Boron-Doped Silicon Diatom Frustules as a Photocathode for Water Splitting

Soundarrajan Chandrasekaran [†], Thomas J. Macdonald [‡], Andrea R. Gerson [§], Thomas Nann [‡*] and Nicolas H. Voelcker [†*]

[†]Mawson Institute, University of South Australia, Mawson Lakes Blvd, Adelaide, SA 5095, Australia.

[‡]Ian Wark Research Institute, University of South Australia, Mawson Lakes Blvd, Adelaide, SA 5095, Australia.

[§]Minerals and Materials Science & Technology, Mawson Institute, University of South Australia, Mawson Lakes, Adelaide, SA 5095, Australia.

* Thomas Nann, e-mail: thomas.nann@unisa.edu.au.

* Nicolas H. Voelcker, e-mail: nico.voelcker@unisa.edu.au.
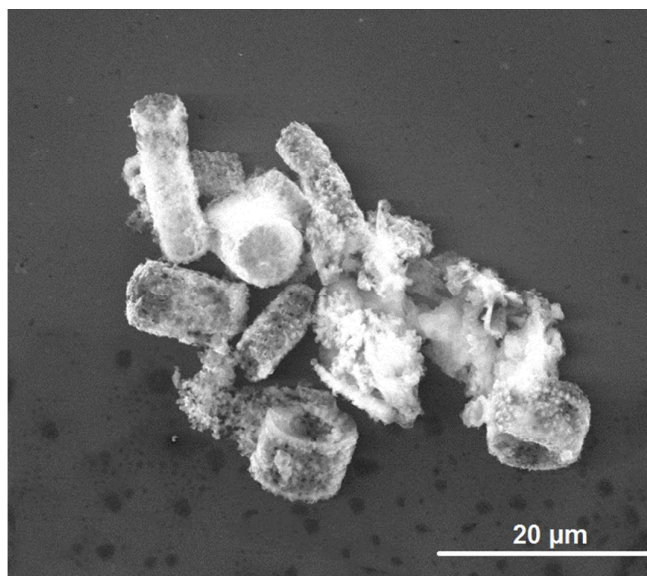
Supporting Information

