

Article

Nanocomposite Inks Based on Nickel–Silver Core–Shell and Silver Nanoparticles for Fabrication Conductive Coatings at Low-Temperature Sintering

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Abstract: Nanocomposite inks composed of nickel–silver core–shell and silver nanoparticles (NPs) can combine the advantages of lower cost, high conductivity, and low-temperature sintering processes, which have attracted much attention in the development of materials for printed flexible electronics. In this context, in the present paper, we report the process of preparation of nanocomposite ink containing nickel–silver core–shell nanoparticles, as the main filler, and silver nanoparticles, as doping material, and their application for the fabrication of conductive coatings. It was found that the addition of a low concentration of Ag NPs to ink formulation based mainly on low-cost Ni–Ag NPs improves the conductive properties of coatings fabricated by ink deposition on a glass substrate. Two types of prepared nanocomposite ink coatings showed promising properties for future application: (1) doped with 0.5% of Ag NPs sintered at 200 °C as low cost for larger industrial application and, (2) containing 1% of Ag NPs sintered at 150 °C for the fabrication of conductive printed patterns on flexible substrates. The conductivity of such nanocomposite films was similar, about of 6×10^6 S/m, which corresponds to 35% of that for a bulk nickel.

Keywords: metallic nanoparticles; nanocomposite ink; low-temperature sintering; conductivity



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1. Introduction

During the last years, printing methods have attracted much attention as low cost, low pollution, and convenient ways for the fabrication of electronic circuits or devices. Conductive inks are important materials for application in the printed market for the production of electronic devices such as radiofrequency identification (RFID) tags, touch screens, or flexible displays [1–3]. Therefore, studies on the development of conductive ink formulations enabling improved devices' performance or providing their new applications are still performed.

To prepare conductive ink with optimal properties, some specific requirements appear, and several specific challenges should be overcome for obtaining high-quality printed patterns. First, the process of ink preparation should be simple and high-yielding. Second, the ink should possess proper physicochemical properties compatible with a method of printing such as direct ink writing, screen printing, inkjet printing, or airbrush spraying. Therefore, conductive ink is a multi-component system that contains a functional conducting material (filler) in a liquid vehicle (aqueous or organic) and various additives (such as surface tension and rheology modifiers, humectants, wetting agents, or defoamers) that provide the optimal working of the printing device and compatibility with the substrate [4,5]. Besides, the printed pattern should be highly conductive, which is of crucial importance for the production of electronic devices.

The most important component of conductive ink is conductive filler (active material), including conductive polymers, carbon nanotubes, graphene, organometallic compounds,

metal precursors, or metallic nanoparticles (NPs) [6–9]. Among these fillers, metallic nanoparticles are considered the most promising candidate for the preparation of conductive inks, because of their high specific surface energy and surface-to-volume ratio, which enhances their sensitivity to heat [10]. Currently, most metal NP conductive inks are based on silver NPs [1–3]. This is mainly because of its high electrical conductivity, chemical stability, and the ability of its oxide form to conduct electricity. Additionally, Ag NPs have a low melting point, which promotes obtaining conductive thin coatings at relatively low sintering temperatures. The disadvantages of silver NPs are their high price and poor mechanical properties, which limits their utilization in industrial applications. Nickel, being cheaper and possessing good conductivity, can be considered as a potential replacement for these expensive nanoparticles. Although Ni NPs can be used in place of silver as fillers in conductive inks, the problem associated with their widespread utilization is the tendency of nickel to oxidize in an ambient atmosphere. Therefore, the protection of nickel NPs from the oxidation process is of crucial importance for the fabrication of printed tracks with high conductivity. The most efficient and long-term approach for the preparation of air-stable Ni NPs is their coating with a layer of noble metals (silver or gold) by transmetalation, which results in the formation of a core–shell structure. In this process, the preformed surface of the core particle acts as a reducing agent for the second metal with higher redox potential [11,12].

High conductivity is the crucial property of inks for their application in printed electronic devices. Therefore, obtaining as low as possible resistance is the main aim of most conductive ink formulations [13]. To achieve low resistivities, usually, after conductive ink deposition, a sintering step is required. It consists of spontaneous coalescence and Ostwald ripening, driven by the surface-to-volume energy ratio of the small nanoparticles [14]. The reason for performing the sintering process is the removal of the stabilizing agent (essential for the stability of colloidal metallic NPs solutions), coating the metal NPs, which forms an insulating layer after the ink deposition process. The stabilizer needs to be removed to improve the conductivity of printed features. This is usually obtained by exposing the printed patterns to elevated temperatures. Generally, to achieve highly conductive printed tracks, a high sintering temperature needs to be applied [15,16]. However, common substrates for printed electronics are made of polymers that have low thermal stability and require a relatively low sintering temperature to prevent destruction by heating. For example, Shen et al. [17] successfully printed silver patterns on paper and polyethylene terephthalate (PET) substrates. They noticed that, upon heating at 180 °C, the resistivity of the obtained tracks decreased to 3.7 $\mu\Omega\cdot\text{cm}$. A simple and low temperature (130 °C) sintering process of inkjet-printed industrial Cu NPs ink was performed by Hermerschmidt et al. [18]. The electrical conductivity of up to 16% of that for bulk Cu was observed when sintering was carried out at 130 °C and more than 25% of bulk Cu was observed above 150 °C.

