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Obtaining Ink Based on Palladium Nanoparticles for Possible Use in Printed Electronics

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Abstract: **The possibility of obtaining conductive ink based on palladium nanoparticles obtained by the polyol method is considered. The composition of the ink is adapted for use in printed electronics. The ink contains 20 mass% palladium, has a viscosity of 17-20 cps and a surface tension of 35-38 N/m. During heat treatment, the specific surface resistance of palladium nanostructures changes from 0.38 to 0.07 Ω. These and other characteristics, such as high stability and good wettability of the substrate, make it possible to use palladium nanoink in printer printing.**

Keywords: **synthesis, palladium nanoparticles, nanoink, printed electronics**

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Contents

1. INTRODUCTION

Printer technologies are of increasing interest for the production of electronic devices such as gas sensors [1], transistors [2], organic light-emitting diodes [3], RFID tags [4], etc. Conductive inks are one of the important components of printing. The inks can be based on various materials such as conductive polymers [5], carbon [6], organometallic compounds and metallic nanoparticles [7]. The leading place among conductive inks is occupied by systems based on metallic nanoparticles. The reason is that their resistivity is close

to the specific gravity of the material (2-3 times higher) and much lower than that of conductive polymers and other materials. Silver nano-ink is most commonly used in printer printing. Silver has undeniable advantages in terms of electrical and thermal conductivity, oxidation resistance, optical and antibacterial properties. We have previously reported on the possibility of using silver nanoparticles in input-organic solvents in 2D printing [8]. However, silver is not without disadvantages: metal atoms can diffuse inside the dielectric under conditions of high humidity, tend to form dark Ag_2S films, which limits the use of silver near sulfur-containing materials (rubber). Therefore, the creation of nano-ink based on nanoparticles of other precious metals is important.

It is known that platinum group metals exhibit chemical inertness with respect to atmospheric constituents, which makes them indispensable for the manufacture of electronic devices.

Palladium is a unique element of the platinum group. The element is widely used in the manufacture of capacitors, some types of relays, contacts, parts of microcircuits. Palladium, having good anti-corrosive properties, improves stability of functioning of parts in any environment, including at significant temperature increase. Palladium is most actively used in electronic, chemical, military and aerospace industries. Scientists are conducting scientific research to expand the use of this precious metal [9]. Palladium nanoparticles are used in the form of dispersions in liquid phases or fixed on the surface of various substrates [11].

The production of palladium nanoparticles and materials based on them still remains interesting and significant. Therefore, the main goal of this work was to synthesize and study the properties of palladium nanoparticles, as well as to produce inks based on them for possible use in printer technology printing.

2. EXPERIMENTAL PART

The following materials were used for the experimental work: palladium chloride (crude, JSC "Aurat"), sodium hydroxide (crude, LLC "RusChem"), polyvinylpyrrolidone (CAS-No: 9003-39-8 (K15), AppliChem), ethylene glycol (h.d, "ECOS-1"), acetone (h.d.a., RusChem LLC), ethanol (hh, "CONSTANT PHARM-M" LLC), deionized water (resistivity is 18 Mohm-cm).

Synthesis of palladium nanoparticles was carried out in an oil bath in a three-neck flask equipped with a reflux condenser, under continuous stirring with a magnetic stirrer. Ethylene glycol, a stabilizer –polyvinylpyrrolidone and a small amount of sodium hydroxide (to create a slightly alkaline environment) were placed in the reaction vessel, then stirred and heated. When the temperature reached 120°C, an aqueous solution of palladium chloride was slowly (drop by drop) introduced into the system. After all precursor solution was added, the reaction mixture was heated to 160°C and kept under stirring for 3 h. During the reaction, a color change from burgundy to black was observed, indicating the formation of palladium nanoparticles.

At the end of the synthesis, the palladium nanoparticles were precipitated by triple excess of acetone by centrifugation for

5 min at a rotor speed of 7000 rpm. The resulting precipitate was decanted and washed several times with ethanol to remove reaction products and excess stabilizer.

