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TITLE:

Elaborate Control of Inkjet Printer for Fabrication of Chip-based Supercapacitors.

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SUMMARY:

This paper provides a technique for manufacturing chip-based supercapacitors using an inkjet printer. Methodologies are described in detail to synthesize inks, adjust software parameters, and analyze the electrochemical results of the manufactured supercapacitor.

ABSTRACT:

There are tremendous efforts in various fields to apply the inkjet printing method for the fabrication of wearable devices, displays, and energy storage devices. To get high-quality products, however, sophisticated operation skills are required depending on the physical properties of the ink materials. In this regard, optimizing the inkjet printing parameters is as important as developing the physical properties of the ink materials. In this study, optimization of the inkjet printing software parameters is presented for fabricating a supercapacitor. Supercapacitors are attractive energy storage systems because of their high power density, long lifespan, and various applications as power sources. Supercapacitors can be used in the Internet of Things (IoT), smartphones, wearable devices, electrical vehicles (EVs), large energy storage systems, etc. The wide range of applications demands a new method that can fabricate devices in various scales. The inkjet printing method can break through the conventional size-fixed fabrication method.

INTRODUCTION:

In the past decades, multiple printing methods have been developed for various applications, including wearable devices[1], pharmaceuticals[2], and aerospace components[3]. The printing can be easily adapted for various devices by simply changing the materials to be used. Moreover, it prevents the wastage of raw materials. To manufacture electronic devices, several printing methods such as screen printing[4], push-coating[5], and lithography[6] have been developed. Compared to these printing technologies, the inkjet printing method has multiple advantages, including reduced material waste, compatibility with multiple substrates[7], low cost[8], flexibility[9], low-temperature processing[10], and ease of mass production[11]. However, the application of the inkjet printing method has hardly been suggested for certain sophisticated devices. Here, we present a protocol establishing detailed guidelines to use the inkjet printing method for printing a supercapacitor device.

Supercapacitors, including pseudocapacitors and electrochemical double-layer capacitors (EDLCs), are emerging as energy storage devices that can complement conventional lithium-ion batteries[12,13]. Especially, EDLC is a promising energy storage device because of its low cost, high power density, and long cycle life[14]. Activated carbon (AC), having high specific surface area and conductivity, is used as electrode material in commercial EDLCs[15]. These properties of AC allow EDLCs to have a high electrochemical capacitance[16]. EDLCs have the passive volume in devices when the conventional fixed-size fabrication method is used. With inkjet printing, the EDLCs can be fully integrated into the product design. Therefore, the device fabricated using the inkjet printing method is functionally better than that fabricated by existing fixed-size methodologies[17]. The fabrication of EDLCs using the efficient inkjet printing method maximizes the stability and longevity of EDLCs and provides a free-form factor[18]. The printing patterns were designed by using a PCB CAD program and converted to Gerber files. The designed patterns were printed using an inkjet printer because it has precise software-enabled control, high material throughput, and printing stability.

PROTOCOL:

1. Design of pattern using PCB CAD program

1.1. Run the CAD program. Click on the **File** button atop the program window. To form a new project file, click on the **New** and **Project** buttons.

1.2. To generate the board file, click on the **File**, **New**, and **Board** buttons in order. Set the grid size, multiple, and alt values by clicking on the mesh-shaped **Grid** button at the top left of the created **Board File** window (or clicking on **View** and **Grid** in order at the top of the window).

1.3. Change both the grid size and alt value from mm to inch so that the inkjet printer can read the PCB CAD pattern. Press **Finest** to make fine adjustments.

1.4. Design the pattern of the current collector and EDLC line in an interdigitated form. Design the gel polymer electrolyte (GPE) pattern and current collector pads in a rectangular form (**Figure 1**).

NOTE: Pattern width: 43 mm, pattern height: 55 mm, line length: 40 mm, line width: 1.0 mm, line-to-line space: 1.5 mm, and pad size: 15 x 5 mm^2.

1.4.1. Since the final pattern consists of three types (conductive line, EDLC, and GPE), set the three layers as follows.

1.4.1.1. Click on **View** and **Layer Settings** in order at the top of the window. Create new layers by clicking on the **New Layer** button at the bottom left of the **Visible Layers** window.

1.4.1.2. In the new window (**New Layer**), set up the name and color for the new layer. For visually distinguishing the layers, set the names of the three layers to **Current Collector**, **EDLC**, and **GPE**, and change the corresponding colors by clicking on the box to the right of Color.

1.4.2. Press **Line** at the bottom left of the screen, click on the main field (black background), and drag to draw a line. To change the thickness of the line, input the value of Width located at the top center in inch scale (1.0 mm = 0.0393701 inch).

1.4.3. To edit the length of a line, right-click on the line and click on **Properties** at the bottom. In the **From** and **To** fields, input the x and y values of the starting and ending points.

1.4.4. To set the reference point of the pattern, set the upper-left corner of the pattern shown in **Figure 1** to (0,0). Draw the rest of the pattern based on the above information.

1.4.5. To set the drawn pattern to the desired layer, right-click on the pattern and click on **Properties**. Then, click on **Layer**, and choose the desired layer.

1.4.6. To draw rectangular patterns of the current collector pad and GPE, press **Rect** at the bottom left of the main window. Click and drag on the screen (main field) where the previously drawn pattern exists.

1.4.7. To edit, right-click on the rectangular surface and click on **Properties** at the bottom. Input the upper left (x,y) value and the lower right (x,y) value of the rectangle in the **From** and **To** fields, respectively. Set the rectangle to the desired layer as mentioned in step 1.4.5.

1.5. Convert the CAD file of the designed pattern into the Gerber file format that is read by the inkjet printer.

1.5.1. Before converting the designed pattern file, save the **Board File** in .brd format. To save, click on **File**, and then on **Save** (or press ctrl + S on the keyboard).

1.5.2. After saving, click on **File** at the top of the window and click on **CAM Processor**. To create a Gerber file of the desired layer, modify the items under **Gerber** of **Output Files** on the left side of the window, as follows.

1.5.3. First, delete the sub-lists such as **Top Copper** and **Bottom Copper** by pressing the '-' below.

Press '+' and click on **New Gerber Output** to create Gerber output.

1.5.4. On the right side of the screen, set the layer name in **Name** and **Function** to **Copper** by pressing the gear on the right. Set **Layer Type** to **Top** and set **Gerber Layer Number** of the current collector, EDLC and GPE to **L1**, **L2**, **L3**, respectively.

1.5.5. In the **Layers** window at the bottom of **Gerber File**, click on **Edit Layers** at the bottom left, and select each desired layer.

1.5.6. To set the name of the output file to be created, set the **Gerber Filename** of **Output** at the bottom of the window to **%PREFIX/%NAME.gbr**.

1.5.7. Finally, click on **Save Job** at the top left of the window to save the settings. Click on **Process Job** at the bottom right to create a Gerber file.

2. Ink synthesis

NOTE: Flexible Ag ink is used as conductive ink for the current collector line and pads.

2.1. Prepare EDLC ink using terpineol, ethylcellulose, activated carbon (AC), Super-P, polyvinylidene difluoride (PVDF), and Triton-X as follows.

2.1.1. Use 2,951 µL of terpineol with high viscosity as the solvent and 1.56 g of ethyl cellulose as a thickener. Set the ratio of AC to Super-P to PVDF as 7:2:1 with a total weight of 1.8478 g. In addition, use 49 µL of Triton-X as a surfactant for mixing.

2.1.2. Mix all the materials for 30 min using a planetary mixer. Place the well-mixed electrode material in a cartridge for the inkjet printer and centrifuge it at 115 x *g* for 5 min.

2.2. Prepare GPE ink using propylene carbonate (PC), PVDF, and lithium perchlorate ($LiClO_4$) as follows.

2.2.1. Use PC as the solvent, PVDF as the polymer matrix, and $LiClO_4$ as the salt. Weigh all components of GPE such that the final molar concentration of $LiClO_4$ is 1 M, and the final weight % of PVDF is 5 wt%.

2.2.2. Stir all the components at 140 °C for 1 h until dissolution. After stirring, cool the GPE ink sufficiently and place it into the ink cartridge.

3. **Inkjet printer software parameter set-up**

3.1. Run the printer program. Click on the **Print** button, select **Simple**, and then select **Flexible Conductive Ink** in order as shown in **Figure 2**.

3.2. Upload the Gerber file of the designed pattern by following the 1 arrow in **Figure 3**. Choose and open the Gerber file of the conductive line (see 2 and 3 arrows in **Figure 3**). Click on the **NEXT** button as indicated by the 4 arrow.

3.3. Fix the PCB board as shown in **Figure 4A**, and mount the probe as shown in **Figure 4B**.

3.4. Adjust the zero point of the PCB printer through the probe by clicking on the **OUTLINE** button (see the 1,4 red arrow in **Figure 5**).

NOTE: The probe moves over the PCB board while showing the outline of the pattern (see the bottom right of **Figure 5**).

3.5. Move the pattern image on the screen by dragging (see the yellow dashed arrow in **Figure 5**). Click on the **OUTLINE** button once more to check whether the probe moves through the desired path. Click on **NEXT** (indicated by the 5 arrow in **Figure 5**).

3.6. Click on **PROBE** to measure the height of the substrate for checking whether the substrate is flat (**Figure 6**).

NOTE: The probing region on the substrate is automatically selected by the program built into the printer.

3.7. Remove the probe once the height measurement is completed. Insert the ink cartridge into the ink dispenser and connect the nozzle (inner diameter: 230 µm) to prepare the dispenser.

3.8. Mount each ink (conductive line, EDLC, GPE) dispenser, and print a sample pattern by pressing the **CALIBRATE** button, while adjusting the parameters of each ink (**Figure 7**).

3.9. Visually check the printing result and record the parameter values for each ink. See **Representative Results** for details.

4. Printing the conductive line

NOTE: Since steps 4.1. to 4.7. overlap with section 3, they are only briefly summarized below.

4.1. Run the inkjet printer program and click on **Print** in the start menu and select **Simple** (**Figure 1**).

4.2. Click on the **Choose File** button next to **Ink** to load the designed pattern file and click on **NEXT** (**Figure 3**).

4.3. Fix the PCB board onto the printer and install the probe (**Figure 4**).

4.4. Check the position of the pattern on the substrate and measure the height of the substrate

(**Figure 5** and **Figure 6**).

4.5. Remove the probe, and then mount the conductive ink (flexible Ag ink) dispenser.

4.6. Change the software parameters of conductive ink by clicking on the **Settings** button (see **Figure 7** and **Table 1**).

4.7. Print a sample pattern to check whether the setting from step 4.6 is successful.

4.8. Erase the sample printing pattern with a cleaning wipe moistened with ethanol.

4.9. Print the designed pattern of the conductive line by pressing the **START** button.

4.10. After printing, cure the conductive line at 180 °C for 30 min. Then, measure the combined weight of the substrate and the conductive line.

5. **Printing the EDLC line**

5.1. Select the **Aligned** option on the start screen of the printer program. Load the EDLC line pattern file and click on **NEXT** (see step 3.2).

5.2. Ensure the position of the conductive line is detected through two alignment points to align the pattern positions of the EDLC line and the conductive line. Then, move to a random point and check whether the location is correct.

5.3. Measure the overall height of the conductive line to check the height of the dispenser nozzle above the conductive line by clicking on the **PROBE** button (see **Figure 6**).

5.4. Change the software parameter values of EDLC inks (**Figure 7** and **Table 1**).

5.5. Print a sample pattern to check whether the software parameter values are appropriate. Erase the sample printing pattern with a cleaning wipe moistened with ethanol. Print the EDLC line by pressing the **START** button.

5.6. Dry the printed EDLC line overnight at room temperature to evaporate the solvent.

5.7. To calculate the weight of the dried EDLC line, measure the combined weight of the substrate, conductive line, and EDLC line.

6. Printing the GPE pattern

6.1. Select the **Aligned** option on the start screen of the printer program. Load the Gerber file of the GPE pattern and click on **NEXT** (see step 3.2).

6.2. Check the alignment points and move to any point to check whether the position is correct.

6.3. Measure the height of the EDLC line to set the default height for the nozzle.

6.4. Change the software parameter values of GPE inks (**Figure 7** and **Table 1**).

6.5. Print a sample pattern to check whether the software parameter values are appropriate.

6.6. Erase the sample printing pattern with a cleaning wipe moistened with ethanol. Print the GPE pattern.

6.7. To have a stabilization process and evaporate the residual solvent, dry the GPE pattern at room temperature for 24 h.

7. Electrochemical test

7.1. Perform the electrochemical measurements for the inkjet-printed supercapacitor device following the below steps. Turn on the potentiostat device and run the program to measure cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS).

7.1.1. Connect the potentiostat to the supercapacitor device printed earlier.

NOTE: Four connection lines are used in the potentiostat: the working electrode (WE), working sensor (WS), counter electrode (CE), and reference electrode (RE).

7.1.2. Connect the WS line to the WE line and the RE line to the CE line as the fabricated device is a symmetric supercapacitor.

7.1.3. Connect the WE\WS line and CE\RE line to the opposite current collector pads on the supercapacitor device.

7.2. Generate a sequence of CVs and run it to get the result.

7.2.1. Run the program to generate the sequence file.

7.2.2. Click on the **New Sequence** button.

7.2.3. Click on the **Add** button to generate step 1.

7.2.4. Check whether the potential displayed by the potentiostat is 0 V or not. If the potential is not 0 V, do as follows.

7.2.4.1. Set **Control** as **CONSTANT** and for **Configuration**, set **Type** as **PSTAT**, **Mode** as **NORMAL**, and **Range** as **AUTO**. For **Voltage (V)**, set **Ref.** as **Eref**, and **Value** as **0**.

7.2.4.2. For **Condition-1** of **Cut Off Condition**, set **Item** as **Step Time**, **OP** as **>=**, **DeltaValue** as **1:00** and **Go Next** as **Next**. For **Misc. setting** push the **Sampling** button and set **Item** as **Time(s)**, **OP** as **>=** and **DeltaValue** as **30**.

7.2.5. Click on the **Add** button to create the next step.

7.2.5.1. Set **Control** as **SWEEP** and for **Configuration**, set **Type** as **PSTAT**, **Mode** as **CYCLIC** and **Range** as **AUTO**. For **Initial (V)** and **Middle (V)**, set **Ref.** as **Eref**, **Value** as **0**. For **Final (V)**, set **Ref.** as **Eref** and **Value** as **800.00e-3**.

7.2.5.2. Use voltage scan rates of 5, 10, 20, 50, and 100 mV/s. Therefore, according to each scan rate, set **Scanrate (V/s)** as **5.0000e-3**, **10.000e-3**, **20.000e-3**, **50.000e-3**, and **100.00e-3**, respectively.

