Engineered biomimicry for harvesting solar energy: a bird’s eye view

Raúl J. Martín-Palma\textsuperscript{a,b,*} and Akhlesh Lakhtakia\textsuperscript{a,c}

\textsuperscript{a}Materials Research Institute, The Pennsylvania State University, University Park, PA 16802, USA; \textsuperscript{b}Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA; \textsuperscript{c}Department of Engineering Science and Mechanics, The Pennsylvania State University, University Park, PA 16802, USA

\(\text{(Received 22 September 2011; final version received 1 February 2012)}\)

All three methodologies of engineered biomimicry – 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, respectively, are being investigated for solar cells. Whereas dye-sensitized solar cells deploy artificial photosynthesis, bioinspired nanostructuring of materials in solar cells improves performance. Biomimetically textured coatings for solar cells have been shown to reduce optical reflectance and increase optical absorptance over a broad spectral regime. Compound lenses fabricated by a bioreplication technique offer similar promise for reduced reflectance by increasing the angular field of view.

\textbf{Keywords:} bioinspiration; biomimetics; bioreplication; solar cell; artificial photosynthesis; antireflective coating; engineering biomimicry

1. Introduction

Living organisms display an astonishing diversity of functionalities. Engineered biomimicry takes ideas and concepts from biology and implements them in different fields ranging from engineering to computing, aiming at the development of novel devices with desirable functionalities. This evolving methodology is highly multidisciplinary, and embraces aspects related to physics, materials science, nanotechnology, biology, chemistry, mechanical properties, computing and control, design integration, optimization, multifunctionality, and economics.

Engineered biomimicry comprises three methodologies: bioinspiration, biomimetics, and bioreplication [1]. Bioinspiration – an age-old methodology that is ever more fruitful with continuing techno-scientific advances – encompasses the design of a new structure or device that displays a certain functionality of a plant or animal without reproducing the biological structure responsible for that functionality. For instance, helicopters hover and so do bumblebees, but their mechanisms for hovering are entirely different. Biomimetics requires the approximate reproduction of the essential mechanism of the biological structure responsible for the display of a specific functionality. Robots that walk on four or more legs on uneven terrain furnish an excellent example of a biomimetic design methodology. The distinction between bioinspiration and biomimetics, however, is not always

\*Corresponding author. Email: raul@psu.edu

© 2013 The Author(s). Published by Taylor & Francis.
clear [2]. Bioreplication [3], the latest methodology in engineered biomimicry, is the direct replication of the responsible biological structure.

Engineered biomimicry has been applied for optical purposes for centuries. Perhaps the best examples are glass lenses used by a visually impaired person, many glass lenses having surfaces of roughly the same shape as that of the crystalline lenses found inside the eyes of numerous animals. Another example is provided by multilayered structures in the exoskeletons of beetles of many species to create color – which is mimicked by the widely used Bragg filters – without the use of pigments [4,5]. Such colors are called structural colors and their first description dates back to Isaac Newton [6], who tried to explain the brilliant plumage of the common Indian peafowl (Pavo cristatus) as rising from optical interference from the thin transparent part of the feathers. This research has now been extended to photonic crystals [7] and applied to the manufacture of unpigmented but colored fabrics [8]. Very recently, achromatic waveplates found in the eyes of crustaceans of a certain species inspired the design and fabrication of similarly performing waveplates [9].

Given our seemingly insatiable appetite for energy and given the focus today on non-polluting sources of energy, it was inevitable that the paths of engineered biomimicry and solar-energy harvesting would meet. Indeed, that is currently happening in three ways, one of which is bioinspired, the second is biomimetic, and the third can be classified as bioreplication.

Plants use sunlight in a chemical process called photosynthesis to convert carbon dioxide into sugars whose solutions act as liquid fuel. Any artificial route to harvest solar energy through a chemical process is bioinspired. Some biological structures such as the eyes of many species possess excellent anti-reflection coatings, and their implementation in conventional solar cells can enhance the light-harvesting efficiency, thereby providing an example of biomimetic methodology. Finally, compound eyes in many insects impart a huge angular field of view, which too can be exploited via bioreplication. All three applications of engineered biomimicry to harvesting solar energy are reviewed in the remainder of this paper.