In order to obtain ink, the impurity-free nanoparticles were ultrasonically redispersed in a mixture of ethylene glycol and ethyl alcohol, taken in a ratio of 4:1, respectively.

The obtained palladium nanoparticles were applied to glass substrates by spin-coating. The obtained films were annealed at 150°, 200°, 250° and 300°C.

Microphotographs in the mode of scanning electron microscopy were obtained on a Zeiss Supra 40 Scanning Electron Microscope with Field Emission cathode with an operating accelerating voltage of 25 kV. The morphology of the samples was determined in the secondary electron detector mode (In-lens SE). Sample preparation consisted of applying a dispersion sample of palladium nanoparticles with a pipette to a silicon substrate, which after complete drying of the preparation was placed in the microscope.

Absorption spectra of the samples were obtained using a spectrophotometer Leki SS2107UV (CJSC LOIP, Russia) in the wavelength range from 200 to 1100 nm. Working samples were prepared by 30-fold dilution of the reaction mass (or dispersion of palladium nanoparticles) with deionized water. The sample volume was 3 ml and the optical path length was 1 cm.

X-ray phase analysis (XRF) was carried out on a DRON-7 setup with a graphite monochromator on CuKα – radiation (λ = 1.54056 Å) with Ni filters.

The concentration of palladium nanoparticles in the nanoink was determined gravimetrically.

The viscosity of palladium nanoink was measured on an AND SV 10A vibrating viscometer.

The surface tension of palladium nano-ink was determined by stalagmometry.

To measure the sheet resistance of palladium thin films, a four-probe method was used. The value of sheet resistance was calculated by the formula:

$$R_s = F \cdot U/I,$$

where R_s – value of Ohm; F – correction factor $F = \pi/\ln 2 = 4.53236$; U – value of electric voltage, V; I – value of electric current, A.

3. RESULTS AND DISCUSSION

Palladium nanoparticles were produced using the polyol method. Simultaneously ethylene glycol, was used as the reaction medium and reducing agent. At the beginning of the synthesis, polyvinylpyrrolidone (PVP), used as a stabilizer, due to the presence of heterocyclic pyrrolidol groups in the structure, entered into donor-acceptor interaction with the noble metal ions, forming complex PVP-Pd^{2+}. According to the literature, the formation of a metal-polymer complex is the result of contact between one palladium ion and three monolinks of the polymer ligand [12]. Thus, palladium ions were coordinated to the polymer molecules prior to the reduction reaction. When heated, ethylene glycol was oxidized to glycolic acid. Glycolic acid was deprotonated in the reaction medium, forming glycolate anions. Receiving electrons from the oxidation products of the polyalcohol, the

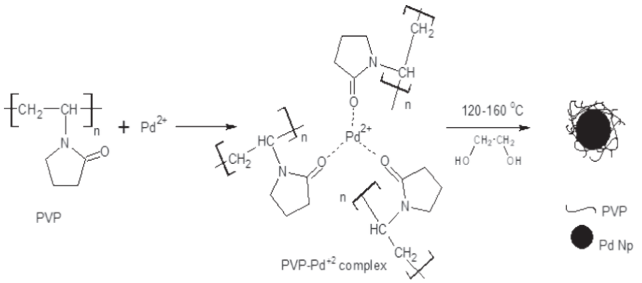


Fig. 1. *Mechanism of formation of palladium nanoparticles.*

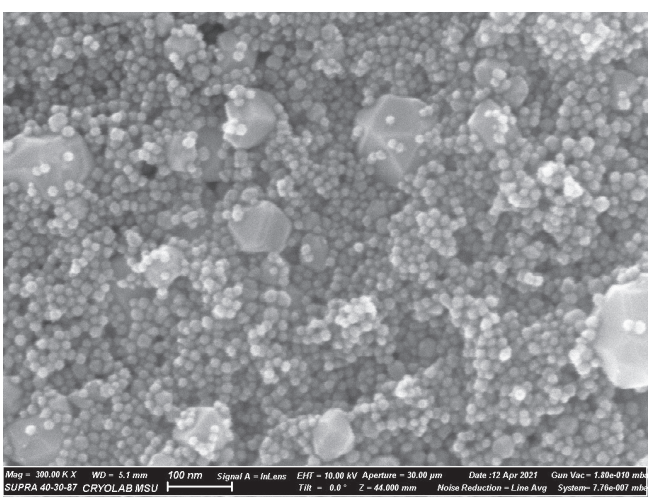
polymer-ion complexes were reduced to form metal colloids.

