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Designing interfaces of hydrogenase–nanomaterial hybrids for efficient solar conversion [☆]

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ABSTRACT

The direct conversion of sunlight into biofuels is an intriguing alternative to a continued reliance on fossil fuels. Natural photosynthesis has long been investigated both as a potential solution, and as a model for utilizing solar energy to drive a water-to-fuel cycle. The molecules and organizational structure provide a template to inspire the design of efficient molecular systems for photocatalysis. A clear design strategy is the coordination of molecular interactions that match kinetic rates and energetic levels to control the direction and flow of energy from light harvesting to catalysis. Energy transduction and electron-transfer reactions occur through interfaces formed between complexes of donor–acceptor molecules. Although the structures of several of the key biological complexes have been solved, detailed descriptions of many electron-transfer complexes are lacking, which presents a challenge to designing and engineering biomolecular systems for solar conversion. Alternatively, it is possible to couple the catalytic power of biological enzymes to light harvesting by semiconductor nanomaterials. In these molecules, surface chemistry and structure can be designed using ligands. The passivation effect of the ligand can also dramatically affect the photophysical properties of the semiconductor, and energetics of external charge-transfer. The length, degree of bond saturation (aromaticity), and solvent exposed functional groups of ligands can be manipulated to further tune the interface to control molecular assembly, and complex stability in photocatalytic hybrids. The results of this research show how ligand selection is critical to designing molecular interfaces that promote efficient self-assembly, charge-transfer and photocatalysis. This article is part of a Special Issue entitled: Metals in Bioenergetics and Biomimetics Systems.

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1. Introduction

Electron-transfer reactions constitute a fundamental process of energy transduction in biology that link biochemical reactions to the metabolic pathways that are essential for cellular life. These pathways function to convert abundant substrates such as solar energy, water, carbon dioxide, nitrogen and oxygen into the energy carrying molecules

necessary for cellular viability [1]. A majority of the conversion steps are redox-driven, where photoelectrochemical potential derived from light-harvesting by photosynthetic reaction centers provides the energy and driving force for downstream enzymatic formation of hydrogen (H_2) and other biofuel compounds [2,3]. These enzymatic steps are coupled to electron-transfer (ET), which is mediated by the diffusion controlled formation of transient protein–protein complexes. The resulting binding surface, or interface, functions as part of the medium through which electrons are transferred. Thus, a co-evolution of protein structures and binding surfaces, cofactor redox potentials and solvent networks contribute to geometric and thermodynamic parameters that control ET rates [4]. Understanding the complexity of the molecular interactions that control electron flow presents one of many challenges to reengineering photosynthetic solar-energy conversion for the large-scale production of energy carriers [5–7].

The functional themes that control biological photoconversion are also fundamental to the development of efficient charge-transfer and catalysis in artificial photosynthetic systems. Interest in developing chemical based approaches to solar fuel production has gained significant momentum in recent years and many strategies are being developed that include mixing synthetic and biological components [8–18]. One approach to motivate and inspire artificial efforts has been to use

Abbreviations: AA, ascorbic acid; BET, back electron-transfer; CB, conduction band; CdS, cadmium sulfide; CdTe, cadmium telluride; CS, charge-separation; CT, charge-transfer; CytC, Cytochrome C; DFT, density functional theory; DHA, dehydroascorbate; EC-STM, electrochemical scanning tunneling microscopy; E_g , band gap energy; ET, electron-transfer; eV, electron volt; FB, flat-band; HT, hole-transfer; MPA, mercaptopropionic acid; MWNT, multi-walled carbon nanotubes; NP, nanoparticle; PC, plastocyanin; PSI, Photosystem I; QY, quantum yield; RuP, ruthenium bipyridine phosphonic acid; SAM, self-assembled monolayer; ST, surface-trap; SWNT, single-walled carbon nanotubes; TEOA, triethanolamine; TiO_2 , titanium dioxide; VB, valence band; VDWA, van der Waal

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enzymes as catalysts in solar conversion devices and photocatalytic complexes [19–26]. The substrate specificities, high turnover rates, low reaction overpotentials and the use of base transition metals (e.g., Fe, Ni, Cu, and Mg) make enzymes an attractive option for use in photocatalytic systems [24]. Significant progress has been made toward interfacing enzymes with organic and inorganic materials for photochemical conversion. Examples include direct immobilization of enzymes on electrodes (e.g., bulk and nanostructured carbon [27–32], TiO_2 [33–35], Au [30,36,37]), and in molecular complexes with photoactive and conductive materials (e.g., macroscopic [38–40] and nanoparticulate inorganic semiconductors [41–45], carbon-based particles and nanorods [46,47]) (Fig. 1). The combination of high catalytic rates exhibited by enzymes and the outstanding photophysical properties and high molar extinction coefficients of nanomaterials has the potential to exceed photosynthetic light-harvesting efficiencies when electronically coupled to enzymes [5,23,48]. Moreover, the demonstration of multi-exciton generation, or a >1 ratio of electron-hole pairs per absorbed photon in nanoparticle (NP) based photovoltaics, is driving even greater interest in these materials for use as light harvesting molecules in the production of solar fuels [49,50].