2. Bioinspiration

Artificial photosynthesis is any chemical process whereby the energy of sunlight is converted into the energy stored in a material. This can be done in several ways. In a photoelectrochemical cell, an anode and a cathode are immersed in water [10]. Either both electrodes are made of a semiconductor or just one is semiconducting but the other is metallic. Water dissociates electrolytically into hydrogen and oxygen when a semiconducting electrode is exposed to light (which includes radiation of wavelengths smaller than \( \sim 1000 \) nm). Hydrogen, which burns cleanly, can be used in a fuel cell. As a semiconducting electrode is also expected to function as a catalyst, a semiconductor may have to be alloyed with an efficient catalyst such as platinum to make that electrode. Clean fuels other than hydrogen may also become viable, and the major problem is the identification of the right materials to achieve efficient conversion.

A dye-sensitized solar cell, sometimes called a Grätzel cell, comprises (i) a transparent anode deposited on a glass with a porous semiconductor such as titanium dioxide that has been impregnated with a photosensitive dye, (ii) a metal sheet acting as the cathode, and (iii) a liquid electrolyte sealed between the two electrodes. Dye molecules excited by exposure to light lose an electron each which diffuses towards the anode, the electrolyte yields an electron to each positively charged dye molecule, and the electron-deficient electrolyte
molecules physically move towards the cathode to replenish themselves from the cathode which receives additional electrons from the external circuit. Thus, rather than a fuel, the output of a dye-sensitized solar cell is electricity itself. This type of third-generation thin-film solar cell is quite inexpensive but its typical efficiency is not yet close to that of silicon solar cells.

Nanostructuring of materials which host a photochemical reaction is expected to improve performance. Recently, it has been proposed that arrays of hollow nanowires of zinc oxide can be sensitized to solar light and used as more efficient building blocks for different types of nanostructured solar cells, including organic, hybrid and dye-sensitized [11]. As may be inferred from Figure 1, looking like sea urchins (pentameristic echinoderms of subclasses *Perischoechinoidea* and *Euechinoidea*), these nanowire arrays combine characteristics of three-dimensional and one-dimensional materials, are highly porous, and have a large specific surface area. These structures are fabricated as perfectly ordered arrays over large areas by an approach that combines colloidal patterning and electrochemistry. Exquisite control of dimensions and morphologies is possible by this hybrid approach.

Additionally, hollow structures of porous tin oxide have been fabricated by wet-chemical processing followed by annealing [12]. These coralline structures grow by assimilating smaller spherical structures. Dye-sensitized solar cells with photoanodes made of these structures have been reported to exhibit enhanced photovoltaic performance in comparison to photoanodes comprising spherical structures. The radial morphology of the coralline structures is believed to be responsible for providing larger effective surface area for dye sensitization and photon capture [12].

3. **Biomimetics**

Given that a significant fraction of light impinging the surface of most materials is reflected back, optical devices [13,14] including solar cells [15,16] incorporate surface texturing to reduce optical reflection resulting in enhanced light absorption. Sub-wavelength surface
features are being increasingly used [14,17] to change the optical reflection characteristics of surfaces – instead of using multilayer antireflection coatings which usually require (i) the use of high-vacuum deposition techniques; (ii) accurate control of layer thicknesses; and (iii) selection of materials with suitable refractive index (appropriate real part and low imaginary part), appropriate mechanical properties (strength, adhesion, etc.) and coefficient of thermal expansion. Randomly sized and spaced pyramids [14,18,19], deep vertical-wall grooves [20], V grooves [21,22], and arrays of nanopillars [6–11,23] on the surface of silicon wafers have been widely utilized to reduce optical reflectance. Several surface-texturing techniques [24] including anodization [25] have also been used.

Nanopillars can be nanocylinders, nanocones, or nanonipples. Their arrays should function as graded-index materials in the visible and near-infrared spectral regimes [26,27]. An array of sub-wavelength nipples is commonly seen in moth eyes and fly eyes, as shown in Figure 2, which has led to many biomimetic efforts to improve solar-cell performance. Techniques employed to fabricate such nanopillar-array coatings comprise traditional bottom-up and top-down approaches [28].

Closely packed arrays of nanonipples were recently patterned on silicon substrates using spin-coated silica colloidal monolayers as etching masks; see the scanning electron microscope image provided in Figure 3 [29]. The anti-reflection coatings made using this bottom-up non-lithographic technique were found to exhibit broadband antireflective performance superior to commercial coatings. Similar biomimetic anti-reflection coatings have also been used for GaAs substrates [30]. The nanonipple array also enhances hydrophobicity [31,32] so that the surface is self-cleaning [33].

