CHAPTER IX

SYNTHESIS OF COLLOIDAL SILVER NANOPARTICLE FOR PRINTED ELECTRONIC

9.1 Abstract

Colloidal silver particle was successfully prepared by wet chemical synthesis. Pure single phase of silver was confirmed by X-ray diffraction. Transmission electron microscope categorized that diameter of particle was 100 and 20 nm, depending on molecular weight of PVP stabilizer. Schematic drawing model was used to predict the packing efficiency of 1:1 wt% of two mixtures. The mixture of silver solution was deposited as thin solid film by desktop inkjet printer. Scanning electron microscope showed that two different sizes of silver particle give higher densely packed structure than the film of single particle size. When 0-20V of voltage was applied, the current density was reached 0.10 J/cm^2, suggesting that silver film has potential to be applied as cathode layer in organic light emitting diodes (OLEDs) device.

9.2 Introduction

Recently, wide attentions have been focused on the development of convenience and low-cost processing techniques to deposit conductive features on nano-bio-composite substrate [7, 9, 144, 200] flexible display. Direct-write techniques, one type of printable electronic [201, 202] with the feature of low conductive ink consumption, have attracted interests of many industrial applications such as printed circuit board and display device, because they promised the simplification of device manufacturing. Among multiple direct-write technologies, a drop-on demand inkjet printing technology [17, 132, 141] is currently used as the high potential method in the printing industry due to low instrument cost and less processing steps compared with other patterning processes. In addition, mark-less and non-contact patterning approaches are also beneficial. This technique has been

applied to use with a variety of nano-scale materials including ceramic, metal, polymer as well as composite.

Conductive ink solution [142, 203, 204], a mixture of metallic and organic solution, had been suspended prior to load into inkjet cartridge in order to prevent agglomeration of particles. The common condition of their particle size must be less than 200 nm and monodispersed. The diameter size of nozzle of inkjet cartridge is less than 200 nm, indicated by printer supplier. In particular, inkjet printer uses water as media to suspend ink particle. It is desirable that ink particle at the end product should be well aligned and give high electrical conductivity after heat treatment at a relatively low temperature. In the case of metal nano-particle, when ink solution was deposited onto the substrate, solvent was then evaporated with moderate heating and obtained a thin solid film of nano-particle. The thin solid film was further heated to a higher temperature in order to remove organic molecules and ensured that nano-particle sinter into a dense metallic film.

In general, nano-particles are based on monodispersed form. Based on the theoretical maximum density, the attainable packing fraction for dried film should be 74% if considering into a perfect face centered cubic lattice. However, the nano-particle can be randomly packed; this fraction is reduced to 62.5%. Higher dispersions and various different sizes of ink nano-particles offer larger packing ratios production. In addition, Rasmussen et al [205] also found that if two different volumes of monodispersed particles were mixed and allowed randomly packed, the packing fraction increased and the dense film product can be then obtained.

In this research work, we wish to extend our research work on bio-nanocomposite substrate. Transparent and flexible feature of nanocomposite substrate was successfully carried out. Additional information of bio-nanocomposite substrate had been discussed elsewhere [9]. The synthesis of silver nanoparticle for inkjet printer technique was performed. Silver nanoparticle was prepared as both large and small size by the reaction of polyvinylpyrrolidone (Mw as 10000 and 40000 g/mol), respectively. The silver precursor after synthetic step was investigated as structural analysis by Fourier transform infrared. X-ray diffraction and TEM image were employed to investigate the crystal phase structure and particle size of silver. Schematic drawing model and SEM image were used to predict and

investigate the packing efficiency of silver thin solid film prepared by desktop inkjet printer. After that, the preliminary experiment of electrical conductivity was performed. This layer was expected to apply as cathode layer in organic light emitting diodes (OLEDs) [146].

9.3 Materials, Instruments And Methods

9.3.1 Materials

$AgNO_3$ (purity >99.9%) was purchased from Sigma Aldrich Canada and used as the starting material. Polyvinylpyrrolidone (10000 and 40000 g/mol) was also purchased by Sigma Aldrich Canada and used as stabilizer (purity >99.9%). Ethylene glycol and methanol were purchased from Bioshop Canada and used as solvent. All of these products were used as received.

