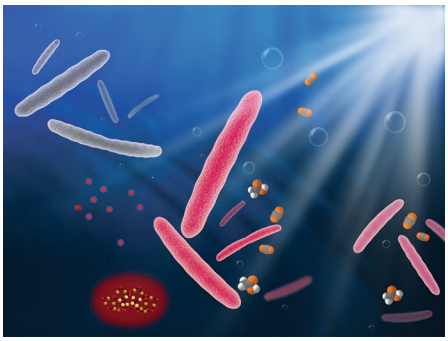
Semi-artificial photosynthesis

Combining the strengths of catalytic biomachineries with those of synthetic materials can yield more efficient and durable solar chemical conversion.

Natural photosynthesis is the process that converts solar energy and stores it in the chemical bonds of organic molecules. Although the overall biomass production amount is impressive — with more than 100 thousand million tonnes of carbon being converted into biomass per year — the solar conversion efficiency is below 1%, because plants do not usually absorb all sunlight, and their metabolic pathways are low-yielding. Scientists therefore believe that they can make artificial systems with better performance than natural ones.

Artificial photosynthetic systems already outperform natural catalytic systems in terms of simplicity, control of charge transport and spectral range of their light adsorption. In contrast, biological systems operate in a more complex and energy-consuming fashion. However, a great deal of work has been stimulated by the higher selectivity towards complex products and self-repair properties of natural photosynthetic systems, especially in conjunction with developments in synthetic biology that allow the synthesis of enzymes and cells with improved catalytic activity and higher stability.

Researchers have found that on interfacing enzymes or even whole cells with synthetic materials in semi-artificial photosynthesis systems, the two components can work in synergy, boosting the solar energy conversion. Take, for instance, photosystem II, the only enzyme in nature that oxidizes water. It does so inefficiently, but when it is integrated with synthetic light absorbers, the water oxidation efficiency is greatly enhanced. Much more efficient electron transfer can be further realized by wiring together the photosystem II, light absorbers and electrode by means of redox polymers, which also obviates the need for diffusional redox mediators. Sokol and co-workers, for example, have constructed a bias-free photoelectrochemical water-splitting system by wiring photosystem II to hydrogenase, a direct connection that does not occur in nature[1]. And Sakimoto et al. report that the non-photosynthetic bacterium *Moorella thermoacetica* can photosynthesize acetic acid from carbon dioxide when it is interfaced with an inorganic photosensitizer, cadmium sulfide[2].



A photosynthetic biohybrid system, based on non-photosynthetic bacteria with incorporated gold nanoclusters, achieves faster electron transfer and more durable solar CO_2 fixation[3].

Semi-artificial colloidal enzyme/cell systems or biohybrid photocathodes can also do reductive chemistry, and considerable research activity has focused on the production of fuels or chemicals such as hydrogen, ammonia, carbon monoxide and hydrocarbons from water, nitrogen and carbon dioxide. Thanks to advances in structural biology, we now understand better the structures of many enzymes. It is also recognized that the electron and energy transfer to active sites in material–enzyme hybrid systems occurs through a series of electron transfer co-factors. With this in mind, it is now possible to control the attachment of enzymes to the electrode to achieve faster energy transfer. However, the purification of enzymes is still difficult, and enzymes can easily destabilize ex vivo. In contrast, the material–cell hybrids are easier to construct and are more durable. Therefore, material–enzyme hybrids seem to have great potential, even though much fundamental research is still needed to characterize the chemical pathways involved.

For material–cell hybrid systems, understanding and maximizing the interfacial charge transport remain a key challenge to enhance efficiency. For the *M. thermoacetica*–CdS system, Sakimoto et al. have shown[2] that the photogenerated electrons from CdS are passed on to the Wood–Ljungdahl pathway within cells to produce acetic acid from CO_2. A paper by Zhang et al. in this issue of *Nature Nanotechnology* reports a photosynthetic biohybrid system in which gold nanoclusters are incorporated inside non-photosynthetic bacteria[3]. In this way, the intimate contact between cellular pathways and the intracellular photosensitizer aids the electron and energy transfer for CO_2 fixation, enhancing the quantum efficiency by 33%. In addition, the system is more durable, as gold is more biocompatible than the CdS used in previous work (the intracellular gold nanoclusters are less toxic and can trap reactive oxygen species that might damage the cells).

Although semi-artificial photosynthesis that interfaces natural catalytic machinery with synthetic materials has made great progress in the past few years, there is a long way to go to surpass purely natural or purely artificial systems. Understanding and manipulating the synthetic–biotic interface remains the key challenge. Enzyme hybrids can be used as a simplified model in which to gain knowledge on how to improve the charge transfer and product yields of whole-cell hybrid systems. And protein engineering or directed evolution could be a future direction to improve the biocatalytic efficacy of enzymes or whole cells. Finally, the significance of the research on semi-artificial systems may not be limited to seeking alternative solar-to-fuel conversion approaches. It can also help us to understand natural biomachineries in various ways, as Kornienko et al. explain in their Review[4]. ❐

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