Video Article

Inkjet Printing All Inorganic Halide Perovskite Inks for Photovoltaic Applications

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Abstract

A method for synthesizing photoactive inorganic perovskite quantum dot inks and an inkjet printer deposition method, using the synthesized inks, are demonstrated. The ink synthesis is based on a simple wet chemical reaction and the inkjet printing protocol is a facile step by step method. The inkjet printed thin films have been characterized by X-ray diffraction, optical absorption spectroscopy, photoluminescent spectroscopy, and electronic transport measurements. X-ray diffraction of the printed quantum dot films indicates a crystal structure consistent with an orthorhombic room temperature phase with (001) orientation. In conjunction with other characterization methods, the X-ray diffraction measurements show high quality films can be obtained through the inkjet printing method.

Video Link

The video component of this article can be found at https://www.jove.com/video/58760/

Introduction

Dieter Weber synthesized the first organic-inorganic hybrid halide perovskites in 1978[1,2]. Roughly 30 years later in 2009, Akihiro Kojima and collaborators fabricated photovoltaic devices using the same organic-inorganic hybrid halide perovskites synthesized by Weber, namely, $CH_3NH_3PbI_3$ and $CH_3NH_3PbBr_3$[3]. These experiments were the beginning of a subsequent tidal wave of research focusing on the photovoltaic properties of organic-inorganic hybrid halide perovskites. From 2009 to 2018, the device power conversion efficiency dramatically increased from 3.8%[3] to over 23%[4], making organic-inorganic hybrid halide perovskites comparable to Si-based solar cells. As with the organic-inorganic halide-based perovskites, the inorganic halide-based perovskites started gaining traction in the research community around 2012 when the first photovoltaic device efficiency was measured to be 0.9%[5]. Since 2012 the all inorganic halide-based perovskites have come a long way with some device efficiencies measured to be over 13% as in the 2017 study by Sanehira *et al.*[6] Both the organic-based and inorganic-based perovskites find applications related to lasers[7,8,9,10], light emitting diodes[11,12,13], high energy radiation detection[14], photo detection[15,16], and of course photovoltaic applications[5,15,17,18]. Over almost the past decade, many different synthesis techniques have emerged from scientists and engineers ranging from solution processed methods to vacuum vapor deposition techniques[19,20,21]. The halide perovskites synthesized using a solution-processed method are advantageous as they can easily be employed as inks for inkjet printing[15].

In 1987, the first reported use of inkjet printing of solar cells was presented. Since then, scientists and engineers have sought ways to successfully print all inorganic solar cells with attractive performance properties and low implementation costs[22]. There are many advantages to inkjet printing solar cells, as compared to some of the common vacuum based fabrication methods. An important aspect of the inkjet printing method is that solution-based materials are used as inks. This opens the door for trials of many different materials, such as inorganic perovskite-based inks, which can be synthesized by facile wet chemical methods. In other words, inkjet printing of solar cell materials is a low-cost route to rapid prototyping. Inkjet printing also has the advantages of being able to print large areas on flexible substrates and print by design at low temperatures in atmospheric conditions. Furthermore, inkjet printing is highly suitable for mass production allowing for realistic low cost roll-to-roll implementation[23,24].

In this article, we first discuss the steps involved with synthesizing inorganic perovskite quantum dot inks for inkjet printing. Then, we describe the additional steps for preparing inks for printing and the actual procedures for inkjet printing a photoactive film using a commercially available

inkjet printer. Finally, we discuss the characterization of the printed films which is necessary to ensure the films are of proper chemical and crystal composition for high quality device performance.

Protocol

CAUTION: Please consult the lab's material safety data sheets (MSDS) before proceeding. The chemicals used in these synthesis protocols have associated health hazards. Additionally, nanomaterials have additional hazards compared to their bulk counterpart. Please use all appropriate safety practices when performing a nanocrystal reaction including the use of a fume hood or glovebox and the proper personal protective equipment (safety glasses, gloves, lab coat, pants, closed-toe shoes, *etc.*).