7.2.5.3. For all scan rates, set **Quiet time(s)** as **0** and **Segments** as **21**. For **Condition-1** of **Cut Off Condition**, set **Item** as **Step End** and **Go Next** as **Next**.

7.2.5.4. For **Misc. setting**, push the **Sampling** button and set **Item** as **Time(s)** and **OP** as **>=**. For each scan rate, set **DeltaValue** as **0.9375**, **0.5**, **0.25**, **0.125**, and **0.0625**.

7.2.6. Click on the **Save As** button to save the sequence file of the CV test.

7.2.7. Click on **Apply to CH** and run the sequence file of the CV test to obtain the result.

7.3. Generate a sequence of GCD and run it to get the result.

7.3.1. Run the program to generate the sequence file.

7.3.2. Click on the **New Sequence** button.

7.3.3. Click on the **Add** button to generate step 1.

7.3.4. Check whether the potential displayed by the potentiostat is 0 V or not. If the potential is not 0 V, do as follows.

7.3.4.1. Set **Control** as **CONSTANT** and for **Configuration**, set **Type** as **PSTAT**, **Mode** as **NORMAL** and **Range** as **AUTO**. For **Voltage (V)**, set **Ref.** as **Eref**, **Value** as **0**.

7.3.4.2. For **Condition-1** of **Cut Off Condition**, set **Item** as **Step Time**, **OP** as **>=**, **DeltaValue** as **1:00** and **Go Next** as **Next**. For **Misc. setting**, push the **Sampling** button and set **Item** as **Time(s)**, **OP** as **>=**, and **DeltaValue** as **30**.

7.3.5. Click on the Add button to create the next step (Charge step).

7.3.5.1. Set **Control** as **CONSTANT** and for **Configuration**, set **Type** as **GSTAT**, **Mode** as **NORMAL**, and **Range** as **AUTO**. For **Current (A)**, set **Ref.** as **ZERO**.

7.3.5.2. Current density varies between 0.01 A/g and 0.02 A/g. Therefore, set the **Value** of **Current (A)** for each current density to **310.26e-6** and **620.52e-6**.

7.3.5.3. For **Condition-1** of **Cut Off Condition** set **Item** as **Voltage**, **OP** as **>=**, **DeltaValue** as **800.00e-3**, and **Go Next** as **Next**. For **Misc. setting**, set **Item** as **Time(s)**, **OP** as **>=** and **DeltaValue** as **1**.

7.3.6. Click on the **Add** button to create the next step (Discharge step).

NOTE: This step is set the same as the Charge step.

7.3.6.1. Set **Value** of **Current (A)** for each current density to **-310.26e-6** and **-620.52e-6**.

7.3.6.2. For **Condition-1** of **Cut Off Condition** set **Item** as **Voltage**, **OP** as **<=**, **DeltaValue** as **0.0000e+0** and **Go Next** as **Next**. For **Misc. setting**, set **Item** as **Time(s)**, **OP** as **>=** and **DeltaValue** as **1**.

7.3.7. Click on the **Add** button to create the next step (Loop step).

7.3.7.1. Set **Control** as **LOOP** and for **Configuration** set **Type** as **Cycle** and **Iteration** as **21**.

7.3.7.2. For **Condition-1** of **Cut Off Condition** set **Item** at List 1 as **Loop Next**. For each current density, set **Go Next** as **STEP-2** for 0.01 A/g and **STEP-5** for 0.02 A/g.

7.3.8. Click on the **Save As** button to save the sequence file of the GCD test.

7.3.9. Click on **Apply to CH** and run the sequence file of the GCD test to obtain the result.

7.4. Generate a sequence of EIS and run it to get the result.

7.4.1. Run the program that can generate the sequence file.

7.4.2. Click on the **New Sequence** button.

7.4.3. Click on the **Add** button to generate step 1.

7.4.3.1. Set **Control** as **CONSTANT** and for **Configuration**, set **Type** as **PSTAT**, **Mode** as **TIMER STOP**, and **Range** as **AUTO**.

7.4.3.2. As the operating potential window in this study is set as 0.0 to 0.8 V, for **Voltage**, set **Value** at **400.00e-3**, which is the average value of the operating potential window. Set **Ref.** as **Eref**.

7.4.4. Click on the **Add** button to generate the next step.

7.4.4.1. Set **Control** as **EIS** and for **Configuration**, set **Type** as **PSTAT**, **Mode** as **LOG** and **Range** as **AUTO**.

7.4.4.2. Set the frequency range as 0.1 Hz to 1 MHz. Therefore, set **Initial (Hz)** and **Middle (Hz)** to **100.00e+6**, and **Final (Hz)** to **100.00e-3**.

7.4.4.3. As mentioned in section 7.4.3.2, set **Value** of **Bias (V)** to **400.00e-3**, and set **Ref.** to **Eref**.

7.4.4.4. To maintain a linear response, set the **amplitude (Vrms)** to **10.000e-3**.

7.4.4.5. Set **Density** as **10** and **Iteration** as **1** for this experiment.

7.4.5. Click on the **Save As** button to save the sequence file of the GCD test.

7.4.6. Click on **Apply to CH** and run the sequence file of the EIS test to get the result.

REPRESENTATIVE RESULTS:

The ink was synthesized according to step 2, and the characteristics of the ink could be confirmed according to reference[18]. **Figure 8** shows the structural properties of conductive ink and EDLC ink, as well as the rheological properties of EDLC ink reported in the previous research[18]. The conductive ink is well sintered to form continuous conducting paths, and the nanoscale roughness is expected to increase the contact area with the EDLC ink (**Figure 8A,B**). EDLC ink is uniformly distributed on the macroscopic scale but has a very rough surface shape on the micro and nanoscale, which possibly provides a high surface area and improves the energy storage capacity. All components are well dispersed and there are no visible elements that could cause clogging during printing (**Figure 8C–F**). **Figure 8G** presents the time-evolution of the apparent viscosity in the EDLC ink. The viscosity value increases with shear time and doesn't show viscoelastic behavior; it indicates a shear-thickening behavior without any stress-induced structural extension, stretching, or rearrangement.

A printed supercapacitor was successfully obtained using the present protocol (**Figure 9B**). The print quality is considered good if the printed pattern has fewer or no defects (compare **Figure 9B** with **9A**), minimal surface roughness, and uniform thickness. The primary parameters that affect the quality of the inkjet printing method are the feed rate, kick, trim length, anti-stringing distance, rheological setpoint, and soft start/stop ratio. In this study, the printing results of the GPE and EDLC line (or layer) were evaluated based on the printing results of the conductive line.

The feed rate and XY-axis travel speed during dispensing determine the overall printing time. They also have a significant impact on the thickness of the line and the prevention of cut-off problems. All lines were uniform with no visible disconnection when the feed rate was minimum (100 mm/min) (**Figure 10A**); however, it took a long time to print the product. In contrast, the overall printing time decreased when the feed rate was maximum (600 mm/min) (**Figure 10D**); however, compared with the results printed with a feed rate of 500 mm/min (**Figure 10C**), the line was cut off or cracked because the dispenser moved rapidly. A feed rate of 300 mm/min is found to be optimal for a proper printing time and to prevent crack formation (**Figure 10B**). Kick controls the pressure applied *via* the stroke length of the piston within the dispenser. All lines were disconnected when the kick was too low (the minimum value is equal to 0.1 mm). However, the high pressure at a high kick (maximum value is equal to 0.7 mm) created a bottleneck resulting in the clogging of the nozzle. Therefore, it is necessary to use an appropriate value of kick (0.35 mm) so that the line does not break, and the nozzle does not clog (**Figure 11**).

Trim length is the maximum distance traveled for one dispensing and has a value ranging from 1 mm to 9999 mm. The printer prints crudely and takes a long time when the trim length is 1 mm. Therefore, the trim length needs to be adjusted based on the total length of the pattern. In this protocol, the trim length was set as 120 mm (**Figure 12**). A stringing can be formed at the end of the nozzle because the adhesion of the ink to the nozzle is higher than the adhesion of the ink to the substrate based on the surface energy of the ink. The anti-stringing distance aids in safely breaking the stringing by pushing the nozzle back (**Figure 13**). The rheological setpoint is a parameter that compensates for the flow rate to maintain the pressure after dispensing. The dispensing amount does not increase even after printing a pattern when the rheological setpoint is at its minimum value (0.0). However, the dispensing amount and the flow rate of the ink increase when the rheological setpoint is at the maximum value (1.0). Moreover, clogging occurs due to the bottleneck effect when the rheological setpoint is high. Thus, the rheological setpoint needs to be adjusted based on the viscosity and compressibility of the ink (**Figure 14**).

The soft start/stop ratio is a parameter that adjusts the difference between the time when the kick (pressurization) starts and when the flow rate is stabilized based on the properties of the ink (**Figure 15**). During the software parameter setup control experiment, it is difficult to observe any variation in printing due to the changes in the passing space and the trace penetration setting value. Therefore, these two parameters must be fixed separately based on the designed pattern. The results of the setup control experiment are as follows: pass spacing, trace penetration, and trim length should be adjusted based on the pattern to be printed. Moreover, feed rate, anti-stringing distance, kick, soft start/stop ratio, and rheological setpoint should be adjusted based on the properties of the ink. Therefore, the software parameter values for different inks (conductive ink, EDLC ink, and GPE ink) were fixed as shown in **Table 1**.

Electrochemical data were obtained as described in step 7 of the protocol. **Figure 16A**,**B**,**C** present the CV, GCD, and EIS data, respectively. The data shown in **Figure 16A** was obtained through the CV measurement. The gravimetric capacitance, areal capacitance, and cell capacitance were calculated to be 5.74 F/g, 142 mF/cm^2, and 178 mF/cell, respectively, for a scan rate of 5 mV/s. GCD graphs (**Figure 16B**) demonstrate a nearly symmetrical curve shape, which is the characteristic property of the EDLC. Moreover, the EIS graph (**Figure 16C**) illustrates a low R_s value (5.29 Ω) and no R_{ct} value, which are typical of EDLC.

FIGURE AND TABLE LEGENDS:

Figure 1: Interdigitated pattern designed with CAD program. The two pads at the top of the pattern are printed only with a current collector ink. The large sky-blue square is printed with a gel polymer electrolyte ink, and the blue lines are printed with the EDLC line ink and current collector ink.

Figure 2: Image of the printer program window. (**A**) The first screen of the program. The red arrow shows where the Print button is. (**B**) The second screen of the program. The red arrow shows where the Simple button is. (**C**) The third screen of the program. Red arrow shows which ink should be selected.

Figure 3: A screenshot showing how to upload the Gerber file of the designed pattern.

Figure 4: A screenshot showing how to fix the PCB board and mount the probe. (**A**) A top-view image of the inkjet printer which holds the PCB board. (**B**) The front-view image of the inkjet printer where the probe is mounted.

Figure 5: A screenshot showing how to check the probe movement when the pattern position is changed.

Figure 6: A screenshot showing how to measure surface height. After clicking on PROBE, the probe goes to the indicated spot on the substrate (denoted by circles), and then moves down and up to check the height of the substrate.

Figure 7: A screenshot showing how to adjust the software parameters and print the sample pattern. (**A**) A screenshot image showing the procedure for printing a sample pattern. The red arrow indicates the button to print the sample pattern and the yellow arrow indicates the button to control the software parameters for the inks. (**B**) A window that appears when the yellow arrow shown in (**A**) is pressed. Software parameters can be modified by changing the values indicated by the 1 arrow. Press the 2 arrow to save the changes in software parameters.

Figure 8: SEM image of the inks and printed layers, and EDLC ink viscosity. (**A,B**) Top-view SEM images of the current collector at (**A**) low magnification and (**B**) high magnification. (**C**) Tilted side-view SEM image of the printed EDLC active layer film. (**D–F**) Top-view SEM images of the EDLC active layer with different magnifications. (**G**) Apparent viscosity of EDLC ink versus shear time for constant 0.3 s^{-1} shear rate experiment. Adapted with permission from reference[18]. Copyright (2020) American Chemical Society.

Figure 9: Photograph of the printed results. (**A**) Printing failure photo; the red circled part is printed unevenly due to printing failure. (**B**) Photograph of the final printed product.

Figure 10: Printing results corresponding to the change in the feed rate. (**A**) 100 mm/min, (**B**) 300 mm/min, (**C**) 500 mm/min, and (**D**) 600 mm/min.

Figure 11: Printing results corresponding to the changes in the kick. (**A**) 0.1 mm, (**B**) 0.2 mm, (**C**) 0.35 mm, and (**D**) 0.7 mm.

Figure 12: Printing results corresponding to the changes in the trim length. (**A**) 1.0 mm and (**B**) 50 mm.

Figure 13: The pictures showing how the dispenser moves by the adjustment of the anti-stringing distance parameter. (**A**) Movement of the nozzle when the anti-stringing distance value is fixed at the maximum value (5.0 mm). (**B**) Photograph of stringing.

Figure 14: Printing results corresponding to the change in the rheological setpoint change. (**A**) 0 and (**B**) 1.0. Red circles in (**B**) show the cracks (or holes) caused by the clogging effect.

Figure 15: Printing results corresponding to the change in the soft start/soft stop ratio. The clockwise rotation of the sawtooth (red arrow) indicates the start of the printing. (**A**) Soft start maximum value and soft stop minimum value, as well as (**B**) soft start minimum value and soft stop maximum value.

Figure 16: The electrochemical test results of the printed supercapacitor. (**A**) CV, (**B**) GCD, and (**C**) EIS graphs.

Table 1. The optimized software parameters for conductive ink, EDLC ink, and GPE ink.

DISCUSSION:

The critical steps in this protocol are involved in the software parameter setup to print the designed pattern by finely adjusting the parameter values. Customized printing can lead to structural optimization and obtaining new mechanical properties[19]. The inkjet printing method with software parameter control can be used for sophisticated printing in various industries by selecting the optimized material for the printing process.

In the fabrication of supercapacitors using inkjet printing, one paper reported that there is still a limit to developing a pattern with uniform and high resolution. It has been reported that high-temperature post-treatment is still necessary, and the optimization process of the material is indispensable[20]. Another paper reported that to use inkjet printing properly, it is necessary to adjust the viscosity and surface tension in a relatively narrow range that depends on the printer. For this purpose, the concentration of the active material of the ink is limited. In some cases, it has been noted that multiple prints are necessary to deposit a sufficient amount of material[21]. In line with this trend, this protocol can help researchers implement patterns with higher resolution by providing precise methods for handling inkjet printers. In addition, with mastery over software control, one can simplify the manufacturing process by adjusting the software parameters such as Feed rate and Kick without having to print several times to deposit enough material.

