Video Article

Printing Fabrication of Bulk Heterojunction Solar Cells and *In Situ* Morphology Characterization

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Abstract

Polymer-based materials hold promise as low-cost, flexible efficient photovoltaic devices. Most laboratory efforts to achieve high performance devices have used devices prepared by spin coating, a process that is not amenable to large-scale fabrication. This mismatch in device fabrication makes it difficult to translate quantitative results obtained in the laboratory to the commercial level, making optimization difficult. Using a mini-slot die coater, this mismatch can be resolved by translating the commercial process to the laboratory and characterizing the structure formation in the active layer of the device in real time and *in situ* as films are coated onto a substrate. The evolution of the morphology was characterized under different conditions, allowing us to propose a mechanism by which the structures form and grow. This mini-slot die coater offers a simple, convenient, material efficient route by which the morphology in the active layer can be optimized under industrially relevant conditions. The goal of this protocol is to show experimental details of how a solar cell device is fabricated using a mini-slot die coater and technical details of running *in situ* structure characterization using the mini-slot die coater.

Video Link

The video component of this article can be found at <https://www.jove.com/video/53710/>

Introduction

Organic photovoltaics (OPV) are a promising technology to produce cost-effective renewable energies in the near future.^{1,2,3} Tremendous efforts have been made to develop photo-active polymers and fabricate high efficiency devices. To date, single layered OPV devices have achieved a >10% power conversion efficiency (PCE). These efficiencies have been achieved on laboratory scale devices using spin coating to generate the film, and translation to larger size scale devices has been fraught with significant reductions in the PCE.^{4,5} In industry, roll-to-roll (R2R) based thin film coating is used to generate photon active thin films on conductive substrates, which is quite different from typical laboratory-scale processes, particularly in the rate of solvent removal. This is critical since the morphologies are kinetically trapped, resulting from the interplay between multiple kinetic processes, including phase separation, ordering, orientation and solvent evaporation.^{6,7} This kinetically trapped morphology, though, largely determines the performance of the solar cell devices. Thus, understanding the development of the morphology during the coating process is of high importance for manipulating the morphology so as to optimize performance.

The optimization of the morphology requires understanding the kinetics associated with the ordering of the hole-conducting polymer in solution as solvent is removed;^{8,9} quantifying the interactions of the polymer with the fullerene-based electron conductor;^{10,11,12} understanding the roles of additives in defining the morphology;^{13,14,15} and balancing the relative rates of evaporation of the solvent(s) and additives.¹⁶ It has been a challenge to characterize the evolution of the morphology quantitatively in the active layer in an industrially relevant setting. Roll-to-roll processing has been studied for the fabrication of large scale OPV devices.^{4,17} However, these studies were performed in a manufacturing setting where large quantities of materials are used, effectively limiting studies to commercially available polymers.

In this paper, the technical details of fabricating OPV devices using a mini-slot die coating system are demonstrated. Coating parameters such as film drying kinetics and film thickness control are applicable to larger scale processes, making this study directly related to industry fabrication. Besides, a very small amount of material is used in the mini slot die coating experiment, making this processing applicable to new synthetic materials. In design, this mini-slot die coater can be mounted onto synchrotron end stations, and thus grazing incidence small angle X-ray scattering (GISAXS) and X-ray diffraction (GIXD) can be used to enable real-time studies on the evolution of the morphology over a wide range of length scales at different stages of the film drying process under a range of processing conditions. Information obtained in these studies can be directly transferred to an industrial manufacturing setting. The small amount of materials used enables a rapid screening of a large number of photo-active materials and their mixtures under various processing conditions.

The semi-crystalline diketopyrrolopyrrole and quaterthiophene (DPPBT) based low band conjugated polymer is used as the model donor material, and (6,6)-phenyl C71-butyric acid methyl ester (PC₇₁BM) is used as the electronic acceptor.^{18,19} It is shown in previous studies that

DPPBT:PC₇₁BM blends form large size phase separation when using chloroform as the solvent. A chloroform:1,2-dichlorobenzene solvent mixture can reduce the size of phase separation and thus increase the device performance. The morphology formation during the solvent drying process is investigated *in situ* by grazing incidence X-ray diffraction and scattering. Solar cell devices fabricated using the mini-slot die coater showed an average PCE of 5.2% using the best solvent mixture conditions,²⁰ which is similar to spin-coating fabricated devices. The mini-slot die coater opens a new route to fabricate solar cell devices in a research laboratory setting that mimics an industrial process, filling a gap in the predicting the viability of these materials in an industrially relevant setting.

