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## One-step microwave calcination of ZrO<sub>2</sub>-coated TiO<sub>2</sub> electrodes for use in dye-sensitized solar cells

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### Abstract

TiO<sub>2</sub> and ZrO<sub>2</sub>-coated TiO<sub>2</sub> working electrodes were produced and calcined at 450 °C in a 2.45 GHz microwave furnace prior to incorporation in dye-sensitized solar cells. The bare TiO<sub>2</sub> working electrodes increased from 0.2% up to 2.4% efficient after microwave calcination at a light intensity of 1 Sun. The efficiency was further increased to 3.1% for the ZrO<sub>2</sub>-coated TiO<sub>2</sub> core-shell electrodes. The increased photovoltaic performance was due to improvements in the open circuit voltage ( $V_{oc}$ ) from 692 to 719 mV and the short circuit current density ( $J_{sc}$ ) from 6.24 to 6.56 mA cm<sup>-2</sup>. **To cite this article: David B. Menzies et al., C.R. Chimie 9 (2006).**

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### Résumé

Des électrodes de travail en TiO<sub>2</sub> et TiO<sub>2</sub>-ZrO<sub>2</sub>, obtenues par calcination à 450 °C dans un four à micro-ondes (2,45 GHz), ont été préparées avant leur incorporation dans des cellules solaires photovoltaïques. L'efficacité des cellules solaires, soumises à une intensité lumineuse de 1 Sun, passe de 0,2 à 2,4% dans le cas des électrodes de travail constituées d'oxyde de titane. Elle atteint 3,1% avec les électrodes de travail pour lesquelles les particules de TiO<sub>2</sub> sont recouvertes de ZrO<sub>2</sub>. Cette augmentation est due à un accroissement de la tension de circuit ouvert ( $V_{oc}$ ) de 692 à 719 mV et de la densité de courant de court-circuit de 6,24 à 6,56 mA cm<sup>-2</sup>. **Pour citer cet article : David B. Menzies et al., C.R. Chimie 9 (2006).**

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**Mots clés :** Four à micro-ondes (2.45 GHz) ; Calcination ; Électrodes de travail en TiO<sub>2</sub>-ZrO<sub>2</sub> ; Cellules solaires photosensibles

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## 1. Introduction

The need for sustainable energy sources in the future is of increasing importance due to the rate of use of non-renewable energy sources and increasing population. Thus, research into solar energy devices such as the dye-sensitized solar cell (DSSC) has been increasing [1–13]. One critical component of the DSSC is the semiconducting layer, typically a nanoporous titania layer [1,8,13]. One of the processing steps involved in the production of these working electrodes is the calcination of the thin metal oxide on the conducting oxide substrate.

In this work, a 2.45-GHz microwave reactor [11] was used to provide the heat required for effective calcination of the semiconducting film. As reported earlier, the use of 2.45-GHz microwaves results in cracking of the transparent conducting oxide (TCO) coating on the glass [11,14]. In this work, the use of external SiC susceptors was utilized to overcome the problems that arise due to the TCO film being a microwave absorbing material.

The use of core-shell nanostructures has been shown to alter the performance of the DSSCs, in many cases causing a substantial improvement [10,12,15–24]. In these studies, the working electrodes were processed using conventional heating. This study examines whether increased photovoltaic performances can be obtained by using a core-shell system (ZrO<sub>2</sub>-coated TiO<sub>2</sub>) calcined by 2.45-GHz microwaves.

## 2. Experimental

TiO<sub>2</sub> working electrodes were produced from a slurry of 4 ml distilled water, 2 g preformed TiO<sub>2</sub> nanopowders (P25, Degussa), 100 µl Triton X-100 (Lancaster) and 25 µl acetylacetone (BDH). The slurry was coated using a doctor blade technique on F:SnO<sub>2</sub> glass (TEC8, Hartford Glass Co.). The ZrO<sub>2</sub> shells were deposited onto the TiO<sub>2</sub> nanostructure via spin-coating a 0.1 M zirconium isopropoxide (Aldrich) solution in isopropanol at 2000 rpm for 10 s. Immediately after spinning, the working electrodes were washed with isopropanol. The ZrO<sub>2</sub>-coated electrodes were then hydrolyzed at 70 °C in a water-soaked desiccator for 30 min. Some of the uncoated and ZrO<sub>2</sub>-coated TiO<sub>2</sub> working electrodes were then calcined in a 2.45-GHz micro-

wave (MPC, Model 941) using a technique reported earlier [11]. The working electrodes were dyed using a 0.3 mM N3 ([Ru(dcbpy)<sub>2</sub>(SCN<sub>2</sub>)] where dcbpy = 4,4'-dicarboxylic acid-2,2' bipyridine) solution in a 1:1 solution of butanol and acetonitrile for 20 h. From profilometry (Taylor Hobson, Talysurf 10) it was determined that the film thickness was 8 ± 1 µm. In addition, the film thickness was unchanged after calcination and sol-gel modification to form a core-shell nanostructure.

