APPLIED PHYSICS REVIEWS **4**, 021103 (2017)

APPLIED PHYSICS REVIEWS—FOCUSED REVIEW

Progress on bioinspired, biomimetic, and bioreplication routes to harvest solar energy

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(Received 11 January 2017; accepted 4 April 2017; published online 28 April 2017)

Although humans have long been imitating biological structures to serve their particular purposes, only a few decades ago engineered biomimicry began to be considered a technoscientific discipline with a great problem-solving potential. The three methodologies of engineered biomimicry—viz., bioinspiration, biomimetic, and bioreplication—employ and impact numerous technoscientific fields. For producing fuels and electricity by artificial photosynthesis, both processes and porous surfaces inspired by plants and certain marine animals are under active investigation. Biomimetically textured surfaces on the subwavelength scale have been shown to reduce the reflectance of photovoltaic solar cells over the visible and the near-infrared regimes. Lenticular compound lenses bioreplicated from insect eyes by an industrially scalable technique offer a similar promise. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4981792]

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I. ENGINEERED BIOMIMICRY

Appearing at diverse locations in Europe and Asia between 60 000 and 125 000 years ago, members of the subspecies that today calls itself *Homo sapiens sapiens* must have looked wistfully at birds, bats, and insects escaping at will into the glorious skies from tyrannical confinement to land. Eventually, humans must have realized that unlike the gliding motion that some birds exhibit for hours and some small mammals exhibit for much shorter durations, aerial motion had to be powered. But all hominins, what to say of humans only, lack large external membranes that birds, bats, and insects flap to fly.

Today, aircraft called ornithopters have flapping wings.[1] These machines, particularly when piloted, are excellent examples of an engineering methodology called biomimetics.[2] But the vast majority of aeroplanes today have fixed wings, despite evolution of their designs for over a century.[3] These fixed-wing aircrafts are examples of bioinspiration,[2] an even older methodology in engineering.

Bioinspiration aims at reproducing the outcome of a certain functionality of a plant or an animal without reproducing either the physical/chemical mechanism or the biological structure responsible for the outcome. Biomimetics aims at the reproduction of the physical/chemical mechanism underlying a specific functionality of a plant or an animal. Establishing the boundary between bioinspiration and biomimetics is not always an easy task, but both methodologies implement biological concepts for the development of devices with desirable functionalities. Both are highly multidisciplinary and embrace diverse aspects related to basic sciences, engineering, mathematics, design, and economics.[2,4,5]

During the last two decades, these two methodologies of engineered biomimicry have been complemented by a third methodology: bioreplication[6]—defined as the direct replication of a structure found in living organisms, and thereby copy one or more functionalities. As an example, bioreplicated decoys of females of the buprestid insect species *Agrilus planipennis* have been shown as highly successful in luring males of the same and related species.[7,8] And we can

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go one step further, by providing a bioreplica with additional functionalities by choosing to incorporate materials in it that are different from the ones used in the biological structure replicated. Thus, the decoys could have had a phosphorescent layer and/or a magnetic layer to display phosphorescence and/or magnetism that *A. planipennis* is not known to display. A phosphorescent decoy could attract diurnally active pests of the same species and nocturnally active pests of other species.

II. ENGINEERED BIOMIMICRY AND OPTICS

The brilliant plumages of many avian species and the emotional urge in humans to adorn their clothes, especially vestments, ensured interaction between engineered biomimicry and optics. Clothes used to be colored primarily with dyes derived from plant and animal sources,[9] until the invention of synthetic dyes during the mid-19th century.[10] Many synthetic dyes are definitely examples of bioinspiration and some even of biomimetics.[11]

The colors of certain plumages arise entirely from the spectral selectivity of optical mechanisms such as scattering and Bragg diffraction.[12–15] These colors are called structural colors. Iridescence is exhibited whenever Bragg diffraction occurs,[16,17] whereas disordered arrays of particles exhibit non-iridescent color due to scattering.[18] Structural colors are realized artificially using the same optical mechanisms as in plants and animals.[19] Thus, artificial structural colors are biomimetic. In nature, structural colors are often combined with pigments.[20,21] Structural colors are beginning to enter the worlds of arts[22] and cosmetics.[23]

Vision proffers several instances of engineered biomimicry. External lenses[24] used by visually impaired persons can have surfaces of roughly the same shape as that of the crystalline lenses found inside human eyes.[25] The apposition compound eyes of many arthropods[26,27] have inspired optical recording devices.[28–30]

