Novel TiO_2 Microstructures for Low Cost Dye Sensitized Solar Cells

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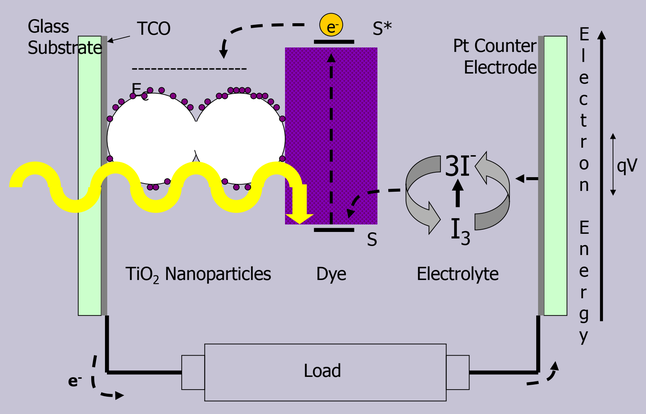
Background

The **dye sensitized solar cell (DSSC)**, invented in 1991 by Grätzel et al. [1], is a 3rd generation PV technology, with commercialization just beginning [2,3]. Maximum efficiencies are less than 10%, but promise lies in low light performance and low cost, estimated at 10-20% of crystalline silicon PV.

The DSSC is fundamentally different from a traditional Si cell in that the photon absorbing material (eg *N719 Dye*) is separate from the charge transport material (nano-anatase). Therefore, e^- - h+ recombination is not as probable, and material restrictions (high purity and crystalline perfection) are relaxed.



The basic components of the DSSC include [4]:

- transparent conducting electrode (TCO)
- porous film of nanocrystalline, wide E_g semi-conductor (TiO_2)
- monolayer of sensitizing dye adsorbed to surface of TiO_2
- Redox electrolyte and counter electrode

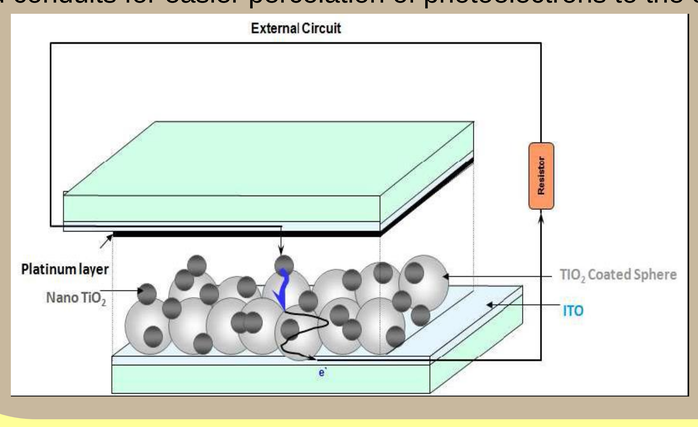
One limitation of the DSSC is the tortuous *e*- percolation path between weakly linked nano-anatase particles giving high internal resistance and low current output. Impedance spectroscopy and numerical simulations suggest that *e*- transport and recombination dominate operation of DSSC, and an optimal bimodal distribution of nanoparticles can benefit performance [5]. Several groups [6] have grown oriented TiO_2 and ZnO nano-rods or -tubes to enable easy transport to the anode, however; the height of nanopillar arrays is limited to 10's nm which limits the amount of light absorption in the cell. Growing large areas in an economical fashion is also difficult to envision.

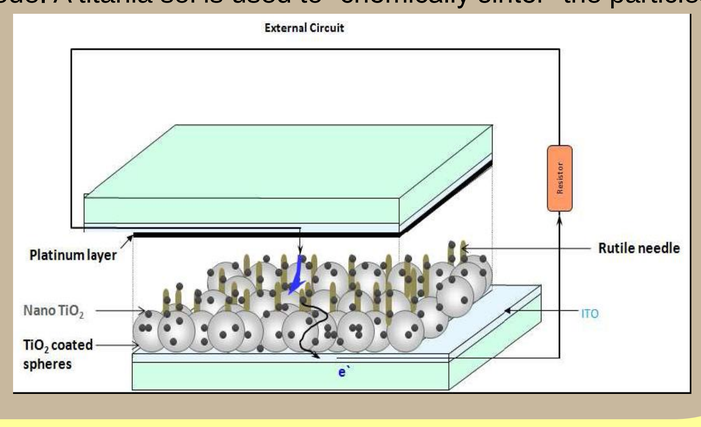
Microstructure has other effects. Diffusion of the electrolyte to and from surfaces is critical to reduce recombination events and undesirable dark current [7]. Enhanced internal light scattering may increase the average photon path length, increasing the probability for photon capture by the dye [8].