9.3.2 Instruments

- Desktop inkjet printer

The Dimatix DMP-2800 inkjet printer (Fujifilm Dimatix, Inc., Santa Clara, CA, USA) was used to deposit conductive solution on 50x50 mm^2 substrate with a disposable piezo inkjet cartridge. The cartridge reservoir contained 2 ml of conductive solution. The temperature of vacuum plate, which secured the substrate in place, was adjusted to 60 °C. The conductive solution was prepared as 1:1 by weight of mixture of both two precursor sources from synthetic step and adding 10 wt% of deionized water. Conductive solution was filtered by nano-size filter (200 nm) and before usage in order to prevent agglomeration among silver particle.

- Fourier Transform Infrared (FTIR)-Attenuated Total Reflectance (ATR)

ATR-FTIR was performed on a Bruker Vector 22 mid-IR spectroscopy (Bruker, Germany), equipped with an ATR crystal (50 mm x 10 mm x 2 mm) at 45° incident angle configuration. All FTIR absorption spectra were recorded over 4500-500 cm^{-1} wavenumbers region at a resolution of 8 cm^{-1} with 1024 scans using a deuterated triglycine sulfate (DTGS) detector. A straight line between two lowest points in the respective spectra region was chosen as a baseline, and the peak areas were integrated from 2000 to 500 cm^{-1}. The position peak of C-H and C-O stretching region will be compared with literature [206].

- Transmission Electron Microscope (TEM)

The particle size of silver was investigated by TEM, Hitachi H-7000. The silver solution was suspended in methanol and dropped on a molybdenum grid. After that, the grid was dried at 50°C for methanol evaporation and kept into the TEM chamber. The image thus obtained was processed with computer for identification of the domains in which certain lattice fringes appear. For this propose, TEM image was captured under 60000X and 150000X magnification. The acceleration voltage of electron beam was set at 100 keV.

- X-ray Diffraction (XRD)

After silver particle was printed on the substrate, process of heat treatment was conducted for solvent removal; thin solid film of silver can be then obtained. The silver film was identified for crystal structure by XRD (Phillips P.W. 1830 diffractrometer) using nickel-filtered CuKα radiation. Diffraction patterns were recorded over a range of 2θ angles from 25-80°. The consistent of result was compared with literature [206].

- Scanning Electron Microscope (SEM)

The thin solid film of silver was investigated by SEM (a JOEL JSM-6301F scanning microscope). The machine was operated at an acceleration voltage of 20 keV, a working distance of 15 mm and a magnification of 30000X was used to identify the dense characteristic of thin solid film of silver. Before investigation, the sample was sputter-coated with Au to enhance the electrical conductivity.

- I-V Probe station

The thin solid film of silver was investigated the relationship of current density and applied voltage by I-V probe station. The forward bias was applied in the range of 0-20V. The range of applied voltage for OLEDs propose was suggested by literature [146, 200].

9.3.3 Methods

- Synthesis of silver nanoparticle and characterization

Colloidal silver particle was synthesized by polyol process. The large particle size of silver colloid was synthesized by dissolving 1 g of 10000 molecular weight polyvinylpyrrolidone (PVP) into 4 ml of ethylene glycol. Then, solution was heated

to 130°C and waited until PVP has been dissolved. In parallel, 1 g of $AgNO_3$ was also dissolved into 4 ml of ethylene glycol and heated to 130°C. PVP solution was then poured into $AgNO_3$ solution. The combined solution was maintained at 130°C for 4 hours before cooled down to room temperature. Once the colloid was synthesized, 10 ml of methanol was added and then the colloid was centrifuged at 500 rpm for 30 min. The solvent was removed and colloid was kept in oven at 150°C.

For the small particle size of colloid, the synthesis followed the similar procedure as large particle size preparation. The 40000 molecular weight of polyvinylpyrrolidone (PVP) was used instead of the 10000 molecular weight.

To mix silver particle of the two different sizes, both post-reaction of silver precursors was mixed and stirred for 2 hours to obtain to homogeneous product of silver precursor mixture.

