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Working Mechanism and Performance of Polypyrrole as Counter Electrode for Dye-Sensitized Solar Cells

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Supporting Information

XPS spectra of as-prepared PPy film polymerized in 0.1 M TsOH; 0.5 M TsOH; 1.0 M TsOH; 2.0 M TsOH; XPS iodine spectra of as-prepared PPy film polymerized in 0.5M TsOH; 1.0M TsOH.

Doping and qualitative analysis of the resultant PPy films have been investigated by using XPS spectra. The XPS survey-spectra of as-prepared PPy films polymerized using 0.1 M pyrrole and 10 mM LiI in aqueous solution with different concentrations of TsOH are presented in Figure S1 ~ Figure S4.



Fig. S1 XPS spectrum of as-prepared PPy film polymerized in 0.1 M TsOH.



Fig. S2 XPS spectrum of as-prepared PPy film polymerized in 0.5 M TsOH.



Fig. S3 XPS spectrum of as-prepared PPy film polymerized in 1.0 M TsOH.



Fig. S4 XPS spectrum of as-prepared PPy film polymerized in 2.0 M TsOH.

It is important to study the existing state of iodine in the PPy thin films, which can be determined by the XPS measurements. Figure S5 and S6 show $I_{3d3/2}$ and $I_{3d5/2}$ XPS spectra of as-prepared PPy films polymerized with 0.5 M and 1.0 M TsOH, respectively.



Fig. S5 XPS iodine spectrum of as-prepared PPy film polymerized in 0.5 M TsOH.



Fig. S6 XPS iodine spectrum of as-prepared PPy film polymerized in 1.0 M TsOH.

The stability of resultant PPy films has been studied using electrochemical technique, as they are supposed to be used as the CEs in the DSSCs. The consecutive CV spectra of the asprepared PPy thin films have been collected both in an acetonitrile solution at room temperature and in N,N-Dimethylformamide (DMF) solution at 80 °C (Figure S7). As evidenced by Figure S7, the redox current density for $I_3^- \rightarrow I^-$ redox reaction slightly changes after 10 cycles of consecutive CV measurements, even at a high temperature. Thus, the asprepared PPy films exhibit relatively good electrochemical stability and, thereby, can be used as the CEs in DSSCs.



Fig. S7 Consecutive CV curves of PPy films polymerized with 2.0 M TsOH at a scan rate of 50 mV s⁻¹: (**A**) in acetonitrile solution tested at room temperature, and (**B**) in DMF solution tested at 80 °C. Both electrolytes contain

0.1 M LiClO₄, 10 mM LiI, and 1 mM I₂. The inset shows the change of redox peaks current Ipc/Ipa $(I_3 \rightarrow I^-)$ with scanning segments of CVs.

It is noted that, theoretically, two semicircles should be observed in the EIS curve. One corresponds to the charge transfer process at interface between counter electrode and electrolyte (at high frequency) and another is the one between photoanode and electrolyte (at low frequency). Indeed, we have observed a small semicircle at high frequency, as given here (Figure S8), corresponding to the process between the PPy CE and electrolyte. Though these semicircles are not well-shaped, it can be seen approximately that this charge transfer resistance also decreases slightly with increasing TsOH concentration, indicating the promotion of electrocatalytic kinetics by TsOH concentration. Since the semicircles are not well-shaped, however, the error would be very large if we use these spectra for simulation.



Fig. S8 Zoom-in of EIS spectra at high frequency (1 kHz ~ 100 kHz) derived from Figure 4 of the main text.

Figure S9 shows the Tafel polarization curves of the symmetrical cells fabricated with two identical as prepared PPy CEs and the same electrolyte in DSSCs. Tafel polarization curve can be used to characterize the electro-catalytic activity of CEs. The current at high potential (J_{lim}) represents the limiting diffusion rate of tri-iodide on electrode, and the slope of curve corresponds to the ions exchange rate on electrode. The PPy CE polymerized with 2.0M TsOH

demonstrates a higher J_{lim} and larger curve slope (J_0), indicating better tri-iodide diffusion and ions exchange ability than other CEs.



Fig. S9 Tafel polarization curve of symmetrical cells fabricated with two identical PPy CEs polymerized with different TsOH concentration and the same electrolyte in DSSC.

Action spectra of the monochromatic incident photon-to-current conversion efficiency (IPCE) were measured with a CIMPS- IPCE system (ZAHNER-Elektrik GmbH & Co.KG), which are shown in Figure S10. The J_{SC} values derived from IPCE spectra are very close to those determined from J-V measurements, which also exhibits the same change trend with the TsOH concentration used for the preparation of PPy CEs as those derived from J-V measurements.



Fig. S10 IPCE curves of DSSCs based on PPy CEs prepared with 0.1 M pyrrole, 10 mM LiI and different TsOH concentration of 0.1, 0.5, 1.0, and 2.0 M, respectively.