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# New Approach for Preparation of Efficient Solid-State Dye-Sensitized Solar Cells by Photoelectrochemical Polymerization in Aqueous Micellar Solution

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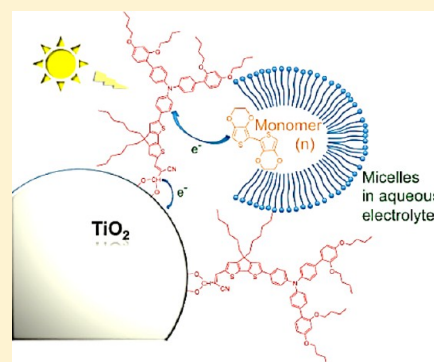
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## Supporting Information

**ABSTRACT:** Hereby, we present a new, cost-effective, and environmentally friendly method of preparing an efficient solid-state dye-sensitized solar cell (sDSC) using a PEDOT conducting polymer as the hole conductor and a recently developed organic sensitizer. PEDOT is generated and deposited on the dye-sensitized TiO<sub>2</sub> electrode by in situ photoelectropolymerization of bis-EDOT in aqueous micellar solution. The advantages of this approach are the use of water as the solvent and the obtaining of a sDSC simply by adding a silver layer on the as-obtained polymer film deposited on dye/TiO<sub>2</sub> without the need for electrolytic solution. The sDSC containing the film prepared as above is compared to those where the organic dye is used to generate the same polymer film but in organic solvent. The energy conversion efficiency values of the two cells appear comparable, 4.8% for sDSC prepared in the aqueous-phase polymerized PEDOT and 6% for the sDSC prepared with in organic-phase polymerized PEDOT.

**SECTION:** Energy Conversion and Storage; Energy and Charge Transport



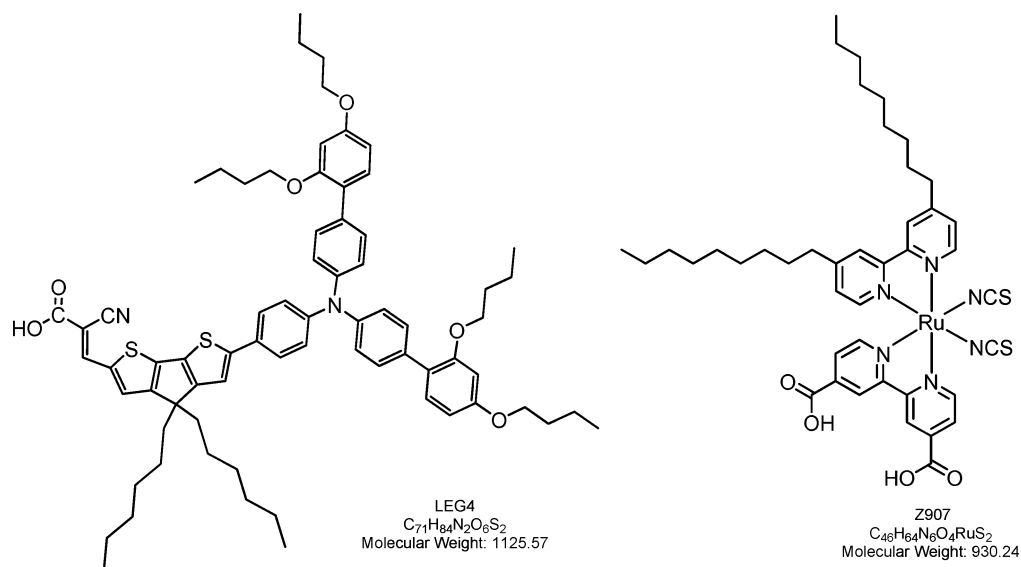
The physical chemistry of dye-coated mesoporous oxide electrodes and their application in dye-sensitized solar cells (DSCs) have attracted considerable interest in the last quarter of a century.<sup>1–3</sup> Several types of DSCs with efficiency exceeding 10% have been published.<sup>4</sup> However, they contain acetonitrile-based electrolytes so that their applicability to devices with long-term stability is doubtful. Therefore, substantial efforts are dedicated to the development of DSCs with either a nonvolatile organic electrolyte (i.e., ionic liquid) or a solid-state hole-transport material (HTM) in solid-state DSCs (sDSCs).<sup>5</sup> Various types of HTMs have been investigated including inorganic hole conductors (e.g., CsSnI<sub>3</sub>, CuI, CuSCN),<sup>6</sup> low molar mass heterocyclic amines (e.g., spiro-OMeTAD, MeO-TPD),<sup>7</sup> and electronic conducting polymers.<sup>8,9</sup> A common limitation of using hole conductors by the conventional spin-coating technique is the low solubility of the HTM molecules and their relative inefficient infiltration into the pores of the mesoporous oxide electrodes so that contact with the dye monolayer is poorly assured.<sup>10–12</sup> When conducting polymers are used as HTMs, there is one way to circumvent this problem, namely, the in situ polymerization of small organic precursors dissolved in solution and located in