Even though energy conservation is on the rise and there is a relentless focus on energy efficiency today in all walks of life, the world continues to consume more energy every year.[31] Solar energy being plentiful and eco-friendly,[32,33] the research worlds of engineered biomimicry and solar-energy harvesting were bound to overlap. That overlap has continued to grow for four decades. Bioinspiration, biomimetics, and bioreplication are all relevant to the harvesting of solar energy, as became evident from research on artificial photosynthesis and textured surfaces for solar cells.[34]

III. ENGINEERED BIOMIMICRY AND SOLAR-ENERGY HARVESTING

Sunlight is absorbed by proteins containing chlorophyll in plants to strip electrons from water and produce oxygen, nicotinamide adenine dinucleotise phosphate (NADPH), and adenosine triphosphate (ATP). A series of subsequent light-independent reactions then incorporate carbon dioxide from the atmosphere to produce carbohydrates such as glucose from NADPH and ATP.[35,36] The carbohydrates are the fuel that powers plants to grow and reproduce. Any synthetic chemical process[37–39] to produce a fuel from the energy of harvested sunlight exemplifies the bioinspired methodology for harvesting solar energy.

The eyes of many arthropod species possess arrays of parallel nanonipples.[40] These arrays function as antireflection coatings.[41–43] The incorporation of arrays of nanoscale aciculate structures on the exposed faces of conventional solar cells enhances the light-harvesting efficiency,[44,45] thereby providing an application of the biomimetic methodology for harvesting solar energy.

Many insects—such as the common housefly (*Musca domestica*), the common North American blowfly (*Eucalliphora lilea*), and the South African horsefly (*Tabanus sulcifrons*)—do not have simple eyes like humans do but have compound eyes.[26,27] Figure 1 shows the compound eye of a fly. Each compound eye comprises several cylindrical eyelets called ommatidia arrayed on a curved surface. Whereas the compound eye has cross-sectional linear dimensions on the order of a millimeter, the cross-sectional diameter of an ommatidium is around 20 μm. Light propagating along the axis of an ommatidium is collected to form an image, but light from other directions reaching an ommatidium does not participate in image formation. The large size, the lenticular shape, and the modular construction of a compound eye together engender an angular field of view that exceeds 180° in the horizontal plane. Different sets of contiguous ommatidia in the compound eye gather light coming from different angular sectors in the field of view.

Solar cells and collectors must have as large an angular field of view as possible in order to maximally harvest the incident light as the sun traverses the sky every day, the solar trajectory also having an annual variation. Theory indicates that multifaceted lenticular texturing of the exposed face of a solar cell at the multiwavelength scale can provide that large angular field of view and enhanced light-coupling efficiency.[46,47] Large-scale replication of an array of insect corneas being feasible,[48,49] a bioreplication methodology for harvesting solar energy is likely to emerge soon.

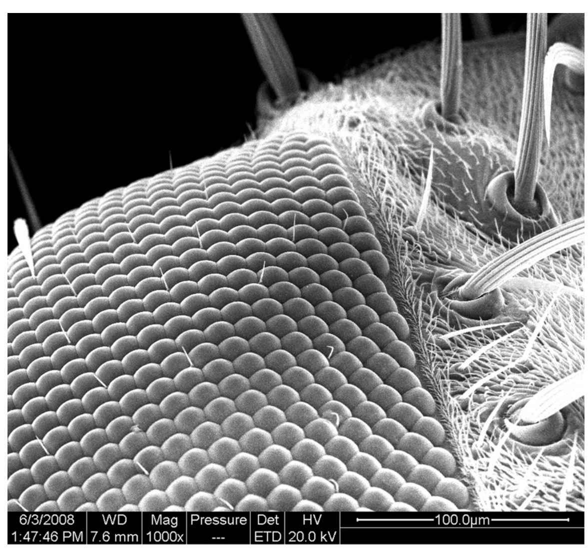

FIG. 1. Scanning electron micrograph of the compound eye of a fly.

IV. BIOINSPIRATION FOR HARVESTING SOLAR ENERGY

A. Artificial photosynthesis

Life arose on our planet about 3.8×10^9 years ago. Several types of archaea and bacteria harvested energy from sunlight and carbon dioxide from their environment to generate carbohydrates.[50] These forms of life not only still exist but also evolved into a plethora of multicellular species of which plants are the best-known photoautotrophs. Indeed, mimicry of the light-harvesting functionality of plants has been a major goal in photochemical research for more than a century.[51]

However, the technoscientific challenges for the development of economical and widely deployable artificial photosynthetic systems are numerous, since major advances are concurrently required in photon management, charge-carrier management, catalysis and photochemistry, materials engineering, and energy storage, not to mention modeling capabilities.[52] More specifically, the current limitations of most artificial photosynthetic systems are related to the inefficient coupling of the catalytic steps required for the formation of chemical bonds and for the accumulation of energy-rich product molecules, i.e., solar fuels.[53] Progress continues to be made.

