



CHAPTER IV

EXPERIMENTAL

4.1 Materials and Methods

4.1.1 Raw Materials

- Bacterial Cellulose Nanocomposite

Polyurethane based resin (PU) based resin was purchased from Sartomer Company, Inc. (Exton, PA, USA). The resin has the density of 1.16 g/ml. It was stored in dark room due to its high light-sensitivity. Bacterial cellulose was extracted from commercially available Nata de coco (Uno Foods, BC, Canada), an indigenous Filipino-originated dessert of which the main component was reported as bacterial cellulose (Iguchi et al. 2000; El-Saied et al. 2004). Analytical grade sodium hydroxide, ethanol was purchased from Bioshop Canada Inc. at the University of Toronto. All chemicals were used as received.

- Ferrofluid solution

Ferrous chloride 4-hydrates ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) (purity >99.9%), Ferrous chloride 6-hydrates ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and Al_2O_3 were purchased from J. T. Baker Chemical Co, Phillipsburg, Canada. Ammonia (NH_4OH), Iron particle and castor oil were purchased from Sigma Aldrich, Canada. All of these products were analytical grade and used as received without further purification.

- PEDOT: PSS preparation

Poly (3, 4-ethylenedioxythiophene) (PEDOT) doped with polystyrene sulfonic acid (PSS) and Triton X-100 were purchased from Sigma-Aldrich Chemical Company (Oakville, ON, Canada). They were used as ink suspension and surfactant, respectively. Surfynol DF-1100 defoamer was from Air Products Company (Allentown, PA, USA). Glycerol in reagent grade (>99% Reagent Plus) was purchased from Bioshop Canada Inc. (University of Toronto, Canada)

- Silver nanoparticle preparation

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.

- ZnS and metal-doped ZnS nanoparticle preparation

Sodium sulphide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) was purchased from Caledon Chemical Company, Canada. Zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$), Cuprous chloride (CuCl) and Manganese sulfate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$) were purchased from J. T. Baker Chemical Company, Canada. Analytical grade of methanol was purchased from Bioshop, Canada. Distilled water and analytical grade of methanol were used as solvent. All the chemical reagents were used as received.

- Hybrid ZnS and PVP nanocomposite preparation

Sodium sulphide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) and Zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) were purchased from Caledon Chemical Company, Canada and J. T. Baker Chemical Company, Canada, respectively. Polyvinylpyrrolidone (PVP) ($M_w \sim 10000$) was purchased from Sigma Aldrich Company, Canada. Analytical grade of methanol was purchased from Bioshop, Canada. Distilled water and analytical grade of methanol were used as solvent. All the chemical reagents were used without further purification.

4.1.2 Methods

- Extraction and purification of bacterial cellulose

Bacterial cellulose was extracted from Nata de coco. The Nata de coco gel was first rinsed with distilled water and blended using a laboratory blender. The bacterial cellulose suspension was then treated in 0.1M NaOH at 80 °C for 20 minutes to remove any remaining microorganisms, medium component and soluble

polysaccharides, following Juntaro et al [10]. The purified bacterial cellulose was then thoroughly washed with distilled water until neutral pH.

- Fabrication of bacterial cellulose nanocomposite

To fabricate the nanocomposite, the bacterial cellulose sheet was first prepared from bacterial cellulose suspension. The water was removed from the suspension through filtration with a Buchner funnel fitted with Polyterafluoroethylene membrane filter (0.1 μm mesh, 90 mm diameter), which was connected to a Buchner flask and a vacuum pump. The volume of the bacterial cellulose suspension was adjusted to achieve a bacterial cellulose disc with the dried weight of 0.25 g. The filtration was continued until the wet sheet of bacterial cellulose was formed. The wet sheet was then dried between two Polyterafluoroethylene membranes under the applied pressure of 58 psi, following the paper handsheet formation standard SCAN C 26:76. The dried bacterial cellulose sheet was then impregnated with PU resin and cured under UV at 25 mW/cm^2 for 3 minutes. As a reference, the neat PU based resin sheet was also fabricated in similar manner. All samples had the thickness of 0.3 mm. All experiments involving the resin were conducted in dark room as the resin was sensitive to light. The fiber content of the nanocomposite was 10 - 50 wt %.

