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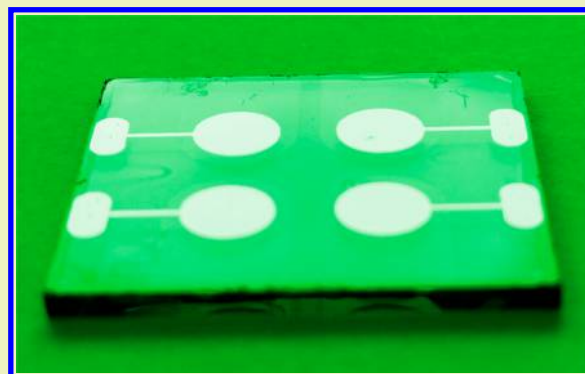
# A Green Approach to Organic Thin-Film Electronic Devices: Recycling Electrodes Composed of Indium Tin Oxide (ITO)

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**S** Supporting Information

**ABSTRACT:** Organic thin-film optoelectronic devices, unlike inorganic analogues, offer the attractive prospect of large, flexible, and inexpensive arrays made by simple procedures such as roll-to-roll printing. In current organic thin-film devices, layers of tin-doped indium oxide (ITO) are widely used as electrodes. Motivated by the increasing price of indium and the high cost of ITO-coated substrates, we have examined ways to recover and recycle ITO substrates in typical devices by environmentally benign methods. A process using only water yields recovered ITO substrates that can be reused at least 10 times to prepare new devices without loss of efficiency.



**KEYWORDS:** Recycling, Tin-doped indium oxide (ITO), Thin-film devices, Solar cells

## INTRODUCTION

Tin-doped indium oxide (ITO) is a conductive solid solution of tin(IV) oxide ( $\text{SnO}_2$ ) in indium(III) oxide ( $\text{In}_2\text{O}_3$ ). It is essentially transparent and colorless in thin layers. Its electrical conductivity, optical transparency, and well-established methods of deposition make it widely used as an electrode in organic thin-film devices such as light-emitting diodes (OLEDs),<sup>1–3</sup> photovoltaic devices (OPVs),<sup>4</sup> and field-effect transistors (OFETs).<sup>5–9</sup> At present, ITO films supported on transparent insulators such as glass are the most frequently encountered electrodes in organic optoelectronic devices.

Despite the popularity of ITO, efforts to develop alternatives are under investigation for multiple reasons.<sup>10</sup> In particular, the growing cost of ITO reflects limited supplies of indium and uncertainty about its availability in the future.<sup>11</sup> Economic analyses have considered the energy required to produce devices, as well as the cost of the basic components. For example, a recent study by Azzopardi et al. attributed 31–51% of the total cost of a standard flexible OPV device to the ITO electrode.<sup>12</sup> In addition, the properties of ITO are not ideal. It can be deposited on flexible substrates such as poly(ethylene terephthalate),<sup>13–15</sup> but layers of ITO crack readily when the underlying substrate is bent, leading to defects in the device.<sup>16,17</sup> Moreover, the preparation of thin layers of ITO requires advanced technology for depositing and doping under vacuum.

Among the potential substitutes are carbon-based alternatives such as nanotubes<sup>18–22</sup> and graphene,<sup>22–24</sup> which have been shown to give flexible layers with 90% transparency and an electrical resistance lower than that of standard ITO.<sup>24,25</sup> Conductive polymers such as poly(aniline)<sup>26–28</sup> and poly(3,4-

ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)<sup>29,30</sup> may also be able to replace ITO in certain applications. Their conductivity is typically lower, but they are more flexible, cheaper, and more easily manufactured and processed by methods that are environmentally benign. Potential inorganic alternatives to ITO include aluminum-, gallium-, or indium-doped zinc oxide (AZO, GZO, or IZO),<sup>31–34</sup> although ITO shows higher resistance to hydrolysis when exposed to water.<sup>35</sup>

Despite the ongoing search for substitutes, most laboratory-scale thin-film organic optoelectronic devices continue to incorporate ITO electrodes, and their performance is increasingly impressive. For example, efficiencies have now reached 10% in photovoltaic devices containing ITO electrodes.<sup>36–42</sup> This has contributed to an international surge of research covering topics such as new photoactive materials, nanomorphology of active layers, and underlying photophysical aspects, all requiring extensive use of glass-coated ITO electrodes. As a result, it has become important to examine the ability to recycle ITO and recover intact working electrodes by suitable treatment of devices no longer needed.