1. Fuel production

Today, bioinspired artificial photosynthesis systems called photoelectrochemical cells (PECs) can be designed to perform the essential light-harvesting, charge-separation, and water-splitting functions to store energy from the sun in chemical bonds.[54] Given the intermittent nature of sunlight on the earth, energy storage has to be a key attribute of artificial photosynthesis systems—just as it is for photoautotrophs such as plants. Water is oxidized to oxygen and the electrons released thereby are used to reduce (i) either carbon dioxide to methane, methanol, formaldehyde, formate, carbon monoxide, and/or oxalate or (ii) protons to hydrogen. In either case, the chemical products have a high energy content per unit mass. Furthermore, they can be stored, transported, and burned to release energy. Thus, the chemical products are fuels. But, artificial photosynthesis is not a fully fledged technology yet.[38,39] Only a handful of working PECs have been reported so far, all of them showing low solar-to-fuel conversion efficiencies.

In a hydrogen-producing PEC depicted in Figure 2, an anode and a cathode are immersed in water. Either both electrodes are made of a semiconductor or just one is semiconducting but the other is metallic. Water dissociates into hydrogen and oxygen when a semiconducting electrode is

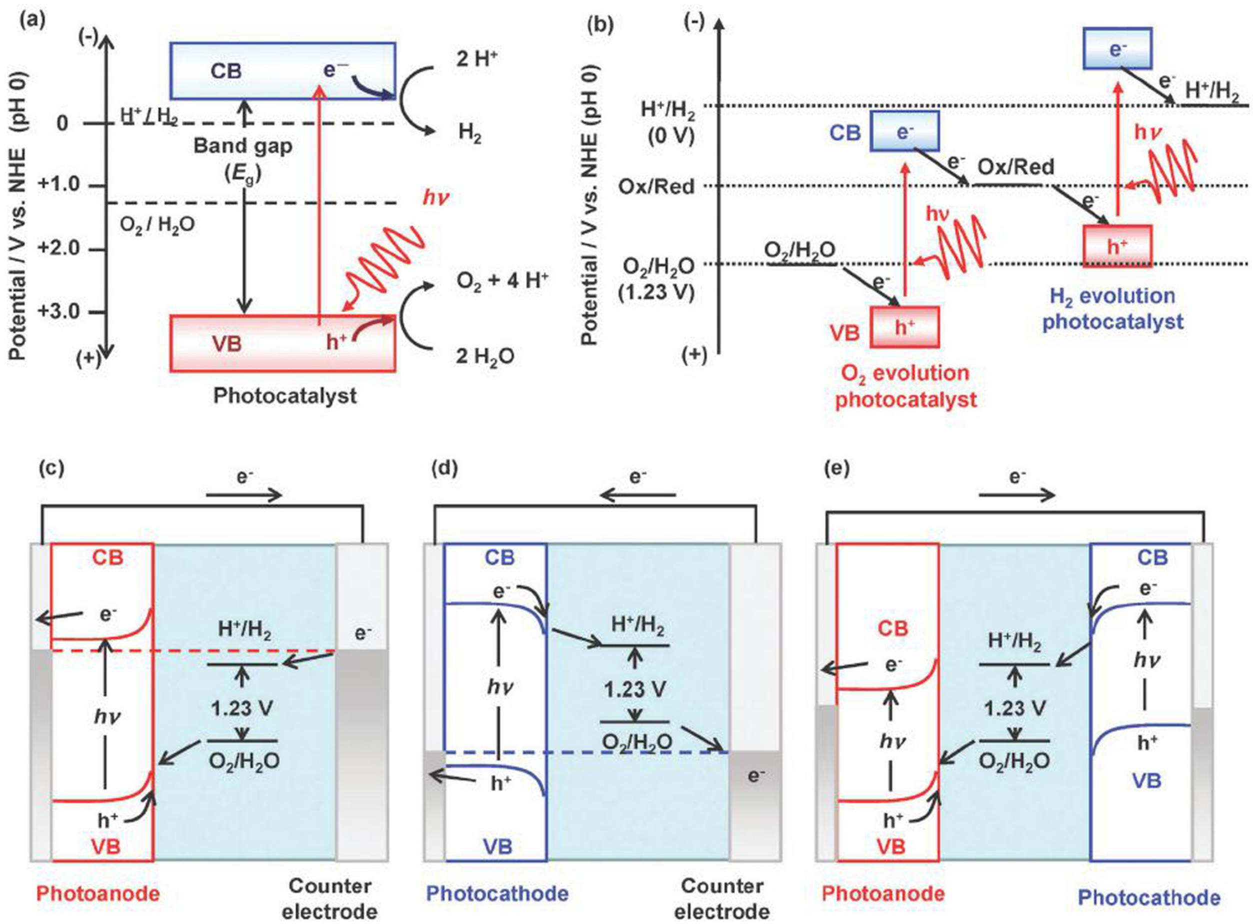

FIG. 2. Representation of the use of semiconductors as photocatalysts for splitting water based on (a) one-step excitation and (b) two-step excitation schemes. PEC for splitting water using (c) a photoanode, (d) photocathode, and (e) photoanode and photocathode in tandem configuration. The band gaps are depicted smaller in (b) and (e) to emphasize that semiconductors with a narrow band gap can be employed. Reproduced with permission from Hisatomi *et al*., Chem. Soc. Rev. **43**, 7520 (2014).[37] Copyright 2014 Royal Society of Chemistry.

exposed to light. Hydrogen, which burns cleanly, is the fuel produced. The process is analogous to natural photosynthesis: The absorption of photons results in the creation of an electron-hole pair, a process which can generate electrochemical potential sufficient as to drive the water-oxidation reaction and/or the proton-reduction reaction, mainly depending on the bandgap of the semiconductor. No electrocatalyst is used in this process.