In this study, a Ni-Ag/Ag nanocomposite ink was developed by mixing nickel–silver core–shell (as a basic active material) and silver nanoparticles (as a doping functional material) at the averages sizes of 220 nm and 30 nm, respectively. The effect of various concentrations of Ag NPs on the conductive properties of ink coatings was analyzed and compared. We found out that Ni-Ag coatings doped with 1% of Ag NPs can be sintered at a much lower temperature (150 °C) in comparison with coatings based on only Ni-Ag NPs. The obtained value of conductivity was about 6.00×10^6 S/m, which corresponds to 35% of bulk Ni conductivity. A similar value was achieved for the nanocomposite film at only a slightly higher sintering temperature of 200 °C, but lower Ag NPs' concentration (0.5%), which is important from an economic point of view and can help decrease the cost of fabrication of conductive materials.

2. Materials and Methods

2.1. Materials

Nickel sulfate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$), sodium borohydride (NaBH_4), sodium carboxymethyl cellulose (CMC) with MW 90,000, and amino methyl propanol (AMP) were purchased from Sigma-Aldrich. The citric acid (CA) and silver nitrate (AgNO_3), as a precursor of the silver shell, were products of Avantor Performance Materials Poland S.A. Silver nitrate, as the precursor of Ag NPs, and potassium hydroxide were purchased from STANLAB (Lublin, Poland). Maltodextrin was a product of Kemikals (Gdynia, Poland). A wetting agent, Surfynol PSA 336 (acetylenic-based formulated surfactant), was obtained from Evonik (Essen, Germany).

2.2. Synthesis of Metallic Nanoparticles

Both types of metallic NPs were synthesized using the “wet” chemical method, by reduction of metals ions by proper reducing agents in the presence of stabilizers. The process of synthesis of Ag NPs was performed as followed. Firstly, an aqueous solution (3000 mL) of potassium hydroxide at a concentration of 0.057 M was prepared. Then, maltodextrin (5 g/L), which acts as a reducing and stabilizing agent, was added and reagents were mixed. After that, silver nitrate at a concentration of 0.015 M was added to the obtained solution. The synthesis was performed for 24 h at a mixing speed of 380 rpm. In the next step, to the synthesized Ag NPs, 3000 mL of methanol was added, which resulted in nanoparticles’ destabilization. This process was performed for 24 h and, after that, the obtained brown precipitation was washed three times with 300 mL of methanol by mixing (360 rpm) and sedimentation process. Then, the obtained precipitation was dried for 24 h at room temperature, which resulted in the Ag NPs based powder formation.

Nickel–silver core–shell NPs were obtained using an improved two-stage process, which was previously developed in our lab [12,19–21]. At the first stage, Ni NPs were synthesized in the presence of two types of complexing agents. At the second stage, the Ni NPs acted as a reducing agent for Ag ions (transmetalation reaction), which resulted in silver shell formation on the surface of Ni NPs.

Ni NPs were obtained by the reduction of Ni ions (by sodium borohydride) in complex with CA and AMP, in the presence of sodium CMC (MW 90,000) as a stabilizer. In the optimized process, aqueous solutions of the following reagents were mixed: 30 mL of CMC (0.5%), 12 mL of NiSO_4 (0.2 M), and 12 mL of CA (0.15 M). Thereafter, to the above mixture, an AMP solution with a concentration of 80% was added to adjust the pH value to 9. Finally, 30 mL of an aqueous solution of reducing agent (NaBH_4) with concentration 0.05 M was injected, using a peristaltic pump (700 rotations speed per minute), into the reaction mixture. The mixture was stirred at 850 rpm for 60 min.

To synthesize Ni-Ag NPs, to the obtained dispersion of Ni NPs, 45 mL of the aqueous solution of AgNO_3 (0.04 M) as the precursor of a silver shell was added. The synthesis was performed for 60 min at room temperature. The obtained Ni-Ag NPs were washed two times (with distilled water) and concentrated (25 wt%) by centrifugation (7000 rpm, 20 min).

2.3. Nanocomposite Ink Formation and Conductive Coatings’ Fabrication

To prepare nanocomposite ink, based on Ni-Ag and Ag NPs, first, to the aqueous dispersion of Ni-Ag NPs, various concentrations (0.1–1.5%) of Ag NPs (in the form of powder) were added. The obtained dispersion was homogenized using an ultrasonic bath for 30 min at 20 kHz. The physicochemical properties of NPs based nanocomposite ink were optimized using various concentrations of Surfynol PSA 336 as a wetting agent. The obtained ink was homogenized using an ultrasonic bath (30 min, 20 kHz). Then, nanocomposite ink of 0.1 mL was deposited on glass substrates (3.5×2.5 cm) using a manual bar coating method (with 0.05 mm of wire winding rod). More information about ink coatings deposition by the bar coating technique can be found in the user instruction [22].

