1. **Molecules, materials, and mechanisms for solar fuel production**

Quick View Other Sources

By Gray, Harry B.

From Abstracts of Papers, 250th ACS National Meeting & Exposition, Boston, MA, United States, August 16-20, 2015 (2015), PRES-37. | Language: English, Database: CAPLUS

Collaborative research efforts in the NSF CCI **Solar** Fuels Program are focused on developing new fundamental understanding of mols. and **materials** that efficiently generate renewable hydrogen **fuel** using the energy of sunlight. Emphasis in these efforts is placed on a mechanistic understanding of reactions relevant to achieving **fuel** formation. Catalysis of water oxidn., the anodic half reaction of overall water splitting, is being intensely studied. Pulsed laser ablation has proven to be a valuable technique for synthesis of small, surfactant-free, mixed-metal nanomaterials with size and compn. control. Deposition of these **materials** on electrodes results in assemblies that are highly active for water oxidn. In-situ spectroscopic studies of these assemblies are providing new insights into possible **mechanisms** of oxygen evolution. In-situ spectroscopies are also being applied to investigate new trimetallic water-oxidn. catalysts. Metal oxides contg. Ni, Fe, and a third metal (M = Al, Ga, Mo, Cr) have been found to be superior in catalytic performance to the Ni-only or Ni-Fe analogs. Understanding the role of the third metal promises better understanding of the mechanism of catalysis in these **materials**. Exptl. cyclic voltammetry has demonstrated that fluorinated iron glyoxime complexes act as hydrogen evolving catalysts at modest overpotentials. Our objective is to use d. functional theory (DFT) calcns. and CV simulations to identify the **mechanisms** that are consistent with the obsd. activity. The calcd. redn. potentials and pKa's have allowed us to propose **mechanisms** for two catalyst derivs. In one case, the mechanism involves a single pathway through an Fe(0) intermediate and a subsequent Fe(II)-hydride intermediate. In a second case, a parallel pathway involving protonation of the ligand gives rise to a qual. different electrochem. response. These mechanistic insights are guiding the synthesis of more active mol. electrocatalysts.