- Nano-scale barrier film preparation

Si-O film was deposited on nanocomposite substrate via PECVD in a parallel plate, capacitively coupled-plasma (13.56 MHz) reactor with an electrode spacing of 4 cm. A gas showerhead, which was electrically isolated from the reactor by a ceramic spacer, acted as the power electrode. On the grounded electrode, a ceramic heater capable of heating up to 400 $^{\circ}\text{C}$ was used to heat the substrate. The substrate temperature was measured by the thermocouple tube which was electrically shielded from plasma. The thermocouple tube was in contact with the backside of the substrate holder. SiH_4 (5%) in O_2 was used as a source gas. During the epitaxial growth process, the N_2 gas flow rate was maintained at 100 sccm. PECVD was conducted at 130 $^{\circ}\text{C}$ in order to prevent any thermal deformation of nanocomposite substrate. The deposition rate was set at 25 nm per minute. Three deposition times were attempted - 2, 4 and 8 minutes; therefore, Si-O layer with the estimated

thickness of 50, 100 and 200 nm were expected to be deposited on nanocomposites. From here on, the bacterial cellulose nanocomposite deposited with Si-O layer with the estimated thickness of 50, 100 and 200 nm, will be referred to as ~50 nm-thick sample, ~100 nm-thick sample and ~200 nm-thick sample respectively.

- Ferrofluid preparation and abrasive technique

The co-precipitation method was used to synthesize ferrofluid. The synthetic process from the salt solution occurred in accordance with the reaction:



A solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.3 M) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (0.3 M) mixed in a molar ratio of 2:1 was prepared. An ammonia aqueous solution of 20 ml was then added with vigorous stirring using mechanical stirrer. The reaction was conducted for 5 hours. A black precipitation was obtained. After that castor oil of 20 ml was added and intensely stirred at 70°C for 1 hour. The precipitation was filter and washed with deionized water several times. The ferrofluid solution was centrifuged and kept in desiccators in order to prevent moisture sensitive problem.

Furthermore, ferrofluid was continually dropped between magnet and nanocomposite. Here, a disc-shaped permanent magnet is attached as the holder and located above the sample; ferrofluid is put into the gap between the magnet and sample. Magnetic nanoparticle clusters are formed along the magnetic field immediately. When the magnet holder is rotated around its axis, the magnet follows the rotation of holder and the clusters are rotated around the magnet axis due to the magnetic force, hence carry the abrasive particle to generate a relative speed between the abrasive particles and the sample. As a result, the surface of sample is smoothed by nano-cutting action of abrasive particle.

- PEDOT: PSS as anode preparation

Poly (3, 4-ethylenedioxythiophene) (PEDOT) doped with polystyrene sulfonic acid (PSS) in aqueous solution as received was diluted with 50 wt% of deionized water. 5 wt% of Triton X-100 was added into the solution as a surfactant, followed by 1 wt% of Surfynol DF-1100 as a defoamer. Glycerol in reagent grade was consequently dropped in 1 wt% to enhance the conductivity of PEDOT: PSS. Then, the conductive

polymer solution was homogeneously stirred and stored in the refrigerator. TEM, tensiometer and Ubbelohde canon type viscometer were employed to investigate particle size, surface tension and viscosity, respectively.

Then, 1 ml of the ink solution was loaded into inkjet cartridge reservoir. The plate temperature was set to 50 °C. 1, 3, 5 and 10 layers were deposited on substrate. Film thickness and electrical conductivity were subsequently determined by profilometer and four point probe measurement, respectively.

- Silver nanoparticle as cathode preparation

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 AgNO₃ was also dissolved into 4 ml of ethylene glycol and heated to 130°C. PVP solution was then poured into AgNO₃ 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.

Then, 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.