After the coating process, the ink layers were dried on a hot plate (60 °C for 15 min) and then the obtained coatings were sintered by heating at various temperatures (130–250 °C) and time (15–90 min).

2.4. Characterization

The size of metallic nanoparticles such as hydrodynamic diameter (according to number distribution), using the dynamic light scattering (DLS) method, using Zetasizer Nano Series of Malvern Instruments, was measured. Each value was determined in three runs with at least 20 measurements. All analyses were performed with aqueous dispersions of NPs at 25 °C.

The metallic coatings were obtained by deposition of hybrid ink formulation using a hand coater (Kontech, Poland). The morphology (shape, size) of synthesized NPs and their coatings were visualized by SEM (LEO Gemini 1530, Zeiss).

The thickness of deposited nanocomposite ink coatings was measured by the EDXRF method (FISCHERSCOPE X-RAY XDL 230). The thermal sintering process was performed on a hot plate in an atmospheric environment. The values of sheet resistance of metallic coatings were measured by a four-point probe method (Milliohm Meter, Extech Instruments). Four equally-spaced, co-linear probes were manually contacted with the deposited metallic coatings, which resulted in electrical contact, and the sheet resistance value was automatically determined. To calculate the values of the resistivity, the values of the sheet resistance were multiplied by the thickness, and the conductivity was established as the reciprocal value to the resistivity [23].

3. Results and Discussion

The procedure of nanocomposite metallic coatings fabrication is a multi-step process, which consists of nanoparticles synthesis, ink-based on those NPs' preparation, its deposition by a proper method, and sintering to transform a nonconductive coating to a conductive one. The process of preparation of conductive coatings, formed from nanocomposite ink, is schematically presented in Figure 1.

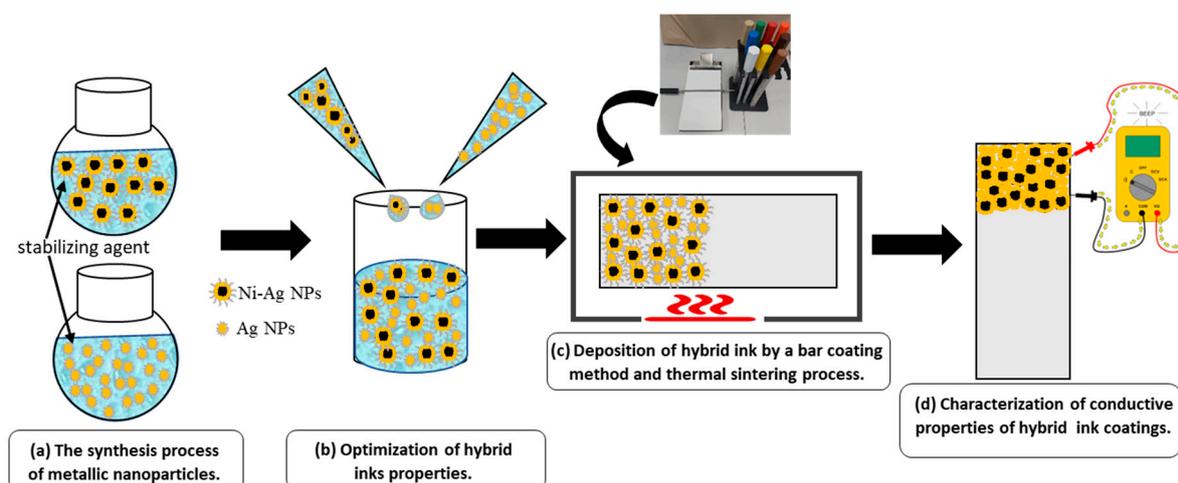


Figure 1. Scheme of the preparation of conductive coatings based on Ni-Ag nanoparticles (NPs): (a) optimization of the process of synthesis of metallic NPs (Ni-Ag and Ag); (b) preparation and optimization of properties of nanocomposite ink (based on Ni-Ag and Ag NPs); (c) deposition process of nanocomposite inks and sintering of obtained coatings; (d) characterization of conductive properties of nanocomposite ink coatings.

3.1. Preparation of Ni-Ag and Ag NPs as a Component of Hybrid Dispersion

To prepare nanocomposite ink consists of two types of metallic nanoparticles, firstly, Ni-Ag core-shell (as a basic active material) and Ag NPs (as a doping part of ink formulation) were prepared.

