Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supplementary Material

A simple one step process for enhancement of titanium foil dye sensitised solar cell anodes

J. Linnemann,[b] J. Giorgio,[a] K. Wagner,[a] G. Mathieson,[a] G. G. Wallace[a] and D. L. Officer*[a]

Surface treatments of Ti foil

Titanium foil pieces (0.25 mm thickness, Hlmet Co. Ltd.) in the size of 10 x10 cm^2 were cleaned in an ultrasonic bath for 10 min using soapy water, rinsed with deionized water and sonicated again in ethanol. The HNO_3 passivation treatment was carried out by immersing the foil in 30% nitric acid in a beaker covered with parafilm for 24 hours. Freshly cleaned foils as well as passivated foils were treated in 30% H_2O_2 solution (50 cm^2 foil in 50 ml) in a closed screw-cap glass vial. H_2O_2 treatments under high reaction rate conditions were performed at 95°C in preheated solutions in an oven for 20 or 60 min. For low reaction rate treatments, the foils were immersed for 48 h at room temperature. After the chemical treatments, the Ti foils were rinsed with deionized water and dried in a N_2-stream.

DSSC assembling

TiO_2 photoanode films were prepared on the Ti foil substrates by screen-printing three 4 μm transparent layers (DSL 18 NR-T paste, Dyesol) and then sintering stepwise using a programmable hot plate with a maximum temperature of 500°C. The active electrode area was 0.64 cm^2. The photoanodes were immersed in a 0.5 mM N719 (Dyesol) solution in a 1:1 volume mixture of acetonitrile and tert-butyl alcohol at room temperature overnight in the dark immediately after sintering or reheating to 450°C. The dye-loaded photoanodes were rinsed with acetonitrile and attached to glass using a hot-melt Surlyn foil (Solaronix). Counter electrodes were prepared by platinising TEC7 fluorine-doped tin oxide (FTO) glass (Hartford Glass) with a ethanolic 10 mM H_2PtCl_6 solution at 400°C for 20 min. Solar cell devices were assembled with a hot press using 25 μm thick Surlyn gaskets (Solaronix). The device was vacuum filled through a hole in the counter electrode with an electrolyte solution composed of 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII), 0.5 M 4-tert-butylpyridine, 0.1 M guanidinium thiocyanate and 0.03 M iodine in a solvent mixture of 85:15 vol% acetonitrile/valeronitrile and subsequently sealed with Surlyn (Solaronix) and a glass cover.

Characterization Measurements

The surface morphologies and cross sections of just cleaned and further treated Ti foils were observed by a scanning electron microscope (JEOL JSM-7500FA) operated at 5 keV. Ion milling of titanium foil was carried out on a Leica TMTIC020 for 4 hours using a 6 kV beam.

Raman Spectroscopy was carried out on a JY HR800 Spectrometer (Jobin Yvon, Horiba). A 632 nm HeNe laser was used at 20 mW with an Olympus Bx4I microscope 50x. SiO_2 was used as calibration material with a vibrational frequency at 520.7 cm^{-1}. Optical reflectance measurements were conducted with a UV-Vis-NIR spectrophotometer (UV 3600, Shimadzu). Electrochemical experiments to determine the capacitance of the foil surface were carried out in a three-electrode configuration with Ag/AgCl reference electrode and a Pt-mesh as counter electrode in an aqueous 1 M Na_2SO_4 electrolyte solution in a potential range from -100 mV to +400 mV vs. Ag/AgCl with several scan rates (10 mV s^{-1}, 50 mV s^{-1}, 100 mV s^{-1}, 200 mV s^{-1}). Area specific differential capacitances c_A were determined by plotting the current densities i at 150 mV against the scan rate ν following equation (2) which is derived as shown in (1).[1]

$$I = \frac{dQ}{dt} = \frac{\partial Q}{\partial E} \cdot \frac{dE}{dt} = C\frac{dE}{dt} \tag{1}$$

$$i(E) = c_A v \tag{2}$$

Current-voltage curves of the DSSCs under simulated 100 mW cm^{-2} AM 1.5 illumination (Oriel) were recorded in a voltage range from -0.25 to 0.85 V using a Keithley 2400 SourceMeter after calibrating the solar simulator using a certified Si diode equipped with a KG5 filter (Peccell). The device area was masked with black paint.

Incident photon-to-current conversion efficiency (IPCE) spectra were recorded using monochromatic light of a setup consisting of a xenon lamp and a monochromator equipped with sorting filters. The light was focused onto a smaller spot than the whole active DSSC area. The short-circuit current response was measured in 5 nm steps with Keithley 2400 SourceMeter and referenced to the response of a calibrated silicon diode (Peccell).

Electrochemical impedance measurements (EIS) under calibrated 100 $mWcm^{-2}$ AM 1.5 illumination were conducted at open-circuit conditions with an AC amplitude of ±10 mV in a frequency range from 0.3 MHz to 2 Hz using a Gamry Reference 600 instrument. The recorded data were analysed and fitted using ZView2.

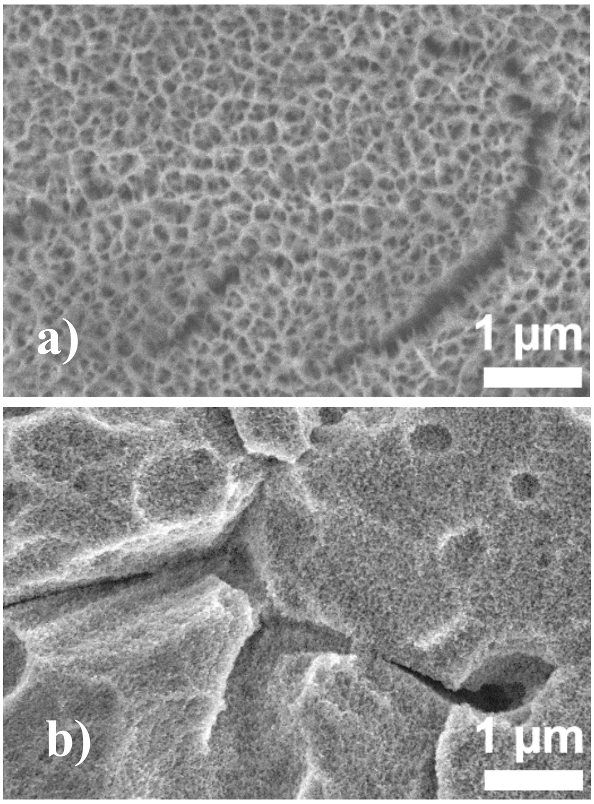

Fig. S1 SEM images of Ti foil after passivation in HNO_3 following etching in H_2O_2 for 60 min at 95°C (a) and for 48 h at room temperature (b).

References

[1] B.E. Conway, Electrochemical Supercapacitors. Scientific Fundamentals and Technological Applications, Kluwer Academic, New York, 1999.