- ZnS and metal-doped ZnS nanoparticle as emissive layer preparation

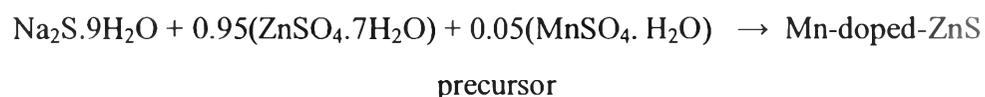
The ZnS ceramic powder was prepared as follow: 10 g of Na₂S. 9H₂O was added to 50 ml of distilled water. The mixture was stirred for 1 hour. In parallel, 10 g of ZnSO₄. 7H₂O was also dissolved into 50 ml of distilled water. Na₂S. 9H₂O solution was then poured into ZnSO₄. 7H₂O solution.

The stoichiometric of chemical reaction was below;

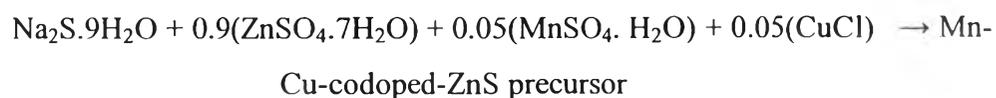


For the individual Mn-doped and Cu-doped ZnS ceramic powder, it was prepared as follow: 10 g of Na₂S. 9H₂O was added to 50 ml of distilled water. The mixture was stirred for 1 hour. In parallel, 9.5 g of ZnSO₄. 7H₂O and each of 0.5 g of CuCl and MnSO₄. H₂O was also dissolved into 50 ml of distilled water. Na₂S. 9H₂O solution was then poured into ZnSO₄. 7H₂O solution.

The stoichiometric of chemical reaction was below;



On the other hand, for the co-metal doped ceramic powder, it was prepared as follow: 10 g of Na₂S. 9H₂O was added to 50 ml of distilled water. The mixture was stirred for 1 hour. In parallel, 9 g of ZnSO₄. 7H₂O and each 0.5 g of CuCl and MnSO₄. H₂O was also dissolved into 50 ml of distilled water. Na₂S. 9H₂O solution was then poured into ZnSO₄. 7H₂O solution.



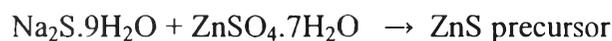
The reaction was continually conducted for 4 hours at room temperature. After the reaction was completed, methanol was employed to use in order to remove impurities, 50 ml of methanol was added and then the mixture was centrifuged at 500

rpm for 30 min. The obtained ZnS and metal-doped ZnS would precipitate. The step of adding methanol was repeated ten times and each of methanols was removed. The mixture was kept in oven at 150°C overnight.

- Hybrid ZnS and PVP nanocomposite for emissive layer properties enhancement preparation

The first step, ZnS nanoparticle was prepared as follow: 10 g of Na₂S. 9H₂O was added to 50 ml of distilled water. The mixture was stirred for 1 hour. In parallel, 10 g of ZnSO₄. 7H₂O was also dissolved into 50 ml of distilled water. Na₂S. 9H₂O solution was then poured into ZnSO₄. 7H₂O solution.

The stoichiometric of chemical reaction was below;



After that, PVP 10 g was subsequently added into ZnS precursor solution. The reaction was continuously stirred for 3 hours at room temperature. After that, the solution was centrifuged at 500 rpm for 30 min in order to remove solvent. The obtained ZnS nanoparticle would precipitate.

Then, second step, the ZnS/PVP solution was 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.

4.2 Characterization

4.2.1 Bacterial Cellulose and Bacterial Cellulose Nanocomposite

Characterization

Physical properties

- Morphological observation by SEM

Scanning electron microscope (SEM, a JOEL JSM-6301F scanning microscope) operating at an acceleration voltage of 15 kV was used to determine the

morphology of the bacterial cellulose sheet. The sample was placed on the carbon tape and sputtered with gold particles.

- Insulator characteristic determined by dielectric properties

Dielectric constant and dielectric loss were measured by a precision LCR meter (Agilent E4980A) at ambient temperature and various frequencies (1 kHz – 100 kHz). The samples were coated by silver paint as electrode on both sides before measurement.