The optimized synthesis process of Ag NPs was performed in alkaline solution (KOH, 0.057 M) by reduction of Ag ions (AgNO_3 at a concentration of 0.015 M) by maltodextrin (5 g/L), which also acted as the stabilizing agent. In the presence of OH^- , from potassium hydroxide, $[\text{Ag}(\text{OH})_2]^-$ was formed. Then, it was reduced to Ag^0 by an aldehyde group ($-\text{CHO}$) from maltodextrin, while oxidation of the aldehyde to the carboxylic group ($-\text{COOH}$) appeared, according to the following reaction [24,25]:



The process of Ag NPs' formation was supported by the changes in the color of the dispersion during the synthesis of silver nanoparticles. After the addition of AgNO_3 to the solution of KOH and maltodextrin, the color of dispersion was a bright gray and, after 24 h of stirring, it changed to a gray-green. After the process of sedimentation, decantation, and washing of the nanoparticles, the color of their precipitation was a brown color and semi-liquid consistency. During the drying process, the precipitation colour changed to silver with a metallic sheen.

The Ag NPs' properties (size, shape), which were analyzed directly after the synthesis process (before destabilization by methanol), were similar to that studied after redispersion of their powder in distilled water. As presented in Figure 2A, the Ag NPs at the average size (as the value of three subsequent runs of the instrument) of about 30 nm were synthesized. They also showed monodisperse size distribution according to the low polydispersity index (~ 0.190) of their dispersion. The obtained Ag NPs were spherical, as can be seen in the SEM image shown in Figure 2B. Besides, the SEM analysis confirmed their size, which was measured using the DLS method.

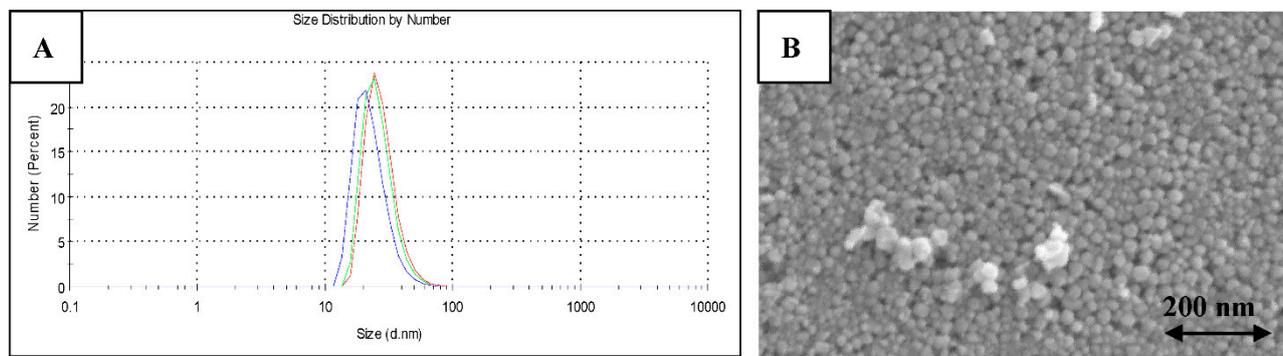


Figure 2. The size distribution (A), as the value of three subsequent runs of the instrument, and SEM image (B) of Ag NPs.

The basic as a low-cost active material of metallic hybrid ink, in the form of Ni-Ag core-shell NPs, was synthesized according to previously developed methods [12,19–21]. These methods involved a two-step process: (1) synthesis of Ni NPs followed by (2) silver shell formation by transmetalation reaction [26]. At the first step, by reduction of Ni^{2+} , in the complex with AMP and citric acid [21], by NaBH_4 as a reducing agent, in the presence of sodium carboxymethyl cellulose (0.5%) as a stabilizer, Ni NPs were obtained. This process was performed at the deficiency (0.05 M) of the reducing agent, which is of crucial importance for the stage of the formation of a silver shell. Due to the deficiency of NaBH_4 , it is fully consumed in the process of reduction of Ni^{2+} , which prevents the reduction of Ag^+ to Ag NPs, instead of their reduction on the surface of Ni NPs with the formation of a core-shell structure by transmetalation reaction.

As we found, the obtained Ni NPs were not stable and totally oxidized in aqueous dispersion after a few (4–5) hours of storage. To stabilize Ni NPs against oxidation, by the reduction of silver ions (0.04 M) on their surface, by transmetalation process, a protective silver shell was formed on the surface of Ni NPs, which results in fabrication of the core-shell structure. The average size (as the value of three subsequent runs of the instrument) of obtained Ni-Ag NPs was found to be 220 nm according to DLS measurement (Figure 3A). The SEM analysis also confirmed their size (Figure 3B) and provided information about the morphology of Ni-Ag NPs. As can be seen in Figure 3B, the synthesized NPs were almost spherical. The characterization of Ni-Ag NPs' properties, in detail, was presented in our previous manuscript [22].

