In Situ Polymerized Carboxylated Diacetylene as a Hole Conductor in Solid-State Dye-Sensitized Solar Cells

Yanping Wang,[†] Ke Yang,[†] Seong-Cheol Kim,[†]
Ramaswamy Nagarajan,[†] Lynne A. Samuelson,[‡] and
Jayant Kumar*,[†]

Departments of Chemistry and Physics, Center for Advanced Materials, University of Massachusetts Lowell, Lowell, Massachusetts 01854, and Nanomaterials Science Team, United States Army Natick Soldier Center, RDECOM, Natick, Massachusetts 01760

Received April 19, 2006
Revised Manuscript Received July 11, 2006

Dye-sensitized nanocrystalline (nc) TiO_2 solar cells (DSSCs) have attracted significant attention over the past decade because of their potential as a high-efficiency and low-cost alternative to conventional inorganic solar cells.[1] The prototypical devices using liquid electrolytes have achieved overall power conversion efficiencies up to 10% under AM 1.5 illumination (100 mA/cm^2).[2] Practical applications, however, have been limited by corrosion and leakage problems associated with a reactive electrolyte. Therefore, numerous efforts have been investigated to replace the liquid electrolyte with a solid-state hole transporting material (HTM).[3−9] The HTMs can be inorganic semiconductors, such as CuI[3], organic small molecular solids such as 2,2′,7,7′-tetrakis(*N*,*N*-di-*p*-methoxyphenylamine)-9,9′-spirobifluorene (spiro-OMeTAD),[4−6] or conjugated polymers, such as polythiophene.[7]

Conjugated polymers are regarded as promising HTMs because of their low cost, tailorability, and processability. However, the efficiencies of the solid-state DSSCs using these polymeric HTMs were quite low compared to devices using nonpolymeric HTMs. There are two main reasons for their poor performance: (1) poor electronic contact between the dye molecules and the polymeric HTMs due to interface dewetting and incomplete incorporation of bulky macromolecules into the TiO_2 nanopores and (2) low hole mobility for amorphous polymeric HTMs due to the disordered arrangement of their molecular chains. To improve integration of the conjugated polymer into the voids of the nanoporous TiO_2 film, Saito et al. employed in situ chemical and photoelectrochemical polymerizations.[8] These devices, using in situ prepared poly(3,4-ethylenedioxythiophene) (PEDOT) as the HTM, performed the best with a reported short-circuit current density (J_{sc}) of 2.3 mA/cm^2 and overall power conversion efficiency (η) of 0.53%.[9]

This work describes the first use of in situ solid-state polymerized carboxylated diacetylene as the HTM in a solid-state DSSC. Solid-state polymerization is a common method used to obtain crystalline polymer from crystalline monomer by facile thermal or photo-irradiation. There are a number of advantages of using this method for the fabrication of solid-state DSSC devices. One major advantage is that by being able to first add the smaller monomer species and then carry out in situ, solid-state polymerization, more polymer may ultimately be integrated into the nanoporous TiO_2 structure. Because polydiacetylenes (PDAs), as prepared via solid-state polymerization, are primarily crystalline and have high charge carrier mobilities, approximately 10^3 larger than those of partially crystalline or amorphous conjugated polymers,[10] this method should provide a novel way to enhance the carrier mobility in solid-state DSSCs. Also, modification of the diacetylene monomer with a carboxylic acid group is expected to provide an intimate contact of the HTM with the ruthenium dye by the formation of hydrogen bonding. Last, this approach is simple and minimizes the exposure of impurities to the DSSC device compared to traditional chemical or photoelectrochemical polymerizations.

A schematic representation of the device structure used in this work is given in Figure 1. A compact TiO_2 film was deposited onto a fluorine-doped tin oxide (FTO) coated glass substrate (Hartford Glass, TEC-15) by a sol−gel process[11] or liquid-phase deposition (LPD). This dense TiO_2 film acts as a hole-blocking layer (HBL) between the FTO and the HTM to minimize charge recombination. The nc-TiO_2 film (Degussa, P25) of ∼3 μm thick was spin-coated and then sensitized with *cis*-bis(SCN)-bis(2,2′-bipyridyl-4,4′-dicarboxylate)ruthenium(II) (Ru-N3) following the usual procedure.[2] The diacetylene monomer of 5,7-dodecadiyndioic acid (DA-3118, GFS Chemicals) was drop-cast onto the surface of the dye-coated TiO_2 electrode from acetonitrile/tetrahydrofuran (50:50 vol %, 0.07 M) and then polymerized by treatment with 254 nm UV for 10 min. A small amount of 4-*tert*-butyl pyridine (tBP) was added into the monomer solution for inhibiting PDA−TiO_2 interfacial charge recombination. Because the PDA layer is believed to be very thin with possible pinholes, a thin but continuous film of regioregular poly(3-hexylthiophene) (P3HT, Aldrich) was spin-coated on top from chloroform to serve as the electron-

