Self-Powered Nanosystems

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Nanotechnology-Enabled Energy Harvesting for Self-Powered Micro-/Nanosystems

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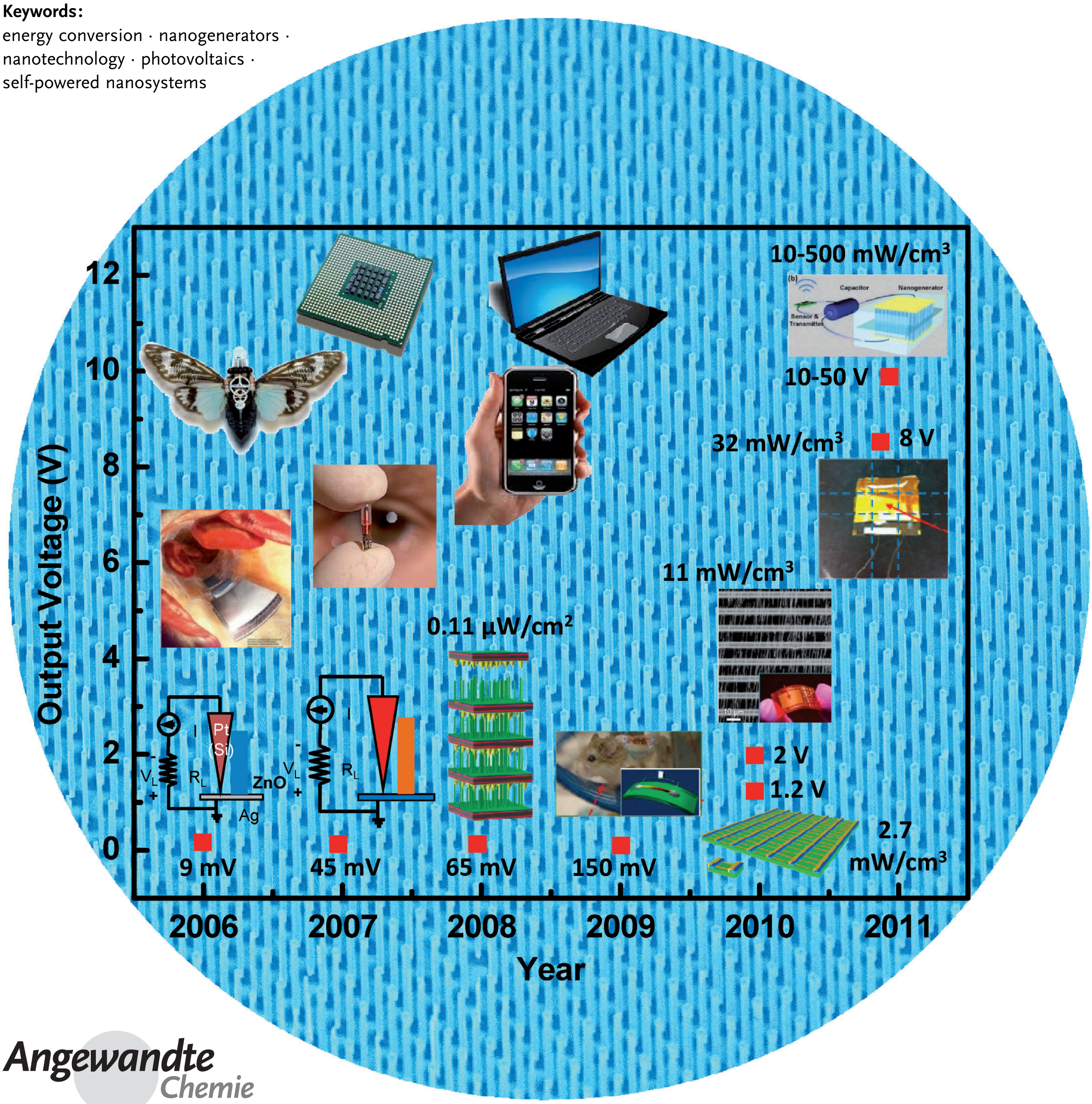

Health, infrastructure, and environmental monitoring as well as networking and defense technologies are only some of the potential areas of application of micro-/nanosystems (MNSs). It is highly desirable that these MNSs operate without an external electricity source and instead draw the energy they require from the environment in which they are used. This Review covers various approaches for energy harvesting to meet the future demand for self-powered MNSs.

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1. Introduction

With the growing threat of pollution, global warming, and energy crises caused by our strong dependence on the dwindling supply of nonrenewable fossil fuels, the search for clean and renewable alternative energy resources is one of the most urgent challenges to the sustainable development of human civilization.[1] In addition to the energy resources which drive human society today, such as petroleum, coal, hydraulic power, natural gas, wind power, and nuclear plants, a focus of active research and development is the exploration of alternative sustainable energy resources, such as solar energy,[2] geothermal power,[3] biomass/biofuel,[4] and hydrogen energy.[5] Although there is potential for the use of these alternative sources for the large-scale supply of power, the energy that can be harvested from these sources is still mainly used for small-scale powering applications.

A dramatic technological trend today is the rapid growth of personal and mobile electronics for applications in communication, health care, and environmental monitoring (Figure 1). Individually, the power consumption of these electronics is low; however, the number of such devices deployed can be huge. Currently, the powering of electronic devices still relies on rechargeable batteries. The amount of batteries required increases in proportion with the increase in the number and density of mobile electronic devices used and may result in challenges for recycling and replacement of the batteries as well as concerns about potential environmental pollution. To effectively extend the lifetime of batteries and even completely replace batteries in some cases, a worldwide effort has begun towards the development of technologies for harvesting energy from our living environment, such as solar energy, thermoelectricity, mechanical vibration, and biofuels. The first target is to power sensors[6] and micro-/nanosystems (MNSs).[7] This Review focuses on recent advances in both the scientific understanding and technology development of energy harvesting specifically for powering future functional MNSs.

