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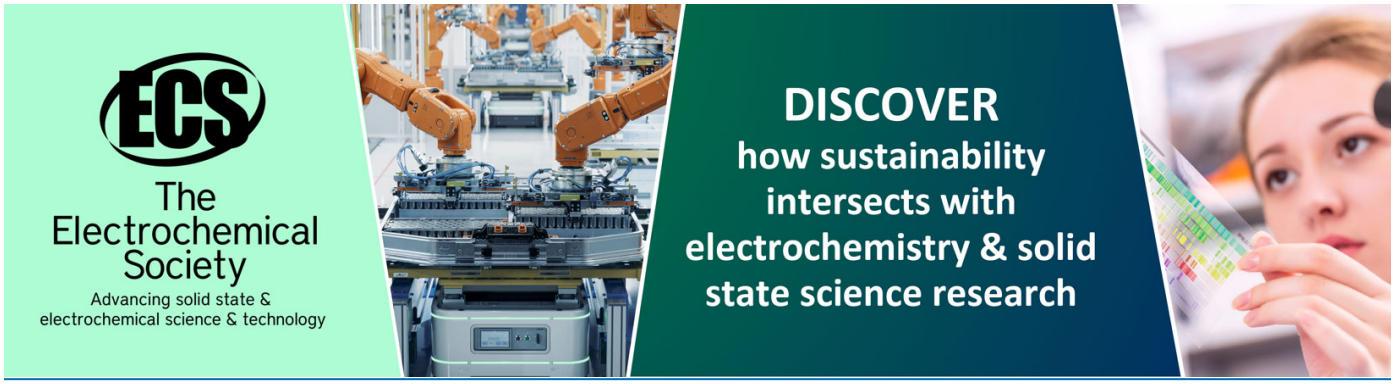

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Laser-ablative fabrication of nanoparticle inks for 3D inkjet-printing of multifunctional coatings

A A Ionin[1], A K Ivanova[1,2], R A Khmel'nitskii[1], Yu V Klevkov[1], S I Kudryashov[1,2], N N Mel'nik[1], A A Nastulyavichus[1], A A Rudenko[1], I N Saraeva[1*], N A Smirnov[1] and D A Zayarny[1]

[1] Lebedev Physical Institute, Leninsky prospect 53, Moscow 119991, Russia
[2] National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Kashirskoe shosse 31, Moscow 115409, Russia

E-mail: *heddwch@mail.ru

Abstract. We report the fabrication of multifunctional coatings via inkjet printing using water-based nanoinks in the form of selenium (Se) and gold (Au) nanoparticle (NP) colloids, prepared by laser ablation of solid targets in deionized water or 50%-isopropyl alcohol solution. Nanoparticles and NP-based coatings were deposited onto silver films, magnetron-sputtered to silica-glass substrates, and characterized by means of scanning and transmission electron microscopy (SEM, TEM), UV-vis-IR, Raman and energy-dispersive X-ray spectroscopies.

1. Introduction

Many techniques, widely used for the nanostructured coatings manufacturing, such as lithography, chemical etching or vacuum sputtering are efficient, although complex and time-consuming, also reducing the spectrum of usable substrate materials due to high temperature or pressure during the machining process. The emerging field of 3D inkjet printing allows overcoming the imposed restrains, making it possible to create the required nanostructured areas with necessary NPs concentration on the surface of any possible material, including elastic and soft plastics, dielectrics, paper etc.

3D inkjet printing with the use of nanoparticle (NP) colloids as an active ink-pigment components is considered an eligible and simple-to-implement technique for manufacturing of thin-film transistors, SERS-substrates, accumulators, solar batteries, memory basic components etc. [1–4], based on the multi-elemental sandwich structure. Two problems emerge while constructing functional coatings with nanoinks: (1) the fabrication of NPs with the required morphology without any contaminations and (2) their precise deposition on given substrates. Chemical and mechanical methods of NPs manufacturing are well known for high impurity, caused by side reaction products or machining process, and are hard to implement. Laser ablation of solid targets in liquid media seem an eligible candidate for NPs preparation, as it ensures the purity of the resulting ablation products as well as their abundant yield and rapid fabrication [5–8].

In this work, we present a technique of mono- and multilayer nanostructure coatings' inkjet printing with NPs colloidal solutions, prepared by laser ablation of solid targets in liquid media, on the magnetron-sputtered silica-supported Ag films. The resulting coatings were characterized by means of scanning electron and transmission microscopy (SEM, TEM), UV-vis-IR, Raman and energy-dispersive X-ray spectroscopy modules.