Similar low-reflection surfaces textured with arrays of nanopillars with different periods (pillar-to-pillar distance, from 150 nm to 350 nm), heights (from around 150 nm to 500 nm) and shapes (pillar width-to-period ratio from around 0.3 to 0.7) were fabricated by electron-beam lithography on silicon wafers [34]. In parallel, numerical simulations

Figure 2. Scanning electron microscope image of the compound eye of a fly.
using the rigorous coupled-wave analysis (RCWA) indicated that as the height and shape of nanopillars as well as the array period affect reflectance, these parameters require optimization for best performance in the specific wavelength range over which the surface is required to function. Subsequently, RCWA was used to theoretically optimize the period of moth-eye arrays for low-reflection surfaces on silicon solar cells [35].

In another approach, moth-eye anti-reflection coatings were made of acrylic resin and deposited on polyethylene terephthalate substrates [36]. The geometry of closely packed arrays of nanonipples was optimized for operation in the 400–1170 nm wavelength range that almost completely covers the solar spectrum for using silicon solar cells. Optical simulations using RCWA indicated that the optimal nanonipples are 300 nm in height, 100 nm bottom width, and 30 nm top width, leading to reflectance lower than 0.87% in the 400–1170 nm wavelength range and a minimum of 0.1% at 400 nm for normally incident light. The same reflectance of a moth-eye coating (with nipples of approximately 200 nm height, 90 nm bottom width, and 50 nm top width) was experimentally determined to be lower than about 1% in the desired wavelength range, with a minimum of 0.55% at 700 nm wavelength.

A fabricated coating textured with nanonipples was placed on top of a crystalline silicon photovoltaic module and characterized indoors and outdoors for performance [37]. Typically, the optical-to-electrical efficiency of the module improved by 5%, which may turn out be cost-effective if the coating production becomes inexpensive.

4. Bioreplication

Bioreplication is the latest methodology in engineered biomimicry, having arrived on the scene just about a decade ago [3]. Its potential application for solar-energy harvesting is based on two observations [38]. The first observation is the wide angular field of view that many dipterans including house flies have. Each eye of a house fly is a compound eye,
comprising numerous elementary eyes (ommatidia) arranged radially on a curved surface, as shown in Figure 2. The second observation is the almost halving of the reflectance, averaged over a huge angular sector and the 400–110 nm wavelength range, predicted through geometrical-optics simulations for a prismatic compound lens (with a surface inspired by the compound eyes of dipterans) adhering to a silicon solar cell [39].

A multistep experimental technique, now called the Nano4Bio technique, has been developed to replicate the corneal layer of a compound eye from an actual specimen. Industrial-scale replication being possible with the Nano4Bio technique [1], the idea is to cover the surface of a solar cell with numerous replicas of compound eyes in order to enhance the angular field of view of the solar cell.

Since the characteristic lengths of a compound eye range from about 200 nm to a few mm, direct fabrication of such a structure will require complex processing and most methods can produce just one replica per biotemplate (i.e. the compound eye). In contrast, the Nano4Bio technique can be used to fabricate multiple high-fidelity replicas of a single biotemplate. As depicted schematically in Figure 4, in the first step of this technique, a modified conformal-evaporated-film-by-rotation (CEFR) technique is deposit a ∼250 nm thick conformal coating of nickel on the biotemplate [40–42]. In the second step, a roughly 60-µm-thick structural layer of nickel is electroformed onto the thin layer to give it the structural integrity needed for casting or stamping. The biotemplate is then plucked off and plasma ashing is carried out to completely remove all organic material, in the third step. What is left behind is a master negative made of nickel. This can be used either as a die for stamping or a mold for casting multiple replicas, in the fourth step. Casting alone has been implemented thus far, with high fidelity obtained at the 2 µm length scale; stamping is expected to improve the reproduction fidelity at even lower length scales. The Nano4Bio technique can produce multiple replicas simultaneously of multiple biotemplates.

5. Concluding remarks
The most recent and significant research activities in the field of engineered biomimicry for harvesting solar energy have been reviewed here. The field can be said to be in its infancy as now, and bioinspired and biomimetic methodologies have seen the most intense activity. Engineered biomimicry could provide advantages over conventional engineering,
as shown for example by a comparative simulation study of bioinspired texturing and V-grooved texturing of the front surface of silicon solar cells [39]. We expect that the next few years will witness increased activity with all three methodologies as well as industrial adoption.

Acknowledgments

RJMP is grateful for funding provided by a cooperative project of Universidad Autónoma de Madrid and Banco de Santander. AL thanks the Charles Godfrey Binder Endowment at the Pennsylvania State University for partial support of his research activities.