Many semiconductors have received attention from the research community to split water into oxygen and hydrogen without the need of an electrocatalyst. Perhaps, titanium oxide was among the earlier semiconductors to receive attention,[55] but other metal oxides (such as Fe_2O_3, Cu_2O, WO_3, and $BiVO_4$), metal sulfides (CdS and CdZnS), chalcopyrites (CuInS, CuGaS, etc.), and graphitic carbon nitride (g-C_3N_4) have been subsequently investigated.[37] The key objective of these investigations is to enhance the absorption of visible light in order to increase the fuel-conversion efficiency.

Intrinsic photocatalytic activity of some large-bandgap semiconductors can be enhanced[37–39] by introducing an oxygen-evolving catalyst[56] and/or a hydrogen-evolving catalyst on their surfaces to trap charge carriers. At the same time, these electrocatalysts can increase the rates of the chemical reactions. Alternatively, as portrayed in Figure 2(e), two different narrow-bandgap semiconductors can be wired in tandem[37,57] as a complete photocatalytic system for splitting water and producing hydrogen.

2. Dye-sensitized solar cells

Dye-sensitized solar cells (DSSCs), often called Grätzel cells, also exemplify the bioinspired approach for harvesting solar energy.[58] These third-generation thin-film solar cells are quite inexpensive but with typical efficiencies not yet comparable to that of silicon solar cells.[59,60]

A DSSC has three main components: a transparent anode deposited on a glass with a porous semiconductor (such as titanium oxide) that has been impregnated with a photosensitive dye, a metal cathode, and a liquid electrolyte sealed between the anode and the cathode. When light excites the dye, each of its molecules loses an electron which diffuses towards the anode, an electrolyte molecule yields an electron to a positively charged dye molecule, and the electron-deficient electrolyte molecule moves towards the cathode to replenish itself from the cathode which receives additional electrons from the external circuit. Importantly, the output of a DSSC is electricity itself rather than a fuel.

3. Photovoltaic-electrolyzer combination

A potentially viable approach in some situations[61,62] is to initially convert solar radiation into electricity and then use the electricity to split water into hydrogen and oxygen via classical electrolysis is afforded by coupling a DSSC (or even a silicon solar cell) to an electrolyzer, resulting in a photovoltaic-electrolyzer combination.[63] The overall efficiency of this combination is likely to be low due to losses in both stages of the solar-to-fuel conversion process.

