

Electronic Supplementary Information (ESI)

TiO₂ Nanoparticles Synthesized by Molten Salt Method as a Dual Functional Material for Dye-Sensitized Solar Cells

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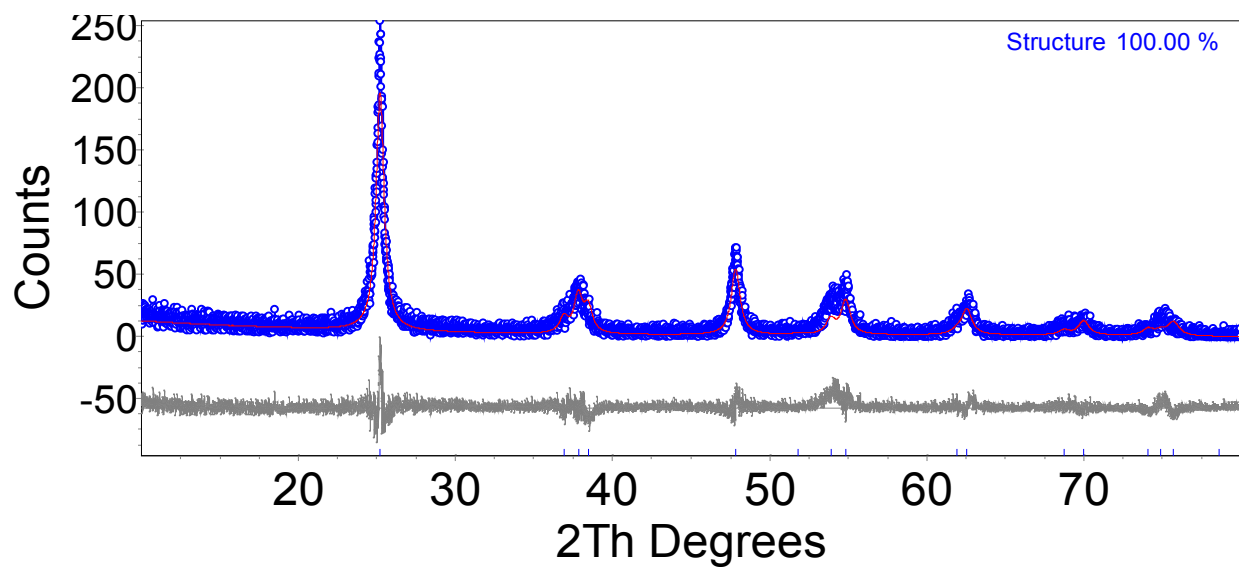
Experimental Details:

(a) Fabrication of Dye-Sensitized Solar Cells: Dye-sensitized solar cells (DSCs) were fabricated by the methods of screen-printing and doctor blading as described below: the FTO plates were first cleaned with acetone, ethanol and water successively and treated with 50 mM aq. TiCl_4 solution at 70 °C for 30 min. The MSM and P25 TiO_2 nanoparticles respectively were made into paste with ethyl cellulose and α -terpineol under controlled ratios, and fabricated on the FTO substrates by twice screen-printing and one time doctor-blading on an area of $\sim 0.25 \text{ cm}^2$. The films were then heated at 450 °C in air for 30 min, followed by a TiCl_4 post treatment and sintered again at 450 °C for 30 min. These electrodes (of thickness $\sim 13 \mu\text{m}$) were immersed in a 1:1 volume mixture of acetonitrile and tert-butanol solution of a ruthenium-based dye [$\text{RuL}_2(\text{NCS})_2 \cdot 2\text{H}_2\text{O}$; $L=2,2'$ -bipyridyl-4,4'-dicarboxylic acid (0.5 mM, N3 Solaronix)] for 24 h to allow dye attachment. The counter electrodes were prepared by spin-coating H_2PtCl_4 (50 mM in isopropyl alcohol) on FTO substrates and sintering at 390 °C in air for 30 min. Acetonitrile containing 0.1 M lithium iodide, 0.03 M iodine, 0.5 M 4-tert-butylpyridine, and 0.6 M 1-propyl 2,3- dimethyl imidazolium iodide was used as the electrolyte.

