# Microbial Membrane-Supported Catalysts: A Paradigm Shift in Clean Energy and Greener Production

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ABSTRACT: From a materials standpoint, biological cells can be regarded as nanomaterial factories, perfected by evolution to execute seemingly complex functions in a seamless, energy efficient manner. This article discusses mechanistic principles of metal-supported microbial catalysts and compares them with the industrial benchmark parameters. Incorporation of a microbial membrane toward direct augmentation in heterogeneous catalysis and clean energy applications is a rapidly growing area of research. Efforts have been made to connect multidisciplinary fundamentals with relevant examples, highlighting potential opportunities and providing an open-ended discussion towards clean energy initiative. As it stands, engineered biogenic materials (EBMs) will bring a paradigm shift, for both developing and developed economies, allowing each to capitalize on pre-existing tools of biobased production, fermentation technology, and synthetic biology—toward high-value product generation with a lower carbon footprint.

KEYWORDS: *Biogenic nanomaterials, Living materials, Microbial energy, Clean production, Heterogeneous catalysis*

Engineered Biogenic Materials (EBMs)

Improved Catalytic Properties
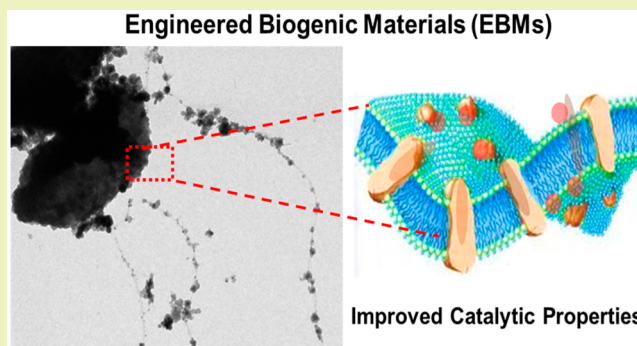
To date, most of our materials have been manufactured either by combining small building blocks (bottom-up) or by breaking down a larger chunk of material (top-down).[1] Comparing this with the onset of industrialization just over a century ago, we have had our fair share of ingenuity (and serendipity), which has also resulted in (a) energy intensive/environmentally degrading production, (b) generation of substantial waste, and (c) limited material regeneration or responsiveness. Therefore, it is imperative that the next generation of materials should not only address the above shortcomings but also surpass the same by incorporating stimuli responsive dynamic architecture with a (genetically) programmable interface. In nature, life and associated materials have been shaped for over 3.7 billion years by continuously evolving with varying extremes of environment, stress/nutrition deficiency, and natural predators.[2] During the course of evolution, living organisms have evolved functional materials across all length scales including molecular level proteins to self-assembled nano/microstructures like cellular compartments, photonic structures, adhesive membranes, etc. Complex inorganic phases (oxides, sulfides, silica, phosphates, and carbonates) are routinely synthesized in all living organisms from unicellular to mammalian via biomineralization.[3]

For chemists and material engineers, understanding surface science, grafting procedures, coating techniques, or the design of additive organic/dopant molecules has become the norm to control the very *unit* of a hybrid material—interfaces. As expected, this lays the foundation for heterogeneous catalysis as well as electrochemical energy devices. In living systems, such interfacial phenomena are governed by a porous framework, often involving asymmetric membrane layers to interact with diverse physiological conditions.[4,5] Here, it should be noted that the term "asymmetric" refers to membrane architecture on the nanoscale facilitating/imparting desirable energy harvesting properties.[6] For instance, the plasma membrane provides selective permeability to a cell by the action of phospholipid bilayer with a hydrophobic head and a hydrophilic tail.[7] In electrochemical catalysis, similar asymmetry is imparted by localizing active sites in micro- and mesopores (nanopores), while macropores facilitate diffusion away from such active sites.[8] Also, asymmetric pore sizes over the membrane minimize ion and electron path length as well as provide larger surface areas leading to enhanced catalytic activity.[9,10] To this end, biogenic materials provide an exhaustive list of substrates for templated synthesis of functional materials with intact membrane specific properties (see Figure 1A).

Engineered biogenic materials (EBMs) can be described as a hierarchical assembly of organic/inorganic molecules via functional and structural components derived from a living system. These biogenic interphases can be from a natural source like plants (lectins as drug carriers),[11] bacteria (engineered outer membrane with vector properties),[12] mammalian cells (protein and cell-derived microvesicles),[13] etc., each agent imparting a distinct set of material proper-
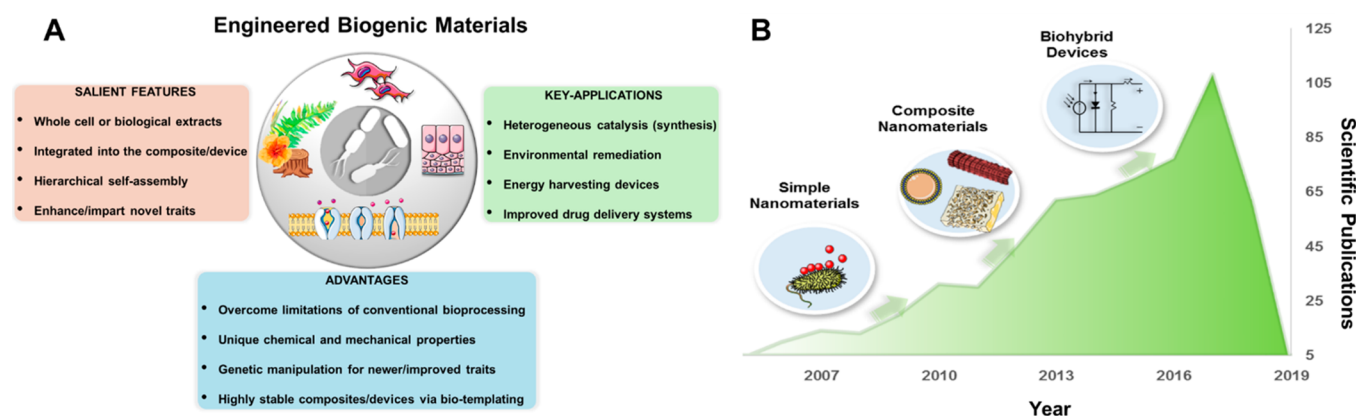
Figure 1. Engineered biogenic materials (EBMs). (A) Introduction and scope of application. (B) Timeline depicting rapidly evolving trends and associated number of publications in the past decade [PubMed search: "biohybrid materials" OR "biogenic synthesis" OR "bionanomaterials"]. Images adapted from Servier Medical Art by Servier and licensed under a Creative Commons Attribution 3.0 Unported License.

