

Article

Long-Term Stable Solid-State Dye-Sensitized Solar Cells Assembled with Solid-State Polymerized Hole-Transporting Material

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Received: 16 July 2019; Accepted: 28 August 2019; Published: 30 August 2019



Abstract: The long-term stability of liquid-state dye-sensitized solar cells (liquid-DSSCs) is a primary problem for the upscaling and commercialization of this technology. The solid-state dye-sensitized solar cell (ss-DSSC) has been instigated to overcome the liquid-DSSC's inherent production and instability issues and advancement has been made to achieve low-cost high-power conversion efficiency. The photovoltaic performance of ruthenium-based complex Z907 dye was studied in ss-DSSCs using a solid-state polymerized conductive polymer as hole-transporting material (HTM). We investigated the long-term stability of both liquid and solid-state DSSCs and the findings revealed an improved photovoltaic performance and long-term stability of ss-DSSC. This mainly depends on the transport phenomena of the HTM throughout the interface. The present results show a pavement for manufacturing highly stable and inexpensive ss-DSSC and the practical use is promising.

Keywords: solid-state dye-sensitized solar cells; device stability; solid-state polymerization; poly-3,4-ethylenedioxythiophene

1. Introduction

Due to controllable optical, electrochemical and conductive characteristics, conjugated conducting polymer materials are of considerable importance for different applications such as chemical sensors, organic light-emitting diodes, electrochromic cells, photovoltaic cells, and organic field-effect transistors [1–6]. In these conducting polymers, hetero-atom substituted conducting polymers have become attractive polymers due to their simple processability, easy modification, and high conductivity [7–11]. Several polymerization procedures have been employed for the preparation of these heterocyclic polymers, such as enzyme-catalyzed polymerization [12], oxidative polymerization, which includes electrochemical polymerization [13], chemical polymerization with a catalyst [14], organic vapor phase polymerization [15], solution casting polymerization [16], and solid-state polymerization (SSP) [17]. In recent years, hole-transporting materials (HTMs) based on solid-state polymerized polymers have been applied in solid-state dye-sensitized solar cells (ss-DSSCs), promising to replace the conventional polymerization methods and the SSP method [18–21]. As monomers can quickly infiltrate into the nanopores of the photoactive layer, they are essential tools to enhance the interfacial contact properties between the photoanode and HTM in ss-DSSCs [18,19]. In SSP, polymerization progresses in crystalline forms and in such a way that the short distances between the monomers are crucial to minimize the activation energy for polymerization.

Device stability is a major problem for widespread practical use of liquid-state DSSC (liquid-DSSC) technology. In this work, long-term stable and high efficient ss-DSSC was achieved by SSP through the enhanced interfacial contact properties of a conductive poly-3,4-ethylenedioxythiophene (PEDOT)

polymer. Here, commercially available 3,4-ethylenedioxythiophene (EDOT) was selected as the starting material, which was firstly brominated by a well-known brominating method using *N*-bromosuccinimide to obtain 2,5-dibromo-3,4-ethylenedioxythiophene (DBEDOT) [18]. Then, brominated DBEDOT was used as a monomer for obtaining the corresponding polymer PEDOT owing to its ease of synthesis, effective polymerization, and low-cost of preparation. Solid-state polymerization progress only in the crystal form because of the short $\text{Br} \cdots \text{Br}$ distance between DBEDOT monomers [17,20]. The specific stacking structure of monomer crystals enables the DBEDOT to encounter a self-coupling reaction, promoting the generation of highly conductive polymer PEDOT without any additives. The conductivity of the as-prepared polymer without any additives attained higher conductivity values compared to other preparation methods [20] and hence, SSP-PEDOT with high conductivity can be a good candidate for a HTM. On the other hand, the long-term stability of this SSP-PEDOT in ss-DSSCs has not yet been reported. Therefore, we studied the long-term stability of ss-DSSC using a stable and well-known amphiphilic ruthenium sensitizer Z907. Promising results were achieved for ss-DSSCs when compared with conventional liquid-DSSCs.