References

[1] D. P. Pulsifer, A. Lakhtakia, R. J. Martín-Palma, and C. G. Pantano, Mass fabrication technique for polymeric replicas of arrays of insect corneas, Bioinsp. Biomim. 5 (2011), 036001.
[2] Y. Bar-Cohen and C. Breazeal, Biologically Inspired Intelligent Robots, SPIE Press, Bellingham, WA, 2003.
[3] D. P. Pulsifer and A. Lakhtakia, Background and survey of bioreplication techniques, Bioinsp. Biomim. 6 (2011), 031001.
[4] S. Kinoshita, S. Yoshioka, and J. Miyazaki, Physics of structural colors, Rep. Progr. Phys. 71 (2008), 076401.
[5] N. Dushkina and A. Lakhtakia, Structural colors, cosmetics and fabrics, Proc. SPIE 7401 (2009), 740106.
[6] A. R. Parker, The diversity and implications of animal structural colors, J. Exp. Biol. 201 (1998), pp. 2343–2347.
[7] J. W. Galusha, M. R. Jorgensen, L. R. Richey, J. S. Gardner, and M. H. Bartl, Oxide-based photonic crystals from biological templates, Proc. SPIE 7401 (2009), 74010G.
[8] A. Saito, Y. Miyamura, Y. Ishikawa, J. Murase, M. Akai-Kasaya, and Y. Kuwahara, Reproduction, mass production, and control of the Morpho-butterfly’s blue, Proc. SPIE 7205 (2008), 720506.
[9] Y.-J. Jen, A. Lakhtakia, C.-W. Yu, C.-F. Lin, M.-J. Lin, S.-H. Wang, and J.-R. Lai, Biologically inspired achromatic waveplates for visible light, Nat. Comm. 2 (2011), pp. 363–363-1-5.
[10] D. A. Tryk, A. Fujishima, and K. Honda, Recent topics in photoelectrochemistry: Achievements and future prospects, Electrochim. Acta 45 (2000), pp. 2362–2376.
[11] J. Elias, C. Lévy-Clément, M. Bechelany, J. Michler, G.-Y. Wang, Z. Wang, and L. Philippe, Hollow urchin-like ZnO thin films by electrochemical deposition, Adv. Mater. 22 (2010), pp. 1607–1612.
[12] J. Liu, T. Luo, S. Mouli T. F. Meng, B. Sun, M. Li, and J. Liu, A novel coral-like porous SnO2 hollow architecture: biomimetic swallowing growth mechanism and enhanced photovoltaic property for dye-sensitized solar cell application, Chem. Comm. (2010), pp. 472–474.
[13] W. H. Southwell, Pyramid-array surface-relief structures producing antireflection index matching on optical surfaces, J. Opt. Soc. Am. A 8 (1991), pp. 549–553.
[14] B. Päivänranta, T. Saastamoinen, and M Kuittinen, A wide-angle antireflection surface for the visible spectrum, Nanotechnology 20 (2009), 375301.
[15] V. M. Bright, E. S. Kolesar, Jr., and D. M. Sowders, Reflection characteristics of porous silicon surfaces, Opt. Eng. 36 (1997), pp. 1088–1093.
[16] R.J. Martín-Palma, L. Vázquez, J. M. Martínez-Duart, M. Schnell, and S. Schaefer, Antireflective porous-silicon coatings for multicrystalline solar cells: The effects of chemical etching and rapid thermal processing, Semicond. Sci. Tech. 16 (2001), pp. 657–661.
[17] S. L. Diedenhofen, G. Vecchi, R. E. Algra, A. Hartsuiker, O. L. Muskens, G. Immink, E. P. A. M. Bakkers, W. L. Vos, and J. Gómez Rivas, Broad-band and omnidirectional antireflection coatings based on semiconductor nanorods, Adv. Mater. 21 (2009), pp. 1–6.
[18] P. Campbell and M. A. Green, High performance light trapping textures for multicrystalline silicon solar cells, Sol. Energ. Mater. Sol. Cell 65 (2001), pp. 369–375.
[19] B. S. Richards, Comparison of TiO2 and other dielectric coatings for buried-contact solar cells: A review, Progr. Photovoltaics: Res. Appl. 12 (2004), pp. 253–281.
[20] E. S. Kolesar, Jr., V. M. Bright and D. M. Sowders, Optical reflectance reduction of textured silicon surfaces coated with an antireflective thin film, Thin Solid Film 290–291 (1996), pp. 23–29.

[21] T. I. Chappell, The V-groove multijunction solar cell, IEEE Trans. Electron. Dev. 26 (1979), pp. 1091–1097.

