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## LOW-TEMPERATURE PROCESSING OF PHOTOELECTROCHEMICAL SOLAR CELLS.

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### ABSTRACT

Photoelectrochemical (or Grätzel) solar cells are normally manufactured by a process involving a sintering heat treatment of the TiO<sub>2</sub> photoanode, to provide mechanical and electrical contact between the nanoparticles. This precludes the use of many low cost substrates and alternative manufacturing approaches. This paper describes a new approach to engineer the nanostructure such that the heat treatment step can be eliminated whilst retaining acceptable device performance. The principles of and processes used to facilitate this are described and the device characteristics reported.

### 1. BACKGROUND

The nanostructure of the TiO<sub>2</sub> photoanode is one of the most important factors determining conversion efficiency and cell stability in photoelectrochemical (dye sensitised) cells. The requirements are for a high surface area, a minimum of trapping and recombination sites, and high degree of porosity with appropriate pore size to facilitate diffusion of the redox species [1]. In addition the photoanode (and other cell components) requires reasonable mechanical integrity and adhesion to the conductive coated glass substrate/electrode to ensure it is sufficiently robust and stable to withstand the assembly, transportation and installation processes and to maintain good electrical contact.

“Conventional” manufacturing processes for these cells [1][2] involve the use of a sintering heat treatment, which is normally used prior to dye coating and subsequent incorporation of the cell electrolyte, and which provides a positive contribution to almost all of the factors outlined above. However, despite its many benefits in terms of cell performance, this sintering process imposes a significant restriction on the range of substrates that can be employed, and on the sequence and ability to integrate the various manufacturing steps. Ideally, it would be preferable if a process route could be determined which might allow the appropriate microstructure to be engineered at low temperatures, whilst providing acceptable device performance.

In this paper we present the findings of a study into the factors limiting and determining performance in the unsintered photoelectrochemical solar cell and report on a novel approach to engineering improved performance in such devices by the fabrication of a duplex TiO<sub>2</sub> photoanode microstructure.

The principal limitation for low temperature processing of photoelectrochemical cells is that, in the absence of a sintering heat treatment, the (anatase) TiO<sub>2</sub> particles remain as discrete entities within the microstructure. Consequently, charge trapping and recombination processes which occur at the particle surfaces/interfaces hinder transfer of injected electrons through the photoanode. It is probable that this stems from two factors, firstly the poor interparticle contact, exacerbated by the presence of dye and/or electrolyte between the surfaces, and secondly by the very small contact area which is present between unsintered predominantly spherical particles [3]. The differences between the idealised sintered photoelectrochemical cell and the unsintered cell are schematically illustrated in figures 1 and 2).

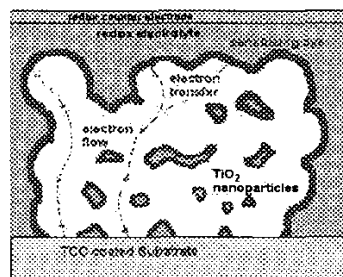


Figure 1: Idealised photoanode structure in conventional sintered photoelectrochemical cell illustrating facile flow of injected electrons within photoanode structure

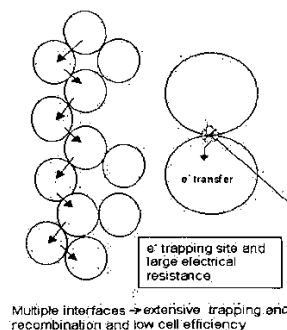


Figure 2: schematic diagram indicating problems of poor electrical contact and recombination at particle interfaces in the unsintered cell

## 2. EXPERIMENTAL

### 2.1 Cell Fabrication and Testing.

All devices described in this work comprised a  $1\text{cm}^2$  device based on an ITO coated glass substrate onto which the  $\text{TiO}_2$  photoanode was deposited from a suitable suspension. The photoanode comprised variously:-  $\text{TiO}_2$  nanoparticles fabricated by ourselves by both nonhydrolytic and hydrothermal, sol-gel type processes; commercially available material (Degussa P25) and various combinations of these, described as duplex microstructures. These are described in more detail subsequently.

