

Supporting Information

Titanium Carbide and Titanium Nitride-Based Nano-composites as Efficient Catalysts for the $\text{Co}^{2+}/\text{Co}^{3+}$ Redox Couple in Dye-Sensitised Solar Cells

Jiangjing He^{1,2}, Jennifer M. Pringle^{1,3}, Yi-Bing Cheng^{1}*

1 Department of Materials Engineering, Monash University, Clayton, Victoria 3800, Australia

2 Australian Research Council Centre of Excellence for Electromaterials Science, Monash
University, Clayton, Victoria 3800, Australia

3 Australian Research Council Centre of Excellence for Electromaterials Science, Deakin
University, Melbourne Burwood Campus, 221 Burwood Highway, Burwood, VIC 3125,
Australia

* Corresponding author. Email: yibing.cheng@monash.edu; Phone: +61 (0)3 990 54930

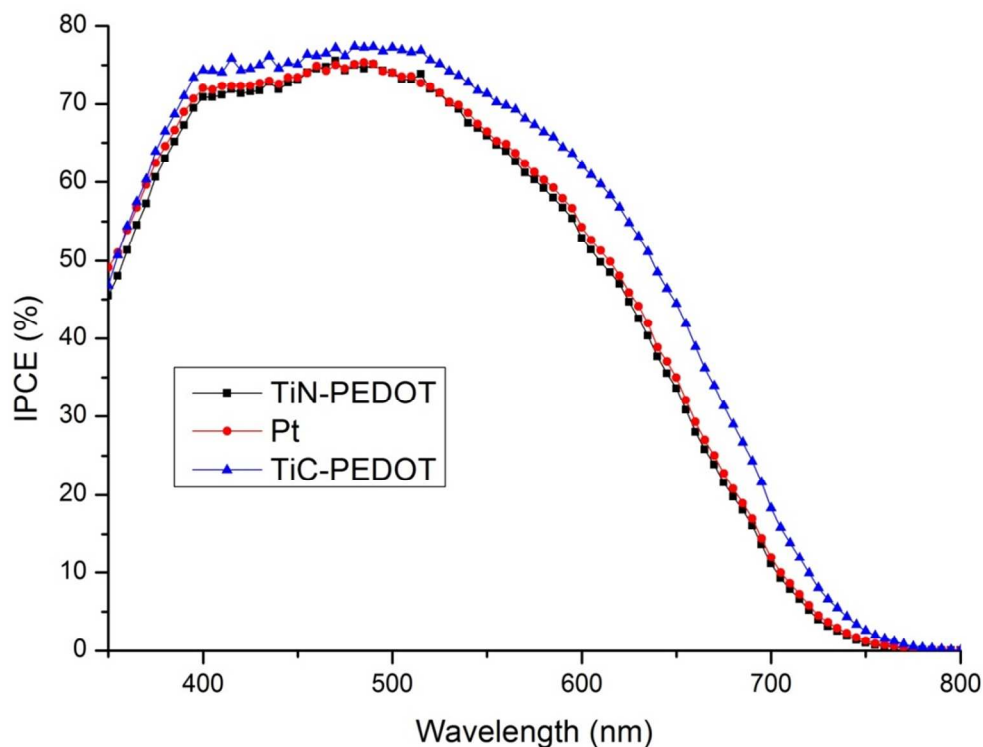


Figure S1. Incident photon to charge carrier efficiency (IPCE) of DSSCs with Pt, TiN-PEDOT and TiC-PEDOT nanocomposite counter electrodes. (TiC-PEDOT 77.4%, TiN-PEDOT 75.5% and Pt 75.3% at 475-480 nm wavelengths).

EIS measurements were also recorded using full solar cells under 1 sun illumination without any applied bias (Figure S2). The EIS spectra can be fitted by using the equivalent circuit model (Scheme S1). All fitted results are summarized in Table S1. However, the cells with Pt counter electrodes show an extra small feature (inset in Figure S2) in the high frequency domain. In order to differentiate the corresponding semicircles to different electrochemical processes, we conducted measurements under the same illumination condition but with additional applied bias across the two electrodes (shown in Figure S3).