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2. Experimental details

2.1. Fabrication of nanoinks and inkjet printing

The ablative fabrication of NP-based inks was implemented using an Yb^{+}-doped fiber laser HTFMark, Bulat (central wavelength $\lambda = 1040$ nm, pulsewidth FWHM $\tau = 200$ ns, average pulse energy up to 1 mJ, repetition rate up to 80 kHz), equipped with a galvanometric scanner and an f-theta objective (focal length F = 160 mm) (figure 1). The 2×2 mm^2 areas of solid targets (golden plate, purity 99.99%, Savings Bank of Russian Federation, and selenium plate, purity 99%, hexagonal γ-phase, homemade) were processed via multipass (10 passes) laser beam scanning with the constant speed of 40 m/s under the 2-mm layer of liquid (deionized water or isopropyl alcohol (IPA) solutions of different concentration). The inkjet printing of nanocoatings on silica glass-supported silver films was implemented via multicartrige printer Epson L800.

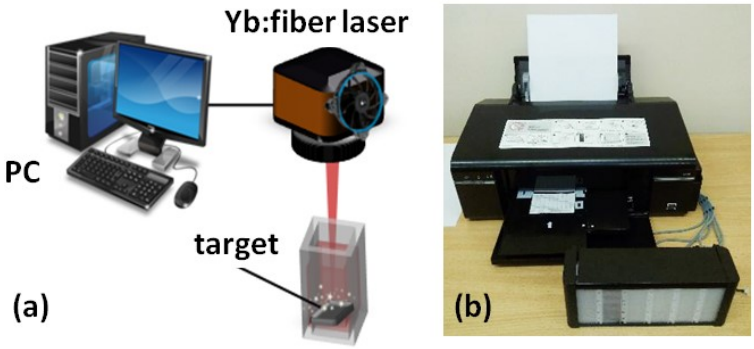

Figure 1. (a) – experimental setup for nanoinks fabrication; (b) – inkjet printer Epson L800.

2.2. Characterization of nanoinks

The resulting ablation products in form of Au and Se colloidal solutions were analyzed in order to define their morphology and properties. The NPs size distribution was estimated with the use of dynamic light scattering (DLS) (PhotocorFC), scanning electron microscopy (SEM, JSM 7001F, JEOL) and transmission electron microscopy (TEM, LEO912 ABOMEGA). NPs for SEM characterisation were deposited onto atomically-smooth silicon wafers and dried at room temperature. Plasmon-related absorption band (for Au nanoinks) and interband absorption peak (Au, Se) positions were detected via UV-vis transmission spectroscopy (V-70, Brucker).

Se colloids, prepared in a 50%-IPA solution (opaque red), exhibited an interband absorption band <400 nm and the strong Mie-resonance absorption band at >400 nm (figure 2b). The position of the main $E_g \approx 233$ cm^{-1} in bulk selenium corresponds to its γ-crystalline structure, while in NPs deposits a new band appears $A_{1g} \approx 250$ cm^{-1} (figure 3), illustrating the amorphization of target material during the laser-induced ejection [9]. The mean Se NPs radii equalled to 75 and 167 nm, which is supported by the SEM and DLS data (figure 2a).

Au hydrosols of reddish-violet colour had an absorption band at ~530 nm (figure 2d), which is red-shifted comparing to the typical Au localised plasmon resonance ($\lambda_{LPR} \approx 520$ nm) [10] and can be explained by the formation of spheroids and overall NPs size increase [11]. The average Au NPs size equalled to ~20 nm, but with a broad polydispersity range (figure 2c).

Se NPs, fabricated in 99% IPA solution (opaque, dark brown colour), were nucleated in form of trigonal selenium (t-Se) nanorods, which was supported by the TEM photographs (figure 4) and Raman spectroscopy (figure 3, blue curve).