In earlier work related to green thin-film devices, Zhou and co-workers built polymer-based solar cells on free-standing transparent substrates of nanocrystalline cellulose.<sup>43</sup> A degree of recycling was achieved by simply immersing spent cells in water at room temperature, which led to redispersal of the nanocrystalline cellulose and separation of membranes

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consisting of the photoactive polymeric layer and adhering electrodes. The membranes were removed by filtration, and their various components were then separated by extracting the photoactive polymeric layer into organic solvents, leaving behind the components of the electrodes, which were recovered by filtration.

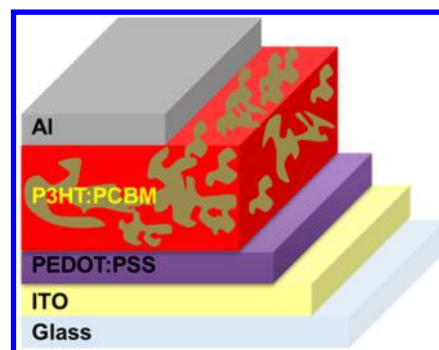
In the present study, we have taken a significant further step forward by developing a method to recover ITO electrodes from representative organic thin-film devices in a way that allows repeated reuse of the electrodes without loss of efficiency. The process is performed in water without using organic solvents. Although our initial study has focused on the use of recycled ITO electrodes in thin-film solar cells, we believe that our method will be effective for recycling ITO electrodes in other types of devices as well.

## EXPERIMENTAL SECTION

**Fabrication of Thin-Film Photovoltaic Devices.** Thin-film devices were fabricated by a standard protocol. ITO-coated glass slides (12 mm  $\times$  18 mm, with a standard resistivity of about 20  $\Omega$ /square) were purchased from Colorado Concept Coatings, Limited, and used as substrates for the construction of devices. The glass/ITO substrates were cleaned in an ultrasonic bath using deionized water, acetone, ethanol, and isopropanol in sequence. The cleaned substrates were then exposed to UV/ozone for 15 min to destroy any residual contaminants.<sup>44</sup> An aqueous dispersion of PEDOT:PSS (PH1000, Clevios) was initially filtered using a PTFE filter (0.45  $\mu$ m) and was then deposited on the cleaned substrate by spin coating in air at 25  $^{\circ}$ C, using a speed of 4000 rpm during 1 min. The samples then were heated in air at 110  $^{\circ}$ C for 30 min. The thickness of the resulting film of PEDOT:PSS was determined by profilometry to be 30  $\pm$  4 nm.

All subsequent manipulations and characterizations were carried out in a glovebox under  $N_2$  with residual concentrations of  $O_2$  and  $H_2O$  below 0.1 ppm. Poly(3-hexylthiophene) (P3HT; Rieke, Inc. and Solaris Chem, Inc.) and phenyl- $C_{61}$ -butyric acid methyl ester (PCBM; Solaris Chem, Inc.) were used as received. Blends of P3HT and PCBM have been extensively used as the active layer in molecular photovoltaic devices.<sup>45,46</sup> P3HT, which acts as an electron donor, exhibits good solubility in standard organic solvents, suitable chemical stability, relatively low band gap ( $\sim$ 2 eV), and high mobility of holes.<sup>46</sup> PCBM, which acts as an electron acceptor, also has adequate solubility and complementary electronic properties.<sup>46</sup> A mixture of P3HT and PCBM (1:0.8 by weight) was stirred at 45  $^{\circ}$ C overnight in chlorobenzene to give a solution containing 10 mg of P3HT per mL. The solution was then deposited on the underlying PEDOT:PSS layer by spin coating at 1000 rpm for 90 s. The thickness of the resulting active layer was measured to be 100  $\pm$  5 nm. Finally, a top electrode of Al (100 nm) was thermally deposited on the P3HT:PCBM layer under vacuum ( $2 \times 10^{-6}$  Torr). This resulted in thin-film devices with the following sequence of layers: glass/ITO/PEDOT:PSS/P3HT:PCBM/Al (Figure 1). To increase the photovoltaic performance of the resulting devices, improved organization of P3HT and PCBM in the active layer was achieved by thermal annealing in a glovebox at 160  $^{\circ}$ C for 30 min.<sup>46</sup>

