Tungsten and molybdenum nano-oxides as promising substrates for analytical method of giant Raman scattering

T I Borodina¹, G E Valyano¹, V T Karpukhin¹,² and M M Malikov¹

¹ Joint Institute for High Temperatures, Russian Academy of Sciences, Moscow, Russia
² E-mail: vtkarp@gmail.com

Abstract. The article discusses the results of the experimental research into composition and crystal structures of tungsten and molybdenum nano-oxides. We prove that the starting material of nanostructures is amorphous, with particle sizes being less than 1-2 nm. These structures are able to serve as an effective substrate for the analytical method based on the surface enhanced Raman scattering (SERS).

1. Introduction
Over the last fifteen years, there has been the growing interest of research into the enhanced effect of Raman scattering probability of laser emission caused by certain molecules in a substance which are located on the surface of nanoparticles of another substance. This effect is the basis of a highly sensitive method for the compositional analysis of gases, liquids, and solids, called the giant Raman scattering (GRS) or the surface enhanced Raman scattering (SERS) [1-2]. The intensity of the scattering is determined by some mechanisms of the resonance interaction between laser emission and electronic structures of molecules in both the sampled substance (analytes) and nanoparticles (substrates). The plasmon and charge-exchange mechanisms are considered to be the conventional ones [3-4]. The plasmon mechanism is the most effective one, with the scattered signal amplitude scaling up to $10^{12} – 10^{14}$ times and even more. Thus, the amplification coefficient ($E_{GRS}$) represents the indicated value. In this case, the best substrates are the ones with the high electrical conductivity such as gold, platinum, and silver. They are most frequently used in biomedical studies [5]. The more complex charge-exchange mechanism is specifically attributed to the semiconductor materials, in particular, to such transition metals as zinc, copper, titanium, ferrum, zirconium, molybdenum, and tungsten [6]. Although the substrates of oxides have significantly less $E_{GRS}$, which is approximately $10^4 – 10^6$, they have some advantages of practical importance: low cost, high chemical and temperature stability, and others.

2. The problem statement and research goal
While conducting the research into GRS, the huge influence of both the substrate composition and nanoparticle structures on the substrate quality was detected. Several studies were dedicated to examining the individually-tailored nanostructures whose surface profile and its traits – the form, sizes of cavities or protrusions on the films, the diameter as well as the number of tubes and threads in a beam – were changed under a specific control; $E_{GRS}$ was also measured [7-8]. Based on these studies, we conducted the research into nanostructures of molybdenum and tungsten oxides. The goal of this research is to examine the nanostructures of molybdenum and tungsten oxides synthesized by the laser
ablation of metals in water as well as to evaluate their possible applicability in the form of substrates for GRS.

3. Materials and methods

3.1. Experimental facility
The experimental facility consists of a pulse-frequency copper-vapor laser as a radiation source with the emission wavelengths of 510 nm and 578 nm; the pulse duration is 20 nanoseconds; the pulse repetition rate is 10 kHz; the average beam output power is 13-15 W. Both the sampled composition and crystal structures are determined by the standard method of X-ray diffraction using the diffractometer DRON-2 (copper line Kα). The morphology of the sampled nanostructures is examined using the scanning electron microscope (SEM) called NOVA NANOSEM 650. The sample preparation for the analysis includes centrifugation of the colloid obtained during the ablation at 15000 r/min and subsequent sediment drying.

3.2. Composition of samples
Figure 1 shows the diffractograms of sediments of the colloidal solutions obtained during the tungsten and molybdenum ablation in water for about 3 hours. As it can be seen from the diffractograms, the sediments consist of both the crystalline and X-ray amorphic components.

![Figure 1. X-ray diffractograms of sediments: 1 - W - oxides, 2 - Mo - oxides.](image)

The crystalline component of W-colloid sediments includes tungsten, its oxides W₂O₅, WO₂ₗₙ, and hydroxides WO₃·H₂O, WO₃·5H₂O. An average particle size of WO₂ₜ phase is 70 nm; WO₃·H₂O phases are 42 nm; WO₃·0, 5H₂O and W₂O₅ W phases are greater than 100 nm. The main part of the material is in the X-ray amorphic state (the particle size is ≈ 1-2 nm). The diffuse halo located in the X-ray diffraction spectrum at the Bragg angles of 2θ = 20-35° indicates this state. The halo angular position suggests that WO₃·H₂O phase could dominate in the X-ray amorphic state. Mo - sample (see Figure 1) features the extensive halo in the region of angles of 2θ ≈ 20-38°. It indicates the presence of molybdenum oxides MoO₃, Mo₃O₁₁, and hydroxides MoO(OH)₂, Mo₅O₃(OH)₈. The absence of prominent lines in the spectrum proves that the bulk of sediments is in the X-ray amorphic state, the same as with tungsten.

