

## **Optimizing catalyst-semiconductor integration in hybrid photoelectrodes for light-driven CO<sub>2</sub> reduction**

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Sonochemical hydrosilylation was used to immobilize three different Re(bipyridine)(CO)<sub>3</sub>Cl catalysts competent for CO<sub>2</sub> reduction onto H-terminated Si (111), where the bipyridine ligands were functionalized with appended alkene functionalities. H-terminated Si (111) samples were submerged in solutions of the catalysts and reacted in an ultrasonic bath. Reaction time was varied to optimize the surface loading of Re catalysts, and samples from various time points were exposed to additional sonication to test the integrity of the Re layer. Catalyst surface loading on Si was quantified by inductively coupled plasma mass spectrometry (ICP-MS) analysis. Catalytic multilayer thickness was measured by variable angle spectroscopic ellipsometry (VASE). ICP-MS results showed an initial linear relationship between catalyst surface loading and reaction time, before loading ultimately plateaued, and revealed that the alkene-appended bipyridine ligand properties influence the reactivity of the catalyst towards hydrosilylation—underscoring the need to optimize the integration procedure based on attachment group. VASE measurements showed a consistency in the thickness of multilayers formed on various samples from the same time point. Finally, electrochemical experiments indicated a qualitative change in the photoelectrochemical behavior of the modified Si electrodes from early to later time points. Preliminary results reveal the need for a more thorough investigation into the nature of these multilayers under different experimental conditions.