Electronic Supplementary Information

Spatial-resolved electrochemical reversibility of conducting polymer thin film imaged by oblique-incidence reflectivity difference

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Experimental Section

**Materials and instruments**

$\text{H}_2\text{SO}_4$, Toluene, acetone, ethanol and KCl were purchased from Sangon Biotechnology Co., Ltd (Shanghai, China). FTO conductive glass were obtained from OPV Tech New Energy Co., Ltd. Aniline and other chemicals were purchased from Aladdin Reagents Ltd. All the chemicals were analytical grade and used as received. The deionized water from a Millipore system was used throughout all experiments. A UV light (BZZ250GF-TC, HuiWo Tech, China, Hg-Xe lamp, main wavelength of 185 and 254 nm) was used for UV irradiation. A profilometer (kosaka ET-150) was used to measure the thickness of PANI film.

**OIRD instrument**

A home-built OIRD instrument (see its photographs in Fig S1) was used for this study. Components include: a He-Ne laser (632.8 nm, 25-LHP-171-230 He-Ne laser from Melles Griod); a photoelastic modulator (PEM 100 photoelastic modulator system from HINDS INSTRUMENTS, I/FS50 Fused Silica, 50 kHz from and Optical and Electronic Heads, Controller, and Cables); Lock-In Amplifier (SR830, dual phase DSP Lock-In amplifier from Stanford Research Systems Inc.); motorized stage (KS202-100 stage with DS102MS controller, from SURUGA SEIKI CO.LTD).

For EC-OIRD measurement, a PDMS cell was coated on the FTO surface to form an electrochemical cell, in which electrolyte solution was added and the counter electrode and reference electrode were inserted. The electrochemical measurement was carried out with a CHI 760 potentiostat.

**Electrochemical measurements**
All electrochemical measurements were performed on a CHI-760 electrochemical analyzer (CH Instruments, Inc., Shanghai) in a standard 3-electrode. The platinum electrode and SCE were purchased from Tianjin Aida Inc., Tianjin and were used as counter electrode and reference electrode respectively. For electrochemical polymerization of PANI thin film, FTO glass (25 mm×75 mm× 2 mm, 14±1Ω/□, ~350 nm of FTO layer) was used as working electrode, and PANI was grown by CV sweep between −0.2 V and 0.9 V at a scanning rate of 20 mV s⁻¹ in 1 M H₂SO₄ containing 0.5 M aniline. The CV scanning was performed for 14 cycles.

Fig. S1. Photographs of homemade OIRD setup. From left to right: optical components; lock-in amplifiers and PEM controller; software interface.
Fig. S2. CV curve for electrochemical growth of PANI thin film.

Fig. S3. In situ OIRD response of a bare FTO upon CV scanning from -0.2 to 0.6 V in 1.0 M H$_2$SO$_4$. 
Fig. S4. Differential OIRD image of a bare FTO after patterned UV-irradiation at 0.51V and 0 V collected in 1.0 M H₂SO₄.

Fig. S5. (a) CV curve of pristine PANI thin film and simultaneous OIRD response in 1.0 M KCl at a scan rate of 10 mV s⁻¹; (b) differential OIRD images of a patterned UV-irradiated PANI film at 0.51V and 0 V collected in 1.0 M KCl.