Table 1. Showing Key Biogenic Studies Which Paved the Way for Current Generation of EMBs for Heterogeneous Catalysis

s. no.	biogenic material	reaction type/key-information
1	*E. coli* supported Pt NPs	Lindlar-type catalyst for hydrogenation of alkynes[21]
2	Pd NPs supported on multiple bacterial membranes	Heck coupling and Suzuki reaction[22]
3	Pd-supported *A. oxidans* and *R. capsulatus*	hydrogenation of 2-butyne-1,4-diol to 2-butene-1,4-diol[23]
4	Pd-supported *Desulfovibrio desulfuricans*	hydrogenation of 2-pentyne; superior performance as compared to industrial catalyst (5% Pd/Al_2O_3)[24]
5	*Pseudomonas aeruginosa* SM1 exhibiting synthesis of multiple NPs	intracellular NPs linked to the presence of respective metal sequestering genes facilitating intracellular reduction[25]
6	recombinant *E. coli* producing 60 different types of nanomaterials	a pioneering study highlighting genetically programmable interface for EBMS[26]
7	Pd catalyst over Fe(III)-reducing bacterium, *Geobacter sulfurreducens*, thereby acting as a magnetically recoverable heterogeneous catalyst	Heck reaction coupling iodobenzene to ethyl acrylate or styrene; rate of reaction equal to or superior to equimolar amount of a commercial colloidal palladium catalyst[27]
8	magnetically recoverable, bimetallic biogenic composite (Au/Ag/Pd–Fe_3O_4) on *S. oneidensis* MR-1	catalytic reduction of nitroaromatic compounds[28]

ties.[14−19] Traditionally, this area has been classified as biohybrid materials, with research at the interface of biologically derived components together with materials fabrication. However, with advances in this area of research, three distinct classes have emerged in the form of Biogenic (biological cell/extracts, nonliving), biomimetic (chemical linkages and synthetic designing of biological interfaces), and bionic materials (living engineered cell factories), each with its distinct set of advantages as discussed elsewhere.[20]

HOW BIOGENIC MATERIALS DIFFER FROM CONVENTIONAL BIOPRODUCTION

The very rationale of studying any material needs to be done with respect to its proposed application. These biogenic materials, owing to their natural inorganic synthesis machinery (biomineralization), and unique membrane properties are an ideal choice for membrane dependent applications, like catalysis and electro/chemical reactions (clean energy). Further, they are characteristically different than a conventional bioproduction assembly where cell culturing is carried out for intra/extracellular products of interest as (a) a living cell produces compounds of interest which need to be extracted and purified (i.e., biosynthesis only). On the contrary, for biogenic materials, the whole cell or parts thereof form an integral unit of the final product (i.e., bioaugmentation). (b) Structural integrity and intracellular metabolites (acting as a "chemical reservoir") can be retained and modified post-cell-culturing via wet-lab chemistry methods, making them an ideal choice for membrane/electrochemical interface

designing; i.e., cellular viability is not required during application. (c) Bioproduction aims for continuous cell culturing (cellular viability) and associated downstream processing, which is an extremely resource intensive endeavor requiring careful justification, especially if relatively simple, cost-effective options are readily available. This is the key reason why bioproduction has been immensely successful for pharmaceuticals/value-added compounds but may not necessarily be so for lignocellulosic biofuels. For instance, once regarded as the prime contender to meet our energy challenges, biofuels, in general, have been under intense scrutiny. Apart from plummeting oil prices, using all the world's harvested biomass for energy would provide just 20% of the world's energy needs by 2050. Evidently, there has been a shift of focus away from biofuels, toward value-added secondary metabolites (like drugs, polymers, antibiotics, hormones, etc.) On the other hand, EBMs require batch culturing as the cells themselves are the "product of interest." Table 1 presents some of the key biogenic studies with relevance to heterogeneous catalysis development.

For instance, *E. coli* supported Pt NP resulted in a metal-supported catalyst with increased selectivity toward alkenic products of up to 1.4 during hydrogenation of the alkyne. Much like a Lindlar-type catalyst, these biogenic materials can also be used for organic synthesis for selective hydrogenation of alkynes, in which an additive partially poisons metal sites but without the associated hazards of toxic heavy metals such as lead being present.[21] In another study, Macaskie et al. tested multiple microbial strains and went on to establish that

biogenic size/location of NPs is dependent on the bacterial strain. Gram-negative strains produce superior Pd NPs for catalysis compared to thise from Gram-positive ones.[22] This study is of considerable interest as it clearly shows the effect of different bacterial species toward fabrication of biogenic catalysts. Palladized cells of *E. coli*, *D. desulfuggricans*, and *C. metallidurans* all showed high activity in the Heck coupling of phenyliodide and ethylacrylate. This represents an industrially relevant advance since the Heck and Suzuki couplings are key bond-forming reactions used in the chemical industry.