Then, the silver precursor was characterized by FTIR for chemical structure analysis. Solid particle after centrifugation step was then investigated by means of TEM and XRD for particle size and crystal phase structure, respectively.

- Silver nanoparticle thin film preparation and characterization

The expected large and small of silver particle sizes as well as the mixture of both were dissolved in 3 ml of water and loaded into the cartridge reservoir of desktop inkjet printer. Each of 3 ink formulations was sonicated for 3 hours prior to printing in order to prevent the agglomeration among ink particles. Then, the amount of solution and plate temperature was controlled at 3 ml and 50°C. After that, deposited-silver film was dried at 180°C over night.

The silver thin film was characterized by SEM for morphological analysis of surface. Then, preliminary experiment of electrical conductivity measurement was conducted by I-V probe station.

9.4 Results And Discussion

- Dissociation of silver nitrate

In this experiment, silver nanoparticles were successfully synthesized by use of polymer in wet chemical synthetic route. PVP was used as the stabilizer for nano-

scale size of particle control. The embedding of such particles in PVP matrix is also advantageous. The formation of silver particle was synthesized from silver ion using reducing agent. It can be trapped along with PVP chain and the size of this particle can be controlled into nano-scale. It can be explained that PVP can prevent the agglomeration and precipitation among each particle size. The bulk particle of silver can be avoided.

On the other hand, in common theory, it is remarkably to note that silver nitrate has the highest lattice energy when comparing to any other silver salts and therefore, it can be dissolved only by polar solvents. Silver ion is a powerful oxidant and can be reduced to metal silver, which can be proved by the similar result in the previous report [207]. In our case, silver nitrate was dissolved in ethylene glycol in order to synthesize silver nanoparticle in the organic phase. The chemical reaction requires some of organic molecule that can dissociate lattices of silver nitrate and form organic-soluble complexes as shown in Figure 9.1. In this concern, polyvinylpyrrolidone (PVP), one type of organic molecule, was used to dissociate silver ion. PVP acts as a protective agent and restricts the mobility of silver ions during the reaction; controlling most of the agglomeration. The in situ produced Ag^{+} ions were bound to PVP through a chemical bonding which later helps Ag^{+} ions to get converted into Ag. According to related theory, it can be explained that coordinative interaction between organic molecule and metal is related to electron donation from the organic molecule to the metal atom and electron reverse-donation from the metal atom to the organic molecule [208].

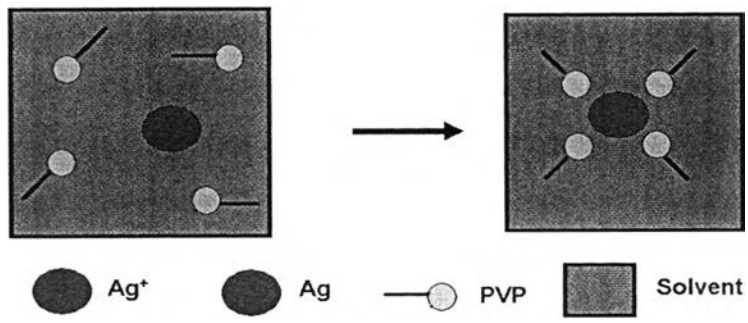

Figure 9.1 Illustration of direct chemical synthetic route of silver nanoparticle from the reaction of silver nitrate and PVP solution

FTIR spectroscopy was used to investigate neat PVP solution, thin solid film of silver and coordinative interaction between silver ions and PVP solution.

