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A modernized laboratory setup for the deposition of metal oxide nanoparticles onto a metallic substrate using a droplet-free electrospray mode with dynamic liquid flow division at atmospheric pressure

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Received March 18, 2024
Revised May 31, 2024
Accepted June 18, 2024

A modernized chesme of a laboratory setup for the deposition of metal oxide nanoparticles onto a metallic substrate has been presented. Using TiO_2 particles as an example, it has been shown that the modernized setup allows for the creation of a uniform coating with a dense packing of spherical particles less than $1\,\mu$m in size, featuring a granular structure and strong adhesion to the substrate.

Keywords: Electrospray, LDI mass spectrometry, titanium dioxide, surface functionalization, LDI target.

DOI: 10.61011/TPL.2024.10.60117.19922

The development of methods for functionalization of the LDI (laser desorption/ionization) target surface is of great importance, since it allows for significant expansion of the capabilities of LDI mass spectrometry [1]. It is especially important to ensure strong adhesion of the functional metal to the target surface in functionalization. This may be achieved, e.g., with the use of such techniques as physical vapor deposition, chemical solution deposition, or deposition of monomers with their subsequent polymerization [2,3]. However, these methods have a number of disadvantages and limitations. For example, chemical solution deposition may yield non-uniform coatings, and restrictions imposed on the choice of solvents may affect the stability and functionality of the resulting coating [2]. When monomer polymerization methods are used for surface functionalization, uneven distribution of monomers and weak adhesion to the matrix may be observed, which potentially lead to instability of the coating and loss of its functionality [3].

Electrospraying of a metal oxide suspension onto the surface is another possible way to functionalize an LDI target [4]. However, this requires careful preparation of the target surface (e.g., oxygen plasma treatment) to ensure adhesion of particles. Apparently, these strict requirements in regard to the deposition of coatings from metal oxide particles are necessary due to the formation of microdroplets during spraying with the use of a classical electrospray ion source [5]. We have demonstrated in [1] that the droplet-free electrospray method provides an opportunity to obtain a uniform coating of the target surface. This is important in terms of ensuring sample homogeneity and minimizing the impact of coating non-uniformity on experimental results. To simplify the process of droplet-free spraying, we proposed [6] the simplest set of equipment for deposition of metal oxide nanoparticles onto an LDI target. It allows one to perform droplet-free electrospraying with dynamic liquid flow division at normal pressure and obtain smooth and stable coatings of titanium dioxide particles with strong adhesion to the substrate.

In the simplest design of the setup [6], a suspension of metal oxides in an aqueous solution of methanol with 0.1% of formic acid was fed into a capillary from an open syringe dropper under atmospheric pressure and the influence of gravity. However, the operating range of this setup was limited. First, uncontrolled flow of the liquid phase (suspension of nanoparticles) associated with evaporation of the solvent from the syringe dropper chamber was observed. This had a negative effect on uniformity of the suspension flow into the capillary, which led to instability of the liquid meniscus and disruption of the droplet-free spray mode. Second, the non-uniformity of counter-flow of air pumped between the capillaries to maintain surface tension of the formed droplet induced bubbling of liquid in the gap between the capillaries and, consequently, made the droplet-free mode unstable and initiated the transition to conventional liquid spraying. Third, the pH level of the solution decreased during spraying due to evaporation of the organic solvent, resulting in a sharp increase in spray current, disruption of the liquid meniscus, and, consequently, electrical breakdown and mechanical damage to the surface of the counter electrode.

To solve the above problems, the simplest set of equipment for deposition of metal oxide nanoparticles onto an LDI target was updated. The syringe dropper was replaced with a closed dropper chamber (*1* in Fig. 1) to maintain a stable and uniform flow and suppress the process of evaporation of the organic solvent. This helped prevent the reduction in the nanoparticle suspension flow rate that was previously associated with a reduction in height of the

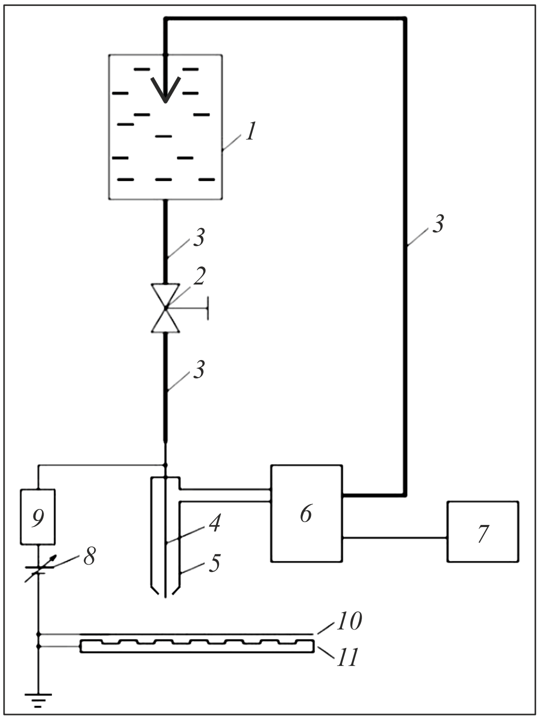

Figure 1. Schematic diagram of a simplified laboratory setup for deposition of nanoparticles of various metal oxides onto a metal substrate. *1* — Closed dropper chamber, *2* — infusion rate regulator, *3* — plastic tubing, *4* — metal capillary 0.8 mm in diameter, *5* — outer dielectric capillary, *6* — R385 6-12V DC air pump, *7* — power supply of the air pump, *8* — Applied Kilovolts adjustable high-voltage power supply, *9* — high-value resistor, *10* — grounded smooth metal removable plate (used to set the spray mode), and *11* — LDI target.

