Fuels and Materials from Sunlight and Water

Thesis by

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To the great teachers that inspired me to become a scientist.

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ABSTRACT

The urgency to develop new technologies that harness energy and natural feedstocks in a sustainable fashion has never been more apparent. With global power consumption growing at an exponential rate, only one resource is truly capable of powering the planet: the sun. Sunlight is reliable, clean, and free.

Significant resources have been pledged to develop and refine solar energy devices that convert photons into electricity (i.e. photovoltaics), but the sun's intermittency and the poor overlap of solar irradiance with global power demand a different strategy. In light of these limitations, we have proposed a device which converts solar energy into reduced chemical fuels (e.g. dihydrogen or methane) that can be indefinitely stored and easily transported. In principle, the only required inputs are sunlight, an earth-abundant feedstock such as carbon dioxide, protons (H^+), and reducing equivalents (e^-). The source of these protons and electrons must be abundant and ubiquitous—we chose water.

Despite the 2-billion-year history of plants performing water oxidation to produce molecular oxygen, protons, and electrons (Photosystem II), our understanding of this complex $4H^+/4e^-$ process has been severely limited. Only recently have high-performing, earth-abundant heterogeneous electrocatalysts been reported that can be scaled up to make functioning devices.

This dissertation describes progress on both the synthetic and mechanistic fronts in developing earth-abundant heterogeneous water oxidation catalysts for solar-driven water splitting. We have synthesized nanoparticulate Ni-Fe catalysts with the highest measured activity on flat electrodes to date. We carefully characterized these materials spectroscopically to determine that edge-site iron was active in catalysis. We then undertook novel *in-situ* spectroelectrochemical techniques in non-aqueous media to identify the active iron species, which is surprisingly a *cis*-dioxo-iron(VI) corner site. The data also indicate that geminal iron-oxo coupling may be the operative mechanism of O-O bond formation, a new scheme with potential biological relevance.

Finally, we have expanded our goal to include sustainably reducing other feedstocks, such as carbon dioxide and hydrocarbons. In doing so, we aim to make pharmaceuticals, polymers, and other high-value products from sunlight and water.

PUBLISHED CONTENT AND CONTRIBUTIONS

Darnton, T. V.;* Hunter, B. M.;* Hill, M.G.; Záliš, S.; Vlček Jr, A.; Gray, H.B. Reduced and Superreduced Diplatinum Complexes. *Journal of the American Chemical Society* **2016**, *138*, 5699. DOI: 10.1021/jacs.6b02559.

B.M.H. performed the electrochemical and spectroelectrochemical characterization, participated in developing the bonding scheme, and co-wrote the manuscript.
* Contributed equally.

Hunter, B. M.; Blakemore, J. D.; Deimund, M.; Gray, H.B.; Winkler, J. R.; Müller, A. M. Highly Active Mixed-Metal Nanosheet Water Oxidation Catalysts Made by Pulsed-Laser Ablation in Liquids. *Journal of the American Chemical Society*, **2014**, *136*, 13118. DOI: 10.1021/ja506087h.

B.M.H. characterized the nanosheet catalysts by infrared (IR) spectroscopy and participated in the writing of the manuscript.

Hunter, B. M.; Gray, H. B.; Müller, A. M. Earth-Abundant Heterogeneous Water Oxidation Catalysts. *Chemical Reviews* **2016**, *116*, 14120. DOI: 10.1021/acs.chemrev.6b00398.

B.M.H. wrote the manuscript along with the other authors.

Hunter, B. M.; Hieringer, W.; Winkler, J. R.; Gray, H. B.; Müller, A. M. Effect of interlayer anions on [NiFe]-LDH nanosheet water oxidation activity. *Energy & Environmental Science*, **2016**, *9*, 1734. DOI : 10.1039/C6EE00377J.

B.M.H. participated in the conception of the project, characterized the exchanged materials by infrared (IR) spectroscopy, and wrote the manuscript along with the other authors.

Hunter, B. M.; Kallick, J.; Kissel, J.; Herzig, M.; Manuel, C; Protsenko, D.; Wong, B. J. F.; Hill, M. G. Controlled-Potential Electromechanical Reshaping of Cartilage. *Angewande Chemie*, **2016**, *128*, 5587. DOI: 10.1002/ange.201600856.

B.M.H. participated in the inception of the method, the hypothesis of cartilage reshaping by water oxidation, and the writing of the manuscript.

Hunter, B. M.; Villahermosa, R. M.; Exstrom, C. L.; Hill, M. G.; Mann, K. R.; Gray, H. B. M-M Bond-Stretching Energy Landscapes for $M_2(dimen)_4^{2+}$ (M = Rh, Ir; dimen = 1,8-Diisocyanomenthane) Complexes. *Inorganic Chemistry*, **2012**, *51*, 6898. DOI: 10.1021/ic300716q.

B.M.H. performed the calculations, analyzed the data, and wrote the manuscript.

Záliš, S; Hunter, B. M.; Gray, H. B.; Vlček Jr, A. Electronic Structures of Reduced and Superreduced $Ir_2(1,8\text{-diisocyanomenthane})_4^{n+}$ Complexes. *Inorganic Chemistry*, **2017**, *56*, 2874. DOI: 10.1021/acs.inorgchem.6b03001.

B.M.H. contributed to the design of the project, primarily in the bonding scheme of superreduced d^8-d^8 “$6p^2$” complexes.

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