(b) Characterization: The as-prepared MSM TiO_2 nanoparticles were characterized by scanning electron microscopy (SEM, JEOL JSM-6701F microscope operated at 30 kV), high-resolution transmission electron microscopy (HR-TEM, JEOL 3010 operated at 300 kV), BET surface area (NOVA 4200E Surface Area and Pore Size Analyzer, Quantachrome, USA), X-ray powder diffraction (XRPD, Bruker-AXS D8 ADVANCE). The absorbance spectra of electrodes and the dye-desorbed solutions (by 0.02 M NaOH solution (50% v/v in water-ethanol mixture)) were measured using UV-visible spectroscopy (Schimadzu UV-3600 UV-VIS-NIR spectrophotometer). Photocurrent measurements and electrochemical impedance spectra (EIS) were measured were carried out using a XES-151 S solar simulator (San-Ei, Japan) under Standard Solar Spectra AM1.5 G conditions. Incident photon-to-current conversion efficiency (IPCE) was measured with an IPCE evaluation system for dye-sensitized solar cells (Bunkoh-Keiki Co. Ltd., CEP-2000). Electrochemical impedance spectra (EIS) were measured by a BAS-Zahner IM6e impedance analyzer (Germany) under 1 Sun illumination at an applied bias of open-circuit voltage.

Neutron powder diffraction (NPD) data were collected on the high intensity powder diffractometer, Wombat, at the Open Pool Australian Light-water (OPAL) reactor facility at the Australian Nuclear Science and Technology Organisation (ANSTO).¹ The sample was placed in a 6 mm vanadium can and data were collected for 5 minutes between $30 \leq 2\theta \leq 130^\circ$ using $\lambda = 1.5407(1) \text{ \AA}$, with the wavelength determined using the NIST 676 Al_2O_3 standard reference material. Wombat has a 2D detector allowing data to be collected over the entire 2θ -range in one acquisition. Rietveld refinements were carried out using the GSAS² suite of programs with the EXPGUI interface.³ To account for absorption in the NPD data, the Lobanov and Alte da Veiga absorption correction⁴ was applied to the Rietveld model.

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XRPD pattern of the TiO_2 nanoparticles obtained by the molten salt method. Symbols are the experimental data and red line is the model calculation.

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Materials	J_{sc} (mA/cm ²)	OCV (V)	Fill factor (%)	Efficiency (%)
P25	12.36±0.1	0.75±0.01	65±0.5	6.03±0.2
MSM TiO ₂	14.48±0.1	0.765±0.01	67.5±0.5	7.48±0.2