2. Materials and Methods

Titanium dioxide (TiO_2 ; 20 nm) paste and the hydrophobic ruthenium dye Z907 were purchased from Solaronix (Aubonne, Switzerland). The fluorine-doped SnO_2 (FTO)-coated glass films were procured from TEC8, Pilkington, Japan ($8 \Omega/\text{cm}^2$, thickness of 2.3 mm). *N*-bromosuccinimide (NBS), ethylenedioxythiophene (EDOT), methyl-3-propylimidazolium (MPII), iodide lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), *tert*-butyl pyridine (TBP), and tetrahydrofuran solvent were obtained from Sigma-Aldrich (Missouri, United States). DBEDOT was prepared as described in our previous report (Scheme S1, SI) [21]. The conductive polymer of PEDOT was thermally synthesized in the solid state from the monomer of DBEDOT (Figure 1 (right); Scheme S1). The FT-IR spectra were recorded using a Fourier Transform Infrared (FT-IR) spectrometer (Perkin Elmer, Massachusetts, United States). The ^1H -NMR spectrum was measured on a Bruker Advance NMR 300 MHz spectrometer (Billerica, MA, United States). The surface morphology of the film was studied by scanning electron microscopy (SEM, Hitachi FE-SEM S4800) (Hitachi High-Technologies Corporation, Tokyo, Japan). The ss-DSSCs were fabricated using the previously reported method [20]. The model device structure and complete ss-DSSC fabrication are shown schematically in Figures 1 and 2, respectively. Detailed photovoltaic characterization and liquid- and ss-DSSC fabrication are presented in the supporting information.

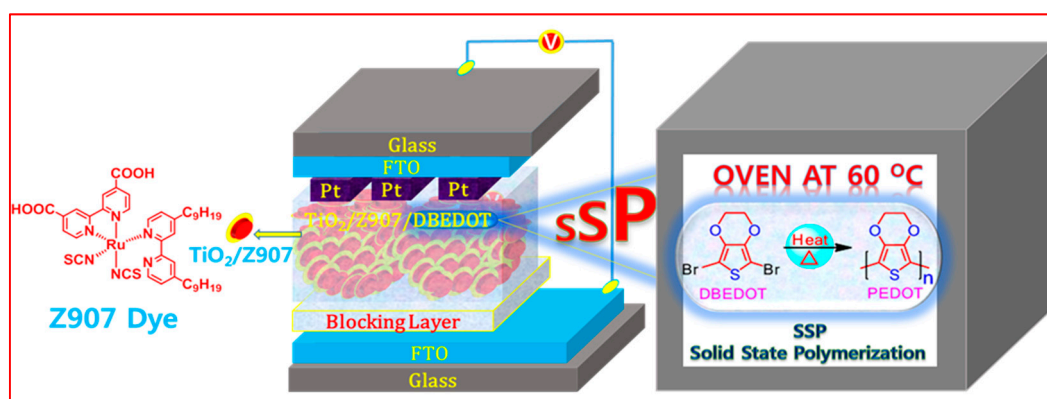


Figure 1. Model fabricated solid-state-dye-sensitized solar cell (left) and simple solid-state polymerization (SSP) of 2,5-dibromo-3,4-ethylenedioxythiophene (DBEDOT) (right) penetrated the cell at 60 °C within the device.