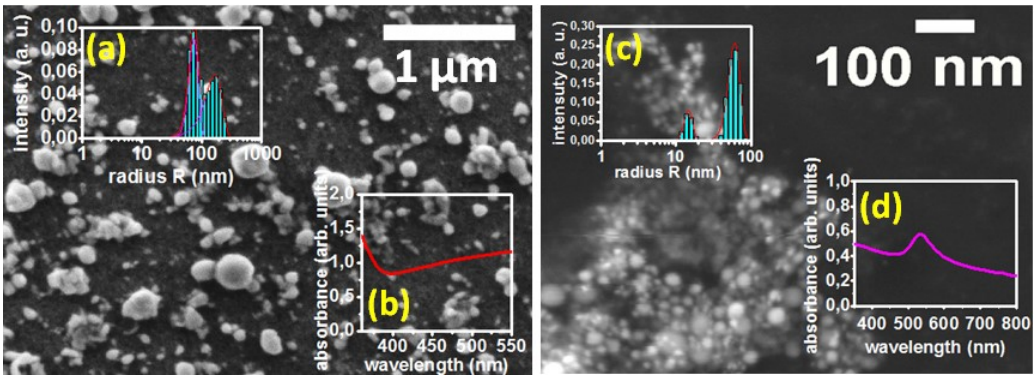

Figure 2. SEM-images of Se (left) and Au (right) NPs, printed on silica-supported silver films. Insets: (a), (c) – the corresponding DLS spectra of NPs size distribution; absorbance spectra of Se NPs (b) and Au NPs (d).

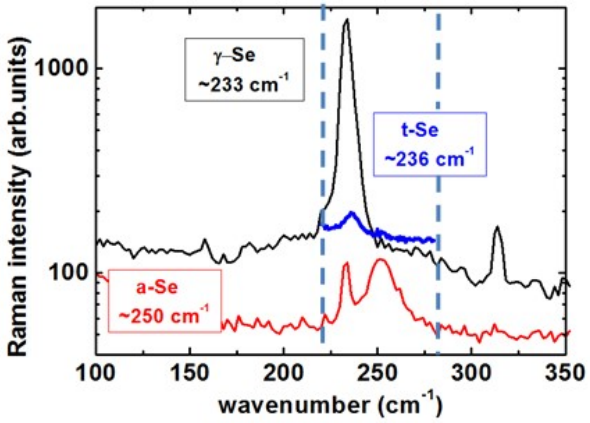

Figure 3. Raman spectra of solid γ-Se (black curve), amorphous a-Se NPs (red curve) and trigonal t-Se nanorods (blue curve).

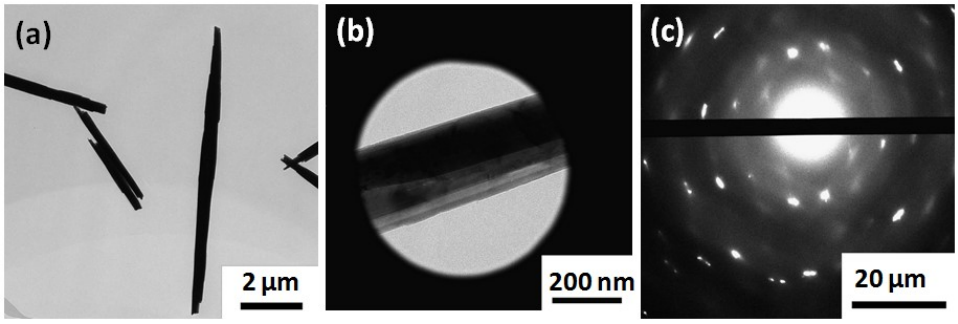

Figure 4. TEM-photographs of Se nanorods (a), (b) and the corresponding electron diffraction pattern (c).

3. Fabrication of 2D and 3D functional nanocoatings

3.1. Inkjet printing

The as-prepared nanoinks (Au NPs hydrosols and Se NPs in a 50%-IPA solution) were used for inkjet printing of nanocoatings on silica-supported silver films via multicartrige printer Epson L800. The resulted coatings were analyzed with the use of optical microscopy (biological microscope Altami-6), SEM and the built-in module for energy-dispersive X-ray spectroscopy (EDS, module INCA, Oxford Instruments), allowing characterization of elemental composition of the nanocoatings.

During the printing nanoinks were ejected in form of 1-pL drops and rapidly dried on the Ag film surface, creating quasiperiodical structure of discrete spots with mean diameter of about tens of μm (figure 5). The percent of spot area filling with NPs expectedly increased during multipass printing, accompanied by the layer height change from hundreds of nm to several μm.