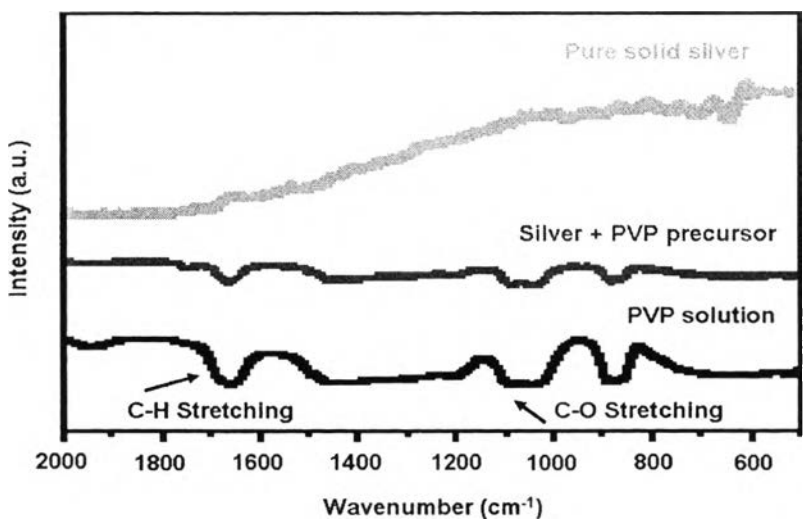

Figure 9.2 FTIR spectra of pure silver, PVP solution, mixture of pure silver nanoparticle and PVP solution

Figure 9.2 exhibits FTIR spectra of the adsorption bands ascribed to PVP molecules, i.e., absorptions at wavenumbers of 1663 and 1180 cm^{-1} due to C=C stretching, C-O stretching vibration, respectively. In contrast, the spectra from neat

silver nanoparticle film was featureless over the identical wavenumbers examined. It can be interpreted that organic molecule from PVP solution was completely eliminated via centrifugation after wet chemical synthetic step. The silver precursor was poured on glass slide and consequently annealed at 200°C for completely PVP solution elimination. In addition, it is obvious that the intensity pattern of stabilizer-mediated Ag nanoparticle was slightly decreased from pure PVP solution. Neat silver nanoparticle film can not be adsorbed in this range of wavenumbers, implying that annealing at 200°C can be completely used for PVP solution elimination.

- Silver nanoparticle formation

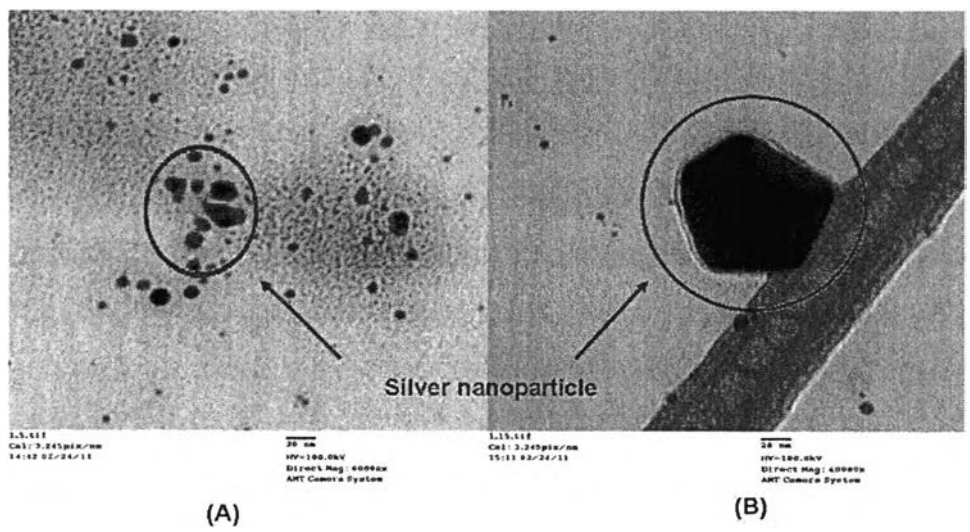

Figure 9.3 Transmission electron microscope of silver nanoparticle (A) silver nanoparticle prepared from PVP (Mw~40000) (B) silver nanoparticle prepared from PVP (Mw~10000) at 60000 X magnifications

The particle size, microstructure and size distribution of synthetic nanoparticle was characterized via TEM. In Figure 9.3, it indicates that a homogeneous distribution of the nanoparticles can be observed. The smaller size of nanoparticles was prepared in PVP (Mw ~40000) with a diameter of roughly 20 nm, while the larger ones were prepared in PVP (Mw~10000) with a diameter of roughly 100 nm. The results were consistent with XRD observation. The size distribution of both small and large silver nanoparticle was quite uniform. In particular, a very large

size and non-spherical shape of a particle can be seen at higher magnification in Figure 9.4. It is important to note that PVP solution play an important role in stabilizing suspension of silver particle and prevention them from agglomeration.