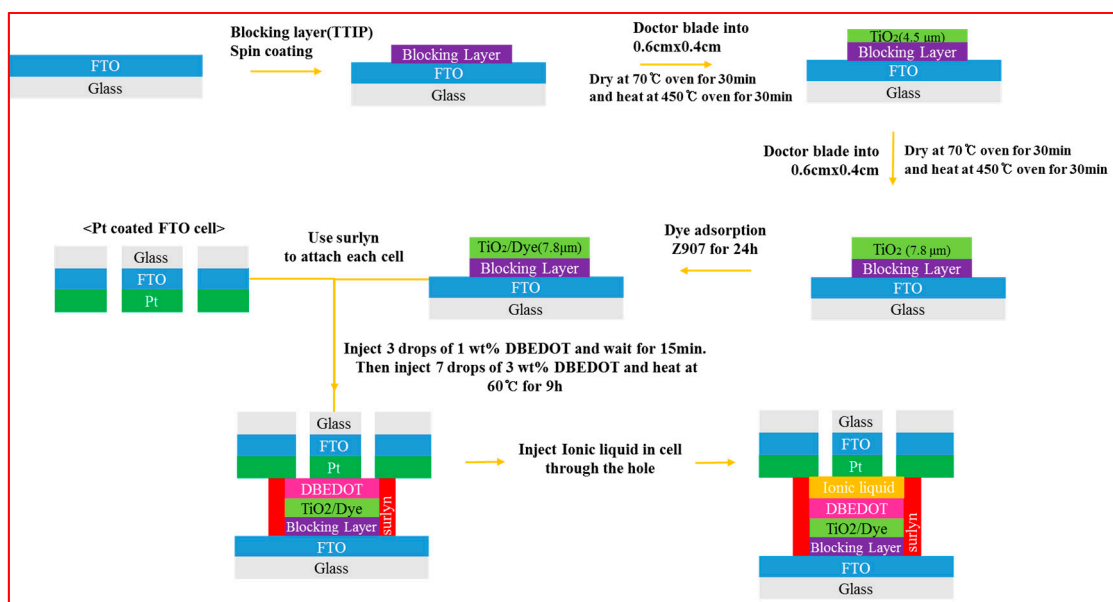


Figure 2. Schematic representation of the solid-state dye-sensitized solar cell fabrication process.

3. Results and Discussions

FT-IR spectroscopy (Supplementary Materials Figure S2a) and X-ray diffraction (XRD) analyses (PANalytical X'Pert PRO MPD, Malvern Panalytical Ltd., Malvern, UK) (Figure S2b) were performed to study the successful penetration of monomer DBEDOT and solid-state polymerization. The peaks of SSP-PEDOT showed good agreement with reported values [19]. After solid state polymerization of the monomer, the SSP-PEDOT polymer exhibited vibrational signals in the range of 1485 and 1540 cm^{-1} coming from the symmetric stretching and conjugated $\text{C}=\text{C}$ asymmetric vibration in the thiophene ring, respectively. The vibrational signals of the SSP-PEDOT-infiltrated photoanode mimicked those of TiO_2 and only PEDOT, representing that monomer, was well infiltrated and polymerized in the photoactive layer. Furthermore, XRD analysis of the SSP-PEDOT film indicated that the peaks of the crystalline SSP-PEDOT film matched earlier reported values well [19]. In addition, in ss-DSSCs, an increased level of interfacial contact between the HTM layer and the photoactive layer had a crucial effect in increasing the photovoltaic performance.

The surface SEM images of the nanocrystalline TiO_2 and nanocrystalline TiO_2 layer with SSP-PEDOT are shown in Figure 3. The surface morphology changes before and after SSP indicate that a PEDOT layer was polymerized on the nanocrystalline TiO_2 film. From Figure 3b it is clear that almost all of the surface was coated with the PEDOT polymer. TiO_2 particles were detectable with a size of $30\text{--}40\text{ nm}$ in the TiO_2 only layer (Figure 3a) and it is well known that TiO_2 particles have a pore size of about $17\text{--}20\text{ nm}$. Therefore, this size was sufficient for the monomer solution to practically infiltrate the pores of the photoactive layer. When the monomer solution was infiltrated and self-coupled in the solid-state at a specified temperature, the particle size of TiO_2 evidently enhanced, and the image (Figure 3b) of the TiO_2 particles became indistinguishable. This emerged because the conductive polymer covered the TiO_2 nanoparticles, suggesting an exceptional interfacial interaction between the dye-loaded TiO_2 and the conductive polymer. In other words, excellent monomer infiltration into the TiO_2 pores, and thus excellent contact between TiO_2 and the polymer, is feasible due to the fact that the monomer has a lower molecular size than the TiO_2 layer pores. This method represents an easy and efficient practice for packing a big molecular weight polymer into the pores of a photoactive layer as the hole-transporting material. Additionally, the photoactive layer pores were packed with MPEI and Li salts (LiTFSI), which suggested further enhancing interfacial contact between the dye-loaded TiO_2 particles and the conductive polymer.