B. Bioinspired materials

Performance is expected to be improved via nanostructuring of materials which host photochemical reactions. As an example, arrays of hollow nanowires of zinc oxide were sensitized to solar light for use as efficient building blocks for different types of nanostructured solar cells.[64] As shown in Figure 3, these nanowire arrays combine characteristics of three-dimensional and one-dimensional materials, are highly porous, have a large specific surface area, and were fabricated large areas by an approach that combines colloidal patterning and electrochemistry. These arrays look like the spines on sea urchins.[65]

As another example, DSSCs with photoanodes made of coralline structures have been reported to exhibit enhanced

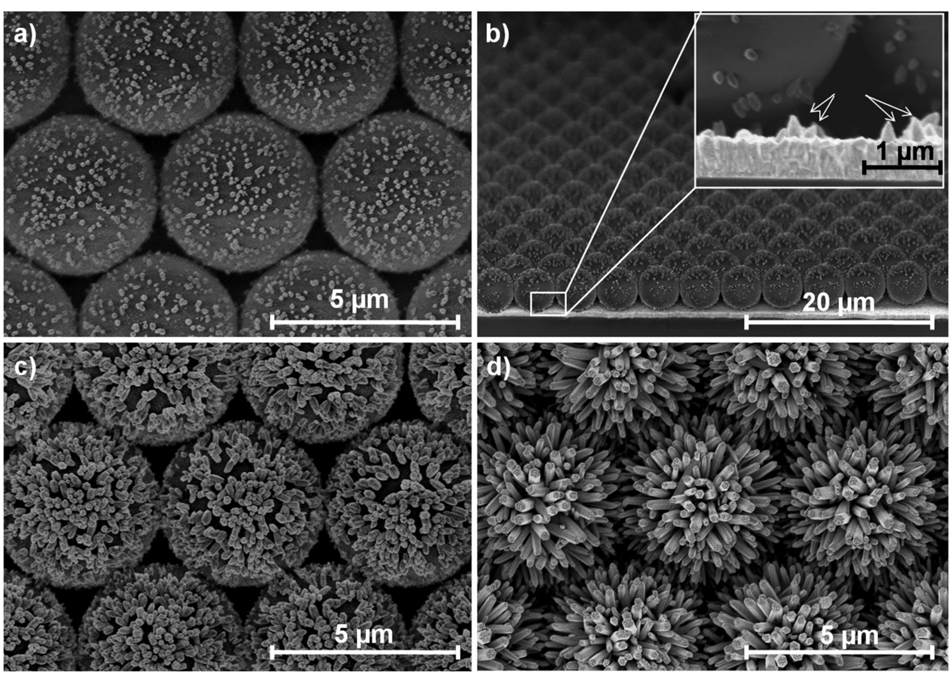

FIG. 3. (a) and (c) Top-view and (b) tilted-view scanning electron micrographs of ZnO deposited on ordered polystyrene (PS) microspheres under different experimental parameters. (d) Ordered hollow urchin-like structure of ZnO nanowires after the removal of polystyrene.[64] Courtesy of Dr. J. Elias (EMPA Materials Science and Technology). Reproduced with permission from Elias *et al.*, Adv. Mater. **22**, 1607 (2010). Copyright 2010 John Wiley and Sons.

photovoltaic performance in comparison to photoanodes comprising spherical structures.[66] The coralline structures of porous tin oxide are grown by assimilating smaller spherical structures. The radial morphology of the coralline structures is believed to be responsible for providing larger effective surface area for sensitization of the dye and for trapping light.

Both urchinoid and coralline materials have a large surface area in relation to the volume, quite like the interior of the small intestine[67] in a human. The small intestine is the seat of absorption in the human alimentary canal: sugars, amino acids, and fatty acids are absorbed in the jejunum, while Vitamin B_{12} and bile acids are absorbed in the ileum. Absorption is a surface-dominated phenomenon, just like any reaction between two chemicals. No wonder, surface crenellation enhances photochemical-reaction yield and photon capture per unit macroscopic area.[64,66]

V. BIOMIMETICS FOR HARVESTING SOLAR ENERGY

Solar cells, like most optical devices, incorporate antireflection coatings for boosting efficiency by reducing the fraction of incident light lost to reflection at the exposed surface. The traditional approach relies on using single- or multilayer coatings.[68,69] However, this approach generally requires (i) the use of high-vacuum deposition techniques, (ii) the accurate control of layer thicknesses, and (iii) the selection of materials with sufficiently low absorption and appropriate phase speed. Moreover, the layers must be mechanically and thermally robust and adhere well to each other as well as to exposed face. Nevertheless, the antireflection-coating technology is an industrially advanced technology,[70–72] so much so that the electrical effects of the coatings are carefully considered.[73]

The exposed faces of solar cells have been textured on the superwavelength scale for many years in order to trap solar energy by multiple reflections of rays. Pyramids,[74] deep grooves with vertical walls,[75] and V-shaped grooves[76] have been etched in the exposed faces of solar cells. Increasingly, however, arrays of subwavelength-scale features are being created on surfaces to change their optical reflection characteristics,[77–79] and the same strategy is also being implemented on solar cells.[80–83]