**Assessment of Performance of Thin-Film Photovoltaic Devices.** Current density–voltage ( $J$ - $V$ ) curves were measured using a Keithley 2400 Source Measure Unit. The photocurrent was measured under standard illumination (AM1.5G, 100 mW/cm<sup>2</sup>) using a 150 W Oriel solar simulator. The intensity of light was determined using a monosilicon detector calibrated by the National Renewable Energy Laboratory. The reported measures of photovoltaic performance (current density, open-circuit voltage, fill factor, and power conversion efficiency) were taken as the average of the values determined for all devices. It should be noted that our devices were built with a cross bar configuration, and photovoltaic performances were measured using a shadow mask with an aperture that determined the active area of the devices (12.6 mm<sup>2</sup>). In this way, overestimations of performance were avoided.<sup>47–50</sup>



**Figure 1.** Schematic representation of thin-film photovoltaic devices subjected to recycling.

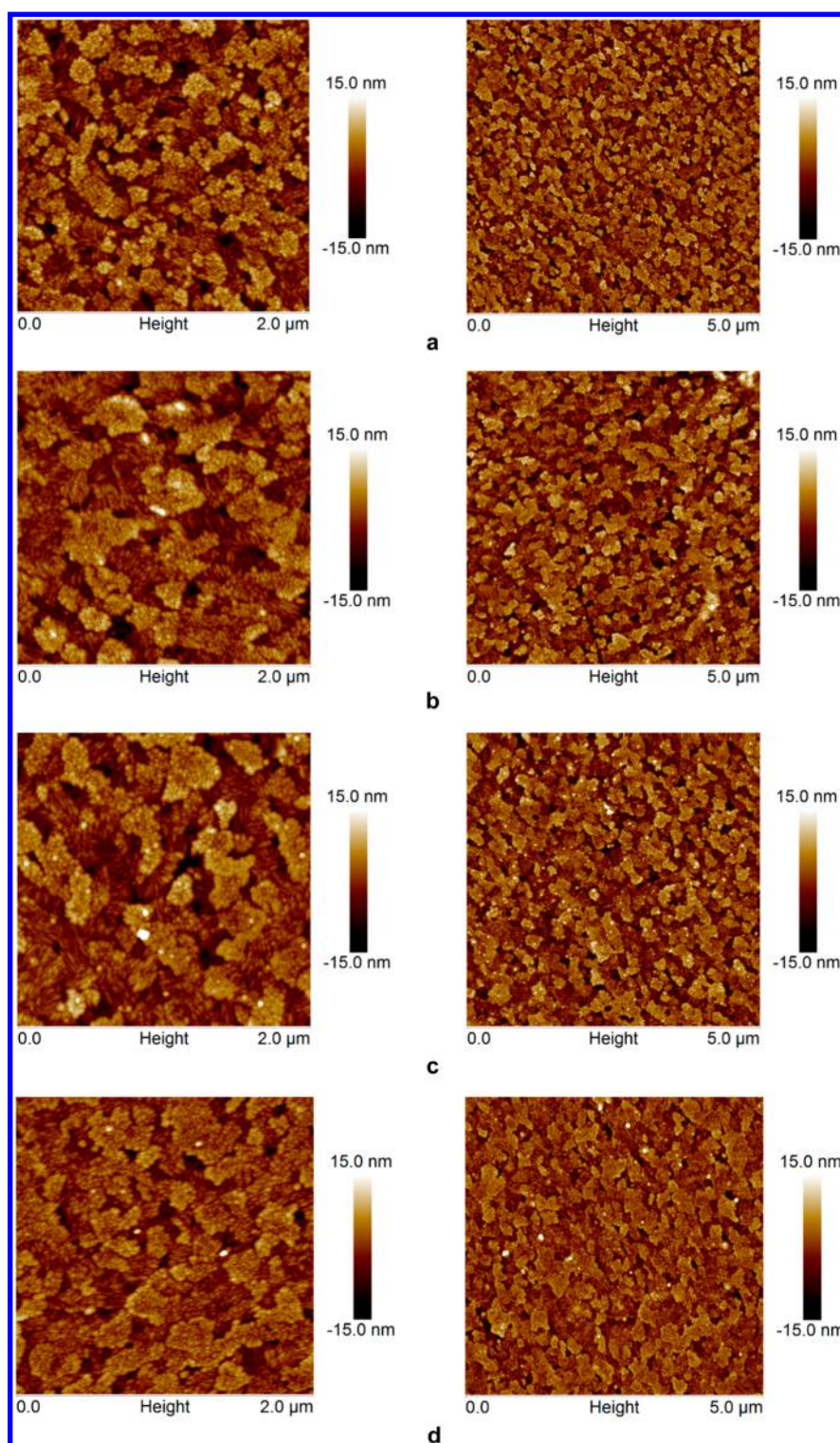
### Recycling by Recovering Glass/ITO Substrates and Reusing Them To Fabricate New Thin-Film Devices.