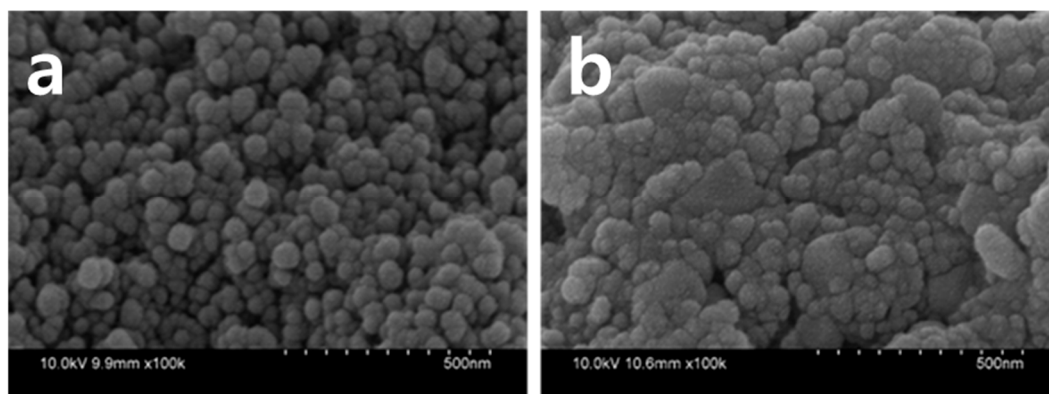


Figure 3. Surface scanning electron microscopy (SEM) images of (a) nanocrystalline TiO_2 layer on the fluorine-doped tin oxide (FTO) glass, (b) nanocrystalline TiO_2 layer with SSP-PEDOT.

Photocurrent density–voltage (J–V) characteristics and incident photon-to-current-conversion efficiency (IPCE) were studied by employing liquid (I^-/I_3^-)-based electrolyte and solid-state polymerized HTM. The corresponding spectra and photovoltaic parameters using amphiphilic Z907-sensitized nanocrystalline TiO_2 solar cells are depicted in Figure 4 and Table 1. The error bars in Table 1 were calculated from the J–V curves of four DSSCs for each condition. Figures S3 and S4 show the IPCE and standard deviation obtained from four identically prepared devices. The photovoltaic performance using a liquid-based reference electrolyte showed the highest PCE of 6%, whereas the PCE decreased to 3.17% in the case of ss-DSSC. Due to the comparatively small conductivity of the organic HTM, the lower photovoltaic performance of ss-DSSC can be ascribed to greater series resistance in the cell.

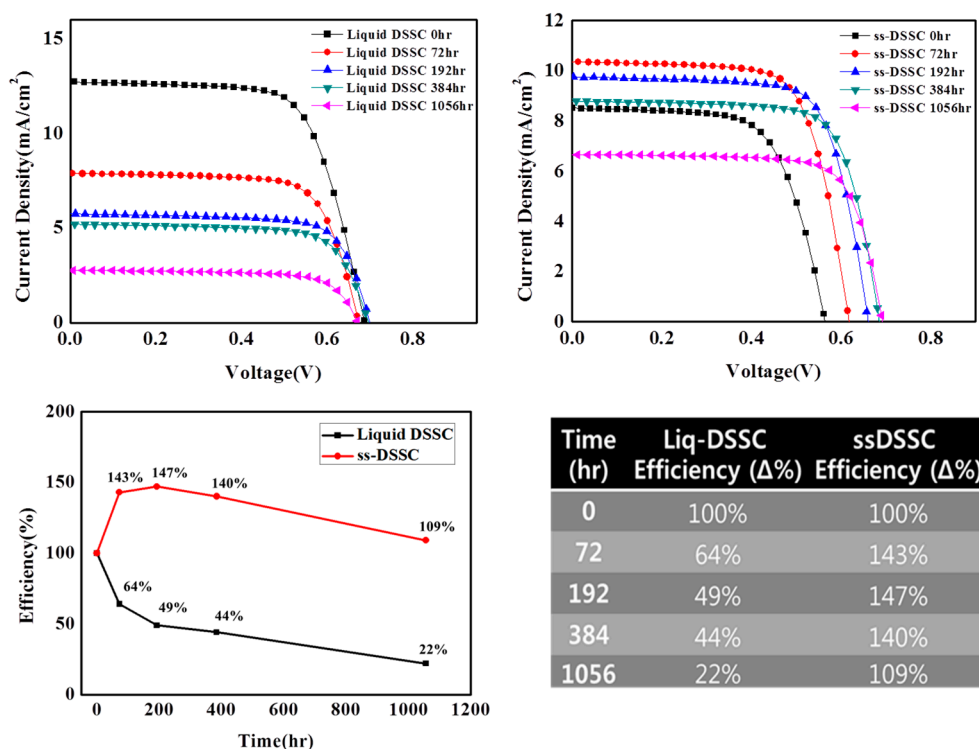


Figure 4. Performances of liquid and solid-state dye-sensitized solar cells at 100 mWcm^{-2} (top) and change in efficiency during the long-term stability test (bottom).