Figure S1. SEM image showing the distorted shape of the boron-doped silicon diatom frustules after treatment with HCl and HF.
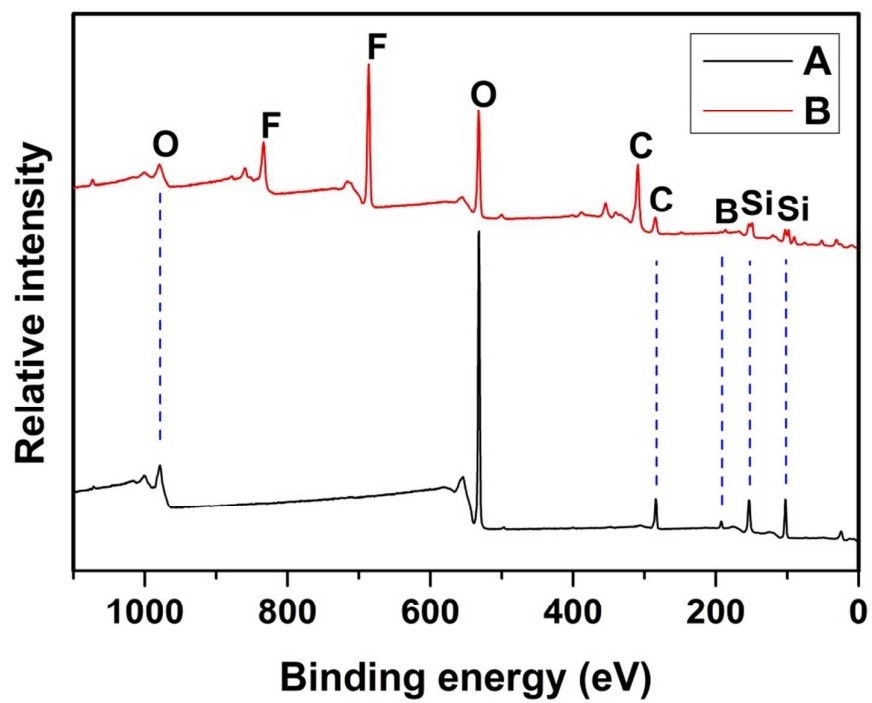
Figure S2. XPS survey spectra of boron-doped silica diatom frustules (A) and silicon diatom frustules (B).
