BIOINSPIRED MATERIALS

Boosting plant biology

Chloroplasts with extended photosynthetic activity beyond the visible absorption spectrum, and living leaves that perform non-biological functions, are made possible by localizing nanoparticles within plant organelles.

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The photosynthetic machinery is utterly ingenious. It uses the antenna effect, wherein many high-cross-section light absorbers — molecules, such as chlorophyll, that are embedded in the protein complexes that make up the photosynthetic unit of plants — funnel their energy (transiently captured as photoexcitations) into a much smaller number of reaction centres, the protein complexes that initiate a chain of reactions to convert the photoexcitations into chemical energy. Across the Earth, absorbed sunlight powers biochemical processes that produce a staggering 100 billion tons of biomass annually.

Human-engineered analogues of photosynthetic systems include dye-sensitized solar cells[1] and energy-gradient devices[2]. However, aspects of the photosynthetic system, such as the spectral cross-section for light harvesting, could be optimized further. Michael Strano and colleagues now report in *Nature Materials* that the localization of nanoparticles within plant chloroplasts aids photosynthesis through the broadening of the spectral capture of light and the scavenging of radical oxygen species[3]. Furthermore, the researchers report the first steps of what they term plant nanobionics: the enhancement of plant functions through the combination of biology and nanotechnology. They also showed that living plant leaves can be embedded with nanoparticle-based sensors to monitor nitric oxide in real time.

Strano and collaborators first showed that two nanoscale systems, single-walled carbon nanotubes (SWNTs) and ceria nanoparticles, can traverse and localize within the lipid envelope of plant chloroplasts. SWNTs and ceria are attractive choices, as they have the potential to couple to the photosynthetic system. In particular, ceria is a well-known quencher of reactive oxygen species that may be produced by rogue photoexcitations, and SWNTs offer a broadband spectral capture, absorbing photons of energies lower than those typically absorbed by plants. Moreover, SWNTs can transport electronic excitations across extraordinary distances[4]. In fact, Strano and co-authors report that SWNTs show photoluminescence at longer wavelengths (785 nm) than natural photosynthetic reaction centres (chlorophyll excitation occurs at 700 nm). To demonstrate augmented photosynthesis in a much broader spectral bandwidth, however, further improvements to the SWNT–chlorophyll (or more generally nanoparticle–chlorophyll) hybrid system would be required. For instance, the reaction centre could be modified so that it can capture and process near-infrared excitations. Interestingly, the authors suggest a further possible element of sensitization within the photosynthetic apparatus by proposing that SWNTs may introduce electrons into the photosynthetic reactions.

Structurally, the photosynthetic machinery is located in the thylakoid membranes within chloroplasts (Fig. 1). However, in some photosynthetic organisms, additional light-harvesting complexes dock on the stromal side of the membrane (in the case of cyanobacteria and red algae) or locate in the lumen (cryptophyte algae)[4]. Strano and colleagues show that SWNTs and nanoceria pass through the outer membranes of the chloroplast and locate in the stroma, and that, remarkably, both nanoparticles influence photosynthetic performance. It would be interesting to investigate the possibility to introduce nanoscale systems that sit in selected positions across the chloroplast system, thus potentially adding spatial localization to the new or augmented functionalities arising from the coupling of the nanoparticles to the biological components. This is particularly critical in the case of SWNTs, as their role in augmenting plant