Software parameter control for precise printing can be done according to the presented protocol. However, some bottlenecks should be addressed to improve the performance of the device based on the printing method. Various problems, such as ink spreading and clogging effect, require the optimization of the characteristics of the ink itself along with adjusting of software parameter values[22]. The two most crucial properties of the ink are viscosity and surface tension[23]. Therefore, the viscosity[24] and surface tension[25] of the ink must be measured and controlled for its optimization. To improve the performance, it is also important to fully understand the properties of the inks and to select materials with appropriate ratios.

In summary, a protocol is established here to use inkjet printing for printing a supercapacitor device. A discussion of software parameters controlling the inkjet printer has been provided here as a useful guide for handling and optimizing sophisticated printing processes. Further progress in printing wearable devices for energy storage, flexible sensors, and the aerospace industry can be achieved through ink material optimization.

ACKNOWLEDGMENTS:
This work was supported by the Korea Electric Power Corporation (Grant number: R21XO01-24), the Competency Development Program for Industry Specialists of the Korean MOTIE operated by KIAT (No. P0012453), and the Chung-Ang University Graduate Research Scholarship 2021.

DISCLOSURES:
The authors have no disclosures.

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Figure 1.

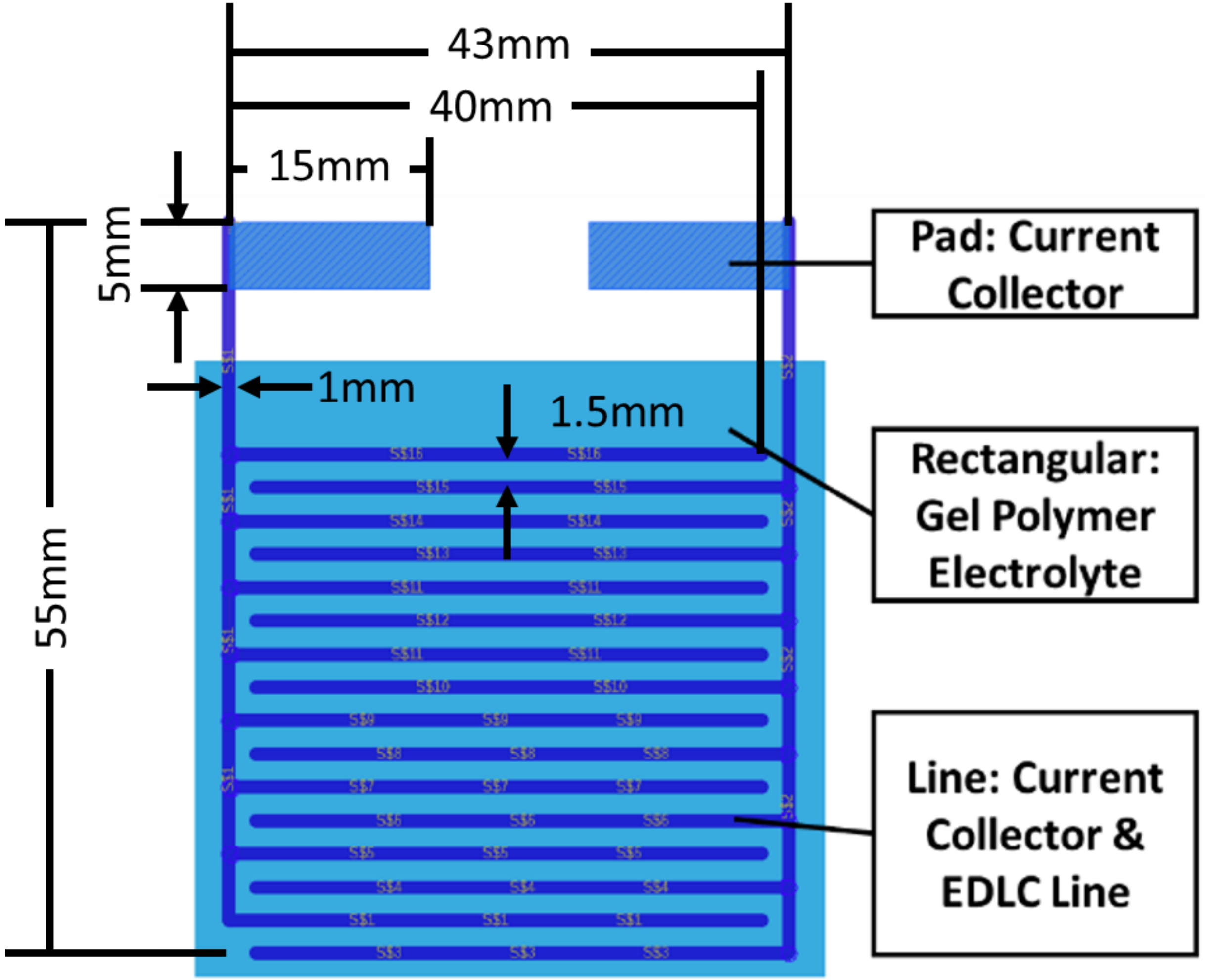
43mm
40mm
15mm
5mm
55mm
1mm
1.5mm
Pad: Current Collector
Rectangular: Gel Polymer Electrolyte
Line: Current Collector & EDLC Line