2. Self-Sufficient Energy Harvesting for MNSs

2.1. Application Requirements for Wireless, Self-Sufficient, and Intelligent MNSs

There has been an increasing need for the design/development of MNSs for wireless applications, and it is predicted that the market for wireless sensor networks (WSNs) alone will grow rapidly from $US 0.45 billion in 2011 to $US 2 billion in 2021.[8] In addition to the conventional technology trajectory of shrinking device dimensions for faster operating speed as per Moore's law, enormous efforts have been focused recently on integrating individual micro-/nanodevices with diversified functionalities into multifunctional MNSs and further into large-scale networks for applications in ultrasensitive chemical/biomolecular sensing,[9] remote and mobile environmental monitoring,[10] structural health monitoring,[11] homeland security,[12] and portable/wearable biomedical devices and personal electronics.[13] To address these application needs, each device/system node within the network should consist of a low-power microcontroller unit, high-performance data-processing/storage components, a wireless signal transceiver, ultrasensitive sensors based on a micro-/nanoelectromechancial system (MEMS/NEMS), and most importantly the embedded powering units.[7b,c,14] The integration of these conventionally discrete devices with dedicated functionality toward smart and self-powered systems is proposed to be one of the major road maps for electronics.[15] The miniaturized dimensions of nanomaterials and the ability to modulate their composition in a well-controlled manner to create properties that are not possible in their bulk counterparts provide the potential to address some of the critical challenges faced by silicon-based microelectronics as technology advances. Furthermore, these characteristics enable the incorporation of diversified functionalities into the systems to complement digital signal/data processing with augmented functional capabilities, such as interactions between the machine and humans or the environment (Figure 2). Numerous nodes of such devices or systems can be spatially distributed and embedded virtually anywhere, from a remote field to civil structures and even the human body, to fulfill their respective purposes. It is therefore essential that these MNSs have an extended life span, especially for applications with limited human accessibility,

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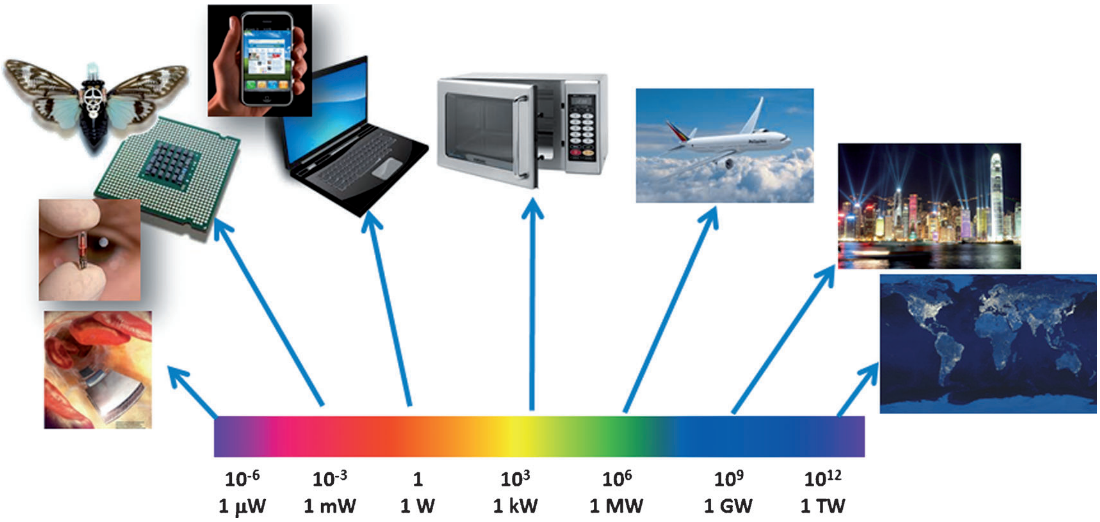

Figure 1. Power requirements for different applications: In the future there will be a great demand for mobile/implantable electronics with extremely low power consumption.

such as monitoring/tracking in a remote or hazardous environment. Despite the rapid progress witnessed recently in the development of batteries with a relatively high energy density,[16] the amount of energy available in these batteries is still finite and low, which severely limits the life expectancy of the systems being powered. Power management at both device and system levels has also been investigated in an effort to increase operation time for a given power supply; however, limitations, such as complexity in its implementation and related costs, may hinder its broad application.[17]

2.2. Power Consumption and Mode of Operation of MNSs

Micro-/nanodevices exhibit operational advantages, such as small electrical/thermal time constants, enhanced sensitivity/responsivity, and high integrated complexity with respect to their conventional counterparts. In addition to the above merits, another key characteristic of micro-/nanodevices is the low operation power, with typical values in the range of microwatts to milliwatts. Typical power consumption in MNSs also includes contributions from other operations of the system, such as signal conditioning, information processing/storage, and data communication. For most application purposes, digitization of the sensed signal is critical during front-end signal conditioning and for analog-to-digital converters (ADCs) with sub-microwatt to microwatt power consumption.[18] Logic processing and storage of the conditioned information are also indispensable for MNSs. Nanomaterials based on logic operations with power consumption in the nanowatt to microwatt range have been demonstrated,[19] and nonvolatile memory devices with sub-microwatt programming-power consumption have also been described.[20] Such memory devices are highly suitable for data storage in future wireless MNSs owing to their long-term data retention and low power consumption.

Generally, the transmission/communication of data consumes the majority of the power in a wireless MNS. For example, modular products for low-power medical, industrial, and consumer applications, such as TI CC2560 from Texas Instruments and BCM4329 from Broadcom, operate at a rate of 3–5 Mbps with power consumption in the milliwatt range.[21] Therefore, the long-term sustainable operation of MNSs requires either data-transmission modules with even lower power consumption or a new MNS operation scheme. Although the power consumption of MNSs could be small, as shown in Figure 1, it is an indispensable component of the entire energy spectrum. More importantly, for small elec-