[22] P. Verlinden, O. Evrard, E. Mazy, and A. Crahay, The surface texturization of solar cells: A new method using V-grooves with controllable sidewall angles, Sol. Energ. Mater. Sol. Cell 26 (1992), pp. 71–76.

[23] K. C. Sahoo, M.-K. Lin, E.-Y. Chang, T. B. Tinh, Y. Li, and J.-H. Huang, Silicon nitride nanopillars and nanocones formed by nickel nanoclusters and inductively coupled plasma etching for solar cell application, Jpn. J. Appl. Phys. 48 (2009), 126508.

[24] G. Beaucarne, P. Choulat, B.T. Chan, H. Dekkers, J. John, and J. Poortmans, Etching, texturing and surface decoupling for the next generation of Si solar cells, Photovoltaics Int. 1 (2008), pp. 66–71.

[25] J. M. Martínez-Duart and R. J. Martín-Palma, Photodetectors and solar cells based on porous silicon, Phys. Status Solidi B 232 (2002), pp. 81–88.

[26] S. J. Wilson and M. C. Hutley, The optical properties of ‘moth eye’ antireflection surfaces, Opt. Acta 29 (1982), pp. 993–1009.

[27] B. S. Thornton, Limit of the moth’s eye principle and other impedance-matching corrugations for solar-absorber design, J. Opt. Soc. Am. 65 (1975), pp. 267–270.

[28] R. J. Martín-Palma and A. Lakhtakia, Nanotechnology: A Crash Course, SPIE Press, 2010.

[29] C.-H. Sun, B. Jiang and P. Jiang, Broadband moth-eye antireflection coatings on silicon, Appl. Phys. Lett. 92 (2008), 061112.

[30] C.-H. Sun, B. J. Ho, B. Jiang, and P. Jiang, Biomimetic sub-wavelength antireflective gratings on GaAs, Optic Lett. 33 (2008), pp. 2224–2226.

[31] D. Quéré, Non-sticking drops, Rep. Progr. Phys. 68 (2005), pp. 2495–2532.

[32] X.-M. Li, D. Reinhoudt and M. Crego-Calama, What do we need for a superhydrophobic surface? A review on the recent progress in the preparation of superhydrophobic surfaces, Chem. Soc. Rev. 36 (2007), pp. 1350–1368.

[33] W.-L. Min, B. Jiang and P. Jiang, Bioinspired self-cleaning antireflection coatings, Adv. Mater. 20 (2008), pp. 3914–3918.

[34] A. Boden and D. M. Bagnall, Tunable reflection minima of nanostructured antireflective surfaces, Appl. Phys. Lett. 93 (2008), 133108.

[35] S. A. Boden and D. M. Bagnall, Optimization of moth-eye antireflection schemes for silicon solar cells, Progr. Photovoltaics: Res. Appl. 18 (2010), pp. 195–203.

[36] N. Yamada, O. N. Kim, T. Tokimitsu, Y. Nakai, and H. Masuda, Optimization of anti-reflection moth-eye structures for use in crystalline silicon solar cells, Progr. Photovoltaics: Res. Appl. 19 (2011), pp. 134–140.

[37] N. Yamada, T. Iijiro, E. Okamoto, K. Hayashi, and H. Masuda, Characterization of antireflection moth-eye film on crystalline silicon photovoltaic module, Optic Express 19 (2011), pp. A118–A125.

[38] F. Chiadini, V. Fiumara, A. Scaglione, D. P. Pulsifer, R. J. Martín-Palma, C. G. Pantano, and A. Lakhtakia, Insect eyes inspire improved solar cells, Optic Photon. News 22(4) (2007), pp. 38–43.

[39] F. Chiadini, V. Fiumara, A. Scaglione, and A. Lakhtakia, Simulation and analysis of prismatic bioinspired compound lenses for solar cells: II. Multifrequency analysis, Bioinsp. Biomim. 6 (2011), pp. 014002-1-7.

[40] R. J. Martín-Palma, C. G. Pantano, and A. Lakhtakia, Replication of fly eyes by the conformal-evaporated-film-by-rotation technique, Nanotechnology 19 (2008), pp. 355704-1-5.

[41] R. J. Martín-Palma, C. G. Pantano, and A. Lakhtakia, Biomimetization of butterfly wings by the conformal-evaporated-film-by-rotation technique for photonics, Appl. Phys. Lett. 93 (2008), pp. 063901-1-3.

[42] D. P. Pulsifer, A. Lakhtakia, and R. J. Martín-Palma, Improved conformal coatings by oblique-angle deposition for bioreplication, Appl. Phys. Lett. 95 (2009), pp. 193701-1-3.