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Preparation of conductive nano silver ink and its application on RFID tags

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Abstract : The recent dramatic progress in the printed electronics and flexible electronics, due to the universality of the substrates including the foldable and stretchable substrates, has opened a new prospect in the field of future electronics. In this paper, silver nanospheres in large-scale are synthesized, the nanosilver ink with 63.88% silver content are prepared and a new type of highly conductive and far identify distance RFID tags are manufactured. Especially there are no resin and other additives containing in our conductive ink which satisfy the rheological characteristics and process of screen printing. The tags exhibit the best radiation performance own to there is no high temperature sintering in need. The surface resistance of the tags could be 80 mΩ/□, and the identify distance reach to 6.0m.

INTRODUCTION

Printed electronics (PE) and flexible electronics, contrary to conventional electronics, can be bent, stretched, compressed, twisted and deformed into complex, non-planar shapes while maintaining good performance, reliability, and integration. So it could be widely used in many fields, examples include flexible and stretchable circuitries, flexible displays, flexible energy devices, smart skins, electronic eye type imagers, soft and human friendly devices, and so on. With the development of the PE and flexible electronics, as the most important conductive functional materials, such as nanosilver, nanocopper, aluminum, and nanogold have gained interests from researchers in academia and industries. Conductive nanosilver inks are most commonly used materials due to their low resistance.

Among those applications with printing technologies, RFID tags have gained extensive attentions of the industries for the wide potential market. IDTechEx's estimates on the potential size of the overall PE market have ranged up to $57 billion by 2019, while it has placed the potential value of the RFID market as high as $25 billion by 2018[1]. Current, most RFID tags are being made with etching technology. It is not only environmentally unfriendly but also a waste subtractive manufacturing process, while printed RFID tags is inherently an additive process which could save the overall production cost. Still, RFID and conductive inks offer plenty of opportunities as new applications emerge.

Therefore, several group have being engaged in the manufacturing of the printed RFID tags, and also various printing technologies have been attempted. For example, L. Yang et al developed the RFID tag module for high frequency applications such as 915 MHz with the inkjet-printing technology[2]. The polymer foils are typically substrates used for flexible electronics including RFID tags, while the coefficient of thermal expansion and moisture content of them contributing to the undesirable permanently thermoplastic deformation which is detrimental to the performance of the devices. The glass transition temperatures of commercially available polymer substrates such as polyethylene naphthalate (PEN), PET, polycarbonate, polyethersulphone cyclic olefin copolymer, and polyimide are 150, 80, 145, 223, 164 and 300 °C, respectively[3]. Various approaches have been reported during the last years to lower the sintering temperature of NP inks. A rapid low-pressure plasma sintering process of inkjet-printed silver nanoparticles for RFID antennas has recently been reported by Wolf, F.M. and his co-workers, although the maximum processing temperature did not exceed 70 °C, plasma sintering is typically a low sintering method, in order to realize the comparable response signal with the screen-printed tags, the tags must be sintered at least 30 min[4]. Magdassi, S., et al have presented a new approach to achieve melt of the nanoparticles and sintering at room temperature[5],5 while the printed conductive pattern can not be easily controlled either by the ink or by the thickness concerning the screen printing method, which fits for the production of RFID tags at different frequencies. Otherwise, Tang, Y., et al. conducted the post processing of the patterns fabricated by silver nanoparticles by the means of soaking in the chloride irons aqueous solution[6], which is a time consuming process. Furthermore, Shin et al studied in the selection of ink and printing process to fabrication the RFID antennas, regrettably, the average thickness and standard deviation of printed RFID antennas are 16.74 μm and 1.08 μm, which is less than the required one for 13.56 MHz but more than for 860 MHz[7].

Here we focus on the preparation of silver nanopheres in large scale. More importantly, we also prepared the nanosilver conductive ink with the nanopaticles and manufactured the RFID tags with screen printing method eventually since it is a high-speed and continuous process and could satisfy the demands for ultra low-cost, high-resolution patterns, it could be an alternative for mass production of next-generation printing devices.

Characterizations of shape and nanostructure heavily rely on scanning electron microscopy (SEM) and other diverse methods that are applied where appropriate. Thermogravimetric analyses (TGA) were performed with a TG209 by Germany NETZSCH under ambient atmosphere in the range from 30 to 800 °C with a heating rate of 10 K/min. Then, surface resistance of the RFID tags was measured by a four point probe measurement and film thickness was measured by a Profile meter named MarSurf XCR20. The identify distance of RFID tags was recorded by Ultra High Frequency All-in-One Card Reader.