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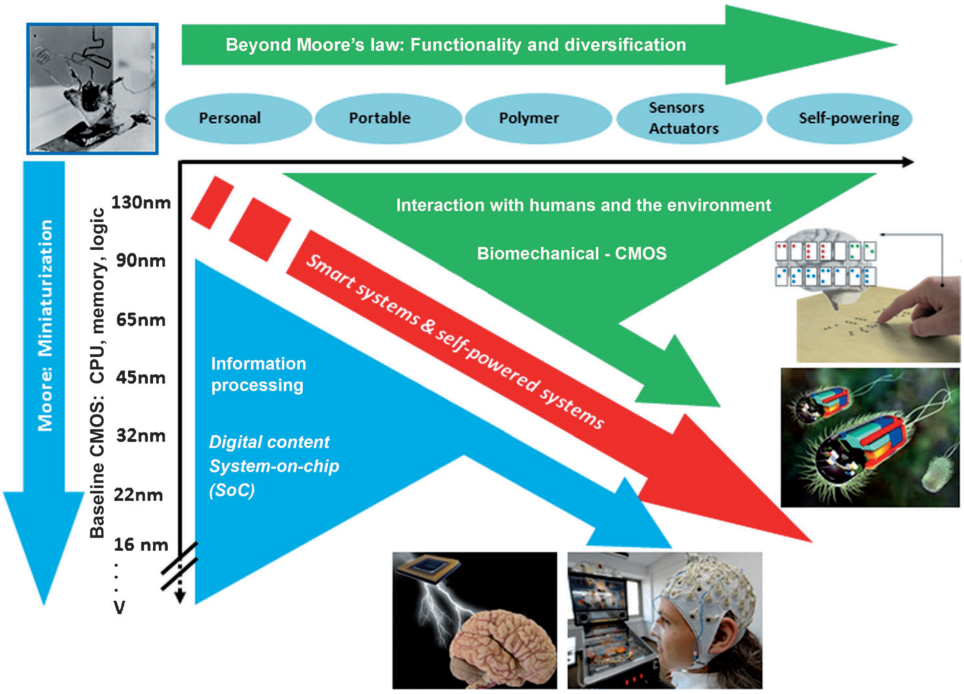

Figure 2. Future perspective of electronics beyond Moore's law. The vertical axis reflects miniaturization and increasing device density, CPU speed, and memory capacity. The horizontal axis reflects the diversity and functionality of personal and portable electronic devices. The future of these devices lies in the integration of CPU speed and functionality. CMOS = complementary metal–oxide–semiconductor, CPU = central processing unit.

tronic devices, energy consumption is not solely measured in terms of cost, as in the case of a large-scale power requirement, but energy is required to enable the operation of the MNS. Pacemakers are a typical example.

Practically, in applications such as environmental and biomedical monitoring, a sampling rate of once every few minutes should be adequate, whereas in other scenarios, such as infrastructure and health monitoring, a measurement rate of once every few hours could be appropriate. The operation of a wireless MNS for such applications should therefore consist of both active and standby modes with low-duty cycles: most of the time, the MNS is dormant with minimum energy consumption, and active operation of the system is only required periodically according to the preset sampling rate (Figure 3). Accumulated power harvested by the system during the standby period between two active periods might be sufficient to drive the operation of the MNS in its active mode. The main requirement for energy harvesting may thus be minimization of the power consumption of the device in its standby mode and during the transitions from the standby mode to the active mode.

2.3. *Self-Powered MNSs*

Intensive efforts during the last two decades towards the design and development of micro-/nanotechnology for various applications have led to systems with unprecedented performance, as enabled by improved capabilities in materials synthesis and increasingly sophisticated micro-/nanofabrication technologies.[22] Although micro-/nanodevices require much lower power consumption than their conventional counterparts,[23] the powering of these systems can still be challenging. Almost all reported MNSs are powered by a traditional power cord or battery, which is in general much larger than the device being powered and hence dictates the size of the entire system. This conventional power-supply scenario also leads to issues of replacement/maintenance, cost, and environmental concerns, and severely hinders the further development and practical deployment of micro-/nanotechnology.[24] A nanosystem should therefore consist of not only functional nanodevices but also nanoscale power sources. The dilemma is, however, that the miniature size of these power sources can largely limit their lifetime and efficiency. The design and development of appropriate energy-harvesting strategies for miniaturized powering packages is thus critical to the fulfillment of the potential and promises of micro-/nanotechnology.[7c,25]

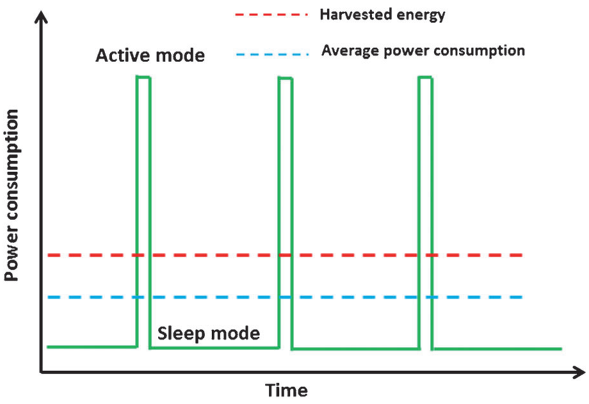

Figure 3. Operation of an MNS with a short active mode and a long sleep mode. The energy harvested during the sleep mode can power the device in the active mode for sensing, data processing, and wireless signal transmission.

Research on micro-/nanotechnology in the near future should therefore be aimed at integrating micro-/nanodevices into multifunctional systems capable of wireless, self-sufficient, and intelligent operations, such as sensing, actuating/responding, communicating, and controlling.[24,26] It is highly desirable for MNSs to be self-powered without a battery, particularly for applications such as remote sensing and implanted biomedical systems,[27] as the life span of the devices would thus be extended, the footprint and cost of entire system decreased, and the adaptability of these MNSs to the environment increased. The development of enabling technology for harvesting energy from the environment and converting it into usable electric power to support the self-sufficient operation of MNSs is the most promising strategy to overcome the current challenges and hurdles presented by conventional powering methods. In contrast to energy stored in storage elements, such as batteries and capacitors, the environment can be viewed as an almost infinite reservoir of energy available for potential applications. The goal of energy-harvesting technologies for self-powered MNSs is thus to develop power sources which operate over a broad range of conditions for extended time periods with high reliability.