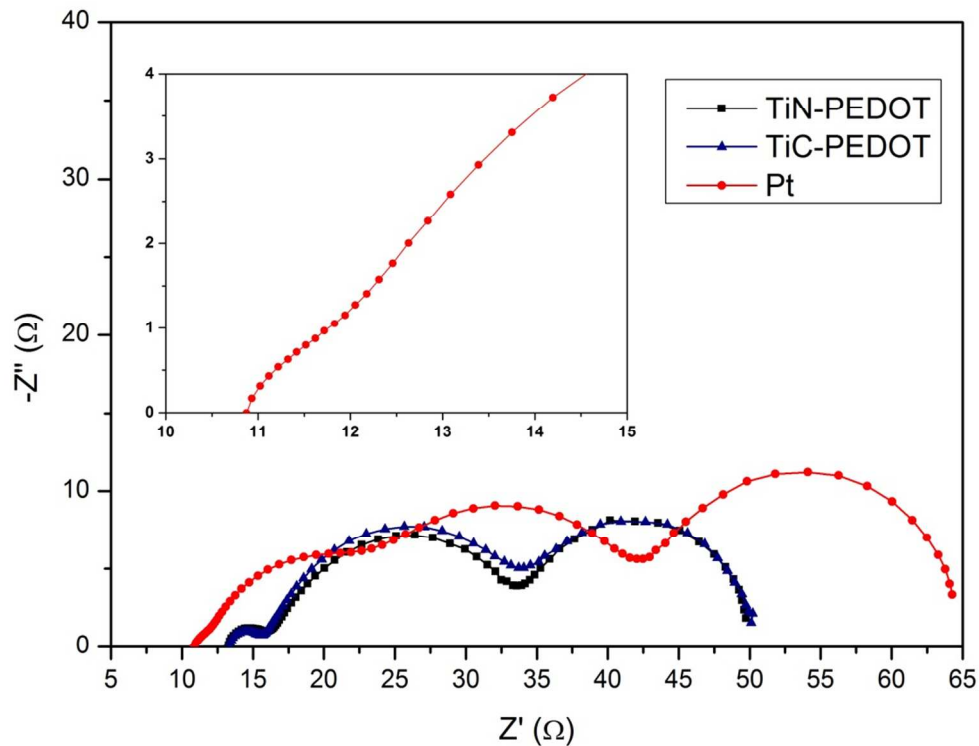
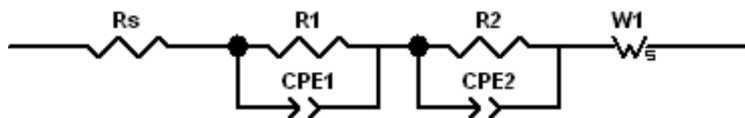


Figure S2. EIS spectra of solar cells with Pt and nanocomposite CEs, tested at open circuit condition under 1 sun illumination. The inset is an expansion of the high frequency region of the Pt cell.



Scheme S1. The Equivalent circuit model used for fitting the spectra in Figure S2. R_s is the series resistance; $R_1 = R_{ct}$ and CPE1 represent the charge transfer resistance and corresponding double layer capacitance at the counter electrode/ electrolyte interface; $R_2 = R_{re}$ is the charge recombination resistance at the TiO_2 /dye/electrolyte interface; CPE2 represents the chemical capacitance of the TiO_2 layer. $W1$ is the Nernst diffusion impedance.

Table S1. Data obtained from the Fits of the Nyquist plots in Figure S2. R_D is the diffusion resistance of the redox species in the electrolyte

Electrode	$R_s (\Omega)$	$R_{ct} (\Omega)$	$R_{re} (\Omega)$	$R_D (\Omega)$
Pt	10.9	20.0	28.5	28.6
TiC-PEDOT	13.4	2.7	21.1	21.3
TiN-PEDOT	13.3	3.0	19.6	20.6

