

Supplementary Information

Solid-state dye-sensitized solar cells fabricated by coupling photoelectrochemically deposited poly(3,4-ethylenedioxythiophene) (PEDOT) with silver-paint on cathode

Kazuhiro Manseki* , Wirat Jarernboon , You Youhai, Ke-Jian Jiang, Kazuharu Suzuki, Naruhiko Masaki, Yukyeong Kim, Jiangbin Xia, and Shozo Yanagida*^a

^aCenter for Advanced Science and Innovation, Osaka University,
Yamadaoka 2-1, Suita, Osaka, Japan;
Fax: +81-6-6879-4132; Tel: +81-6-6879-4132;
E-mail: kmanseki@gifu-u.ac.jp, s.yanagida@casi.osaka-u.ac.jp

† *A typical cell fabrication is employed as follows:* a transparent conducting substrate, FTO (F doped SnO₂ coated on soda-lime glass, sheet resistance 13 Ω/□, Nippon Sheet Glass) is used for an anode electrode. A dense TiO₂ blocking layer with around 80 nm in thickness is then deposited by spin-coating in order to avoid a short circuit between FTO substrate and hole conducting materials. Mesoporous TiO₂ layer with various thickness are prepared from colloidal paste of TiO₂ (Nanoxide-T: Solaronix) by doctor blade technique on the FTO covered with the compact TiO₂ layer. Substrates thus obtained are sintered at 500 °C for 15 min. The film thickness is measured by a profiler (Sloam, Dektak3). After calcination, TiO₂ electrodes are immersed into 3.0×10⁻⁴ M cis-Ru(dhtbpy)(dcbpy)(NCS)₂, dhtbpy = 4,4'-di(hexylthienylvinyl)-2,2'-bipyridyl; dcbpy = 4,4'-dicarboxy-2,2'-bipyridyl, which is known as HRS-1, of acetonitrile/tert-butanol (1:1, (v/v)) and kept in a dark for 24 h at 60 °C. In-situ photoelectrochemical oxidative polymerization is carried out in a mixed solution of 0.01 M 2,2'-bis(3,4-ethylene-dioxythiophene) (bis-EDOT, Azuma) and 0.1 M lithium bis(trifluoromethane-sulfonyl) imide (LiTFSI, Fluka) in acetonitrile by applying constant potential (+0.2V vs Ag/AgCl) using the dyed TiO₂ electrode dipped in the solution. The reaction is monitored by electrochemical system (BAS 100B/W) for 20 min under irradiation of a 500W xenon lamp (22 mW/cm², λ > 520 nm). After the polymerization, TiO₂ electrodes are rinsed with acetonitrile and dried at room temperature, then treated with the ionic liquid of 0.2 M LiTFSI mixed with 0.2 M tBP(4-tert-butylpyridine) in 1-ethyl-3-methylimidazolium bis(trifluoromethane-sulfonyl)imide (EMIm-TFSI), and kept in a dark for 12 h. Then the ionic liquid on the electrode surface is wiped off and silver paste (D-362, σ~1.4×10⁵ S m⁻¹, Fujikura Kasei) or carbon paste (XC-223, σ~3.3×10³ S m⁻¹, Fujikura Kasei) is applied directly onto the wiped electrode. Typical active area of electrode is 0.25 cm² (5mm square) and solar cell performance is measured with a mask under AM 1.5 (100 mW cm⁻²) irradiation conditions (YSS-80, Yamashita Denso) at room temperature, and incident photon to current conversion efficiency (IPCE) is evaluated using a commercial setup for IPCE measurements system

(PV-25 DYE, JASCO) under 5 mW cm⁻² monochromic light illumination. Electrochemical impedance spectroscopy (EIS) is measured by an impedance analyzer (1260, Solartron analytical) connected with a potentiostat (1287, Solartron analytical) under illuminated condition (AM 1.5, 100 mW cm⁻²) at 25 °C. EIS is recorded over a frequency range of 1 Hz – 200 kHz.