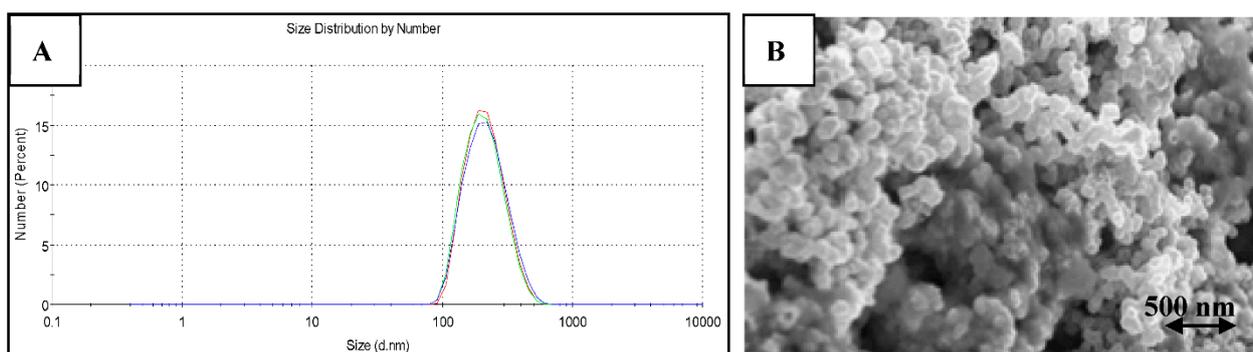


Figure 3. The size distribution (A), as the value of three subsequent runs of the instrument, and SEM image (B) of Ni-Ag NPs.

3.2. Fabrication of Ink Formulation and Conductive Coatings

The main filler of metallic nanocomposite inks consisted of Ni-Ag NPs. Therefore, for their preparation, the aqueous dispersion of Ni-Ag NPs was doped with different concentrations (0.1–1.5%) of Ag NPs in the metallic powder form. After their mixing, the dispersions of Ni-Ag and Ag NPs were homogenized in an ultrasonic bath. Then, the properties of nanocomposite ink formulation were optimized for the coating on a glass substrate using a bar coating method. To obtain high-quality deposited films, various concentrations (0.01–0.075%) of Surfynol PSA 336 (wetting agent) were used. It was found that the most visually uniform coatings of nanocomposite ink (similar for all Ag NPs' concentrations) were obtained for 0.05% and 0.075% of the wetting agent, as can be seen in Figure 4. Regarding the conductivity of coated films, the concentration of organic materials in ink formulation should be as low as possible. Therefore, for the further experiment (sintering process), as the optimal concentration of Surfynol PSA 336, 0.05% was selected.

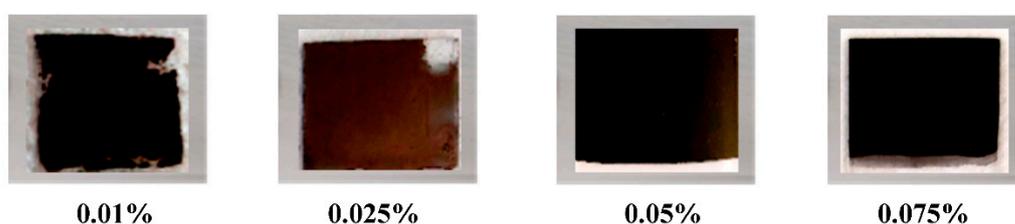


Figure 4. The effect of the Surfynol PSA 336 (wetting agent) on the quality of obtained metallic coatings composed of Ni-Ag and Ag NPs, after drying (60 °C, 15 min).

In the next stage of the research, the sintering process of deposited coatings of inks (with an optimal concentration of wetting agent) composed of Ni-Ag NPs doped with different concentrations (0.1–1.5%) of Ag NPs was performed. This process was required because of the presence of organic materials (stabilizer, wetting agent) in ink formulation, which was acted as an electrical insulator and led to the lowering of metallic coatings'

conductivity. Accordingly, after the drying process (60 °C, 15 min) of deposited coatings, their resistance was too high for determination with the available equipment. Therefore, after the drying process, the coated metallic films were sintered at 100 °C. The obtained value of sheet resistance (about 1 k Ω /□) was too high for any practical applications. In this context, the sintering process of the deposited metallic coatings was performed by heating them at a higher temperature, ranging from 130 to 300 °C. Then, using the four-probe electrodes method, the value of sheet resistance of the obtained coatings was determined. Their values were multiplied by the thicknesses (using the EDXRF method), which were similar (about 2 μ m) for all deposited films, and the values of resistivity were calculated. Finally, the conductivities as the reciprocal values of resistivity were calculated. The dependence of values of conductivity of metallic films of nanocomposite inks (with different concentrations of Ag NPs) on the sintering temperature is presented in Figure 5.