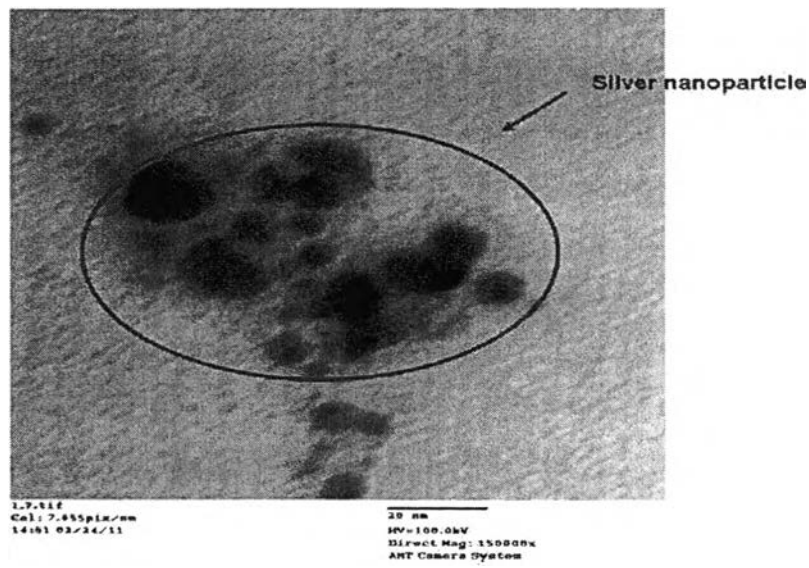

Figure 9.4 Transmission electron microscope of silver nanoparticle prepared from PVP (Mw~40000) at 150000X magnification

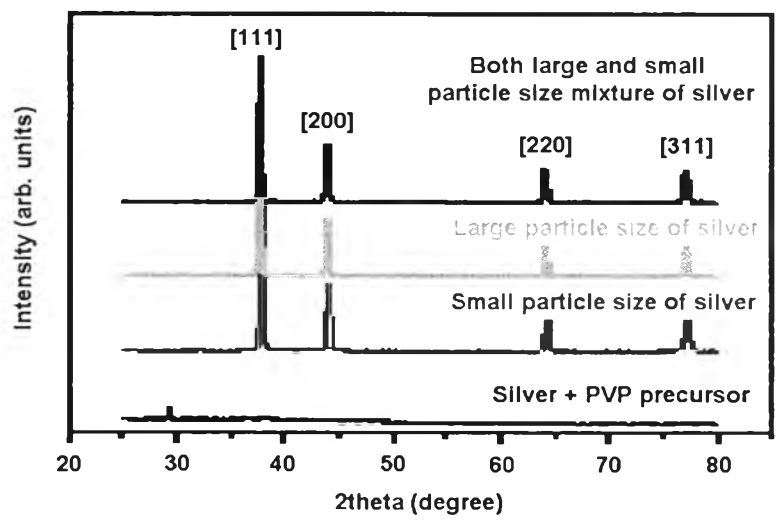

Figure 9.5 X-ray diffraction of silver nanoparticle

XRD was used to investigate the crystalline structure of the materials. Figure 9.5 exhibits the XRD patterns of specimens deposited with different silver particle sizes. No silver diffraction peak was detected for the mixture of silver nitrate and PVP solution. The precursor solution did not contain crystallite structure of silver.