Protocol

1. Photon-active Blend Ink Preparation

1. Weigh 10 mg of DPPBT polymer and 10 mg of PC₇₁BM material (chemical structures shown in **Figure 1**). Mix them in a 4 ml vial.
2. Add 1.5 ml chloroform and 75 μ l of 1,2-dichlorobenzene into the mixture.
3. Put a small stir bar into the vial, close the vial with a polytetrafluoroethylene (PTFE) cap, and transfer the vial to a hot plate. Stir at ~400 rpm, and heat at ~50 °C overnight before use.

2. ITO and Wafer Substrate Cleaning and Preparation

1. Load pre-patterned indium tin oxide (ITO) glass substrate (1 inch by 3 inches, with half removed ITO) or silicon wafer into a Teflon cleaning rack and put the rack into a glass container (**Figure 2**). Add dilute detergent solution (300 ml, 1% universal detergent solution) into the glass container and put the glass container into sonicator and sonicate for 15 min.
2. Remove the detergent and rinse the ITO glass with deionized (DI) water a couple of times. Then add 300 ml DI water into the container, and put the glass container into sonicator for another 15 minutes.
3. Remove the water from the container. Add 300 ml acetone into the container, and sonicate for 15 min.
4. Remove the acetone. Add 300 ml 2-isopropanol into the glass container, and then sonicate for 15 min.
5. Move the cleaning rack out into an oven. Set the oven temperature to 100 °C, and wait 3-5 hr until the ITO glass is completely dried.
6. Take out cleaned substrates. Transfer them into an UV-ozone cleaner or oxygen plasma cleaner. Use high-powered UV-ozone or plasma to clean them for ~15 min according to manufacturer's protocol.
7. Put the cleaned substrate onto a spin-coater, add 150 μ l poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) solution onto the cleaned substrate, and spin coat at 3,000 rpm to coat a ~30 nm thick PEDOT:PSS (PEDOT:PSS 4083) thin film onto either the ITO glass or silicon wafers.
8. Take off spin coated substrates. Transfer the fresh coated substrates onto a heating plate and anneal at 150 °C for 15 min.

3. Active Layer Printing

1. Load substrate. Put the PEDOT:PSS coated ITO substrate onto the base plate of mini slot die coater. Turn on the vacuum pump that is connected to the vacuum chuck of the slot die coater to hold the substrate tightly. (See **Figure 3** to locate different components.)
2. Adjust the position of substrate to put it right beneath printer head. This can be done by using the linear manipulator beneath the substrate plate.
3. Adjust the head tilting using the 2-D tilting manipulator that holds the printing head. Make sure that the head stands vertically on top of the loaded substrate. Note that in this process, the printing head can be lowered close to the substrate. Use the gap between printing head and substrate to show whether the head is tilted or not. This will be extremely useful when a wafer substrate is used, since a minor image of printing head will show up and it will be much easier to check the tilting.
4. Tune the head-to-substrate distance to zero. The vertical motor is coupled with a force sensor. When the printing head is floating, a constant force reading will be obtained (from the weight of printing head and tilting manipulator assemblies). Once printer head touches substrate, the reading will reduce, marking the zero position. See **Figure 4** for the step distance setting. Use jog mode in tuning the distance.
NOTE: The vertical manipulator translational plate is connected to its base using springs and the spring constant varies slightly. Thus small changes in force sensor are inevitable during the experiment.
5. Set a head-to-substrate value to run the experiment. In this experiment, set the head to substrate gap to 100 μ m.
6. Adjust the linear translational stage motor that will be used to print. Find the starting point and end point. Record these values. The travel distance of the linear motor is 100 mm. Here, set 10 mm motor position as the starting point and 80 mm motor position as the end point.
7. Set the printing speed to 10 mm/sec by using the motor controlling software interface (**Figure 4b**). Set the motor acceleration speed to 100 m/sec.
 1. If the motor does not work properly or the software has an error, please restart the software and click "enable" and then "home" in the software interface. Note that during printing process, the printing head remains fixed and the substrate moves to dispense the solution and mimic the industrial printing process.
8. Load DPPBT:PCBM solution (room temperature) into 1 ml syringe and mount the syringe to the syringe pump that is connected to the slot die printer. Set the printing parameters in controlling software (syringe diameter and solution feeding speed, 0.3 ml/min in this case).
9. Start the printing experiment.
 1. Move the substrate to the starting point by typing the starting point position in the position window in controlling software. See **Figure 4c** for details.
 2. Start to pump solution into slot die head by clicking the start in the syringe pump software. Alternatively, manually operate the syringe pump. For each coating, around ~100 μ l of solution will be used. Normally, use 300 μ l solution for first time printing and use ~100 μ l solution for repeated printing.

