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Abstract:	The photoactive layer, of a typical, organic thin film bulk-heterojunction (BHJ) solar cell commonly uses fullerene derivatives as electron accepting materials. However, fullerene derivatives are air-sensitive; therefore, air-stable materials are needed as alternative materials. In the present study, we propose and describe the properties of Ti-alkoxide as an alternative electron accepting material to fullerene derivatives for highly air-stable BHJ solar cells. On the other hand, it is well-known that controlling the morphology in the photoactive layer, which is constructed by fullerene derivatives as the electron acceptor, is important for obtaining a high overall efficiency by the solvent method. However, the conventional solvent method is useful for using high-solubility materials such as fullerene derivatives. However, for Ti-alkoxides, the conventional solvent method is insufficient because they only dissolve in specific solvents. Here, we demonstrate a new approach to morphology control using the molecular bulkiness of Ti-alkoxides without the conventional solvent method. That is, this method is one approach for obtaining highly efficient air-stable organic-inorganic bulk-heterojunction solar cells.
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Cover Letter

August 29, 2016

Dr. Jaydev Upponi
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Dear Dr. Upponi:

Thank you for your letter dated August 17, 2016, which details your review of our article. We have given careful consideration to your feedback, and the comments from the reviewers, and are hereby resubmitting the manuscript for your consideration.

Our replies to each individual comment are provided in a separate document.

Thank you for your consideration. We look forward to hearing from you again.

Sincerely,

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TITLE:

Morphology control for fully-printable organic-inorganic bulk heterojunction solar cells based on a Ti-alkoxide and semiconducting polymer

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SHORT ABSTRACT:

A method for fully-printable, fullerene-free, highly air-stable, bulk-heterojunction solar cells based on Ti alkoxides as the electron acceptor and the electron-donating polymer fabrication is described here. Moreover, a method for controlling the morphology of the photoactive layer through the molecular bulkiness of the Ti-alkoxide units is reported.

LONG ABSTRACT:

The photoactive layer of a typical organic thin-film bulk-heterojunction (BHJ) solar cell commonly uses fullerene derivatives as the electron-accepting material. However, fullerene derivatives are air-sensitive; therefore, air-stable material is needed as an alternative. In the present study, we propose and describe the properties of Ti-alkoxide as an alternative electron-accepting material to fullerene derivatives to create highly air-stable BHJ solar cells. It is well-known that controlling the morphology in the photoactive layer, which is constructed with fullerene derivatives as the electron acceptor, is important for obtaining a high overall efficiency through the solvent method. The conventional solvent method is useful for high-solubility materials, such as fullerene derivatives. However, for Ti-alkoxides, the conventional solvent method is insufficient, because they only dissolve in specific solvents. Here, we demonstrate a new approach to morphology control that uses the molecular bulkiness of Ti-alkoxides without the conventional solvent method. That is, this method is one approach to obtain highly efficient, air-stable, organic-inorganic bulk-heterojunction solar cells.

INTRODUCTION:

Organic photovoltaic devices are considered promising renewable energy sources due to their low manufacturing cost and light weight[1-7]. Because of these advantages, a large number of scientists have been immersed in this promising area. In the past decade, dye-sensitized, organic thin-film, and perovskite-sensitized solar cells have achieved significant progress in power conversion efficiency in this area[8].

Specifically, organic thin-film solar cells and BHJ organic thin-film solar-cell technology are efficient and cost-effective solutions for the utilization of solar energy. Furthermore, the energy conversion efficiency has reached over 10% with the use of low-band-gap polymers as the electron donor and fullerene derivatives as the electron acceptor (Phenyl-C61-Butyric-Acid-Methyl Ester: [60]PCBM or Phenyl-C71-Butyric-Acid-Methyl Ester: [70]PCBM)[9-11]. Moreover, some researchers have already reported the importance of the BHJ structure in the photoactive layer, which is constructed with low-band-gap polymers and fullerene derivatives to obtain a high overall efficiency. However, fullerene derivatives are air-sensitive. Therefore, an air-stable electron-accepting material is required as an alternative. A few reports previously suggested new types of organic photovoltaic cells that used n-type semiconducting polymers or metal oxides as electron acceptors. These reports supported the development of air-stable, fullerene-free, organic thin-film solar cells[12-15].