The implementation definitely has a biomimetic provenance. Arrays of parallel and identical nanopillars are commonly seen on the eyes of many arthropods.[40] Rigorous theoretical analysis shows that the array functions as a coating of a nonporous material whose refractive index changes with depth from almost that of air (i.e., unity) to a considerably higher value,[42,43] in conformance with experimental results.[84] Thus, the array provides a gradual transformation of the optical impedance from that of air to that of silicon, thereby functioning as an anti-reflection coating to enhance the light-harvesting efficiency.[44,45] Another example is furnished by nanotip arrays mimicking the structure of cicada wings.[85] These arrays are efficient light harvesters over the 300–1000 nm region of the solar spectrum and for angles of incidence as oblique as 60°. Not surprisingly, these types of arrays have been fabricated by employing several commonplace different bottom-up and top-down techniques.[86]

Nanostructures of diverse shapes can be fabricated. Arrays of closely packed nanonipples, patterned on silicon substrates using spin-coated silica colloidal monolayers as etching masks, were found to exhibit broadband antireflective performance superior to commercial antireflection coatings.[80] The same strategy proved efficacious on GaAs substrates too.[87] Arrays of closely packed nanocones of TiO_2 fabricated on a TiO_2 coating deposited on a GaAs single-junction solar cell increased the power conversion efficiency to 19.66%, in comparison to 18.98% for the TiO_2-coated GaAs solar cell and to 14.74% for the bare GaAs solar cell.[88] Not only that, but the reflection reduction was significant over a wide range of incidence angles. Figure 4 compares the optical performance of TiO_2 single-layer antireflection coatings (SLARC) and sub-wavelength structures (SWS) grown on GaAs substrates. A side-benefit of nanopillar arrays is their superhydrophobicity,[89,90] so that reflection reduction is accompanied by self-cleaning capability[91] that is attractive for field deployment of solar cells.

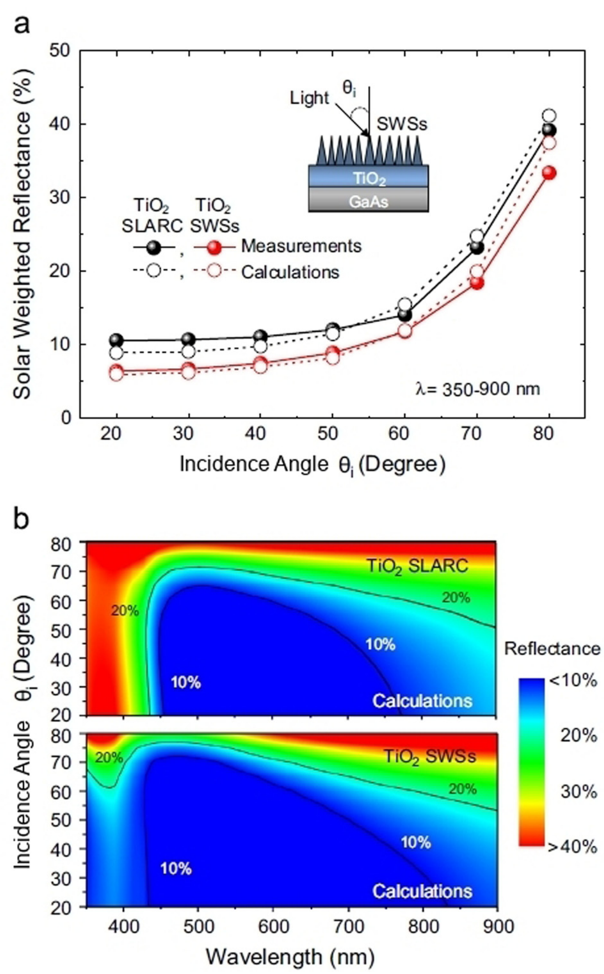

FIG. 4. (a) Estimated solar weighted reflectance as a function of the incidence angle for a TiO_2 single-layer antireflection coating (SLARC) and subwavelength structures (SWSs) grown on GaAs substrates. (b) Calculated reflectance spectra for different incidence angles. Reproduced with permission from Leem *et al.*, Sol. Energy Mater. Sol. Cells **127**, 43 (2014). Copyright 2014 Elsevier.[88]

