

A Molecular Cobalt Catalyst Architected and TiO₂ Modified p-GaInP₂ Photoelectrode for Hydrogen Production

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Fundamental Question Impacting Solar Fuels

- > Semiconductors are unstable under illumination, if you don't have thermodynamics, you have to depend on catalysis.
- > Could directly attaching homogeneous catalysts to the semiconductor surface provide the same or better catalytic activity as precious metals and stabilize the surface?

Advantages of Homogeneous Catalysts for PEC

- Molecular catalysts can offer a variety of structures and can use many different active metal ions.
- High activity with abundant materials is possible
- They can be transparent catalysts in contrast to solid metals
- Attachment can form a strong electronic coupling and mass transfer is not an issue for the catalyst.
- Catalyst can easily be changed to do other reactions like reduce CO₂ or nitrogen
- For a PEC system, long-term catalyst stability is less of an issue since the system will have a daily off-time during the night, where it is possible to regenerate the catalyst layer.
- The ultimate goal then is an attachment scheme that is basically a spontaneous self-assembled surface layer.

Homogeneous catalyst used in this study

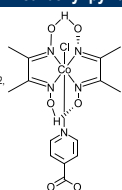
Co(oxm)(pyCOOH) [oxm = bis-glyoxime; pyCOOH = 4-carboxy pyridine]

Catalyst
Accounts of Chemical
Research 42, 1995-2004
(2009)

Chemical Society Reviews 42,
2338-2356 (2013)

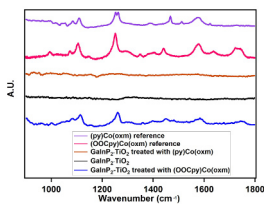
Linkage
Nature 356, 563-565
(1998).

J. Mater. Chem. 13,
1048-1053 (2003)



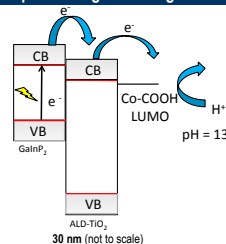
The linkage is expected to be through a covalent coordination of the carboxylate group to the TiO₂ surface

To improve the linkage stability, an additional 10-cycle (~0.4 nm) TiO₂ ALD layer was deposited after catalyst attachment



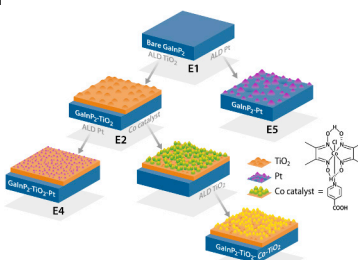
ATR-IR spectra of electrode surfaces show attachment with the carboxylate group and no attachment without [pyCOOH].

Conceptual Energetic Configuration

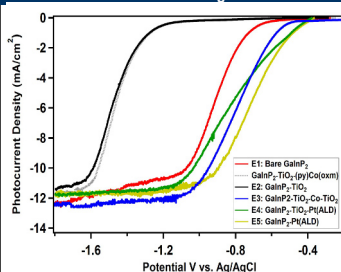


Here the TiO₂ layer was used as-grown; it was not annealed so it remained amorphous. The actual position of the conduction band and valence band for the TiO₂ is unknown.

Surface modification strategies for the p-GaInP₂ photoelectrodes.

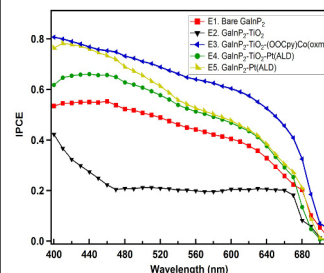


Photocurrent-voltage curves



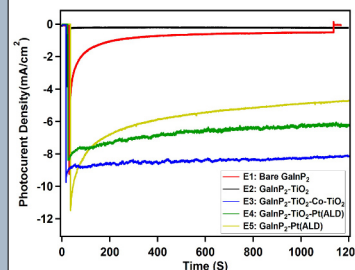
Photoelectrochemical current density (J) versus potential (V) behaviors of the photocathodes under 1 sun illumination (100 mW cm⁻²) in argon purged 0.1 M NaOH solution (pH=1). The Co-modified photocathode shows significant photoelectrochemical performance enhancement over an untreated electrode, very close to the Pt catalyzed electrode.

IPCE performance of electrodes 1-5 at -1 V vs. Ag/AgCl in pH 13 aqueous solution



A significant enhanced IPCE for the Co molecular catalyst modified electrode (3) was observed. Electrode 3 displays a high IPCE up to ~80% across the visible range, ca. 50% higher than the bare electrode, and ca. 20% higher than Pt modified electrode 4. Our interpretation for this high IPCE is twofold, i) that the catalyst is transparent throughout the visible spectra and ii) the TiO₂ layer acts like an antireflective coating. The lower IPCE of electrode 4 and 5 can be explained by the blockage of light by the Pt particles.

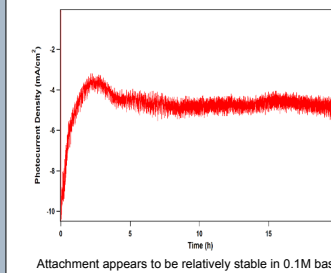
Current density-time profile of electrodes 1-5 at -1 V vs. Ag/AgCl (or 0 V vs. RHE) under 1 sun illumination for 20 min



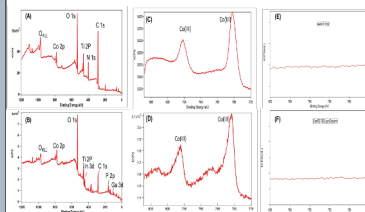
Turnover number and turnover frequency for 20 min test

Entry	Electrodes	Catalyst amount (mmol)	Catalyst J, 20 min at 0 V vs. RHE (mA/cm ²)	Total charge (Coulombs)	TON	TOF (sec ⁻¹)
1	GaInP ₂ -only	-	-0.6	0.12	-	-
2	GaInP ₂ -TiO ₂	-	-0.3	0.009	-	-
3	GaInP ₂ -TiO ₂ -(COOPy)Co(oxm)-TiO ₂	0.5	-8.2	0.40	4070	3.4
4	GaInP ₂ -TiO ₂ -Pt	0.38	-6.2	0.23	3129	2.6
5	GaInP ₂ -Pt	6.1	-4.7	0.40	342	0.28

20 h at -1 V vs. Ag/AgCl (or 0 V vs. RHE) under 1 sun illumination at pH 13



Attachment appears to be relatively stable in 0.1M base



Satellite peaks indicate change in cobalt environment, likely catalyst decomposition, but the species has not yet been identified. Experiments at BESSY show similar results.

Next steps

- Use transient reflectance spectroscopy to study interface
- Determine the electron transfer rate for semiconductor to catalyst and then catalysis to products and how that depends on the attachment scheme
- Determine degradation products
- Change linkage to phosphonic acid – phosphonic acid group should attach directly to the electrode surface.
- Combine with dipoles to control band edge energetics

Acknowledgment



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