1. Precursor Synthesis

1. Cesium oleate precursor synthesis
   NOTE: Cesium oleate is synthesized under a N_2 environment.
   1. Add 0.203 g of cesium carbonate (Cs_2CO_3), 10 mL of octadecene (ODE), and 1.025 mL of oleic acid (OA) to a three necked round bottom stirring flask. The three necked round bottom flask for cesium oleate precursor is labeled 1 in **Figure 1a**.
   2. Place a thermometer or thermocouple into one of the necks *via* a rubber stopper.
   3. Place a rubber septum into one of the remaining necks and then attach the third and final neck to a nitrogen gas line *via* a Schlenk line. Place the mixture under a gaseous nitrogen atmosphere.
   4. Heat the mixture to 150 °C with constant stirring at a stirring speed of 399 mm/s using a 2.54 cm magnetic stir bar until the Cs_2CO_3 fully dissolves.
   5. Lower the temperature to 100 °C to avoid precipitation and decomposition of the cesium oleate and leave stirring at the same stirring speed as in step 1.1.4.

2. Oleylamine-$PbBr_2$ precursor synthesis
   NOTE: Oleylamine-$PbBr_2$ precursor is synthesized under a N_2 environment.
   1. Add 37.5 mL of ODE, 7.5 mL of oleylamine (OAm), 3.75 mL of OA, and 1.35 mmol of $PbBr_2$ into another three necked round bottom stirring flask. The three necked round bottom stirring flask for OAm-PbBr2 is labeled 2 in **Figure 1a**. **Figure 1b** shows the unmixed precursor solution.
   2. Place a thermometer or thermocouple into one of the necks and place some sort of polymer film around thermometer/thermocouple to seal neck, see **Figure 1**.
   3. Place a rubber stopper in one of the remaining necks and then attach the third and final neck to a nitrogen gas line via a Schlenk line. Place mixture under gaseous nitrogen atmosphere.
   4. Heat the mixture to 100 °C with constant stirring at a stirring speed of 599 mm/s using a magnetic stir bar until the $PbBr_2$ is fully dissolved. The precursor solution under constant stirring is shown in **Figure 1c** and the fully dissolved precursor solution is shown in **Figure 1d**.
   5. Heat the mixture to 170 °C with constant stirring, notice the mixture undergoes a color change to dark yellow once reaching 170 °C as seen in **Figure 1d**. Leave stirring under 170 °C heat.

2. CsPbBr$_3$ Quantum Dot Synthesis

1. Using a 2 mL glass syringe, with a 10 cm long 18 gauge needle, extract 1.375 mL of cesium oleate precursor from three neck flask through the rubber septum as shown in **Figure 2a**.
2. Quickly inject, *via* the rubber septum, the 1.375 mL of cesium oleate precursor into the three neck flask containing the OAm-$PbBr_2$ precursor, as shown in **Figure 2b**. There should be an observable color change, a brilliant yellow-green, as shown in **Figure 2c**.
3. After injecting the cesium oleate precursor, wait 5 s, remove the three neck flask from the heat, and immerse the three-neck round bottom flask into an ice/water bath at 0 °C, as shown in **Figure 3a**.
4. Separate the solution in the three neck flask equally into 2 test tubes, roughly 25 mL per test tube.
5. Add 25mL of acetone to each supernatant solutions, then separate with centrifuge using parameters below.
6. Separate the quantum dots using a centrifuge at 2431.65 x g for 5 min at room temperature setting, as shown in **Figure 3b**.
7. Separate the supernatant and centrifuged quantum dots, as shown in **Figure 3c**, by pouring the supernatant into an empty test tube.
8. Finally, dissolve the separated quantum dots in 10-25 mL of hexanes or cyclohexanes. This solution can then be used as an ink in the inkjet printer cartridges for printing thin films.
   NOTE: A commercially available inkjet printer was used to print all the quantum dot thin films of the inorganic halide-based perovskite inks. In this protocol substrates of amorphous glass and Indium tin oxide coated polyethylene terephthalate (ITO/PET) were used during measurements. To ensure that the substrate surface is clean before printing, the substrates were cleaned using an acetone wash followed by a methanol wash.

3. Cleaning the Printer Head

1. First make sure the printer is plugged in and the power turned on to gain access to the ink cartridges and printer head.
2. Remove the ink cartridges from the printer head, open the top of the printer and wait for the ink cartridges to return to the center position and the red lights underneath the ink cartridges to be illuminated, and then remove all cartridges.
3. Move the print head slightly to the right and pull out the guard on the ink tray so that it allows the tray to stay in place as shown in **Figure 4**. Reach to the back of the ink tray and pinch the plastic divider separating the two halves of the print head. Pull gently and the print head will be easily removed.

4. To clean the print head, prepare a dish with a few millimeters of warm water. Place the print head in the water with the slits at the bottom submerged. Avoid contact between the green electronic parts on the back and the water because this has the potential to do damage to the print head.
5. Use a pipette and warm water to drop water on the resistors. Leave the print head sitting in warm water for 1-2 h.
6. Once finished soaking in warm water, place the printer head on a lab tissue and leave to dry at least 20 min. Avoid wiping the bottom of the print head because the fibers from the wipe can get stuck in the slits where ink is dispensed.
7. Return the print head to its position and push the guard back to its original position.