3. Quickly start the translational motor when the solution starts coming out from the printing head, and the substrate will move to the end position. Please note this is a critical step. Preload the translational motor ending position into the position window, and click enter to start the motor movement.
4. Stop the syringe pump and lift the printing head by using the vertical motor. Turn the vacuum off and take the substrate off the base plate. Note that the dead volume for this printing head is 250 μ l, and thus filling the first time takes more than 250 μ l of solution.
5. Load the printed substrate into a vacuum oven for 3-5 hr to remove residual solvent.
6. Put a Petri dish beneath the printing head. Pump 10 ml chloroform into the printing head to clean the head. Collect the contaminated chloroform solution with the Petri dish. Use cotton swabs to clean the printing head while pumping the cleaning solution. After each coating run, clean the printing head, especially when a different solution is used.
NOTE: The DPPBT:PCBM solution shows a dark green color. When the cleaning is complete, no color can be seen from the chloroform solvent.

4. Cathode Electrode Deposition

1. Load the active layer coated substrate onto shadow masks (**Figure 5**) and mount the mask into the evaporation chamber.
2. Put two thermal evaporation boats in between the electrode studs (**Figure 6a**). Load one boat with LiF salt (barely covering the boat, ~0.2 g) and one boat with aluminum metal (4 pellets).
3. Close the evaporation chamber and pump down the evaporation chamber to about 2×10^{-6} Torr.
4. Set the chamber to deposit 1 nm of LiF followed by 100 nm of aluminum. In the current case, use 20% power for LiF deposition and use 26% power for Al deposition. Shown in **Figure 6b** is the evaporator control interface of the system used in this study.
5. Stop evacuation pumps and fill the chamber with nitrogen gas. When pressure returns to atmosphere pressure, take the substrates out.

5. Photovoltaic Performance Measurement

1. Prepare a glass slide that is half the width of the ITO glass that is used in device fabrication. Carry out this step in a glove box. Paste epoxy glue to one side of the glass substrate, and cover the device area using the epoxy glue coated glass slides (see **Figure 11** for sample device). When the epoxy has cured, the device will be fully sealed.
2. Start the solar simulation lamp and set to AM 1.5 radiation with 100 mW/cm². Stabilize the lamp for about 15 min before measurement. Shown in **Figure 7** is the PV measurement system used in this study.
3. Mount the device under the solar simulator at the instrument suggested distance. Connect the anode and the cathode to the measurement circuit. Record a current-voltage curve using an electrical multimeter using manufacturer's protocol.
4. Determine the performance of the device as follows:
J_{sc}: short circuit current, the maximum current that a solar cell device can deliver;
V_{oc}: open circuit voltage, the maximum voltage that a solar cell device can deliver;
FF: fill factor, the maximum area in I-V curve divided by J_{sc} * V_{oc};
PCE: power conversion efficiency, J_{sc} * V_{oc} * FF / (100 mW/cm²).