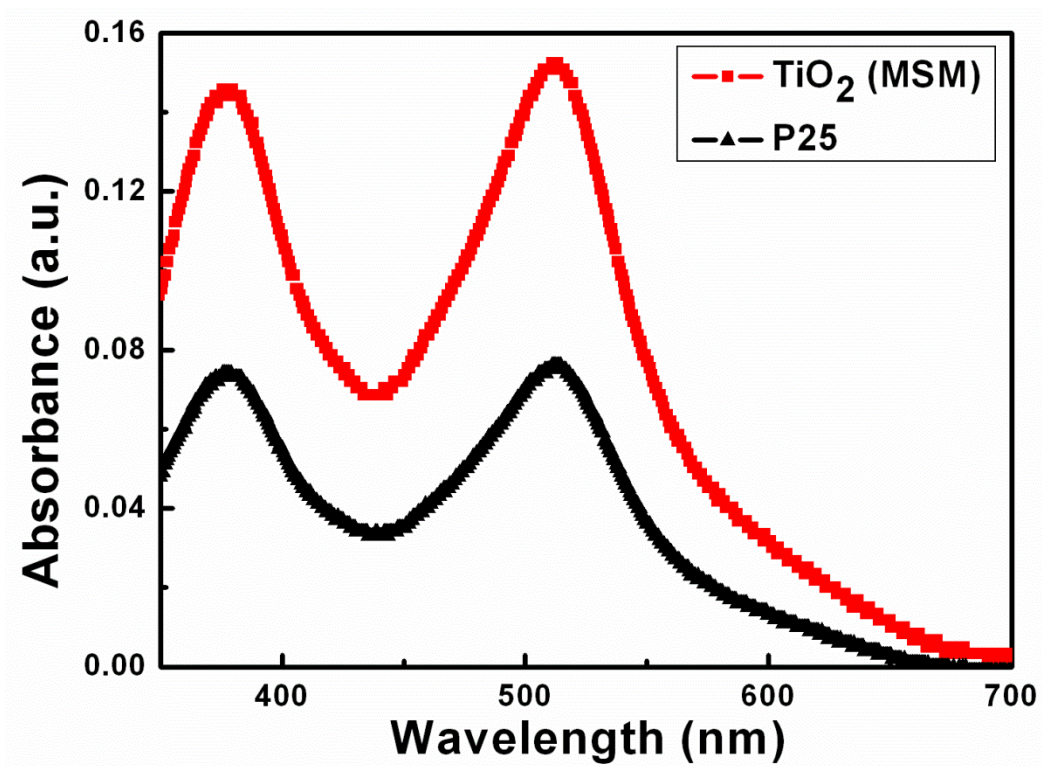
I-V parameters of solar cells with different electrodes (based on 5 devices for each material)

ESI-4

Thickness of electrodes	J_{sc} (mA/cm ²)	OCV (V)	Fill factor (%)	Efficiency (%)
9 μ m	11.87±0.1	0.765±0.01	67.5±0.5	6.13±0.2
11 μ m	13.38±0.1	0.765±0.01	67.5±0.5	6.91±0.2
13 μ m	14.48±0.1	0.765±0.01	67.5±0.5	7.48±0.2
15 μ m	14.05±0.1	0.75±0.01	66±0.5	6.95±0.2

I-V parameters of MSM TiO₂ electrodes with different thickness

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UV-Visible spectra of the solutions containing desorbed dyes from the electrodes