More diffraction peaks appeared in the case of silver thin film deposition including large, small of silver particle size and the mixture of those. The peaks can be remarkably observed at 37.5°, 43.7°, 63.9° and 76.8° corresponding to the face-centered cubic structure of silver crystal planes (111), (200), (220) and (311) of silver metal which are consistent with those of bulk silver [53, 209]. It can be determined that silver is well crystallized. In Figure 9.5, it is evident that the intensity of the diffraction peak increased from the small particle size to large particle size and the mixture of those due to higher dense thin film materials. This is consistent with the previous report [88, 210]. In addition, the particle sizes of silver nanocrystals can be calculated from peak of XRD spectra based on the Scherrer 's equation:

$$D= k\lambda/(\beta\cos\theta)$$

where D is the average particle size, k is a constant taken as 0.9 for calculation, β is the full width at half maximum (FWHM) in radians, λ is the wavelength of the X-ray, and θ is the diffraction angle. From the Scherrer 's equation, the synthesized silver has been calculated to be roughly 26 nm and 110 nm for the expected small and large particle size based on the (111) peak, respectively. This is close to the value deduced from TEM image.

- Silver thin film preparation, packing efficiency of silver nanoparticle and electrical conductivity

Both large and small sizes of silver nanoparticle were successfully synthesized from wet chemical synthetic route. The mixture of both large and small particle sizes was performed in order to enhance the electrical properties and to prevent crack [189] and pinhole [211] phenomena, while thin solid film of silver was fabricated as electrode layer of electronic device. The crack and pinhole phenomena can be occurred at the grain boundary of silver film or free space among silver particle. The connection between grains of silver is easily to crack due to higher residual stress when silver film is bended. The free space among silver particle exhibits less amount of silver, so when silver film is bended, the non-connection between aligned silver occurred.

Figure 9.6 represents the schematic drawing model. It was used to predict the two dimensional packing of silver nanoparticle size. In order to prevent the occurrence of space among large particle size of silver colloid, smaller particle size

can be fulfilled in this space. The combination of both large and small particle size of silver colloid were expected to provide dense thin solid film of silver.

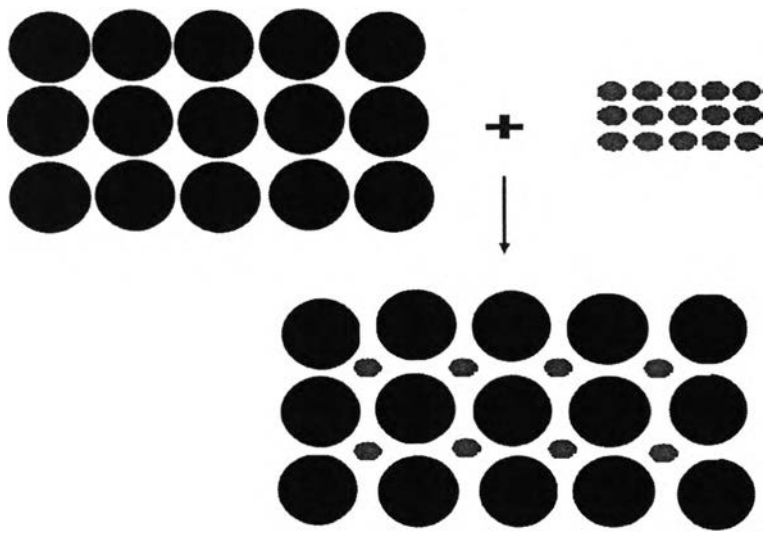

Figure 9.6 Schematic drawing of ideal arrangement of small and large particles in printed silver lines