For practical reasons, the thickness of the  $\text{TiO}_2$  layer was standardised at  $1.5\mu\text{m}$  in the case of devices comprising the hydrothermal and non-hydrolytic derived material this being constrained by the onset of cracking and debonding of the deposited coating in these systems. In the case of the duplex structures, a standardised photoanode thickness of  $25\mu\text{m}$  was used. Cells were sensitised by immersion in an N3 dye solution, with a conventional iodine based redox electrolyte, in acetonitrile/ethylene carbonate. A platinum counter electrode was used.

Cells were tested under simulated AM1.5 radiation at an intensity of  $650\text{w/m}^2$ , under a range of reverse bias conditions with  $V_{oc}$ ,  $J_{sc}$  and Fill factor being determined.

### 2.2 Particle morphology

Initial investigations focussed on the ability to improve device performance by engineering changes in particle morphology via the use of alternative processing routes. In this investigation a comparison was made between anatase nanoparticles produced by novel non-hydrolytic process routes [5] and particles produced by a more conventional hydrothermal processing technique, similar to that reported by Grätzel and co-workers [2][6]. The process conditions were adjusted to provide comparable particle sizes in each case. These processes are to be reported in detail elsewhere [5].

### 3.2 Duplex structures.

An alternative (and low cost) source of the  $\text{TiO}_2$  nanoparticles for photovoltaic cells is available in the form of commercially available powders. The material P25 produced by Degussa is frequently used in studies on these devices in sintered form, although the device performance is generally inferior to the hydrothermal material.

Attempts were made to develop cells with microstructures based on this material, and in combination with the hydrothermal derived material. Combinations with the two materials were produced using different ratios of P25 and hydrothermal material.

## 3. RESULTS AND DISCUSSIONS

### 3.1 Hydrothermal and Non Hydrolytic Processes

The hydrothermal and non-hydrolytic processes used enabled somewhat different morphologies to be obtained in the anatase material, whilst retaining essentially 100% anatase phase and comparable particle size. The former process tends to produce more rounded quasi-spherical particle morphologies whilst the latter tends to produce a greater proportion of straight sided/angular particles,

which can be considered as a quasi-cubic particle morphology (figures 3(a) and 3(b) respectively).

It was postulated that the quasi cubic morphology provided by the non-hydrolytic process route might allow, better interparticle contacts to be obtained in the unsintered cell, thereby obviating the need for the sintering process (figure 4).

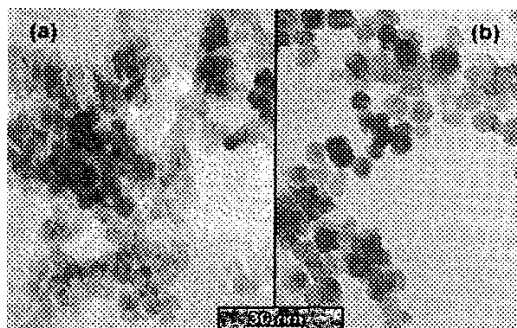


Figure 3 particle size/morphologies obtained by the (a) hydrothermal and (b) non hydrolytic process routes.

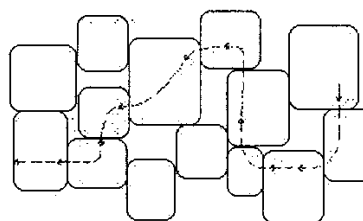


Figure 4: schematic diagram indicating potential improvements from changes in nanoparticle morphology leading to improved contacts in unsintered PV cells.

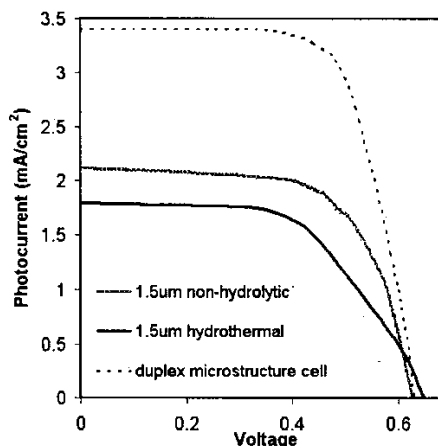


Figure 5: Comparative performance characteristics of various unsintered solar cells.