- Surface roughness analysis

AFM was performed with a Digital Instruments Nanoscope III Scanning Probe Microscope (Digital Instruments, CA, USA) in ambient conditions (22°C, 45-55% relative humidity) over areas of 40 μm x 40 μm . The instrument was equipped with silicon nitride tip and operated in the lateral contact mode.

Mechanical properties

- Tensile properties

The tensile tests were conducted in accordance to the ISO Standard number ISO 527:1996. The sample was cut with a Zwick cutter into dog-bone specimen type 5A. The samples had the overall length and the gauge length of 75 and 20 mm, respectively. The initial distance between grips was 50 mm and its width at the grip end was 12.5 mm. The width at the narrowest part was 4 mm and the thickness was 0.3-0.5 mm. The testing speed was 1 mm/min. The specimens were preconditioned at 20°C in 54% relative humidity in a desiccator containing a saturated solution of $\text{Mg}(\text{NO}_3)_2$ for at least 48 hours prior to testing. The tensile test were conducted using as Instron universal material testing machine (Instron 4502, Instron Corporation, MA, USA) equipped with a 1 kN load cell. At least 5 specimens were tested per sample to obtain a statistical average.

Optical properties

- UV-Vis spectroscopy

A Varian Cary 5000 UV-Vis NIR spectrophotometer (Agilent Technologies, CA, USA), equipped with transmittance accessory, was employed to record the electronic spectrum of the nanocomposite samples over the wavelength of 200 - 900

nm. This technique allowed the study of the transmittance spectra of the samples in the thin film form. The transmittance accessory consisted of 110 nm diameter integrating sphere and an in-built high-performance photomultiplier. Each sample was placed in a sample cell specifically designed for the instrument. A base line was recorded and calibrated using a polytetrafluoroethylene (PTFE) reference cell.

- Ellipsometer

Spectroscopic ellipsometer (M-44 ellipsometer, J.A. Woollam, NE, USA) equipped with silicon carbide plate for controlling position was used to determine the refractive index (RI) of nanocomposites at ambient temperature. The instrument had a variable angle stage, allowing adjustment of the incident angle. It performed on a rotating polarizer principle, in which the polarization of the incident light was varied. Reflected intensity was recorded with a grating charged-coupled device (CCD) over the wavelength of 400 - 900 nm. The measurements were repeated 5 times. Subsequent curve fitting allowed for the determination of refractive index and its variation with wavelength.

Thermal properties

- Thermomechanical analysis (TMA)

Coefficient of thermal expansion (CTE) measurements of the nanocomposite and the bacterial cellulose sheet were carried out in Mettler Toledo TMA/SDTA 841 Thermo Mechanical Analyzer. Samples with the size of 2.5 cm x 3 mm x 0.5 mm were tested in tensile mode. The sample was placed into TMA instrument and purged with high purity Argon for 15 minutes. Surfaces contacting the base of the thermostatic chamber of the instrument and the measuring probe were controlled to be parallel to each other. The constant force of 0.1 N was applied to the sample as the temperature was increased from 30 °C to 120 °C at the rate of 5 °C/min. The calculation of CTE was performed following the ASTM E831 standard.

- Thermogravimetric analysis (TGA)

Thermal degradation behaviors of the PU based resin and the bacterial cellulose nanocomposites were determined by thermogravimetric analysis (TA-5000 TGA, TA Instruments, DE, USA). Each sample (10 mg) was heated with a heating rate of 10 °C/min in nitrogen atmosphere from 30 °C to 500 °C. The TGA balance

flow meter was set at 20 psi N₂, while the purge flow meter was adjusted to 20 psi of synthetic air.

- Differential scanning calorimetric (DSC)

DSC of the PU based resin and bacterial cellulose nanocomposite was performed in the temperature range of -50 °C to 100 °C at the heating rate of 10 °C/min (TA-10000 DSC, TA Instruments, DE, USA). The glass transition temperatures were determined from the heat flow curve.