Objective & Approach

The long term goal of our work is to design a DSSC material coating system which can be assembled on site. Engineered TiO_2 pastes or slurries capable of being applied by casting, rolling or other cost effective thick film processes are necessary.

Our premise is that DSSC is an example of a device which can benefit from a heterogeneous, hierarchical mixture of TiO_2 particle sizes and morphologies. Below are schematics of two novel microstructures. While nanocrystalline anatase provides the high surface area, rutile needles and/or hollow glass microspheres with dense TiO_2 film provide enhanced light scattering and conduits for easier percolation of photoelectrons to the electrode. A titania sol is used to "chemically sinter" the particles.



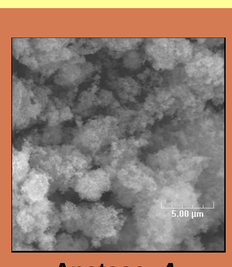


Materials & Procedures

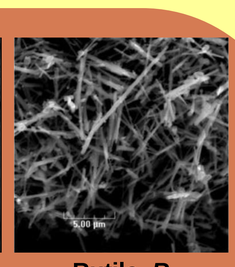
Our pastes included both commercial anatase (*A*) and micron particles mixed with a titania sol (*SG*) as the liquid vehicle [9]. The sol was prepared by dissolving titanium isopropoxide in ethanol with acetic acid as a chelating agent, and hydrolyzing with H_2O_2 [10]. Films from a mixture of the sol and anatase are referred to as SGA (*tn* and *tk* refer to thin and thick). SGAR refers to formulation with acicular rutile (*R*) as an additive. Two *A* to *R* mass ratios were used, 1:1, and 7:1. Titania spheres (*TS*) were another additive produced by dissolving titanium isopropoxide in isopropanol and acetic acid and spray dried [11]. SGATS is one of these film types. The last additive is called coated spheres (*CS*), prepared by treating glass microspheres (Trelleborg, Inc.) in the titanium sol above, filtering, hydrolyzing in air, suspending in ethanol, and spray drying [11]. Corresponding films include SGACS, etc.

12 of the 25 formulations prepared are included in this discussion (Tables below). Powders and mixtures were characterized by multipoint BET (Nova 2200, Quantachrome Instr.), and scanning electron microscopy (Hitachi S-800). A Dektak profilometer (Veeco) was used to measure thickness and roughness of the films.

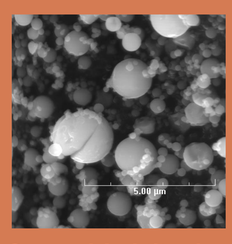
Films were cast onto FTO coated borosilicate glass (Hartford Glass, Inc.), dried, annealed at 450˚C, soaked in a 3.10 x10^{-5} M ethanol solution of N719 ruthenium 535-bis TBA dye (Solaronix, Inc.), rinsed in ethanol, and allowed to dry. The dyed anode and sputter coated Pt counter electrode were placed face to face with a 30 µm or 60 µm thick spacer, and secured with a clamp. Immediately prior to testing, the electrolyte (0.5M KI/0.05M Iodine in ethylene glycol) was introduced.



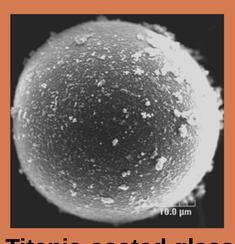
Anatase, *A* (Degussa P25)



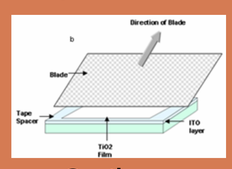
Rutile, *R* (FTL300, Ishihara)



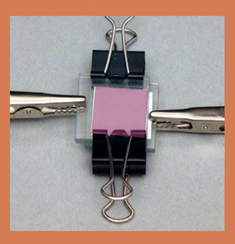
Spray dried titania spheres, *TS*



Titania-coated glass micro-sphere, *CS*



Casting



Assembled cell

Solar cell performance was measured using simulated AM1.5 light with P_{in}= 100mW/cm^2 (Sciencetech 1.6KW SS).