To some extent, the results obtained from these two systems do appear to confirm these tentative theories. Cells obtained with the quasi-cubic morphology (non-hydrolytic process) were found to exhibit superior performance to that of the spherical particles

(hydrothermal process) in unsintered cells. Under comparable conditions the fill factor and conversion efficiency did show a significant performance gain (figure 5), although some questions remain regarding the differences in  $V_{OC}$  and the shape of the IV curve under low reverse bias conditions. Further work is ongoing to investigate this further.

Unfortunately, the performance of unsintered cells developed with both conventional hydrothermal and non-hydrolytic  $TiO_2$  as the photoanode was found to be strongly time dependent. In particular, the photostability of both systems was poor, with significant degradation in cell performance observed after just tens of minutes light exposure at 1 sun. It is believed that this can be attributed to the relatively high density of these as deposited films. (figure 6).



Figure 6: Cross section through unsintered non-hydrolytic derived  $TiO_2$  photoanode on ITO coated glass indicating limited porosity/high green density.

The heat treatment used in the fabrication of high performance photoelectrochemical cells, in fact performs several vital functions that it is necessary to replicate if the goal of a low temperature process route is to be realised.

The primary function is to develop necking between particles and between particles and substrate by partial sintering, enhancing electrical and mechanical contact as previously outlined. However, an important second function is in enhancing the porosity of the deposited layer. This is achieved by the addition of organic materials, which are subsequent burnt out leaving residual porosity in the deposited layer. However, the objective of a low temperature process route in this work is incompatible with such an approach, since the organic materials cannot be subsequently removed and thus form a barrier for both electron migration and dye/electrolyte impregnation.

In the case of the unsintered cells from both the hydrothermal and non-hydrolytic processes, the coatings deposited were relatively dense. It is believed that this adversely affected the diffusion rates of the redox ions in solution through the pore structure [4]. In these systems the rates of charge injection effectively exceeded the rates at which the regeneration of the dye by the diffusion redox species could take place. Such an effect would be expected to increase the propensity for undesirable back and photodegradation reactions to take place. Confirmatory evidence for this supposition was that the cell performance could be partially recovered after "resting" under low illumination conditions for some time, and for the occurrence of these effects only under relatively high levels of illumination.

### 3.2 Duplex Microstructure Cells.

The porosity and pore size achieved in the unsintered photoanode coating are largely determined by the particle size of the nanoparticles used. The photoanode microstructure of the cell is necessarily a compromise between the requirement for high surface area (small particle size) and high porosity (larger particle size). Given the very different process conditions, it is probable that the optimum compromise microstructure for these factors will be different for low temperature processed cells in comparison with sintered photoanode devices.

Initial attempts were made to fabricate cells utilising the commercial P25 material as the unsintered photoanode. This material offers both a larger particle size compared to both the hydrothermal and non-hydrolytic synthesised materials, and also has a very well defined "quasi cubic" particle morphology (figure 7) potentially offering good interparticle contacts as outlined in figure 4/ section 3.1.



Figure 7: Size and morphology of P25  $TiO_2$  nanoparticles.

However, attempts to directly utilise this material in unsintered PV cells were found to be largely unsuccessful. In particular, the adhesion of the P25 nanoparticles both to the substrate and between particles was too low to provide sufficient mechanical integrity to allow reliable unsintered cells to be fabricated.

An alternative approach was therefore investigated in which a duplex pore structure was engineered from larger quasi-cubic particles combined with a secondary  $TiO_2$  component (termed nanocement) comprising much finer nanoparticles, providing both enhanced surface area and bond strength. This is illustrated schematically in figure 8.