In another study, Pd catalyst samples were prepared upon bacterial biomass supports (Gram-positive *A. oxidans* and Gram-negative *R. capsulatus*) and tested in the partial hydrogenation of 2-butyne-1,4-diol to 2-butene-1,4-diol.[23] A maximum selectivity toward 2-butene-1,4-diol of 0.98 was observed in a solvent composed of 5% isopropyl alcohol (2-propanol) in water at a conversion of 75% 2-butyne-1,4-diol for the Pd/*A. oxidans* catalyst. The Pd/*R. capsulatas* catalyst showed a maximum selectivity of 1.0 at a conversion of 62.6%. At a typical catalyst loading of 0.29 g/L (Pd/*R. capsulatus*), analysis of the mass-transfer steps in the reactor showed that ~63% of the resistance to mass transfer lies at the catalyst (liquid−solid) particle and ~37% lies at the gas bubble interface. The biogenic Pd-catalyst was proven to be a highly selective catalyst for partial hydrogenation reactions and has the advantage that it can be prepared inexpensively from metal-waste-bearing solutions.

While, biogenic materials have also witnessed unprecedented progress in the medical (drug delivery)[29,30] and healthcare (like tissue engineering) areas,[17] their application in non-medical areas has been rather limited. While the early developmental phase of biogenic materials was focused on nanomaterial synthesis and characterization,[15,31−33] a paradigm shift has been witnessed upon the incorporation of genetic engineering,[34,35] supramolecular chemistry,[36,37] and "renewed" (or rather mandatory) interest in green chemistry.

In another interesting study, Rotello et al. demonstrated hierarchical nanostructures via protein−nanoparticle coengineering.[38] They utilized glutamic acid modified GFP proteins for Au NP synthesis via a protein corona formation. This study draws a parallel with several other studies including the first report from our side demonstrating intracellular nanoparticle formation due to a specific set of genes. We demonstrated that in nanoparticle synthesis via *Pseudomonas aeruginosa* SM1, Co NPs were internalized due the presence of the cyanocobalamin (Vit B12) gene, and Li NPs owing to the presence of Li sequestering genes imparted a high-salt tolerance—a characteristic feature in Pseudomonas sp.[25] Nonetheless, their molecular level understanding and application in the area of catalysis and clean energy has been rather recent as highlighted in Figure 1B. In another study, *Desulfovibrio desulfuricans* was used for hydrogenation of 2-pentyne.[24] The metal nanoparticles grown within the cell envelope were regularly dispersed and were of uniform particle size, ~1.7 nm as determined by chemisorption. The bio-Pd is also easily separated from the product mixture and remained active and selective when reused in a subsequent hydrogenation. An interesting comparison was made with the conventional 5% Pd/Al$_2$O$_3$ catalyst and successfully demonstrated that biogenic catalysts are a superior choice where it is desirable to maximize yield of a specific component. For example, at 92% alkyne conversion, the bio-Pd catalyst gave a cis/trans ratio of 2.5 and pentene/pentane ratio

of 3.3, as opposed to respective values of 2.0 and 2.0 with 5% Pd/Al$_2$O$_3$.

Several microbial/biogenic material synthesis reviews exist for fungal biomass, wood, algae, etc. which can be seen elsewhere.[39−43] The focus of this article has been kept toward a mechanistic understanding of metal interfaces via a microbial membrane (bacteria) and how the inherent membrane-support metallic interface supports electron transfer for catalysis and green energy applications. Effort has been made to explain why the bacterial membrane has the potential toward metal supported catalysis based upon (i) hierarchical, molecular self-assembly of metallic particles; (ii) membrane mediated surface asymmetry for process efficiency, and (iii) structural/chemical variations via genetic engineering of the host cell.

■ EBMs FOR CATALYSIS: HOW THE MICROBIAL MEMBRANE ACTS AS AN IDEAL TEMPLATE FOR CATALYST DESIGNING

Living cells routinely exhibit autonomous structuring of matter on the nanoscale by controlling reactions and self-organization, not only in terms of space (which nano/chemical engineering has largely mastered) but also in terms of time. To design hierarchical structures, biological systems often impose boundary conditions that limit material growth in their reaction microenvironment acting as kinetic controls. These kinetic controls are the result of complex (and multiple) metabolic processes with embedded error-correction mechanisms. For instance, magnetotactic bacteria utilizes an expression cassette of approximately 30 genes for the biosynthesis of magnetite inside the living cell; transferring this expression cassette also transfers this biomineralization ability to any non-native organism.[44] Inspired by the structural sophistication and impressive (often, novel) material properties, researchers in supramolecular chemistry and biomineralization communities have shown renewed interest in metallic nanomaterial synthesis via living systems.[45,43] Traditionally, two theories have found extensive merit in the chemical synthesis of nanoparticles:[46] LaMer burst nucleation followed by Ostwald's ripening (LSW theory) and Constant slow nucleation followed by autocatalytic growth (Watzky−Finke). Irrespective of the mode of nucleation, all nanoparticle synthesis approaches follow the law of conservation of energy as the total free energy of a nanoparticle is the sum of surface free energy and crystal/bulk free energy as shown in Figure 1A.

