

Development of a Method to Characterize Active Sites in Photocatalysis using *operando* Transmission Electron Microscopy

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Hydrogen gas has the potential to be a clean source of sustainable energy due to its high energy density. However, greenhouse gas emissions are still a major byproduct of current hydrogen production methods. Photoelectrochemistry provides a promising, environmentally friendly route to hydrogen production; [1,2] however, the atomic scale mechanisms of the photocatalysts that facilitate the water splitting reaction are currently poorly understood. Further understanding of the chemical physics governing the active hydrogen evolution sites would allow for better design of photoelectrochemical devices and thus lead to improved reaction efficiencies. This will overcome one of the major barriers impeding this promising technology.

We have developed a unique *operando* photoelectrochemistry transmission electron microscope (TEM) liquid cell sample holder which can be used to characterize these reactions in real time at nanometer length scales. This system builds upon our prior developments of *operando* electrochemical liquid cell holders [3, 4], by including the additional provision of an optical fiber directed at the sample to provide full solar spectrum illumination.

In order to provide accurate, quantitative information, it is necessary to accurately deposit the photocatalyst of interest onto microfabricated electrodes. In this research, a precise sample deposition technique utilizing an inkjet printer has been developed along with stable suspensions of known photocatalysts, leading to site-specific deposition onto the electrode chips. Specifically, this experimental design allows for correlation between I-V characteristics (Figure 1) and real time, high magnification imaging and spectroscopy, elucidating information about photocatalytic mechanisms at the nanoscale. The following photocatalysts used were chosen because the proposed mechanism for each exhibits a spatial dependence: plasmonically enhanced catalysis for Au nanoprisms and catalytically active edge sites for MoS₂ flakes. These experiments will lay the groundwork for the use of this novel experimental design to investigate a wide variety of photoelectrochemical systems, and will allow determination of the mechanisms by which selected photocatalysts induce water splitting and the identification of defect features that serve as the active sites.

References:

[1] Nowotny, J.; Sorrell, C. C.; Sheppard, L. R.; Bak, T. *Int. J. Hydrogen Energy* **2005**, *30*, 521

[2] Walter, M. G. *et al. Solar water splitting cells. Chem. Rev.* **110**, 6446–6473 (2010).

[3] N. Singh, T.S. Arthur, T.S. O. Tutusaus, J. Li, K. Kisslinger, H.L. Xin, E.A. Stach, X. Fan, and R. Mohtadi, *ACS Appl. Energy Mat.* **1**, 4651-4661, 2018

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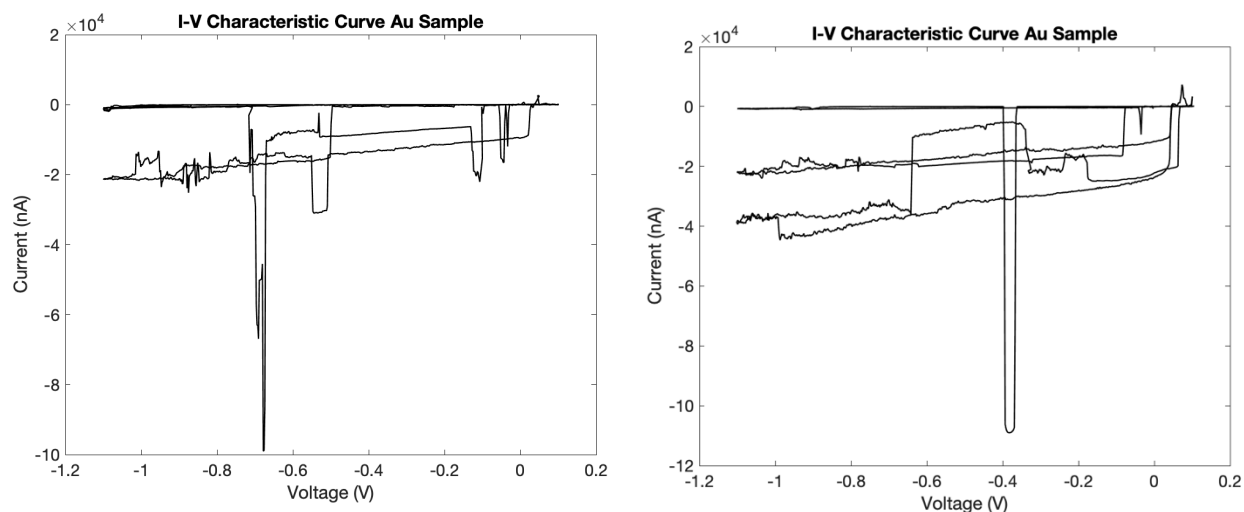


Figure 1. Quantitative I-V measurements taken during cycling without (left) and with (right) full spectrum light provision to the sample. Note the changes in both the onset of I-V excursions and differences in their onset as indicated by the differences in voltage.

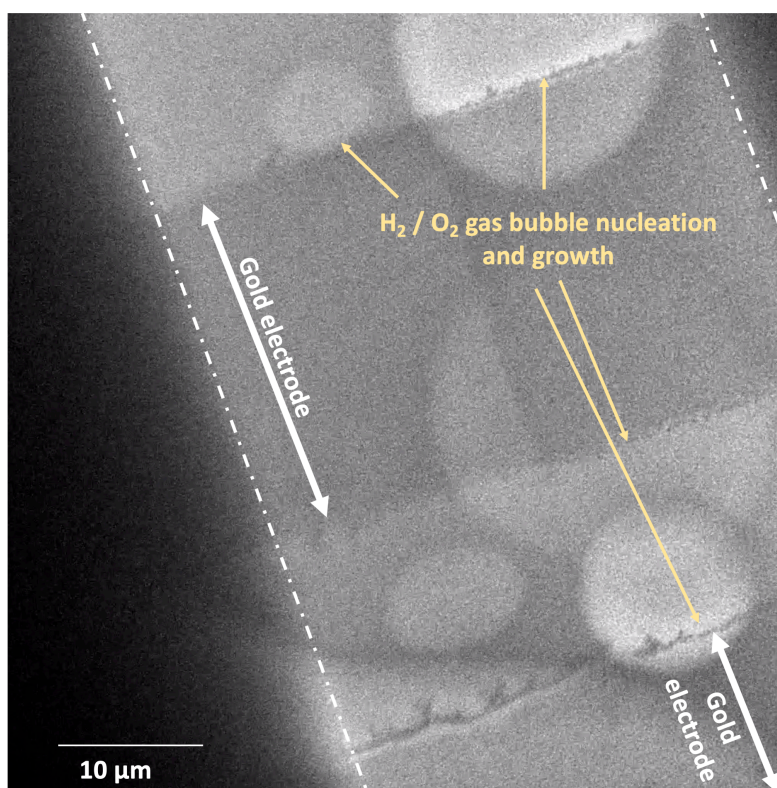


Figure 2. Low-magnification bright field TEM image extracted from a real time video of the splitting of water by Pt electrodes. The silicon nitride viewing window is between the dotted white lines, and the gold electrodes are indicated. The nucleation and growth of gaseous H_2 and O_2 is visible as indicated.