Article to Materials Chemistry A

Supplementary Information

Transparent and Flexible Organic Semiconductor Nanofilms with Enhanced Thermoelectric Efficiency

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Experimental Section

Characterization

Electrical conductivity (σ) of the PEDOT:PSS film on a glass substrate was measured by the van der Pauw method with a four-point contact configuration on a Keithley 2400 source-measure unit equipped with a 2182 nano-voltameter and a 7001 switch system. Prior to the measurement, four gold electrodes (2×2 mm) were patterned onto the PEDOT:PSS film to ensure stable ohmic contacts. The Seebeck coefficient was measured on a temperature gradient setup built in-house from a Peltier cooler and a Peltier heater. The Peltier devices were controlled by a Keithley 2400 source-measure unit and a Keithley 2200-30-5 power supply. A thermocouple (TC) was placed on each of the hot and the cold region's gold electrode of the film samples at a separation of 1 cm. The temperature difference between the TCs was fixed at 5 °C. Accordingly, thermoelectric efficiency values were calculated from the relationship $ZT = \sigma S^2 T/\kappa$ where S stands for the Seebeck coefficient (also called the

thermopower), σ and κ are the electrical and thermal conductivities, respectively, and T is the absolute temperature. Here, a product of electrical conductivity and the square of Seebeck coefficient is referred to as the power factor (σS^2). The average thickness of the films was measured on an AS500 (KLA-Tencor Co.; USA) alpha-step surface profiler. To confirm the component ratio of PEDOT to PSS and chemical compositions on the film surface, X-ray photoelectron spectra (XPS) were acquired on a Thermo K-Alpha XPS (Thermo Fisher Scientific, West Palm Beach, FL, USA) instrument. The Raman spectra were acquired on a LabRAM ARAMIS (HORIBA Jobin Yvon, Tokyo, Japan) spectrometer with 514.5 nm (green) Ar laser excitation in the range 850–1700 cm^{-1} at room temperature. The ultraviolet-visible-near-infrared (UV-Vis-NIR) absorption spectra were acquired on a Lambda 750 (PerkinElmer, USA) at 300 - 1400 nm to investigate the doping/dedoping states of the film as a function of hydrazine concentration. The film optical transmission was measured on an UV–1601PC UV–Vis spectrophotometer (Shimadzu, Japan). The carrier concentration and carrier mobility were measured on a HMS-3000 Hall measurement system (Ecopia, Republic of Korea). The thermal diffusivity (λ) was measured on an LFA 457 MicroFlash system (Netzsch, Germany). The specific heat capacity (C_p) was evaluated on a DSC 200 F3differential scanning calorimeter (Netzsch, Germany). The thermal conductivity (κ) was calculated from the relationship $\kappa = \lambda \times C_p \times \rho$, where ρ is the density.[1]

1. Thermal conductivity

Samples	Density (g/cm^3)	Specific heat capacity (J/g·K)	Thermal diffusivity (mm^2/s)	Thermal Conductivity (W/m·K)
DTP-100	1.357	1.340	0.209	0.381
DDTP-0 M	1.270	1.190	0.198	0.299
DDTP-1.1× 10^{-4} M	1.220	1.210	0.210	0.310

Table S1. Thermal conductivity for different PEDOT:PSS samples and other parameters used for the calculation of thermal conductivity