4. Printing Perovskite Quantum Dot Inks

NOTE: This protocol uses an inkjet printer that includes the ability to print CD labels onto CDs with the aid of a rigid CD disc tray. It is recommended before printing perovskites, that one cut out a preferred shape and size of the substrate and then print the exact size and shape of the desired substrate on the CD disk itself using black ink, as shown in **Figure 5**.

1. Draw a straight line at the edge of the disk and continue it onto the CD disc tray. This way, the CD template can be lined up the same way every time and ensure the inks print in the desired location.
2. Place the substrate over the ink images printed on the disk. The substrate can be held in place using double sided tape or some other adhesive, as shown in **Figure 5**b.
3. Before filling the ink cartridges, ensure the orange cover is installed correctly on the bottom of the ink cartridge, as shown in **Figure 6a**. This will prevent ink from spilling out the bottom of the cartridge.
4. Once the ink solution is made, as in step 2.9, and the cover is on the cartridge, use a pipette to inject the quantum dot ink into the top of the ink cartridge, as shown in **Figure 6**a.
   NOTE: The quantum dot ink will be absorbed by the sponge until it becomes saturated and the remaining ink will be stored in the compartment beside the sponge. Avoid over-filling this compartment, because ink can escape from the top when it becomes nearly full.
5. Once the cartridge is filled to the desired amount, plug the top with the rubber stopper and carefully remove the orange bottom cover. Be prepared for a little ink to escape through the bottom when performing this action.
6. Place the ink cartridge in the printer head and be sure it snaps into place, as shown in **Figure 6b**, be sure to insert the remaining cartridges, either empty or full before continuing to next step, as shown in **Figure 6**c.
7. Close up the printer and wait for the printer head to return to the far right-hand side of the printer.
8. Make sure the color of the images being printed corresponds to the ink cartridge color containing the quantum dots. A solid image of cyan, magenta, or yellow have been found to work best (black is tricky because there are two black cartridges).
9. Click print at the bottom right-hand corner and follow the on-screen instructions.
10. While the printer is warming up, check that the disk is properly aligned on the disk tray, such that the image on the screen will print exactly where expected.
11. An instruction will appear on the screen that directs the user to open the disk cover on the printer and insert the disk tray containing the disk into the machine. Perform this action and then press the resume (orange blinking) button on the printer or click the "OK" button on the screen, as shown in **Figure 7a** and **7b**.
12. At this point the printer will accept the disk tray and print perovskites on the substrate, after printing is complete; check that the inks actually printed onto the substrate as clogging is a common problem.
    1. Hold an ultra violet (UV) lamp over the substrate, if the printing did not work there will be something similar to **Figure 7**c; otherwise there will be luminescing film as in **Figure 7**d if the above protocol worked properly.

Representative Results

Crystal Structure Characterization

Characterizing the crystal structure is vital regarding the synthesis of the inorganic perovskites. X-ray diffraction (XRD) was performed in air at room temperature on a diffractometer using a 1.54 Å wavelength Cu-K$_\alpha$ light source. Using the above protocols should lead to a room temperature orthorhombic crystal structure for the CsPbBr$_3$ quantum dot inks as shown in **Figure 8**a.

The XRD results, as shown in **Figure 8**a, indicate that the crystalline CsPbBr$_3$ QD inks maintain an orthorhombic room temperature perovskite structure after the inkjet printing process, in good agreement with reports in literature[8,15,25,26]. The Scherrer equation[27] can be used in conjunction with a standard Lorentzian distribution fitting function of the (220) Bragg peak, to determine the quantum dot size , which in this case is roughly 5.5 nm in diameter. The Scherrer equation is shown below,

$$D = \frac{k\lambda}{\beta \cos \theta}$$

where D is the diameter of the quantum dot, *k* is a dimensionless shape factor, *λ* is the X-ray wavelength, *β* is the full-width at half-maximum of the peak in radians, and *θ* is the Bragg diffraction angle. A shape factor, *k* = 0.89 which is used for cube like nanoparticles, was utilized in the calculations[28].