It is shown from the Figure S3 the size of the low-frequency arc grows with the forward bias, indicating it is corresponding to the diffusion as the mass transport resistance of redox species would increase with bias.¹ Meanwhile, the 3rd semicircle, which arises from the charge-transfer resistance from the TiO_2 to the electrolyte, i.e. recombination resistance, decreases due to the increase of electron concentration in the TiO_2 .² Eventually at 0.2V, the recombination arc merged into the diffusion arc. It seems the 2nd semicircle shrinks slightly with the applied bias. Although the arc corresponding to the counter electrode-electrolyte interface usually remain constant with the forward bias, the authors think the shrinkage might because of the influence from the decreases of 3rd arc. Besides, the arc is at kHz region, which is the characteristic frequency domain of the charge-transfer resistance of the counter electrode.³ The origin for the extra high-frequency spectrum remains unclear, and requires further investigation.

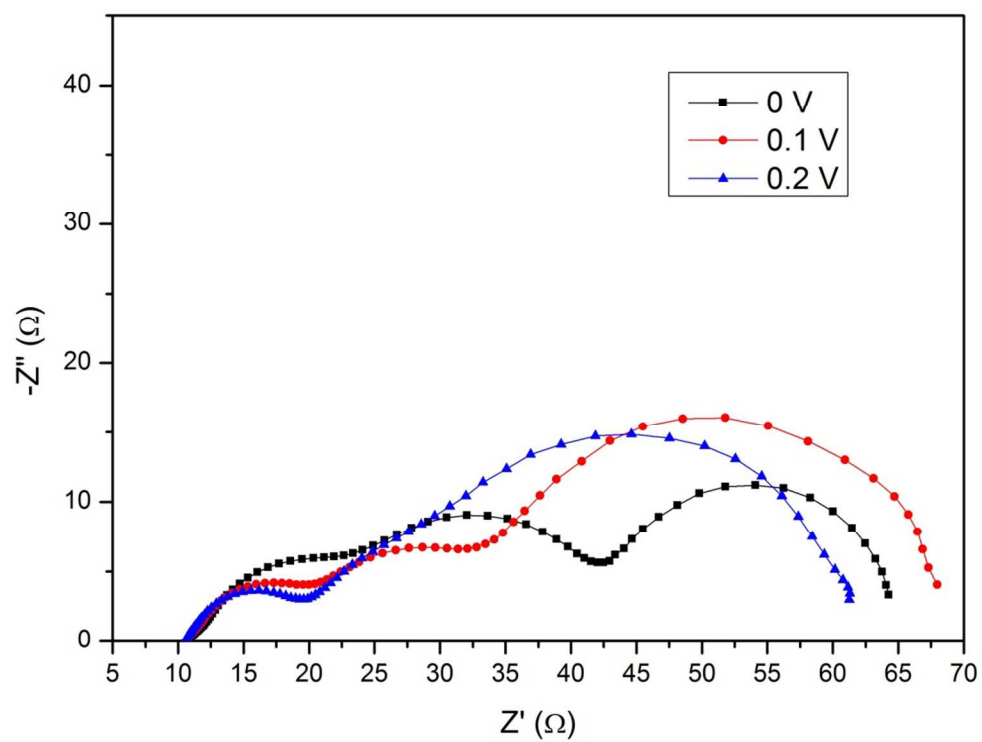
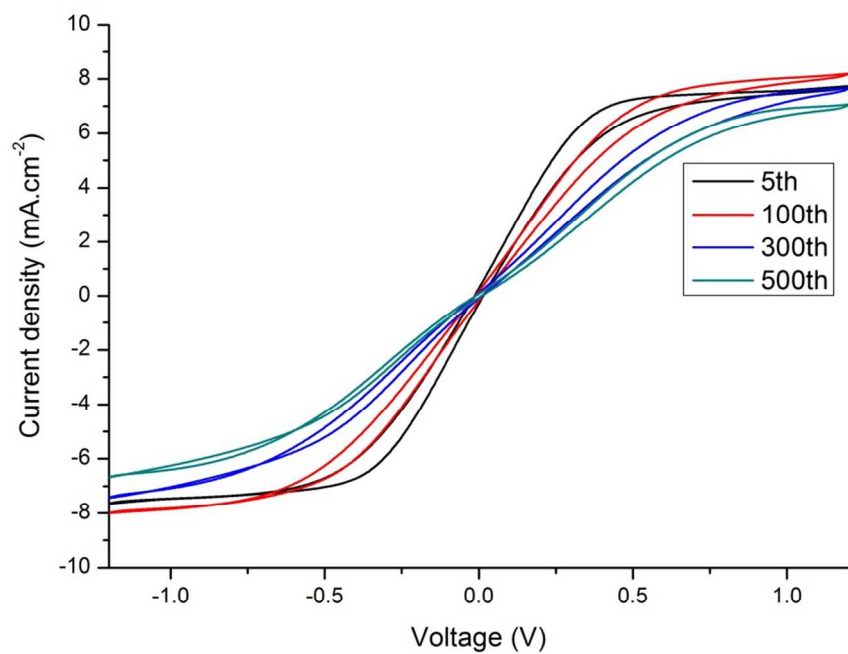