Since surface free energy is always positive and crystal free energy is always negative, it is possible to find a maximum free energy which a nucleus will pass through before being stabilized, i.e., the critical radius (R_c). In Figure 2A, eqs 1 and 2 describe the surface free energy of a spherical particle by accounting for both curved surface area and volume of the sphere. Kwon and Hyeon[47] provided an explanation for the rate of formation of particles (N) in time (t) as shown in eq 3 and concluded that three experimental parameters can be varied, including supersaturation (S), temperature (T), and the surface free energy. The largest effect on nucleation rate comes from supersaturation, where a change from $S = 2$ to $S = 4$ causes an increase in the nucleation rate of about ~10^{70} and a variation in the surface free energy caused by different surfactants. Experimentally, the largest effect on nucleation rate comes from supersaturation and a variation in the surface free energy caused by surfactants. Unlike homogeneous nucleation, in heterogeneous nucleation, nuclei are formed on the first surface of the foreign body, which may not
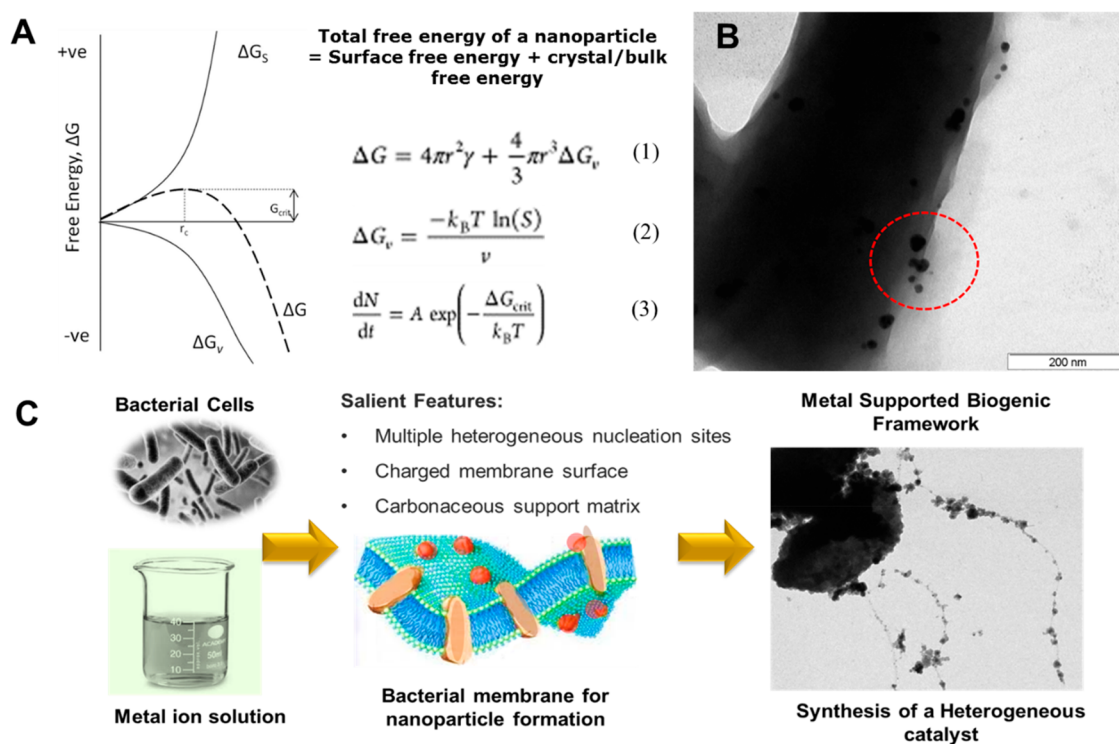
Figure 2. Understanding biogenic nanoparticle synthesis and associated composites. (A) Fundamental principles of thermodynamics guiding nanoparticle formation. (B) Bacterial membrane polysaccharide showing nanoparticle formation and (C) schematic representation of biogenic heterogeneous catalyst over bacterial membrane matrix.

necessarily be spherical in shape (assumption of classical nucleation theory). Therefore, free energy needed for heterogeneous nucleation is also dependent on the surface contact angle.

This is where biogenic synthesis of metallic interfaces gets interesting—Microbial cells are charged entities providing multiple sites for nucleation ($\theta \leq \pi$) together with continuous production of lipopolysaccharides acting as surfactants. Figure 2B shows an image of a metallic nanoparticle being synthesized/stabilized on the bacterial cell surface of *Pseudomonas sp.* (unpublished work; from author's personal repository). To this end, we also provided the first unified theory for multiple monometallic nanoparticle synthesis exploiting bacterial cells as a highly versatile agent.[25] This study not only demonstrated extracellular synthesis of multiple monometallic nanoparticles (NPs) but also made an interesting observation that nanoparticles, which are synthesized intracellularly, happen owing to the presence of a respective metal reducing gene in the bacterial plasmid. Removal of intracellular water (with calcination or pyrolyzation) will invariably yield a metal decorated carbonaceous membrane (as show in Figure 2C), doped with trace elements, for green, cost-effective, highly efficient catalytic activity as demonstrated previously.[48−50]

The importance of exploring such biogenic machinery can also be understood from a recent study by Choi et al. where they scanned through the periodic table to select 35 elements for the biosynthesis of 60 different nanomaterials via a recombinant *E. coli* strain (as shown in Figure 3A).[26] Recombinant *E. coli* cells coexpressed metallothionein—a metal binding protein and phytochelatin synthase responsible for metal-binding phytochelatin peptide. Another important aspect of this study was the biosynthesis of previously

unsynthesized NPs (20 single element and 13 multielement NPs), together with enhanced control on producibility and crystallinity (via Pourbaix diagram), thereby facilitating the design of functional NMs. While one may argue that nanoparticles can also be synthesized by much simpler processes, like citrate reduction or oil-microemulsion, the novelty/practicality of biogenic synthesis via a bacterial system stands out during the designing of a heterogeneous catalyst. Simply speaking, a heterogeneous catalyst is an active metal layer/particle supported over an inert (carbonaceous) matrix, catalyzing a reaction in a liquid/gas environment.[51,52] Lloyd et al. demonstrated an active Pd catalyst over an Fe(III)-reducing bacterium *Geobacter sulfurreducens*, thereby acting as a magnetically recoverable heterogeneous catalyst.[27] The resulting biogenic Pd−Fe catalyst was tested toward the Heck reaction coupling iodobenzene to ethyl acrylate or styrene. Interestingly, rates of reaction were equal to or superior to those obtained with an equimolar amount of a commercial colloidal palladium catalyst, and near complete conversion to ethyl cinnamate or stilbene was achieved within 90 and 180 min, respectively (as shown in Figure 3B).