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* Corresponding author. E-mail address: jayant_kumar@uml.edu.

[†] University of Massachusetts Lowell.

[‡] U.S. Army Natick Soldier Center.

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10.1021/cm0609045 CCC: $33.50

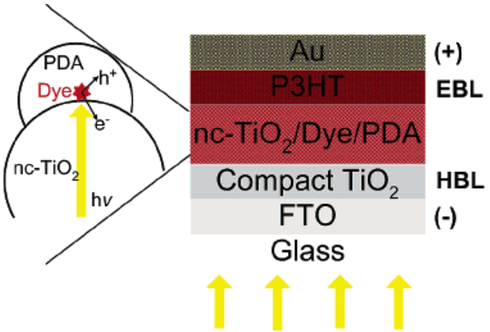

Figure 1. Device structure.

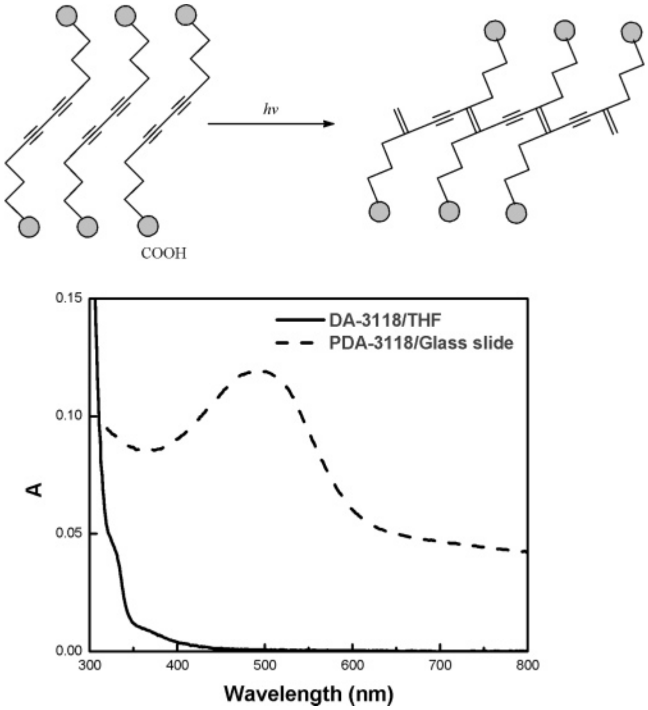

Figure 2. Solid-state polymerization of DA-3118 (top) and UV−vis absorption spectra of DA-3118 in tetrahydrofuran and PDA-3118 on a glass slide (bottom).

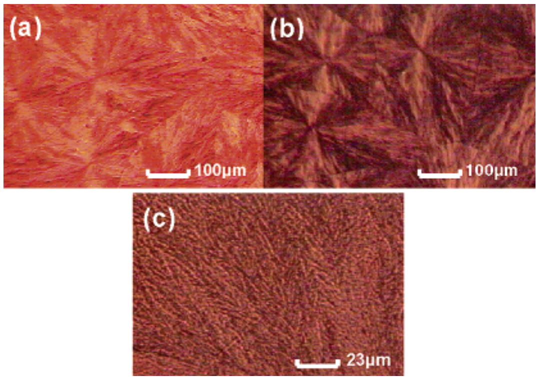

Figure 3. Optical micrographs of crystalline PDA-3118 in the Ru-N3 absorbed nanoporous TiO_2 film. (a) Transmitted brightfield 130×. (b) Transmitted polarization 130×. (c) Transmitted brightfield 560×.