2. Hall measurements

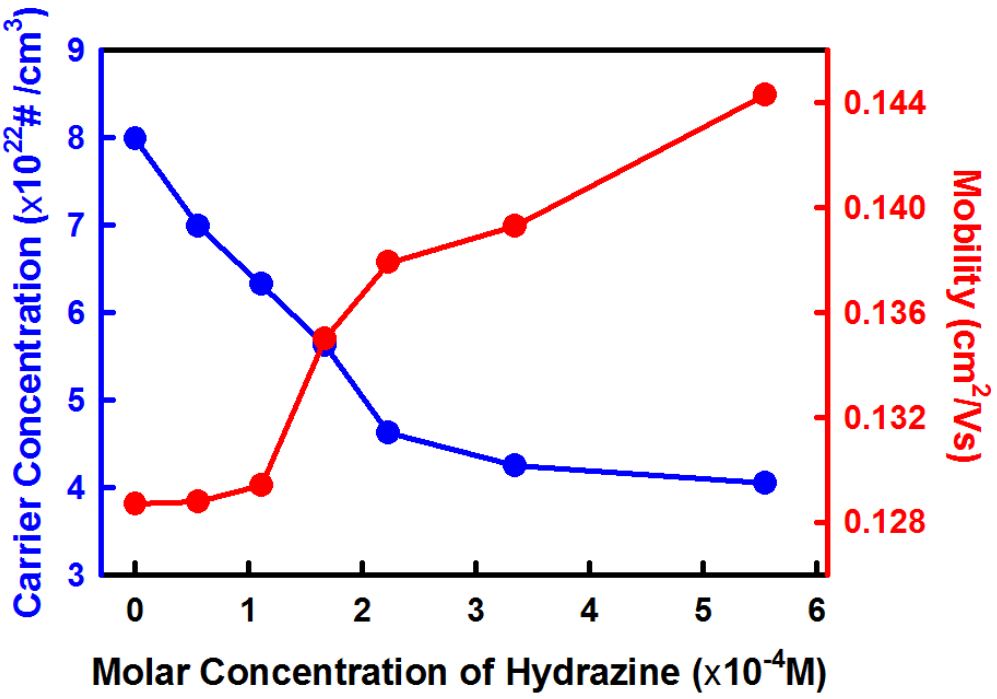

Fig S1. Variation of carrier concentration (n) and mobility (μ) of hydrazine/DMSO-dedoped PEDOT:PSS (DDTP) films as a function of hydrazine concentration. The electrical conductivity (σ) is proportional to $n \times \mu$.

3. Reduction mechanism

The dedoping process with hydrazine/DMSO can be divided into two steps according to the role of hydrazine; the neutralization of PSS and reduction of PEDOT, as shown in (a) Route 1 and (b) Route 2, respectively. In Route 1, the dedoping of PEDOT occurs via two steps: the reversible reaction of hydrazine (1) and combination between $–SO_3H$ and $N_2H_5^+$ via deprotonation (2). This step neutralizes the doped PEDOT by reducing the coulomb interaction between PEDOT and PSS. In Route 2, 'over-dedoping' of PEDOT occurs by reduction of ethylenedioxy part in EDOT units. Hydrazine first attacks the carbon of ethylenedioxy part, and which opens the ring of ethylenedioxide (***Int*$_1$**). Second, one hydrogen atom transfers from the hydrazine group to the negatively charged oxygen and the hydrazino group ($-HNNH_2$) attacks the thiophene ring to form ***Int*$_2$**. Another hydrogen atom of ***Int*$_2$** transfers from the hydrazino group ($-HNNH_2$) to the hydroxyl group (-OH) and forms ***Int*$_3$** and ***Int*$_4$**. This gives a water molecule (H_2O) or a water molecule and a cis-diazene ($-N_2H_2$), and the two deoxygenated product.[2-4]