Optical Absorption and Photoluminescence Spectroscopy Characterization

It is well known that the optical properties of these inorganic perovskite quantum dots are sensitive to quantum dot size and stoichiometry of the inorganic (cation) and halide (anion) atoms. Small changes in either the size or stoichiometry of the quantum dots will lead to different absorption and luminescence profiles. Optical absorption and photoluminescence were performed with a Deuterium-Halogen light source equipped with an UV-Near Infrared (UV-NIR) high resolution spectrometer, where the deuterium lamp wavelength range is 210-400 nm and the Halogen lamp wavelength range is 360-1500 nm. In **Figure 8**b, the photoluminescence profile (black curve) for $CsPbBr_3$ is shown and the peak position is ≈ 520 nm. Similarly, in **Figure 8**b, the optical absorption profile (red curve) for $CsPbBr_3$ is shown with an excitonic peak observed around 440 nm. The above protocol if successfully executed should result in a photoluminescence and absorption profile as shown in **Figure 8**b.

Electronic Transport Characterization

A sourcemeter, a picoammeter, and a multimeter were used to measure the current-voltage (I-V) curves. An impedance analyzer was used to measure capacitance-voltage (C-V) curves. I-V and C-V measurements were taken for printed films under dark and light conditions, as shown in **Figures 8c** and **8d**. Without illumination a dark current of 1.3 pA at 1.0 V applied voltage was measured. Under illumination, with light source fluences of 14.1 mW/cm^2, the measured current increased linearly to 2.64 mA at 1.0 V applied voltage. The appearance of a significant non-zero current, under light illumination, indicates that the film is photoactive. The films can exhibit very high on/off ratios, as high as 10^9, which suggests good potential applications related to photodetection.