The success of these efforts and the potential for high conversion efficiencies have led to more effort to understand the factors that control the fundamental processes of molecular assembly, ET and photocatalysis. As in biological ET, the interface in enzyme-semiconductor complexes has an essential role in each of these processes. Interfaces mediate molecular assembly and the spatial relationship of molecules, alter the energy landscape through surface passivation and mediate charge-transfer reactions, all of which control photocatalytic performance. This review will present a brief summary of basic ET theory for context, discuss how NP interfaces control solar conversion energetics, and highlight examples of enzyme-NP photocatalytic hybrids that include complexes of [FeFe]-hydrogenases and semiconducting NPs for solar-driven H_2 production.

2. Biological electron-transfer

A general model for ET mechanisms in proteins and protein complexes has emerged from extensive experimental and theoretical efforts, and generally conforms to the basic principles of nonadiabatic ET

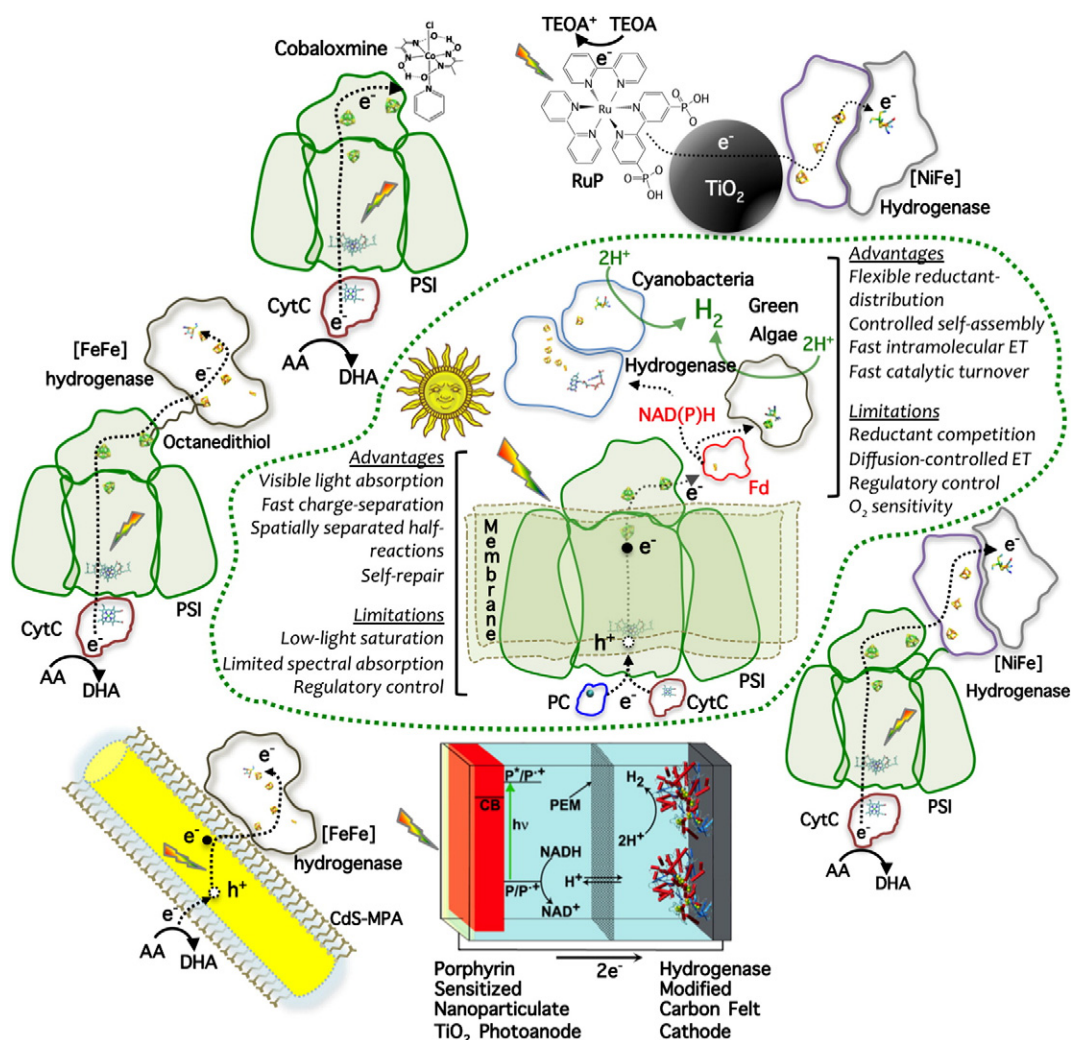


Fig. 1. Bio-inspired, enzyme-based hybrid complexes and devices directly couple the catalytic power of enzymes and catalysts with light-harvesting by natural photosystems (PSI), artificial NPs, or photoelectrochemical cells for solar H_2 production. The center panel shows the biomolecules that together function to direct solar energy capture and conversion by cyanobacterial or algal photosynthesis to enzymatic H_2 production by hydrogenases. Some of the advantages and limitations of photobiological H_2 production systems are identified. Examples of biomolecular, bio-inspired and enzyme-NP hybrid systems are shown clockwise from the left: PSI-CytC chemically linked to a [FeFe]-hydrogenase by octanedithiol [51]; cobaloxmine adsorbed to PSI [52]; [NiFeSe]-hydrogenase adsorbed to particulate, dye-sensitized TiO_2 [45]; [NiFe]-hydrogenase genetically fused to the *psaE* subunit of PSI [53–55]; [FeFe]-hydrogenase adsorbed onto a carbon electrode in a dye-sensitized photoelectrochemical cell (adapted with permission from ACS, [29]); and [FeFe]-hydrogenase adsorbed to MPA passivated CdS nanorods [42].

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