Figure 2

Figure 2

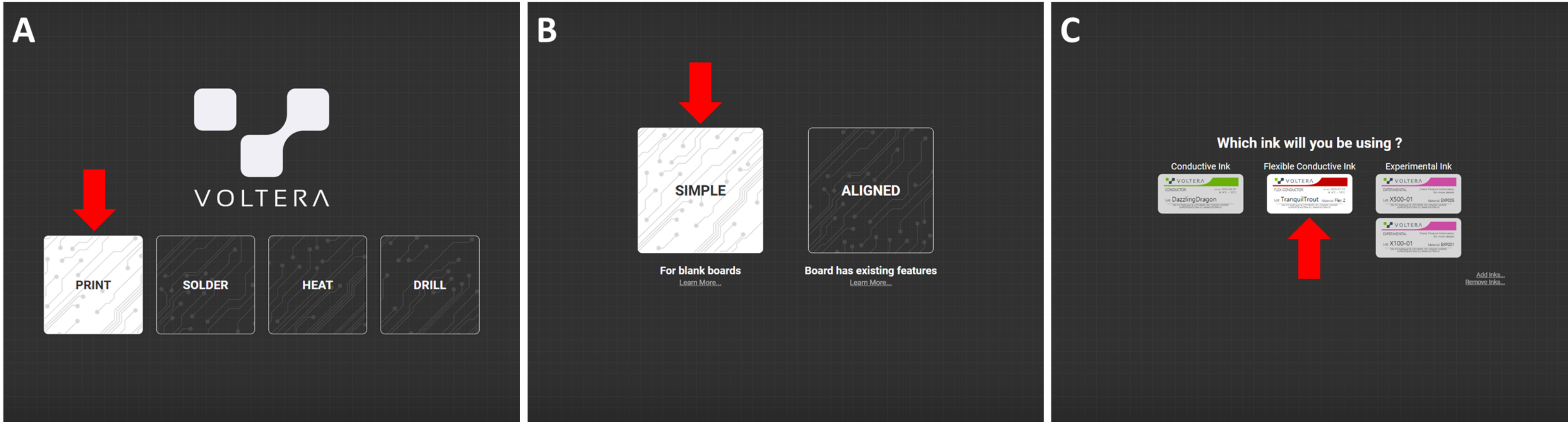

Figure 3

Figure 3

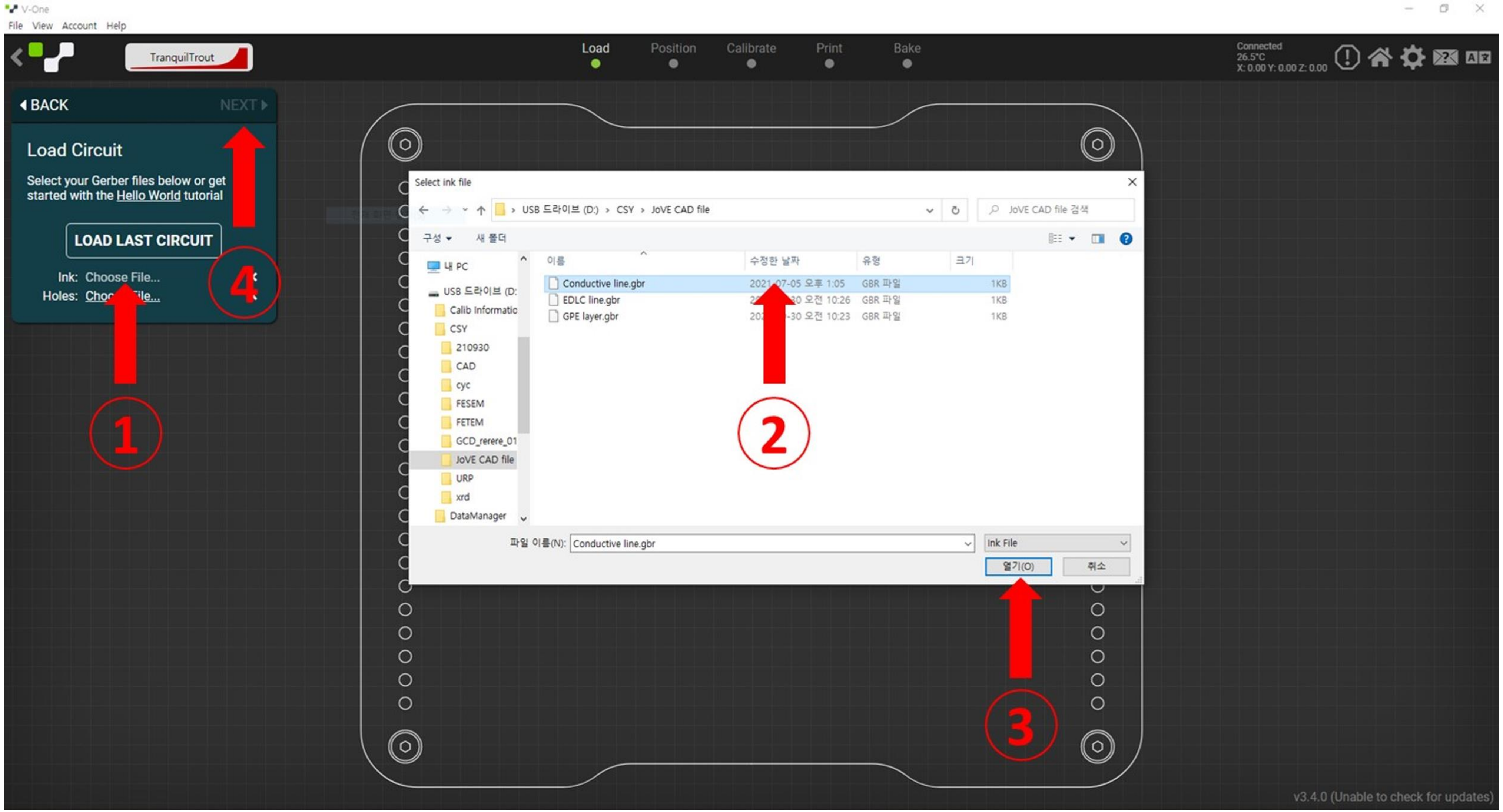

Figure 4

Figure 4

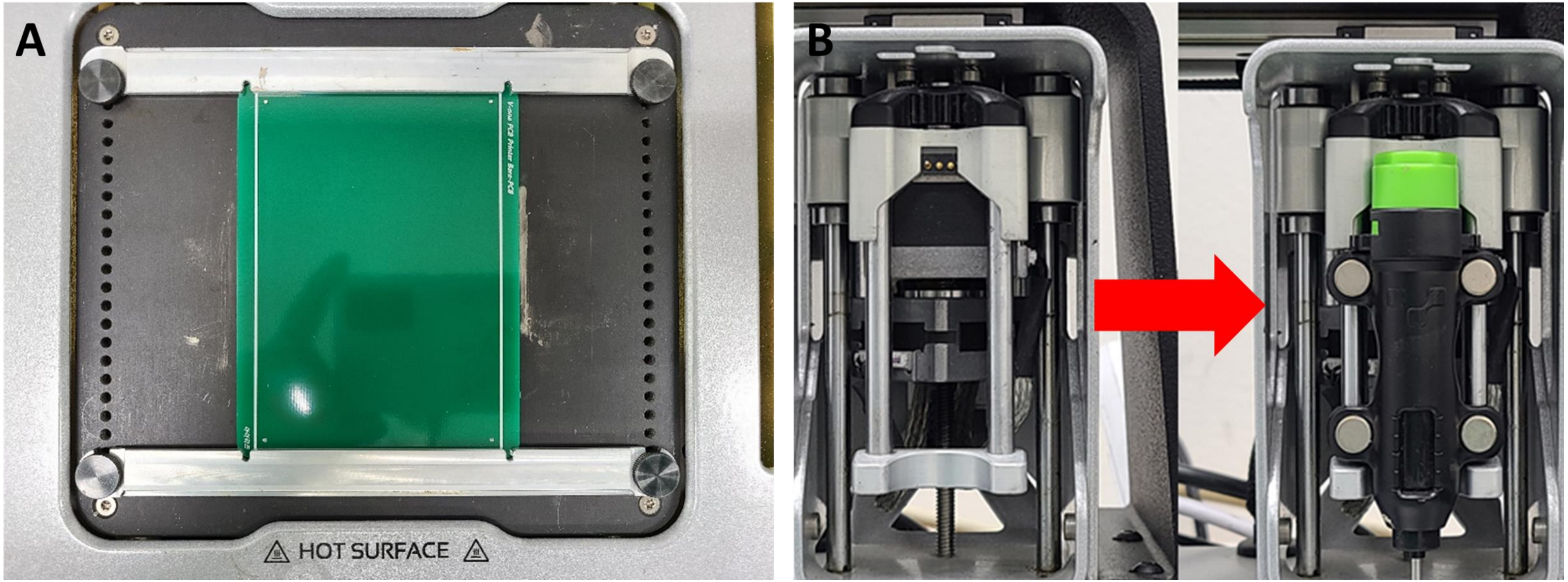

Figure 5

Figure 5

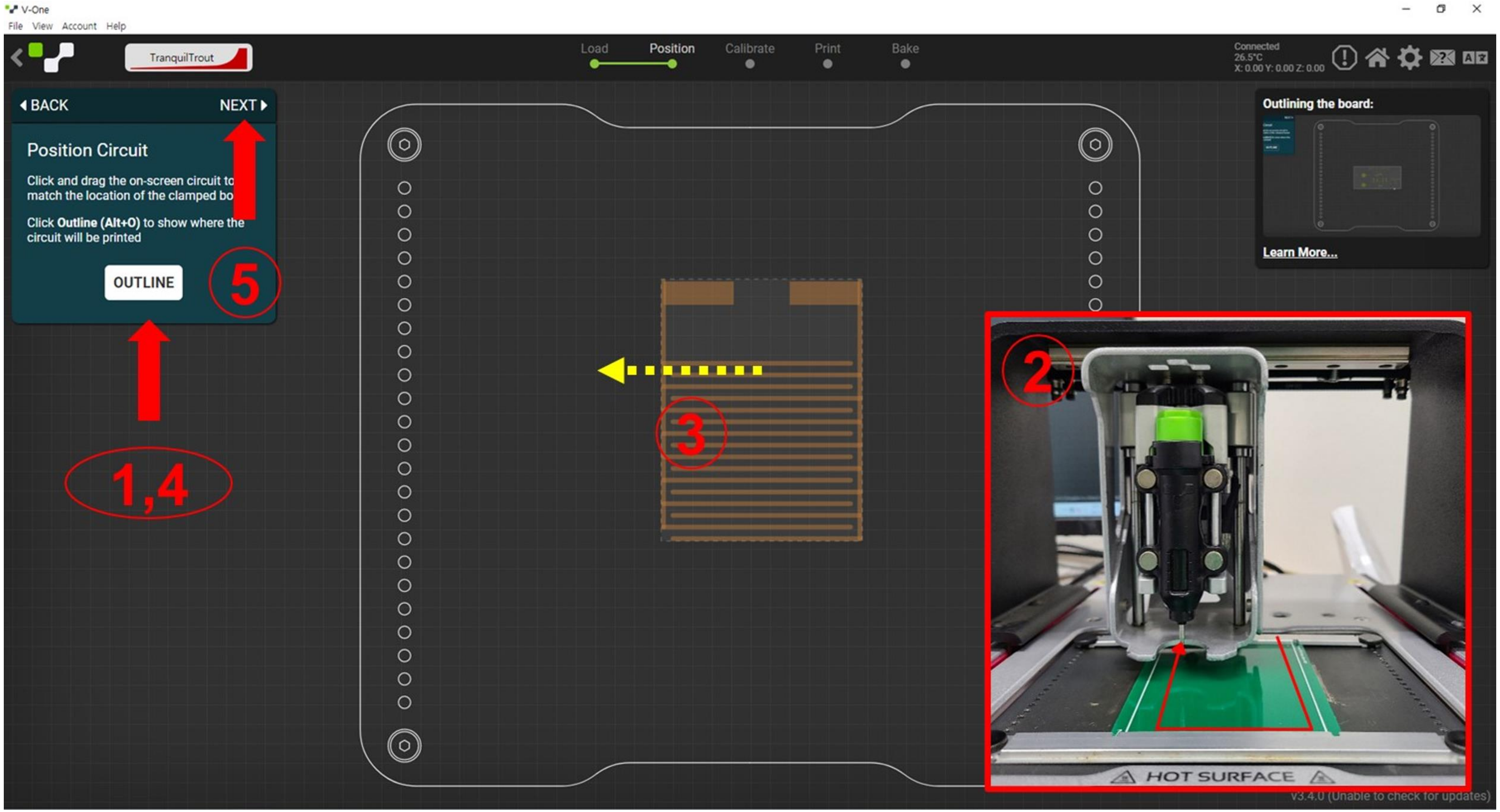

Figure 6

Click here to access/download;Figure;Figure 6.pdf

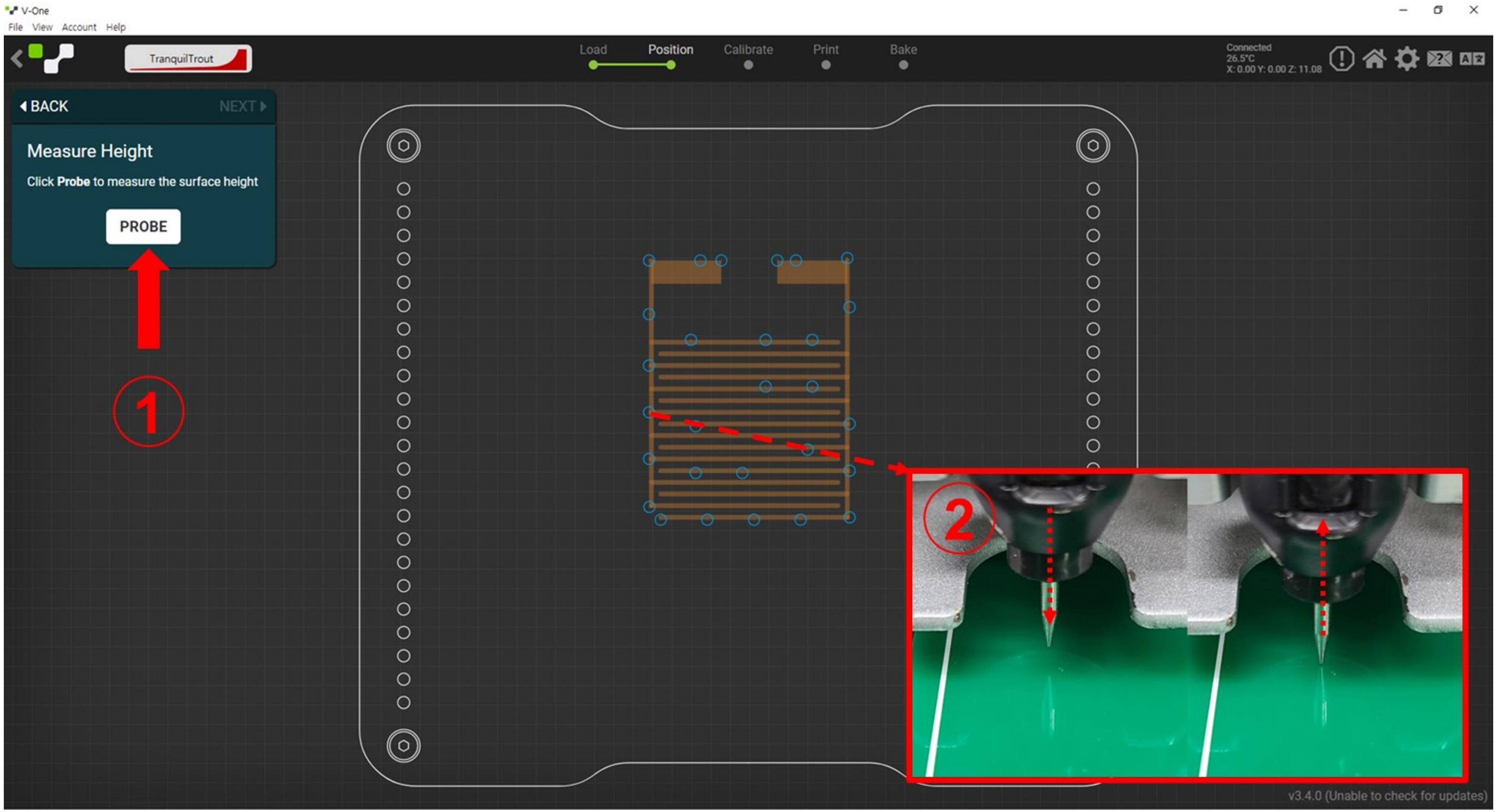

Figure 7

Figure 7

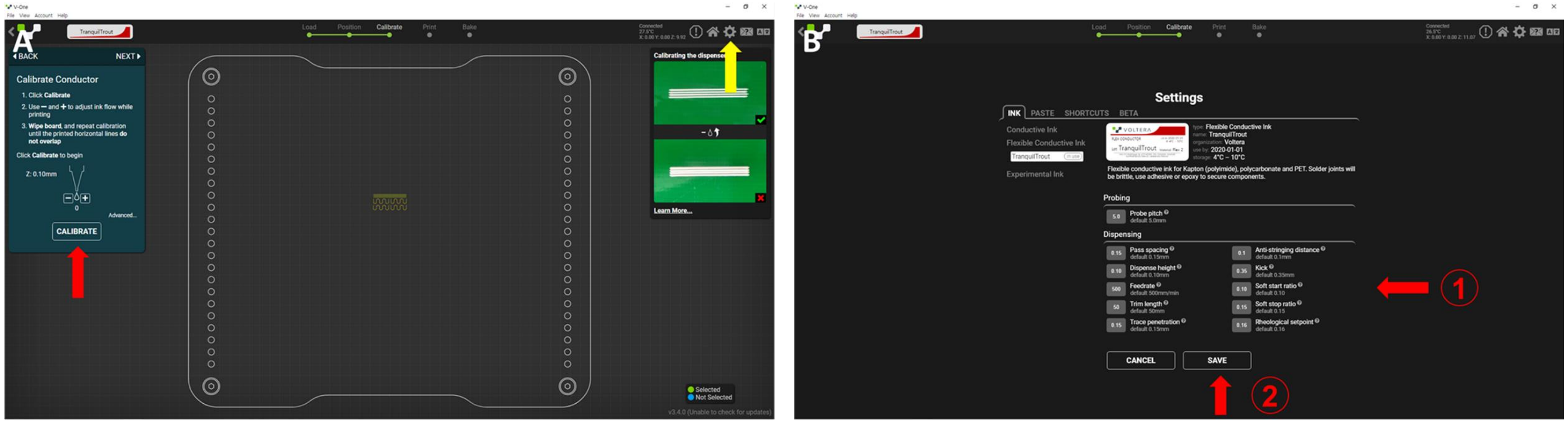

Figure 8

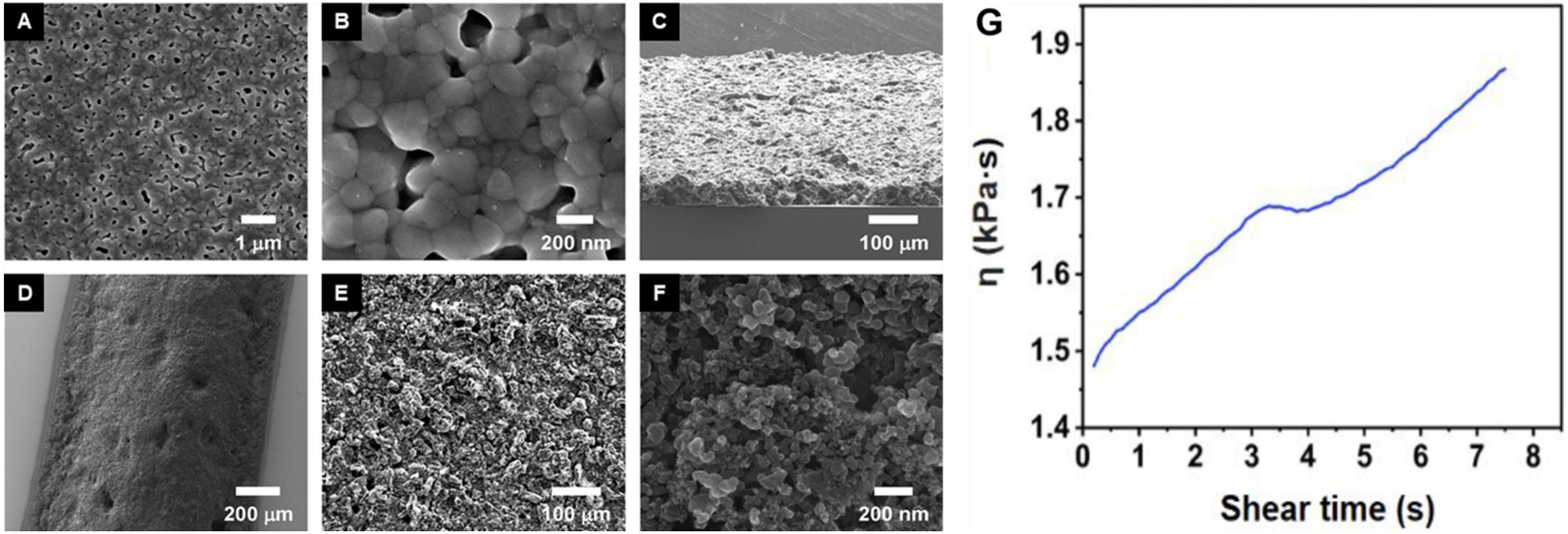
A
1 µm
B
200 nm
C
100 µm
D
200 µm
E
100 µm
F
200 nm
G
η (kPa·s)
1.9
1.8
1.7
1.6
1.5
1.4
0
1
2
3
4
5
6
7
8
Shear time (s)

Figure 9

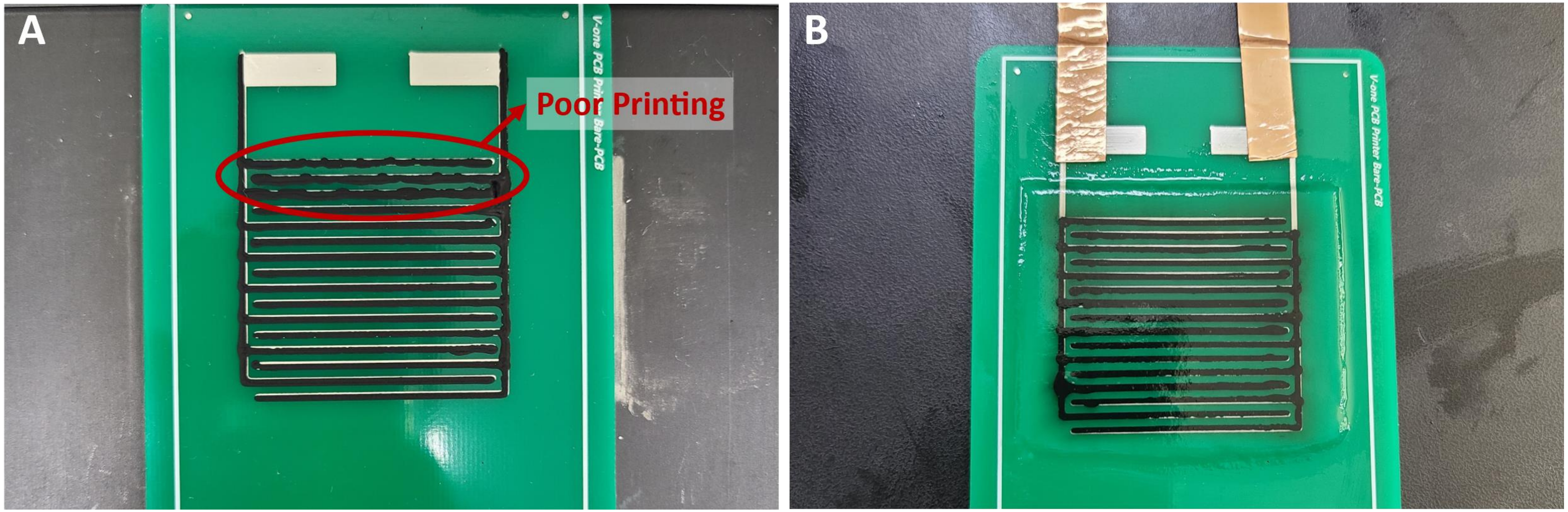
A
Poor Printing
V-one PCB Printer Bare-PCB
B
V-one PCB Printer Bare-PCB