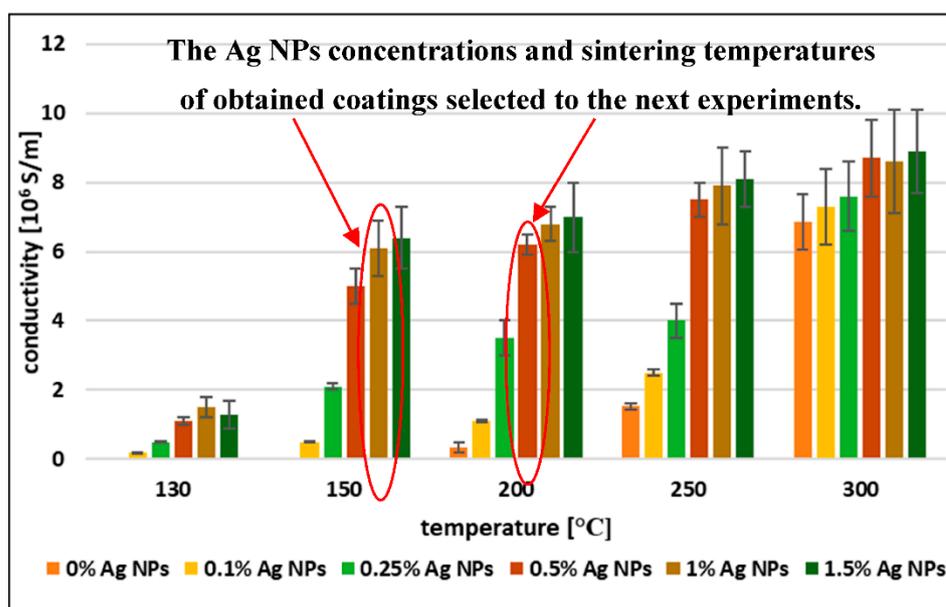


Figure 5. The dependence of the conductivity of metallic films based on Ni-Ag NPs (main filler) on the doped concentration of Ag NPs and sintering temperature (heating duration 30 min).

As can be seen in Figure 5, the addition of Ag NPs affects the conductive properties of coatings of nanocomposite inks composed mainly of Ni-Ag NPs. The increasing of conductivity of metallic films, after their doping of Ag NPs, at all ranges of sintering temperature can be noticed, although the highest effect of their addition was observed at a low sintering temperature (130–200 °C). The conductivity of metallic coatings of inks composed of only of nickel-silver core-shell NPs was very low after the sintering process at a temperature of 130–150 °C (resistivity above 1.5 k Ω ·cm). The sufficiently high conductivity of such metallic films of about 6.86×10^6 S/m was obtained after the sintering at 300 °C [21]. The doping of ink with low Ag NPs concentration (0.1%) results in a significant increase of conductivity of metallic coatings to 0.2 and 0.5×10^6 S/m (resistivity of 495 $\mu\Omega$ ·cm and 248 $\mu\Omega$ ·cm, respectively) sintered at 130 and 150 °C, respectively. The lowering of the sintering temperature of Ni-Ag-based coatings after the addition of Ag NPs could be the result of the much lower melting point of silver (930 °C) in comparison with nickel (1455 °C). As shown in previous research, the nano-size lowers the demand for energy to achieve the nanoparticles' conjunction within the grains, which allows for their sintering at a temperature far below the melting point of metal on a macro scale [27]. The increasing of Ag NPs' concentration to 0.25% affects the further increase of metallic coatings' conductivity after sintering at all applied ranges of temperature. The highest conductivity growth spike was observed after doping of Ni-Ag ink coatings with 0.5% of Ag NPs, especially at the sintering temperature range of 130–250 °C. Although, the

highest effect of such a concentration of nanoparticles on the coating conductivity (also considering error bars) was observed after sintering at 200 °C. The obtained conductivity was high, at about 6.2×10^6 S/m. At the lower temperature sintering of 150 °C, at the concentration of 1% of Ag NPs, the highest growth spike of conductivity was noticed. At the temperature sintering of 250 °C, the conductive properties of metallic coatings were almost not changed, and even the concentration of Ag NPs of the doped ink coatings was increased from 0.5 to 1.5%. After the sintering process of deposited nanocomposite films at the highest temperature (300 °C), the improvement of their conductivity at all ranges of applied concentration of Ag NPs was negligible. The value of conductivity changed from 7.3 to 8.9×10^6 S/m with the increasing concentration of Ag NPs from 0.1 to 1.5%. This slight effect of increasing the concentration of nanoparticles on the conductive properties of nanocomposite coatings at higher sintering temperature (250–300 °C) could be related to the properties of Ni-Ag and Ag NPs. This is because the lower melting point of Ag NPs in comparison with Ni-Ag provides their total merging at a lower sintering temperature. Therefore, further increasing of the concentration of Ag NPs does not affect the conductivity at a higher sintering temperature.