EXPERIMENTAL DETAILS

The preparation of the silver nanospheres has been reported by our group[8], in a typical synthesis process, solution A contained 300ml deionized water solution, some amount of PVP and 5% NaOH. 100g silver nitrate was dissolved in 300ml deionized water to form solution A, Solution C contained some amount of hydrazine hydrate and 75ml of deionized water. Then, temperature of solution A was kept at 6~10 °C under vigorous stirring and solution B and solution C were fed into solution A with speed of 3ml/min. It is noteworthy that the molar ratio of the PVP to silver nitrate must be under 0.8 for avoiding the post high temperature sintering. Then, the dispersion was washed by acetone for 3 times to remove the excess PVP, free ions to obtain wet silver nanoparticles.

The nano-silver dispersion obtained contained much ion and excess PVP which impact the conductivity of the silver dramatically. So, the dispersion was purified with the solvent deposit method. In detail, two times of acetone in volume were added into the vigorous stirring dispersion with. After the dispersion breaking into two layers, the supernate was removed and wet precipitation was obtained. To obtain wet silver nanoparticles, the process was repeated for three times. The silver nanoparticles were finally dispersed by adding ethylene glycol without other toxic additives.

Semi-automatic screen printer was used to proof and PET acted as substrate. After proofing, sintering at 120 °C for 30s was taken and then the conductivity the ink layer is tested.

RESULTS AND DISCUSSION

Characterization of silver nanopaste

To investigate the thermal stability of the silver nanoparticles, the mass decrease was recorded by TGA (Figure 1)[8]. The TGA curve shows a decrease of 32.23 wt% at an initial step from 30 to 200 °C, which corresponds to the boiling temperature of ethylene glycol. A single deflection point and gradual decreases from 300 to 600 °C indicate the capping agent is removed. Finally, the residual mass is 63.88 wt% that is the nanosilver containing in the conductive ink. To lower down the sintering temperature and minimize the sintering time of the silver paste with maintaining a good conductivity, the silver paste should be produced without leaving a highly content of resin such as polymer binders. It can be seen the ratio of PVP to silver is 0.048 which can show good conductivity. Furthermore, there are no toxic dispersion solvent and other resin containing in our conductive ink, and it is environmental friendly for moving forwards to industrial production.

The selection of appropriate printing method is intimate connection with the electrical properties and rheological characteristics of the conductive ink. The measured dynamic viscosity against shear strain rate is plotted in Figure 2. The viscosity of the conductive ink is 17 Pa·s at a shear rate of 1/s. The rheological characteristics and adhesion are suitable for the screen printing method according to Helmut, K[9]. The color of silver conductive ink we prepared is greyish-green (Figure 3).

Performance of the printed patterns

For nanoparticle ink, the polymer capping agent that protects the particles from agglomerating must be removed in order to make them direct physical contact. And the terminal destination is to make the printed feature a continuous conductive network. The Figure 4(a) shows the SEM of the printed patterns after sintering at 120 °C for 30s. Obviously, there is no distinct residual polymer is found corresponding to the TGA curve, compared to Figure 4(b) where is a commercially silver paste. For the latter, the post sintering must be conducted at 120 °C for 30min. So it is possible for the roll to roll production of the RFID antenna with our silver conductive ink.

For the printed RFID antennas, the average thickness on a flexible PET film was about 3.6 μm (Figure 5), which is a reference value because of the slightly