3. Micro-/Nanotechnology-Enabled Technologies for Energy Harvesting

There are a variety of sources available for energy scavenging by MNSs from the ambient environment, including, but not limited to, energy in natural forms, such as wind, water flow, ocean waves, and solar power; mechanical energy, such as vibrations from machines, engines, and infrastructures; thermal energy, such as waste heat from heaters and joule heating of electronic devices; light energy from both domestic/city lighting and outdoor sunlight; and electromagnetic energy from inductor coils/transformers as well as from mobile electronic devices. Moreover, the human body itself provides a tremendous amount of energy that is available for harvesting and potential utilization in self-powered MNSs: mechanical energy due to vibration/motion from body movement, respiration, and even blood flow in vessels; thermal energy from body heat; and biochemical energy generated during physiological processes and metabolic reactions. In this section, various energy-harvesting techniques are reviewed, and their application prospects in future self-powered MNSs are discussed.

3.1. Photovoltaic Technologies for Solar-Energy Harvesting

Solar energy is by far the most abundant exploitable renewable energy resource. More energy is provided to the earth by sunlight irradiation within one hour than is consumed by human society globally in one year.[28] Semiconductor materials that exhibit a photovoltaic (PV) effect can be used to convert solar radiation into electricity through a photovoltaic process. PV technology has been growing and expanding rapidly. The total global energy production by PV processes reached 64 GW (1 GW = 10^9 W) by the end of 2011.[29] Despite this considerable capacity, however, PV technology only accounts for 0.1% of electricity generation globally,[30] largely as a result of the inability of existing PV technologies to produce electricity with an efficiency that fulfils the grid parity set by conventional power-generation routes.[31] Enormous efforts and resources have therefore been devoted to the development of new-generation PV technologies that operate with enhanced efficiency at lower cost.

Practically all PV devices, or solar cells, incorporate a p–n junction. Such junctions occur in various possible configurations. Solar cells containing multiple p–n junctions have recently been investigated intensively for the more efficient absorption of light with different wavelengths with the aim of reducing the inherent sources of energy loss in conventional single-junction cells. A conversion efficiency of 42.3% was achieved by combining multijunction cells and concentrator technology.[32] However, the high efficiency of multijunction cells is offset by their increased complexity and manufacturing cost, which limit their application mainly to aerospace exploration, for which a high power-to-weight ratio is desirable. The dominance of PV technology historically by inorganic solid-state junction devices is now being challenged by the emergence of a new generation of PV technologies built, for example, on nanostructured materials or conducting polymers. Such technologies offer the prospect of converting solar energy into electricity at low cost. Subsequent discussions on solar-energy harvesting are focused on micro-/nanotechnology-enabled PV technologies and their potential applications in MNSs.

3.1.1. Dye-Sensitized Solar Cells

The dye-sensitized solar cell (DSSC), invented by Michael Grätzel and Brian O'Regan in 1991,[33] enables optical absorption and charge separation/injection by associating a dye sensitizer (a light-absorbing material) with a wide-band-gap semiconductor of nanocrystalline morphology as the photoanode. This type of solar cell is based on the combination of interpenetrating networks of mesoscopic semiconductor materials with electrolytes,[34] as alternatives to the p–n junctions of inorganic solid-state semiconductors in conventional solar cells.

A three-dimensional network of randomly dispersed TiO_2 nanoparticles has typically been adopted as the photoanode in DSSCs since their first introduction.[33,35] Although its fabrication is straightforward and cheap, the disordered network of TiO_2 nanoparticles presents numerous grain boundaries and hence multiple trapping sites.[36] These trapping sites not only promote the increased recombination of electrons but also hinder the collection of the excited electrons and thus compromise the overall conversion efficiency. Structural configurations with higher degrees of order than the random assemblies of nanoparticles are expected to facilitate the transport/collection of electrons and hence improve the efficiency of solar cells. Rapid progress has also been made in the application of ZnO nanomaterials as transparent photoanodes in DSSCs.[37] The coupled piezoelectric, semiconductor, and photoexcitation properties of ZnO together with the straightforward methods available for the synthesis of various ZnO nanostructures at low temperatures could potentially facilitate the wider application of ZnO in DSSCs.[22e,38] Novel strategies, such as the integration of ZnO or TiO_2 nanowires with 3D optical fibers or planar waveguides, have been shown to address issues such as insufficient internal surface area and deficient dye loading, which are shortcomings of DSSCs based on 1D nanostructures. Such strategies offer the potential for the manufacture of DSSCs with high flexibility, adaptability, and enhanced efficiency for concealed applications.[37b,39]

Advances have also been made in the development of photosensitizers and electrolytes to enhance the efficiency of energy conversion in DSSCs. The combination of a donor-π-bridge-acceptor Zn–porphyrin dye and a tris(bipyridyl)cobalt(II/III)-based redox electrolyte was recently demonstrated to boost the power-conversion efficiency of a DSSC to 12.3%, which is comparable to the performance of thin-film PV devices.[40] The liquid redox electrolyte conventionally used in DSSCs is associated with sealing and long-term-stability issues. It can be replaced by a solid p-type semiconductor to enhance the stability of DSSCs.[41] Currently, DSSCs suffer from stability issues caused by both intrinsic and extrinsic factors, such as degradation of electrolytes and dye molecules by elevated and varied temperatures, humidity, prolonged illumination, and sealant leakage. If DSSCs are to be deployed practically at a level comparable to the use of standard silicon PV technology, substantial effort has to be devoted to the improvement of their stability through scientific development and engineering. It is also technically feasible to engineer DSSCs into flexible formats with mechanical robustness and adaptability for novel applications.[42]

DSSCs could be suitable for powering distributed MNSs for self-sufficient, maintenance-free applications, since ideally DSSCs convert sunlight into electricity in a self-sustainable manner, without suffering any permanent chemical transformation or consumption of the materials in the system.[43] Although their conversion efficiency is still less than that of the best thin-film cells, DSSCs could still possibly compete with conventional options for electricity generation if their price/performance ratio was improved to meet grid parity by taking advantage of emerging fabrication techniques, such as a roll-to-roll printing process for the large-scale manufacture of DSSCs at low cost with reasonable efficiency.