After the analysis of the obtained results and considerations of two criteria (which are important for metallic inks regarding their large-scale industrial application), (1) high conductivity of the obtained tracks and (2) the fabrication of flexible devices, we have selected two types of formulated nanocomposite inks: (1) doped with 0.5% of AgNPs and (2) doped with 1% of Ag NPs, which, after the deposition process, were sintered at 200 and 150 °C, respectively. In this context, we considered the economic point of view, in which the lowering of the costs of fabrication of conductive circuits is of crucial importance, and as low as possible a concentration of silver is favorable, although it should provide sufficient conductivity of metallic coatings. Therefore, as the first candidate for the conductive coatings' fabrication, nanocomposite ink doped with 0.5% of Ag NPs sintered at 200 °C was chosen. Besides, for the fabrication of conductive patterns on flexible, heat-sensitive substrates, the sintering temperature should be low enough to not damage their structures. In this context, for the next experiments, we selected and applied the nanocomposite ink containing a proper concentration of the Ag NPs (1%) and conditions of the sintering process (150 °C) of obtained coatings. It allowed to formed film with high conductivity of about 6.1×10^6 S/m, which was similar to the one obtained for the ink coating doped with 0.5% of Ag NPs after sintering at 200 °C.

Another factor that strongly influences the conductive properties of metallic coatings is the sintering time. Therefore, the dependence of the conductivity of Ni-Ag based coatings doped with 0.5% or 1% Ag NPs on the time of sintering at an optimal temperature of 200 °C and 150 °C, respectively, was studied. The obtained results are presented in Figure 6.

As presented in Figure 6, similar values of conductivity (at all ranges of sintering time) were obtained for both types of coatings: doped with 0.5% and 1% of Ag NPs, which were sintered at 200 °C and 150 °C, respectively. The highest growth spike of conductivity was observed after 30 min of the sintering process. Its value increases from about 3×10^6 S/m, after 15 min of heating, to about 6×10^6 S/m for both types of sintered nanocomposite coatings. The consideration of their conductivity (and measurement error estimation) obtained after increasing of time of sintering (45–75 min) indicates that its values were almost not changed. Therefore, 30 min was selected as the optimal time of the sintering process of both types of analyzed nanocomposite coatings. The obtained conductivities correspond to 35% of that for a bulk nickel. In our previous work, we presented the conductive properties of metallic coatings based on Ni-Ag NPs with bimodal size distribution. We have obtained the highest conductivity, 20% of that for bulk nickel, for films containing Ni-Ag NPs with an average size of 70 and 250 nm after sintering at 300 °C for 30 min [20]. Therefore, the conductivity of nanocomposite coatings obtained in present research, when we treat the deposited films as a structure of nanoparticles (Ni-Ag and Ag) with bimodal size distribution, is 1.75 times higher in comparison with that obtained for the ink coatings composed of only Ni-Ag NPs at different size distribution. Besides, as

we presented in our previous work, the temperature sintering was much higher (300 °C) than that applied in the present paper (150 °C or 200 °C) to achieve highly conductive nanocomposite coatings. In comparison, the resistivity recently reported for coatings, based on the mixture of silver nanoparticles at the size 12 and 80 nm, after sintering at 150 °C was 33 $\mu\Omega\cdot\text{cm}$, which was almost 1.5 times higher than the value (19 $\mu\Omega\cdot\text{cm}$) obtained at the same sintering temperature in our research. Besides, the coatings presented in our paper were mainly composed of Ni-Ag NPs, doped with only 1% of Ag NPs; therefore, their additional advantage, in comparison with that based on Ag NPs, is a lower price [28]. Mohammadi et al. [29], achieved the highest electrical conductivity (4.22×10^5 S/m) for the mixture of Ni and Ag NPs (50:50 wt%) after sintering at 300 °C. However, the obtained value was much lower in comparison to the ones achieved in the presented studies, even if the applied sintering temperature was higher. The value of sheet resistance previously obtained for coatings based on Ni-Ag NPs was found to be 11 $\text{m}\Omega/\square$ [11]. However, this value was obtained at a much higher sintering temperature (850 °C). Furthermore, the thickness of the sintered coating was not determined; therefore, it is difficult to compare the conductive properties of the metallic coatings.

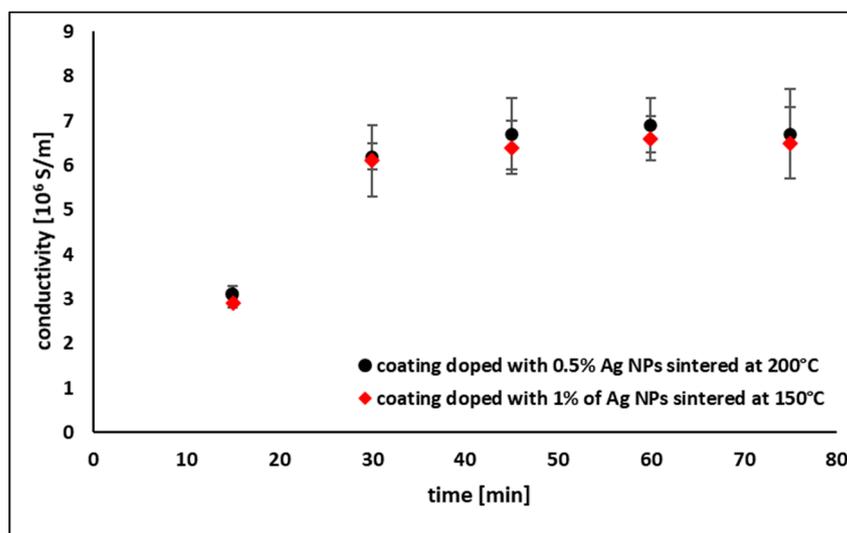


Figure 6. The dependence of the conductivity of metallic films based on Ni-Ag NPs (main filler) doped with 0.5% (circles) or 1% (rhombus) of Ag NPs on the sintering time at the sintering temperature of 200 °C and 150 °C, respectively.