The films exhibit very low capacitance under dark conditions when no illumination is present, as can be seen in **Figure 8**d. Under light illumination the zero-bias measured capacitance increases to 14.45 nF. When under light illumination a measured non-zero capacitance at zero-bias is another indication that the films are photoactive.
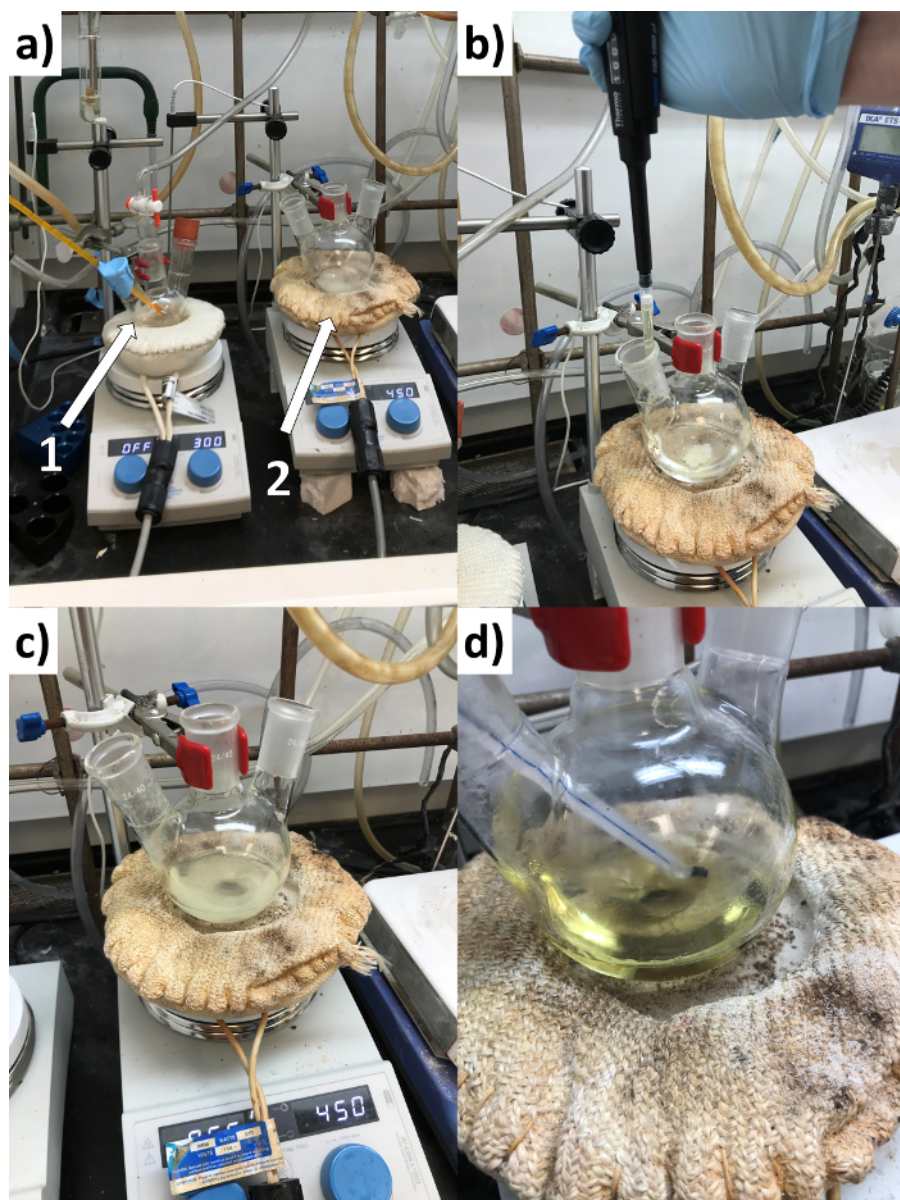
Figure 1: Quantum Dot Precursor Synthesis. (a) The cesium oleate precursor in three necked flasks labeled 1 and the OAm-PbBr$_2$ precursor in three necked flask labeled 2. (b) Putting oleylamine and PbBr$_2$ into three necked flask. (c) Mixing and heating OAm-PbBr$_2$ precursor solution. (d) OAm-PbBr$_2$ precursor has fully dissolved, notice the dark yellow color change. Please click here to view a larger version of this figure.
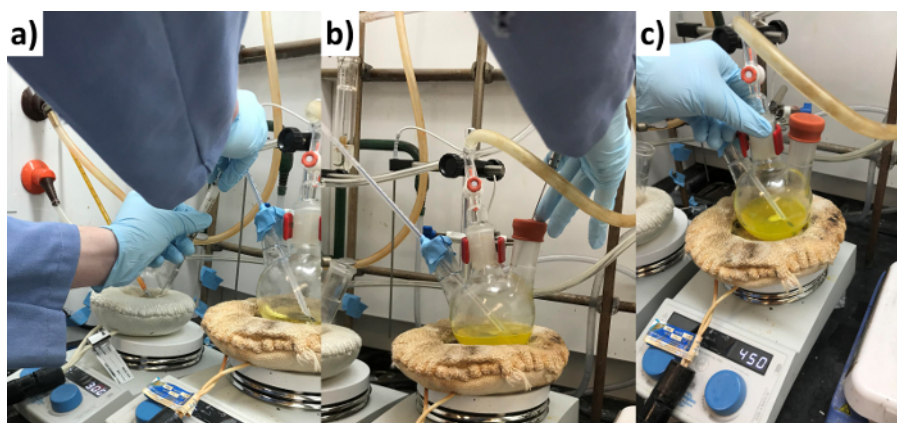
Figure 2: Precursor Injection Method. (a) Extracting 1.375 mL of cesium oleate for injection. (b) Injecting cesium oleate into OAm-PbBr$_2$ solution. (c) Rapid color change and formation of quantum dot solution. Please click here to view a larger version of this figure.
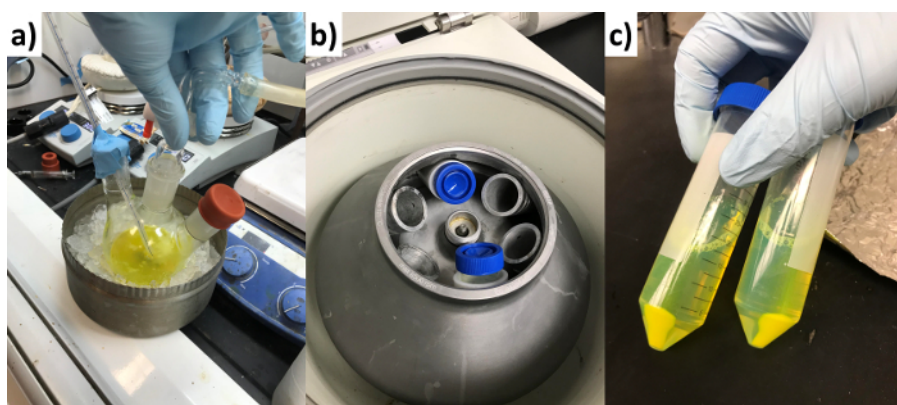

