

Supplementary Information

Photo-Electrochemical Oxygen Evolution Reaction by Biomimetic CaMn_2O_4 Catalyst

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1. Photo-Electrochemical Cell

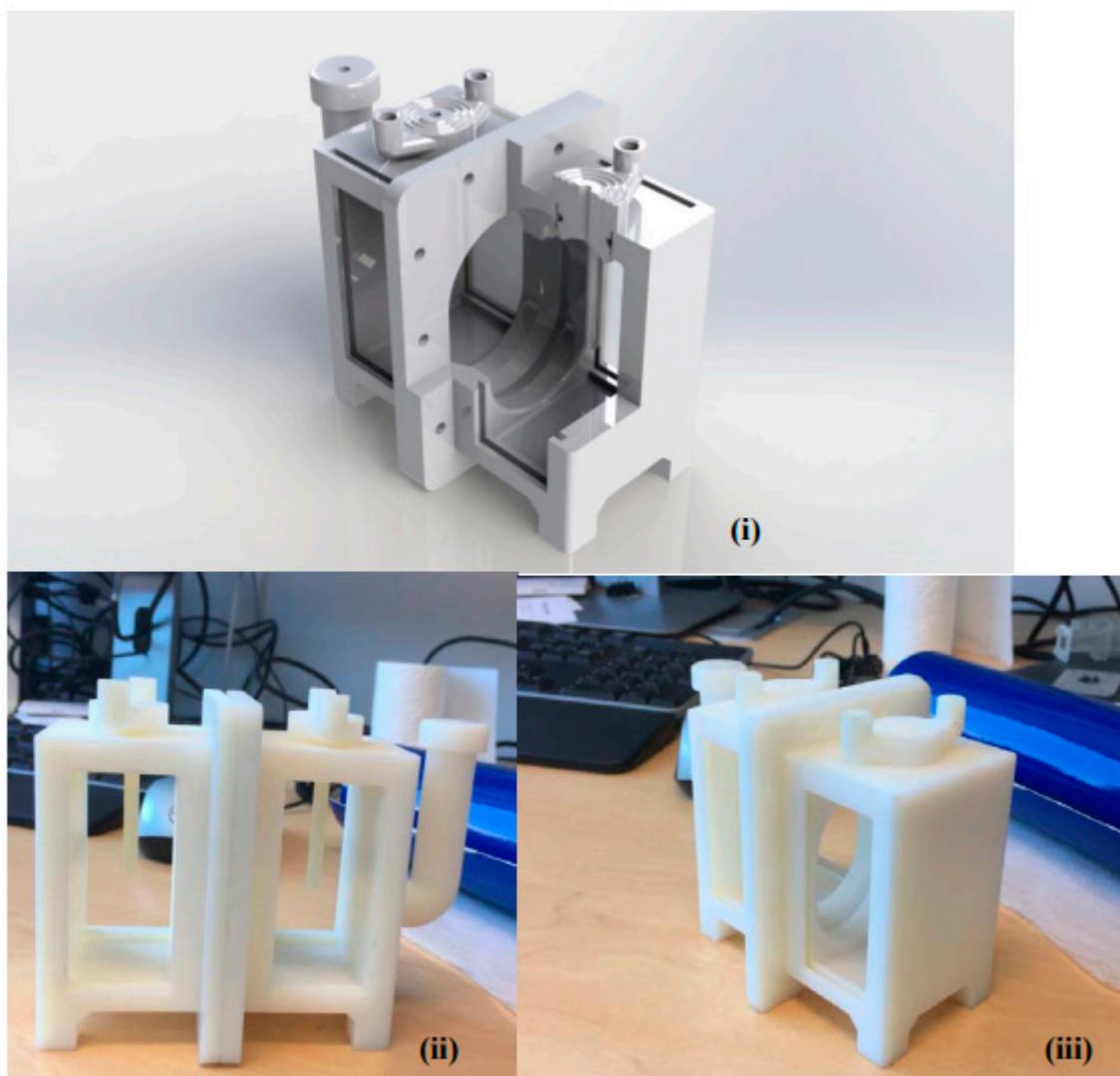


Figure S1(a). (i) Partially cutaway, cross-sectional view (computer-generated) of the sealed cell used in the gas analysis studies; (ii) and (iii) Photographs of the cell prior to being fitted with quartz windows (Reprinted with permission from ref [1]. Copyright (2018) American Chemical Society).