Figure 10

Figure 10

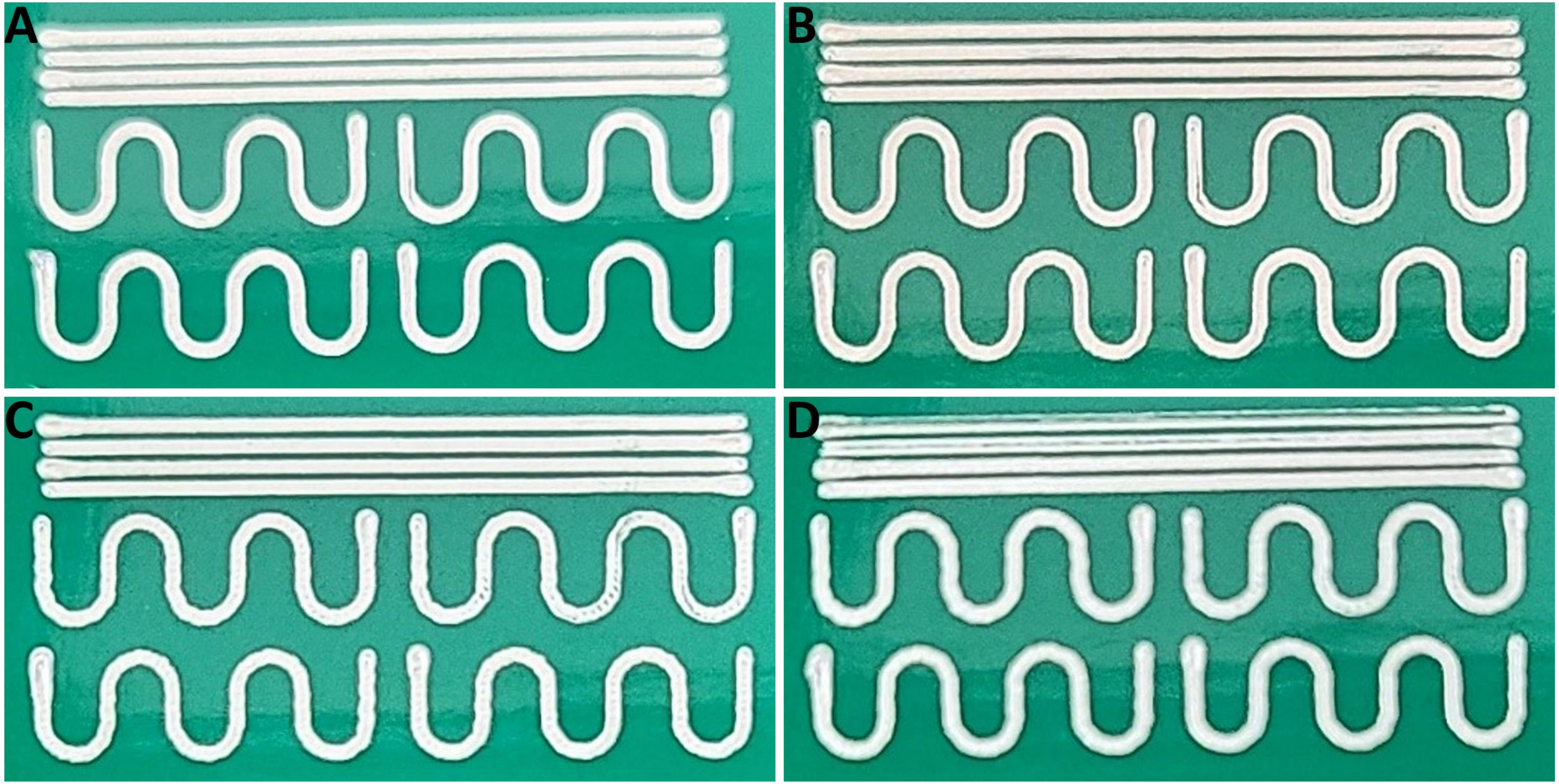

Figure 11

Figure 11

Click here to access/download;Figure;Figure 11.pdf

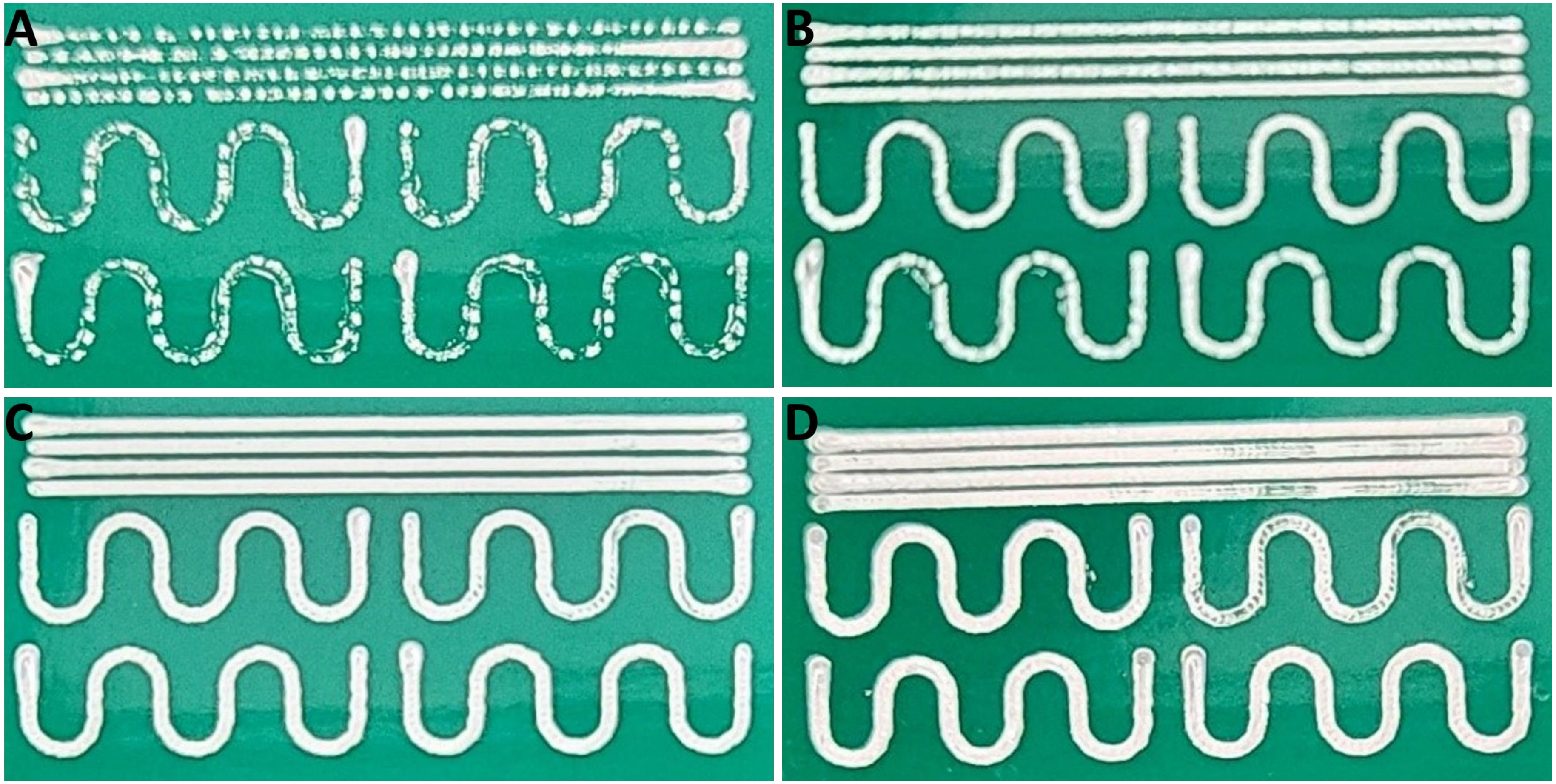

Figure 12

Figure 12

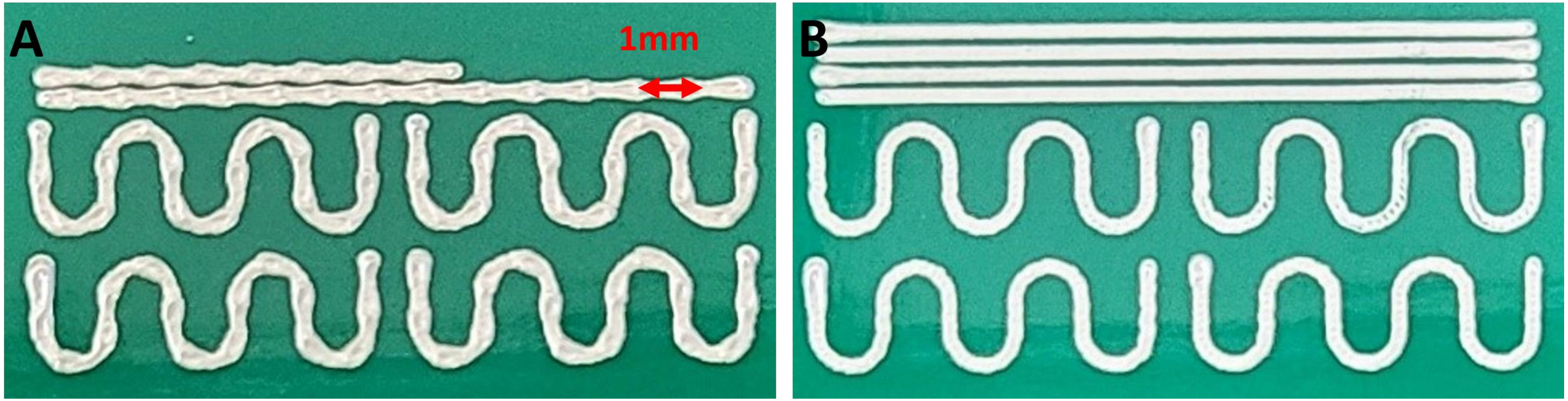

Figure 13

Figure 13

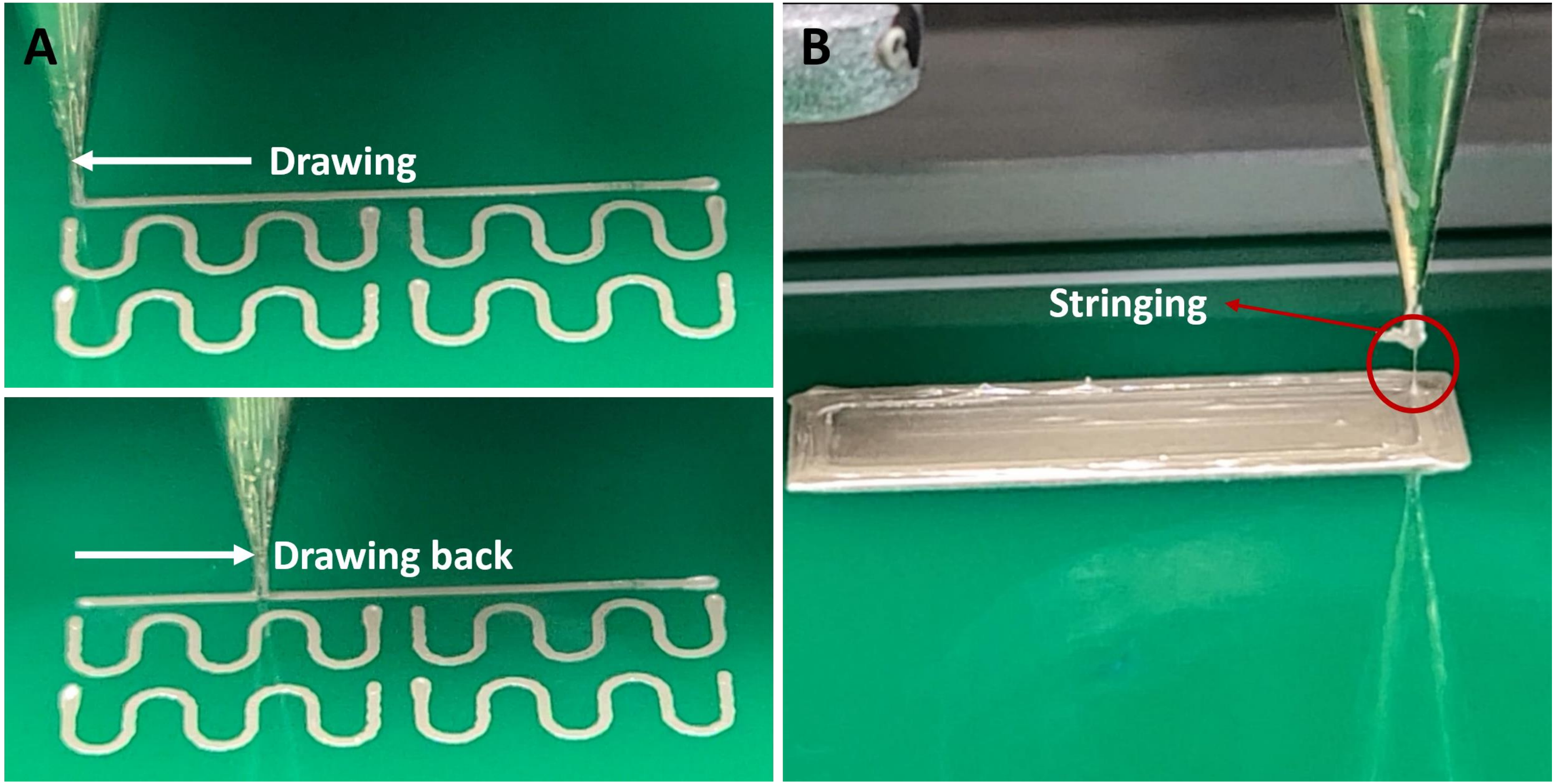

Figure 14

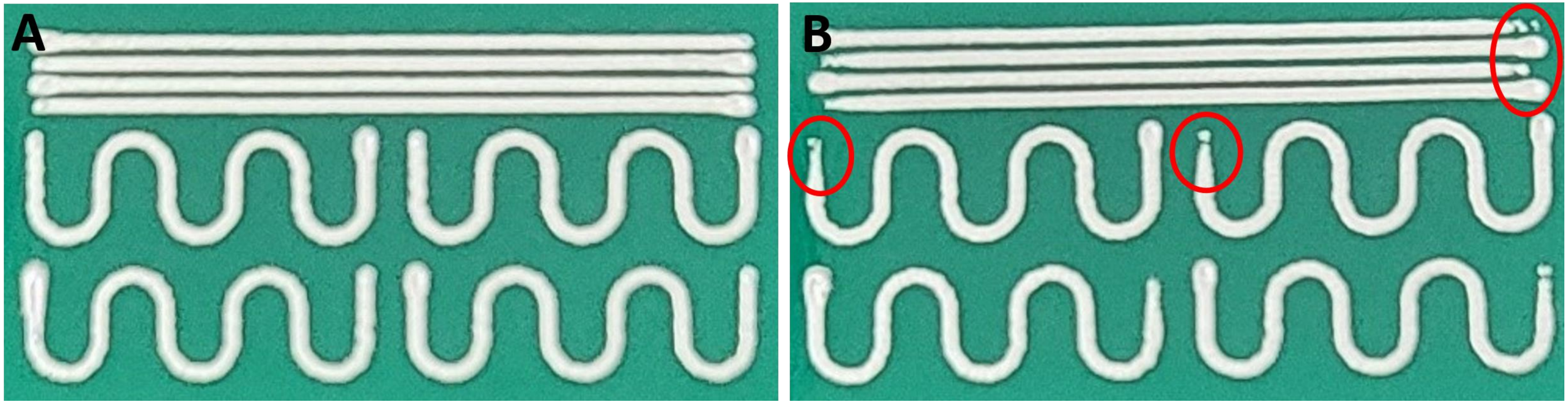

Figure 15
Figure 15

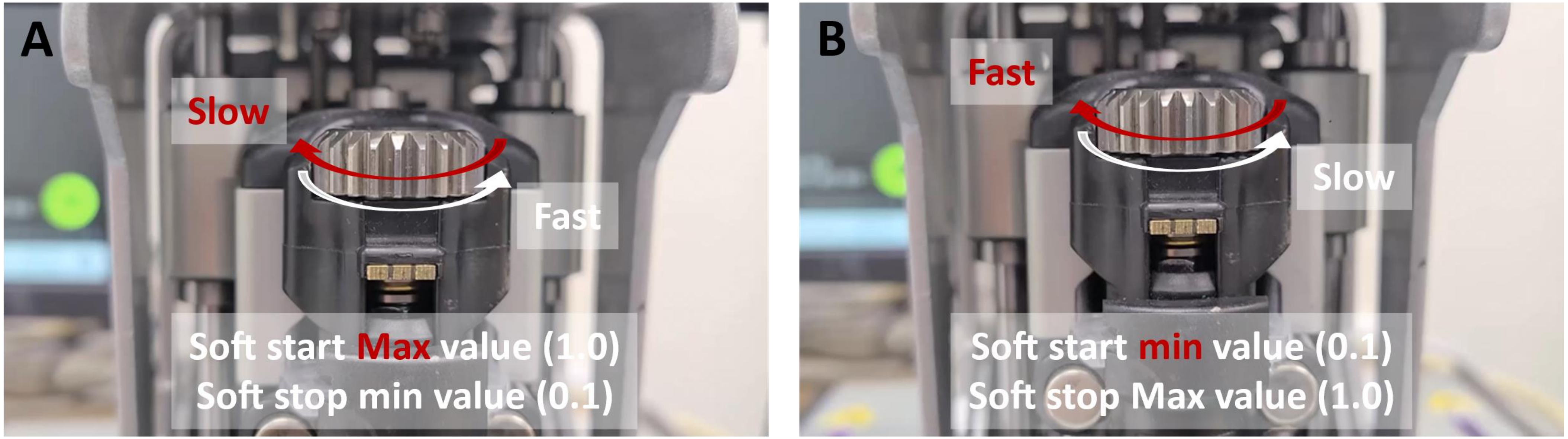

Figure 16

Figure 16

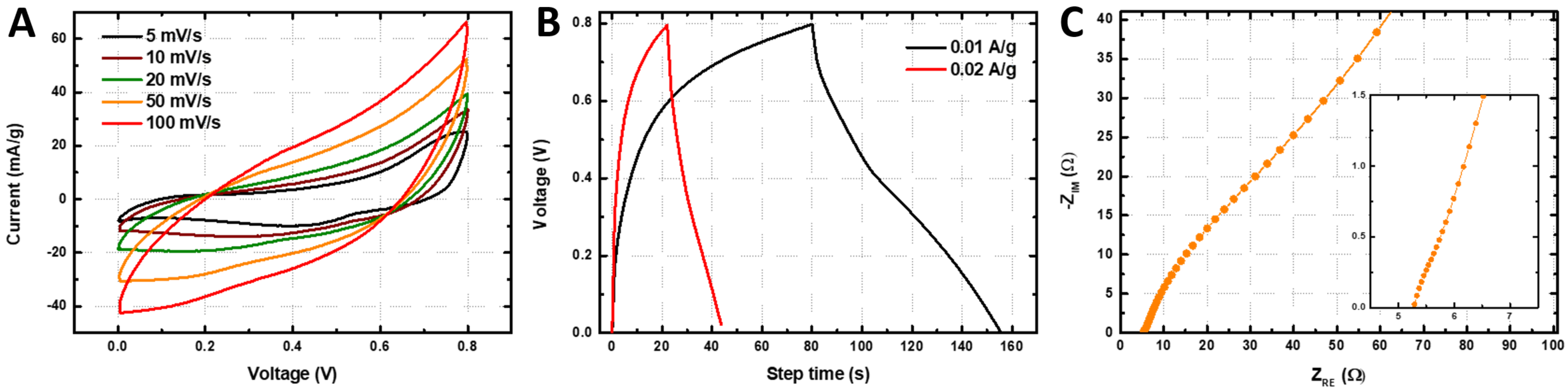

Table 1 Click here to access/download;Table;table 1.xlsx

Parameter	Conductive ink	EDLC ink	GPE ink
Pass spacing (mm)	0.15	0.15	0.15
Dispense height (mm)	0.12	0.14	0.16
Feedrate (mm/min)	500	300	300
Trim length (mm)	120	120	120
Trace penetration (mm)	0.15	0.15	0.15
Anti-stringing distance (mm)	0.4	0.7	0.1
Kick (mm)	0.35	0.3	0.4
Soft start ratio	0.1	0.8	0.8
Soft stop ratio	0.15	0.1	0.15
Rheological setpoint	0.16	0.2	0.16

Click here to access/download
Table of Materials
JoVE_Materials.xls

Response to Referee's Comments

Manuscript ID: JoVE63234

Title: Elaborate control of inkjet printer for fabrication of chip-based supercapacitors

We appreciate the constructive comments and suggestions from the editor and referees, which were very helpful to improve the clarity of our manuscript. Based on the comments, we have made changes to improve our manuscript. Consequently, we now believe that the quality of the manuscript is considerably improved to be suitable to publish in *Journal of Visualized Experiments*. We have given a response to each comment, including the detailed changes that were highlighted in the manuscript.

Response to the Editorial Comments:

Comment 1:

Please take this opportunity to thoroughly proofread the manuscript to ensure that ther e are no spelling or grammar issues.

Answer)

Thank you very much. We revised the manuscript and proofread it.

Comment 2:

Please rephrase the Summary to clearly describe the protocol and its applications in c omplete sentences between 10-50 words: "Here, we present a protocol to …."

Answer)

Thank you for your valuable comment. To clarify the topic and applications of our protocol, we have made the following changes in the *SUMMARY* section.

In *Page 1 SUMMARY section*

This paper provides a technique for manufacturing chip-based supercapacitors using an inkjet printer. In detail, methodologies are described to synthesize inks, adjusting software parameters, and analyze the electrochemical results of the supercapacitor manufactured through electrochemical tests.

Comment 3:

Please revise the text to avoid the use of any personal pronouns (e.g., "we", "you", "our" etc.).

Answer)

Thank you for your valuable comment. The entire paper has been thoroughly reviewed for the points you mentioned. the revised points are highlighted in the revised manuscript.

Comment 4:
JoVE cannot publish manuscripts containing commercial language. This includes trademark symbols (™), registered symbols (®), and company names before an instrument or reagent. Please remove all commercial language from your manuscript and use generic terms instead. All commercial products should be sufficiently referenced in the Table of Materials.
For example: WYPALL, Voltera, etc.

Answer)
Thank you for your valuable comment. The entire paper has been thoroughly reviewed for the points you mentioned, and they are highlighted in the revised manuscript.

Comment 5:
5. Please ensure that the Introduction includes all of the following:
a) A clear statement of the overall goal of this method
b) The rationale behind the development and/or use of this technique
c) The advantages over alternative techniques with applicable references to previous studies
d) A description of the context of the technique in the wider body of literature
e) Information to help readers to determine whether the method is appropriate for their application

Answer)
To improve the quality of the introduction, the manuscript has been revised as below.

In *Page 1* ***Introduction*** *section*
In the past decades, multiple printing methods have been developed for various applications, such as wearable devices[1], pharmaceuticals[2], and aerospace components[3]. The printing can be easily adapted for the various devices by simply changing the materials to be used. Moreover, it prevents the wastage of raw materials. To manufacture electronic devices, sorts of printing methods have been developed, such as screen printing[4], push coating[5], and lithography[6]. Compared to these printing technologies, the inkjet printing method has multiple advantages, including reduced material waste, compatibility with multiple substrates[7], low cost[8], flexibility[9], low-temperature processing[10], and ease of mass production[11]. However, the application of the inkjet printing method has barely been suggested for certain sophisticated devices. Therefore, this protocol established detailed guidelines to use the inkjet printing method for a specific electronic device.