direct contact with the dye, which takes place directly inside of the pores. The photoelectrochemical polymerization (PEP) is typically applied as the most convenient method for in situ polymerization, preferably in a three-electrode cell; a constant current (chronopotentiometry) or constant potential (chronoamperometry) is applied while the electrode potential is monitored versus a suitable reference electrode, so that it does not exceed a positive threshold to avoid either overoxidation of the formed polymer or generation of polymer at sites where the conducting glass substrate might be directly exposed to the electrolyte.<sup>13–18</sup> However, previous development of such a technology was mainly performed in an organic solvent, typically acetonitrile, due to the solubility limitation of the precursor compounds, monomers or oligomers, which is unfortunately unfavorable in terms of environmental concerns and large-scale production costs. Moreover, in organic solvent, a large part of the organic oligomers start to be oxidized at high potential values, which makes it quite difficult to find valuable

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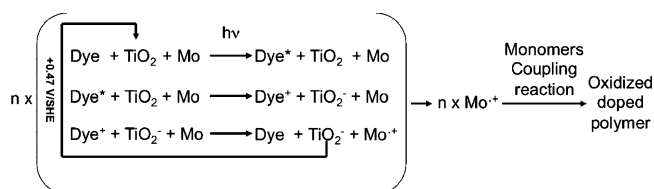
**Figure 1.** Molecular structures of the two sensitizers LEG4 and Ru-Z907.

dye/precursor couples where the photooxidized dye can act as an oxidant to readily trigger the HTM deposition by *in situ* PEP.