3.1.2. *Organic Solar Cells*

As a result of the increasing requirement for inexpensive renewable energy sources, organic-polymer-based PV devices (OPV) have been introduced as one option for the production of energy from light at very low cost.[44] The ability to chemically manipulate electrical conductivity through the molecular/electrochemical doping of polymers, together with the development of facile and cheap processing techniques, has significantly boosted the application of polymer-based solar cells. In organic solar cells, excitons are separated into free electron–hole pairs by the effective field created across the heterojunction between two dissimilar organic materials, known as the donor and acceptor molecules.[45] Typical device architectures for organic solar cells include the single layer, the bilayer heterojunction, the bulk heterojunction, and the diffusive bilayer heterojunction.[45b] The conversion efficiencies for single-layer and bilayer organic solar cells have been below or around 1%, and most recent attention has been focused on solution-processed polymer bulk-heterojunction (BHJ) solar cells, for which conversion efficiencies of around 6–8% have been attained by systematically engineering the polymer properties and morphology and the device structure.[46]

The optical absorption coefficient is high for organic molecules, and the cost of fabricating organic solar cells with decent conversion efficiencies could be much lower than the cost of fabricating the current thin-film solar cells. In analogy with DSSCs, emerging fabrication techniques, such as roll-to-roll processing, enables the manufacturing of organic solar cells to be scaled up to a level at which OPV devices are viable and competitive for powering flexible MNSs and even consumer electronics.[47] However, there are still problems associated with OPV cells, such as their relatively low conversion efficiency, their vulnerability to variations in humidity/temperature, and instability in device performance. Organic materials in OPV cells are susceptible to chemical degradation caused by oxygen, moisture, and even reactions with electrode materials, as well as physical degradation resulting from morphological changes and the spatial diffusion of materials inside the cells at the microscale.[48] In addition to the conversion efficiency, improvement of the stability, cost, and processing of OPV cells deserves considerable attention for the deployment of OPV techniques to become practical. In-depth investigations need to be carried out to gain an understanding of and, more importantly, alleviate degradation (such as the oxidation of organic material upon illumination) and low efficiency due to microphase separation during annealing and operation.

3.1.3. *Quantum-Dot and Plasmonic Solar Cells*

Semiconductor quantum dots (QDs), within which the charge carriers are confined spatially by potential barriers, have attracted widespread attention as a result of their novel optoelectronic properties,[49] which can be tailored by simply varying the dimensions of the QDs.[50] QD-based solar cells have also drawn a lot of attention during the past few years owing to the possibility of boosting energy-conversion efficiency beyond the traditional Shockley–Queisser limit for silicon-based solar cells.[51] Significant progress has been made in photoelectrodes based on 3D arrays of QDs of various materials.[52] The relatively delocalized while still quantized states found in QD arrays can facilitate multiple-exciton generation (MEG), which involves the generation of multiple electron–hole pairs upon the absorption of a single photon and can hence considerably increase the conversion efficiency of solar cells. However, measurement of the exact efficiency of MEG is experimentally challenging, and apparent inconsistencies between the reported values of quantum yield have led to much controversy in this field.[53] A detailed discussion on the controversy, status, and prospects of research on MEG in nanocrystal QDs can be found elsewhere.[54]

QDs can also function similarly to the dye photosensitizers in DSSCs,[55] whereby QDs possess several advantages, such as the ability to tune their optical properties by changing their dimensions, better junction formation, and more significantly the larger-than-unity quantum efficiency due to efficient MEG effects.[53] Structures consisting of interpenetrating junctions formed between QDs and organic semiconductor polymers also exhibit the potential to convert light into electricity effectively.[56] The recently demonstrated doping of QDs with metal impurities enables even more sophisticated control of the properties of the QDs in addition to simple variation of their dimensions; record high efficiency of 5.4 % was reported when CdS QDs were doped with Mn^{2+}.[57]

The emerging field of plasmonics has made it possible to guide and localize light at the nanoscale for the development of novel photonic/optoelectronic applications.[58] Design approaches based on metallic nanostructures that support surface plasmons can also be used to improve absorption in PV devices and thus enable more efficient photon management and a significant reduction in the physical thickness of PV devices.[59] Metallic nanostructures enhance the performance of PV devices by trapping and coupling freely propagating plane waves from the sun into the absorbing semiconductor thin film, and by coupling sunlight into surface-plasmon modes supported at the metal/semiconductor interface as well as guided modes in the semiconductor slab. These plasmonic couplings are beneficial in their enhancement of PV performance, as enabled by recently developed inexpensive and scalable techniques for fabricating patterned metallic nanostructures with sophisticated control over the nanoscale dimensions. However, owing to the resonant nature of the plasmonic effect, absorption can only be enhanced at certain wavelengths. In a recent study it was shown that broadband absorption in plasmonic solar cells could be enhanced and a conversion efficiency of 8.1 % attained by the controlled engineering of plasmonic nanostructures to strongly scatter the incident light in a large angular range with the minimization of detrimental particle absorption.[60]

3.1.4. Solar Cells Based on Low-Dimensional Nanostructures

As evident from the above discussions, improvement of the performance of PV devices largely depends on the optimization of photon absorption and photoinduced-carrier collection.[61] However, the simultaneous optimization of both processes is nontrivial for solar cells based on conventional structures owing to the dilemma between the improvement of optical absorption and the minimization of recombination. Novel structural configurations, such as ordered arrays of one-dimensional nanostructures, are expected to not only improve light absorption and assist interface/junction formation, but also facilitate the transport and collection of electrons.[61,62]

The use of ordered arrays of low-dimensional nanostructures to improve the photon absorption of PV devices has been investigated both theoretically and experimentally:[63] strong broadband optical absorption superior to that found for thin-film structures was observed. The ability to manage photon absorption efficiently through the use of intentionally engineered nanostructures enables significant reduction of the total amount of active materials required for the fabrication of solar cells. The composition, shape, morphology, and dimensions of the nanowires (NWs) and the periodicity of the array can all be manipulated to tailor the absorption spectrum of the as-fabricated solar cell.[64] In a conventional planar thin-film solar cell, the high-quality crystalline film must be thick enough for carriers to be collected and incident photons absorbed along the same axis. Solar cells built on an array of vertically aligned one-dimensional nanostructures, however, can improve the collection of the photoinduced electrons by orthogonalizing and separating the paths of light propagation and electron collection, as shown schematically in Figure 4 a. Consequently, the diffusion path for photoexcited minority carriers can be decreased, and the efficient collection of carriers can be made possible even in materials of low crystalline quality.[37a,63b,65] This helps relax the stringent requirements in materials manufacturing and thus reduces the cost substantially.