Figure 4, Figure 5 show the detailed J–V curves and change of photovoltaic parameters of the same samples during the stability test up to 1056 h with the liquid and solid-state DSSCs. After 192 h, the PCE for the ss-DSSCs was significantly enhanced due to a significant increase in photo-current density and photo-voltage values. Then a gradual small decrease in J_{sc} , with a small increase in V_{oc} , caused a slight increase in the overall PCE by 9% after 1056 h (Figure 4, Figure 5). On the other hand, in the case of liquid-DSSCs, the efficiency was significantly diminished over the period of time due to a gradual decrease in J_{sc} , whereas the V_{oc} was almost unchanged. In other words, the power conversion efficiency of the cell using liquid-state electrolytes shows a decrease of 80% after 1056 h. Overall, the significantly enhanced PCE achieved for ss-DSSC over a period of time stemmed from the application of highly conductive PEDOT solid-state polymerization, which allows the small monomers to penetrate deeply into the pores of a thick mesoporous photoactive layer. It should be observed that solid-state conductive polymer has a maximum penetration depth of about 11 μm (better than 4–5 μm when using photoelectrochemical polymerization) [19]. Thus it is expected that the penetration depth can be further increased over a period of time, leading to more dye adsorption and photovoltaic performance.

Table 1. Time dependence of photovoltaic parameters (J_{sc} , V_{oc} , FF, and η) of liquid and solid-state dye-sensitized solar cells based on the Z907 sensitizer.

Sample	J_{sc}	V_{oc}	FF	η
Liquid DSSC 0 h	12.70 ± 0.1	0.68 ± 0.002	0.68 ± 0.02	5.97 ± 0.27
ss-DSSC 0 h	8.54 ± 0.36	0.56 ± 0.005	0.66 ± 0.01	3.19 ± 0.20
Liquid DSSC 72 h	7.83 ± 0.12	0.68 ± 0.011	0.70 ± 0.01	3.73 ± 0.02
ss-DSSC 72 h	10.38 ± 0.44	0.61 ± 0.006	0.71 ± 0.01	4.51 ± 0.24
Liquid DSSC 192 h	5.75 ± 0.15	0.70 ± 0.01	0.73 ± 0.02	2.94 ± 0.20
ss-DSSC 192 h	9.78 ± 0.23	0.65 ± 0.001	0.72 ± 0.002	4.61 ± 0.12
Liquid DSSC 384 h	5.25 ± 0.45	0.68 ± 0.02	0.69 ± 0.03	2.46 ± 0.12
ss-DSSC 384 h	8.80 ± 0.20	0.68 ± 0.004	0.73 ± 0.005	4.36 ± 0.09
Liquid DSSC 1056 h	2.80 ± 0.19	0.67 ± 0.009	0.70 ± 0.02	1.30 ± 0.12
ss-DSSC 1056 h	6.66 ± 0.25	0.69 ± 0.004	0.75 ± 0.004	3.42 ± 0.15