In the process of synthesis, carbonyl C=O groups of polyvinylpyrrolidone side chains began to actively interact with the surface of the formed nanoparticles, thereby slowing down their further growth and providing the stabilization process. **Fig. 1** shows the mechanism of palladium nanoparticles formation.

The process of nanoparticle formation was monitored using UV spectroscopy. In the absorption spectrum (**Fig. 2**) recorded at the initial stage of synthesis, there is a peak in the near ultraviolet region (271 nm) corresponding to the PVP-Pd^{2+} complex.

In the process of PVP-Pd^{2+} complexes reduction, the peak began to flatten out and at the end of the synthesis, the spectrum acquired a wide absorption region falling smoothly into the visible region, which is characteristic of metallic palladium nanoparticles.

The study by scanning electron microscopy made it possible to establish the morphology of the obtained nanoparticles. Small and large spherical particles are present in nano-ink (**Fig. 3**). Large palladium particles have a pronounced multifaceted crystalline structure, in turn, small particles are



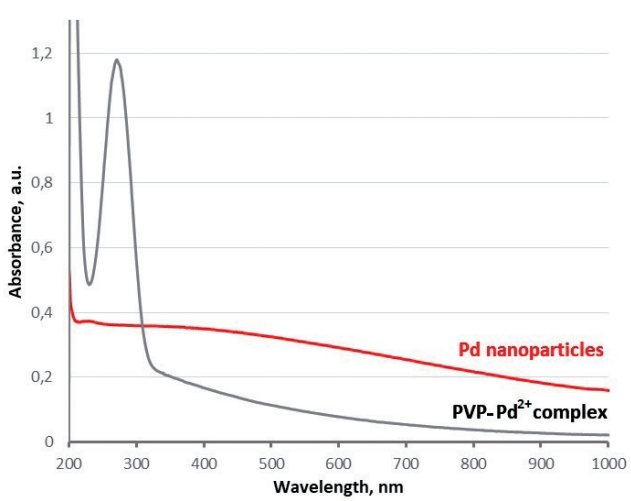


Fig. 2. *UV-visible absorption spectrum of palladium nanoparticles.*

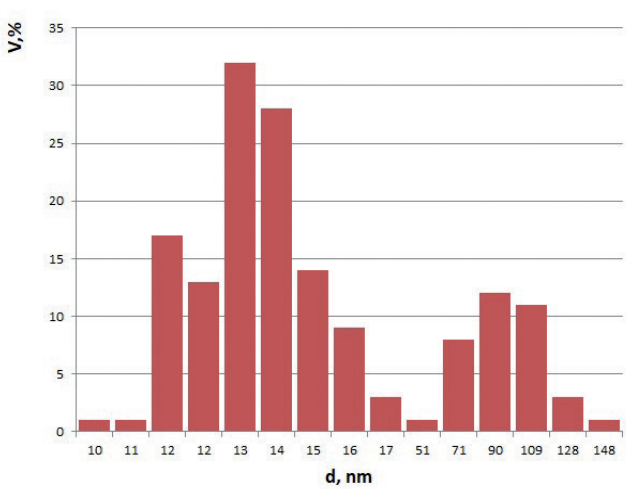


Fig. 3. *SEM-image of palladium nanoparticles and histogram of nanoparticles size distribution.*

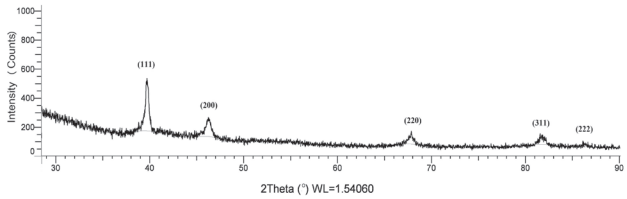


Fig. 4. *XRD of palladium nanoparticles.*

characterized by a smoother surface relief. Results of analytical processing of SEM images allowed making a conclusion about bimodal character of nanoparticles distribution. The dominant maximum in particle content in the sample belongs to palladium nanoparticles with the average size of 13 nm. The average size of large particles was 90 nm.

