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 efficiency of ensembles of photosynthetic nanoreactors be increased by more than one order-of-magnitude*? To answer this question, **EPN** is taking a bottom-up approach to synthesis, characterization, and modeling of solar water splitting nanoreactors. Fundamental knowledge gained will be used to identify the physicochemical principles that in aggregate are responsible for ensemble behaviors. This information will guide **EPN** toward achieving its scientific mission, and may lead to transformative pathways to meet the DOE H_2 Earthshot cost target of $1 per kg-$H_2$.

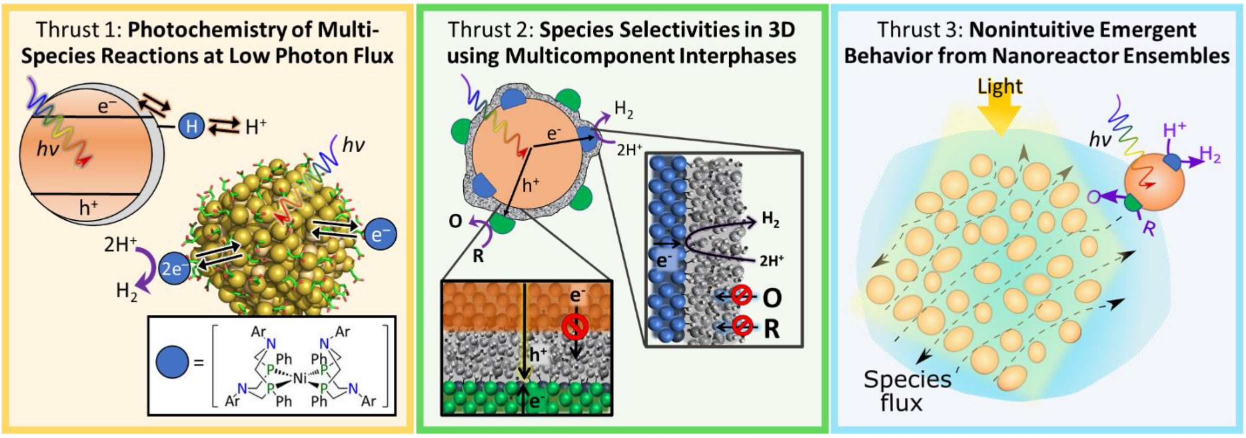

Fig. 1 | **EPN**’s multifaceted research thrusts aimed at unveiling design rules for solar water splitting nanoreactors.

EPN’s three thrusts shown in *Fig. 1* benefit from integrated efforts and close collaborations in nanomaterials synthesis, advanced microscopies and spectroscopies, and multiscale physics-based and data-driven computational modeling. Building on knowledge gained from planar model systems, synthesized nanoreactors will be studied in isolation and as ensembles containing several-to-millions of nanoreactors. Outcomes will inform codesign strategies for the four interacting microenvironments critical to **EPN**: *(i)* the semiconducting solid phase; *(ii)* multicomponent electrocatalytic interphases; *(iii)* the intervening aqueous liquid phase between adjacent nanoreactors; and *(iv)* the collective terrestrial and solar blackbody radiation fields. By controlling properties of these four microenvironments, **EPN** will reveal means to achieve high quantum yields and energy conversion efficiencies for each elementary step, from transport of incident solar photons to formation of chemical products. Because each nanoreactor inherently cogenerates both oxidation and reduction reaction products in close proximity, exquisite control over species selectivities is paramount. A core hypothesis within **EPN** is that reaction selectivities can be controlled independently for electrons, holes, reactants, and products, through precise molecular-level design and synthesis of multicomponent interphases. To better understand how ensemble behaviors arise from elementary steps, **EPN** will also evaluate reactivity from smaller, well-defined ensembles of interacting nanoreactors. This is important, because simulations indicate that solar-to-hydrogen energy conversion efficiencies for ensembles of photosynthetic nanoreactors can exceed those of standard photoelectrochemical devices. This outcome arises from the low absorbed photon flux per nanoreactor, resulting in small photocurrents and small overpotentials, combined with the multiplicative output of having many nanoreactors in an ensemble.

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 containing multicomponent functional interphases will be 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 will be 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 will be interpreted using a multiscale simulation network, which 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 will be 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. These links are crucial to bridging knowledge gaps for the influence of multicomponent functional interphases on ensemble reactivities, leading to desired redox selectivities. Furthermore, knowledge gained from **EPN** will provide 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 includes diverse minority representation (AANAPISI, ANNH, HSI, NASNTI, PBI/HBCU) 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** is developing a program aimed at training the next generation of scientists and engineers interested in microscopy, while strengthening the STEM pipeline between PUIs and R1 institutions through mutually beneficial research partnerships. Each PUI is intentionally situated near an R1 institution to help facilitate exchange of R1 graduate students and PUI undergraduate students between institutions.

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