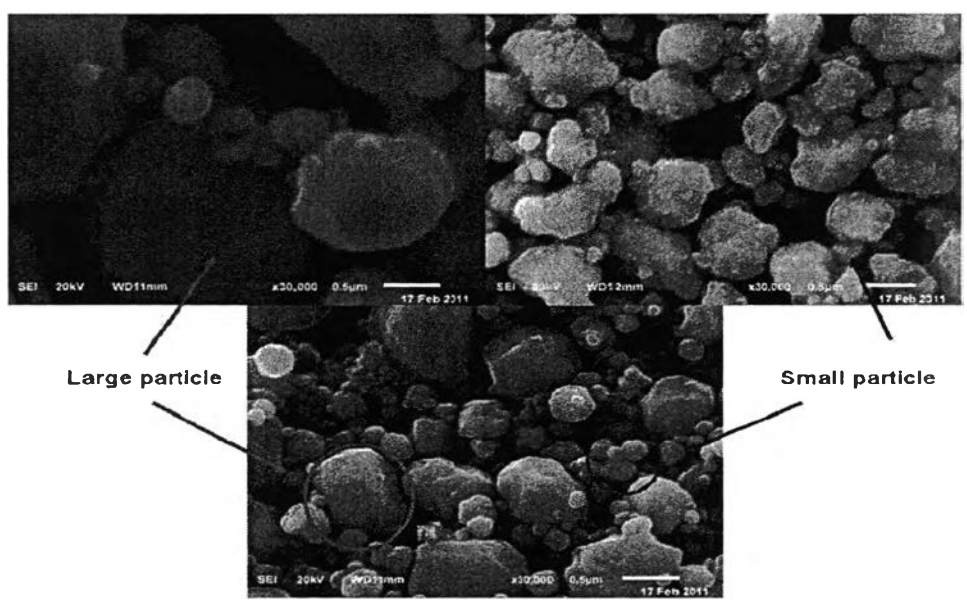

Figure 9.7 SEM image of silver nanoparticle

After the heating step, both of large and small particle sizes of silver were well packed. The free space among silver particle in mixture case is less than the individual one. In Figure 9.7, the dried silver of both large and small particle size provided the average diameter as 100 and 20 nm, respectively. However, each procedure of both synthetic steps may offer a significant amount of polydispersity in

particle size. The size of silver particle may be higher or lower of 100 and 20 nm. After silver particle was heated to 200°C for solvent evaporation, the free space can be then observed. In case of small particle size (right top), the large space was not well observed, while this is opposite for large particle size (left top). In case of the large and small particle size mixture, the dried silver film exhibited denser packing than film of only large or small particle size. The necking area among particles was expected to enhance if silver dried film was heated with higher temperature [212, 213].

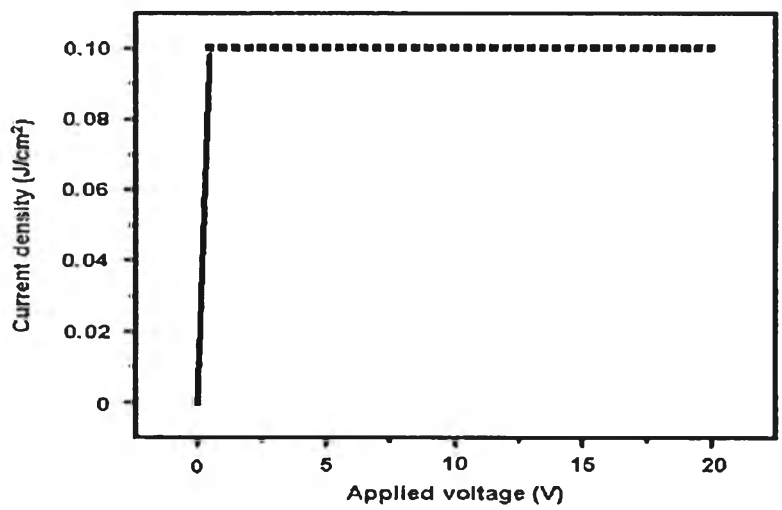

Figure 9.8 Current density (J/cm^2) vs Applied voltage (V) for synthesis of silver thin film

Once silver nanoparticle was printed as a thin solid film, the relationship of current density and applied voltage was measured using I-V probe station. From the measurement in Figure 9.8, under forward bias voltage from 0-20V, the current density exhibited as 0.1 J/cm^2. This constant current density and range of applied voltage are commonly utilized for OLEDs device [146, 200]. All the measurements were conducted at ambient atmosphere with no encapsulation. The consistent result of our synthetic silver offered the identical data as the commercial silver paint electrode. The preliminary experiment of electrical conductivity was successfully performed for further development of cathode layer in OLEDs in the near future.

9.5 Conclusion

Dense thin solid film of silver was successfully developed. From the ease of synthetic route, both large (100 nm) and small (20 nm) particle sizes of silver were successfully synthesized. The mixture of both large and small particle size of silver solution was printed as thin solid film of silver. The preliminary experiment of electrical conductivity suggested that it can be applied as cathode layer for OLEDs device.

9.6 Acknowledgement

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