Identification of the phase composition of the obtained nanoparticles was carried out based on the XRD. The diffractogram (**Fig. 4**) shows reflexes in the region of reflection angles 2θ = 40, 46, 68, 82, and 87 deg corresponding to the palladium phase with cubic crystal structure (JCPDS 05-0681). The low intensity and broadened nature of the coherent scattering regions indicate the nanoscale nature of the particles under study.

In order to investigate the temperature treatment behavior of palladium nanoparticles the films were obtained from the ink and annealed at 150-300ºC.

SEM microphotographs (**Fig. 5***a,b*) show that nanoparticles at 150ºC-200ºC

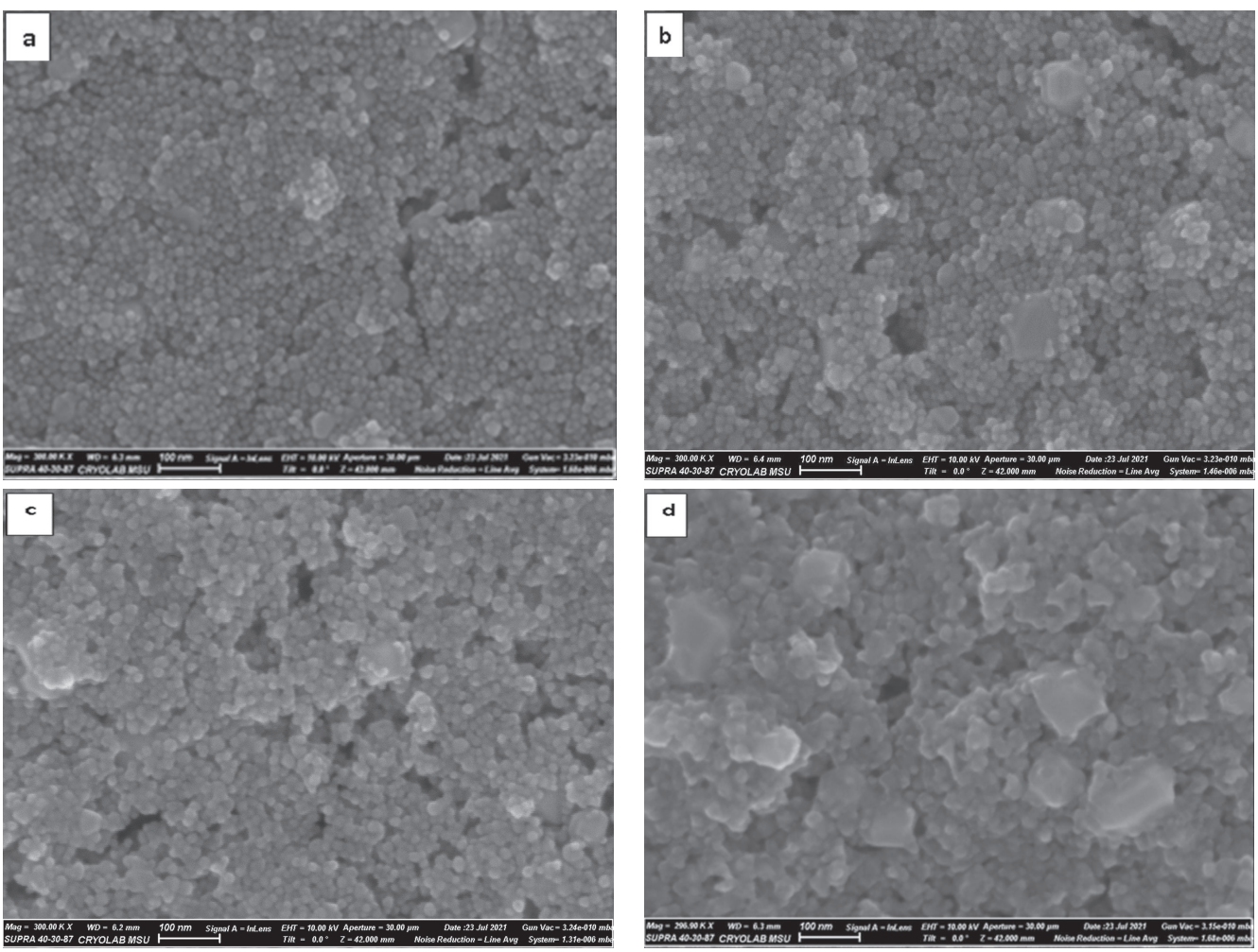


Fig. 5. *SEM images of annealed palladium nanoparticles at the following temperatures: a – 150ºC, b – 200ºC, c – 250ºC, d – 300ºC.*

do not form a continuous film and have outlined contours. During the temperature treatment at 250°C (Fig. 5*c*), a pronounced convergence of palladium nanoparticles is observed due to the destruction of the stabilizing "coat" and the formation of agglomerates. Metallic films obtained at 300°C (Fig. 5*d*) are characterized by an obvious blurring of the boundaries between small-sized nanoparticles, the surface acquires a smoothed structure.

The lower melting temperature of palladium films (300°C) relative to compact metal (1554°C) is characteristic of nanoscale objects. This circumstance opens ample opportunities for using palladium as an alternative material in flexible microelectronics.

Variation of surface resistivity values with treatment temperature is shown in **Fig. 6**.

With increasing of annealing temperature the decrease of surface resistivity from 0.38 to 0.07 Ohm is observed (Fig. 6)