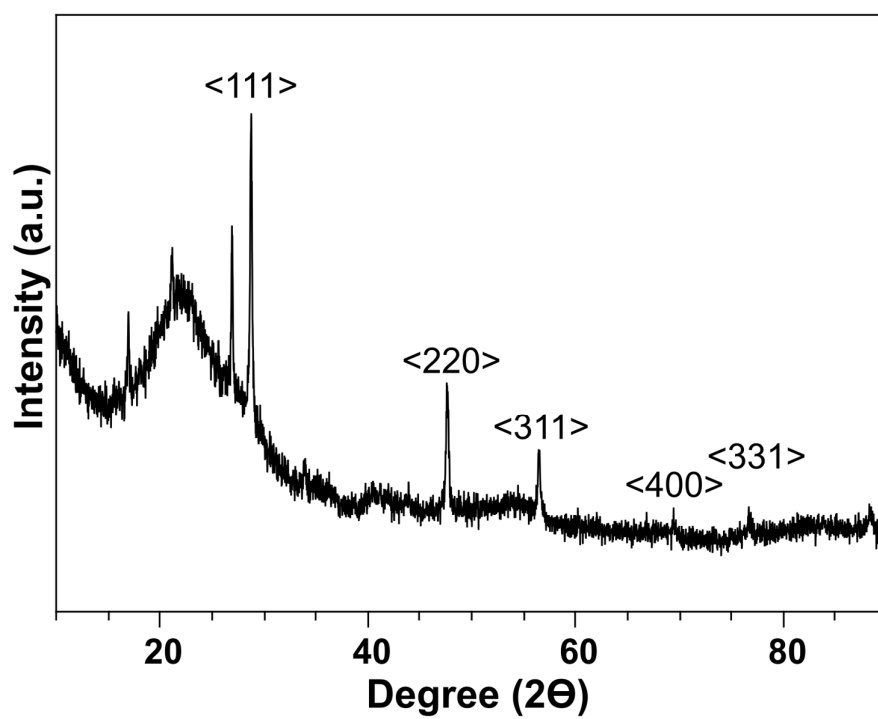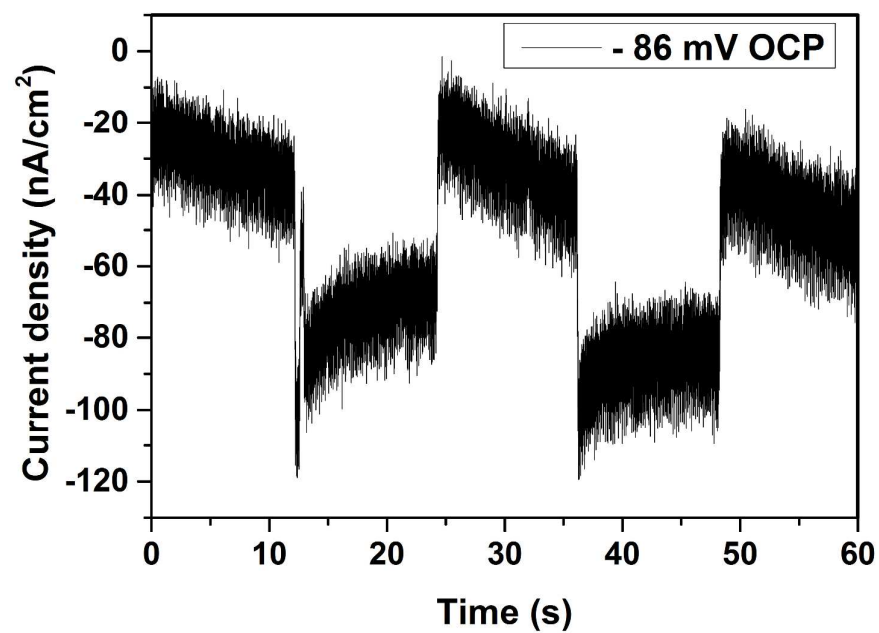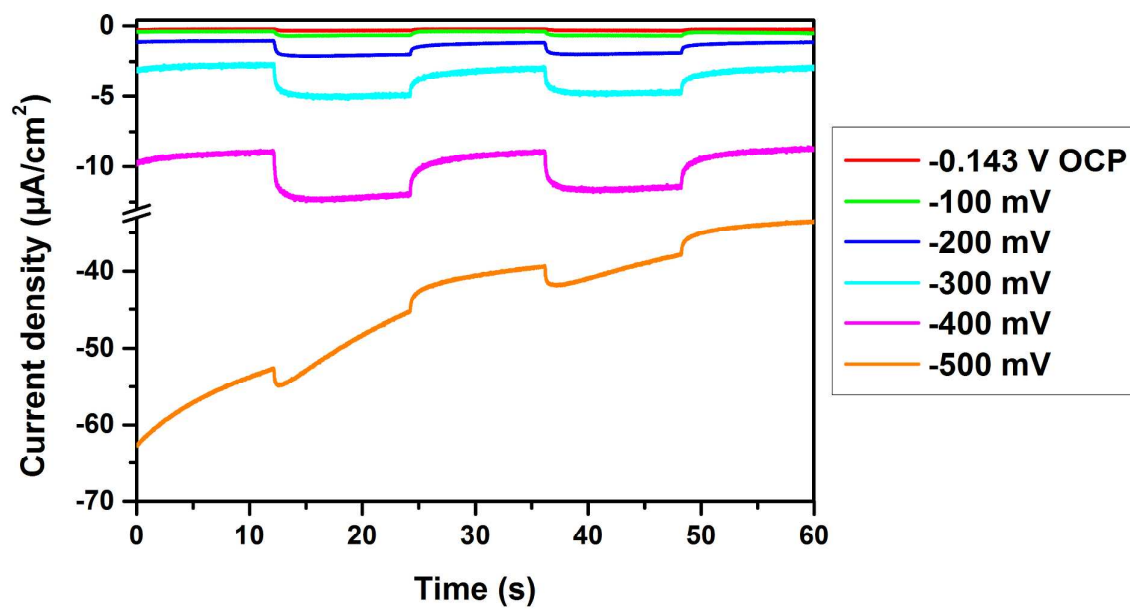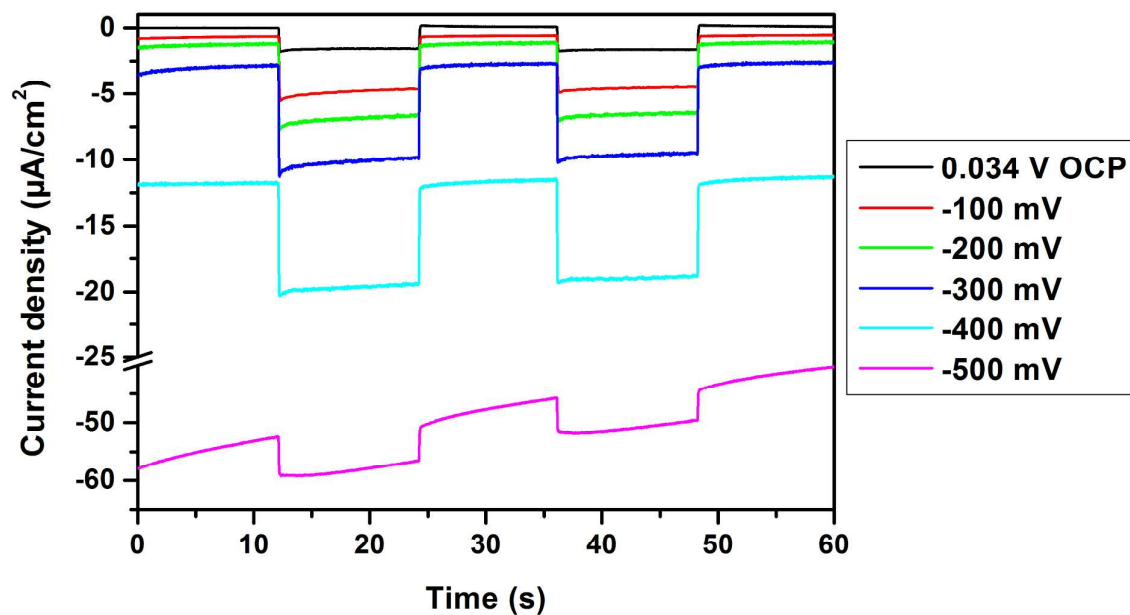
Figure S3. XRD spectrum of boron-doped silicon diatom frustules. Strong silicon peaks (JCPDS card number 27-1402) were observed.