Electron-beam lithography has been used to texture silicon surfaces with arrays of nanopillars with different periods (150–350 nm), heights (150–500 nm), and pillar width-to-period ratios (0.3–0.7).[44] Subsequent theoretical studies indicated that the height and shape of nanopillars as well as the array period require optimization for best performance in the specific wavelength range over which the surface is required to function, given the strong effect of these parameters over reflectance. Significantly, such optimization is possible.[82]

The exposed surface of the semiconductor in the solar cell need not be textured. Instead, a coating deposited on top of the semiconductor can be textured on the subwavelength scale. Layers of SiO_2, TiO_2, and/or SiN_x were deposited on $Ga_{0.5}In_{0.5}P$/GaAs/Ge triple-junction solar cells, the uppermost layer textured as an array of hexagonally packed nanocones.[92] Shadow-sphere lithography, electron-beam evaporation, and reactive ion etching were the fabrication techniques used. The resulting devices show a power conversion efficiency enhancement of around 6.4%. From a practical point of view, reflection reduction was quite insensitive to fabrication parameters.

Even more simply, a polymeric array of nanonipples could be deposited on a solar cell. This has been both theoretically and experimentally studied for operation over the 400–1170-nm wavelength regime.[83] Tightly packed arrays of acrylic-resin nanonipples of 300 nm height, 100 nm bottom diameter, and 30 nm top diameter were found to be optimal when deposited on a silicon substrate with an interposing polyethylene-terepthlate layer. For normally incident unpolarized light, the reflectance was predicted to be lower than 0.87% throughout the wavelength regime of interest, with a minimum of 0.1% at 400-nm wavelength. The reflectance of a nanonipple array (200 nm height, 90 nm bottom diameter, and 50 nm top diameter) was measured to be lower than about 1% in the chosen wavelength regime, with a minimum of 0.55% at 700-nm wavelength. When field tests were carried out,[45] the conversion efficiency of the solar-cell modules was found to improve by about 5%, which may turn out to be cost-effective if the biomimetic-coating production becomes inexpensive.

Superwavelength-scale texturing of the exposed faces of solar cells can also be biomimetic. The aim then is to mimic the compound eye as a tightly packed array of ommatidia. Geometrical-optics simulations for a prismatic compound lens on a silicon solar cell were used to identify the optimal shape of the lens leading to minimum reflectance spectrally averaged over the 400–1100-nm wavelength regime.[46] For these simulations, the cross-section of the compound lens is the arc of a circle (0th-order texturing) decorated by arcs of smaller circles (1st-order texturing). The simulations indicated that the spectrally averaged reflectance is almost half of that of a flat surface; furthermore, 2nd-order texturing did not improve the optical performance. Accordingly, a properly designed and coated biomimetically textured surface can significantly improve the light-harvesting capabilities of solar cells.[47,93]

Following a somewhat similar approach, arrays of inverted cones of silicon to funnel light down to a solar cell were fabricated.[94] This morphology mimics the arrangement and shape of photoreceptors in the *fovea centralis* region of the human retina, this region being responsible for high-acuity binocular vision. An absorption enhancement of about 65% over thin continuous silicon films of comparable thickness was demonstrated. This enhancement should yield power conversion efficiencies about 60% larger than those of nanowire-based solar cells.

Biomimetically structured surfaces have also been used in photovoltaic/thermoelectric hybrid systems aiming towards omnidirectional broadband light trapping.[95] These surfaces could be used in Si-based hybrid systems to significantly improve the full-spectrum harvesting of solar energy.

VI. TOWARDS BIOREPLICATION FOR HARVESTING SOLAR ENERGY

The potential application of bioreplication for harvesting solar energy relies on a key experimental observation, namely, the wide angular field of view that the compound eyes of many arthropods have—as already discussed in Sections III and V. However, given that the typical features of compound eyes range from about 200 nm to a few millimeters, fabrication of such structures requires complex sequences of processing over five orders of length scales. Besides, most bioreplication methods can produce just one replica per biotemplate (i.e., the original compound eye of the chosen insect).[6] Industrial-scale production requires techniques that yield numerous replicas per biotemplate.