Counter electrodes were produced by coating a thin film of a 5 mM H<sub>2</sub>PtCl<sub>6</sub> solution in isopropanol on F:SnO<sub>2</sub> glass. The electrodes were then dried at 50 °C for 15 min and then heated at 2 °C min<sup>-1</sup> to 385 °C for 15 min before annealing to room temperature. Counter electrodes were sealed to the working electrodes by heating a Surlyn gasket (200 µm thick, Dupont) and sandwiching the two glass plates together. The electrolyte [0.5 M LiI (Lancaster), 0.04 M I<sub>2</sub> (Lancaster) and 0.05 M 4-*tert*-butylpyridine (Aldrich) in acetonitrile] was administered by a hole in the counter electrode and subsequently heat sealed with a glass slide backed with Surlyn.

DSSCs were tested under illumination of a 21-V 80-W tungsten lamp (Phillips, 13160). A Keithley 2400 source meter recorded the current across a linear voltage sweep from -0.2 to 0.9 V utilizing Labview 6.1 software (National Instruments). Light intensity corresponding to 1 Sun was determined by an externally calibrated photodiode.

## 3. Results and discussion

Unsintered electrodes were incorporated into DSSCs and were found to be very inefficient (Fig. 1). This is due to poor inter-particle connection between the nanoparticles and thus a lack of efficient pathways for the electrons to migrate to the conductive F:SnO<sub>2</sub> substrate. DSSCs were also constructed from ZrO<sub>2</sub>-coated TiO<sub>2</sub> electrodes which were produced by spin-coating of a zirconium isopropoxide solution onto the TiO<sub>2</sub> electrode followed by hydrolysis at 70 °C. The additional organic species present in the ZrO<sub>2</sub>-coated TiO<sub>2</sub> working electrodes did not affect the dye attachment with similar currents recorded in the DSSCs (Fig. 1). The addition of the zirconia film mainly influences the V<sub>oc</sub> (Table 1). This is due to the reduction in the charge recombination from the photoinjected electrons in the

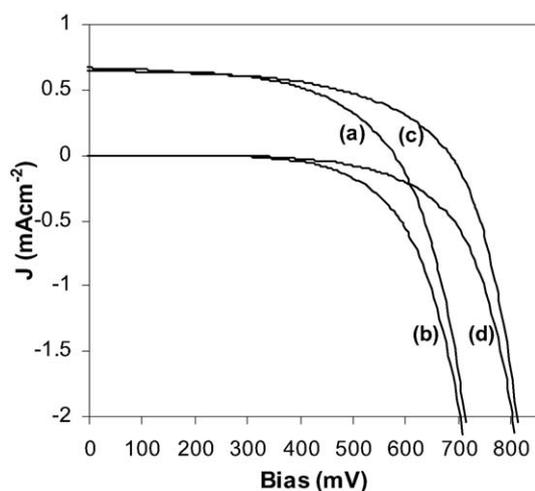


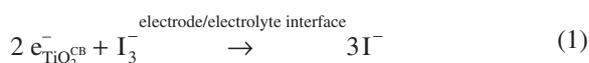
Fig. 1.  $J$ - $V$  curves for  $\text{TiO}_2$  under (a) 1 Sun and (b) dark current and for  $\text{ZrO}_2$ -coated  $\text{TiO}_2$  under (c) 1 Sun and (d) dark current. Both samples were not sintered.

Table 1

Photovoltaic data of DSSCs constructed from  $0.25\text{-cm}^2$  working electrodes determined under 1 Sun illumination where A corresponds to unsintered and B corresponds to microwave sintered working electrodes

Data	Bare $\text{TiO}_2$		$\text{ZrO}_2$ -coated $\text{TiO}_2$	
	A	B	A	B
$J_{sc}$ ( $\text{mA cm}^{-2}$ )	0.67	6.24	0.65	6.56
$V_{oc}$ (mV)	577	692	687	719
FF	0.54	0.56	0.53	0.65
Efficiency (%)	0.21	2.4	0.24	3.1

titanium dioxide conduction band ( $\text{TiO}_2^{\text{CB}}$ ) to the oxidized electrolyte species ( $\text{I}_3^-$ ). This charge recombination reaction results in the  $\text{I}_3^-$  being reduced to  $\text{I}^-$  (Eq. (1)) and therefore reducing the cell efficiency (Fig. 2).



This theory is supported by the dark-current data. The dark-current measurements, although not quantitative, give an overall indication of the charge recombination and more specifically the relative recombination rates of the DSSCs. Thus, the introduction of the  $\text{ZrO}_2$  film (Fig. 1) results in a reduction in that recombination reaction by having a 100-mV positive shift.