Devices prepared with pristine ITO substrates are considered to be reference cells and are labeled  $C_0$ , whereas cells derived from recycled ITO substrates are labeled  $C_n$ , where  $n$  is the number of previous uses of the substrate. After measurements of performance were completed, reference cells were immersed in water in a Branson 3510 ultrasonic cleaner and sonicated at 45  $^{\circ}$ C. After 15 min, ITO substrates were freed of supernatant layers of Al, P3HT:PCBM, and PEDOT:PSS. Substrates could also be cleaned by sonication at 25  $^{\circ}$ C, but the process was slower ( $>60$  min). Cleaned substrates were then used to prepare new thin-film devices according to the protocol described above, starting with the same ultrasonic washings with solvents and exposure to UV/ozone, followed by deposition of PEDOT:PSS, P3HT:PCBM, and the top electrode of Al. The resulting cells, containing ITO recycled once, are labeled  $C_1$ . These cycles were repeated to demonstrate the ability to create new devices incorporating ITO recycled multiple times. In each cycle, we simultaneously fabricated devices using pristine ITO substrates, and we used these devices as benchmarks to allow their photovoltaic performance to be compared with that of recycled cells obtained in the same cycle. Sets of at least 16–20 devices of each type (pristine and recycled ITO) were prepared and characterized to assess the reproducibility of our methods. In standard testing, the PEDOT:PSS layer remained in contact with the underlying ITO substrate for approximately 48 h, which is the normal interval between the deposition of PEDOT:PSS and the steps of recycling. However, we also tested ITO substrates recovered from devices of the same type after extended storage in ambient light for periods of over one year.

**Characterization of Morphology of ITO by Atomic Force Microscopy (AFM).** AFM images were acquired in air at 25  $^{\circ}$ C using a Digital Instruments MultiMode microscope and extended Nano-scope IIIa controller (Bruker, Santa Barbara, CA). Intermitent contact imaging (“tapping mode”) was performed at a scan rate of 1 Hz using Al-coated etched silicon cantilevers (ACTA probes from Applied NanoSystems, Inc.) with a resonant frequency around 300 kHz, spring constant of  $\sim$ 42 N/m, and tip radius of  $<10$  nm. All images were acquired with medium tip oscillation damping (20–30%).

**Characterization of the Surface of ITO by X-ray Photoelectron Spectroscopy (XPS).** XPS studies were conducted using a VG ESCALAB 3 MKII spectrometer at a base pressure below  $1 \times 10^{-10}$  Torr with nonmonochromated Mg  $K\alpha$  radiation ( $h\nu = 1256.4$  eV). For all data collected, the size of the spot analyzed was 2 mm  $\times$  3 mm, and the electrons were detected at a takeoff angle of 90 $^{\circ}$ . The power of the X-ray source was 300 W (15 kV and 20 mA). For survey scans, the pass energy was set to 100 eV, with an energy step size of 1 eV. For high-resolution scans, the pass energy was set to 20 eV, with an energy step size of 0.05 eV. Spectra were analyzed with VG Advantage software v. 4.12; high-resolution spectra were fitted using symmetrical Gaussian–Lorentzian curves, keeping the fwhm of component peaks for each element fixed and allowing the binding energy and intensity of peaks to vary. Charge correction was performed with respect to  $C_{1s}$  of adventitious carbon at a binding energy of 285 eV.