According to thermogravimetric analysis, the palladium content in the ink was 20 wt%.

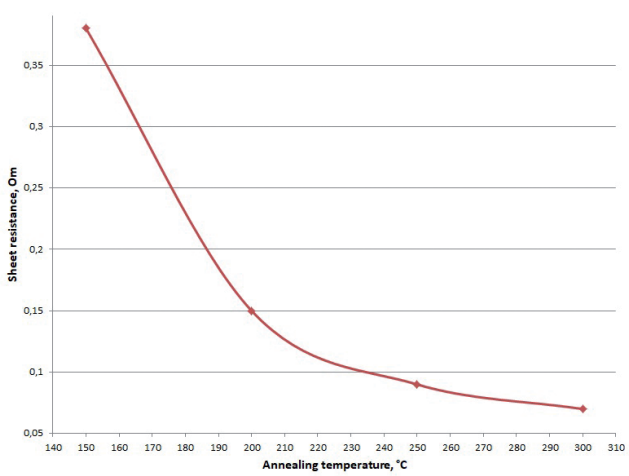


Fig. 6. *Dependence of surface resistivity of palladium films on processing temperature.*

The use of a combination of high and low – boiling solvents in the composition of the ink contributes to good wettability to various materials (glass, ceramics, polymer) and provides optimal values of viscosity (17-20 cP) and surface tension (35-38) N/m for successful printing. The obtained palladium nano-ink is stable for more than 6 months and can be recommended for use in printed electronics.

4. CONCLUSION

In this work, the synthesis of palladium nanoparticles by the polyol method was proposed. The obtained nanoparticles and inks based on them were investigated and characterized by a complex of physical and chemical methods.

According to the results, nanoparticles contain small (d = 13 nm) and large (d = 90 nm) spherical particles. The phase composition of the nanoparticles in the sample corresponds to palladium with a cubic crystal structure. The SEM data of metallic films obtained from palladium nano-ink under temperature treatment (150°-300°C) report a change in surface morphology. As the annealing temperature increases, the boundaries between nanoparticles are blurred and the surface acquires a smoothed structure. This effect is reflected in the decrease of the films surface resistivity from 0.38 to 0.07 Ohm.

The obtained nano-ink has relatively high time stability (more than 6 months), is characterized by good wettability to various materials (glass, ceramics, polymer), contains 20% wt% palladium and can be recommended for use in the field of printed electronics.

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