## **Diatom Frustules as Light Traps Enhance DSSC Efficiency**

Jeremiah Toster,<sup>†</sup> K. Swaminathan Iyer,<sup>†</sup> Wanchun Xiang,<sup> $\perp$ </sup> Federico Rosei,<sup>‡</sup> Leone Spiccia<sup> $\perp$ </sup> and Colin L. Raston<sup>\*,†</sup>

<sup>†</sup>Centre for Strategic Nano-Fabrication, School of Chemistry and Biochemistry, The University of Western Australia, Crawley, WA-6009, Australia.

<sup>‡</sup>National de la Recherche Scientifique, Université du Quebec, 1650 Boul. Lionel Boulet, J3X1S2, Varennes (QC) Canada

<sup>1</sup>School of Chemistry and ARC Centre of Excellence for Electromaterials Science, Monash University 3800 Victoria Australia

## **Materials and Method**

Diatoms (80 mg) were plasma treated by exposing them to an air plasma source at a frequency of 40 kHz at 110 W for three five minute periods, with agitation between each ion bombardment. Hexane (100 mL) was bubbled with argon for 10 minutes and titanium(IV) isopropoxide (200  $\mu$ L) was added. The plasma treated diatoms were then added to the hexane titanium(IV) isopropoxide solution and mixed open to air. Hydrolysis was carried out by pumping hydrated air into the solution until it went white. Subsequently the frustules were calcined at 500°C for four hours, resulting in surface bound anatase nanoparticles  $\leq$ 20 nm in diameter. The process was then repeated to increase the thickness and connectivity of the titania coating.

Titania coated diatoms were calcined at 500°C for 4 hours and made into a paste by mixing with ethyl cellulose and terpineol (2:1:7 diatom/titania:ethyl cellulose:terpineol). The paste was screen printed onto FTO glass and calcined at

500°C for 2 hours. The working electrode was immersed into a solution of the N719 ruthenium dye overnight and then washed with ethanol, sealed to a platinum counter electrode and back filled with the iodide/tri-iodide electrolyte.

## **Cell Assembly**

A mixture of terpineol (28 mL) and ethyl cellulose (3.9956 g) was added to the diatom titania samples in a ratio of 4:1. Each sample was screen printed onto a 0.16 cm<sup>2</sup> active area and heated to 120°C for 6 minutes, and then a second layer was printed. This was sintered at 500°C for 2 hours then submerged in a solution of 1 mL TiCl<sub>4</sub> (2M) and 49 mL of H<sub>2</sub>O for 30 minutes at 70°C. The cell was then washed with ethanol and water and allowed to cool to 70°C before immersion into the N719 dye solution for 24 hours. The platinum counter electrode was made by drilling a hole in cleaned FTO glass and dropping H<sub>2</sub>PtCl<sub>6</sub> to cover the surface of the glass and heating to 450°C for 15 minutes. After sealing, the working and counter electrodes together with the iodide/tri-iodide electrolyte was added through the drill hole and dispersed through the cell by putting under vacuum. The drill hole was then sealed using a cover slip and sealant, then the exposed glass was soldered to increase conductivity and to connect wires to the working and counter electrodes.

## AFM analysis



SEM targeting of AFM tip onto the surface of the diatom frustule.



AFM of untreated diatom frustule



AFM of diatom frustules after single titania coating

cycle.

XRD



From the XRD (after 1 cycle and calcination at 500°C for four hours) it was established that the titania is in the anatase phase, evident by the primary anatase (101) peak at 25.3° and the absence of the rutile (110) peak around 27°.

 $D=0.9\lambda/\Delta cos\theta$ 

 $\lambda = 0.154 \text{ nm}$   $\Delta = 0.008366 \text{ rad}$   $\theta = 12.65^{\circ}$ 

D=16.6 nm

IPCE



The

IPCE data shows the titania only sample being less efficient than titania coated diatoms after 2, 3 and 4 cycles.