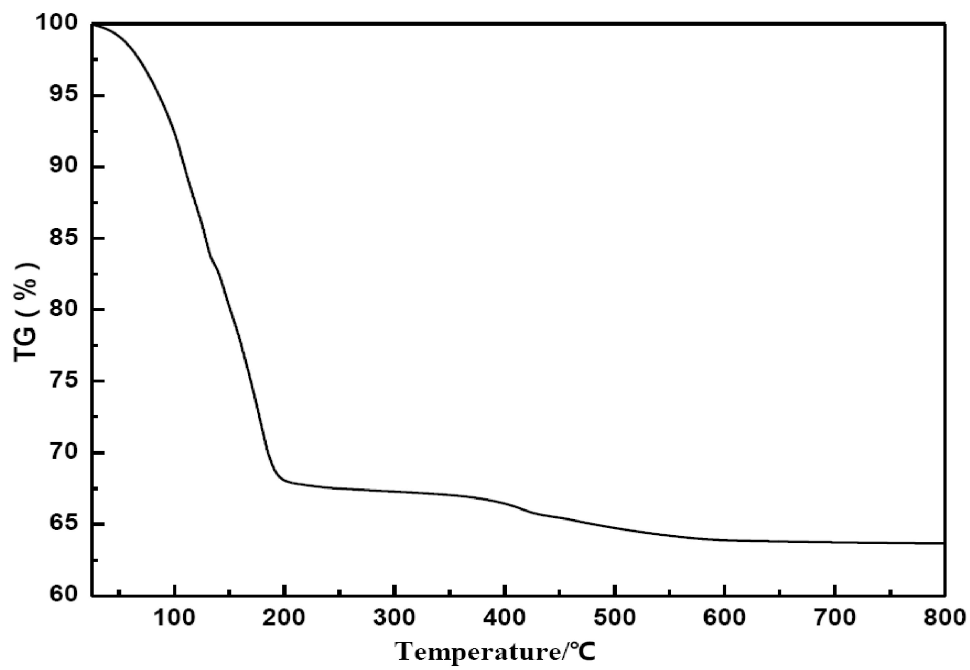

Figure 1 : TGA (heating rate =10 K/min) of the silver nanopaste.

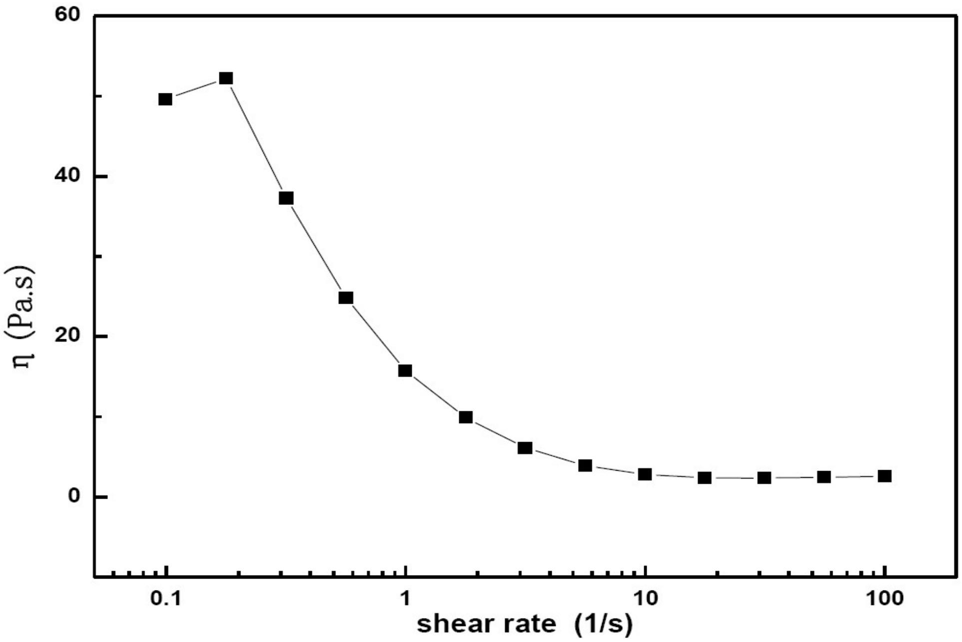

Figure 2 : Dynamic viscosity of silver nanopaste that we prepared.