The Nano4Bio technique has been developed and optimized during the past few years to replicate the corneal layer of compound eyes from actual biological specimens.[48] As this technique can produce multiple replicas of multiple biotemplates simultaneously, it is suited very well for industrial production. In the first step of the four-step Nano4Bio technique schematically depicted in Figure 5, a modified conformal-evaporated-film-by-rotation (CEFR) technique is implemented for the deposition of a ∼250-nm-thick conformal coating of nickel on the biotemplate.[96,97] In the second step, a structural layer of nickel is electroformed onto the thin layer. In the third step, plasma ashing is carried out to completely remove all organic materials. In the fourth step, the master negative made of nickel can be used either as a die for stamping[49] or as a mold for casting[48] multiple replicas. Casting alone has been implemented thus far to produce about 200 replicas from a single master negative. Stamping is expected to improve the reproduction fidelity at the ∼100-nm length scale. The Nano4Bio technique has been demonstrated to make an array of multiple master negatives[48,98] instead of a solitary one.

A biomimetic surface textured on the superwavelength scale with the Nano4Bio technique can significantly improve the light-harvesting capabilities of solar cells, according to electromagnetic simulation studies.[46,47,93] The surface would comprise lenticular compound lenses replicated from insect eyes.

While a great deal of attention has been devoted to anti-reflection structures found in insect eyes and wings, the benefits of plant surfaces for light harvesting in photovoltaic devices are still largely unexplored. In a recent work, the

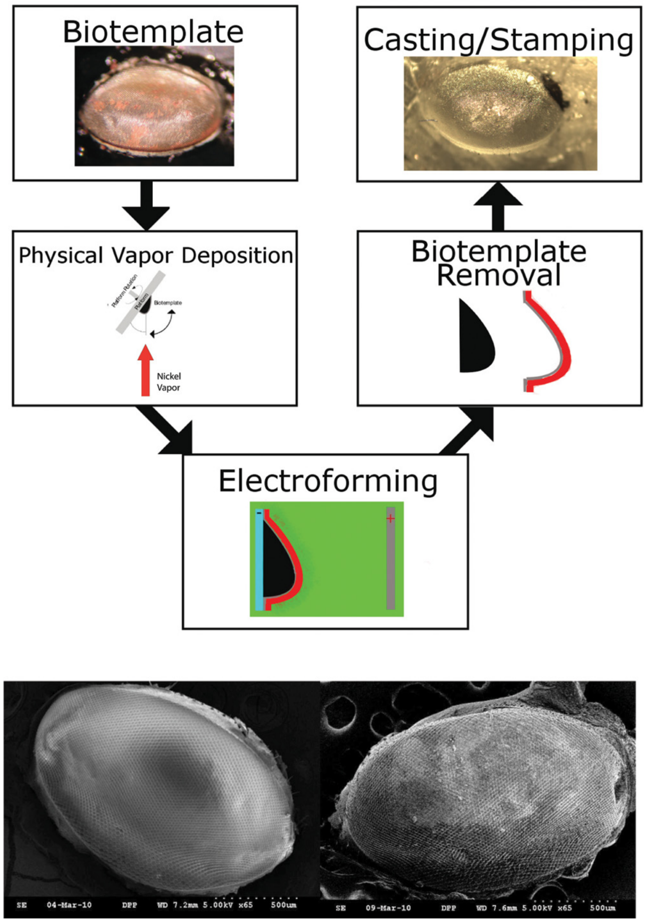

FIG. 5. (Top) Schematic representation of the Nano4Bio technique.[48] (Bottom, left) Cornea of a blowfly and (bottom, right) polymer replica of a cornea produced with the Nano4Bio technique.

hierarchical structures decorating the petals of *El Toro* Rose were bioreplicated in transparent resist layers to develop highly efficient light-harvesting elements for photovoltaic devices.[99] The bioreplicated light-harvesting elements enhanced the photocurrent in optimized organic solar cells by up to 13% for normal incidence and up to 44% at an angle of incidence of 80°.

VII. CONCLUDING REMARKS

Engineered biomimicry is a rapidly evolving area of research. It is also quite a complex area, given the number of disciplines involved, ranging from biology to materials science to manufacturing. Although the broad field of engineered biomimicry is still in its infancy, all three of its methodologies—bioinspiration, biomimetics, and bioreplication—are represented in current research on harvesting solar energy. Both processes and porous surfaces inspired by plants and certain marine animals are being investigated. Biomimetically textured surfaces and coatings for photovoltaic solar cells have been shown to reduce reflectance over a broad spectral regime covering most of the energy of sunlight. Compound lenses fabricated by an industrially scalable bioreplication technique offer a similar promise. However, more attention from the research community and more funding from private and government sources are needed to elevate a patchwork of research efforts to the stage of industrial vibrancy.

ACKNOWLEDGMENTS

A.L. thanks the National Science Foundation for partial financial support under Grant No. DMS-1619901, and the Charles Godfrey Binder Endowment at the Pennsylvania State University for ongoing support of his research activities.

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