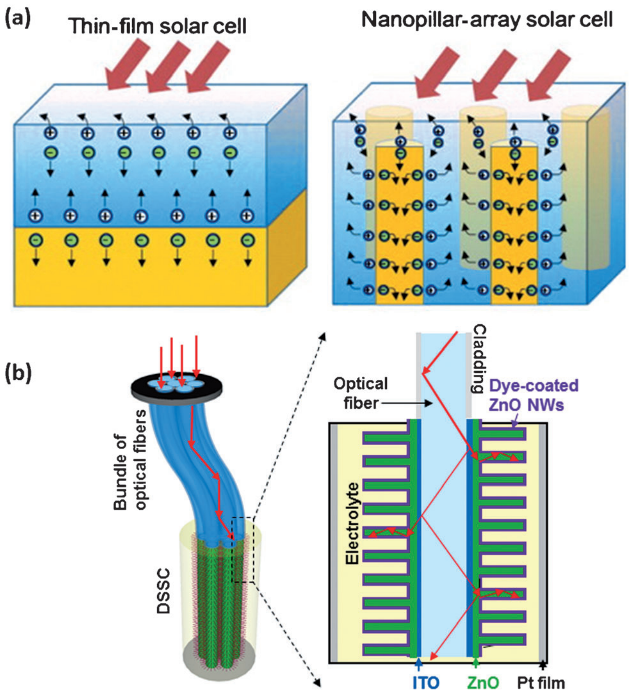

Figure 4. Schematic illustration of a) charge separation in planar thin-film solar cells and nanowire/nanopillar-based solar cells (from Ref. [63b], Copyright 2009 Nature Publishing Group) and b) an optical-fiber-based three-dimensional solar cell (from Ref. [39b]). ITO = indium tin oxide.

One-dimensional nanostructures have been investigated intensively and utilized in all types of PV devices mentioned above.[66] For example, energy-conversion efficiencies of about 10 and 3 % have been reported for DSSCs based on TiO_2 NWs and ZnO NWs, respectively.[37a,67] A solar cell based on an array of Si NWs with a projected efficiency of

17.4% and another based on an array of InP nanopillars with an efficiency of 8.1% have also been demonstrated.[68] Moreover, the performance of solar cells based on NW arrays has been improved strategically by enhancing dye adsorption[69] and reducing surface recombination.[70] Innovative structural configurations, such as tandem/core-shell structures and 3D convolution between NWs and light-transmitting media, have also been investigated in efforts to improve the conversion efficiency of solar cells based on 1D nanostructures (Figure 4b).[39,71]

By taking advantage of the improved photon capturing and photocarrier collection enabled by the engineering of structures at the nanoscale, it is possible to fabricate high-efficiency solar cells, preferably in flexible forms, through scalable processes at very low cost for potential powering applications in future MNSs. However, several technical challenges, such as carrier recombination, mechanical and chemical stability, morphology control, and process scalability, must be met before 1D-nanostructured solar cells with their promised benefits can be implemented practically. In addition to the advancement of understanding of the fundamental aspects that affect the solar-cell performance, engineering issues, such as scaling, module integration, and device packaging, should be addressed.[62]

3.2. Artificial Photosynthesis for the Production of Solar Fuel

Although PV technology enables the direct generation of electricity from sunlight, it is incapable of efficiently producing fuel within which the energy from sunlight can be stored for use at a later time when sunlight is not available.[72] Furthermore, the distribution of sunlight over time is not constant; thus, viable approaches for collecting and storing solar energy in readily accessible media are required.[72b] The conversion of light into stored chemical energy by artificial photosynthesis, a chemical process which replicates natural photosynthesis, has been the focus of much recent attention. Photoelectrolysis, or water splitting, is a form of artificial photosynthesis that converts water into hydrogen and oxygen through the use of sunlight. An artificial photosynthetic system for producing solar fuel typically requires antenna/reaction center complexes for the generation of electrochemical potential from sunlight and appropriate catalysts for the oxidization of water and reduction of precursors to hydrogen.[72a] Considerable progress has been made in the design of technologies that mimic natural photosynthesis and the development of efficient water-splitting technology.[73] The use of multijunction configurations has been the predominant approach for the development of efficient photoelectrochemical water-splitting cells, whereby the incorporation of semiconductors with different band gaps offers the advantages of complementary absorption and improved stability.[73c,74] Efforts have also been focused on the engineering of new materials to optimize processes at both anodes and cathodes and the integration of photoelectrolysis cells with other structures, such as PV cells, which can provide additional voltage to drive the water-splitting reactions and hence increase overall efficiency.[73c,75] In this way, a monolithic and multijunction integrated PV/electrolysis configuration in a $GaInP_2$/GaAs system was developed with 16% solar-to-hydrogen conversion efficiency.[76]

There has been increasing interest in the use of nanostructured materials as the photoanodes in photosynthesis applications as a result of the benefits offered by the large surface area, short lateral diffusion length, and low reflectivity in these nanostructured materials.[77] The use of structured photoelectrodes based on semiconductor NWs with a preferred band gap or an intermediate energy level introduced within the band gap has also been investigated in efforts to improve the water-splitting efficiency through enhanced light absorption in the visible region of interest and enhanced electron-transfer efficiency due to the single-crystalline nature of low-dimensional semiconductor nanostructures.[78] The creation of high-aspect-ratio photoelectrode surfaces by engineering the morphology of nanostructures also enables the use of less expensive catalysts with lower catalytic activities. Furthermore, the ability to modulate the composition of nanomaterials at the atomic scale and to synthesize nanostructures of various morphologies, both in a controlled manner, may improve conversion efficiency in artificial-photosynthesis applications through more effective management of the light absorption.