Interestingly, the addition of nitrogen and phosphorus doping dramatically increases the catalytic potential of most C-supported metal catalysts, which also occurs naturally in all microbial membranes, making them superior to those of traditional organometallic catalysts.[53−55]

In another study, Tuo et al. demonstrated a magnetically recoverable, bimetallic biogenic composite (Au/Ag/Pd − Fe₃O₄) toward the catalytic reduction of nitroaromatic compounds.[28] Alexander and co-workers[56] demonstrated bacterial redox systems to induce the radical polymerization of synthetic monomers at the cell surface as a template synthesis (i.e., externally). They extrapolated this idea the

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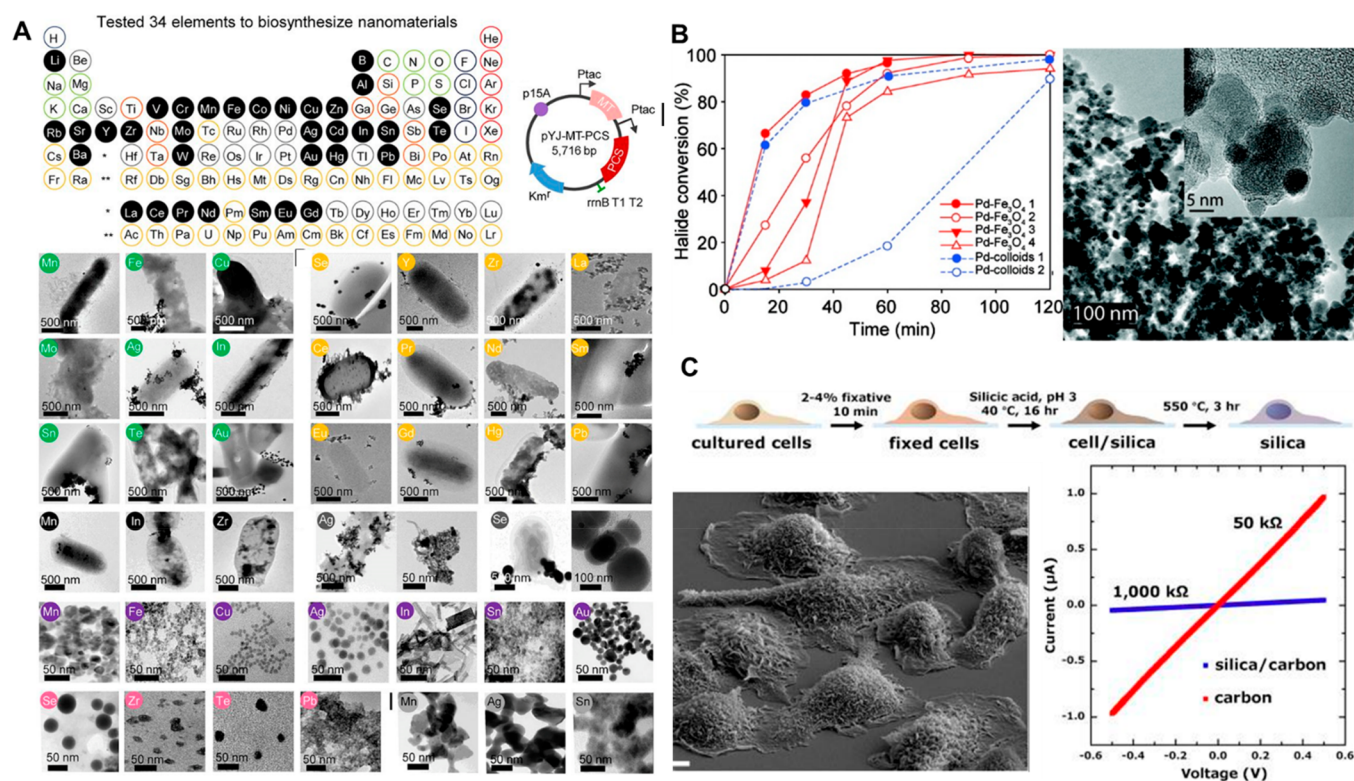
Figure 3. Biogenic synthesis of inorganic materials. (A) Monometallic nanoparticles (a total of 60 different nanomaterials). (B) Heterogeneous catalyst (Pd layer over iron reducing bacteria *G. sulfurreducens*) for coupling reaction and (C) 3D-silica shells grown over mammalian cells as an enhanced conductor postpyrolization. Part A reprinted with permission from ref 26. Copyright 2018 National Academy of Sciences. Part B reprinted (adapted) with permission from ref 27. Copyright 2010 American Chemical Society. Part C reprinted with permission from ref 57. Copyright 2012 National Academy of Sciences.

toward synthesis of "fluorescent tags" over the bacterial surface, facilitating rapid isolation of pathogens. Similarly, Kaehr et al. demonstrated mammalian-cell templated growth of 3D silica architecture via a slow-polymerization of silicic acid species.[57] Upon pyrolysis (900 °C, N_2) followed by silica dissolution (with basic solutions), the obtained carbonized replicas possessed enhanced conductivity as shown in Figure 3C. The biogenic preparation method, apart from its green chemistry approach, provides a metal-supported catalyst as a single-step process, allowing catalytic NPs to be attached to the support material during calcination/pyrolysis. A biogenic heterogeneous catalyst is a low-cost, environmentally friendly, biotechnological route of cleaner production. Further, bimetallic interfaces (like Au and Pt) and bacterial magnetite NPs for magnetic separation clearly indicate the versatility of the bacterial production of industrially relevant membrane supported catalysts for a wide range of chemical modifications. Also, with recent advances in molecular biology, the "desired support matrix" can be encoded into the host organism, to create multifunctional particles with greater usability and facile separation.[58−60]