Morphologies of metallic films of nanocomposite inks doped with 0.5% and 1% of Ag NPs after the drying process (60 °C, 15 min) are presented in Figure 7A,B, respectively. As can be seen after this process, in the structure of both deposited metallic coatings, isolated holes are presented and there is no visible neck formation between nanoparticles. They are not connected; therefore, the nanocomposite ink coatings are not conductive after the drying process. The sintered nanocomposite films containing 0.5% (at 200 °C) and 1% (at 150 °C) of Ag NPs are shown in Figure 7C,D, respectively. It can be noticed that both sintered nanocomposite coatings are more smooth in comparison with that after the drying process. The individual nanoparticles are merged, and coalescence and neck-forming between them can be observed. The formation of molten nanocomposite ink layers results in a transformation of nonconductive metallic coatings (after the drying process) to ones characterized by high conductivity.

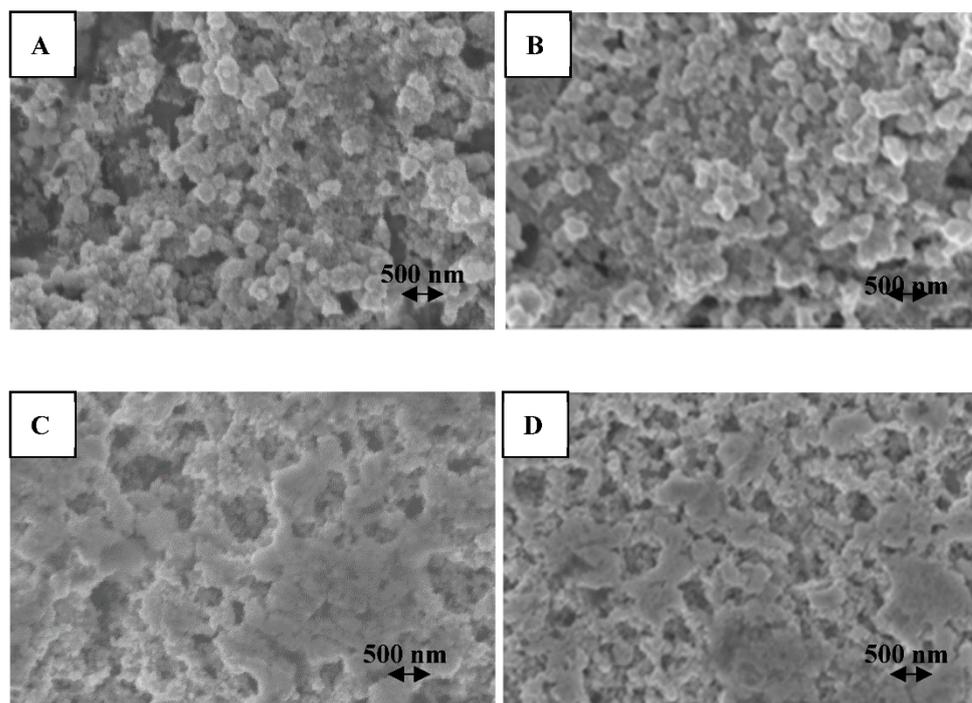


Figure 7. SEM images of metallic coatings of nanocomposite inks after drying at 60 °C: (A) doped with 0.5% and (B) doped with 1% of Ag NPs; after sintering: (C) doped with 0.5% (200 °C) and (D) doped with 1% of Ag NPs (150 °C). The drying process was performed for 15 min while sintering was performed for 30 min.

4. Conclusions

In summary, we demonstrated the process of the preparation of nanocomposite ink based on Ni-Ag “core–shell” and Ag NPs for the fabrication of conductive coatings. It was shown that ink composed of such metallic nanoparticles being used for conductive films preparation provides better conductivity as compared with original Ni-Ag NPs used for ink formulation. According to the future application of such nanocomposite films in flexible printed electronics, the most promising properties, such as high conductivity and sintering at low temperature (150 °C), were shown for the nanocomposite coatings doped with 1% of Ag NPs. Besides, as the ink coatings with good conductive properties can decrease the costs of large-scale fabrication of such films based on silver, the most suitable is the nanocomposite ink containing 0.5% of Ag NPs sintered at 200 °C.

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