Issues such as the low photocatalytic efficiency and scaling up of the manufacturing process need to be addressed properly before artificial photosynthetic systems can be deployed in practical applications at low cost. It is equally important to develop artificial photosynthetic systems from earth-abundant materials in an affordable and environmentally benign manner for energy conversion and storage.[72b] However, it can be expected that artificial photosynthetic systems will play an important role in providing sustainable and clean energy to MNSs in applications such as environmental monitoring and remote sensing. Thus, the ability of artificial photosynthetic systems to convert harvested solar energy into fuel and store it in the system for later applications will enable the operation of self-powered MNSs.

3.3. Harvesting of Thermoelectric Energy

The past decades have witnessed an increasing interest in the development of thermoelectric (TE) materials for electrical-power generation through direct energy harvesting from natural heat sources and waste heat dissipated from engines.[79] This type of energy harvesting is expected to help reduce the consumption of fossil fuels and hence the emission of CO_2. In addition to the macroscale harnessing of heat, attention has also been paid to the scavenging of heat dissipated from humans to support miniaturized sensors in applications such as biomedical monitoring and body-area networks.[80]

Electricity generated directly by a temperature gradient, or thermoelectricity, is based on the Seebeck effect, whereby an equilibrium is established between the diffusion of carriers from the hot side to the cold side of the material and the drift of carriers from the cold side to the hot side as a result of the induced electric field. The electrochemical potential that builds up inside the material in response to the temperature gradient can power an external consumer load.[79a] The efficiency of thermoelectric (TE) conversion is largely determined by $ZT = S^2 T/\rho\kappa$, in which ZT is the TE figure of merit of the materials and S, ρ, κ, and T are the Seebeck coefficient, electrical resistivity, thermal conductivity of the material, and absolute temperature, respectively.[81] A large ZT value corresponds to efficient TE conversion and is thus desired for practical applications, for which TE conversion must be competitive with conventional power generation.[82] It may be possible to make TE conversion competitive as an energy source by reducing the thermal conductivity of the material used, increasing the electrical conductivity, and maximizing the concentration of charge carriers. Intensive efforts in the search for and engineering of materials with optimized TE characteristics have followed two main approaches: the development of advanced bulk TE materials and the investigation of low-dimensional material systems.[83]

3.3.1. Advanced Bulk Thermoelectric Materials

A synergistic "rattling" effect enabled by void-filling by extrinsic guest atoms has resulted in significant enhancement of the performance of skutterudite-based TE devices. For example, a ZT value of 1.25 was achieved at elevated temperatures by simultaneously reducing the lattice thermal conductivity and further optimizing the carrier concentration.[84] A similar strategy has also been investigated in clathrates and half-Heusler intermetallic alloys,[79c,83c] with recent progress yielding $ZT = 1.35$ at 900 K for $Ba_8Ga_{16}Ge_{30}$ and $ZT = 0.4$ for n-type clathrates at room temperature.[85] These results demonstrate the potential of such materials to replace conventional high-temperature TE materials, such as p-type Si–Ge alloys, in future applications.[86] Metal oxides have also been investigated for high-temperature TE applications, with promising results, in particular for p-type TE materials.[87] Research in the design of various derivatives of chalcogenide compounds, which are conventionally the most widely used TE materials for near-room-temperature and mid-temperature applications, has yielded TE devices with superior performance:[88] not only has TE performance in conventional temperature ranges been improved, but the application of these materials has been extended to even lower temperatures.

Despite the potential exhibited by bulk TE materials and the progress made, the low efficiency of current TE devices prohibits their wider application. Recent efforts in the fabrication of nanostructured bulk TE materials, however, have led to significant progress in the enhancement of TE conversion. Bulk nanocomposite TE materials have shown the most promise for commercial applications owing to the feasibility of their large-scale production and their compatibility with existing TE-device configurations.[79a,b] Nanocomposites have caused a remarkable increase in the ZT value in various materials systems[88c,89] owing to the fact that the nanostructures within these materials are smaller than the phonon mean free path while larger than the charge-carrier mean free path. As a result, the scattering of phonons at the interfaces is stronger than the scattering of charge carriers.[79a] High-performance solar thermoelectric generators (STEGs) based on bulk nanostructured Bi_2Te_3 alloys were recently described. With an efficiency in the solar conversion of thermal into electric power of around 4.6%, a value seven to eight times higher than the previously reported best value for a flat-panel STEG, these STEGs exhibit potential for practical large-scale applications (Figure 5).[90] Although much progress has been made, many factors, such as the control of nanostructure formation and mechanisms for the enhanced TE performance of nanocomposites, need to be better understood. Furthermore, high-performance TE materials need to be developed without the incorporation of toxic materials, such as tellurium and lead, for sustainable and environmentally friendly applications.

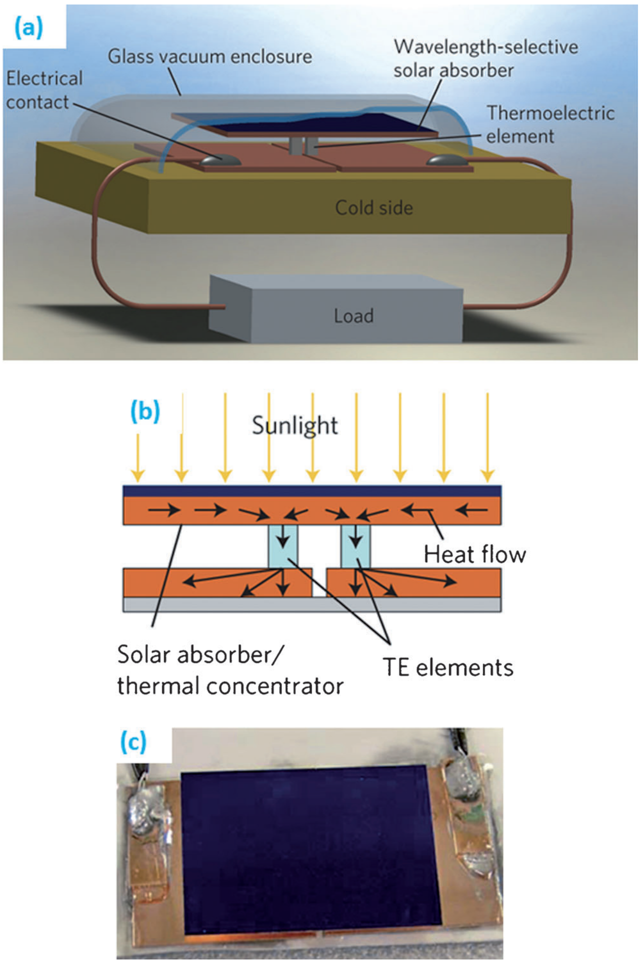

Figure 5. Structure of solar thermoelectric generators (STEGs) based on bulk nanostructured materials. a) STEG cell; b) schematic illustration of thermal concentration; c) photograph of a real STEG device (top view; from Ref. [90], Copyright 2011 Nature Publishing Group).