**Figure 2.** Topographic AFM images of the surfaces of pristine and recycled films of ITO. (a) Reference  $C_0$  ( $R_{\text{RMS}} = 4.17$  nm for sample shown; average  $R_{\text{RMS}} = 4.13 \pm 0.10$  nm). (b)  $C_1$  ( $R_{\text{RMS}} = 3.85$  nm for sample shown; average  $R_{\text{RMS}} = 3.78 \pm 0.09$  nm). (c)  $C_3$  ( $R_{\text{RMS}} = 3.97$  nm for sample shown; average  $R_{\text{RMS}} = 4.18 \pm 0.09$  nm). (d)  $C_8$  ( $R_{\text{RMS}} = 3.25$  nm for sample shown; average  $R_{\text{RMS}} = 3.32 \pm 0.09$  nm).

**Measurements of Resistance Using the 4-Point Probe Method.** The sheet resistance of glass/ITO substrates was measured using a 4-point probe system (Microworld S302 K-Standard). Measurements were performed on 8–12 substrates.

**Measurements of Thickness of Layers.** The thickness of layers of was measured using a Dektak 150 stylus profilometer (Veeco). Measurements were performed on at least eight substrates.

## RESULTS AND DISCUSSION

### Overview of Procedure for Recycling ITO Electrodes.

The feasibility of recycling ITO electrodes was tested by using thin-film photovoltaic cells as representative devices. The devices were fabricated with a standard architecture (Figure 1) according to the protocol set out in the Experimental Section. Subsequent sonication of the devices in water removed upper

layers and freed the underlying glass/ITO substrates, which could be recovered, examined by various analytical methods, and reused to produce new devices. Water is presumably effective because it can penetrate and solubilize the adjacent ionic layer of PEDOT:PSS.

#### Surface Properties of Recycled ITO Substrates.

Analysis by AFM confirmed that the surfaces of commercial thin films of ITO are textured, and it suggests that grains are formed during the process of sputtering under vacuum, with an overall roughness that can vary somewhat even within a single batch of ITO. However, Figure 2 shows that the morphology of ITO changes little as a result of recycling. Pristine ITO shows clusters with diameters of 100–200 nm, which can be resolved into individual grains with diameters of 20–40 nm (Figure 2a). It should be noted that the surfaces of at least two samples were analyzed by AFM, and both individual and average values of root-mean-squared roughness ( $R_{\text{RMS}}$ ) are shown in Figure 2.

Both pristine and recycled ITO (Figure 2a) show cornflake-like clusters of small grains, although the clusters are slightly larger after recycling and the surface is somewhat smoother. These small changes may result from contact with PEDOT:PSS. The dispersions of PEDOT:PSS used for spin coating have a pH of  $\sim 2$  and may initially etch the underlayer of ITO,<sup>51</sup> but subsequent recycling does not appear to lead to further changes of morphology.

Analysis of the surfaces of pristine and recycled ITO by XPS showed no contamination by sulfur derived from PEDOT:PSS or other sources.<sup>52</sup> Table 1 summarizes relative atomic