4.2.2 Si-O (Super Thin Glass) Characterization

- Attenuated total reflectance - Fourier transform infrared spectroscopy (ATR-FTIR)

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. The position of Si-O region was taken from literature [142].

- X-ray Photoelectron Spectroscopy (XPS)

XPS was performed using Thermo Scientific ESCALAB 250Xi XPS spectrometer (Thermo Fisher Scientific Inc., MA, USA) with a monochromatic Al-K α X-ray source. The spot size for analysis was approximately 400 μ m. Samples were analyzed at 90° take off angle with respect to the surface. A low resolution survey spectrum ranging from 0 to 1300 eV was conducted at 150 eV pass energy. To determine the relative atomic percentage, high-resolution spectra in the ranges of 150-200 eV, 280-300 eV and 520-530 eV binding energy were obtained for Si1s, C1s and O1s region, respectively. The bond and depth profile analysis was determined by curve fitting. The data was analyzed using Avantage onboard software supplied by Thermo Scientific with the instrument.

- Atomic Force Microscope (AFM)

AFM was performed with a Digital Instruments Nanoscope III Scanning Probe Microscope (Digital Instruments, CA, USA) in ambient conditions (22 °C, 45-55% relative humidity) over areas of 25 x 25 μm^2 at the normal load ranging from 5 to 130 nN at a scan rate of 0.5 Hz (resulting a scanning speed of 2 $\mu\text{m/s}$). Square pyramidal Si_3N_4 tips with a nominal 30-50 nm radius mounted on triangular Si_3N_4 cantilevers with a spring constant of 0.58 N/m were used. Adhesive forces were determined from the force calibration plot (FCP).

- Water Vapor Transmission Rate (WVTR)

WVTR was measured in accordance with ASTM E96-66 standard. The controlled environment inside a closed desiccator was maintained at $50 \pm 2\%$ relative humidity throughout the experiment by a saturated aqueous solution of $\text{Ca}(\text{NO}_3)_2$, which will control the humidity to be 51% at 24.5 °C. The experiment was performed at room temperature (25 °C). Sample thickness was approximately 2.0-2.5 mm. The dried sample from the oven was put in the desiccator for at least 2 hours prior to the experiment to equilibrate the sample with the atmospheric moisture inside. Demineralized water was put into a permeability Payne cup (2.5 cm diameter). The water level was kept at least 2 cm from the sample to avoid contact between the sample and the water. The sample was then attached to the Payne cup. The sample weight change as a function of time was monitored everyday for 2 weeks. The WVTR was calculated as;

$$\text{WVTR} = G/(t.A)$$

where G is the gain weight, t is the time and A is the test area

4.2.3 Ferrofluid Characterization

- X-ray Diffraction (XRD)

After solid particle was casted on glass slide, process of heat treatment was conducted for solvent removal; solid particle can be then obtained. The film was identified for crystal structure by XRD (Phillips P.W. 1830 diffractometer) using nickel-filtered $\text{CuK}\alpha$ radiation. Diffraction patterns were recorded over a range of 2 θ angles from 20-70°. The consistent of result was compared with literature

(Hartshorne, Backhouse et al. 2004; Racuciu and Creanga 2007; Borin, Zubarev et al. 2011).

- Transmission Electron Microscope (TEM)

The solid particle size of ferrofluid solution was investigated by TEM, Hitachi H-7000. The 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 50000X and 100000X magnification. The acceleration voltage of electron beam was set at 100 keV.

- Rheometer

The rheological properties of the magnetic compound fluid were measured with RH2000 Rheometer, The shear rate range and applied pressure were set between 0-10 s⁻¹ and 0.1 Pa, respectively. The measurements were repeated five times and the statistical average data was used to plot curve.

- Atomic Force Microscope (AFM)

AFM was performed with a Digital Instruments Nanoscope III Scanning Probe Microscope (Digital Instruments, CA, USA) in ambient conditions (22°C, 45-55% relative humidity) over areas of 5 µm x 5 µm and 1 µm * 1 µm. The instrument was equipped with silicon nitride tip and operated in the lateral contact mode. The measurements were repeated five times for comparable topological analysis.