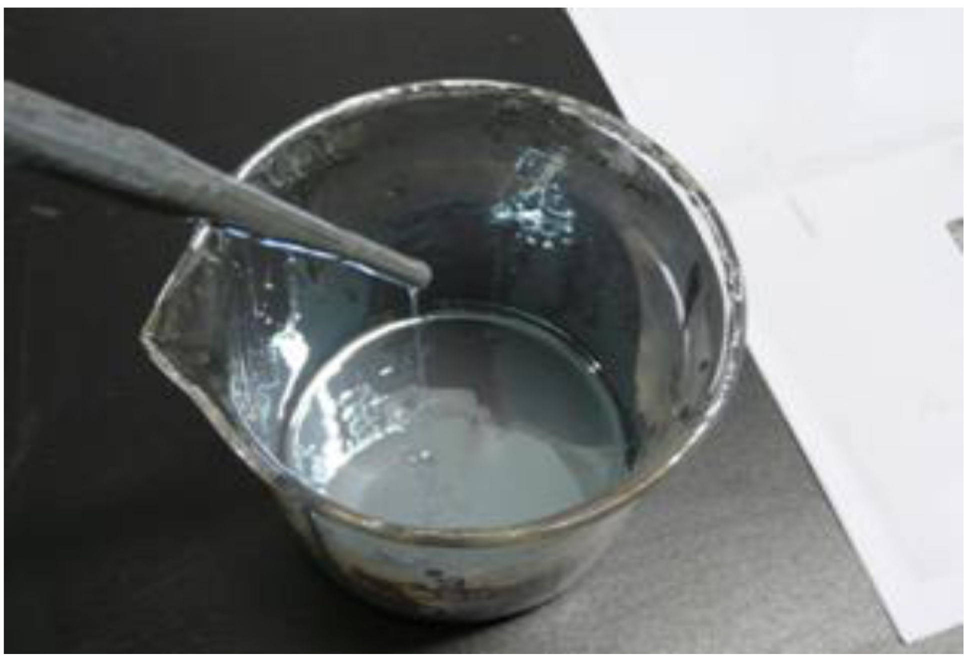

Figure 3 : The picture of silver conductive ink that we prepared.

distorted of the substrate. Therefore, the printing process and developed silver nanopaste are found suitable for the production of tags at frequencies, 960 MHz[6]. However, the silver nanoparticles are accumulated at the edge of the pattern while the central region is relative thin. That is, the curing drop exhibits the so-called coffee ring effect[10], which induced by the differences in the evaporation rates of the conductive ink and cause an additional flow to the system from regions with low surface tension to regions with high surface tension[11].

The photograph of the tag as well as the local digital microscope image of the printed antennas with different magnitudes is shown in Figure 6. Both images confirm a good and uniform printing quality, indicated by the sharp edge and high surface flatness of the printing image. The electrons do not penetrate into a conductor, and the current density of which is not uniform at high frequencies, which is different from direct

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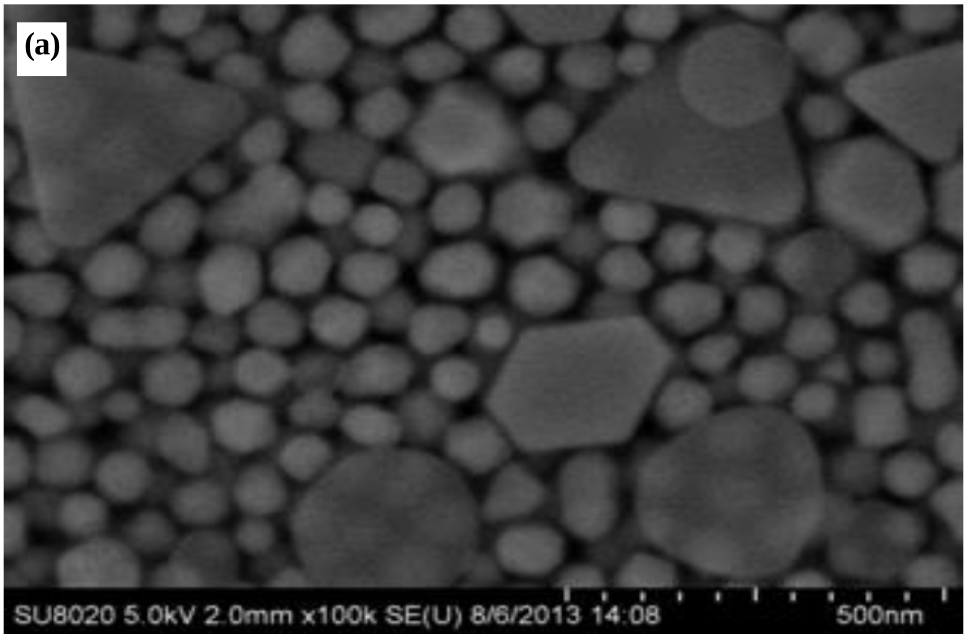

