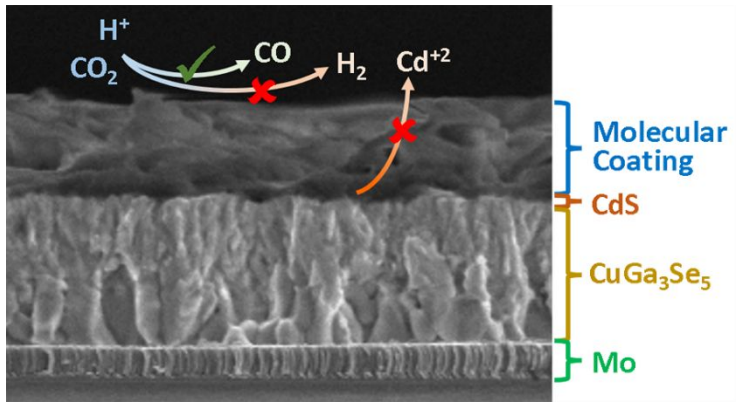
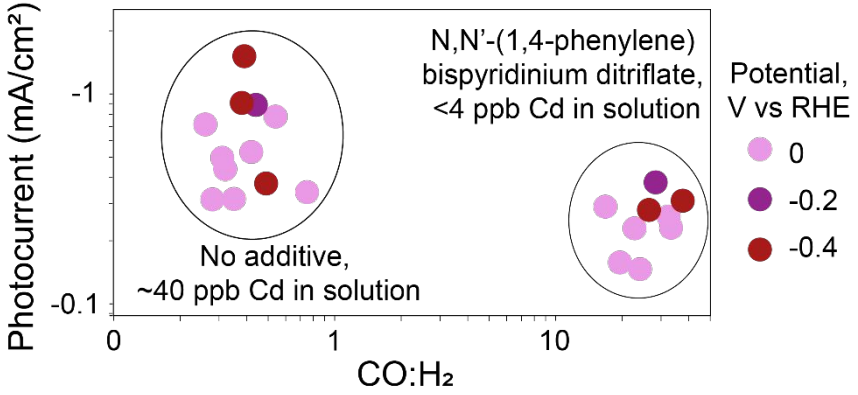
Improved selectivity and durability for CO_2 photoreduction





Each point represents a 10 min photoelectrolysis. Presence of the additive consistently improves selectivity and durability.

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Scientific Achievement:

Nonconductive molecular coatings deposited during operation of solar fuels photocathodes provide a 30-fold increase in selectivity toward CO_2R products while also lowering corrosion at least 10-fold. This discovery establishes hybrid molecular-solid state photocathodes as a promising route for obtaining the efficiency, durability, and selectivity required for a scalable solar fuels technology.

Significance and Impact:

Harvesting solar energy for sustainable generation of chemicals and fuels relies on the development of photocathodes that can utilize visible light to drive the electrochemical reduction of CO_2. Semiconductors that effectively utilize visible light suffer from corrosion and lack of product selectivity, which can both be addressed by molecular coatings.

Research Details:

- The coating is generated *in situ* from the electrolyte additive N,N'-(1,4-phenylene) bispyridinium ditriflate and remains intact when the additive is removed from electrolyte
- The >90% selectivity toward CO is a major improvement compared to the primary H_2 product observed without the additive, and Cd corrosion is lowered to below detectability.
- The $CuGa_3Se_5$ absorber had a CdS coating, which helps generalize the strategy since this coating is also used for broad range of $Cu(In,Ga)Se_2$ (CIGS)-based photocathodes.

Lai, Y.; Watkins, N. B.; Muzzillo, C.; Richter, M.; Kan, K.; Zhou, L.; Haber, J. A.; Zakutayev, A.; Peters, J. C.; Agapie, T.; Gregoire, J. M. Molecular Coatings Improve the Selectivity and Durability of CO_2 Reduction Chalcogenide Photocathodes. *ACS Energy Lett.* **2022**, doi: 10.1021/acsenergylett.1c02762.

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