6. Synchrotron X-ray Measurement

1. Set up a helium box to suppress air scattering in the X-ray measurement. Mount the mini-slot die coater into the helium box. Shown in **Figure 8** is the experiment setup of grazing incidence X-ray diffraction experiments using a helium box at Advanced Light Source.
2. Mount an optical interferometer onto the printing machine to monitor the thickness change over the solvent evaporation. In this experiment, use an UVX model (e.g., Filmetrix F20). The materials that are used in this experiment have strong light absorption from 300-900 nm wavelength.
 1. Use a source lamp of optical interferometer that avoids material absorption. Use an 1,100-1,700 nm wavelength lamp in this experiment. Pre-calibrate the instrument before experiment following its operation procedures.
3. Put the PEDOT:PSS coated wafer substrate onto substrate holder of the printer and adjust the head and substrate position following step 3.2-3.5. Turn on the vacuum pump and make sure that the wafer substrate sticks to the substrate holder tightly.
4. Purge the helium box to remove air. Note that oxygen level should be less than 0.3 v%, which can be monitored by oxygen sensor.
5. Align the substrate at the position where the X-ray impinges on the substrate (the end position in printing), and set the incidence angle, 0.16° in this case. Align according to beam-line protocol.
6. Set the X-ray exposure time and data acquisition method. Here, use 2 sec as the exposure time, and followed by 3 sec of delay time (to avoid server beam damage). Thus each experiment period will be 5 sec. Carry out a continuous queue of 100 repeats; thus take 100 pictures.
7. Name the experiment and choose the data path to save experimental files. Shown in **Figure 9** is the Advanced Light Source beamline 7.3.3 user interface where the above-mentioned settings can be easily located.
8. Move the substrate to the starting position by entering the starting position in motor controlling software. Start the X-ray shutter and the detector will continuously record diffraction/scattering signals.
9. Start the syringe pump to feed solution into printing head. When the solution begins to eject from the printing head (monitored by a surveillance camera), quickly start the printing process.
NOTE: When the pre-chosen measurement position is reached, 2-D detector will capture the scattering signal from solution. Film thickness will be monitored by interferometer. Thus the thin film morphology evolution will be recorded.
10. Lift up the printer head and clean the head when experiment is done.

Representative Results

Shown in **Figure 3** is the mini-slot die coating system. It consists of one coating machine, one syringe pump and a central control box. The coating machine is the essential part, which is made of a slot die head, one horizontal translational stage, and one vertical translational stage. The slot die head is mounted to the base of a vertical translational motor through a 2-D tilting manipulator. **Figure 10a** shows the printer main body without mounting the printing head from which the 2-D tilting manipulator is highlighted. **Figure 10b** shows the mounting of the printing head to the 2-D tilting manipulator. **Figure 10c** shows an enlarged image of printing head and base plate. A force sensor is built into the vertical translational stage. In experiments, the vertical translational stage is used to adjust head-to-substrate distance, and the 2-D tilting motor is used to adjust the head to be strictly vertical. The force sensor is used to monitor the weight of the slot die head system. Once the head touches the substrate, a jump from positive reading to a negative reading will be observed, indicating the head position. The head is moved up to the desired height to give a certain gap. During printing, the slot die head is fixed and the bottom horizontal translational stage moves. With liquid being dispensed from head slit, a uniform film can be obtained. It should be mentioned that both printer head and substrate plate have refined temperature control systems. A temperature range from room temperature to 150 °C can be used during printing for this system. **Figure 11a** shows an ITO substrate coated with conjugated polymer:PCBM blends. The film is quite smooth visually. It should be noted that the beginning and end of the coated film is not always uniform, due to the formed meniscus and the drying from the edges. If the substrate is long enough or if the substrate is coated in a continuous manner (as with a R2R printer), this issue can be solved.

Freshly coated substrate (glass/ITO/PEDOT:PSS/active layer) is transferred into a vacuum oven over a short period and then loaded into shadow masks. The mask is loaded into evaporator to deposit cathode thin layer. Shown in **Figure 5** is a shadow mask that is used in the experiment. **Figure 11b** shows a completed device after the cathode layer deposition. The device performance is measured using a solar simulator under 100 mW/cm² AM 1.5 condition. Shown in **Figure 12** is a representative current-voltage curve of a mini-slot die coated device. An average power conversion efficiency of 5.2% is achieved for slot die coated devices, which is close to that achieved by spin coating (~5.6% PCE).