suspension column and evaporation of the organic solvent. The pressure of air accumulated in the chamber ensured a constant flow rate of the suspension into the capillary when excess solvent was supplied into the closed chamber.

To increase the stability of the droplet-free mode, a change was made to the setup that ensured uniformity of the counter-flow of air pumped through the gap between metal capillary *4* and outer dielectric capillary *5* (Fig. 1). The outer capillary was made conical and tapering towards the metal capillary to minimize the gap between them (Fig. 2). This eliminated the effect of bubbling in the gap and, as a consequence, stabilized the meniscus shape.

As a result of the changes made, the flow rate of the liquid phase remained constant throughout the entire spraying process. In addition, the rate of air and excess liquid pumping through the gap between the capillaries, which was set at the start, was maintained at a constant level throughout the entire experiment. In view of this, the required control over droplet-free spraying was reduced to selecting the voltage that regulates the spray current. This was achieved by introducing a high-value resistor (KEV-2 510 MΩ) into the capillary power supply circuit, which led to an increase in current stability during spraying and, consequently, helped stabilize the droplet-free spray mode and exclude the possibility of electrical breakdown.

The case of spraying a suspension of titanium dioxide (TiO_2) nanopowder with a particle size of $\sim$ 21 nm (Sigma-Aldrich) onto the surface of an LDI target (polished steel target MTP 384, Bruker) was chosen as a test scenario for the modernized laboratory setup for deposition of metal oxide nanoparticles onto a metal substrate was tested using. A suspension in 30% aqueous methanol with 0.1% of formic acid with a particle concentration of 5 mg/ml was used in the experiment. The suspension was premixed with a vortexer and held in an ultrasonic bath for 10 min. The following spraying parameters were set to obtain a titanium dioxide spot 2 mm in diameter: the current strength was 133 ± 5 nA; the distance between the target and the metal capillary was $\sim$ 5 mm; the length of the needle section protruding from the housing was 0.7 mm; the dropper with the suspension was secured to a stand at 70 cm above the table; the working suspension volume was 20 ml; and the sputtering time was 10 min. It was found in the process of droplet-free electrospraying of the suspension that a fairly uniform coating could be obtained at these parameters. This was verified by the results of examination of the coating with a HITACHI S3400N (Japan) scanning electron microscope (SEM). The following SEM parameters were set: a probe current of 1.7 nA, an accelerating voltage of 20 kV, and a working distance of 10 mm (for secondary electrons). The obtained results are indicative of dense packing of spherical particles smaller than 1 μm (Figs. 3, *a*, *b*).

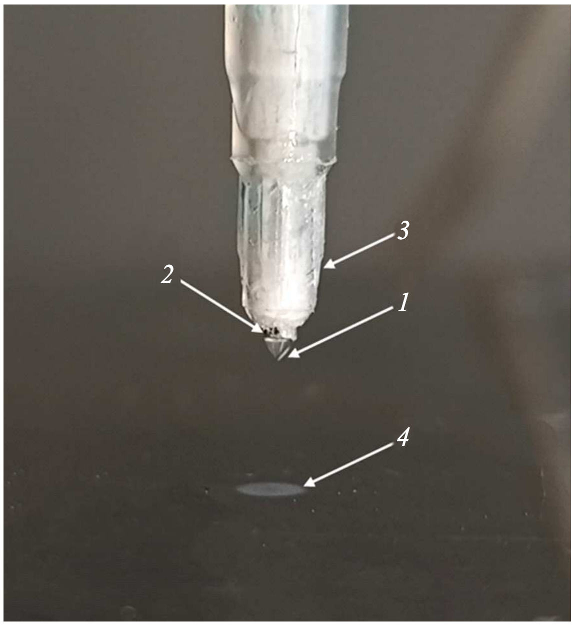

Figure 2. Spraying of a TiO_2 nanopowder suspension onto a polished LDI target. *1* — Meniscus of the sprayed suspension in the droplet-free mode, *2* — end face of the metal capillary, *3* — outer coaxial dielectric capillary, and *4* — dry mechanically stable TiO_2 spot.