However, in contrast to fullerene systems or n-type semiconducting polymer systems, obtaining a satisfactory performance of the BHJ structure in the photoactive layer, which has charge separation and charge transfer abilities, is difficult in metal oxide systems[16-17]. Furthermore, fullerene derivatives and n-type semiconducting polymers have high solubility in many solvents. Therefore, it is easy to control the morphology of the photoactive layer by selecting an ink solution as the solvent, which is the precursor of the photoactive layer[18-20]. In contrast, in the case of metal alkoxide systems used in combination with an electron-donating polymer, both semiconductors are insoluble in almost all solvents. This is because metal alkoxides do not have a high solubility in the solvent. Therefore, the selectivity of solvents for morphology control is extremely low.

In this article, we report a method for controlling the morphology of the photoactive layer by using molecular bulkiness to fabricate printable and highly air-stable BHJ solar cells. We describe the importance of morphology control for the progress of fullerene-free BHJ solar cells.

PROTOCOL:

1. Preparation of indium-tin-oxide (ITO) glass for solar cell fabrication

1.1) Cut the ITO/glass substrate.

1.1.1) Using a glass cutter, cut the ITO/glass substrate (10 cm × 10 cm) into pieces measuring approximately 2 cm × 2 cm.

1.2) Chemically etch the ITO conductive layer.

1.2.1) Using a digital multimeter, check that the top of the ITO/glass piece has a conductive side.

1.2.2) Place masking tape on both sides of the ITO/glass piece, leaving a central area of 2 mm × 2 cm in the middle. Using masking tape, protect the rest of the ITO conductive layer from the etching.

1.2.3) Pour a few drops of HCl (1 M) onto the ITO conductive layer to remove the ITO conductive layer from the surface of the ITO/glass piece. After approximately 3 min, wipe off the HCl using a cotton swab, and then remove the masking tape.

1.3) Pretreat the ITO/glass piece.

1.3.1) Place the ITO/glass pieces in a glass case and fill the case with water.

1.3.2) Place the glass case in a water bath that is two-thirds full of water and attach an ultrasonic cleaner. Then, turn on the ultrasonic cleaner for approximately 15 min to remove the few traces of chemical etchant remaining on the ITO/glass piece. Wash these pieces in an ultrasonic bath with water, acetone, and isopropyl alcohol, respectively, for 15 min each, and then dry them in a stream of dry air. Perform ultrasonication at an oscillatory frequency of 42 kHz.

1.3.3) Place the ITO/glass pieces inside an ultraviolet-ozone (UV-O_3) cleaner and run the machine for 30 min.

2. Preparation of the precursor solution for the photoactive layer

2.1) Dissolve 0.5 mg of poly[2,7-(9,9-dioctylfluorene)-alt-4,7-bis(thiophen-2-yl)benzo-2,1,3-thiadiazole] (PFO-DBT) as an electron donor and 1.0 mg of Ti-alkoxide in 1 mL of chlorobenzene. Select the following Ti-alkoxides as electron acceptors: Ti(IV) isopropoxide, ethoxide, butoxide, and butoxide polymer. Then, dissolve 0.5 mg of PFO-DBT and 1.0 mg of [60]PCBM in 1 mL of chlorobenzene as a reference.

NOTE: Here, the HOMO-LUMO levels are as follows[21]. PFO-DBT: 5.4-3.53 eV, Ti(IV) isopropoxide: 7.49-3.86 eV, ethoxide: 7.55-3.90 eV, butoxide: 7.53-3.76 eV, and butoxide polymer: 7.57-3.83 eV.

2.2) On a magnetic hot stirrer, heat the precursor solution to 70 °C while stirring it with a stir bar at a rotational speed of 700 rpm. Do this for 20 min in the absence of light, until the solution is visually clear to the naked eye. Cool the solution to room temperature, again in the absence of light, for future use.

3. Fabrication of the photoactive layer

3.1) Deposit the film by spin-coating.

3.1.1) Heat the precursor solution of the photoactive layer and the ITO/glass piece to 70 °C. For 10 min, heat the precursor solution on a magnetic hot stirrer heated to 70 °C and use a stir bar at a rotational speed of 700 rpm. Heat the ITO/glass piece on a ceramic hot plate heated to 70 °C for 5 min.

3.1.2) Place the ITO/glass piece at the center of the vacuum stage of the spin coater, heat it with a heat gun to around 70 °C, and turn on the vacuum.

