

Experimental methods

Materials and reagents

FTO glass substrates ($10 \Omega/\square$, Nippon Sheet Glass) were cleaned with 5% Hellmanex in water, ultrapure water and ethanol (96 %, Merck) in an ultrasonic bath.

The dye solution used in this study contains 0.5 mM N719 dye (Dyesol, Queanbeyan (Australia)) in a 1:1 (v/v) mixture of acetonitrile and tert-butyl alcohol. The electrolyte solution contains 0.6 M 1-butyl-3-methylimidazolium iodide, 0.03 M iodine ($\geq 99.99\%$), 0.10 M guanidinium thiocyanate (99%) and 0.5 M 4-tertbutylpyridine (Fluka, 98%) in an 85:15 mixture of acetonitrile and valeronitrile. TiO₂ paste (JGC Catalysts and Chemicals Ltd., Kitakyushu-Shi (Japan)) and all other chemical compounds (Sigma–Aldrich (Australia)) were used without further purification.

Preparation of ZrO₂ spacer layers

To make the ZrO₂ screen-printing paste, 2 g ZrO₂ nanoparticles (Ztech, 50-100 nm particle size) were mixed with 1 g ethyl cellulose (Elthoxyl content 49 %, Aldrich) and 7 g terpinol (Anhydrous, Fluka). The mixture was then dissolved in 40 ml of absolute ethanol (99.7 %, Merck). The slurry was ball milled for 4h and was then rotatory evaporated to remove ethanol. After screen printing, films were dried at 125 °C and then sintering at 450 °C for 30 min.

Scanning electron microscopy

SEM images were obtained using a JEOL 7001F (JEOL, Tokyo, Japan) field emission gun electron microscope. Samples were sputter coated with 1 nm Au–Pd prior to imaging.

Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) measurements were performed using a VSP2 potentiostat (Biologic Scientific Instruments) equipped with an EC-Lab

(version 10.21) software. The frequency of an AC perturbation was varied from 500 kHz to 0.1 Hz. EIS results were fitted to equivalent circuits using a ZViewTM (version 3.2c) software.

Photocurrent–voltage characterization

The output of a sun simulator (Oriel, USA) equipped with a 1000 W xenon lamp was adjusted using a calibrated silicon photodiode cell before each measurement. Devices were tested under simulated AM1.5 sunlight (1000 W/m²). Cells were covered by a 6 mm × 6 mm black mask during testing. The incident photon to electron conversion efficiency (IPCE) was measured using a xenon light source (Oriel, Model 66901), a monochromator (Oriel, Model 74100), and a SourceMeter (Keithley, Model 2400).