MICROBIAL MEMBRANES FOR CLEAN ENERGY: POTENTIAL TO FULFILL THE PROMISE OF BIOBASED CLEAN ENERGY INITIATIVE

With a rather successful shale gas revolution, crude oil prices witnessed a shocking bust from $100 per barrel to below $30. Needless to say, this also dampened the interest in biofuels, more specifically, lignocellulosic biofuels. At the same time, advances in material processing and the automobile industry

resulted in highly efficient solar cells as well as electric vehicles. This brings out an important discussion that, if the aim truly is to generate carbon-neutral clean energy, how are biofuels performing when compared to other clean technologies, like solar photovoltaics (PVs)? In fact, there has been a growing debate for quite some time questioning the very premise of certain biofuels.[61−64] Serchinger and Heimlich made an argument that bioethanol production via sugar cane (highest yielding crop) converts only 0.5% of solar radiation into sugar, of which a mere 0.2% is ultimately converted to bioethanol. Solar PVs on the other hand, provide an efficiency of over 10%, which is 55−70 times more useable energy per hectare than biofuels. Also, solar cells do not require additional resources (like land/soil quality, water, fertilizers, downstream processing). Finally, for transportation, PVs bypass the internal combustion engine's efficiency of 20% (with fossil fuels or biofuels) with around 60% efficiency, as demonstrated with electric engines. In fact, from the energy conversion perspective, the biggest advantage of electrochemical processes as compared to combustion lies in bypassing the Carnot theorem-based efficiency limitation of the thermal processes.[65,66] Needless to say, progress in cellulosic ethanol has been showing symptoms of "losing steam," while solar PV conversion efficiencies have been growing ever since. Clearly, a redirection of efforts toward development of biobased PV technologies or biogenic batteries is of considerable interest.

Generally, the idea of microbes and electricity invariably points toward microbial fuel cells (MFC).[67] It is essentially an electrochemical setup that utilizes microbial metabolic processes (see Figure 4A), thereby, converting chemical
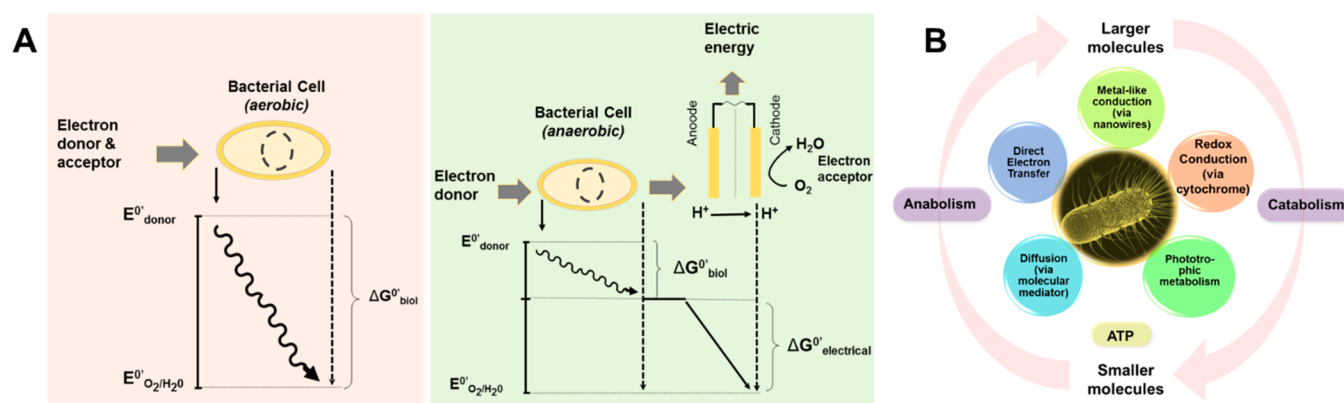
Figure 4. Electron transport in microorganisms. (A) Extracellular electron transfer (EET) in aerobic and anaerobic conditions and (B) different modes of usable electricity generation in microbial systems.

energy to electrical energy. When microorganisms consume a substance such as sugar under aerobic conditions, they produce carbon dioxide and water. However, in the absence of oxygen (anaerobic condition), they produce carbon dioxide, protons/hydrogen ions, and electrons, as follows:

$$C_{12}H_{22}O_{11} + 13H_2O \rightarrow 12CO_2 + 48H^+ + 48e^-$$
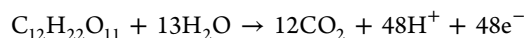
Due to its limited oxygen solubility (11.3 mg/L at $10C^2$), combined with a ∼10 000-fold lower diffusion coefficient (oxygen in water as compared with air),[68] water represents a bottleneck for oxygen transport.[69] Nonetheless, all living biological cells, to an extent, can be treated as a solar/fuel cell, each with its distinct electron transport mechanism coupled with their respective metabolism (as shown in Figure 4B). In this regard, iron-based active sites supported on nitrogen-doped carbon materials (Fe/N@C) have been explored to tackle important applications in electrocatalysis for energy applications.[70,71] For a more in depth study of MFCs and associated challenges, readers are requested to refer elsewhere.[72−75]