NOTE: The vacuum is created by using a vacuum pump with a pumping speed of 30 L/min. The ultimate pressure of the vacuum pump is 26.6×10^3 Pa.

3.1.3) Pour a few drops of the precursor solution of the photoactive layer onto the ITO/glass piece and start the spin coater at 2,000-6,000 rpm for 60 s in air.

NOTE: The volume of precursor solution is 0.5 mL, measured with a 1-mL spuit.

3.1.4) Dry the surface of the photoactive layer for 10 min at room temperature in an air atmosphere in the absence of light to obtain a 50 nm-thick film as the photoactive layer.

3.2) Remove the extra film.

3.2.1) Wipe the extra photoactive layer from the surface of the ITO/glass piece with a cotton swab wetted with chlorobenzene.

3.2.2) Dry the photoactive layer again for 10 min at room temperature in an air atmosphere in the absence of light.

NOTE: The temperature of our experiment room is maintained at 25 °C.

4. Fabrication of the electrode

4.1) Print the organic electrode.

4.1.1) Using a screen printer, print an organic electrode by placing poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS) on the photoactive layer[22]. The metal mask is 50 µm-thick, and the printing area is 5 mm × 20 mm.

4.1.2) Dry the organic electrode for 30 min at room temperature in an air atmosphere in the absence of light.

5. Lamination for the solar cells

5.1) Cut the glass substrate into pieces with dimensions of 1.5 cm × 2.5 cm using a diamond cutter. Spread an epoxy resin onto the glass substrate using a plastic spatula. Place the glass substrate with epoxy resin on the photoactive layer to protect it.

6. Preparation for measuring the solar-cell performance

6.1) Clean the electrodes by wiping them with a cotton swab wetted with acetone. Attach a supporting electrode onto the ITO using an ultrasonic soldering system. Operate the soldering iron at a 42-kHz frequency and at 230 °C.

7. Measurement of the solar-cell performance

7.1) Measure the current-voltage (J-V) characteristics of the solar cells by using a direct-current voltage current source/monitor integrated system, with the solar simulator calibrated to provide a simulated AM1.5G of 100 mW/cm^2 by the silicon photodiode.
NOTE: More detailed information about the measurement of the J-V curves can be found elsewhere[23, 24].

8. Analysis of the phase-separation structure

8.1) Prepare individual films of photoactive layers constructed with Ti-alkoxide and PFO-DBT, using same method for solar-cell fabrication, without the organic electrode and without the lamination process.

8.2) Use an optical microscope or a scanning electron microscope (SEM) to observe the morphology of the photoactive layer at a high magnification (50,000×) in order to analyze the phase-separation structure.
NOTE: More detailed information about SEM operation can be found elsewhere[25, 26].

REPRESENTATIVE RESULTS:

We have presented a protocol for fabricating fully-printable organic-inorganic BHJ solar cells, as well as a method for controlling the phase-separation structure. The solar-cell performance has been extensively investigated[27-31] when Ti(IV) isopropoxide and ethoxide were used as electron-accepting materials (**Figure 1**). These solar cells exhibited a short-circuit current density (Jsc) that is approximately eight times higher than that of devices using the “Ti(IV) butoxide polymer” (**Table 1**). The resulting morphologies in the photoactive layer were adequate for photo-generation and the existence of free carriers and their transportation. In other words, it is possible to control the carrier management structure by selecting the bulkiness of the Ti-alkoxide. Some previous works have shown that the phase-separation structure for carrier management in the photoactive layer of a BHJ solar cell using fullerene derivatives is an important factor[32-34]. This is also important for the organic-inorganic system investigated in this work.

We can explain the relationship between Jsc by the carrier management and the phase separation structure using the three individual models summarized in **Table 2**. Furthermore, we investigated the phase-separation structure through SEM, and SEM images were compared with the phase-separation models (**Figure 2**). When the Ti(IV) butoxide polymer was used, the charge-generation field was insufficient. Consequently, this results in a lower Jsc value. That is, the self-organization of the Ti(IV) butoxide polymer is primarily promoted by the molecule's packing. When "Ti(IV) butoxide" was used as an n-type semiconductor, the phase domains were isolated, which is inadequate for the charge transfer of the free carriers to obtain a high Jsc value. The chemical structure of Ti(IV) butoxide is bulkier than that of Ti(IV) isopropoxide and ethoxide. Therefore, the chemical bulkiness of Ti(IV) butoxide excessively hindered the self-organization of the p-type semiconducting polymer. On the other hand, when Ti(IV) isopropoxide or ethoxide was used, these morphologies provided a good balance between domain size and phase continuity from the viewpoint of charge generation, the existence of free carriers, and their transportation.

