Electronic Supplementary Information

Improving the Efficiency and Stability of Inverted Perovskite Solar Cells with Dopamine-Copolymerized PEDOT: PSS as Hole Extraction Layer

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1 Materials

3-Hydroxytyramine hydrochloride (DA), with a purity of 98%, from Energy Chemical Co. Ltd. (Shanghai, China), was kept in temperature of 0 °C. Polystyrene sulfonic acid (PSS, Mw=75000 Da, 30 wt.%) was brought from Alfa. 3, 4-ethylenedioxy thiophene (EDOT), preserved with low temperature of 0 °C, was purchased from Bayer AG. Ammonium persulphate ((NH₄)₂S₂O₈, APS) was obtained from Sigma and used as oxidant in this experiment. The concentration of 1.0% by weight of PEDOT: PSS (Baytron PVPAI 4083) was used for contrast. All other chemicals were of analytical grade. The water used in laboratory was deionized water.

2. Experiment sections

2.1 Preparation of DA-PEDOT: PSS

The mixed solution containing PSS (20 g, with a mass fraction of 30%) and EDOT monomer (1 g) was adjusted to pH=2. After stirring for 30min, oxidizing agent APS (2.17 g) and DA monomer (0.2 g) were simultaneously added. Subsequently, the color changed from light yellow to dark blue after 24h stirring at room temperature. Thus, the rough product DA-PEDOT: PSS was obtained. The rough product was dialyzed by a dialysis membrane (Special products laboratory, USA, MWCO of 1000 Da) to remove inorganic salt and the pure product (PEDOT+PDA): PSS was available.
2.2 Characterization of Techniquest

FTIR spectra were performed using the KBr pellets in the 4000-400 cm$^{-1}$ region by Auto system XL/I-series/Spectrum 2000 spectrometry (Thermo Nicolet Co., Madison, WI, USA). Element contents of C, H and S were rationed by Vario EL cube (Elementar, Germany) with about 5.0 mg packed in aluminized paper. UV-vis absorption and transmittance spectra were measured by Shimadzu UV-3600 spectrophotometer (Japan) and Shimadzu UV-2600 spectrophotometer (Japan), respectively. The films thicknesses were tested by a step profiler (Dektak150, Veeco, USA). Dynamic light scattering (DLS) experiments were performed on a Zeta PALS instrument (Brookhaver, America). Cyclic voltammetry (CV) test was conducted with a film on glassy carbon electrode against Ag/AgCl (3M KCl solution) reference electrode at scanning rate 100mV/s. The conductivity and sheet resistance of PEDOT: PSS and (PEDOT+PDA): PSS films were measured with a KDY-1 four point probes resistivity/resistance measurement system. The films were prepared by dropping the sample on glass and air drying at room temperature. UPS and XPS measurements were conducted on a Thermo Scientific ESCALAB 250Xi with a He(I) UV source (21.22 eV) in ultrahigh vacuum. For testing UPS and XPS, the samples were spin-coated onto ITO glass and kept in an oven at 110 °C for 15 min before the measurement, and all of the experimental processes were conducted in ultrahigh vacuum environment. Atomic force microscopy (AFM) images were observed by a Park XE-100 in tapping mode. Surface wettability was measured using a static contact angle instrument (Powereach JC2000 C1, Shanghai, China).