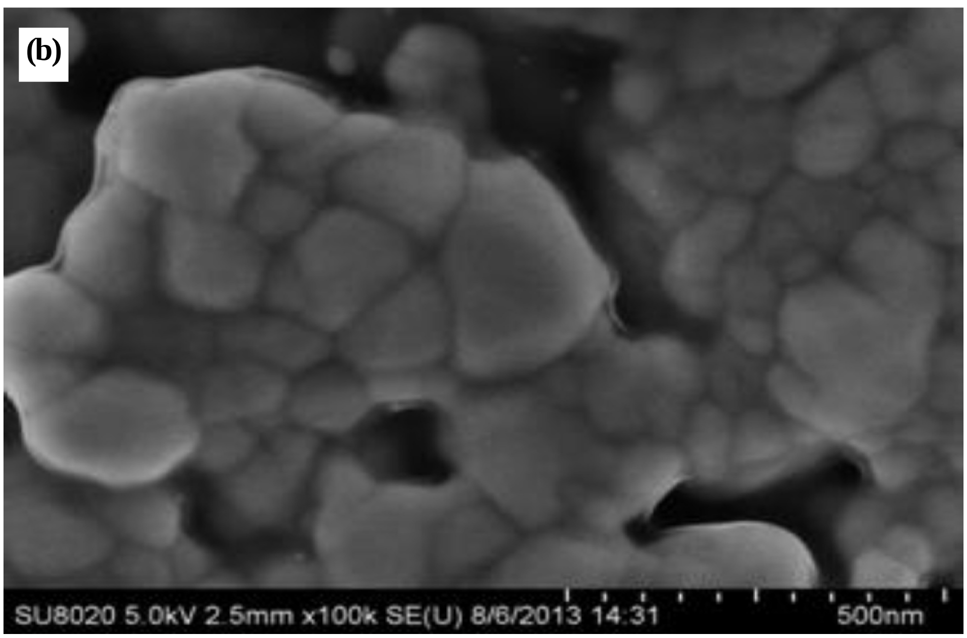

Figure 4 : SEM images of printed pattern with (a) the developed silver paste and (b) commercially ones after sintering