The typical heating rate for the working electrodes in the 2.45-GHz microwave was controlled maintaining a forward power of 450–500 W up to 450 °C and then maintaining the temperature by varying the forward power. Incorporation of these electrodes in DSSCs

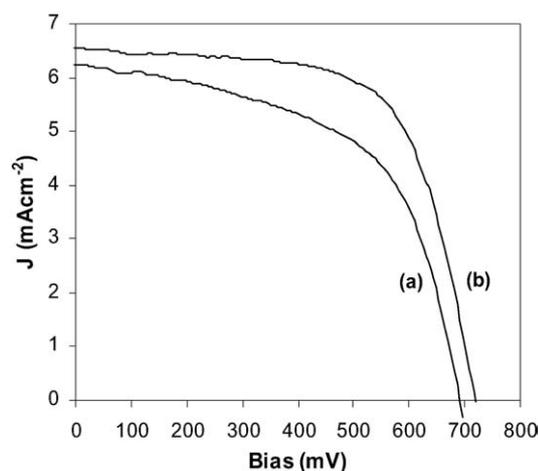


Fig. 2.  $J$ - $V$  curves for the DSSCs comprising 2.45-GHz microwave sintered (a)  $\text{TiO}_2$  and (b)  $\text{ZrO}_2$ -coated  $\text{TiO}_2$  working electrodes.

was found to improve the photovoltaic performance from that seen with the unsintered  $\text{TiO}_2$  (Table 1), up to 2.4% efficiency. This increase is due to increased interparticle connections forming better pathways for electron migration through the film to the TCO glass support.

As was the case for the unsintered working electrodes, the photovoltaic performance was enhanced by the addition of the  $\text{ZrO}_2$  shell, consistent with previous work [10,15]. However, in this work the core-shell nanostructure was formed in a one-step process where the precursor solution was coated onto unsintered  $\text{TiO}_2$  electrodes. The common method by which core-shell nanostructured working electrodes are fabricated is coating sintered working electrodes with the dilute sol-gel precursor solution. This is then calcined to remove residual organics prior to dye adsorption. The one-step process displayed in this work is not optimal; however, it only requires one microwave heat-treatment as opposed to two conventional heat treatments.

From the photovoltaic data (Table 1) it can be seen that the current, voltage and fill factors are all increased with the presence of the  $\text{ZrO}_2$  shell coating. This can be said to be due to an ‘energy barrier’ at the surface of the semiconducting working electrode to act as an insulator between the photoinjected electrons in the  $\text{TiO}_2^{\text{CB}}$  and the oxidized dye molecules and the oxidized electrolyte species ( $\text{I}_3^-$ ). The dark current measurements (Fig. 3) show that the presence of the  $\text{ZrO}_2$  shell the cell has a slight positive increase in the voltage. This means that the recombination rate is reduced from the

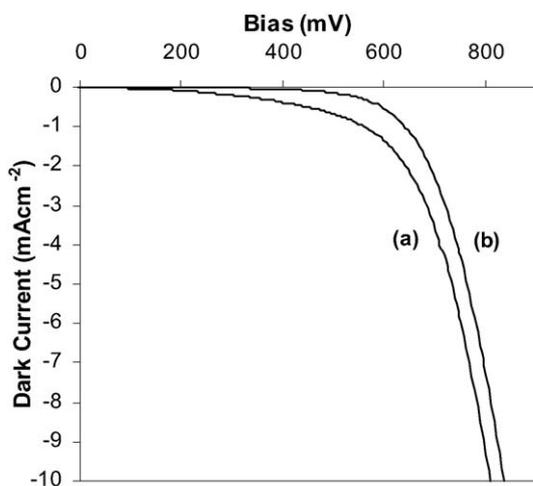


Fig. 3. Dark current curves for the DSSCs comprising 2.45 GHz microwave sintered (a)  $\text{TiO}_2$  and (b)  $\text{ZrO}_2$ -coated  $\text{TiO}_2$  working electrodes.

photoinjected electrons in the  $\text{TiO}_2^{\text{CB}}$  to either the oxidized dye molecules or the  $\text{I}_3^-$ . Thus, the yield is increased with these one-step microwave calcined working electrodes in DSSCs.

#### 4. Conclusions

This work has shown that a thin  $\text{ZrO}_2$  coating can effectively increase the efficiency of the DSSCs. In addition, it is demonstrated that microwave processing can sinter the  $\text{TiO}_2$  particles together resulting in a useful nanostructured  $\text{TiO}_2$  working electrode. Microwave sintering of both bare  $\text{TiO}_2$  and  $\text{ZrO}_2$ -coated  $\text{TiO}_2$  working electrodes was found to have a dramatic improvement in the performance of the DSSCs. The microwave-processed  $\text{TiO}_2$  electrodes were found to be 2.4% efficient, whereas the  $\text{ZrO}_2$ -coated  $\text{TiO}_2$  electrodes performed greater at 3.1% efficient. This data compares well with that from DSSCs comprising conventionally sintered  $\text{ZrO}_2$ -coated  $\text{TiO}_2$  electrodes.

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