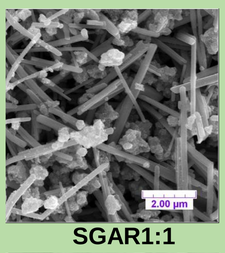
Results

The table below gives measured BET surface area (SA_m) and pore characteristics (radius and volume) for a few mixtures, along with values predicted via weighted calculations (SA_c) for all.

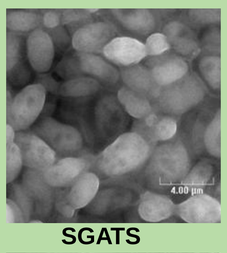
The figures illustrate the variety of microstructures produced. SGAR1:1 shows that the anatase does not uniformly decorate the rutile, but rather agglomerates to some extent. (No attempt at orientation of rutile needles was made in this sample, and none is seen.) In SGATS, the titania spheres have collapsed and fused to one another along with *A* and titania sol. SGACS has microspheres embedded in *A*. SGARCS shows two neighboring glass microspheres, enveloped in a mix of *A* and *R*.

Physical characteristics of TiO_2 films

		t	R	SA_c	SA_m	r_p	V_p
		µm	µm	m^2/g	m^2/g	nm	cc/g
A	A annealed	13.9	.71		56.1 48.3	16	.14
1	SGA-tn	6.64	.47	56.1			
2	SGA-tk	14.1	.72	56.1			
3	SGR			6.0	6.01	7.5	.14
4	SGAR 1:1 annealed	18.4	1.1	31.1 27.2	31.3 18.4	15 17	.07 .10
5	SGAR 7:1	18.2	1.3	49.8			
6	SGTS	6.2		10.8			
7	SGATS	15.8	.79	50.4			
8	SGARTS	19.5	1.5	45.5			
11	SGCS	31.7	2.3	8.3			
17	SGACS	41.8	3.8	50.1			
18	SGARCS annealed	44.7	5.6	45.2 35.5	27.7 38.0	15 19	.97 .24
24	SGARTSCS	44.9	6.0	41.8			



SGAR1:1

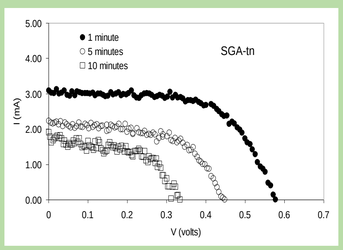


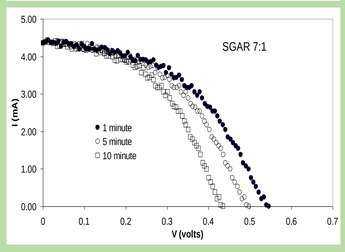
SGATS

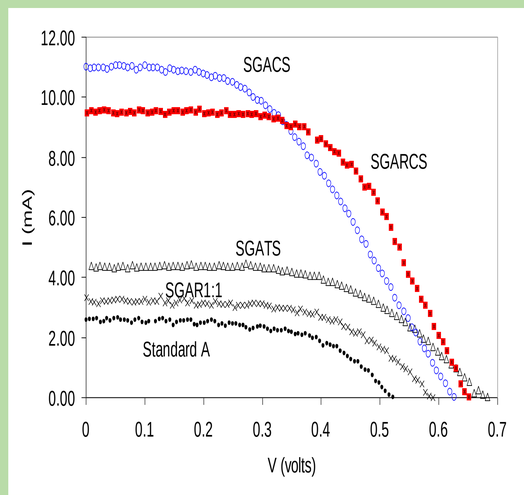
SGACS

SGARCS

The I-V response of assembled solar cells are shown below. The table compares the maximum power output (P_{max}) for experimental cell-types. Generally, cells show decay in output with time (well known challenge with DSSCs), pronounced for SGA-tn and also standard film A. In addition to increasing initial P_{max}, incorporation of *R* in (SGAR 7:1) significantly stabilized the response with exposure time, as did other micro-particles. While the presence of nanocrystalline anatase is required for photovoltaic response (ie null response from SGR and SGTS), addition of microparticles almost always improved performance. The best cells were those containing *TS* or *CS*. The P_{max} is up to 5 times that of the standard cell *A*. Most improvement comes by increase in photocurrent. The beneficial effects of *CS* can in part be explained by comparing pore characteristics. Annealed SGARCS has a larger r_p=19nm, and significantly larger V_P0.24cc/g than the simple anatase film (16nm and 0.14cc/g), thereby opening up a larger amount of meso-porosity for better diffusion of dye and electrolyte.