4.2.4 PEDOT: PSS Solution and Film Characterization

- Dimatix Inkjet Printer

The Dimatix DMP-2800 inkjet printer (Fujifilm Dimatix, Inc., Santa Clara, CA, USA) was used to deposit conductive solution on 50x50 mm² substrate with a disposable piezo inkjet cartridge. The cartridge reservoir contained 2 ml of conductive polymer solution. The temperature of vacuum plate, which secured the

substrate in place, was adjusted to 60 °C. The conductive solution was diluted with 50 wt% deionized water and filtered by nano-size filter before usage.

- Transmission electron microscope (TEM)

The particle size of conductive polymer was investigated by Transmission Electron Microscopy (TEM) Hitachi H-7000. The image obtained was processed with computer for identification of the domains in which certain lattice fringes appear.

- Profilometer

The film thickness was measured by Talysurf-10 profilometer, (Taylor Hobson Ltd., Leicester, UK) equipped with a diamond cursor running on the object surface and following local surface irregularities. The cursor was linked with an optical transducer. The vertical displacements were recorded by a photoelectric cell. The diamond point was 2.5 μm in thickness. Each measurement was 2.5 mm in length with an interval of 50 μm separating two parallel measurements. For the give test line, the roughness was defined in micrometer as the arithmetical mean of peaks above and under baseline. The mean thickness was an average of five successive measurements.

- Four points probe electrical properties measurement

The electrical conductivity was measured by the four point probe technique. This device was specified to have in-line fixed four probes made of solid tungsten carbide needles with 0.4 mm diameter. The nominal radius of a probe tip was 100 μm . Equal probe spacing, S , was 1 mm and downward force was approximately 0.2 kg per probe. A constant current, I , was applied to the bar specimen through two outside probes, V , was then determined. A DC precision power source and nanovoltmeter were used for all measurements. The electrical current $I = 1 \text{ mA}$ was maintained in all measurements.

- Tensiometer

The surface tension was measured by tensiometer technique with Wilhelmy plate. The paper was cut into 10 mm wide and 1 mm thick. For each withdrawing

velocity of the Wilhelmy plate, at least ten times of dynamic meniscus were recorded and the coordinates of their contours were obtained.

Viscometer

The viscosity was investigated by Ubbelohde canon type viscometer. The measurement used a capillary based method of measuring viscosity. The measurement was repeated five times and the statistical average was reported. This experiment was conducted at room temperature. Water was used as reference.

Atomic force microscope (AFM)

The surface morphology and topology were investigated by AFM (Digital Instruments Nanoscope III Scanning Probe Microscope, Digital Instruments, CA, USA). The instrument was equipped with silicon nitride tip and operated in the non-contact mode. The scanning parameters were as follows: scanning rate 5 $\mu\text{m/s}$, resolution 300 and scan range at 50x50 μm . The image was taken from the optimized force between tip and sample at ambient temperature.

4.2.5 Silver Nanoparticle Characterization

- 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 [15].

- 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 diffractometer) using nickel-filtered $\text{CuK}\alpha$ radiation. Diffraction patterns were recorded over a range of 2θ angles from 25-80°.

- 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.

4.2.6 ZnS and Metal-Doped ZnS Characterization

- Fourier transform infrared spectroscopy (FTIR)

FTIR was performed on a Bruker Vector 22 mid-IR spectroscopy (Bruker, Germany), 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. Potassium bromide (KBr) acting as a non-absorbing medium was mixed with a solid sample (0.3-0.5 wt %) by an agate mortar and pestle to prepare a pellet specimen.

- X-ray diffraction (XRD)

The synthesized ceramic powders were stored in an oven above 150°C overnight for water absorption prevention. The crystal structure of the powders was analyzed by XRD (Phillips P.W. 1830 diffractometer) using nickel-filtered $\text{CuK}\alpha$ radiation. Diffraction patterns were recorded over a range of 25-80°.

