

Figure 1. Key Results for Electrode Design and Its Influence on Photoelectrochemical Reduction of Nitrogen

(A) Schematic illustration of electrode fabrication.

(B) Influence of a PTFE layer on the accessibility of water.

(C) Rate of NH₃ formation (column diagrams) and faradic efficiencies (point plots) on a Au/Ts surface (orange) and on Au-PTFE/Ts (purple) at a series of potentials over a 4 h time period.

Adapted from Wang and co-workers.⁷

–0.2 V versus RHE in the resulting electrode.

This paper presents an encouraging strategy for the micro-control of water

with controlled accessibility as a way to enhance reactivity at electrode-catalyst-reactant interfaces. A challenge remains in generalizing the strategy to optimize and further improve its overall

energy efficiency as a way to compete commercially with the already well-established HBP.

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Preview

Surface versus Bulk: Charge Carriers Play by Different Rules

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In this issue of *Chem*, El-Zohry et al. employ a novel time-resolved electron microscopy technique to report that photoinduced charge-carrier diffusion on a semiconducting cadmium telluride single-crystal surface exhibits unusual features that are not only distinct from those of the bulk crystal but also considerably dependent on the crystal facet orientation.

Since the discovery of the photoelectric effect, the prospect of using light to create labile electrons has captured the imagination of many scientists. The key to the success of

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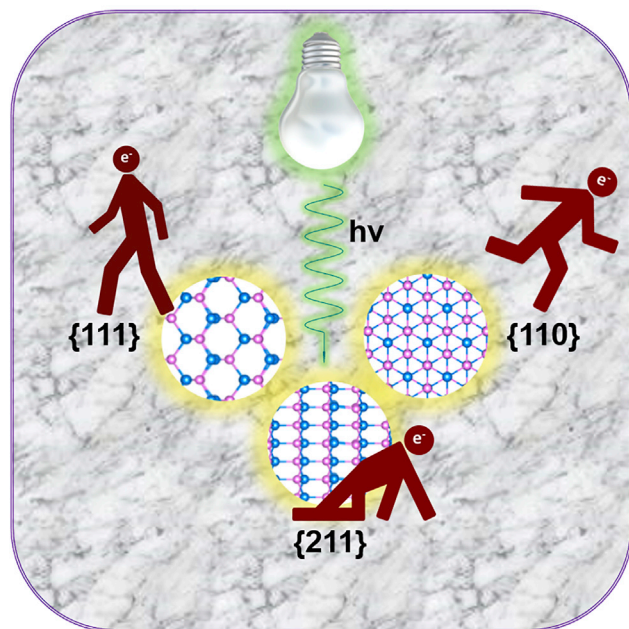


Figure 1. Facet Dependence of Photogenerated Charge-Carrier Diffusion Behavior on a Cadmium Telluride Single-Crystal Surface

optoelectronic devices, such as solar cells, which are inspired by natural photosynthesis, lies mainly in the efficiency and skill with which photoinduced charge carriers generated in semiconductor materials can be intelligently manipulated for useful exploitation.¹ It often helps to view the overall performance of such devices in terms of several constituent processes, including charge-carrier generation, i.e., electron-hole pair (exciton) creation, in photoactive materials upon impingement of light; their mutual separation into free charge carriers; and their eventual diffusion toward electrodes for extraction.²

Although the surface mobility of charge carriers is an intriguing aspect of device performance, it is a much less explored phenomenon than diffusion in the bulk. Experimental techniques endowed with high spatial and temporal resolutions, such as time-resolved optical microscopy, are a good choice for such investigations. However, the relevant signals in such studies can originate from sample depths that are dependent on the

wavelengths of the optical excitation and the probe laser beam used.³ Although one-photon and two-photon excitation schemes have been utilized to differentiate between contributions from the surface and the bulk, the thickness of the relevant "surface" in such cases can range from a hundred nanometers to a few microns.⁴