FIGURE LEGENDS:

Figure 1: J-V characteristics of solar cells for different chemical bulkiness of Ti alkoxide. This figure is modified from Reference 21. J-V characteristics are drastically changed by selecting the Ti alkoxide molecule.

Figure 2: Scanning electron microscope (SEM) images for analyzing phase separation structures. This figure is modified from Reference 21. The morphology of the photoactive layer is obtained at a high magnification (50,000×). The phase separation structures of Ti(IV) isopropoxide or ethoxide were acceptable and had an adequate continuity.

Table 1: Solar-cell performance for different chemical bulkiness of Ti alkoxides. This figure is modified from Reference 21. The J-V characteristics of the BHJ solar cells for each Ti-alkoxide are shown in Figure 1, and the corresponding performance parameters are listed in this table.

Table 2: The representative phase-separation models for analyzing existent free carriers. This figure is modified from Reference 21. Ideally, morphologies, such as that of model B, are required from the viewpoint of the existence of many free carriers.

DISCUSSION:

In order to utilize the molecule's bulkiness in this method, it is important to know the conditions for film formation by spin coating. First, the p-type and n-type semiconductors must be able to be dissolved in the solvents. When some material remains, it will become the large core of the domains in the photoactive layer. The use of an adequate commercial filter for individual solvents is recommended to remove the remaining material. Next, the precursor solution in which the molecules dissolve must be uniformly and homogeneously printed as the photoactive layer on the ITO/glass substrate in approximately 60 s. This process is executed with the following three steps. First, the precursor solution and ITO/glass substrate are maintained at a temperature of approximately 70 °C. Second, the substrate is promptly set on the stage of the spin coater. Finally, a few drops of the precursor solution are poured and spread on the surface of the substrate, as soon as possible, and the spin coater is promptly started. The heated substrate prevents a rapid decrease in the temperature of the precursor solution on the ITO/glass substrate. This method controls the educts from the precursor solution by a rapid thermal change. The effect of the heated precursor solution promotes smooth spreading on the substrate, due to the decrease in the viscosity, and facilitates the formation of a uniformly flat thin film. Furthermore, the spin-coating process is carried out uncovered by the lid. This promotes the evaporation of the solvents from the substrate during the ~60-s process.

If problems occur when using the abovementioned method due to the experimental and equipment conditions, the following methods are recommended. If the heated substrate cannot move on the stage of the spin coater, the substrate can be heated with a heat gun immediately before use. Furthermore, if more time is needed to drop the precursor solution, heating the precursor solution to approximately 75-80 °C is recommended.

Moreover, the phase-separation structure and phase-domain size will be different depending upon the selected individual electron donor. When an electron donor except PFO-DBT is selected, a change in the p/n ratio and a mixture of two Ti-alkoxides with different bulkiness as the electron acceptor are useful methods for obtaining a suitable phase-separation structure. Our method for controlling the phase-separation structure is different from the conventional solvent method[18-20, 33]. Therefore, our method can be modified to electron donors and acceptors that have solubilities in only a few limited solvents.

Finally, we have demonstrated a method for the fabrication of fully-printable, fullerene-free, bulk-heterojunction solar cells based on the use of Ti-alkoxides as the electron acceptor and a semiconducting polymer as the electron donor. Furthermore, this protocol demonstrated that it is effective to control the phase-separation structure by using the molecular bulkiness, without using the conventional solvent method. This method may be applicable to systems using several n-type and p-type semiconductors, which only dissolve in a few solvents. We also mention the limitations of this method. We think that this method is useful only in a two-ingredient system. This is because this method can control the phase separation by hindering self-organization using the bulkiness of one molecule out of two kinds of molecules. Therefore, we cannot say that a three-ingredient system will be applicable. We will investigate the applicability to these systems in the future. We expect that, in addition to completely organic solar cells, hybrid solar cells will also become popular in the near future.

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DISCLOSURES:

The authors declare that they have no competing financial interests.