■ MICROBIAL MEMBRANE FOR CLEAN ENERGY: CURRENT PROGRESS AND CHALLENGES

Biogenic materials offer a unique advantage in capturing cleaner forms of energy as (i) a material advancement and not merely a process development (as cellular viability is not an issue) and (ii) inherent microbial membrane architecture to introduce structural asymmetry important for charge storage and transfer. Since most of the biological membranes are bilayer (or multilayer structures), membrane asymmetry has been the hallmark of biological membranes (as spatial confinement). Electrochemical energy conversion is also largely about spatial separation.[76] Redox reactions are split into spatially separated electrochemical half-reactions: oxidation (i.e., anode reaction) and reduction (i.e., cathode reaction).[77] In energy storage, membranes are routinely employed as electrode separators (especially in batteries), as well as facilitators of ion transport between the two electrodes. The advantages of using membrane architecture provides selective mass transport by reducing conducting resistance and promoting directional mobility of the ions (thereby improving the overall energy generation efficiency of the device). Biogenic membranes are an interesting choice here, as such ion transport channels are often thermodynamically unfavorable, requiring an external energy input to drive the process

forward. To this end, the rise of Janus architecture (asymmetric surface properties like lipophilicity/lyophobicity or positive/negative surface charges), offered by biogenic nanomaterials, provides an intrinsic "inner" driving force at the separation barrier to enhance transport along the designated direction.[78]

Lei et al. coupled hydrophilic chitosan film embedded oxidases together with a superhydrophobic carbon fiber mesh.[79] The resulting Janus membrane was employed as a biosensor with an over 30 times performance improvement (linear detection of a substrate). This was attributed to the superhydrophobic layer that provided a triphase interface, facilitating oxygen diffusion and driving the enzymatic reaction forward. As a consequence, oxidase kinetics for substrate detection did not suffer limited oxygen. A similar idea was also utilized for the fabrication of a biocatalytic membrane with up to 80 times improvement in catalytic efficiency.[80] Such an asymmetric nature of biogenic interfaces can bring new opportunities in imparting/enhancing novel properties, especially in clean energy/microelectronics, which are not viable with conventional membranes.[81]

Rho et al. genetically engineered filamentous bacteriophages displaying 3,4-dihydroxy-L-phenylalanine (DOPA), and the resulting cellular construct was used as a molecular support for a cobalt oxide based oxygen evolution catalyst.[82] The catechol group of DOPA served as a dopant as well as an electron mediator playing two roles; i.e., it stabilizes Co^{2+} and slightly enhances the oxygen evolution reaction (OER) activity in a low overpotential region. The use of EBMs for lithium ion batteries has also come a long way. Yang et al. fabricated a bacteria mediated micro-yolk−shell structure (via bacterial reduction of metallic Mn^{2+} ions) toward $Mn_2P_2O_7$−carbon@ reduced graphene oxides (RGO) for lithium-ion battery anodes.[83] The $Mn_2P_2O_7$ particles were completely encapsulated within the carbon film, which was obtained by carbonizing the bacterial wall (Figure 5A). The resulting carbon microstructure reduced the electrode−electrolyte contact area, yielding high Coulombic efficiency. The inherent cell membrane structure facilitates yolk@shell morphology (with its internal void spaces) and is ideal for sustaining the volume expansion of $Mn_2P_2O_7$ during charge/discharge processes. Further, carbon shells act as an ideal barrier toward limiting solid−electrolyte interphase formation. Also, calcination of the biogenic membrane yields thin carbonaceous films, similar to that of RGO films, which are proven to have high conductivity and robust mechanical flexibility. As a result, high
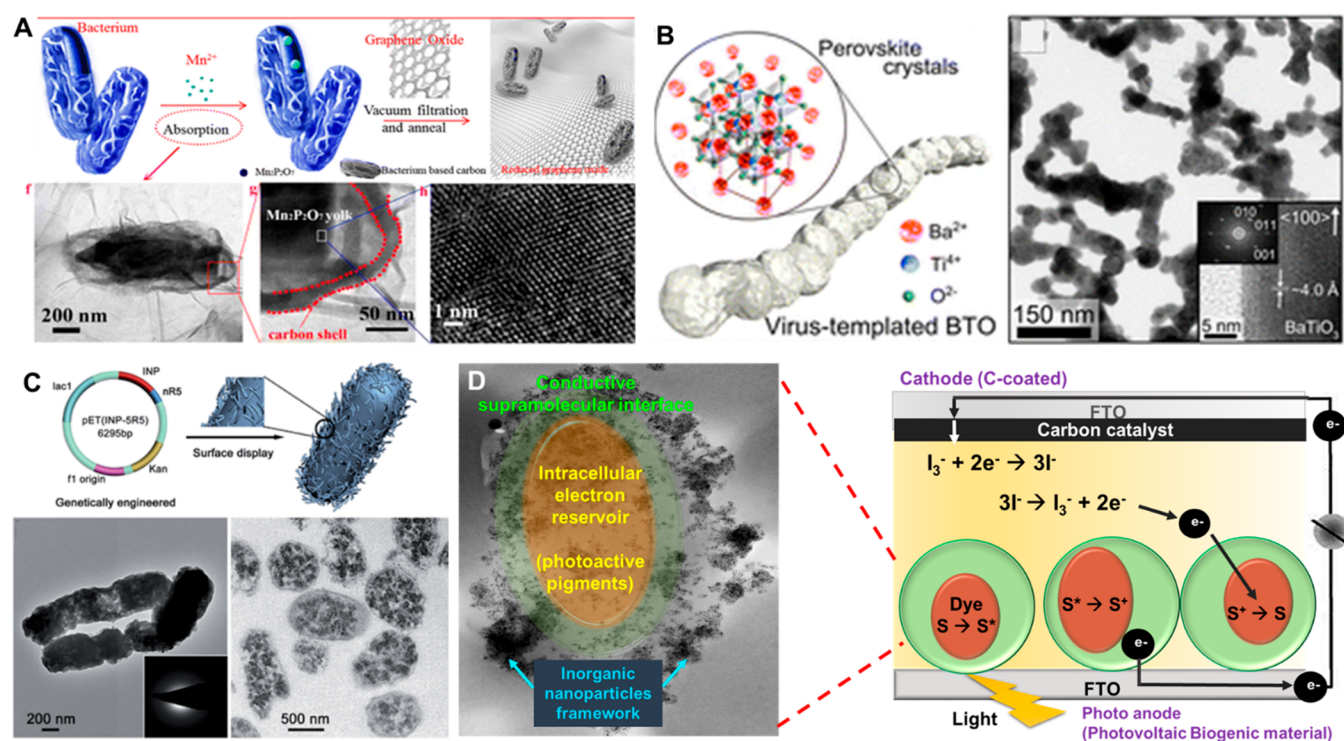
Figure 5. EBMs for a wide range of clean energy applications. (A) *E. coli* based yolk−shell morphology capacitor; (B) M13 viral template as a nanogenerator; (C) silafin producing *E. coli* for anatase-based ultralong cycling lifetime capacitor; (D) tryptophan interface over lycopene producing *E. coli* cells toward dye-sensitized solar cell fabrication. A and B reprinted (adapted) with permission from refs 83 and 84, respectively. Copyright 2016 and 2013 American Chemical Society, respectively. Part C distributed under Creative Commons license with permission from ref 97. Copyright 2016 The Royal Society of Chemistry. Part D reprinted (adapted) with permission from 98. Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA.