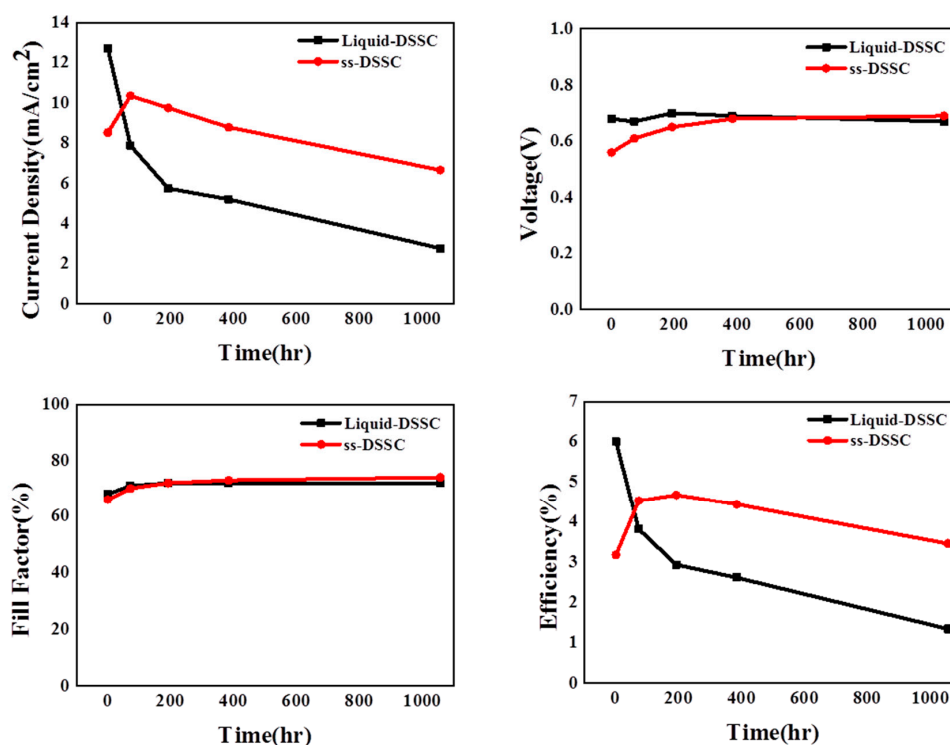


Figure 5. Time dependence of photovoltaic parameters (J_{sc} , V_{oc} , FF, and η) of liquid- and solid-state-dye-sensitized solar cells based on the Z907 sensitizer.

In this study, the stability tests support the information gained from the DSSC and surface morphology studies. The enhanced stability using a SSP-conductive polymer as a HTM can be ascribed to the increased penetration depth between TiO₂ nanoparticles and conductive PEDOT to contribute to the ionic conductivity and the long-term efficiency stability. Devices using liquid-based electrolytes suffered harsh J_{sc} and efficiency decreases, which could be due to the TiO₂/dye/electrolyte interface degradation coupled to electrolyte leakage leading to damage of the stability of liquid-DSSC. To understand the cause of the high stability of the promising SSP-PEDOT hole-transporting material in ss-DSSCs, a detailed investigation is warranted.

4. Conclusions

The solid-state DSSC was fabricated successfully with a solid-state polymerized conductive polymer as a HTM, and long-term stability was investigated using the amphiphilic ruthenium dye Z907. The J–V characteristic of the ss-DSSC increased as a function of time, unlike liquid-DSSCs. The surface morphology images showed the successful deposition of all layers of ss-DSSC and all the TiO₂ nanoparticles were covered by conductive polymer. The ss-DSSC showed excellent stability and significantly increased photovoltaic performance over 1000 h, which is far better than liquid-DSSCs. This behavior might be due to increased pore penetration of HTM over the time. For the first time, a long-term stable device has been achieved by integrating an amphiphilic ruthenium sensitizer Z907 with a solid-state polymerized conductive polymer. A thorough insight into the modification of interface chemistry through a change of other optimized polymers with more suitable dye structures and preparing more porous photoanode films can contribute to the development of long lasting and high performing ss-DSSCs, which are in progress.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4352/9/9/452/s1>, Scheme S1: Synthesis of monomer DBEDOT and polymer SSP-PEDOT; Figure S1: 1H-NMR spectrum of monomer DBEDOT; Figure S2: FTIR (left) and XRD patterns (right) of the nanocrystalline TiO₂ and nanocrystalline TiO₂ layer with SSP-PEDOT; Figure S3: IPCE spectra of liquid- and solid state-DSSCs; Figure S4: Standard error bars of photovoltaic parameters for four different samples.

Author Contributions: Y.J.J.: Synthesis, solution NMR and all DSSC measurements; S.T.: manuscript preparation, supervision, and contribution to synthesis and all other measurements; K.-y.L.: project concepts and contribution to manuscript preparation; J.H.K.: project leader, concepts and contribution to manuscript preparation.

Funding: This research was funded by the Korea Institute of Energy Technology Evaluation and Planning (KETEP) and the Ministry of Trade, Industry & Energy (MOTIE) of the Republic of Korea (No. 20163010012310). This study was supported by a grant from the Fundamental R&D program for Core Technology of Materials (10050966) funded by the Ministry of Knowledge Economy, Republic of Korea.

Conflicts of Interest: The authors declare no conflict of interest.

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