Supercapacitors, including pseudocapacitors and electrochemical double-layer capacitors (EDLCs), are emerging as energy storage devices that can complement conventional lithium-ion batteries[12,13]. Especially, the EDLC is a promising energy storage device because of the low cost, high power density, and long cycle life[14]. Activated carbon (AC), having high specific surface area and conductivity, is used as an electrode material for commercial EDLCs[15]. These properties of AC allow EDLCs to have high electrochemical capacitance[16]. EDLCs have the passive volume in devices when the conventional fixed-size fabrication method is used. However, based on inkjet printing, the EDLCs can be fully integrated into the product design. Therefore, the device manufactured by the inkjet printing method is esthetically and functionally better than fabricated by existing fixed-size methodologies[17]. The fabrication of

EDLCs using the efficient inkjet printing method could maximize the stability and longevity of EDLCs and provide a free-form factor[18]. The printing patterns were designed by using a PCB CAD program and converted all to Gerber files. The designed patterns were printed using an inkjet printer because it has precise control through software, high material throughput, and printing stability.

Comment 6:

Please note that your protocol will be used to generate the script for the video and must contain everything that you would like shown in the video. Please add more details to your protocol steps. Please ensure you answer the "how" question, i.e., how is the step performed? Alternatively, add references to published material specifying how to perform the protocol action. Please add more specific details (e.g. button clicks for software actions, numerical values for settings, etc) to your protocol steps. There should be enough detail in each step to supplement the actions seen in the video so that viewers can easily replicate the protocol.

Answer)

Thank you for your valuable comment. To answer the "how" questions corresponding to the editor's comments 7-21, we tried to provide a clearer protocol by adding and/or modifying a few steps for each and presenting additional figures.

Comment 7:

Line 58-59: Where are the values of grid size and alt changed? In CAD software? Pl ease include the details of the button clicks/ commands used, if any. Please ensure to bold the button clicks/commands.

In *Page 2 line 61 - 67*

1.1. To design a pattern by using a PCB CAD program, firstly run the CAD program. Click the 'File' button at the upside of the program window, and to form a new project file, click the 'New' and 'Project' buttons.

1.2. To generate the board file, click the 'File' and 'New' and 'Board' buttons in order. There can set the grid size, multiple, and alt values by clicking the mesh-shaped 'Grid' button at the top left of the created 'Board file' window.

Comment 8:
Line 60-63: Please elaborate on the designing step. Please ensure to include all the d etails necessary so that the protocol can be repeated/reproduced elsewhere.

In *Page 2 line 74 - 98*
1.4.1. Since the final pattern consists of a total of three types (Conductive line, EDLC, and GPE), three layers must be set.

1.4.1.1. Click ‘View’ and ‘Layer settings’ in order at the top of the window and create new layers by clicking the ‘New Layer’ button at the bottom left of the ‘Visible Layers’ window.

1.4.1.2. There must be a new window (‘New Layer’) that can set up a name and color of a new layer. For convenience, set the names of each layer to 'Current collector', 'EDLC', and 'GPE', and change the color by clicking the box to the right of 'Color' so that they can be visually distinguished.

1.4.2. Press 'Line' at the bottom left of the screen then click on the main field (black background) and drag to draw a line. To change the thickness of the line, input the value of 'Width' located at the top center in inch scale. (1.0 mm = 0.0393701 inch)

1.4.3. To edit the length of a line, right-click on the line and click 'Properties' at the bottom. On the right side of From and To, there are two input fields, which are the x and y values of the starting and ending points, respectively.

1.4.3.1. To set the reference point of the pattern, set the upper left corner of the pattern shown in **Figure 1.** to (0, 0), and draw the pattern by inputting the rest based on the above-mentioned information (**Protocol 1.4.**).

1.4.3.2. To set the layer of the drawn pattern, click 'Layer' in the 3rd line at the bottom of the 'Properties' window mentioned above and set it to the desired layer.

1.4.4. In the case of the current collector pad and GPE, it exists as a rectangular surface rather than a line. To draw them, press 'Rect' at the bottom left of the window, and then click and drag on the screen (main field) where the pattern exists.

1.4.5. Just like editing 'Line', right-click on the rectangular surface and click 'Propertie s' at the bottom. Input the upper left (x,y) value of the rectangle in 'From', and input the lower right (x,y) value in 'To' to edit. Also, set the desired layer as mentioned in **Protocol 1.4.3.2.**.

Comment 9:
Line 64: How are the files converted?

In *Page 3 line 99 - 116*
1.5 Convert CAD file of designed pattern into the Gerber file format that can be read by the inkjet printer.

1.5.1. Before converting the designed pattern file, the ‘Board file’ should be saved in ‘.brd’ format.

1.5.2. After saving, click 'File' at the top of the window and click 'CAM processor'. To create a Gerber file of the desired layer, modify the items under 'Gerber' of 'Output Files' on the left side of the window.