capacity, long cycle-life, and excellent rate performance can be expected of such biogenic composites/devices. In another study, anisotropic $BaTiO_3$ (BTO) incorporated nanogenerators were synthesized on an M13 viral template through the genetically programmed self-assembly of metal ion precursors (Figure 5B).[84] The practical significance of such EBMs can be understood by the fact that even without the use of additional structural stabilizers, these virus-enabled flexible nanogenerators exhibit a high electrical output up to ∼300 nA and ∼6 V, underlining the fact that commercial electrical devices are driven by the harvested energy from the virus-templated BTO nanogenerator. Readers interested to know more about novel catalytic materials and biobased membrane energy technologies can take a look here.[85]

While electron−hole pair generation has been the driving force of photosynthesis, imparting similar material properties to a biological system for the generation of electrical energy has been rather limited.[86] This should not be confused with findings on the bioconversion of solar energy into value-added products.[87−89] A new class of hybrid biophotovoltaic materials has been reported comprised of plant/microbial photosystems proteins,[90,91] comprised of light-driven proton pumps like bacterirhodopsin,[92] direct entrapment of plant/bacterial photosynthetic reaction center proteins for electrodes,[93,94] photosensitizer fabrication[95] or green fluorescent protein (GFP mediated biophotonics),[96] etc. Ping et al.[97] reported genetically engineered *E. coli* cells producing silaffin to regulate the synthesis of nanostructured anatase (Figure 5C). The resulting material was found to be highly robust with a higher specific capacity of 207 mA h g^{-1} after 200 cycles at a current rate of 1C and an ultralong cycling lifetime of 5000 cycles with

an outstanding retention capacity of 149 mA h g^{-1} at a higher rate of 10C. We also demonstrated the importance of supramolecular interfaces toward the fabrication of biogenic photovoltaic materials in overcoming low-light conditions as shown in Figure 5D.[98] The novelty of this research lies in the creation of a one-pot photovoltaic material synthesis, overcoming high costs associated with clean-room fabrication and maintenance of microbial cells, as in case of fuel cells. The underlying tryptophan based supramolecular interface[99,100] facilitated electron transfer across a multilayered membrane structure with an open circuit potential $V_{OC} = 0.289$ V, a short circuit (I_{SC}) current of 0.19 mA, and a corresponding short circuit current density (J_{SC}) of 0.686 mA/cm². While this has resulted in the conversion of incident sunlight to usable electricity (η) at about 0.057%, which needs significant improvement, this study opened a new area of multidisciplinary exploration.

■ VISION FOR THE FUTURE: EBMS FOR OVERCOMING CURRENT ENERGY AND MANUFACTURING CHALLENGES

Multidisciplinary studies discussed in this article incorporate fundamentals of chemistry, electro-catalysis, synthetic biology, and material science. Microbial membrane-based composites and devices are designed via a synergistic fusion of biotic and abiotic components to function under extreme operating conditions. Investigating these biointerfaces for better design of electrocatalytic materials has already made considerable progress in biomimetics as well as bionics.[99,100] While this article has been focused toward microbial biogenics, concepts

discussed here can be extrapolated for other biobased materials like wood/lignin, algae, and mammalian cells. For instance, agro-waste represents a considerable opportunity for developing economies toward biogenic catalyst and electrocatalyst development. There is a practice of burning agro-waste (stubble burning) in certain regions, resulting in significant deterioration of air quality.[101,102] Conventionally, briquettes made from carbonized biowaste have been used successfully as an effective means for municipal solid waste (MSW) management. However, efforts have been made to convert waste into catalysts and process development for MSW valorization.[103,104] An article by Balu et al. presents a broad overview of recent holocellulosic-based chemical and fuel production technologies via heterogeneous catalysis.[105] Utilization of such biowaste products has the potential to fuel the next generation of smart materials owing to its robustness and inexpensive production.[106]

In conclusion, EBMs investigate the very building blocks of life and its organization in nature. This, in turn, generates a wealth of knowledge, as demonstrated in the area of biomimetics and bionics, fuelling our scientific progress in health, energy, materials, and manufacturing. Several developing economies have the required operating apparatus already in place to initiate a dedicated research effort in this direction. Last but not the least, with growing population, depleting natural resources, and ever-growing energy needs, biogenic materials have the potential to ease our techno-economic challenges in an eco-friendly, cost-effective manner.

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Notes
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