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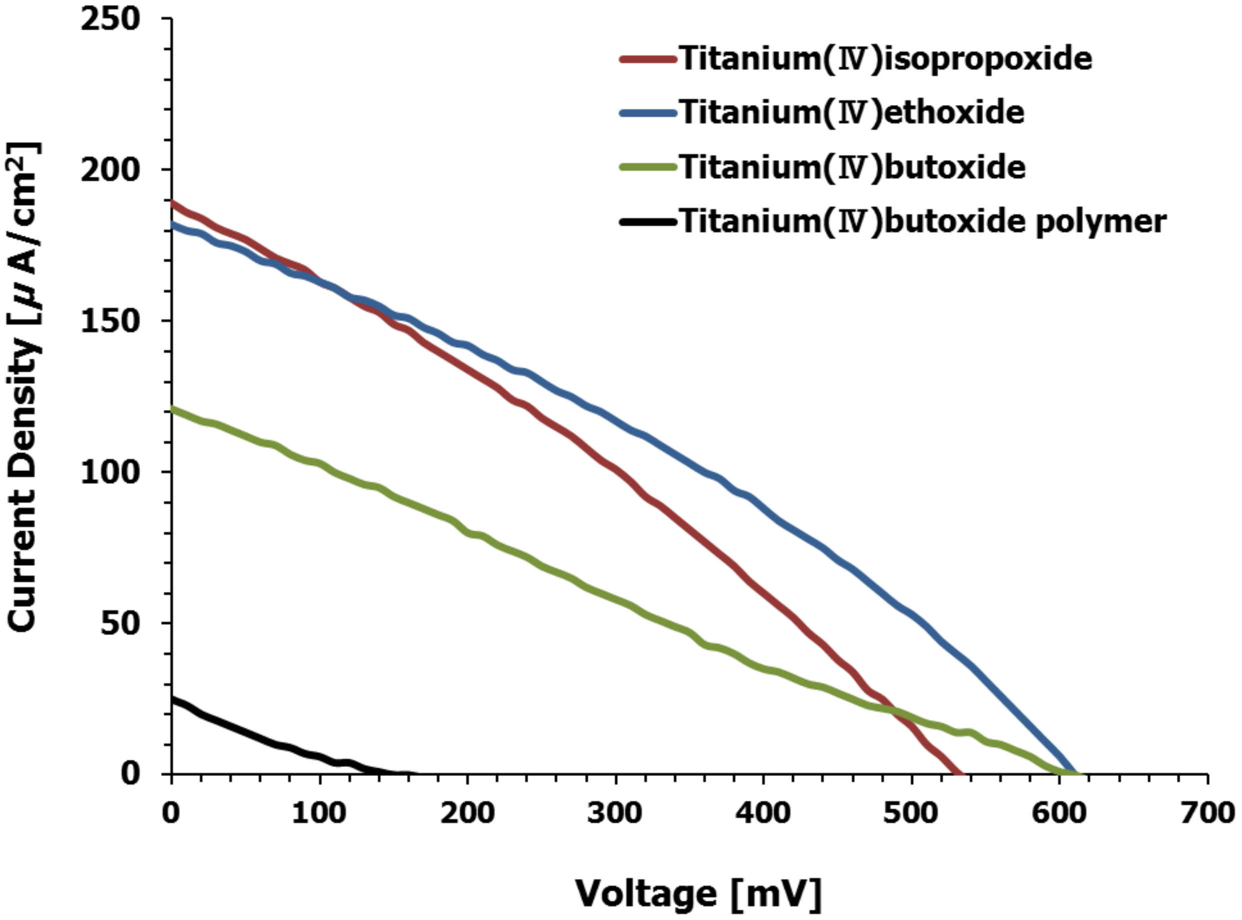
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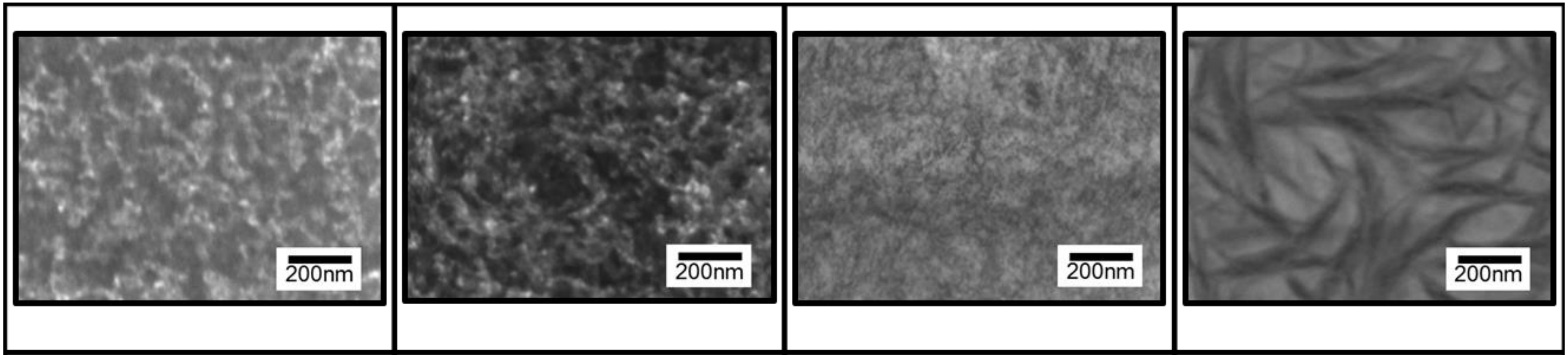
700
Voltage [mV]