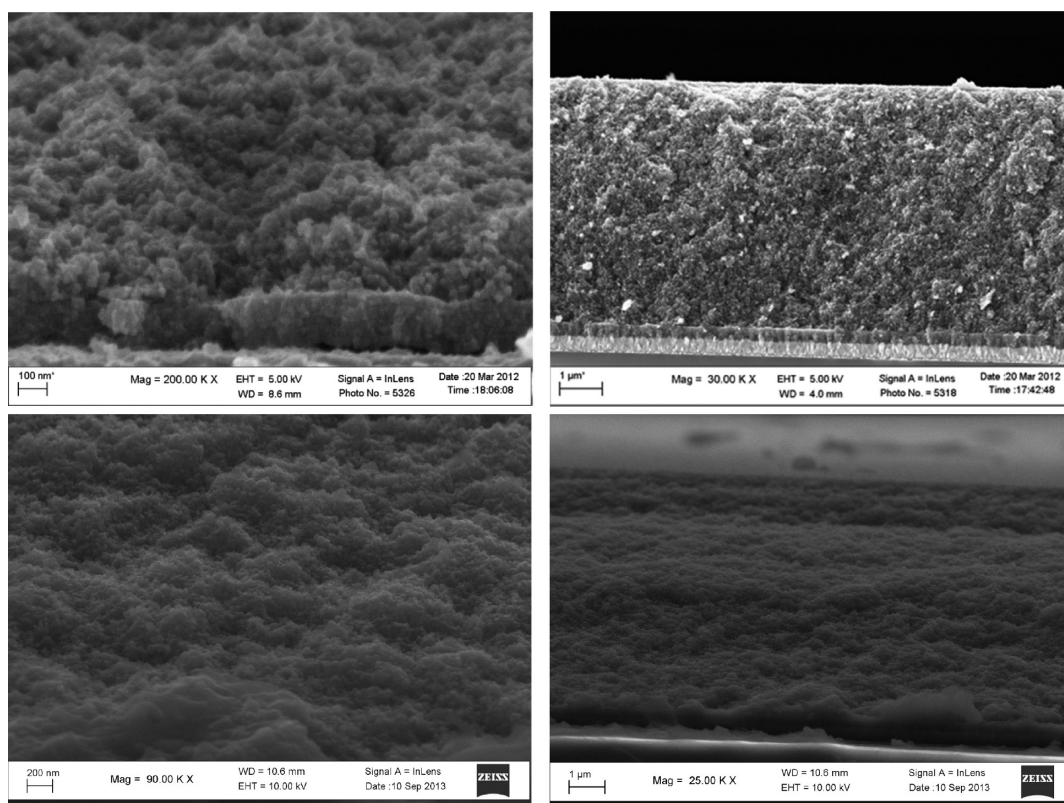
In this work, we present a new method to perform *in situ* PEP in aqueous media of the precursor bis-EDOT in the presence of a surfactant, for example, TritonX-100, in order to fabricate sDSCs. In addition to their ability to dissolve organic hydrophobic precursors, aqueous media containing surfactants or cyclodextrins have been reported to notably decrease the oxidation potential values of the precursor and to allow the obtainment of conducting polymers.<sup>19–25</sup> Therefore, they can be effectively used instead of organic media for this purpose. In this respect, we investigated the photovoltaic properties of the all-sDSCs using PEDOT as the HTM with organic charge-transfer dye LEG4 as the sensitizer. For comparison, the *in situ* PEP in organic solvent, particularly acetonitrile in this case, has also been carried out with bis-EDOT monomer in association with either LEG4 or Ru-Z907 (Figure 1); as a sensitizer, the latter is an intensively studied Ru complex dye, with respect to both traditional liquid electrolyte and sDSCs. Typical values for the oxidation potential corresponding to the onset of bis-EDOT polymerization in (a) acetonitrile and (b) micellar aqueous medium are 0.9 and 0.6 V versus the standard hydrogen electrode (SHE), respectively, as further explained in the Supporting Information. These values are less negative than the redox potential of dyes LEG4/TiO<sub>2</sub> (1.0 V) and Ru-Z907/TiO<sub>2</sub> (1.0 V in a) and LEG4/TiO<sub>2</sub> (0.8 V in b), respectively. Therefore, PEP is a spontaneous process. The advantages of aqueous-phase polymerization are the lower cost and the environmentally friendly character of the process based on an aqueous medium. Besides, the use of an aqueous medium containing surfactants generally leads to better surface organization of the conducting polymer deposition.<sup>20</sup> In contrast to several similar cases of devices encountered in the literature, where the polymer/dye/TiO<sub>2</sub> electrode was dipped in a nonvolatile electrolyte (typically ionic liquid) for several hours, the devices presented in this work do not contain any such electrolyte. The present DSCs are in the solid state, and the conductivity of the HTM layer arises from the doped polymer in its partially oxidized state.

Ultimately, the organic dye LEG4 exhibited excellent compatibility with PEDOT as the HTM in sDSCs, and the devices respectively displayed 6.0% and 4.8% power conversion efficiency with PEDOT produced from either the organic or aqueous phase by *in situ* PEP. Although it is the first time that PEDOT produced by aqueous-phase *in situ* polymerization is employed as the HTM in sDSCs, the devices showed impressive performance as competitive as those with PEDOT generated in the organic phase, as previously reported. The mechanism of PEP is briefly illustrated in Scheme 1.

#### Scheme 1. Photoelectrochemical Polymerization



The high uniformity of the PEDOT layer inside of the porous electrode is essentially required in order to guarantee adequate contact with the dye layer for efficient regeneration after electron injection into the TiO<sub>2</sub> conduction band. As clearly shown in Figure 2, in both sDSCs using PEDOT as the HTM polymerized from either the organic or aqueous phase, the surface of dye-sensitized TiO<sub>2</sub> is homogeneously coated by the PEDOT layer generated by *in situ* PEP across the whole cross section of the solar cell devices. The magnifications of the SEM images of the bottom part close to the compact, recombination current blocking, TiO<sub>2</sub> underlayer and the F-doped tin oxide (FTO) conducting layer (Figure 2, top-left and bottom-left images) show that the dye-sensitized TiO<sub>2</sub> surface is coated by a PEDOT layer even deeply down to the bottom of the device, as indicated by a blurring of the edges of the porous particles in the images. Moreover, in the device using PEDOT polymerized from the aqueous phase, the dye-sensitized TiO<sub>2</sub> surface seems to be slightly more uniformly coated by polymer layer compared to those based on organic-phase polymerized PEDOT, which is probably due to the better surface organization of the conducting polymer deposit in the presence