1.5.2.1. First, delete the sub-lists such as 'Top Copper' and 'Bottom Copper' by pressing the '-' below.

1.5.2.2. Press '+' and click 'New Gerber output' to create Gerber output.

1.5.2.3. On the right side of the screen, set the layer name in 'Name' and 'Function' to 'Copper' by pressing the gear on the right. Set 'Layer type' to 'Top' and set 'Gerber layer number' of the current collector, EDLC and GPE to 'L1', 'L2', 'L3' respectively.

1.5.2.4. In the 'Layers' window at the bottom of 'Gerber File', click 'Edit layers' at the bottom left, and select each desired layer.

1.5.2.5. To set the name of the output file to be created, set the 'Gerber filename' of 'Output' at the bottom of the window to '%PREFIX/%NAME.gbr'.

1.5.2.6. Finally, click 'Save Job' at the top left of the window to save the settings, and then cli ck 'Process Job' at the bottom right to create a Gerber file.

Comment 10:
Line 68-78: The Protocol should be made up almost entirely of discrete steps without large paragraphs of text between sections. Please simplify the Protocol so that indivi dual steps contain only 2-3 actions per step and a maximum of 4 sentences per step.

In *Page 3 line 119 - 132*
2.1. For EDLC ink, terpineol, ethyl cellulose, activated carbon (AC), Super-P, polyvinylidene difluoride (PVDF), and Triton-X were used.

2.1.1. Use 2951 μL of terpineol with high viscosity as the solvent and 1.56 g of ethyl cellulose as a thickener. Set the ratio of AC to Super-P to PVDF as 7:2:1 with a total weight of 1.8478 g. In addition, use 49 μL of Triton-X as a surfactant for mixing.

2.1.2. Mix all the materials for 30 min using a planetary mixer. Place the well-mixed electrode material in a cartridge for the inkjet printer and centrifuge it at 115 rcf (relative centrifugal force) for 5 min.

2.2. For the GPE ink, propylene carbonate (PC), PVDF, and lithium perchlorate ($LiClO_4$) were used.

2.2.1. Use PC as the solvent, PVDF as the polymer matrix, and $LiClO_4$ as the salt. Weigh all components of GPE to be the resulting molar concentration of $LiClO_4$ is 1M, and the weight % of PVDF is 5 wt%.

2.2.2. Stir all the components at 140 °C for 1 h until dissolution. After stirring, cool the GPE ink sufficiently and place it into the ink cartridge in the same way as done for the EDLC ink.

Comment 11:
Line 72: Please convert centrifuge speeds to centrifugal force (x g) instead of revoluti ons per minute (rpm).

In *Page 3 line 124-126*
2.1.2. Mix all the materials for 30 min using a planetary mixer. Place the well-mixed electrode material in a cartridge for the inkjet printer and centrifuge it at 115 rcf (relative centrifugal force) for 5 min.

Comment 12:

Line 81: Please specify where the “Print” and “Simple” button/clicks are located.

In *Page 4 line 135*

3.1. Run the printer program, click the “Print” button, select “Simple”, and select the “Flexible Conductive ink” in order as shown in **Figure 2**.

In *Page 9 line 353 – 356*

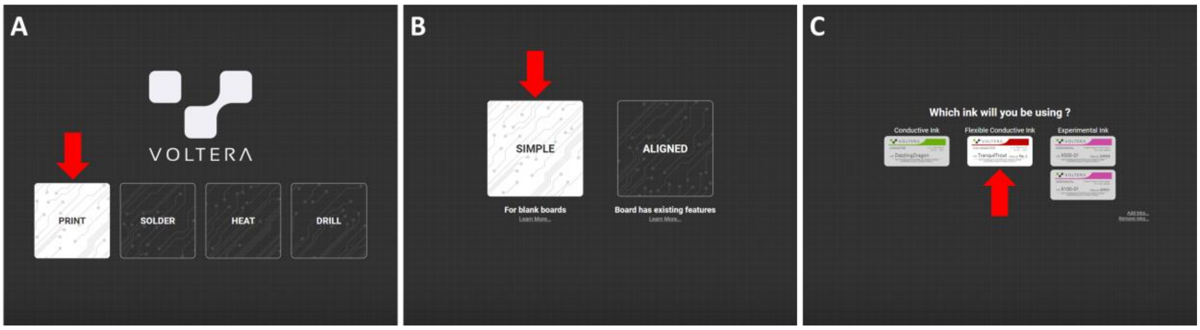

Figure 2. Image of the printer program window. (**A**) The first screen of the program and red arrow shows where the “Print” button is. (**B**) The second screen of the program and red arrow shows where the “Simple” button is. (**C**) The third screen of the program. Red arrow shows which ink should be selected.

Comment 13.
Line 82: How is the file uploaded?

In *Page 4 line 137-139*
3.2. Upload the designed pattern Gerber file by click the first red arrow of **Figure 3.**, choose the Gerber file of the conductive line as the second arrow, and click the third arrow in order. And click the "Next" pointed to by the 4th arrow.

In *Page 9 line 358*

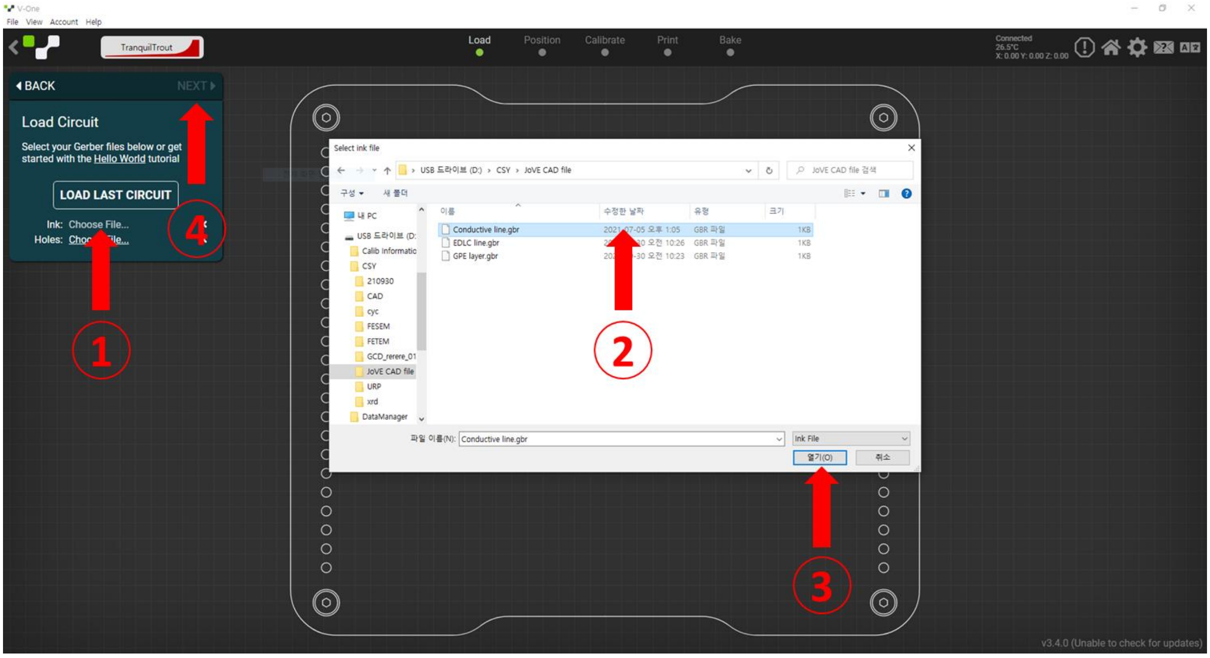

Figure 3. The screenshot image of how to upload the designed pattern Gerber file.

Comment 14:
Line83-84: How is the PCB board fixed? What is set at zero point and how?

In *Page 4 line 140*
3.3. After placing and fixing the PCB board as shown in **Figure 4A.**, mount the probe (**Figure 4B.**).

In *Page 9 line 360-361*

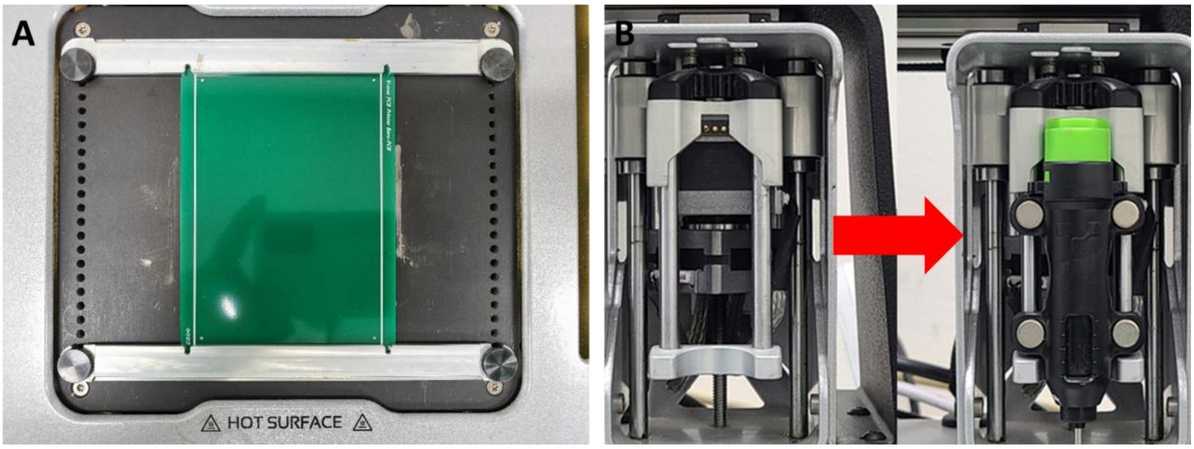

Figure 4. (**A**) The top view image of the PCB printer which holds the PCB board. (**B**) The front view image of the PCB printer which mounted the probe.

In *Page 4 line 142-144*
3.3.1. First, adjust the zero point of the PCB printer through the probe (it is done automatically by clicking the 'Outline' button). The probe will be moved over the PCB board while showing the outline of the pattern, as shown at the bottom right of **Figure 5.**

In *Page 9 line 363*

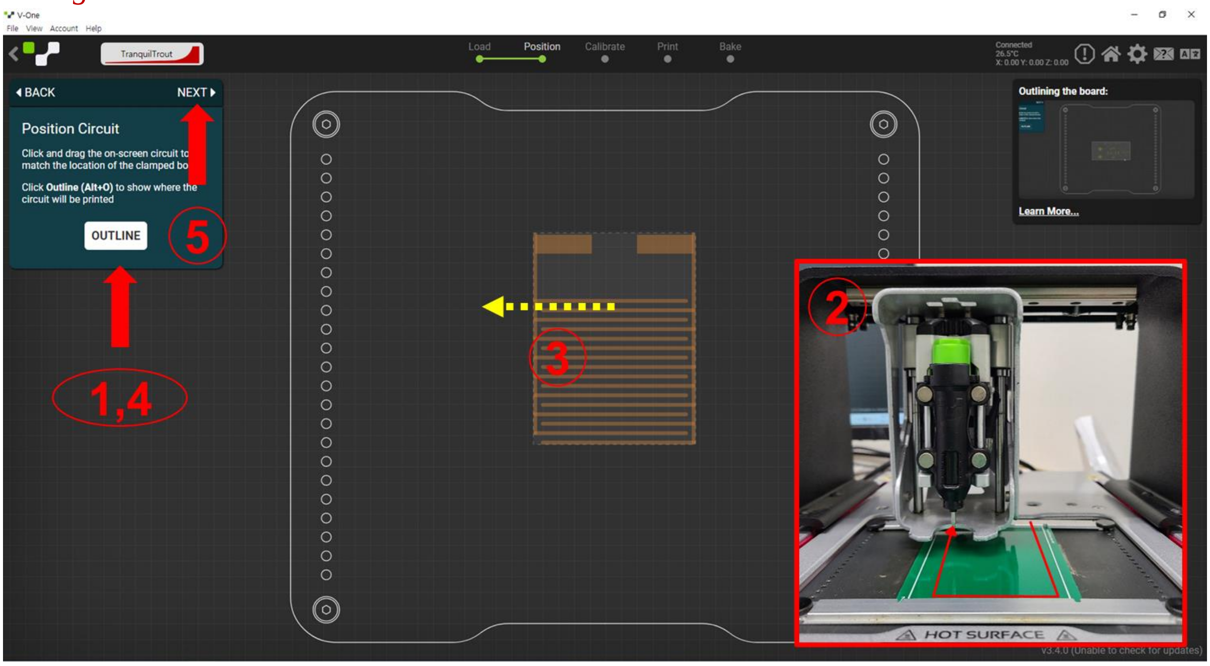

Figure 5. The screenshot image which include the schematic information.

Comment 15:

Line 85: How is it checked? Click "Next" where?

In *Page 4 line 145-147*
3.3.2. And then move the pattern image through dragging the mouse (yellow dash arrow of **Figure 5.**). Then click the "OUTLINE" button once more to check the probe move through the desired path and click the "Next".

In *Page 9 line 363*
Figure 5. The screenshot image includes the schematic information.

Comment 16:
Line 87-88: How is the height measured?

In *Page 4 line 148-149*
3.3.3. Measure the height of the substrate to check whether the substrate is flat (whether there is a height difference or not.). **Figure 6.**

In *Page 9 line 365-367*

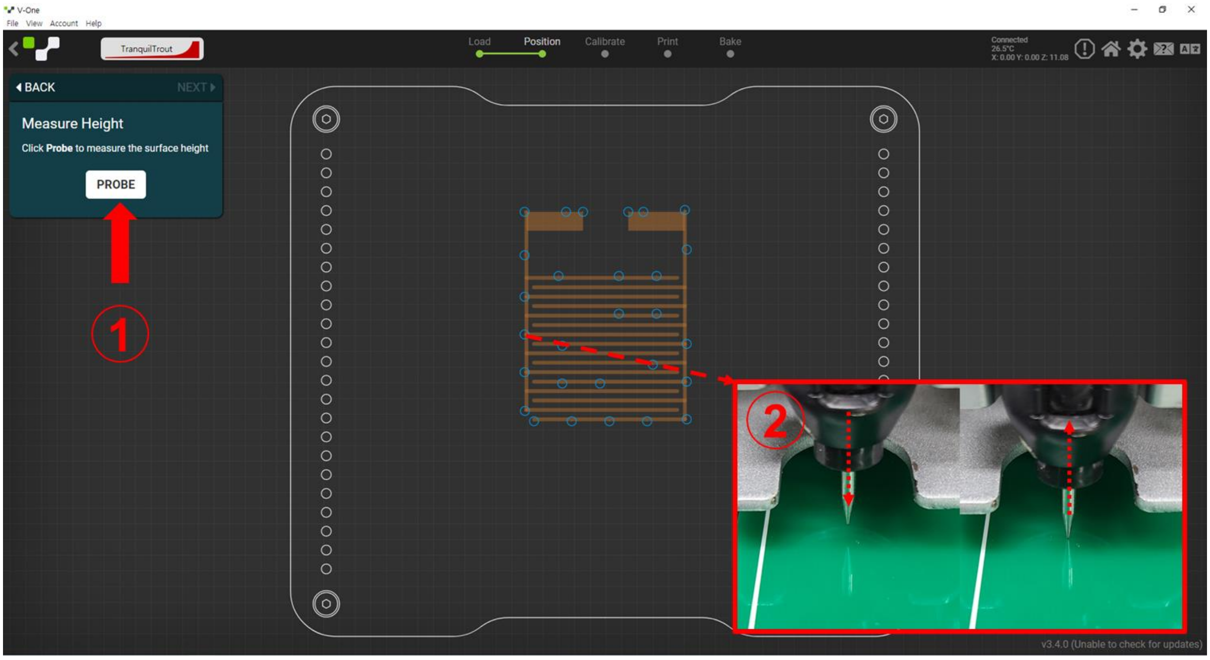

Figure 6. The screenshot image includes the schematic information. Click the "PROBE", then the probe will move to the spot indicated on the screen and move down and up to check the height of the substrate.

