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Preparation and Characterization of Silver Citrate Nano-emulsion and Nano-silver Film

Li-Xin MO[1, a], Lu-Hai LI[1, b], Ya-Ling LI[1, c], Zhong-Xiao LI[1, d], Ming Wang[1, e]

[1]Lab. of Printing & Packaging Material and Technology, Beijing Institute of Graphic Communication, No.25, Xinghua Beilu, Huangcun, Daxing District, Beijing 102600, P.R.China
[a]Lixin_mo@yahoo.com.cn, [b]liluhai@bigc.edu.cn, [c]liyaling@bigc.edu.cn, [d]lizhongxiao@bigc.edu.cn, [e]tomy831@hotmail.com

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Abstract. To prepare the nano-scale silver carboxylate emulsions and investigate their applications in the preparation of nano-scale silver films, the silver citrate emulsion was synthesized through the reaction of silver nitrate with sodium citrate in the presence of polyvinylpyrrolidone (PVP) as a surface modification agent in water. The emulsion was coated onto the surface of the PET substrate to form a thin latex layer of silver citrate. And this was followed by drying at about 100 °C. Then, the silver citrate thin film was deoxidized by aqueous ascorbic acid. Finally, a translucent silver thin film was formed on the surface of the PET substrate. Properties of the silver citrate emulsion and the silver film on the PET were characterized by X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), laser particle size analysis, scanning electron microscopy (SEM), thermogravimetry(TG) ,UV-visible absorption spectroscopy, atomic force microscopy(AFM) and digital multimeter analysis. It was found that the silver citrate particle surface-modified by PVP has a nano-rod structure and homogeneous size distribution. The nano-rod was about 20 nm in diameter and 200 nm in length. For the UV-visible absorption spectrum of the thin film exhibited an absorption peak at 430 nm, the silver thin film prepared on the surface of the PET substrate was a typical nano-scale sliver film. Measurements of the sliver thin film at room temperature indicated that the silver film was electrically conductive, and the surface resistance was 2.42 kΩ/cm.

Introduction

Many preparation ways of nano-silver have been reported. One of the most popular deoxidizing routes is to protect the nano-silver in reaction using some kind of polymers. To gain the nano-scale silver particle, PVP (Polyvinylpyrrolidone) is one of the useful protective agents. By the protecting of PVP, 30~100 nm spherical nano-silver powder could be produced by the deoxidization of silver nitrate[1,2]. The dispersion and dimension of silver powder is greatly influenced by the ratio between reactants, the amount of PVP, the reaction time and reaction temperature. Many substances can be used as deoxidizing agent, such as metal Fe, Al, Zn, Cu, organics formyl and formate, hydrazine hydrate, aldehyde, ammonia, alcohol, gluose, fatty acid, vitamin C (ascorbic acid) and so on. The dispersants always used are PVP, poly (vinyl alcohol) (PVA), gelatine, ethanol amine and so on. But almost all the products are limited in small concentration. And most of the reported solid nano-silver is congregated into bigger grain, then the nano-dimension property is decreased greatly.

To get the conductive silver circuit, people always print the conductive ink on substrate by screen printing firstly, then the printing layer must be thermally treated to several hundred Celsius degree. In such a way, the thickness of the circuit is always more than 20 μm. Based on the principle that the smaller the silver particle the lower the melting point, the nanosilver ink-jet ink was innovated, and the heat-treating temperature was decreased to about 100 °C. But the higher temperature and cost can't be avoided. In the present and future, the thin, low cost and flexible

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conductive nanosilver film is prospective to the development of radio frequency identification (RFID), display electrode, printing circuit plate (PCP) etc.

In this paper, the synthesis and characteristic of silver carboxylate emulsion is reported and discussed, the study is focused on the easy way to form a conductive nanosilver film on the flexible substrate such as PET film.

1. Experimental

1.1 Instruments and agents

UV-2501PC (Shimadzu) , SS-550 scanning electron microscope (Shimadzu) , XRD-2000 X-ray diffractometer (Rigaku) , digital multimeter (DT9205A+, China HAITI Corp.) , scanning probe microscope system (CSPM4000, Guangzhou Benyuan Ltd., China) , FTIR-8400 (Shimadzu), TG-209C (NETZSCH), S3500 (Microtrac), silver nitrate, Vc (A.P., Tianjin HengDa Photosensitive Material Corporation) , PVP(C.P., K30, Guangzhou South Chemical Glass Corporation) , sodium citrate (C.P., Hunan Huari Pharmacy Co. Ltd. China) .