The *in situ* GIXD and GISAXS experiments are useful methods to track the morphology evolution of the printed BHJ ink. The polymer crystallization can be tracked by the GIXD experiment and phase separation can be tracked by GISAXS. In experiments, the mini-slot die coater is mounted onto a goniometer inside the helium box (**Figure 13**). The cable connection will be paired and thus, the instruments can be operated outside of the synchrotron hutch. Shown in **Figure 14** is the operating center at the X-ray beamline. The top left computer controls the beamline parameters; the central computer is the beamline operating interface that controls the X-ray shutter and records data; the left computer is the analogue window for two surveillance camera inside the hutch, one focuses on the sample position and one focuses on the slot die head slit and thus can monitor the solution status; the bottom left computer runs horizontal and vertical translational stage motor software and syringe pump control software. Shown in **Figure 15** is a typical *in situ* grazing incidence small angle scattering experiment during solvent drying. The time evolution is color-coded. In the earlier stage of drying (an excess of solvent existed), a red scattering curve is seen, and blends mixed well. A scattering peak gradually developed at around 0.02 Å⁻¹, indicating a ~60 nm of phase separation. This information, when coupled with *in situ* GIXD results, will tell us the kinetics of polymer crystallization and phase separation.

Figure 1: Chemical structure of conjugated polymer DPPBT and chemically modified fullerene PC₇₁BM used in this study. [Please click here to view a larger version of this figure.](#)

Figure 2: 1/3 removed ITO substrates and Teflon rack used in ITO glass cleaning. [Please click here to view a larger version of this figure.](#)

Figure 3: (a) Main body of Mini-slot die coater. The printing head is mounted on the tilting manipulator. The two knobs above the slot die head are used to just tilting of the printing head. A round shape stepper motor is mounted vertically to provide vertical movement of the printing head. The main horizontal translation stage is mounted on the baseboard to provide linear motion to coat the film. Both printing head and substrate base can be heated. (b) Control box with syringe pump mounted on top. The left cube is the controller for the vertical motor; the middle cube is the horizontal motor controller; the right three panels are temperature controller for the head (top), temperature controller for the base (middle), and force sensor. [Please click here to view a larger version of this figure.](#)

Figure 4: Mini-slot die printer motor controlling software interfaces. (a) Main software interface: the vertical stepper motor controlling software is on the top and linear translational motor software is in the bottom; (b) speed setting and acceleration setting interface for both vertical and horizontal translational motor; (c) position setting for horizontal translational motor. [Please click here to view a larger version of this figure.](#)

Figure 5: Shadow mask used in cathode layer deposition. Device substrates will be loaded into the cut area of the mask. The mask will be mounted onto the evaporation chamber, and electrode metal will be deposited through the cut rectangle areas. [Please click here to view a larger version of this figure.](#)

Figure 6: (a) Evaporator and electrode studs layout. In operation, tantalum metal boat will be mounted in-between electrode studs. Electrode metal will be loaded in boat; and electrical current will heat the boat to thermally evaporate electrode metal. (b) Evaporator control interface. [Please click here to view a larger version of this figure.](#)

Figure 7: Standard photovoltaic measurement system. (a) Solar simulator; (b) Solar simulator controller; (c) Solar simulator flux controller. Please click here to view a larger version of this figure.

Figure 8: Grazing incidence X-ray diffraction experiments using helium box. The helium box is used to generate an experimental atmosphere that has less air scattering. Slot die printer is installed inside the helium box during experiment. Please click here to view a larger version of this figure.

Figure 9: The synchrotron beamline control software interface. This interface controls the beamline experiment. The left panel is used to align samples; the right panel controls the X-ray exposure time, experiment name, and displays the scattering signal. Please click here to view a larger version of this figure.

Figure 10: Mini-slot die printer major parts enlarged. (a) Main body of the slot die coater. A vertical motor is coupled with a load cell force sensor and integrated onto a vertical manipulator. A 2-D tilting manipulator is mounted on the vertical manipulator. (b) The printer head that is mounted onto the 2-D tilting manipulator. (c) Zoom in picture of printer head. The head is very close to base plate at this point. [Please click here to view a larger version of this figure.](#)

Figure 11: Photon active layer coated substrate (left) and completed devices after cathode layer deposition (right). [Please click here to view a larger version of this figure.](#)

Figure 12: Current-voltage curve of slot die coated device. Short circuit current, open circuit voltage can be read from the curve-axis intercepts. [Please click here to view a larger version of this figure.](#)

Figure 13: Mini-slot die coater loaded inside helium box in synchrotron station. (a) Front view; (b) side view. Optical interferometer is mounted to monitor the thickness of the coated film. [Please click here to view a larger version of this figure.](#)