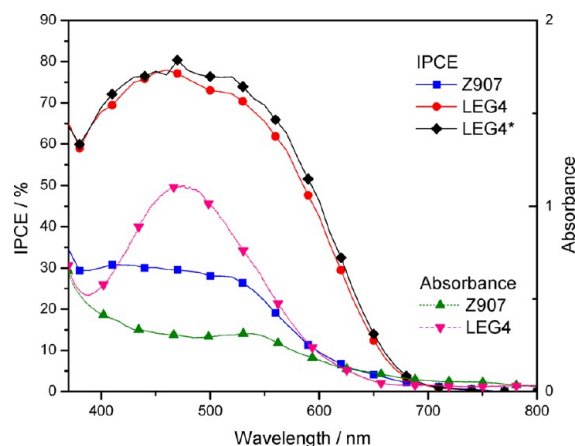


**Figure 2.** SEM images of sDSCs using PEDOT as the HTM generated by photoelectrochemical in situ polymerization. The device using organic-phase polymerized PEDOT: overall cross section of the device (top-right); magnification of the bottom part of the device on the cross section (top-left). The device using aqueous-phase polymerized PEDOT: overall cross section of the device (bottom-right); magnification of the bottom part of the device on the cross section (bottom-left).

of surfactant in aqueous-phase PEP.<sup>20</sup> In practice, an over-standing layer of PEDOT is needed to avoid short circuit by direct contact between Ag and TiO<sub>2</sub> in the sDSC architecture. The thickness of such a layer can be controlled and optimized by adjusting the duration of in situ PEP and, consequently, the total amount of generated polymer.

When the metal-free organic LEG4 sensitizer is used in the sDSC in combination with in situ generated PEDOT by PEP as the hole conductor, the device shows quite high incident photon-to-current conversion efficiency (IPCE), approaching 80% in its maximal absorption spectral window from 450 to 550 nm (Figure 3); IPCE declines steeply after 550 nm all the way down to 750 nm. In contrast, the cell using the Ru coordination complex Ru-Z907 (Figure 1) as the sensitizer exhibits fairly low IPCE across the whole spectral window, with its maximal value of around 30% close to 420 nm. Moreover, both IPCE curves are highly consistent with the absorption spectra of the dye molecules. This result indicates that the major contribution to photocurrent in both spectra is attributed to the dye absorption, while the contribution of PEDOT absorption is negligible. Therefore, the fact that the integrated short-circuit current density of the LEG4-based device (9.80 mA cm<sup>-2</sup>) is 1.4 times greater than that of the Ru-Z907-based device (3.58 mA cm<sup>-2</sup>) mainly derives from the large difference in their absorption spectra. The extinction coefficient of LEG4 is much higher than that of Ru-Z907, which results in a huge light absorption difference and, consequently, a difference in photocurrent.

In agreement with the IPCE spectra, the device using organic-phase polymerized PEDOT as the HTM in association



**Figure 3.** The IPCE of sDSCs using organic-phase polymerized PEDOT as the HTM in association with LEG4 (red trace with the circles) or Ru-Z907 (blue trace with the squares) as the sensitizer; the sDSC using aqueous-phase polymerized PEDOT as the HTM in association with LEG4 (black trace with the diamonds). Absorption spectra of the two sensitizers on mesoporous TiO<sub>2</sub> electrodes: LEG4 (pink dashed trace with the down triangles) and Ru-Z907 (green dotted trace with the up triangles).

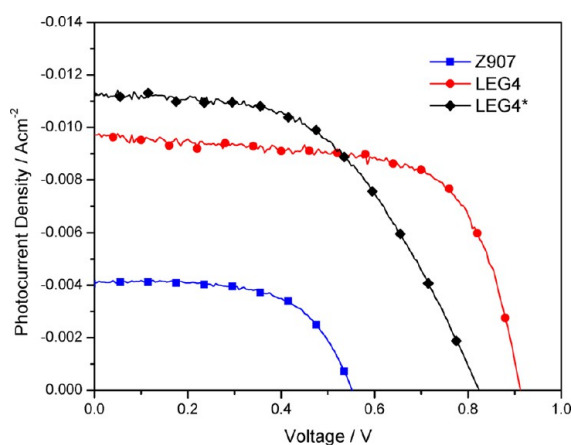
with LEG4 shows a high short-circuit current density ( $J_{sc}$ ) of 9.71 mA cm<sup>-2</sup> (Table 1 and Figure 4), which is more than twice of that for the cell using organic-phase polymerized PEDOT with Ru-Z907 sensitizer. This fact is ascribed mainly to the much weaker absorption spectra of Ru-Z907 and partially to the difference in dye loading as well. Moreover, the Ru-Z907-