Ti(IV) isopropoxide

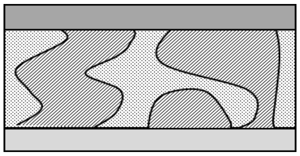
Ti(IV) ethoxide

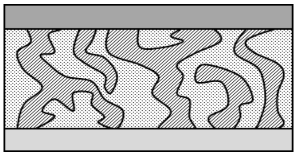
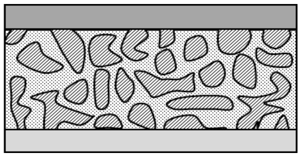
Ti(IV) butoxide

Ti(IV) butoxide polymer

	Titanium(Ⅳ) isopropoxide	Titanium(Ⅳ) ethoxide
Jsc [μA/cm^2]	191	182
Voc [V]	0.53	0.61
FF	0.31	0.33
PCE [%]	0.031	0.036

Titanium(Ⅳ) butoxide	Titanium(Ⅳ) butoxide polymer
121	25
0.61	0.16
0.23	0.18
0.017	0.0007

Model	(A) 
Phase Separation (Overall carrier management)	coarse
Continuity (Free carrier existents and transportation)	continuous
p/n Interfacial Length (Charge generation)	low
Current Density	low

(B)	(C)
	
medium	fine
continuous	isolation
medium	high
high	low

Name of Reagent/ Equipment	Company	Catalog Number	Comments/Description
Ti(IV) isopropoxide, 97%	Sigma Aldrich	205273	
Ti(IV) ethoxide	Sigma Aldrich	244759	Technical grade
Ti(IV) butoxide, 97%	Sigma Aldrich	244112	Reagent grade
Ti(IV) butoxide polymer	Sigma Aldrich	510718	
Poly[2,7-(9,9-dioctylfluorene)-alt-4,7-bis(thiophen-2-yl)benzo-2,1,3-thiadiazole] (PFO-DBT)	Sigma Aldrich	754013	
[6,6]-phenyl-C61 butyric acid methyl ester ([60]PCBM) 99.5%	Sigma Aldrich	684449	Research grade
poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS)	Heraeus	Clevios S V3	
1N Hydrochloric acid	Wako	083-01095	
Chlorobenzene 99.0%	Wako	032-07986	
Acetone 99.5%	Wako	016-00346	
Indium-tin oxide (ITO)-coated glass substrate	Geomatec	0002	100×100×1.1t (mm)
Glass substrate	Matsunami Glass	S7213	76×26×1.2t (mm)
Cotton tail	As one	1-8584-16	
Epoxy resin	Nichiban	AR-R30	
Plastic spatula	As one	2-3956-02	
Ultrasonic cleaner	As one	AS482	
Magnetic hot stirrer	As one	RHS-1DN	
Ceramic hotplate	As one	CHP-17DN	
Spin coater	Kyowariken	K-359 S1	
Vacuum pump	ULVAC	DA-30S	
UV-O_3 cleaner	Filgen	UV253E	
Screen printer	Mitani Electronics	MEC-2400	

Ultrasonic Soldering system	Kuroda Techno	SUNBONDER USM-5
Direct-current voltage and current source/monitor integrated system	San-Ei Electric	XES-40S1
Scanning electron microscope	JEOL Ltd.	JSM-7800