2.3 Fabrication and Characterization of PSCs

The configurations of PSCs were ITO/HTLs/MAPbI$_{3-x}$Cl$_x$/PC$_{61}$BM/BCP/Ag. ITO-coated glass substrates were cleaned via a series of ultrasonication in detergent, acetone, DI water, isopropyl alcohol and followed by UV-ozone plasma treatment. (PEDOT+PDA): PSS layer was spin-coated onto the pre-patterned ITO glass
substrate and annealed using a hot plate at 140°C for 15 min to remove residual solvents. PEDOT: PSS (Baytron PVPAI 4083) based device was also fabricated as comparison with the same method. The substrates with (PEDOT+PDA): PSS or PEDOT:PSS were then transferred into a glove box filled with highly pure N₂. Then MAPbI₃₋ₓClₓ precursor solution (1.26 M PbI₂, 0.14M PbCl₂ and 1.35 M MAI in cosolvent of DMSO: GBL at Vol ratio of 3:7) was spin-coated to form a perovskite layer of about 280 nm on the modified ITO substrate. After annealing at 100°C for 20 min, the PCBM layer (~55 nm) was deposited by spin coating onto the surface of perovskite layer. After that, 0.5 mg/mL BCP solution was spin coated onto PCBM layer. The devices were completed by thermal deposition a layer of 100 nm A gas cathode in a vacuum of <1×10⁻⁶ Torr. The devices area was 0.07cm² defined by shadow mask.

The photovoltaic performance of the PSCs was tested in air with a computer-programmed Keithley 2400 source/meter and a Newport’s Oriel class solar simulator, which simulated the AM1.5 sunlight with energy density of 100 mW/cm² and was certified to the JIS C 8912 standard. IPCEs of PSCs were measured with a 300W Xenon Lamp (Oriel 6258) and a Cornerstone 260 Oriel 74125 monochromator. The photovoltaic stability of PSCs was investigated by storing the unencapsulated devices in N₂ inert atmosphere for 28 days. The UV-visible absorption spectra were measured on a Perkin-Elmer Lambda 950 spectrophotometer. Photoluminescence spectra were collected on an Edinburgh Instruments FLS920 spectrofluorometer, the excitation wavelength was 630 nm. Scanning electron microscopy (SEM) images were obtained on a JSM-7800F SEM. Thin film X-ray diffraction (XRD) measurements were conducted on a Bruker D8 Advance XRD instrument.
Figure S1. The IR spectra of (a) PEDOT: PSS: PDA, (b) EDOT and (c) DA·HCl
Figure S2. UV-vis absorption spectra of PEDOT: PSS and DA-PEDOT: PSS aqueous solutions
Figure S3. Transmittance spectra of PEDOT: PSS and DA-PEDOT: PSS on ITO substrates.
Figure S4. $1/C^2$-V curves of devices with PEDOT:PSS and DA-PEDOT:PSS as the HTLs.
Figure S5. Contact angle of solutions of PEDOT:PSS and DA-PEDOT:PSS droplets on glass.
Table S1. Photovoltaic parameters of PSCs by applying PEDOT: PSS and DA-PEDOT: PSS solutions with different concentration as HELs.

<table>
<thead>
<tr>
<th>HELs</th>
<th>Jsc (mA/cm²)</th>
<th>Voc (V)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEDOT: PSS</td>
<td>18.74 (20.63)</td>
<td>1.00 (0.97)</td>
<td>0.71 (0.98)</td>
<td>13.31 (15.21)</td>
</tr>
<tr>
<td>DA-PEDOT: PSS (1.2 wt%)</td>
<td>14.11</td>
<td>0.96</td>
<td>0.38</td>
<td>5.15</td>
</tr>
<tr>
<td>DA-PEDOT: PSS (0.6 wt%)</td>
<td>19.47</td>
<td>0.95</td>
<td>0.62</td>
<td>11.47</td>
</tr>
<tr>
<td>DA-PEDOT: PSS (0.3 wt%)</td>
<td>19.79 (20.10)</td>
<td>1.04 (1.09)</td>
<td>0.66 (0.70)</td>
<td>13.58 (14.77)</td>
</tr>
<tr>
<td>DA-PEDOT: PSS (0.15 wt%)</td>
<td>20.53 (20.10)</td>
<td>1.06 (1.05)</td>
<td>0.70 (0.76)</td>
<td>15.23 (16.65)</td>
</tr>
</tbody>
</table>

The performance in bracket were obtained from samples filtered with 0.22 um filter film before spin-coating.