Table 1. Data of  $I$ – $V$  Characteristics for sDSCs<sup>a</sup>

sDSC	$V_{oc}/\text{mV}$	$J_{sc}/\text{mA cm}^{-2}$	FF/%	$\eta/\%$
Ru-Z907	550	4.06	63	1.4
LEG4	910	9.71	67	6.0
LEG4*	830	11.21	52	4.8

<sup>a</sup>Ru-Z907 or LEG4 denotes the cell using organic-phase polymerized PEDOT as the HTM in association with LEG4 or Ru-Z907 as the sensitizer, respectively. LEG4\* denotes the cell using aqueous-phase polymerized PEDOT as the HTM in association with LEG4 as the sensitizer.



**Figure 4.**  $I$ – $V$  characteristics of sDSCs: the devices using organic-phase polymerized PEDOT as the HTM in association with LEG4 (red trace with the circles) or Ru-Z907 (blue trace with the squares) as the sensitizer; the device using aqueous-phase polymerized PEDOT as the HTM in association with LEG4 as the sensitizer (black trace with diamonds).

based device only provides an open-circuit potential ( $V_{oc}$ ) of 550 mV, merely more than half of that produced by the LEG4-based cell, which is probably due to slower recombination for LEG4. A comparison of the dye molecular structures of the two sensitizers in question indicates that the electron-donor part of Ru-Z907 (the HOMO of the dye) is located quite close to the anchor group, while the donor part of LEG4 (triphenylamine group) is relatively far from its anchor (cyanoacetic acid group), with a thiophene group as the spacer. Therefore, the probability of recombination between injected electrons and oxidized dye molecules in the Ru-Z907-based device is much greater compared to that for the LEG4-based cell. In addition, the structure of Ru-Z907 is more planar than that of LEG4, with fewer side chains as protecting groups, which leads to inefficient protection of the  $\text{TiO}_2$  surface and, therefore, higher probability of recombination between injected electrons and holes localized in the HTM layer. Hence, the device using Ru-Z907 eventually provides a relatively low power conversion efficiency of 1.4%, while the LEG4-based device shows 6% with the same HTM, namely, PEDOT produced by in situ PEP from the organic phase.

On the basis of the results and the discussion above, LEG4 was therefore selected as the sensitizer for further study of aqueous-phase in situ polymerized PEDOT as the HTM. The solubility of bis-EDOT, the precursor material for PEP, is fairly low in water. Therefore, micelles are introduced into the system by adding 50 mM of the surfactant coded TritonX-100 in order to enhance the bis-EDOT solubility close to 1 mM. The in situ PEP was performed by the same protocol as that in previous

experiments in acetonitrile, that is, by imposition of a constant current. Compared to the previous results of the device based on PEDOT produced from the organic phase, the sDSC using aqueous-phase polymerized PEDOT as the HTM in association with LEG4 as the sensitizer shows a slightly higher IPCE of above 80% at its maximal absorption wavelength, with similar curvature of the spectrum (Figure 3) and a competitive power conversion efficiency of 4.8% with a  $V_{oc}$  of 830 mV and, impressively, a high  $J_{sc}$  of  $11.2 \text{ mA cm}^{-2}$  (Table 1, Figure 4). In comparison, the integrated  $J_{sc}$  of  $10.3 \text{ mA cm}^{-2}$  calculated from the IPCE spectrum is slightly lower, which is probably due to the significantly lower intensity of the light source applied for IPCE measurement. As can be seen, the cell using aqueous-phase polymerized PEDOT provides a higher  $J_{sc}$  by  $1.5 \text{ mA cm}^{-2}$  but lower  $V_{oc}$  by 80 mV, which naturally introduces the interesting issue of higher  $J_{sc}$  accompanied with lower  $V_{oc}$ . Normally, the higher  $J_{sc}$  is a result of better IPCE and less recombination. It is proposed that such differences in  $J_{sc}$  and  $V_{oc}$  are due to the properties of PEDOT produced by two different procedures.