ESI-6

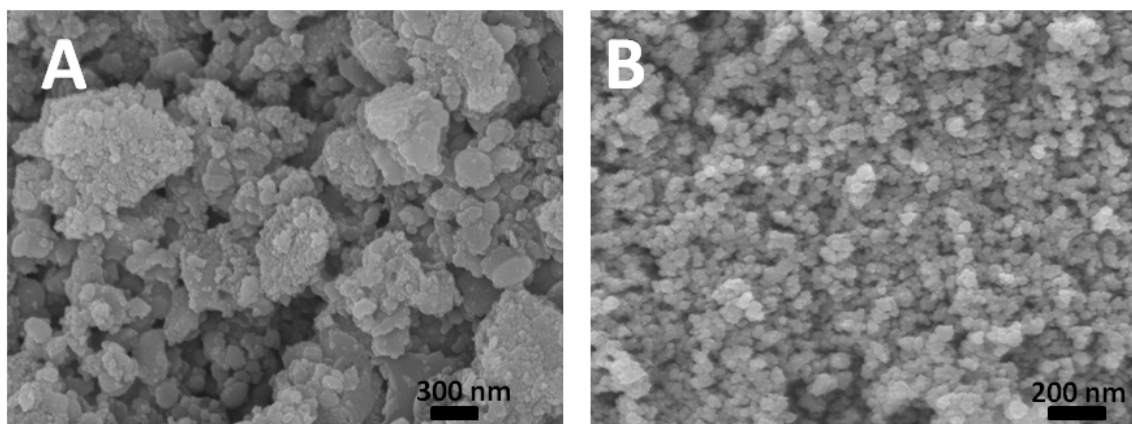
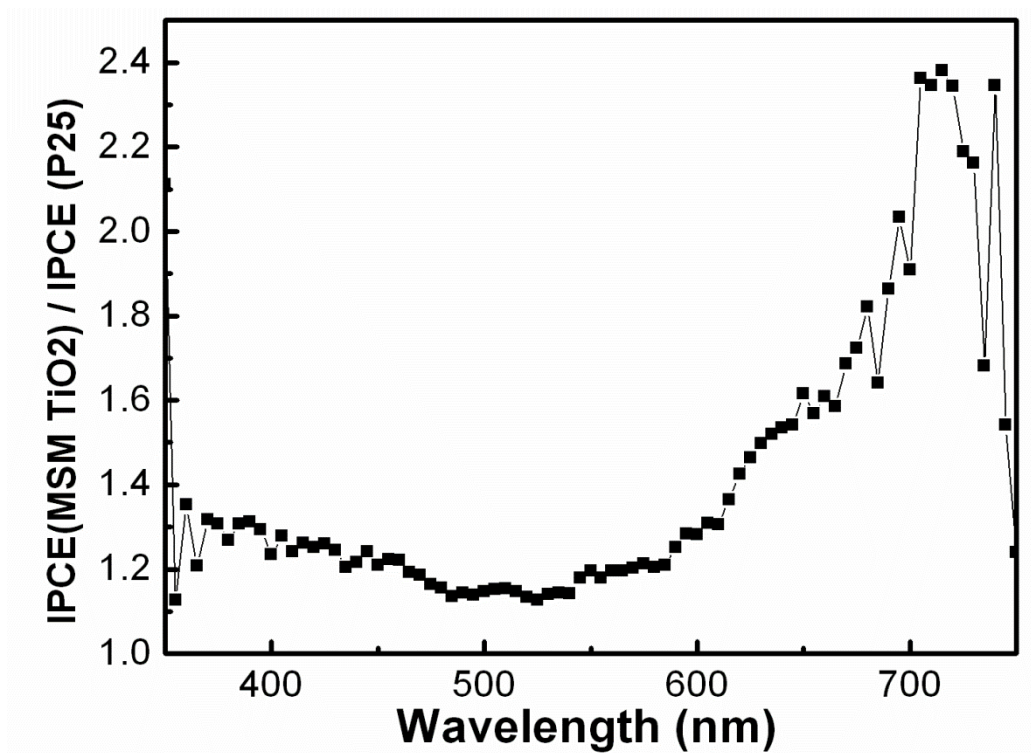


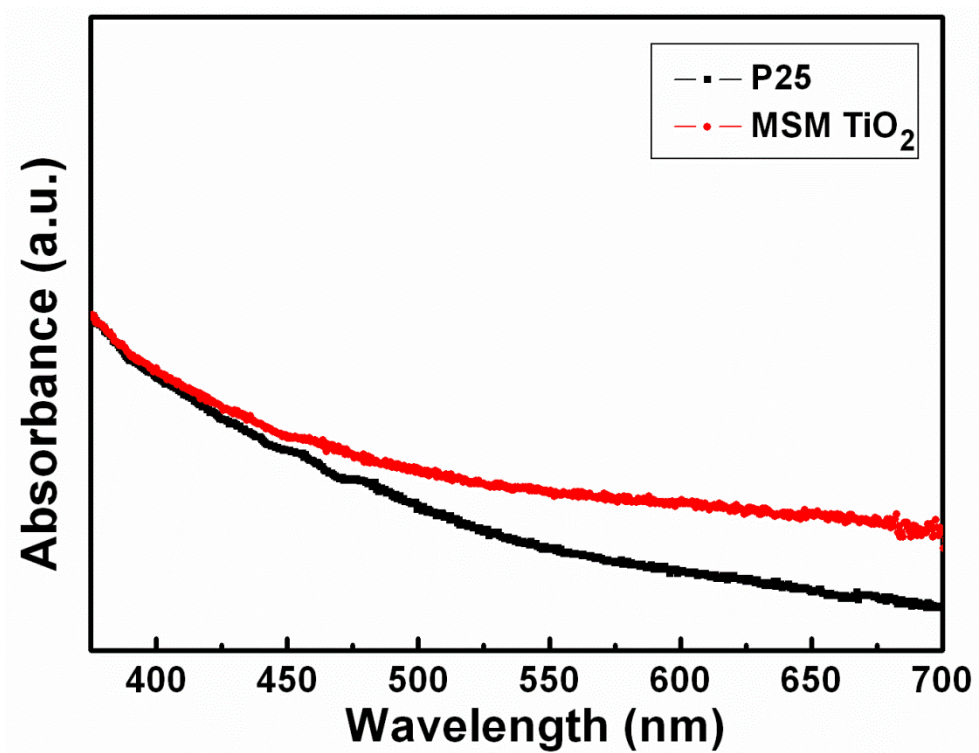
Fig. A shows the SEM image of the TiO₂ obtained using the molten salt method. The TiO₂ nanoparticles were agglomerated into aggregates with sizes ranging from 100 to 500 nm. Fig. B shows the respective image of P-25 TiO₂.