Figure 14: Controlling system of *in-situ* mini slot die coating experiment in Advanced Light Source Beamline 7.3.3. Each interface is labeled in the figure. [Please click here to view a larger version of this figure.](#)

Figure 15: Typical GISAXS morphology evolution. Curve fitting is necessary to obtain the information of phase separations. [Please click here to view a larger version of this figure.](#)

Discussion

The method described here focuses on developing a film preparation method that can be easily scaled up in industrial production. Thin film printing and synchrotron morphology characterization are the most critical steps with the protocol. In previous lab scaled OPV research, spin coating is used as the dominant method to fabricate thin film devices. However, this process uses high centrifuge force to spread out BHJ solution, which is quite different from industrial based roll-to-roll fabrication. Thus the knowledge and experience obtained from the spin coating study cannot be directly transferred to large area device fabrication. The mini-slot die coating device presented in the current studies is akin to the industrial film coating device and thus will be ideal for pre-industrial testing. Parameters that control the film morphology, which correspond to device performance, need to be reinvestigated. The material cost in mini-slot die coating is minimal and thus large quantity of device fabrication conditions can be optimized.

A synchrotron measurement is used to determine the morphology evolution of bulk heterojunction (BHJ) solar cell thin films. We carry out grazing incidence X-ray diffraction (GIXD) and grazing incidence X-ray scattering (GISAXS) to monitor the evolution of the structure. It is ideal to run these two experiments together. If not possible, they can be done separately. The only difference between GIXD and GISAXS is the sample-to-detector distance, and thus we only describe the experiment details once. PEDOT:PSS coated silicon wafers will be used as coating substrates. The printing process is the same as the process for device fabrication. It is critical that the printer position on the substrate is well calculated to make sure the right q range can be reached and the substrate starting point and end point can be exposed to X-rays. Also note that in the GIXD experiment, the sample-to-detector distance is small, and the detector is mounted quite close to the helium box. In the GISAXS experiment, a flying tube is necessary to reduce air scattering since the sample-to-detector distance is quite large (~4 m in this experiment setting). Please note that both GIXD and GISAXS measurements are done at the ending position. When the printing process reaches the ending position, the linear translational motor stops, and continuous X-ray scattering/diffraction data is generated. Note that the travel distance for the linear translational stage is 10 cm. At the starting position, the substrate is far from the X-ray beam, and only the transmission signal of background is recorded in the 2-D X-ray detector. When the substrate moves to the measurement position, it will change from transmission scattering to grazing incidence scattering, and this transition can be used as the starting marker of the experiment.

The small size of mini-slot die coater is well-suited for research laboratory use. The consumption of photo-active materials is quite low. Normally, 10 mg of conjugated polymer can make 1-2 ml of solution. The dead volume in the printing head is about 0.25 ml. In each coating experiment, ~0.1 ml is used. Thus, this new method is efficient with material usage. Normally 100-200 mg of materials will be enough to screen a vast matrix of processing conditions, such as blending ratio, solvent choice, thermal annealing, making mini-slot die coating an efficient method in new materials screening. During the printing experiment, make sure that the syringe pump does not exceed its limit. Clean the head properly to dispose of solid buildup inside the head slits; otherwise, it will jam the system. When changing from one solution to another, perform a thorough cleaning; otherwise cross contamination can happen. The photon active polymer shows its distinct color, which can be used as an indicator as whether the head is fully cleaned or not.

The mini-slot die coater can be used in various fields related to thin film processing. In OPV device processing, new parameters can be included. For example, the slot die head temperature can be controlled, and thus a hot solution coating can be achieved. The substrate can also be heated; thus the solvent evaporation rate can be fine-tuned. Different coating speeds can also be used, to vary the shear rate to control morphology. In the current experiments, only the simplest experiment using a hard substrate is demonstrated. Plastic conductive substrates can also be used to fabricate flexible devices. Compared to spin coating, mini-slot die coating provides a processing that is similar to industrial fabrication, which is critical in helping optimizing industrialization of the OPV technique. One major limitation of this technique is that the device fabrication cannot be continuous, which would need a roll-to-roll coating machine. However, the mini-slot die coating can quickly optimize the processing conditions and fast material screening. These observations provide useful insights for roll-to-roll large panel production.

Disclosures

The authors have nothing to disclose.

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