In the organic phase, the 10 mM concentration of bis-EDOT was employed to carry on PEP, which is about 10 times higher than the bis-EDOT concentration used in the aqueous phase. The precursor is located sufficiently in direct contact with dye molecules, with a high concentration inside of the pores. Once the electrode is illuminated by light, upon excitation, dye molecules inject electrons into  $\text{TiO}_2$ , with holes left in the oxidized form of the dye; the holes tend to rapidly oxidize the precursor in the surroundings (Scheme 1). A large concentration of oxidized precursor leads to faster polymerization and to a large amount of oligomers. As a result, the main possible reaction that will follow this step is the oligomer–oligomer coupling, which is very slow because of the low reactivity of the oligomers. Therefore, short polymer chains with relatively low molar mass are generated in the organic phase. On the other hand, in the aqueous phase, the precursor is mainly incorporated into the micelles penetrating the pores, so that the local concentration of the precursor at close proximity to the dye molecules is very low. Moreover, during PEP, the monomer is also released from the micelles by slow, diffusion-controlled delivery before it meets the oxidized dye. Consequently, the polymerization probably proceeds by coupling between very reactive oxidized precursors and less reactive oligomers, rather than between oligomers. Such a different mechanism eventually leads to longer polymer chains, with larger molecular weight. Therefore, the aqueous-phase polymerized PEDOT would be expected to possess a less positive redox potential, that is, a polymer HOMO lying higher in energy than that in the case of the previous nonaqueous polymerization. An alternative explanation for the higher HOMO is that the better organization observed in the aqueous medium is also responsible for the low oxidation potential of the polymer prepared in this environment. A higher-lying polymer HOMO results in an enhanced dye regeneration rate, favoring a higher  $J_{sc}$ . Contrarily, the less positive redox potential will contribute to lower  $V_{oc}$ . Moreover, the better contact between the dye and polymer for aqueous PEP would facilitate the dye regeneration by the reduced polymer, contributing to higher  $J_{sc}$ . However, the recombination of  $\text{TiO}_2$  electrons and oxidized polymer is also faster; this is a second reason for a lower  $V_{oc}$  and, moreover, for a lower fill factor (ff). A further reason for the lower ff is the possible inclusion of Triton-X into the polymer layer generated by aqueous PEP; this could

contribute to a higher resistance in the hole-conducting film. The polymer obtained by the procedures described above is at the oxidized state and doped as well. When used as obtained in the sDSC, the conductivity is assured by the oxidized state. In this case, the couple PEDOT/oxidized PEDOT plays the role of the HTM. Consequently, there is no need for solvent when holes are transported through the polymer layer. The relatively fast hole conduction for devices generated by both types of PEP is evidenced by the linearity between  $J_{sc}$  and light intensity up to 1 Sun (Figure SI-1, Supporting Information).

In summary, a recently developed organic sensitizer LEG4 has been introduced for an all-sDSC application with PEDOT as the HTM produced by in situ PEP. A new method to perform in situ PEP in an aqueous solution of the bis-EDOT monomer, in association with micelles, has been developed. LEG4 exhibited excellent compatibility with PEDOT as the HTM in sDSCs, and the devices respectively displayed 6.0% and 4.8% power conversion efficiency, with PEDOT produced from either the organic or aqueous phase by in situ PEP. Although it is the first time that PEDOT produced by aqueous-phase in situ PEP is employed as the HTM in sDSCs, the devices showed impressive performance, as competitive as those with PEDOT produced in the organic phase, reported previously. Therefore, it can be stated that the technique of aqueous-phase in situ polymerization could be an environmentally friendly alternative method with a scale-up potential for all-sDSC fabrication with high power conversion efficiency in the future.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

The Information on device fabrication, UV-vis spectroscopy measurements, incident photon to current conversion efficiency (IPCE) measurements, photocurrent density versus voltage measurements, photocurrent versus light intensity measurements, energy conversion efficiency of measured solar cells and variations, scanning electron microscope measurements, and electrochemical (cyclic voltammetric) measurements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Author Contributions

<sup>†</sup>L.Y., J.Z., and A.J. contributed to this work equally.

### Notes

The authors declare no competing financial interest.

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