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Title of Article: **Morphology control for fully printable organic-inorganic bulk heterojunction solar cells based on Ti-alkoxide and semiconducting polymer**

Author(s): **Takehito Kato, Chihiro Oinuma, Munechika Otsuka, Naoki Hagiwara**

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CORRESPONDING AUTHOR:

Name:	**Takehito Kato**
Department:	**Department of Mechanical Engineering,**
Institution:	**National Institute of Technology, Oyama College**
Article Title:	**Morphology control for fully printable organic-inorganic bulk heterojunction solar cell based on Ti-alkoxide and semiconducting polymer**

Signature: Takehito Kato   Date: 29/08/2016

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·Please keep the editorial comments from your previous revisions in mind as you revise your manuscript to address peer review comments. For instance, if formatting or other changes were made, commercial language was removed, etc., please maintain these overall manuscript changes.

Author’s reply:

We would like to express our sincere gratitude to you for carefully reviewing our work. We agree with all your comments and have revised the manuscript accordingly. We have replied to each of the comments from the editor and reviewers in this letter. Our manuscript was checked for language a professional editing service, for which we have additionally submitted a proofreading certificate. Thank you for carefully reviewing our article.

·Formatting: References – Please format references according to JoVE style. DOI are missing, and the volume is not formatted correctly.

Author’s reply:

We have revised the reference section to conform to JoVE’s guidelines, and had it checked by a professional editing service.

·Please copyedit the manuscript for numerous grammatical errors, some of which are indicated below. Such editing is required prior to acceptance and should be performed by a native English speaker.

-Title – Should be “solar cells based on a Ti-alkoxide”

-Line 41 – “a typical, organic thin film bulk-heterojunction (BHJ) solar cells” – singular/plural error

-Line 43 – “as an alternative materials”

-Line 49 – “as some solvents such as fullerene derivatives” – please clarify

-Line 51 – “solve” should be “dissolve”

-Line 78 – “in metal oxide system”

-Line 83 – “metal alkoxide do have not”

-Please correct “in the dark condition” to be both clear and grammatically correct at

each occurrence (6 total). Is this done in the dark or are solutions otherwise protected from light?
-3.2.1, 6.1, Materials table – "cotton tail" – This is a rabbit. Likely you mean "cotton ball" or swab.
-8.1 – "by the Ti alkoxide and PFO-DBT using same methods" – multiple errors
-Line 257 – Please clarify "the good surface interaction".
-Line 258 – "uncovered without the lid"

Author's reply:
Our manuscript was corrected using a professional editing service, for which we have additionally submitted a proofreading certificate.

·Additional detail is required:
-1.2.3 – Is this dropped onto the area not protected by the tape? Is the solution removed prior to removing the tape? If so, how? (Removal of the tape seems out of order.)
-2.2 – Please clarify "in the dark condition". What dark condition? This is likely not grammatically correct. Is the solution clear after 20 min or is the solution stirred for an additional 20 min after becoming clear?
-3.1.1 – How is this different from 2.2? Does this mean that after the solution has been cooled, it needs to be reheated? At what temperature is the ITO heated?
-3.1.3 – How much is a few drops?
-5.1 – How are these cut? Please clarify how spreading and covering with epoxy are different. Are two different epoxies used?
-6.1 – How is the attachment of the supporting electrode performed? Please provide a citation if no detail is provided.

Author's reply:
We have added more detailed information to clarify these points.

·Discussion: How does this method differ from the conventional, solvent method? Please clarify and include independent citations when discussing significance. Please also discuss the limitations of the method.

Author's reply:
We have added the limitations of our method to the "Discussion" section. Moreover,

we have included independent citations concerning conventional methods to facilitate comparison with our method.

·If your figures and tables are original and not published previously, please ignore this comment. For figures and tables that have been published before, please include phrases such as "Re-print with permission from (reference#)" or "Modified from.." etc. And please send a copy of the re-print permission for JoVE's record keeping purposes.

Author's reply:

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Author's reply:

We have revised the reference section to conform to JoVE's guidelines, and had it checked by a professional editing service.

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Author's reply:

Our manuscript was corrected using a professional editing service, for which we have additionally submitted a proofreading certificate.

·NOTE: Please include a line-by-line response letter to the editorial and reviewer comments along with the resubmission.

Author's reply:

We have agreed with and replied to each of the comments from the editor and reviewers in this letter. Thank you for carefully reviewing our article.