1. 2 Synthesis and analysis of nanosilver citrate emulsion

11.46 g (39.0 mmol) sodium citrate was dissolved in 150 ml pure water, then it was mixed with 40 ml 11.5% (w/w) PVP aqueous solution at room temperature. The mixture was light yellow. Then 38 ml silver nitrate water solution was dropped in under stirring. With the dropping of silver nitrate, a white emulsion was formed in the flask. Keep stirring for 40 min at room temperature after dropping. The silver citrate was separated and dried. The IR, TG and XRD spectra of silver citrate were recorded. The disperse condition of silver citrate was measured by Microtrac 3500, and the morphology of the silver citrate was observed by SEM.

1.3 Preparation of nanosilver film

To get a silver PVP film, the PVP modified silver citrate emulsion was coated on the surface of 100 μm thick PET film by Mayer rod. The coating was dried completely under room temperature. Then the coating of silver citrate was deoxidized by 3% (w/w) vitamin C water solution, the solution was brushed on the silver citrate by Mayer rod too. The deoxidized coating was dried at 60 °C using hot air and a light brown silver film was obtained. The morphology and resistance of the silver film was tested on scanning probe microscope system and digital multimeter, the absorptivity was tested on UV-2501PC.

2. Results and Discussion

2.1 Structure confirm of silver citrate

Figure 1 is the infrared spectrum of silver citrate, there are no C=O stretching peaks of carboxylic acid in 1640~1720 cm^{-1} but the stretching characteristic peaks of carboxylate C=O were found in 1593.1 cm^{-1}(asymmetry flex vibration of C=O) and 1390.6cm^{-1}, 1431.1cm^{-1} (symmetry flex liberation of C=O). It can be deduced that the product was carboxylate. Since sodium citrate, silver nitrate and sodium nitrate are dissoluble in water, it was confirmed that the carboxylate product dispersed in water was silver citrate.

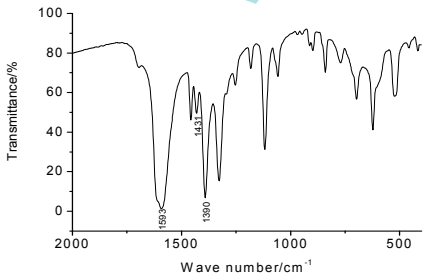

Figure.1 IR spectrum of silver citrate

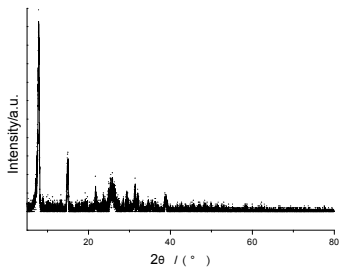

Figure.2 XRD pattern of silver citrate

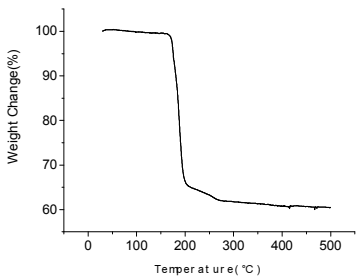

Figure.3 TG curve of silver citrate

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Figure 2 is the XRD pattern of the chemical synthesized in the above reaction. The diffraction angle 2θ is 7.782°, 15.004°, 21.700° and 31.254°. Each of the major diffraction peaks is corresponding to the standard diffraction peaks of silver citrate (JCPDC NO.01-0030) , indicating that the synthesized product is silver citrate.

Figure 3 is the TG curve of the synthesized compound. It is found that the leftover ratio after TG analysis is 60.46%. Just like the ratio of silver in silver citrate. It is thus confirmed that there are 3 silver atoms in one molecule.

2.2 Dispersion of silver citrate emulsion surface-modified by PVP

Figure 4 indicated that the particle of silver citrate emulsion had a size of 60-150nm, mostly 100 nm. This shows that well-dispersed silver citrate nano-particles were prepared by chemical method with polyvinyl pyrrolidone (PVP) as surface-modifying agent. PVP accelerated the reaction between silver ions and sodium citrate, because it stabilized Na^+. PVP protected the silver citrate particles from growing and agglomerating [5, 6].

2.3 SEM analysis of silver citrate emulsion surface-modified by PVP

The silver citrate emulsion surface-modified by PVP was observed by scanning electron microscope. The result is shown in Figure 5.

The silver citrate particle which was surface-modified by PVP has a nano-rod structure. The nano-rod was about 20 nm in diameter and 200 nm in length.

2.4 UV-vis of nano-silver film produced from silver citrate/PVP film

Figure 6 is the UV–vis spectrum of Ag/PVP. The absorptivity peak is located at 430 nm. This corresponded to the nanostructure of the silver film. For the silver particle coagulated in solid state, the absorptivity peak red shifted to 430nm comparing the reported absorptivity peak at 390nm in liquid [7].