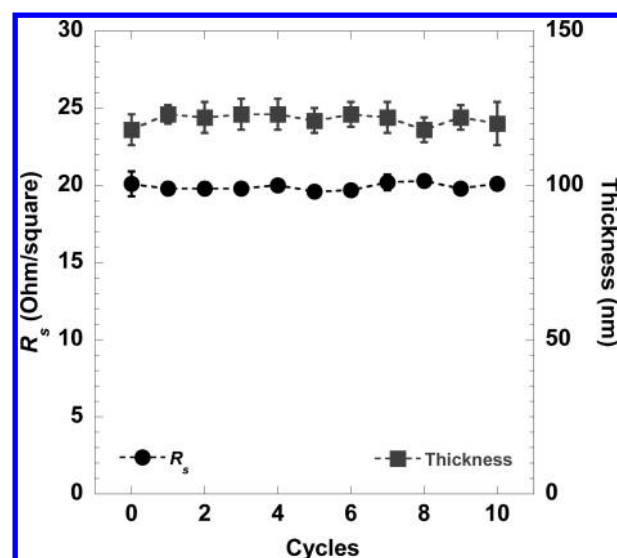
**Table 1. Relative Atomic Concentrations for Pristine ITO ( $C_0$ ) and Recycled ITO ( $C_1$ ) as Measured by XPS (atomic %), along with Corresponding In/Sn and O/In Ratios**

|       | C 1s | O 1s | In 3d <sub>5/2</sub> | Sn 3d <sub>5/2</sub> | In/Sn | O/In |
|-------|------|------|----------------------|----------------------|-------|------|
| $C_0$ | 11.0 | 58.3 | 26.7                 | 4.6                  | 5.8   | 2.18 |
| $C_1$ | 13.7 | 57.8 | 24.2                 | 4.3                  | 5.6   | 2.39 |

concentrations measured on the surface of pristine ITO ( $C_0$ ) and recycled ITO ( $C_1$ ). It should be noted that these samples were cleaned ultrasonically with solvents and exposed to UV/ozone before analysis, as in the protocol used to fabricate photovoltaic devices. Ex situ analysis by XPS could not distinguish between carbon remaining on the samples due to insufficient cleaning and carbon derived from atmospheric recontamination. Differences observed in the composition of pristine ITO ( $C_0$ ) and recycled ITO ( $C_1$ ) are small, which is consistent with the close similarity of the AFM images.

Measurements using a 4-point probe showed that the sheet resistance of ITO substrates remains essentially constant, even after recycling 10 times (Figure 3). This observation confirms observations by AFM that surface morphology is virtually unchanged and supports the conclusion that layers of ITO are not significantly altered by the fabrication of cells and subsequent recycling. In particular, the thickness of the layers was found to remain essentially constant at  $\sim 120$  nm (Figure 3).

**Performance of Photovoltaic Devices Prepared with Pristine ITO (Reference Cells).** Photovoltaic devices prepared using pristine ITO substrates according to the protocol set out in the Experimental Section showed efficiencies of about 2.5%, which is standard for cells incorporating active layers of P3HT:PCBM.<sup>45</sup> It should be noted that our devices have the simplest possible architecture



**Figure 3.** Sheet resistance and thickness of layers of ITO on glass substrates before and after recycling ( $C_0$ – $C_{10}$ ).

(glass/ITO/PEDOT:PSS/P3HT:PCBM/Al), were produced without incorporating buffer layers such as LiF or other metal oxides, and were characterized using a mask with the same area as the Al electrode, so their performance was not overestimated.<sup>47,48</sup>

**Performance of Photovoltaic Devices Prepared with Recycled ITO.** Characteristics of devices incorporating recycled ITO ( $C_1$ – $C_{10}$ ) are summarized in Figure 4 and compared with those of cells containing pristine ITO ( $C_0$ ). Values of open-circuit voltage ( $V_{oc}$ ), current density ( $J_{sc}$ ), fill factor, and power conversion efficiency (PCE) showed no major changes. In our protocol for assessing the effects of using recovered ITO, each cycle of fabrication included devices made using pristine ITO substrates. This allowed us to compare the performance of new and recycled cells obtained in the same cycle of fabrication, thereby permitting the calculation of normalized values of PCE that take into account minor variations between batches of cells. When this is done, no significant variation in the normalized values of PCE can be seen.<sup>52</sup> Similar results were obtained when ITO-coated glass substrates obtained from other suppliers were recycled.<sup>52</sup> Together, these data thereby establish the feasibility of reusing ITO electrodes many times.