3.3. Morphology of samples
Figure 2 shows the typical pattern elements of the W-sediment surface. The sediment represents the cracked continuous mass (see Figure 2a). The 400 nm-scale picture shows that some parts of the continuous mass consist of laminar-foam formations of various forms, ranging from hundreds of
nanometers to tens of microns in size, containing several “arrowy” inclusions (see Figure 2b). In its turn, there are some spherical structures of tens nanometers in size on their surfaces (see Figure 2c).

4. Findings and discussion

The examination of Mo- sediments showed that there are two basic components in their microstructure (see Figure 3a): the cracked dense amorphous masses and the aggregates of rounded particles located on the surfaces and in the near-surface layer of the masses. There are also foam formations of up to ten microns in size in some regions.

It is possible to see the layered structure of the amorphous mass (see Figure 3c) when magnified more times in the regions of cracking (see Figure 3b). The boundaries of particles are obscure in the dense masses (see Figure 3d). The examination of individual aggregates of rounded particles and foam formations demonstrates that they consist of both continuous and hollow spheres ranging from units to several dozens of nanometers in size (see Figure 3e). After analyzing the surface structures of the largest particles (see Figure 3f), it is possible to conclude that both hollow and continuous particles are formed by the structures of substantially smaller sizes.

The examination of nanostructures of tungsten and molybdenum oxides allows determining their specific features. The first and the main feature is the amorphous mass which serves as the basic building material of all structural components (aggregates of both the continuous and hollow particles of the diverse forms, foam formations, and others). The diffractograms show that the mass is in the X-ray amorphic state; the size of its particles (clusters of atoms and molecules) does not exceed 1-2nm. The transition metals with a high ionization potential (molybdenum, tungsten, and others) are known to be prone to formation of the cluster structures [9]. Second, it is possible to speak about a ‘laminar’ structure of virtually all types of nanostructures. Third, the highly-developed surface of nanostructures is specifically attributed to the oxides. The articles [7-8] consider the direct correlation between the
surface development of nanostructures and their sizes and $E_{GRS}$ as follows: the less the sizes are and the greater the surface development is, the higher $E_{GRS}$ is.

Thus, the specific features of nanostructures of tungsten and molybdenum oxides allow assuming the possibility of their application as substrates, which ensure the high $E_{GRS}$ of the Raman scattering. It is necessary to note that the authors’ previous experiments with zirconium oxides having the same nanostructures resulted in obtaining $E_{GRS} \approx 10^4$ [10].

5. Conclusion
The research into the nanostructures of tungsten and molybdenum oxides shows that the method of laser ablation of metals in water allows synthesizing the nanostructures of oxides, which have good prospects for their application as substrates for GRS.

References
[1] Zuev V 2007 Surface polaritons and plasmons: spontaneous emission of an atom near a small body size Optics and Spectroscopy 5(102) 742-753 (Preprint FIAN No 3 (in Russ))
[2] Emelyanov V and Koroteev N 1981 Effect of the giant Raman scattering of light by molecules UFN 135 345
[3] Yamamoto Y and Tamitake I 2016 Why and how do the shapes of surface enhanced Raman scattering spectra change? Recent progress from mechanistic studies J. Raman Spectrosc. 47 78-88
[4] Lombardi J and Birke R 2014 Theory of Surface-Enhanced RAMAN Scattering in Semiconductors J. Phys. Chem. 118 (20) 11120-30
[5] Mamichev D, Kuznetsov I, Maslov N and Zanaveskin M 2012 Optical sensors based on surface plasmon resonance for highly sensitive biochemical analysis Molekuljarnaja medicina. 6 12
[6] Wei J, Bing Z and Yukihiro O 2016 Semiconductor materials in analytical applications of surface - enhanced Raman scattering J. Raman Spectrosc. 47 51-8
[7] Yu-Lien Deng Yi-Je Juang 2014 Black silicon SERS substrate: Effect of surface morphology on SERS detection and application of single algal cell analysis Biosens and Bioelectronics 53 37-42
[8] Rigo I, Veres M, Himics L, Toth S, Czitrovszky A, Nagy A and Furjes P 2016 Comparative analysis of SERS substrates of different morphology Proc. Engineering 168 371-74
[9] Novogenov V 2001 Introduction into inorganic chemistry (Barnaul: Altai State Univ. Press)
[10] Karpukhin V, Malikov M, Borodina T, Val’yano G and Gololobova O 2017 An investigation of the effect of surface-enhanced Raman scattering on zirconium and molybdenum nanostructures synthesized by laser ablation in a liquid environment Laser Ablation: Advances in Research and Applications (New York: Nova science publishers) pp 179-192