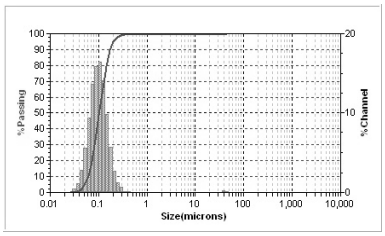

Figure.4 Dispersion of silver citrate

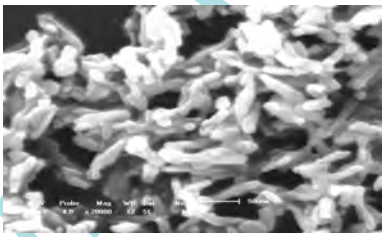

Figure.5 SEM of the silver citrate

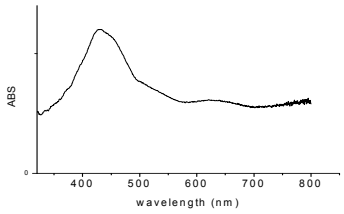

Figure.6 UV-vis spectrum of silver film

2.5 XRD analysis on silver film

The silver film prepared by redox reaction was tested by X-ray diffraction (Cu Kα, K=0.1542 nm, scanning rate 15°/min, angle 1.0 °). There are four strong peaks located at 38.125°, 44.238°, 64.407° and 77.36° (Figure 7). Figure 7 indicated that there are still some silver citrate in the coating, and all silver citrate disappeared after being treated by water. Figure 7(a) is the XRD pattern of PET film. The peaks at 2θ=26.32° and d=3.383 appearing in three curves (a, b, c) are the same, attributed to PET.

Because of the starvation of water during the deoxidizing reaction, the formed silver crystal is not perfect in film. This leads to the broadening of the diffraction peaks in figure 7(b). After dipped in water and further reaction, a better crystal was formed gradually (Figure 7c). It was believed that the additional water treatment should promote the redox reaction and wash away the impurities. By comparing of the XRD patterns of the films, it can be concluded that the further deoxidizing of silver citrate could be accelerated by water.

2.6 AFM analysis of silver film

To confirm the nano dimension of the silver film, the AFM morphology was measured using a

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scanning probe microscope system in rap model. Figure 8 indicated that most of the silver particles were small than 100 nm, and part bigger than 100 nm. For PVP takes some place in silver/PVP coating in the surface of PET film, and it was dissolved from the coating during washing, so some position of the silver film is blank.

2.7 The analysis of conductivity of silver film

The surface resistance of the silver film was measured randomly at 10 points using DT29203 multimeter under room temperature. The distance between any two neighbor test points is 1 cm. The results are listed in table 1.

It is obvious that the resistance is greatly affected by post-treatment after reaction. The resistance of water-treated film is ranked as no water treat >water brushing >water washing >water dipping. The resistance of silver film decreased with the increase of water amount and treating time. It is considered that water offered a reaction environment and washed the impurity away, which makes the silver film more dense. The action of alcohol on decreasing the resistance of the silver film is much less than that of water.

After the treatment of water, the crystal structure of the silver film was improved and the surface resistance of the film on PET was decreased greatly.

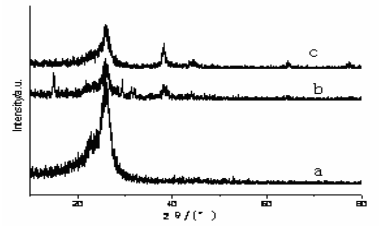

Figure.7 XRD patterns of Ag/PVP film (a).Blank PET (b).Not washed (c).Water washed

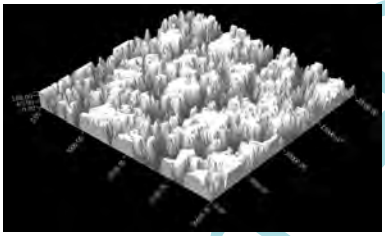

Figure.8 AFM of Silver/PET film (scanningrange20000nm×20000nm)

Table 1 Resistance of silver film treated in different modes

Post-treatment ways	Resistance[Ω/cm]
No water	>>100M
Scraped by water	14.91M
Washed by water	49.87K
Dipped in water 10min	2.42K
Scraped by alcohol	>>100M
Dipped in alcohol 10 min	2.56M

Summary

(1)The nano-scale silver citrate emulsion could be produced by the reaction of sodium citrate and silver nitrate in the presence of polyvinylpyrrolidone (PVP) as a surface modifying agent in water. The silver citrate is of three silver atoms.

(2)A nano-silver film was produced by the redox reaction of silver citrate/PVP film and Vc on a PET substrate. The thickness of the film is less than 0.2 μm.

(3) Morphology and conductivity of the silver film is influenced by the treatment after reaction. Conductivity of the film dipped by water is much better as compared with being dipped by alcohol.

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