Figure S3. Nyquist plots of Pt cell tested under 1 sun illumination with additional applied bias



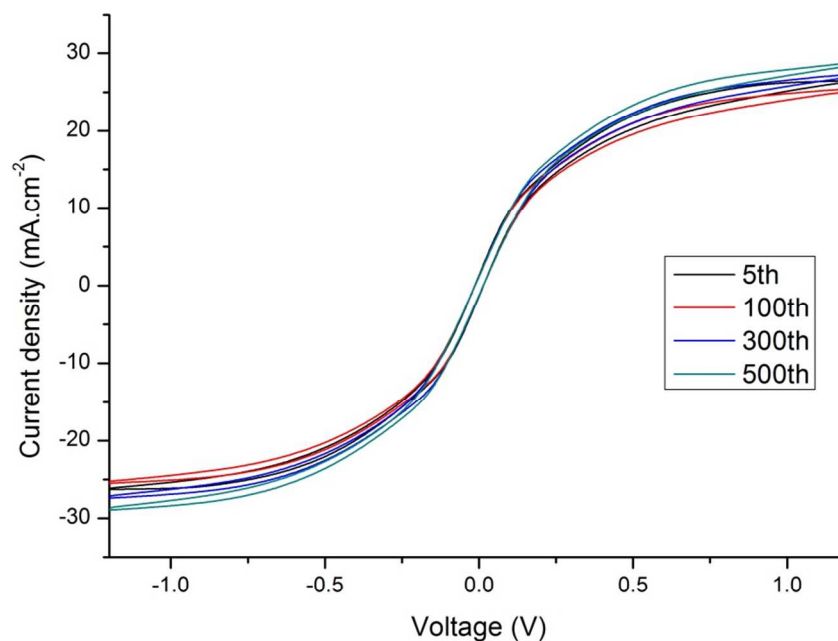


Figure S4. Cyclic voltammograms of closed dummy cell with (top chart) Pt-FTO electrodes and (bottom chart) TiN-PEDOT electrodes, scan rate 50 mV/s, with repeated cycling (up to 500 cycles). The same electrolyte composition as used in the DSSCs was used in this analysis.

REFERENCES:

1. Fabregat-Santiago, F.; Bisquert, J.; Palomares, E.; Otero, L.; Kuang, D.; Zakeeruddin, S. M.; Grätzel, M., Correlation between Photovoltaic Performance and Impedance Spectroscopy of Dye-Sensitized Solar Cells Based on Ionic Liquids. *The Journal of Physical Chemistry C* **2007**, *111* (17), 6550-6560.
2. Fabregat-Santiago, F.; Bisquert, J.; Garcia-Belmonte, G.; Boschloo, G.; Hagfeldt, A., Influence of Electrolyte in Transport and Recombination in Dye-Sensitized Solar Cells Studied by Impedance Spectroscopy. *Solar Energy Materials and Solar Cells* **2005**, *87* (1-4), 117-131.
3. Halme, J.; Vahermaa, P.; Miettunen, K.; Lund, P., Device Physics of Dye Solar Cells. *Advanced Materials* **2010**, *22* (35), E210-E234.