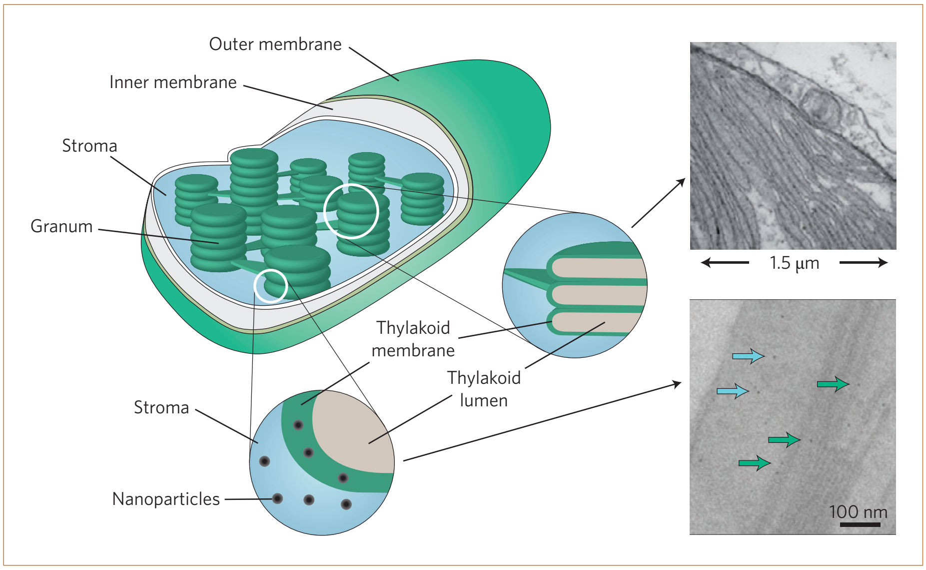

Figure 1 | Natural and nanobionic chloroplasts. The photosynthetic apparatus is mostly embedded in the thylakoid membranes of chloroplasts. Flattened thylakoids are stacked into grana, as shown by a micrograph of the cryptophyte alga *Proteomonas sulcata* (top right). Strano and colleagues show that the nanoparticles localize in both the thylakoid membrane and the stroma (bottom left schematic; green and blue arrows, respectively, in the bottom right micrograph[3]). Schematic and top right image courtesy of T. Mirkovic, Univ. Toronto.

functionalities is strongly dependent on achieving a well-defined coupling with the photosystems. Ceria nanoparticles, however, require less precise positioning relative to the thylakoid membrane because their role is to prevent damage to the photosystems by quenching reactive oxygen species that are widely dispersed throughout the chloroplast.

Biology offers powerful tools that might be harnessed to control the precise positioning of nanoparticles within photosynthetic systems and probe their interaction with the photosynthetic apparatus. For example, proteins employ targeting sequences stitched onto their ends that help them home in on specific membranes. This is exemplified by phycobiliproteins in photosynthetic cryptophyte light-harvesting complexes[5]: the nuclear-encoded α-subunit phycobiliprotein must be transported into the chloroplast where it meets its chloroplast-encoded partner, the β-subunit; then they assemble with light-absorbing chromophores before being transported across the thylakoid membrane into the lumen[6]. The combination of biological functionalization and targeting strategies with functional artificial nanomaterials may one day allow researchers to emulate the precise assembly, transport and positioning of biological components.

Bionics and bioinspiration may thus hold promise for boosting energy harvesting. In contrast to most engineered systems, natural systems such as plants and algae exhibit powerful advantages, such as their capacity to self-propagate, self-repair and self-protect. Hence, there are opportunities for synergy between biology and technology. For instance, solar-energy solutions have drawn insights from natural systems[7,8]. Still, in the energy-conversion process, natural systems are compellingly efficient despite lacking long-range crystalline order and extreme compositional purity. Moreover, the natural biological machinery operates in an environment that includes oxygen, water and fluctuations in environmental variables, such as temperature and illumination. Such a 'warm, wet and noisy' environment — as Schrödinger would describe it[9] — is challenging from an engineering perspective. Energy-harvesting technology thus stands to gain a great deal from designs that learn from and mimic relevant natural processes.

Yet natural energy-harvesting systems also stand to be improved. Evolution may have naturally selected biological systems for certain optimal properties, but this does not mean that they possess a high overall efficiency of capturing energy and storing it for later use[10]. For example, light harvesting on the femtosecond timescale is tightly interconnected with the biochemical production of sugars and their export from the chloroplast. Also, most photosynthetic activity is highly attenuated on a sunny day by a protective process called nonphotochemical quenching. Therefore, substantial gains may be readily possible by optimizing rate-limiting steps or bottlenecks. For example, photosynthetic production under high solar irradiance can be boosted if sugars are exported from the leaf more effectively by increasing the size of the transport pipes (the phloem)[11]. Because photosynthesis in such ramped-up photosynthetic systems may also boost photodegradative pathways, the nanoparticle-based approach of Strano and collaborators may prove useful. Indeed, additives such as ceria nanoparticles could scavenge reactive oxide species and thereby extend the lifetime of photosynthetic activity, especially in *ex vivo* systems that do not benefit from the inbuilt self-repair mechanisms of plants.

Clearly, opportunities abound for understanding mechanisms and limitations of natural photosynthetic systems, and for discovering unique and inspiring solutions to light-harvesting problems. However, the path towards bionic systems will be a complex one to walk because of the combination of the exquisite optimization of natural systems with their baffling bottlenecks[12]. Still, we can learn from highly optimized systems such as carbon-fixing enzymes (such as RuBisCO) to try to reduce carbon dioxide efficiently[13], and also elucidate upgrades to functional elements in the enzyme so as to be able to capture carbon dioxide selectively and more efficiently in the enzyme's active site[14].

Energy harvesting — based on natural biological platforms or engineered ones — requires urgent breakthroughs. Humanity is bound to increase power consumption from the present 15 TW to 30 TW by 2050[15]. Eighty-five per cent of the present 15 TW of demand is met by burning fossil fuels. To decelerate climate change while doubling energy production is thus a tall order. As we seek to make more effective use of free, clean and abundant sunlight, nature's abundant, robust and distributed solar harvesters merit ever-deepened study, and some of their most efficient elements deserve emulation. Bioinspired engineering for energy harvesting will find many opportunities to discover, emulate, improve and engage the exquisite, yet sometimes bizarre, products of 3.5 billion years of evolution. ❐

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