Reviewers' comments:

Reviewer #1:

Manuscript Summary:

The authors showed the fabrication of the fully printable BHJ solar cells using Ti-alkoxides as the electron acceptors, and control the morphology of the active layers through the molecular bulkiness of the Ti-alkoxides. They demonstrated that using the molecular bulkiness can be applicable to other hybrid solar cells systems. The protocol of the experiment is clear and logical, and is appropriate for publication in Journal of Visualized Experiments pending revision to address the following issues.

Major Concerns:

In this manuscript, the authors have fabricated the control devices by using the PFO-DBT/[60]PCBM blend as active layer, and mentioned that the Ti-alkoxides could be an air-stable electron acceptor to obtain highly air-stable solar cells compared with PCBM based devices. The authors should provide the evaluation of the air-stability of the Ti-alkoxides based devices.

Author's reply:

We would like to express our sincere gratitude to you for carefully reviewing our work. Currently, we have checked the superiority by a short-term air-stability test. Subsequently, we started a long-term test. Especially, the light-incident test will require a very long time. Therefore, we are still continuing to collect data from the air-stability test. Upon completion of the air-stability test, we will investigate the internals of the solar cell by various empiric tests to further determine the stability of the Ti-alkoxide system. Therefore, in the near future, when we have new conclusions about the stability of the Ti-alkoxide syst em, we will submit a new paper. Thank you for carefully reviewing our article.

Minor Concerns:
The energy levels of the Ti-alkoxides based acceptors and PFO-DBT should be provided, since the energy levels of the donor and acceptor can have significant influence on the voltage values of the solar cells and charge separation between the donor and acceptor.

Author's reply:
Thank you for carefully reviewing our article. We agree with your comment. We have included the HOMO-LUMO levels in the revised article. Moreover, we indicated references regarding the energy levels of the materials.

Additional Comments to Authors:
No comments.

Reviewer #2:
Manuscript Summary:
N/A

Major Concerns:
A. In my knowledge, the key process is spin coating process with heat.
More specific explanations are needed.
The temperature and temperature gradient will be changed, corresponding to conditions.
For example, the volume of the dropped precursor solution, before spin coating process.
What is the real temperature of substrates, before dropping process?
What is the temperature of substrates, when you use the drier?
B. The solar cell with Ti isopropoxide shown 8 times higher JSC.
You mentioned that this originates from the morphology.
How can you assume that other conditions are same? (for example, electrical propertis of Ti alkoxides, and chemical damages between solvent and polymers)

Author's reply:

Thank you for carefully reviewing our article. We agree with your comment. The temperature of the substrate surfaces are 55–70 °C. The substrate is placed on the stage, which was heated by a heat gun. The temperature of substrate was measured by thermography. The volume of precursor solution is 0.5 ml by using a 1-mL spuit. This amount can cover the ITO surface on the substrate. We have added more detailed information regarding this experiment. Moreover, the temperature of our experiment room is maintained at 25 °C. Therefore, the drying temperature is 20–30 °C. When we used these conditions for the experiment, we obtained reproducible performance and phase separation structure of the solar cells. We would like to express our sincere gratitude to you for carefully reviewing our work.

Minor Concerns:

More specific process to prepare Ti alkoxides should be mentioned. Did you purchase (Sigma?) or prepare by yourself?

Author's reply:

Thank you for your comment. We purchased Ti(IV) isopropoxide, Ti(IV) ethoxide, Ti(IV) butoxide, and a Ti(IV) butoxide polymer from Sigma-Aldrich.

Additional Comments to Authors:

N/A

Reviewer #3:

Manuscript Summary:

This paper used a Ti alkoxide layer as the electron acceptor for bulk-heterojunction solar cells.

Major Concerns:

The power conversion efficiency was very low. The reviewer concerns about the practical applicability of the proposed method in solar cell assembly.

Author's reply:

Thank you for carefully reviewing our article. We agree with your comment. One of the reasons for the low device performance was that we did not use buffer layers. However, in this study, we focused on controlling the phase-separation structure;

therefore, we did not insert buffer layers so that we could evaluate the simplest system. In future, we plan to implement the fabrication of highly efficient solar cells based on a technique that would enable us to control the phase-separation structure reported in this article using buffer layers.

Minor Concerns:
N/A

Additional Comments to Authors:
N/A

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