The essentially unaltered performance reflects the fact that the morphology and composition of the layer of ITO remain substantially unchanged, despite direct contact with the adjacent conductive layer of PEDOT:PSS, which ensures the transport and collection of holes.<sup>53–56</sup> Our study has focused primarily on recycling ITO substrates in prototypical laboratory-scale devices that have been used for relatively short periods of time. However, we have also tested ITO substrates recovered from devices of the same type after exposure to ambient light for over one year. Again, devices made with the recycled substrates show no significant variation in the values of  $V_{oc}$ ,  $J_{sc}$ , fill factor, and PCE.<sup>52</sup> These observations indicate that our protocol for recycling ITO substrates is likely to be broadly effective even after extended use.

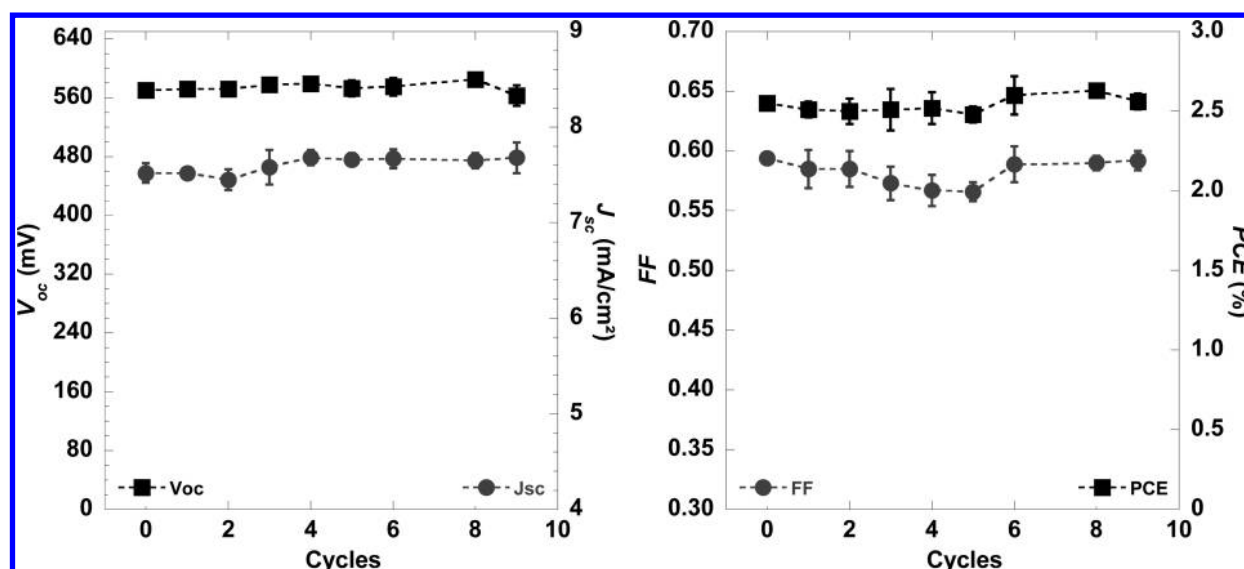


Figure 4. Performance of photovoltaic devices incorporating pristine ( $C_0$ ) and recycled ITO-coated glass substrates ( $C_1$ – $C_9$ ).

## CONCLUSIONS

Our work has established a reliable process for recovering and recycling ITO electrodes used as an underlying substrate for fabricating representative organic thin-film optoelectronic devices. In our process, sonication in water is used to remove the upper layers of the devices, including the top Al electrode, P3HT:PCBM active layer, and adjacent thin film of PEDOT:PSS. Minor morphological and compositional changes in the ITO underlayer are observed but do not appear to alter the performance of photovoltaic devices made using recycled ITO.

Even after extended use in working devices, ITO electrodes can be recycled by our process at least 10 times without losing their ability to be incorporated in photovoltaic devices that meet normal standards of efficiency. Recycling the components of photovoltaic devices with alternative architectures and compositions is currently under investigation. In addition, our method promises to be useful for recovering and recycling ITO electrodes in other thin-film devices such as OLEDs and OFETs. Furthermore, our method is expected to preserve layers of ITO with complex patterns created by techniques such as photolithography and wet chemical etching, thereby allowing more sophisticated and costly devices to be reused.

## ASSOCIATED CONTENT

### Supporting Information

Additional experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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