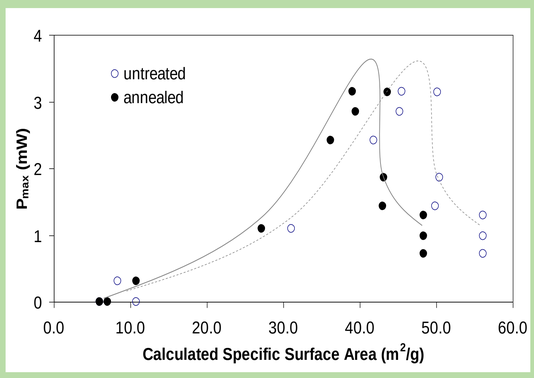


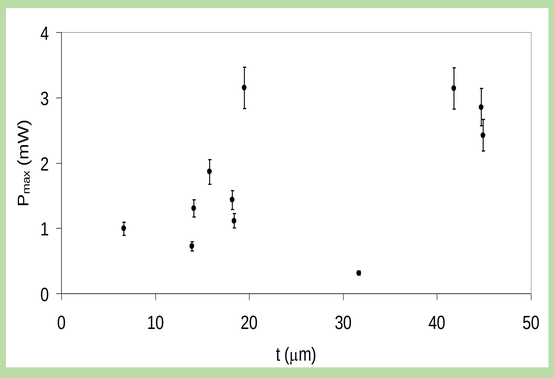


Photovoltaic parameters (average of 3 cells)

	exposure→		1m			5m	
		V_{oc}	I_{sc}	P_{max}	V_{oc}	I_{sc}	P_{max}
		mV	mA	**mW**	mV	mA	mW
A	A	.54	2.4	**.72**	.42	2.4	.47
1	SGA-tn	.60	2.8	**.99**	.42	2.1	.46
2	SGA-tk	.60	3.3	**1.3**	.48	2.7	.73
3	SGR	-	-	-	-	-	-
4	SGAR 1:1	.59	3.09	**1.11**	.54	3.4	1.0
5	SGAR 7:1	.63	4.0	**1.43**	.54	4.3	1.1
6	SGTS	-	-	-	-	-	-
7	SGATS	.66	5.5	**1.86**	.59	4.7	1.50
8	SGARTS	.67	8.03	**3.15**	.58	7.6	2.40
11	SGCS	.45	.956	**.31**	.32	.96	.17
17	SGACS	.65	9.57	**3.14**	.52	8.4	2.10
18	SGARCS	.62	8.52	**2.85**	.52	8.1	2.01
24	SGARTSCS	.64	6.50	**2.42**	.50	6.5	1.67

PV ouptut is correlated with film characteristics in the figures below, which suggest that strictly higher specific surface area is not necessarily the answer for highest PV output. Performance is determined by other characteristics as well, such as the nature of the pores and their size distribution and light scattering from micro-particles as discussed earlier. For hierarchical microstructures, the plot suggests increased performance with thicker films, different from the typical conclusion when using only monodispersed nanoparticles…usually showing decreased performance above about t=10µm. Of course thicker films (more material) are required to achieve greater total surface areas in hierarchical films. We believe that increased number of scattering events and more efficient light trapping is also responsible for this trend.





Conclusions

We have demonstrated that the performance of DSSCs can be improved significantly by using photoanodes with heterogeneously microstructured titania. Although ideal, vertically aligned rutile has not yet been achieved, our study shows that inclusion even of randomly oriented rutile needles offers improvement. The incorporation of titania-coated glass microspheres is an approach which allows good quality thick films and repeatable, high PV output, up to five times that of a DSSC made using the standard nano-anatase photoanode. Our results suggest that while total surface area is important, so too is the connectivity of the titania, the nature of the pore network, and the extent of light scattering within the photoanode. We have presented a relatively simple approach using commercially available materials to create hierarchical structures.

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Acknowledgements

The authors acknowledge financial support from the US Dept. of Energy grant # FC26-06NT42854.