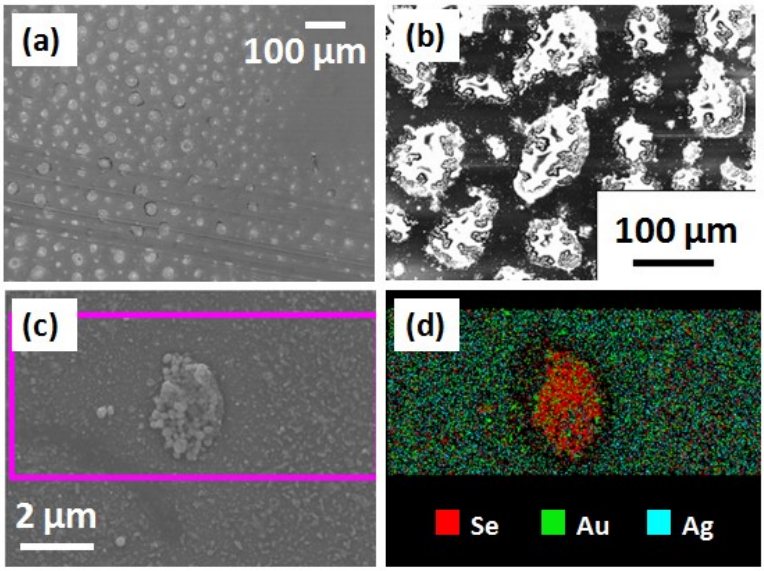

Figure 5. SEM-images of inkjet printed multilayers of Se and Au NPs on the silica-supported Ag film (a), (b), (c) and the corresponding EDS-map (d): Se 0.79 at. %; Au 0.38 at. %; Ag 7.69 at. %.

Au nanionks inkjet printing over the Se-layer resulted in a second inhomogenously deposited layer, which seems to be isolated from the supported metal film, as it exhibits a strong surface charge, detected during its SEM-visualization as the corresponding over-saturated bright areas (figure 5b). The resulted 3D-structure can be considered as a simple semiconductor-based photoresistor.

3.2. Sedimentation of colloids

Se NPs, prepared in the 99% IPA solution, were deposited on silica-supported Ag films and dried at room temperature. During the evaporation of liquid medium amorphous NPs organized in form of t-Se nanorods (vide supra in Section 2: figures 3, 4; 6). This phenomenon can be explained in terms of Ostwald ripening process, which involves the dissolution of unstable a-Se NPs and their aggregation into the c-axis oriented hexagonal structure of the Se helical chains [12]. The resulting nanorods have the mean diameter of 600 nm and the average length of 10 μm. The increase of laser exposition time from 5 to 15 min resulted in a more rapid NRs formation, which lead to the colloid colour change from opaque brick-red to dark gray and was detected during SEM-analysis (figure 6).

4. Conclusion

In this work we report the preparation of nanionks with high pigment (Au, Se NPs) concentration, provided by efficient laser ablation of solid targets in liquid media, and the following manufacturing of multifunctional nanocoatings via inkjet printing and sedimentation of colloids. The resulting coatings were composed of spherical NPs (Au, Se, prepared in a 50% IPA solution) and nanorods (Se colloids @ 99% IPA, air-dried on a substrate). Monolayer nanocoatings of plasmonic NPs can be used as highly-sensitive elements for SERS chemo- and biosensors, and a sandwich structure of Ag/Se/Au NPs can be basically considered as a simple microscale photoresistor.

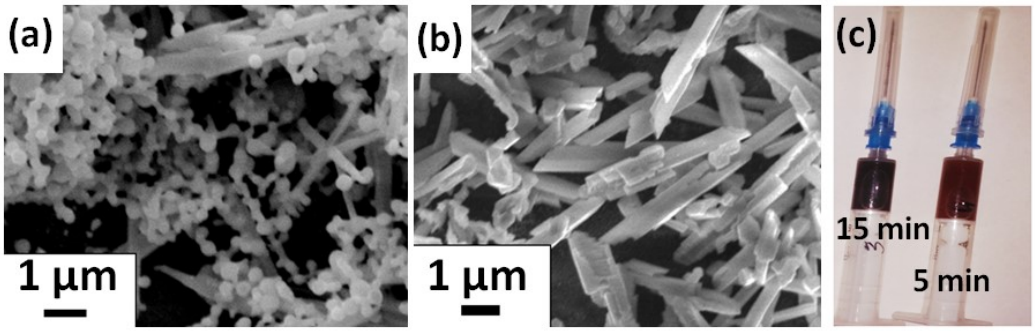

Figure 6. SEM-images of dried Se NRs deposits on silica-supported Ag films with 5 min (a) and 15 min (b) laser exposition of Se target; (c) – a photograph of the corresponding Se-colloids in medical syringes.

Acknowledgments
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