Ensembles of Photosynthetic Nanoreactors (EPN)
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Mission Statement: *To understand, predict, and control the activity, selectivity, and stability of solar water splitting nanoreactors in isolation and as ensembles.*

The overarching question that guides the scientific mission of **EPN** is: *How can the solar-to-hydrogen energy conversion (STH) efficiency of ensembles of photosynthetic nanoreactors be increased by more than an order-of-magnitude to outperform state-of-the-art photoelectrochemical (PEC) devices*? The key discovery that supports a pathway to answering this question comes from **EPN** numerical simulations, which indicate that STH efficiencies for ensembles of photosynthetic nanoreactors can exceed those of standard PEC devices. The cause of this efficiency enhancement is low absorbed photon flux per nanoreactor, and thus small fuel-forming reaction rates that result in less overpotential than observed for typical PEC photoabsorbers, combined with the multiplicative output from having many photoabsorbers in an ensemble. Toward achieving its scientific mission, **EPN** is guided by scientific research goals that span 4 thrusts, each with directed research approaches and associated methods (*Fig. 1*). Fundamental knowledge gained is being used to identify the physicochemical properties that in aggregate are responsible for ensemble behaviors, which may lead to transformative pathways to meet the DOE H_2 Shot cost target of $1 per kg-$H_2$.

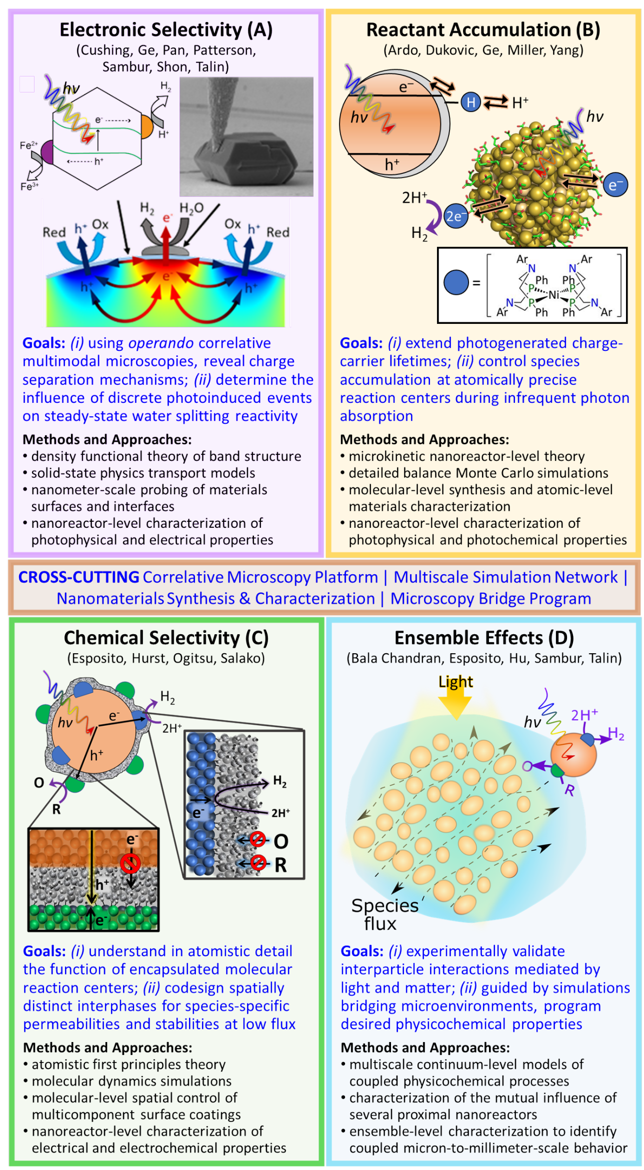

Fig. 1 | **EPN**'s 4 multifaceted thrusts that are revealing design rules for ensembles of solar water splitting nanoreactors.

A key hypothesis within **EPN** is that molecularly-precise multicomponent interphases can be synthesized with nanoscale spatial control to independently control reaction selectivity for each of electrons, holes, chemical reactants, and chemical products. Building on knowledge gained from planar model systems, synthesized nanoreactors are being studied in isolation and as ensembles containing several-to-millions of nanoreactors. Outcomes from simulations and experiments are informing codesign strategies for the four interacting microenvironments critical to **EPN**: (1) semiconducting solid phases; (2) multicomponent electrocatalytic interphases; (3) intervening aqueous liquid phases between adjacent nanoreactors; and (4) collective blackbody and solar radiation fields. Through coupled control of these microenvironments, **EPN** is uncovering pathways to achieve high quantum yields and energy efficiencies for all elementary steps, from transport of incident solar photons to formation of chemical products. To better understand how ensemble behaviors arise from outcomes of elementary steps, **EPN** is isolating and characterizing the effectiveness of individual steps, as well as observed reactivity from several coupled steps.

Inherent to the naturally interwoven aspects of **EPN** is the need for a convergent multidisciplinary center-scale effort with diverse and synergistic theoretical and experimental capabilities. Nanoreactors are being characterized using a correlative microscopy platform that aligns experimental microscopic and spectroscopic capabilities across multiple complementary techniques to quantify underlying properties of single nanoreactors. Generally, it remains unknown whether experimentally measured ensemble activity is dominated by several high-efficiency nanoreactors or a few nanoreactors that serve as catastrophic shunts. This is being revealed through development and use of cross-platform-compatible liquid microscopy cells and light excitation sources that allow for identical-location *in situ* correlative microscopic characterization of individual nanoreactors exhibiting varying performance. Experimental observations are being interpreted using a multiscale simulation network that connects modeling expertise across a multitude of length and time scales to simulate the interplay of optical, species, and thermal processes. Theoretical models of stochastic and ensemble processes are being refined based on outputs from atomistic/molecular-level simulations. With experimentally validated physics-based predictions for ensemble performance, data-driven machine-learning models will be used to solve the inverse problem of designing nanoreactors to achieve desired ensemble performance metrics. This will motivate integrated efforts and close collaborations in nanoreactor development that will be achieved using bottom-up nanomaterials synthesis and characterization. Furthermore, knowledge gained from **EPN** is providing guidance to research and development of batteries, fuel cells, membranes, and other photochemical devices, each that benefit from atomic-level control over functional interphases.

EPN is diverse, including AANAPISI, ANNH, HSI, NASNTI, and PBI minority serving representation and primarily undergraduate institutions (PUIs). It is organized into three clusters by geographic location (California, Colorado, Northeast) to foster regional collaborations and a culture of camaraderie. To complement **EPN**'s world-class innovative research, **EPN** has developed a Microscopy Bridge Program aimed at training the next generation of scientists and engineers interested in microscopy and solar fuels, while strengthening the STEM pipeline between PUIs and R1 institutions through mutually beneficial research partnerships. Institutional proximity helps facilitate two-way student and PI exchanges.

Ensembles of Photosynthetic Nanoreactors (EPN)	
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