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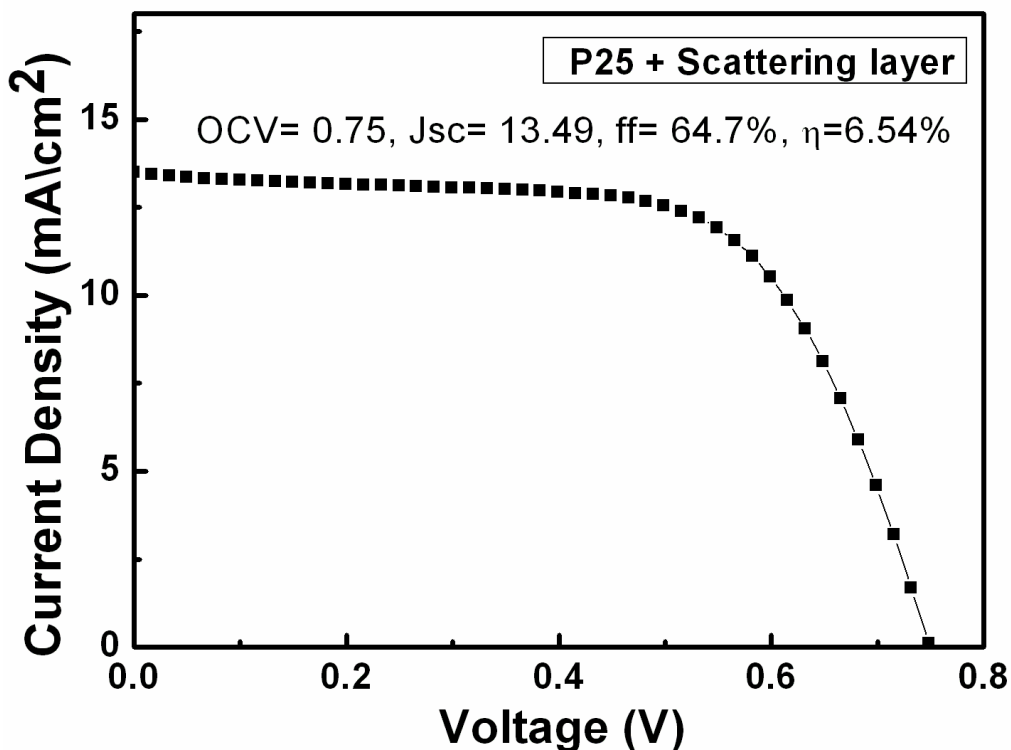
Plot of $IPCE_{(MSM TiO_2)} / IPCE_{(P25)}$

ESI-8



UV-visible spectra of MSM TiO₂ and P25 TiO₂ electrodes (the traces are normalized with respect to the absorbance at 375 nm)

ESI-9



Photocurrent-photovoltage characteristic curves of double layer electrode of P25 with a TiO₂ scattering layer.

References

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