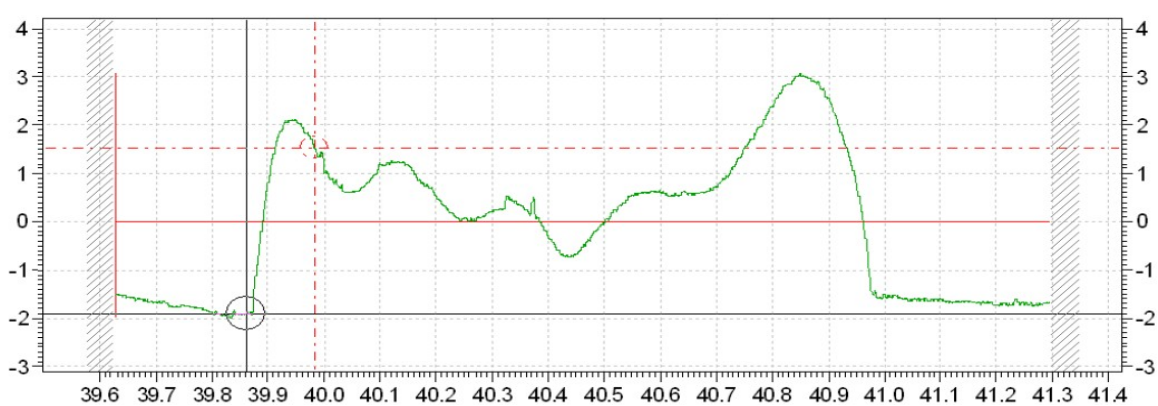

Figure 5 : The thickness curve of the printed pattern

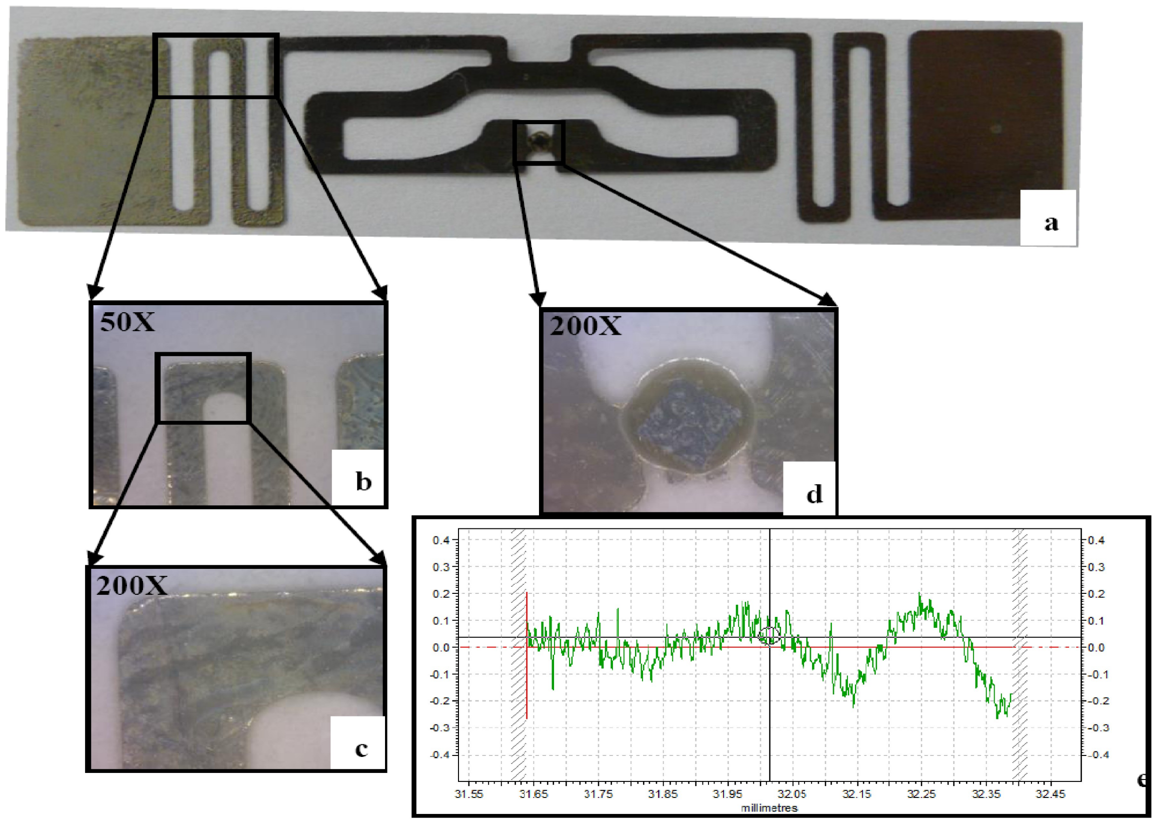

Figure 6 : Printed RFID tag with nano silver ink after sealing the chips: photograph of the tags (a); the local digital microscope image of the printed antennas with different magnitudes (b,c); the amplified digital microscope image of the chip position of the antenna (d); The surface roughness curve of the printed pattern (e).

current. The surface roughness affects the alternating current resistance of a printed RFID antenna[2,12]. In general, according to rheological characteristics of the paste for screen printing the surface roughness of the pattern is not comparable to etched ones, and worsen than that, the surface roughness resistance per unit length of a conductor also attributes to surface roughness at the smaller microscopic scale[6]. The the surface roughness and standard deviation of printed RFID antennas are 0.0706 μm and 0.016 μm (Figure 6(e)).

The surface resistance on the nanoparticle pattern was measured to be 80 mΩ/□. Resistivity is given as resistivity (ρ) = surface resistance × film thickness/ 10; by this equation, the resistivity of the pattern was calculated to be 2.88×10^{-7} Ω·m, which enables fabrication of conductive patterns on some electronic devices, which is lower than. The viscoelasticity and rheological characteristics of the conductive ink that fit for the screen printing must be in the consideration, which influence the conductivity of the conductive paste to some extent, so the resistivity of the printed patterns is higher than the silver paste that reported currently as low as 10^{-8} Ω·m[4,5].

The performance of the RFID tags

To experimentally detecting the radiation performance of the RFID antennas, the antenna was sealed with a UHF transponder chip, it is noteworthy that complete unit is called label or tag after equipped (Figure 6). The tags was then send to the China National RFID Products Quality Supervising Test Center to test the identify distance with Ultra High Frequency All-in-One Card Reader. The RFID tags were tested by sending signals at 960 MHz from the reader to the tag, and the process was repeated for 20 times for each tag shown by the testing report. The RFID tags worked without losing the signal from the reader that fixed 6.0 m from which. Once using a longer distance to the tags, the answer signal is weaker. The report also reveals the working temperature of the tags is -30 to 70 °C.

CONCLUSION

In conclusion, highly conductive features on flexible PET film have been successfully fabricated by screen printing with the developed silver nanoparticle ink. The printed pattern was sintered at temperature as low as 120 °C within 30s to a conductivity $2.88 \times 10^{-7}\ \Omega\cdot m$. The rheological of the paste composed of silver nanoparticles was conducted suitable for the screen printing method. The radiation performances of printed RFID tags screen printing with the developed silver nanoparticles are perfect, with the identify distance be 6.0 m. And the working temperature of the tags is -30 to 70 °C

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