Comment 17:
Line 89-90: Please specify the nozzle size?

In *Page 4 line 150-152*
3.3.4. When the height measurement is completed, remove the probe, insert the ink cartridge i nto the ink dispenser, and connect the nozzle (inner diameter: 230µm) to prepare the dispenser.

Comment 18:
Line 91-92: How is the sample pattern printed?

In *Page 4 line 153-154*
3.4. Mount each ink (conductive, EDLC, GPE) dispenser, and print a sample pattern while adjusting the parameters of each ink. **Figure 7.**

In Page 9 line 369-373

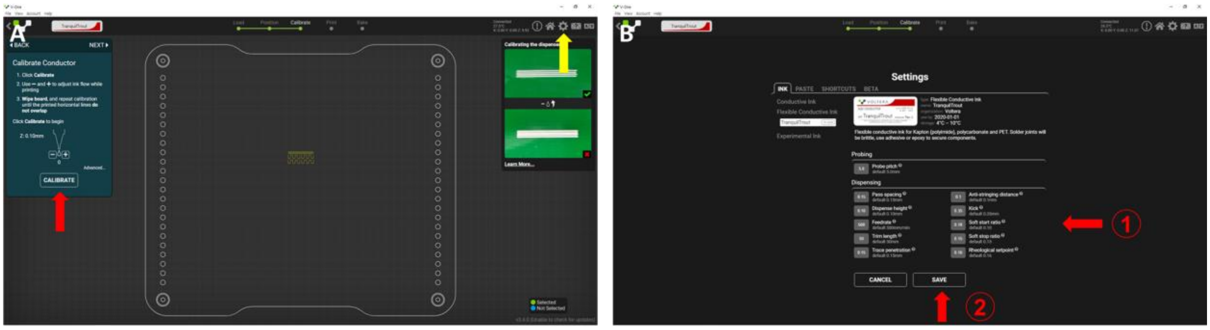

Figure 7. (**A**) The screenshot image showing the procedure of printing sample pattern. The red arrow indicates the button to print the sample pattern and the yellow arrow indicates the button to control the software parameter. (**B**) A window that appears when the yellow arrow of (**A**) is pressed. Software parameters can be modified by changing the values of the first red arrow pointed. Press the second arrow to save the change of the software parameters.

Comment 19:
Line 93: How is the printing result checked visually? Is any instrument used?

In *Page 4 line 155-156*
3.5. Visually check the printing result and record the parameter values for each ink. NOTE: The details are expressed in **REPRESENTATIVE RESULTS.**

Comment 20:
Line 95-106: Please ensure that all the button clicks/ options are included in the prot ocol steps.

In *Page 4 line 159-160*
NOTE: Since steps 4.1. to 4.7. overlap with those shown in **PROTOCOL 3.**, they are summarized as much as possible.

Comment 21:
Line 117: Change the parameter values to what?

In *Page 4 line 166-167*
4.6. Change the software parameter of conductive ink by pressing the setting button. (**Figure 7.** and **Table 1.**)

In *Page 5 line 183*
5.4. Change the software parameter values of EDLC inks. (**Figure 7.** and **Table 1.**)

In *Page 4 line 196*
6.4. Change the software parameter values of GPE inks. (**Figure 7.** and **Table 1.**)

Comment 22:
Please highlight up to 3 pages of the Protocol (including headings and spacing) that identifies the essential steps of the protocol for the video, i.e., the steps that should be visualized to tell the most cohesive story of the Protocol. Remember that non-highlighted Protocol steps will remain in the manuscript, and therefore will still be available to the reader.

Answer)
We highlighted it as a yellow box.

Comment 23:
As we are a methods journal, please revise the Discussion to explicitly cover the following in detail in 3-6 paragraphs with citations:
a) Critical steps within the protocol
b) Any modifications and troubleshooting of the technique
c) Any limitations of the technique
d) The significance with respect to existing methods
e) Any future applications of the technique

Answer)
Thank you for your valuable comment. I recognized that the contents corresponding to b) and d) were insufficient among the details you mentioned. Therefore, the details of the discussion have been reinforced by adding a paragraph as follows.

In *Page 10 line 425-436*
In the fabrication of supercapacitors using inkjet printing, one paper reported that there is still a limit to developing a pattern with uniform and high resolution. It has been reported that high-temperature post-treatment is still necessary, and it is also mentioned that the optimization process of the material is indispensable.[19] Also, in another paper, it was reported that to use inkjet printing properly, it is necessary to adjust the viscosity and surface tension in a relatively narrow range that depends on the printer, and for this purpose, the concentration of the active material of the ink is limited. In some cases, it has been noted that multiple prints are necessary to deposit a sufficient amount of material.[20] In line with this trend, this protocol can help researchers implement patterns with higher resolution by providing precise methods for handling inkjet printers. In addition, if those who have mastered the software control freely, can simplify the manufacturing process by adjusting the software parameters such as Feedrate and Kick without having to print several times to deposit enough material.

Comment 24:
Please revise the table of the essential supplies, reagents, and equipment. The table should include the name, company, and catalog number of all relevant materials in separate columns in an xls/xlsx file. Please sort the Materials Table alphabetically by the name of the material.

Answer)
Thank you for your valuable comment. According to your comment, the Materials Table has been sorted alphabetically, and the molecular weight of the polymer and additional information has been added according to the reviewers' comments.

Response to the Reviewer 1:

In this manuscript authors tried to provide a repeatable protocol in fabricating super-capacitors based on electrical double layers of active carbons via inkjet method. Details are presented well and it may be helpful for researchers in the field. Some minor points should be added before publishing.

Comment 1:

It is strongly suggested to provide some data regarding structural and rheological properties of the ink.

Answer)

Thank you for your valuable comment. We provide the structural and rheological properties of ink as below. In addition, the following information was added and highlighted in the REPRESENTATIVE RESULTS section of the main content.

In *Page 7 line 295-306*

The ink was synthesized according to Protocol 2, and the characteristics of the ink could be confirmed according to the referenced paper.[18] **Figure 8.** shows the structural properties of conductive ink and EDLC ink and the rheological properties of EDLC ink through previous research. It was confirmed that the conductive ink was well sintered to form continuous conducting paths, and the nanoscale roughness is expected to increase the contact area with the EDLC ink (**Figure 8A, B**). EDLC ink was uniformly distributed on the macroscopic scale but had a very rough surface shape on the micro and nanoscale which possibly provides the high surface area and improving the energy storage capacity. All components are well dispersed and there are no visible elements that could cause clogging during printing (**Figure 8C-F**). **Figure 8G** presents the time evolution of the apparent viscosity in the EDLC ink. The viscosity value increased as the shear time increased, and it did not show viscoelastic behavior, which was judged to have shear-thickening behavior without any stress-induced structural extension, stretching, or rearrangement.

In *Page 9 line 386-391*

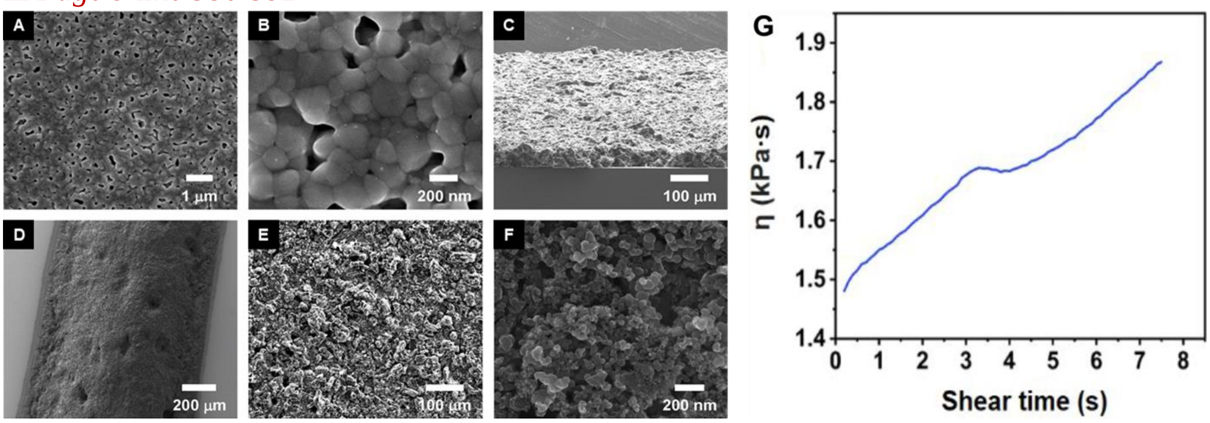

Figure 8. (**A-F**) SEM images of the inks and printed layers. (**A**) Top-view image of the current collector (low magnification). (**B**) Top-view image of the current collector (high magnification).

(**C**) Tilted side-view of the printed EDLC active layer film. (**D-F**) Top-view images of the EDLC active layer with different magnifications. (**G**) Apparent viscosity of EDLC ink versus shear time for constant 0.3 s-1 shear rate experiment. Adapted with permission from [ref]18. Copyright (2020) American Chemical Society

Comment 2:
Some reports like (Inkjet-Printing Technology for Supercapacitor Application: Current State and Perspectives) and (Ti-rich TiO2 Tubular Nanolettuces by Electrochemical Anodization for All-Solid-State High-Rate Supercapacitor Devices) could be added to the references.

Answer)
Thank you for your valuable comment. Thanks to the papers you recommended, my views on fields such as supercapacitors and the use of supercapacitors using inkjet printing have been broadened, and I have been able to support the background knowledge that is lacking in the introduction and discussion of this paper. The corrections and additions are as follows.

In *Page 2 line 44-47*
Supercapacitors, including pseudocapacitors and electrochemical double-layer capacitors (EDLCs), are emerging as energy storage devices that can complement conventional lithium-ion batteries.[12,13]

13. Qorbani, M., Khajehdehi, O., Sabbah, A. & Naseri, N. Ti-rich TiO2 Tubular Nanolettuces by Electrochemical Anodization for All-Solid-State High-Rate Supercapacitor Devices. *ChemSusChem.* **12** (17), 4064-4073, (2019).

In *Page 10 line 408-410*
It has been reported that high-temperature post-treatment is still necessary, and it is also mentioned that the optimization process of the material is indispensable.[20]

20. Sajedi-Moghaddam, A., Rahmanian, E. & Naseri, N. Inkjet-Printing Technology for Supercapacitor Application: Current State and Perspectives. *ACS Applied Materials & Interfaces.* **12** (31), 34487-34504, (2020).

Response to the Reviewer 2:

This manuscript presents the protocol of controlling inkjet printer to fabricate supercapacitors. However, I do not think the work is of broad interest to the society. Below are my comments.

Comment 1:

The fabricated supercapacitors are not of good EDLC performance. Although the authors claim (in Line 272) that the CV curves are of typical box shape of an EDLC, the CV curves in Figure 9 actually indicates lens-like shape with not-identified peaks. The obtained gravimetric capacitance of 5.74 F/g is not of significance as compared with many other printed supercapacitors.

Answer)

Thank you for your valuable comment. This paper was written by JoVE's policy. We focused on how to fabricate the energy storage device with inkjet printing method, not a new or advanced electrochemical performance. The electrochemical results are just an example, and we know that novelty is not a requirement for publication in JoVE. As the reviewer said, its performance is insufficient compared to other supercapacitors up to now. However, the researcher who has an interest in the printing method can refer to this paper.

Comment 2:

The majority of the protocol is for the description of the software operation, even including button clicking. However, in my opinion, such a protocol is of limited interest. In addition, the process parameters may be strongly case-dependent, as all of them need to be changed/optimized once different inks and substrates are used.

Answer)

In this paper, we proposed the optimization steps for the printing of supercapacitor in detail. By editorial comments, it was also required to add more details to the protocol steps. We think that the experimental details are very important for the readership of *JoVE*. If you try to use different materials for inks and substrates, you can follow the steps in this paper and adjust the values according to your materials.

Comment 3: The key information of many materials is missing, such as the suppliers and molecular weight of polymers. It will greatly reduce the reproducibility of the protocol.

Answer)

Thank you for your valuable comment. JoVE does not include commercial expressions in the manuscript. Therefore, additional information such as the suppliers and molecular weight of polymers are mentioned in the Table of Materials. We mentioned it in more detail in the Comments/Description part in the Table of Materials to reflect your opinions.

Comment 4:

In Line 274, it is claimed the EDLCs attain gravimetric capacitance of 5.74 F/g and areal capacitance of 19.9 F/cm^2. Does it imply the material loading is about 3 g/cm^2? Then how much is the thickness of the printed devices?

Answer)

Thank you for your valuable comment. Thanks to your comment, I found some errors in the calculation of areal capacitance and cell capacitance. As a result of the recalculation, areal capacitance came out to be 142 mF/cm^2, and cell capacitance came out to be 178 mF/cm^2. These results have been edited and inserted into the text as follows.

In *Page 8 line 340-341*

The gravimetric capacitance, areal capacitance, and cell capacitance were 5.74 F/g, 142 mF/cm^2, and 178 mF/cell, respectively, for a scan rate of 5 mV/s.

Comment 5:

In the title, inkjet printer is mentioned. But in the main text, it looks a direct filament writing printer (Line 53) is used. It is better to explain the inconsistency.

Answer)

Thank you very much. The term ‘direct filament writing’ should be changed to ‘direct ink writing’. As follows the reviewer's comment, the manuscript is revised.

In *Page 2 line 56-57*

The designed patterns were printed using an inkjet printer because it has precise control through software, high material throughput, and printing stability.

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