- Scanning electron microscope (SEM) and energy dispersive analysis (EDX)

The powders were investigated by SEM (a JOEL JSM-6301F scanning microscope). The machine was operated at an acceleration voltage of 20 keV at a working distance of 15 mm to identify the morphological properties of powders. Before investigation, the samples were sputter-coated with Au to enhance the electrical conductivity.

- X-ray fluorescence (XRF)

XRF (A Phillips 1404 XRF Wavelength Disperse Spectrometer) was used to determine the trace element of sample. It equipped with an array of five analyzing

crystals and fitted with a Rh X-ray tube target was used. A vacuum was used as the medium of analyses to avoid interaction of X-rays with air particle. 1 g of sample was mixed with 6 g of H_3BO_3 and consequently pressed under 10 tons of force.

- Laser confocal microscope and photoluminescence spectroscopy

Laser confocal microscope and luminescence experiments were performed using an Olympus BX41 fibre-coupled confocal microscope. Excitation of the dopant ions is performed using a continuous argon laser. The excitation beam was focused on the sample surface by means of an 100 achromatic microscope objective (NA0.9) down to approximately 0.3 mm spotsize. To separate the excitation beam and the sample luminescence, an interferential filter that removes the excitation wavelength (notch filter) was used. The fluorescence was focused into a fibre-coupled high-resolution spectrometer (SPEX500M) and then detected using a CCD camera.

4.2.7 Hybrid ZnS and PVP Nanocomposite Characterizations

- Fourier transform infrared spectroscopy (FTIR)

FTIR was performed on a Bruker Vector 22 mid-IR spectroscopy (Bruker, Germany), All FTIR absorption spectra were recorded over $4500-500\text{ cm}^{-1}$ 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. Potassium bromide (KBr) acting as a non-absorbing medium was mixed with a solid sample (0.3-0.5 wt %) by an agate mortar and pestle to prepare a pellet specimen.

- X-ray diffraction (XRD)

The synthesized ceramic powders were stored in an oven above 150°C overnight for water absorption prevention. The crystal structure of the powders was analyzed by XRD (Phillips P.W. 1830 diffractometer) using nickel-filtered $\text{CuK}\alpha$ radiation. Diffraction patterns were recorded over a range of $25-80^\circ$.

- Scanning electron microscope (SEM) and energy dispersive analysis (EDX)

The powders were investigated by SEM (a JOEL JSM-6301F scanning microscope). The machine was operated at an acceleration voltage of 20 keV at a working distance of 15 mm to identify the morphological properties of powders. Before investigation, the samples were sputter-coated with Au to enhance the electrical conductivity.

- Laser confocal microscope and photoluminescence spectroscopy

Laser confocal microscope and luminescence experiments were performed using an Olympus BX41 fibre-coupled confocal microscope. Excitation of the dopant ions is performed using a continuous argon laser. The excitation beam was focused on the sample surface by means of an 100 achromatic microscope objective (NA0.9) down to approximately 0.3 mm spotsize. To separate the excitation beam and the sample luminescence, an interferential filter that removes the excitation wavelength (notch filter) was used. The fluorescence was focused into a fibre-coupled high-resolution spectrometer (SPEX500M) and then detected using a CCD camera.

- Transmission electron microscope (TEM)

The particle size of ZnS was investigated by TEM, Hitachi H-7000. The ZnS 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 40000X magnification. The acceleration voltage of electron beam was set at 75 keV.

- Desktop inkjet printer

The Dimatix DMP-2800 inkjet printer (Fujifilm Dimatix, Inc., Santa Clara, CA, USA) was used to deposit conductive solution on 50x50 mm² substrate with a

disposable piezo inkjet cartridge. The cartridge reservoir contained 2 ml of ZnS/PVP solution. The temperature of vacuum plate, which secured the substrate in place, was adjusted to 60 °C. ZnS/PVP solution was filtered by nano-size filter (200 nm) and before usage in order to prevent agglomeration among silver particle and control the ink particle size (<200 nm), suggesting by desktop inkjet supplier.