Figure 3: Ice Bath and Centrifuging. (a) The synthesized quantum dot solution placed in ice bath (b) Two tubes with equal amounts of solution placed in centrifuge. (c) The quantum dot powder at the bottom of test tube with the supernatant solution on top, post centrifuging. Please click here to view a larger version of this figure.
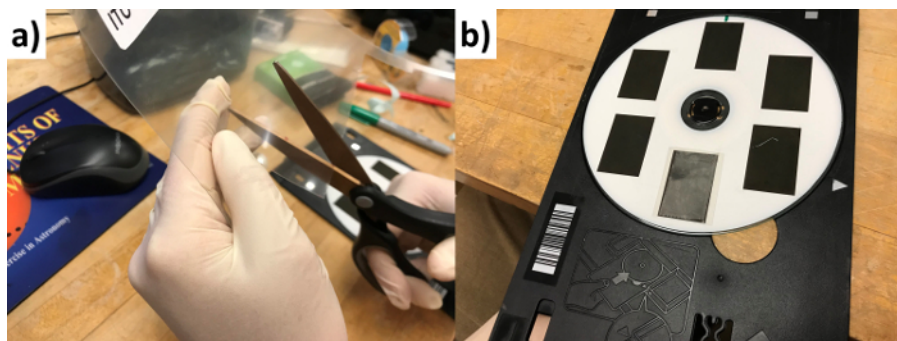

Figure 4: Cutting Substrate and Attaching to Printing Template. (a) Cutting out ITO/PET substrate. (b) The printing template with attached substrate. Please click here to view a larger version of this figure.
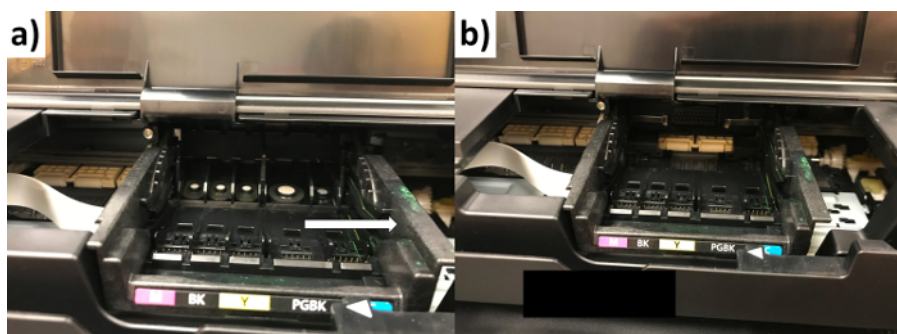
Figure 5: Removing Print Head. (a) The print head can be removed by pushing right slightly as indicated by arrow. (b) After the print head has been removed. Please click here to view a larger version of this figure.
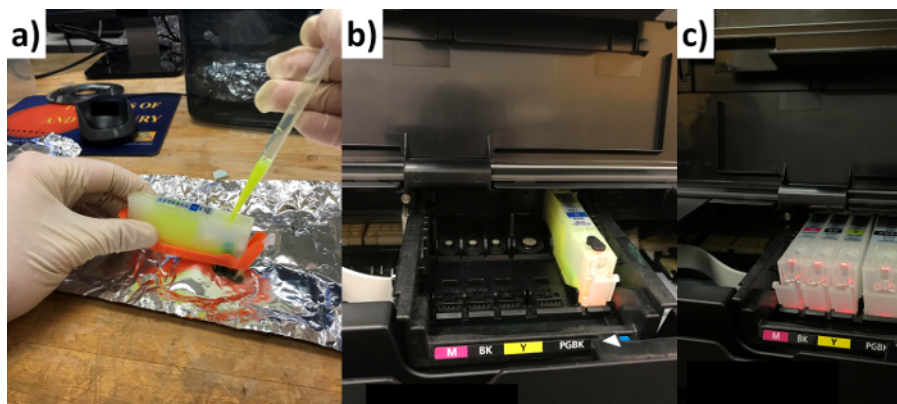