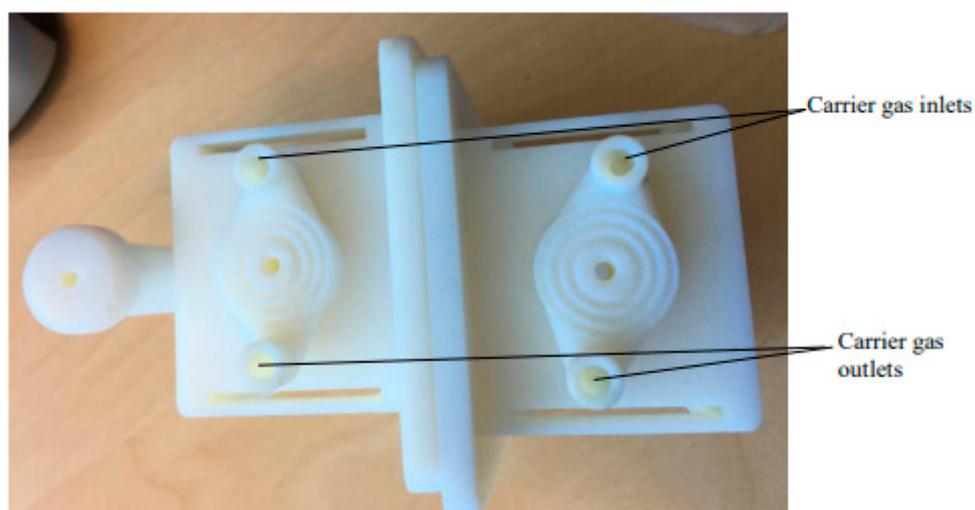


Figure S1(b). Photograph of the top of the cell showing gas inlets/outlets (Reprinted with permission from ref [1]. Copyright (2018) American Chemical Society).

2. Studies on the Gas Bubbles Produced by the $\text{CaMn}_2\text{O}_4/\text{PPy}$ Electrodes

A custom-built apparatus was used for photocurrent testing of samples on FTO glass with simultaneous gas analysis, as shown in Figure S1 (a-b). The apparatus comprised a fully-enclosed electrochemical cell containing two sealed, half-cells whose electrolytes were separated only by a Nafion 117 proton exchange membrane (5 x 4 cm). The working electrode sample and a Ag/AgCl reference electrode were placed in the one half-cell whereas a platinum mesh electrode was placed in the other half cell. One wall of the former half-cell was a quartz sheet. The working electrode was illuminated using a SoLux daylight MR16 halogen light bulb. The electrode that contains irregular-shaped CaMn_2O_4 powders was connected to a potentiostat (CHI Instrument, USA). The gas outlets for the working and counter electrode half cells were connected to a dedicated Shimadzu GC-8A gas chromatograph (GC), via polymer-and-stainless-steel tubing. After fitting the electrodes, the electrolyte was poured into both half cells, which was bubbled with Ar gas overnight to make the cell air free without any external bias. In the gas streams passing through each half-cell, only Ar was detected, which also acted as a carrier gas for the connected GC throughout the photocurrent experiment. Thereafter, the Ar passing through each half cell was sampled, injected and analysed using the gas chromatograph, with the results plotted over 30 min of elution time. A voltage bias of 1.00 V (vs. Ag/AgCl) with and without light-illumination was then applied to the cell, whereafter the carrier gas was tested as described above, for electro-catalysis product gases using the GC. The identities of the gases in the carrier Ar were determined by their retention times.

Figure 6 shows the GC traces over 30 min of elution time for gases generated by the $\text{CaMn}_2\text{O}_4/\text{PPy}$ films on FTO working electrode, with and without light illumination. In addition to the argon carrier gas, a large peak corresponding to oxygen was detected. A minor peak associated with hydrogen, which presumably crossed-over the Nafion membrane from the other half-cell, was also observed. No other gas species was detected. Upon light illumination, the amount of O_2 relative to Ar increased.

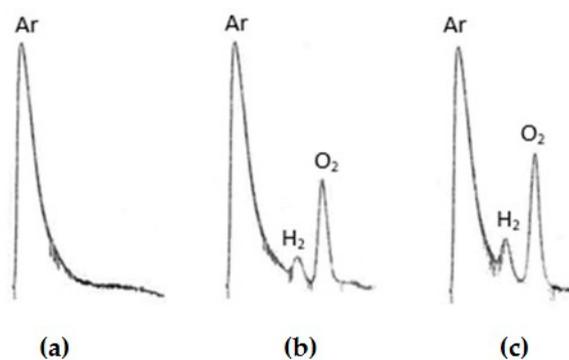


Figure S2. GC traces of collected gases (a) reference, (b) in the dark, and (c) under light irradiation.

References

1. Alsultan, M.; Balakrishnan, S.; Choi, J.; Jalili, R.; Tiwari, P.; Wagner, P.; Swiegers, G.F. Synergistic Amplification of Water Oxidation Catalysis on Pt by a Thin-Film Conducting Polymer Composite. *ACS Appl. Energy Mater.* **2018**, *1*, 4235–4246.