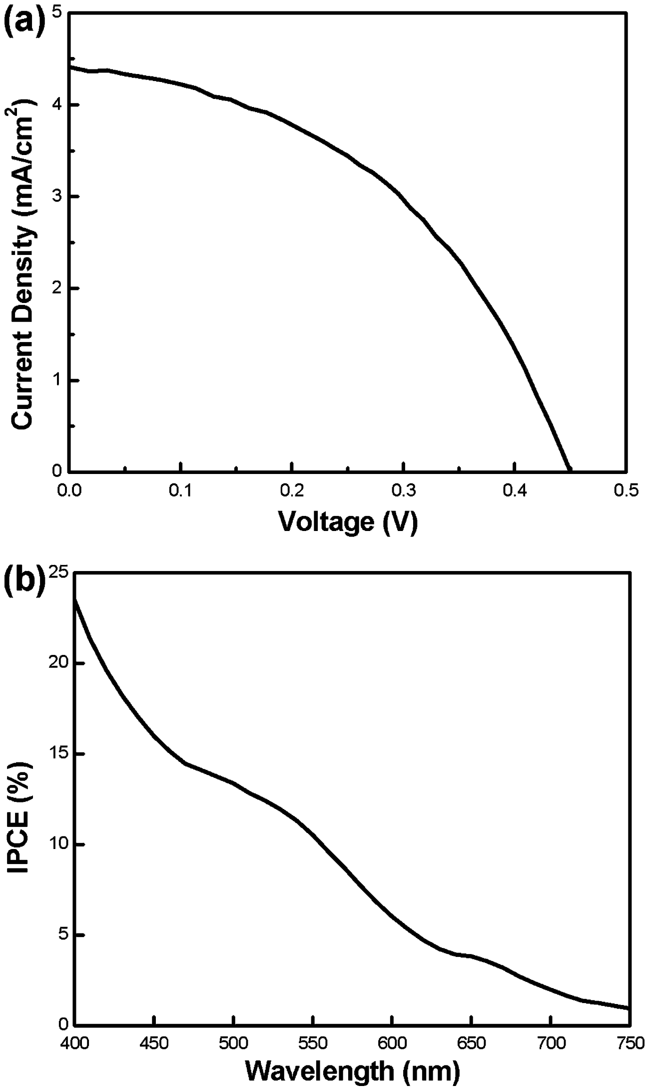

Figure 4. Photovoltaic performance of a tyical cell. (a) *I*−*V* characteristics. (b) Photocurrent action spectrum. The compact TiO_2 HBL was made by a sol−gel process and tBP was added in the DA-3118 monomer solution.

blocking layer (EBL). This P3HT EBL avoids the direct contact of the gold electrode with the TiO_2. Finally, a gold film of ∼40 nm thick was thermally deposited as the hole-collecting electrode. The current−voltage characteristics of each device were measured at the simulated AM 1.5 condition (100 mW/cm^2) with an active area of 2.5 mm × 2.5 mm.

As shown in Figure 2, the monomer and polymerized DA-3118 has two carboxylic acid groups that are expected to covalently bind to the TiO_2 surface and/or form hydrogen bonding to the Ru-N3 dye. In this way, an intimate interface was created between the dye molecules and the HTM. Also shown in Figure 2 are the UV−vis absorption spectra of DA-3118 and PDA-3118.

The microscopic image in Figure 3a shows the large PDA-3118 crystalline domains (∼400 μm) present in the dye-absorbed nanoporous TiO_2 film. The characteristic anisotropic pattern can be observed under the polarized light, as shown in Figure 3b. At the higher magnification as shown in Figure 3c, it can be seen that those crystalline domains are composed of a number of well-arranged microstructures (1−2 μm). Such structures could be due to a combination of TiO_2 nanoparticles with the surrounding, in situ polymerized PDA-3118 nanocrystals. More morphology studies via electronic microscopy are in progress.