Figure 6: Loading Ink Cartridges with Quantum Dot Inks. (a) Injecting inks into ink cartridges *via* a pipette. (b) Inserting filled ink cartridge into print head. (c) Inserting remaining empty ink cartridges into print head. Please click here to view a larger version of this figure.
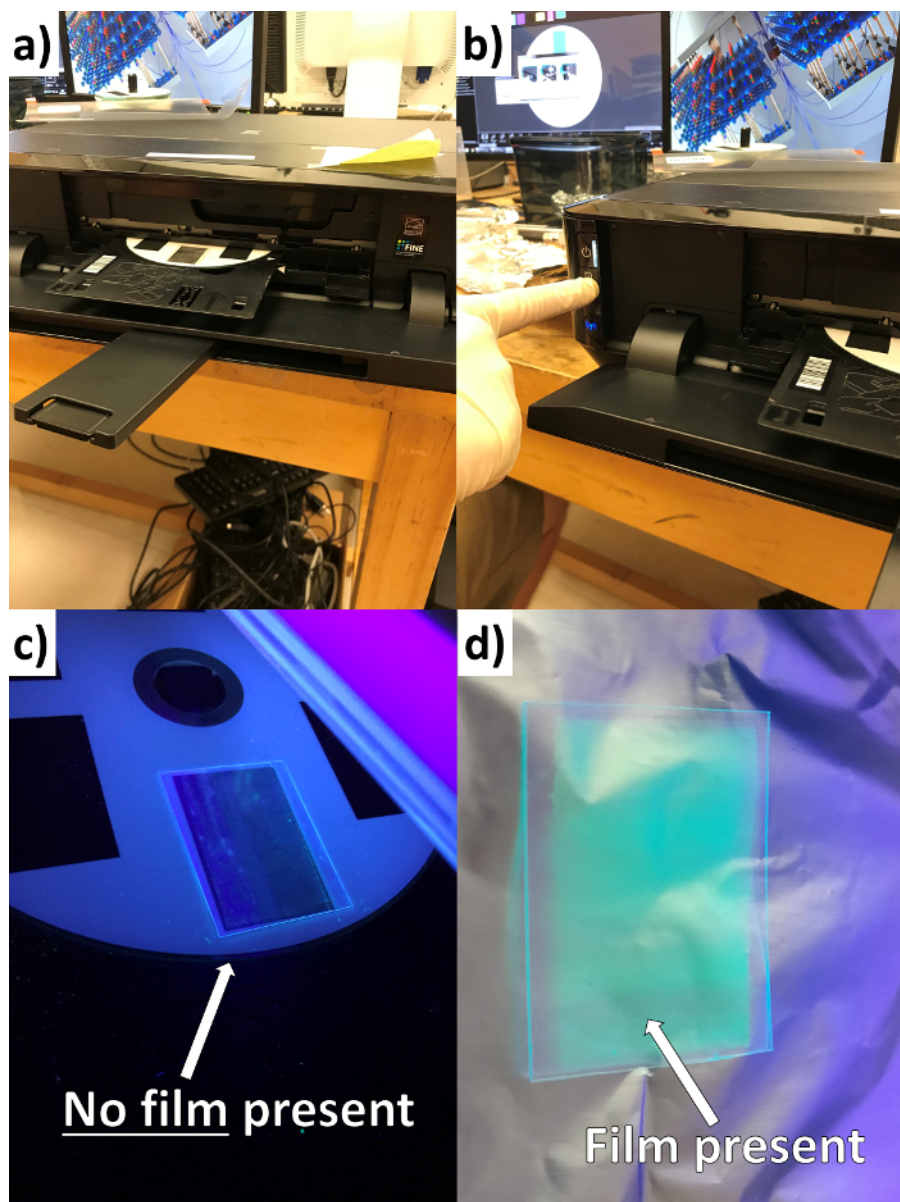
Figure 7: Printing and Quality Check. (a) Inserting the disk tray into the printer. (b) Pressing the orange blinking button to start printing procedure. (c) A failed printing as no film is present under UV illumination. (d) A successful printing as indicated by the presence of film under UV illumination. Please click here to view a larger version of this figure.
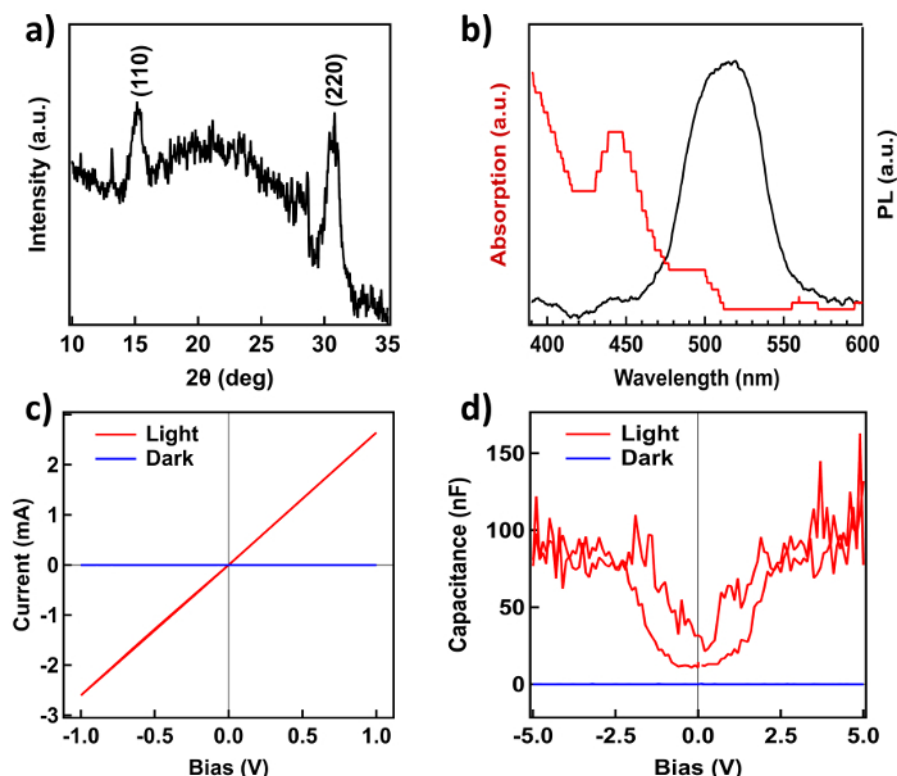
Figure 8: Post Printing Characterization. (a) X-ray diffraction spectrum for $CsPbBr_3$. (b) Optical absorption spectrum (red curve) and photoluminescence spectrum (black curve). (c) Current-voltage spectrum for $CsPbBr_3$ under illumination (red curve) and in the dark (blue curve). (d) Capacitance-voltage spectrum for $CsPbBr_3$ under illumination (red curve) and in the dark (blue curve). Please click here to view a larger version of this figure.

