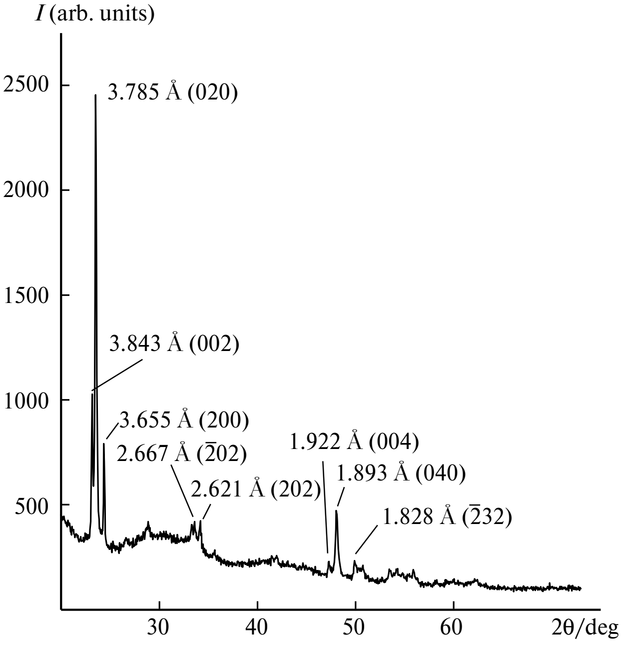

Fig. 1. X-ray diffraction pattern of the sample obtained in entry *1* (see Table *1*). The peaks of WO_3 are designated.

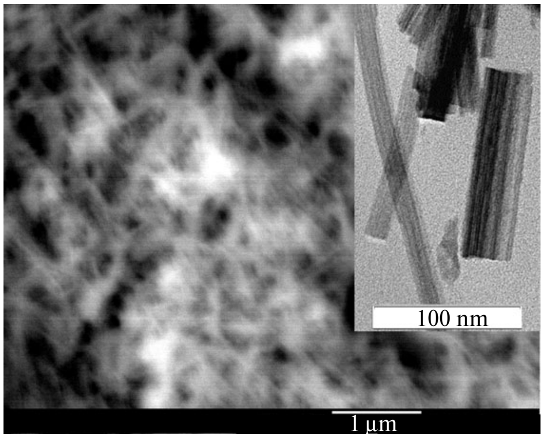

Fig. 2. SEM and TEM (inset) images of WO_3 nanorods.

The oxidation rate was calculated by the equation

$$dN_{H_2}/dt = k\rho S v, \qquad (2)$$

where dN_{H_2}/dt is the rate of hydrogen formation (mmol min^{-1}), ρ is the molar density of water (mmol cm^{-3}), S is the total surface area of the sample (cm^2), and v is the average thermal rate of water molecules (cm min^{-1}). The product of the density $\rho(t)$ by the average thermal rate $v(T)$ characterizes the flow of H_2O molecules onto the surface ⟨W⟩. The Arrhenius temperature dependence was accepted for the rate constant k in Eq. (2): $k = k_0\exp[-E/(RT)]$, where E is the apparent activation energy. Formula (2) takes into account that an increase in the number of moles of H_2 is equal to a decrease in the number of water moles in the reactor.

The dependence dN_{H_2}/dt in entry *1* was determined by the experimental values of $P(T)$ and the specified rate of temperature increase. The number of moles $N_{H_2}(T)$ corresponding to the measured values of P was determined using the Redlich—Kwong equation of state for an H_2O—H_2 mixture as in Ref. 7. The experimental data of entry *1* are well described by Eq. (2) in the studied temperature range at the following values of constants: $k_0 = (2.33\pm0.06)\cdot10^{-9}$ and $E = 37.18\pm0.17$ kJ mol^{-1}. With allowance for a weak decrease in ρ in entries *2—4* and the condition $T = $ const, the value of k was calculated by the formula $k = N_{H_2}/(\rho_0 v S t_{ox})$, which follows from

Eq. (2) (t_{ox} is the time from the onset to end of oxidation of the sample in the experiment). A comparison of the values of *k* presented in Table 1 shows that in entries *2* and *3* constants *k* are higher than those in entries *1* and *4*. It is most likely that this is due to different pre-treatments of the surface of the ⟨W⟩ samples. The lower value of *k* in entry *3* compared to entry *2* at the same values of *T* and ρ_0 is evidently due to the addition of Kr. Krypton was added to the reactor (2.1 MPa at 298 K) before SCW spraying. Perhaps, the addition of Kr decreased the lifetime of H_2O molecules in the adsorbed state on the ⟨W⟩ surface. This resulted in a decrease in the nucleation rate, as evidenced by the increase in t_L (see Table 1).

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References

1. K. Huang, Q. Pan, F. Yang, S. Ni, X. Wei, D. He, *J. Phys. D: Appl. Phys.*, 2008, **41**, 155417.
2. X. Li, G. Zhang, F. Cheng, B. Guo, J. Chen, *J. Electrochem. Soc.*, 2006, **153**, H133.
3. C. M. White, D. T. Gillaspie, E. Whitney, S. H. Lee, A. C. Dillon, *Thin Solid Films*, 2009, **517**, 3596.
4. M. Shibuya, M. Miyauchi, *Advan. Mater.*, 2009, **21**, 1373.
5. M. Feng, A. L. Pan, H. R. Zhang, Z. A. Li, F. Liu, H. W. Liu, D. X. Shi, B. S. Zou, H. J. Gao, *Appl. Phys. Lett.*, 2005, **86**, 141901.
6. A. A. Vostrikov, A. V. Shishkin, N. I. Timoshenko, *Izv. Akad. Nauk*, *Ser. Khim.*, 2006, 2205 [*Rus. Chem. Bull.*, *Int. Ed.*, 2006, **55**, 2291].
7. A. A. Vostrikov, O. N. Fedyaeva, I. I. Fadeeva, M. Ya. Sokol, *Sverkhkrit. flyuidy: teoriya i praktika* [*Supercritical Fluids: Theory and Practice*], 2010, **5**, 12 (in Russian).
8. A. A. Vostrikov, O. N. Fedyaeva, A. V. Shishkin, M. Ya. Sokol, *Pis´ma v Zh. Tekhn. Fiz.*, 2010, **36**, No. 17, 1 [*Tech. Phys. Lett.* (*Engl. Transl.*), 2010, **36**, No. 9, 779].
9. A. A. Vostrikov, D. Yu. Dubov, *Zh. Eksp. Teor. Fiz.*, 2004, **98**, 222 [*JETP* (*Engl. Transl.*), 2004, **98**, 206].
10. R. A. Lidin, L. L. Andreeva, V. A. Molochko, *Konstanty neorganicheskikh veshchestv: spravochnik* [*Constants of Inorganic Substances: Manual*], Drofa, Moscow, 2006, 685 pp. (in Russian).
11. V. S. Fomenko, *Emissionnye svoistva materialov* [*Emission Properties of Materials*], Naukova Dumka, Kiev, 1981, 339 pp. (in Russian).

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