Transparent p-type Semiconductors for Efficient Tandem-Dye Sensitised Solar Cells

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p-Type and Tandem Dye-Sensitized Solar Cell

Our group has made substantial advancements in developing p-type dye-sensitized solar cells (p-DSCs) using NiO as the photocathode, however NiO has several limitations and our current research is focused on developing novel materials to improve the overall efficiency of p-type electrodes.

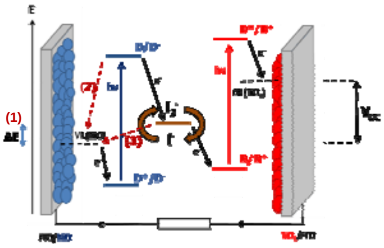


Figure 1: Schematic of tandem cell structure

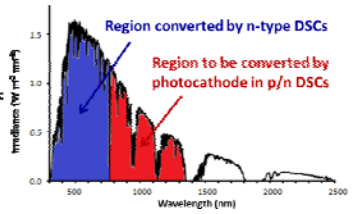


Figure 2: Spectrum of solar irradiance highlighting the target absorbance of our devices.

Efficiency (η) is limited by:

1. Small ΔE between the redox potential of the electrolyte and valence band (VB) of the NiO.
2. Charge recombination between reduced dye and holes in NiO VB.
3. Recombination between electrolyte and holes in NiO VB (hole lifetime).

Motivation and Objectives

The development of tandem devices is limited by the current performance of transparent p-type electrodes. Studies have been limited to few systems; NiO and Cu(I) based oxides/sulphides, with the record efficiency for a p-DSC at 2.51%. Improved photocathodes are required to achieve greater efficiencies that match TiO_2 photoanodes.

Material	Redox mediator	V_{OC} (mV)	J_{SC} (mA cm^{-2})	FF	Efficiency (%)	Band Gap	Valence Band (V vs. NHE)
NiO	$Co(en)_3^{3+/2+}$	709	4.44	42	1.30	3.5	0.51
	I_3^-/I^-	284	5.35	37	0.56		
CuO	I_3^-/I^-	115	0.30	31	0.01	1.4	0.52
$CuGaO_2$	I_3^-/I^-	199	2.05	45	0.18	3.4-3.7	0.60
$CuCrO_2$	I_3^-/I^-	102	0.49	40	0.02	2.95-3.30	0.80
	$Co(en)_3^{3+/2+}$	734	1.23	53	0.48		
$CuAlO_2$	I_3^-/I^-	103	0.954	38	0.04	3.6 (1.2)	
LaOCuS	$Co(dtb\text{-}bpy)_3^{3+/2+}$	150	0.039	26	0.002	3.1	0.52
$NiCo_2O_4$	I_3^-/I^-	189	8.35	50	0.785	3.3	0.50

Objectives

- The development and testing of new p-type materials with an array of dyes and electrolytes.
- Optimisation of screening and characterisation methods.
- Exploration of the structure-property relationships of new materials and investigation of their effects on electron/hole dynamics, concentrations and transport.

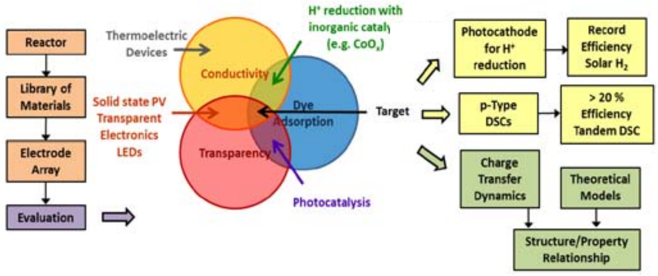
Approach

Synthesis of Materials

A combination of conventional hydrothermal, sol-gel, solid state and co-precipitation routes are being developed for the synthesis of transparent p-type materials.
The figure on the right shows a custom-built high-throughput co-precipitation reactor, being developed for rapid deposition of arrays of compounds onto conductive glass substrates for application and testing in cells.

Tuning p-type Conductivity

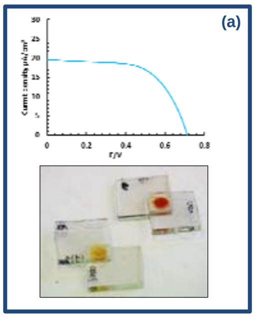
Instead of taking a doping approach, we are optimising parent systems. For example, delafossite copper chromium oxides with **varying Cr/Cu ratio** are expected to influence O vacancy concentration, thereby improving the p-type behaviour of this material and hence device performance.



We will be developing new p-type semiconductors with:
(A) A lower valence band edge than NiO to increase Voc,
(B) A larger dielectric constant to reduce recombination of holes with electrons in the sensitizer and electrolyte,
(C) A greater hole mobility to increase charge collection efficiency.

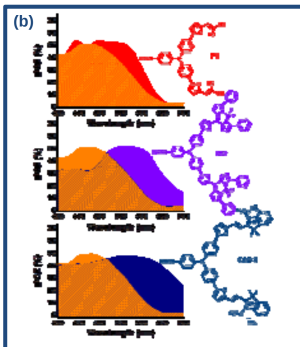
Preliminary Results

Dyes/QD Absorbers

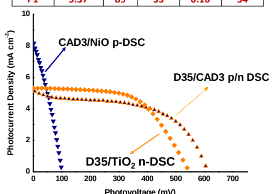


(a) Tandem QDSSC utilising CdSe on NiO and $CdSe_{0.83}S_{0.17}$ on TiO_2

(b)



Dye	J_{SC} [mA cm^{-2}]	V_{OC} [mV]	FF [%]	η [%]	IPCE [%]
CAD3	8.21	101	31	0.25	50
GS1	5.87	106	31	0.20	53
P1	5.37	89	33	0.16	54

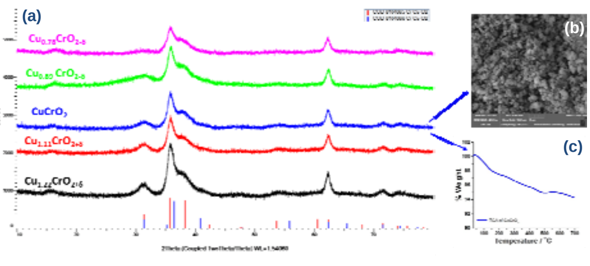


Cell	Dyes	J_{SC} [mA cm^{-2}]	V_{OC} [mV]	*FF* [%]	η [%]
p	CAD3	6.25	101	32	0.2
np	D35/ CAD3	3.95	575	56	1.2

(b) Overlaid IPCE plots for a P1, GS1, CAD 3 NiO p-DSC and a D35 TiO_2 n-DSC (orange), as well as current–voltage plots for the record cells.

A range of novel organic push-pull dyes will be synthesised, starting with BODIPY chromophores. A significant bathochromic shift will be desired to compliment current n-type dyes in tandem cells. Additionally, an investigation of the binding methods of quantum dots onto these new materials could yield p-type electrodes with highly tuneable absorbing properties.

Hydrothermal copper chromium oxides



(a) PXRD of the samples with varying Cu/Cr ratio can be indexed with two well known polymorphs (hexagonal and rhombohedral) of stoichiometric $CuCrO_2$ (marked with blue and red vertical lines). The materials prepared typically exhibit (b) nanocrystalline morphology and (c) significant thermal stability up to 700 ºC in Ar atmosphere .

References

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