Discussion

There are many parameters involved in the inkjet printing process that affect the final printed film. The discussion of all those parameters is beyond the scope of this protocol, but as this protocol focuses on a solution-based synthesis and deposition method, it is appropriate to give a short comparison to other well-known solution-based deposition methods: the spin-coating method and the doctor-blade method.

The spin-coating method is very fast, produces uniform films, and is low cost. The film thickness can be varied by adjusting the viscosity and rotational speed of the spin coater. Spin-coating is known to be very wasteful, because most of the material is ejected off the surface after spinning. Spin-coating is also slow because the process is sample by sample, thus spin-coating is not suitable for large scale processing. On the other side is the doctor-blade method which is also low cost and simple. The real advantage is the uniform thickness of the films, but the doctor-blade method is very slow and wastes a huge amount of materials. Inkjet printing like both the spin-coating and doctor-blade methods is low cost. The ability to print by design is a major advantage to inkjet printing compared to doctor-blading and spin-coating. Also, inkjet printing is highly efficient in terms of materials used *versus* materials wasted. Inkjet printing is also well suited for large areas and rapid prototyping. These features suggest inkjet printing has a high potential for roll-to-roll manufacturing with an added combinatoric feature.

Although inkjet printing is a promising deposition technique there are some limitations: printer head clogging, limited number of printable solvents, and film homogeneity. The biggest limitation in terms of versatility relates to the solvents used in the printer, not every solvent is appropriate and in some cases can damage the printing components. For example, it is probably not a good idea to use acetone as the ink solvent, as this will dry out or dissolve some of the printer components. Some solvents will cause the expansion of rubber gaskets in the print head and other areas. If any piece seems to have expanded during the printing process, place it in warm water for 10 min and allow it to dry completely, returning it to normal size.

Clogged printer heads are another obstacle and keeping them clean is a critical step in this protocol. The printer components must be kept clean prior to and post printing. The print head contains metallic resistors with rubber gaskets surrounding them in each of the ink cartridge slots. The gaskets serve the purpose of keeping a seal between the ink cartridge and the printer head. It is important to keep the print head and gaskets as clean as possible. Furthermore, be gentle when removing gaskets as they can be damaged upon removal.

The realization of low-cost and high-performance printable solar cell materials is one avenue for achieving high efficiency, high stability, and low-cost energy generation in niche applications, that may still allow for large scale deployment, but where silicon-based materials are not competitive. Moreover, the readily roll-to-roll compatible inkjet printing method provides a foundation for realistically scalable "printable" electronics. With a vast number of available substrates and inks, inkjet printing allows access to the fabrication of lightweight, flexible, low-power electronic devices for a broad range of applications. From transistors to quantum dot displays to photovoltaics, inkjet printing is an exciting

field of device fabrication and shows great promise. If used in conjunction with a set of design rules inkjet printing can be used as a tool for engineering printable materials with desired properties for applications.

Disclosures

The authors have no financial conflicts of interest and have nothing to disclose.

Acknowledgements

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