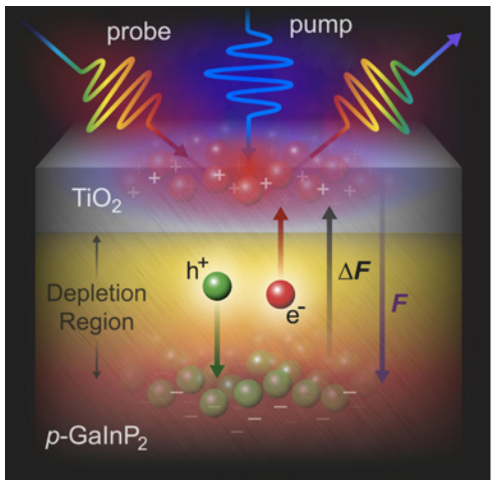
NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Uncovering the Operating Principles of Photoelectrodes

Highlights in Research & Development

NREL researchers have developed a new probe to help design more efficient sunlight-to-fuel photoelectrodes.

Semiconductor photoelectrodes used in photoelectrochemical (PEC) cells directly convert solar energy into stored energy as chemical fuels. The photoconversion process occurs under inherently non-equilibrium conditions and is therefore difficult to probe. Yet, understanding the mechanism of how photons are converted to charge carriers that can then do chemical work represents a key factor in optimizing PEC performance.



Schematic of the transient photoreflectance measurement. A pump pulse modulates the reflectance of a broadband pulse and creates free charge carriers within the depletion region of a semiconductor. The free carriers modulate (ΔF) the built-in field (F), which, in turn, alters the reflectance. The change in reflectance as a function of pump-probe delay time is used to directly monitor the formation and decay of fields at the interface. Illustration by Alfred Hicks, NREL

Scientists at the National Renewable Energy Laboratory (NREL) have developed an ultrafast spectroscopic probe that can elucidate the photoconversion processes that occur near semiconductor junctions. Electric fields at such junctions are critical components for charge separation that drives the photoconversion process.

NREL's novel spectroscopic probe takes advantage of the Franz-Keldysh effect, where an electric field produces an oscillatory modulation to the reflectance of a white-light probe. Using this probe, NREL scientists have uncovered the beneficial role of a semiconductor/oxide interface, specifically a $GaInP_2/TiO_2$ junction, in the photoconversion process. A key finding is that it forms a *p-n* junction.

Equilibration of chemical potential across the *p-n* junction creates internal electric fields. Light absorption by the semiconductor produces energetic electrons near this buried junction. The fields promote rapid electron transfer across the interface so that they can participate in chemical reactions at the surface of the photoelectrode. The positive charges left behind are pushed away from the interface, thus preventing inefficiencies.

Since the presence of free charges can partially screen those fields, the reflectance is modulated through the Franz-Keldysh effect. Thus, by monitoring the electric fields, the operation of the photoelectrode can be probed *in-situ*.

Peering further into interfaces such as $GaInP_2/TiO_2$ can provide critical insight that will enable additional advances in efficiency and stability of photoelectrodes for solar-driven water splitting.

Technical Contact: Matthew C. Beard, matt.beard@nrel.gov

References: Y. Yang, J. Gu, J.L. Young, E.M. Miller, J.A. Turner, N.R. Neale, M.C. Beard, "Semiconductor interfacial carrier dynamics via photoinduced electric fields," *Science* 350, 1061–1065 (2015). DOI 10.1126/science.aad3459

O. Khaselev, J.A. Turner, "A monolithic photovoltaic-photoelectrochemical device for hydrogen production via water splitting," *Science* 280, 425–427 (1998). DOI: 10.1126/science.280.5362.425

Key Research Results

Achievement

NREL scientists developed an ultrafast spectroscopic probe that is specifically sensitive to the carrier dynamics at critically important semiconductor interfaces.

Key Result

NREL has used this probe to elucidate the beneficial role of a $GaInP_2/TiO_2$ junction. A *p-n* junction forms that promotes rapid electron transfer but suppresses interfacial charge recombination.

Potential Impact

A better understanding of interfaces such as $GaInP_2/TiO_2$ that are being developed as photoelectrodes for solar-driven water splitting may lead to improved efficiency and stability.

NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.

15013 Denver West Parkway
Golden, CO 80401
303-275-3000 | www.nrel.gov

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