(A)

(B)

(C)

Figure S4. (A) Current density measurement for bare boron-doped silicon diatom frustules carried out in PBS electrolyte at 0 V. (B) Current density measurement for boron-doped silicon diatom frustules coated with InP and catalyst carried out in PBS electrolyte at bias potentials from 0 V to -500 mV in steps of 100 mV. (C) Current density measurement for boron-doped silicon diatom frustules coated with InP and catalyst carried out in 0.1 M H_2SO_4 electrolyte at bias potentials from 0 V to -500 mV in steps of 100 mV.
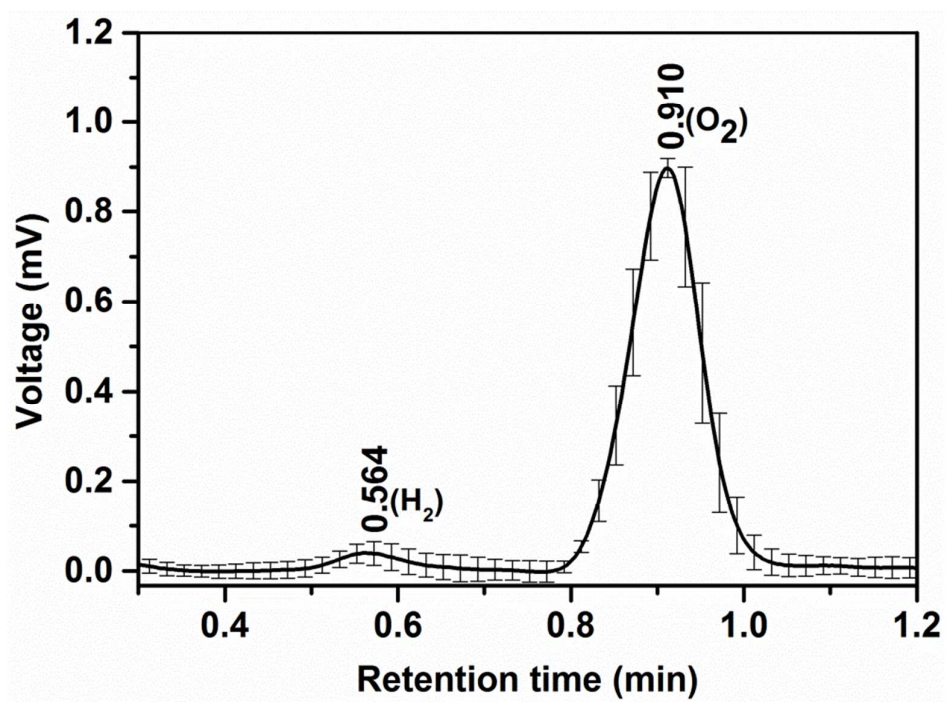
Figure S5. GC of H_2 (200 ppm) standard for 310 µl gas sample.

Theoretical moles of H$_2$ produced

According to $\mathbf{R\ (H_2)} = \dfrac{\mathbf{I}}{\mathbf{nF}}$, a photocurrent of 6 µA should produce 0.112 µmol of H$_2$ for 1 h.

$$\mathbf{R\ (H_2)} = \frac{6 \times 10^{-6}\ A}{2\ \frac{mol\ e^-}{mol\ H_2} \times 96485\ \frac{C}{mol\ e^-}}$$

$$= 3.1 \times 10^{-5} \times 10^{-6}\ A\ mol\ H_2\ C^{-1}$$

For 1 h of water splitting reaction $= 3.1 \times 10^{-5} \times 10^{-6}\ A\ mol\ H_2\ C^{-1} \times 3600\ s$

(where Charge (C) = Current (A) x Time (s))

Amount of H$_2$ evolution for 1 h = 0.112 µmol (or) 112 nmol.

Calculation for moles of H$_2$ produced from gas chromatography

Average area of pure H$_2$ (310 µl, 200 ppm) = 0.00455 mV min

Consider, 99.5% of pure H$_2$ has 995000 ppm of H$_2$.

To convert the average area of pure H$_2$ (310 µl, 200 ppm)

into high pure $H_2 = \left[\dfrac{0.00455\ mV\ min}{200\ ppm}\right] \times 995000\ ppm = 22.63625\ mV\ min.$

Average area of high pure H$_2$ (310 µl) = 22.63625 mV min.

Area of sample H$_2$ (310 µl) after 1 h = 0.00655 mV min

From the areas of pure and sample H$_2$, the H$_2$ evolution is calculated based on the formula from Zhang *et al.* [1]

$$\text{Amount of } H_2 \text{ evolution} = \left[\frac{0.00655\ mV\ min}{(22.63625\text{-}0.00655)\ mV\ min}\right] \times 1\ ml \times \frac{mol}{22.4 \times 1000\ ml}$$

(where 1 ml is the volume of the headspace.)

Amount of H$_2$ evolution for 1 h = 12.9 nmol.

Reference:

1. Zhang, K.; Jing, D.; Xing, C.; Guo, L. Significantly Improved Photocatalytic Hydrogen Production Activity over Photocatalysts Prepared by a Novel Thermal Sulfuration Method. *Int. J. Hydrogen Energy* **2007,** *32*, 4685-4691.