In this issue of *Chem*, El-Zohry et al. employ a novel analytical technique called four-dimensional scanning ultrafast electron microscopy (4D-SUEM) to report some unusual charge-carrier diffusion behavior encountered on semiconductor surfaces, namely, different facets of a cadmium telluride (CdTe) single crystal.⁵ This method typically mimics conventional laser-based ultrafast pump-probe measurement protocols but differs from other methods in the use of pulsed photoelectrons as the probe pulse. The use of pulsed probe photoelectrons instead of photon pulses drastically improves the spatial resolution because of the De Broglie wavelength of the accelerated electrons under a strong field.⁶ Additionally, the relevant signal (second-

ary electrons) in their measurements essentially originates from the first few nanometers of the sample surface, which allows the authors to observe photogenerated charge-carrier diffusion with unprecedented surface selectivity.⁷ This technique has recently been successful in gaining surface-selective insights into charge-carrier diffusion of a wide variety of photoactive materials, such as indium gallium nitride nanowire arrays and copper indium gallium selenide nanocrystal films.⁸

For their investigation, the authors chose single crystals of CdTe, which is a semiconductor material of considerable interest to the solar-cell research community and is preferred for its low cost yet significant power conversion efficiency.⁹ CdTe single crystals with three crystal facets (namely, {110}, {111}, and {211}) were studied; each was characterized, as per density functional theory (DFT) calculations, by distinct polarization properties that originate from the unique bonding and termination environment of their topmost surfaces. The samples were photoexcited by an optical pump pulse with 2.4 eV energy, and the subsequent evolution of the time-resolved secondary electron contrast images was processed for the generation of 2D false color plots of the different images at various time delays between the pump and the probe pulses.

Their 4D-SUEM measurements were limited to a time window of 6 ns because of constraints in their setup; however, they offer several interesting results. These include the observation of carrier diffusion over a scale of several tens of microns, which the authors aptly term super diffusion. In addition, by analyzing the kinetic traces of a few selected coordinates along the contour of the data plots, they reported fast diffusion components that were a few hundred picoseconds in duration. Using these two parameters, they were able to evaluate the diffusion coefficients by assuming a simple 2D

diffusion model. In particular, for the {110} and {111} facets, they estimated diffusion coefficients that were approximately four orders higher than those reported for the bulk.¹⁰ The {111} facet provided smaller diffusion length and diffusion components than {110}; however, these were still substantially higher than those in the bulk. In stark contrast, the scenario was found to be very different for the {211} facet, which was characterized by trapping dynamics rather than facile diffusion of the photogenerated charge carriers as a result of its greater propensity to become oxidized and generate surface trapping sites.

Interestingly, their Hall measurements provided bulk diffusion coefficient values that were of similar order irrespective of the facet orientation. This highlights the fact that the authors provide novel evidence as to how crystal facets and their surface termination assume important roles (very distinct from those of the bulk) in dictating diffusion behaviors (Figure 1). The present study offers the

fascinating prospect of modulating charge-carrier mobilities by suitable facet engineering. Although directly relevant to a plethora of optoelectronic devices involving inorganic semiconductors, the insights from this study can be well extended to several other photoactive materials, including but not limited to soft conducting polymers that form the basis of organic photovoltaics.

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Preview

Reversible CO₂ Sequestration by Precipitation from Water via an Organic Sorbent

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CO₂ capture by chemical methods is highly energy intensive and costly; therefore, more efficient sorbents and more cost-effective technologies are needed. In this issue of *Chem*, Custelcean and coworkers describe a CO₂ sorbent that has several significant advantages over the benchmark sorbent in use today.

For at least 2.1 million years prior to c. 1760, when the Industrial Era began, the concentration of atmo-

spheric CO₂ ranged between approximately 180 and 290 ppm.¹ Large amounts of anthropogenic CO₂ emis-

sions after c. 1760, mostly from burning fossil fuels and land-use changes,² resulted in a continuous and accelerating increase in the atmospheric CO₂ concentration, exceeding the upper limit considered safe (350 ppm³) in the late 1980s.⁴ Although the contribution of CO₂ to the greenhouse effect was quantified by Svante Arrhenius well over a century ago,⁵ and despite studies hinting at the possibly catastrophic consequences of global warming to life on Earth, humanity overall has

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