Figure 4a shows the current−voltage characteristics of a typical cell in the presence of tBP, using the sol−gel prepared compact TiO_2 HBL. Under AM 1.5 illumination (100 mW/cm^2), the cell achieved J_{sc} of 4.25 mA/cm^2, V_{oc} of 0.46 V, fill factor (FF) of 0.45, and η of 0.89%. The average η of the three cells tested was 0.82%. The statistical variation can be primarily attributed to the fact that the thickness of the spin-coated nc-TiO_2 film is not uniform. These proof-of-concept J_{sc} and η values are very encouraging and believed to be some of the highest reported for the polymeric HTM-based DSSCs. The photocurrent action spectrum (IPCE) is shown in Figure 4b. The given values are not corrected for the reflection and absorption losses caused by the FTO-coated glass substrate and the glass slide for mounting the cell. The IPCE curve resembles the absorption spectrum of the Ru-N3 dye but exhibits relatively small values in the range of 500−550 nm. We can preliminarily conclude that the observed photocurrent arises from the photoinduced electron transfer by the dye. Part of the incident light is absorbed and/or scattered by the PDA-3118 and does not contribute to the photocurrent. Even though there is parasitic absorption or scattering caused by the PDA to some extent, the IPCE values from 500 to 550 nm are all higher than 10%.

In principle, conjugated polymers can function as a sensitizer and HTM at the same time. To extend this concept toward this PDA system, a cell was constructed in the absence of Ru-N3. Its photovoltaic performance, however, was quite poor with J_{sc} of 0.11 mA/cm^2, V_{oc} of 0.51 V, FF of 0.35, and η of 0.02%. The photocurrent action spectrum shows (figure not given) that most of the photocurrent arises from the band-gap excitation of TiO_2 at ∼400 nm for anatase and 420 nm for rutile, respectively, indicating that the PDA-3118 is not acting as an efficient sensitizer. This observation agrees with the literature, where Sariciftci et al.[12] reported the absence of photoinduced electron transfer from the PDA to C_{60} and attributed the reason to the large exciton binding energy of PDAs, up to 0.5 eV. In this case, the short exciton diffusion length in the PDA, compared to other conjugated polymers, also reduces the separation of excitons into free charge carriers. As a result, it can be concluded that the photocurrent demonstrated in these cells is created by the Ru-N3 and the PDA-3118 primarily serves as an efficient HTM.

To study the inhibition effect of tBP on the interfacial charge recombination, devices I and II were fabricated with and without tBP, respectively. In each of these devices the compact TiO_2 HBL was prepared by LPD as a proof-of-concept. The comparison of their current−voltage characteristics, as shown in Table 1, indicated a significant improvement in both V_{oc} and η for device II which has the tBP. This better photovoltaic performance can be partly attributed to the role of tBP as an inhibitor for the PDA−TiO_2 interfacial charge recombination, as has been reported with other solid-state DSSCs.[5]

Table 1. Comparison of Different Devices

device	TiO_2 HBL	tBP	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η^a (%)
I	LPD^b	no	3.22	0.14	0.29	0.10
II	LPD^b	yes	3.48	0.41	0.32	0.42
III	sol−gel	yes	4.25	0.46	0.44	0.82

^{a} η: average of two to three cells. ^{b} LPD: hydrolysis of aqueous $TiCl_4$ solution.

A comparison of devices II and III in Table 1 shows the effect of LPD versus sol−gel TiO_2 HBL preparation. It can be seen that in the presence of tBP, the sol−gel prepared TiO_2 HBL in device III works much better than the LPD-prepared TiO_2 HBL in device II. The reason for this difference is that the LPD-prepared TiO_2 film is not as dense as the sol−gel prepared TiO_2 film. Smestad et al. have also proved by cyclic voltammetry that the sol−gel prepared TiO_2 film and the spray pyrolysis prepared TiO_2 film are equivalent for hole blocking.[13]

These results show the first demonstration of in situ solid-state polymerized diacetylene-3118 in DSSCs. The PDA-3118 was found to be an efficient hole conductor but poor light sensitizer in a solid-state DSSC. Because many parameters of the cell assembly have not yet been optimized, further improvement of the photovoltaic performance is expected and underway. In particular, future work will focus on in detail characterizing the PDA-3118 morphology inside the TiO_2 nanopores, improving the PDA-3118 crystallite orientation, inhibiting interfacial charge recombination, and reducing the parasitic absorption by using PDAs that have less absorption overlap with the dyes.

Acknowledgment. The authors acknowledge the financial support of the U.S. Army Natick Soldier Center (no. DAAD16-01-C-0011) and NSF (INT-0243011). The authors also thank Dr. Krishna Mandal of EIC Laboratories for supplying the Ru-N3 and Prof. Daniel J. Sandman for his helpful discussions about PDAs.

CM0609045

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