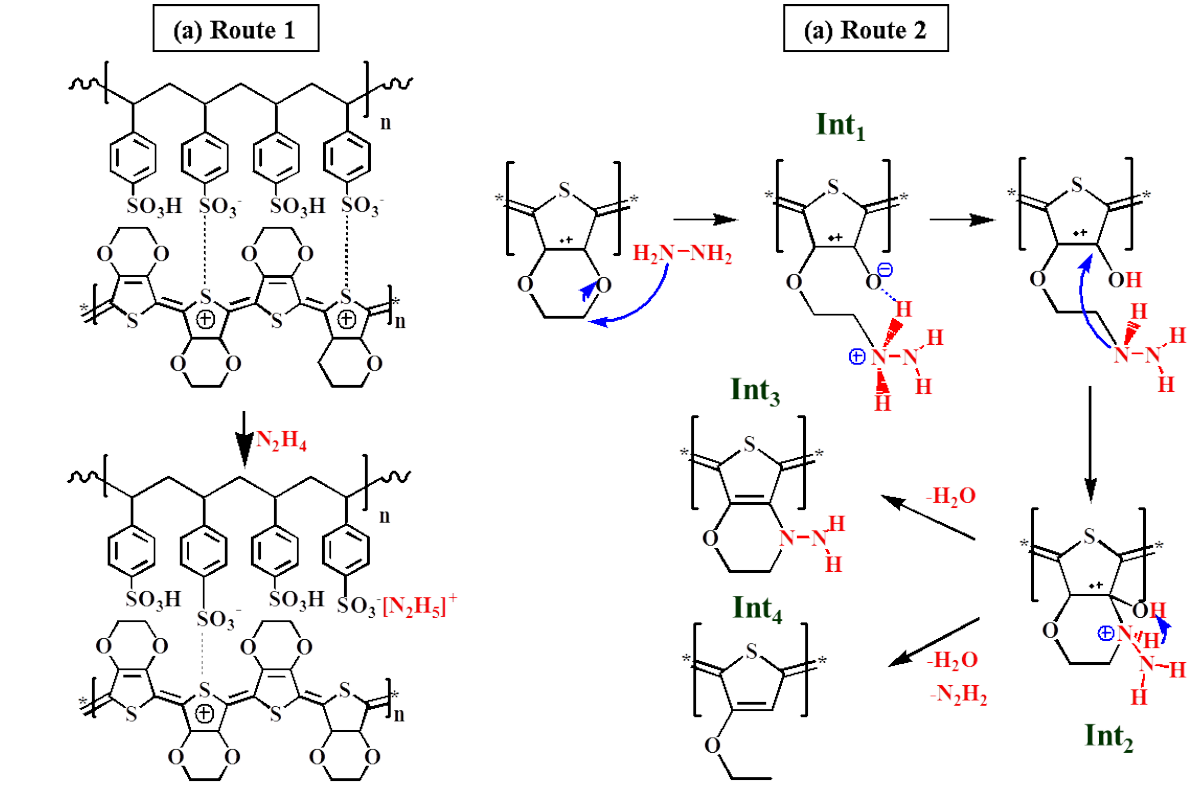

Fig S2. Dedoping and reduction mechanism of PEDOT:PSS films treated by hydrazine/DMSO (i.e. DDTP films): (a) dedoping of PEDOT:PSS film by the neutralization of PSS and (b) reduction of PEDOT molecules with excess amount of hydrazine as a reducing agent.

4. X-ray photoelectron spectra (XPS)

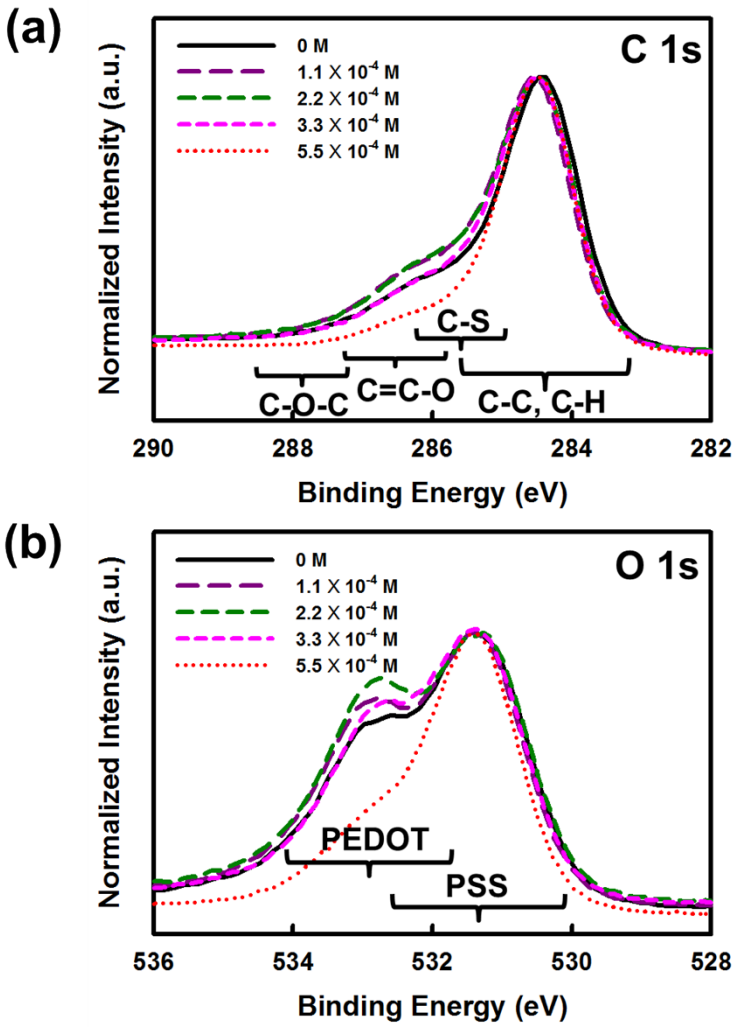

Fig S3. XPS spectra of the PEDOT:PSS films treated by hydrazine/DMSO with different hydrazine concentration (i.e. DDTP films): (a) C 1s and (b) O 1s XPS peaks.

References

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