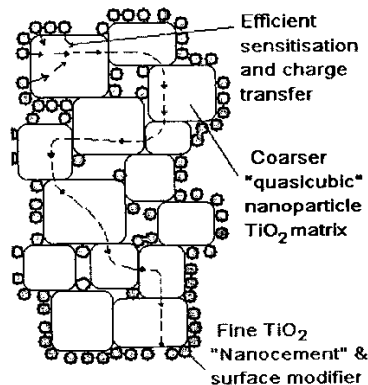


Figure 8: schematic diagram indicating potential improvement from duplex microstructure

The results reported here were for cells with photoanode comprising a major constituent of P25

(particle size circa 25nm) with between 10 and 30 wt% of hydrothermally derived particles with particle size of the order of 10nm. The larger particle size and quasi cubic morphology of the larger particles reduce the number and severity of the interfacial recombination sites, whilst the finer component serves both to increase available surface area and improve mechanical integrity and electrical contact both between TiO<sub>2</sub> particle and between particles and substrate.

The pore structure of the device can also be engineered by adjusting the relative proportions of the two components. For example figures 9(a)- (d).

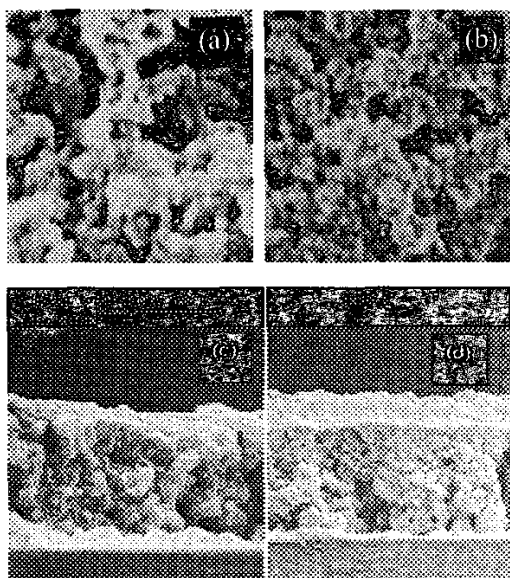


Figure 6: Engineering of different pore structures from duplex microstructures. (a) Surface and (c) section with 10 wt%; (b) surface and (d) cross-section with 30 wt % additions of "nanocement" TiO<sub>2</sub> at equivalent magnification

A further advantage conferred by the use of the duplex microstructure was that the maximum achievable layer thickness, could be significantly increased. Allowing photoanode layer thicknesses up to approximately 30µm to be produced without significant cracking or debonding.

### 3.3 Device performance

Photovoltaic performance in the duplex microstructure devices was significantly improved (figure 7) with significant improvements in both photocurrent and fill factor in comparison to the non-hydrolytic and hydrothermally derived unsintered cells (Table 1). In addition the photostability of these devices was substantially enhanced with no degradation observed over tens of hours illumination at 1 sun. In the current investigation, difficulties in effecting sealing of the redox electrolyte precluded more extended testing, and further work is required to confirm the long-term durability.

Cell photoanode (All unsintered)	J <sub>sc</sub> (mA)	V <sub>oc</sub> (V)	FFI factor	Efficiency (%)
1.5µm hydrothermal derived TiO <sub>2</sub>	1.8	0.65	0.56	1.0%
1.5µm non hydrolytic TiO <sub>2</sub>	2.12	0.63	0.65	1.3%
25 µm duplex microstructure P25+10% Hydrothermal "nanocement"	3.4	0.63	1.48	2.3%

Table 1 summary of cell performance data for various low temperature processed cells

### 4. Conclusions

The study has confirmed the importance of photoanode microstructure in determining device performance, and indicates that the optimum form of the TiO<sub>2</sub> nanoparticles in the photoanode differs for a low temperature processed device in comparison to a more conventional sintered photoanode device. The duplex microstructure approach reported here is a novel design solution to the problems of developing such a cell under low temperature conditions.

The overall efficiencies obtained, whilst not remarkable in comparison with the best photoelectrochemical cells produced using sintering heat treatments [2], are very good for an unsintered device and offer the prospect of further performance improvements in cells produced without high temperature heat treatment through further optimisation. Ultimately this may well allow the goal of an ultra low cost cell with acceptable output and stability to be realised.

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