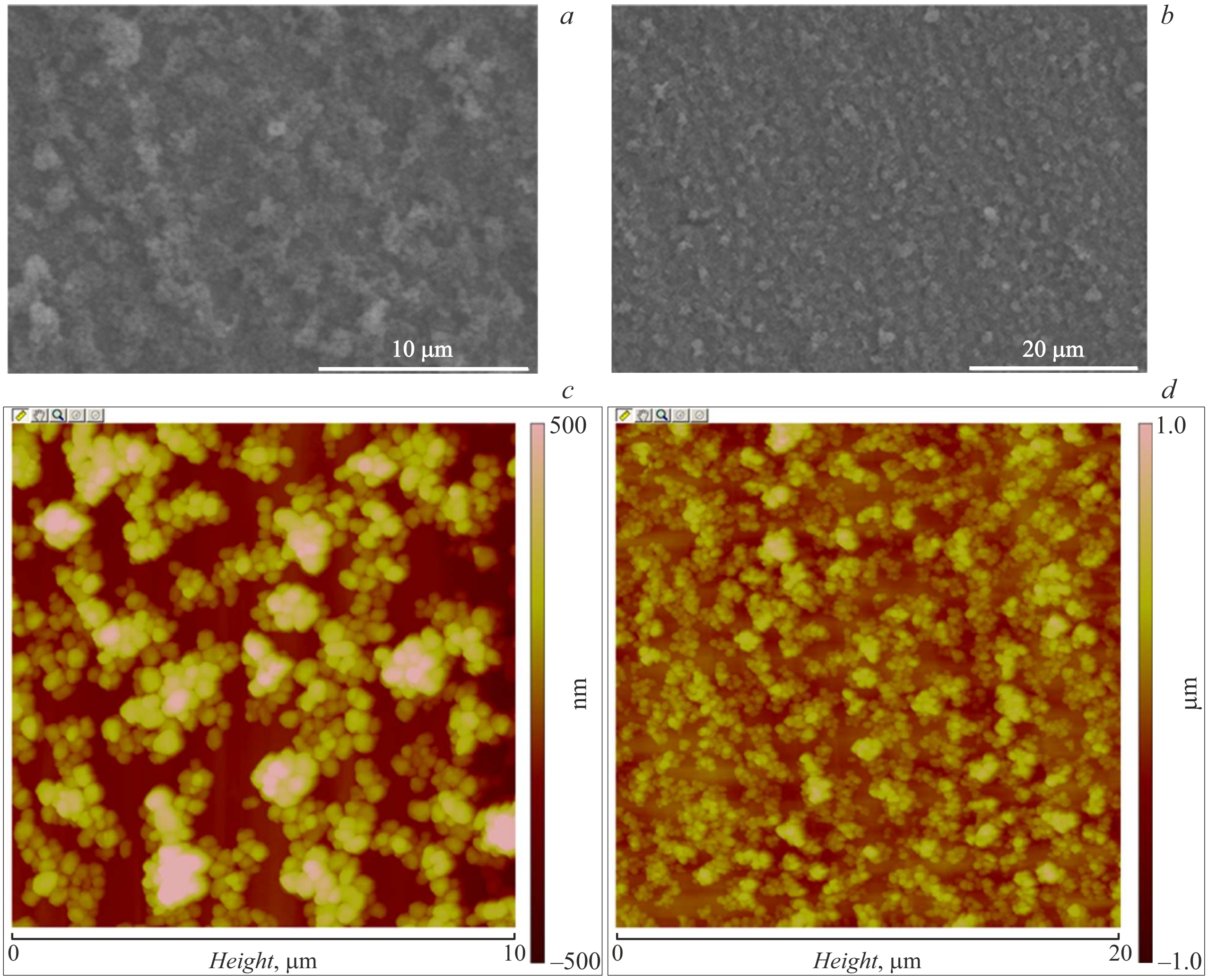

Figure 3. Images of the surface of the LDI target functionalized with titanium dioxide. *a*, *b* — SEM images with scale bars of 10 and 20 μm; *c*, *d* — AFM images with frame sizes of 10×10 and $20 \times 20\,\mu$m.

Atomic force microscopy (AFM) was used to study the surface relief formed by sprayed titanium dioxide in detail. AFM images (Figs. 3, *c*, *d*) were obtained using a DI Nanoscope Multimode V (Veeco, United States) scanning probe microscope in the intermittent contact mode (Tapping Mode$^{\text{TM}}$) with an HA_NC etalon (NT-MDT, Russia) probe (frequency, 226 kHz; force constant, 12 N/m; tip curvature radius, < 10 nm) at a scan rate of 0.3 Hz. The layer of sprayed titanium dioxide had a granular structure with spherical aggregates 350−500 nm in diameter forming clusters with a diameter of $1-1.5\,\mu$m. The average surface relief height was $1.5\,\mu$m.

The obtained results suggest that modernization of the simplest set of equipment for deposition of metal oxide nanoparticles onto an LDI target by droplet-free electrospraying under normal conditions made it possible to maintain a stable droplet-free electrospray mode and exclude the possibility of mechanical damage to the LDI target surface.

Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by D.Safin