3.3.2. Low-Dimensional Nanostructured TE Materials

Inspired by previous theoretical predications[91] and enabled by the recently acquired ability to synthesize nanostructured materials of various dimensions,[92] new effective approaches for the modulation and improvement of the TE properties of materials were previously unavailable. These new possibilities mostly involve changes induced by dimension confinement in the electronic band structures as well as enhanced phonon scattering due to the increased size of interfaces and surfaces.[93] The ability to synthesize nanostructured materials with well-defined dimensionalities makes the quantum confinement of electrons in space possible, which further increases the electronic density of states (DOS) near the Fermi level and hence enhances the thermoelectric power factor. Owing to the increased surface-to-volume ratio and thus the amount of surface/interface states, phonon scattering can be significantly enhanced at surfaces and interfaces in nanomaterials without sacrificing electronic conduction, which has been considered the main contributing factor in the substantial enhancement of TE conversion in some applications.[91c,94]

Semiconductor NWs have been investigated as promising TE materials, although the accuracy of ZT measurement in these experiments remains doubtful. One practical challenge in characterizing the TE properties of low-dimensional nanostructures lies in the increasing surface scattering of electrons, which renders these measurements sample-dependent.[95] Among these low-dimensional TE materials, silicon NWs with small diameters exhibit interesting and promising TE properties, with reported a ZT value of 0.6 at room temperature[92b] and a ZT value approaching those of commercial devices at 200 K. However, the fabrication techniques for these nanostructures cannot be readily incorporated with commercial devices and scaled up. Uniformity in TE conversion and other properties of the as-fabricated nanomaterials remain another practical issue which needs proper attention before these nanomaterials can be implemented in any practical applications for TE energy harvesting.

TE generators have been reliably providing power in remote terrestrial and extraterrestrial applications during the past decades.[79b] By integrating material design with advanced fabrication techniques, TE systems can not only harness waste heat from engines at the macroscale to address environmental issues globally, but can also serve as one of the sources for powering small electronic systems in applications such as MNS-based health monitoring by directly converting dissipated heat from the human body into electricity.[80b,96]

3.4. Nanotechnology-Enabled Piezoelectric Mechanical-Energy Harvesting

Vibration-based mechanical energy is ubiquitous in the environment and more accessible than solar and thermal energy. Mechanical vibrations with frequencies spanning a broad spectrum, from a few hertz to several kilohertz, exist abundantly in the ambient, with available energy density ranging from a few hundred microwatts to milliwatts per cubic centimeter.[97] This energy can potentially facilitate the continuous and adaptable operation of sensors as well as electronic devices and systems, especially under circumstances in which other energy sources, such as solar or thermal energy, are not readily available.[7a,98] Several methods have been developed for the conversion of mechanical energy into electricity through the use of electromagnetic induction, static-electricity generation, and piezoelectric materials.[99] The harvesting of mechanical energy by piezoelectric materials in particular has received enormous attention owing to the ability of these materials to convert mechanical energy into electricity directly and the feasibility of this approach for integrated applications. Traditionally, lead zirconate titanate, or PZT, has been the material used most for mechanical-energy harvesting.[100] Nevertheless, the extremely brittle nature of PZT ceramic and the incorporation of lead create issues such as the reliability, durability, and safety of this material for long-term sustainable operation and hinder its application.

Recently, piezoelectric ZnO NWs have been demonstrated to show promise in the harvesting of mechanical energy at the micro-/nanoscale in various nanogenerator (NG) configurations.[101] They exhibited potential as a sustainable, efficient, and environmentally friendly power source for self-powered MNSs. Notably, piezoelectric NWs excel their bulk counterparts in terms of their enhanced piezoelectric effect, superior mechanical properties, and extreme sensitivity to vibrations of ultrasmall magnitude.[97b,102] The kernel of electricity generation under external strain in piezoelectric NWs is the absence of central symmetry in the crystal structure and the existence of piezoelectric potential, or piezopotential, which is also the fundamental concept in the emerging field of piezotronics.[15,103] Theoretical calculations for ZnO NWs in a clamped–free configuration with an external force applied at the free end showed that piezopotential can be induced on the side surfaces of NWs owing to distortion of the crystal lattice; the calculated distribution of the electric field across the NW is shown in the inset in Figure 6.[104]

Theoretical investigations for piezoelectric nanomaterials in various morphologies and configurations have also been carried out subsequently to facilitate fundamental understanding and the design of related devices.[105] In a typical configuration of doubly clamped NWs on flexible substrates, the calculated distribution of piezopotential was shown to be along the *c* axis of the ZnO NW and along the straining direction, with values up to even the hundred-volt range if the substantially decreased carrier concentration was taken into account.[105b] This significant result has directed subsequent advances in the field of NGs (inset in Figure 6). However, previous research suggested that carrier density in ZnO NWs plays an important role in the NG output performance.[106] The experimentally observed output voltage is much lower than the theoretically calculated piezopotential of the material if the material has been doped, as the positive side of the piezopotential induced by mechanical deformation is partially screened by free electrons, which occur dominantly in n-type ZnO NWs. The negative side of the piezopotential is preserved as long as the donor concentration is not too high, as in the case of unintentionally doped as-grown n-type ZnO. Further theoretical calculations predict that the piezopotential is reduced by almost a factor of 10 at the positive side relative to the value at the negative side when the n-type doping level reaches $1\times10^{17}\,\mathrm{cm}^{-3}$. It can therefore be

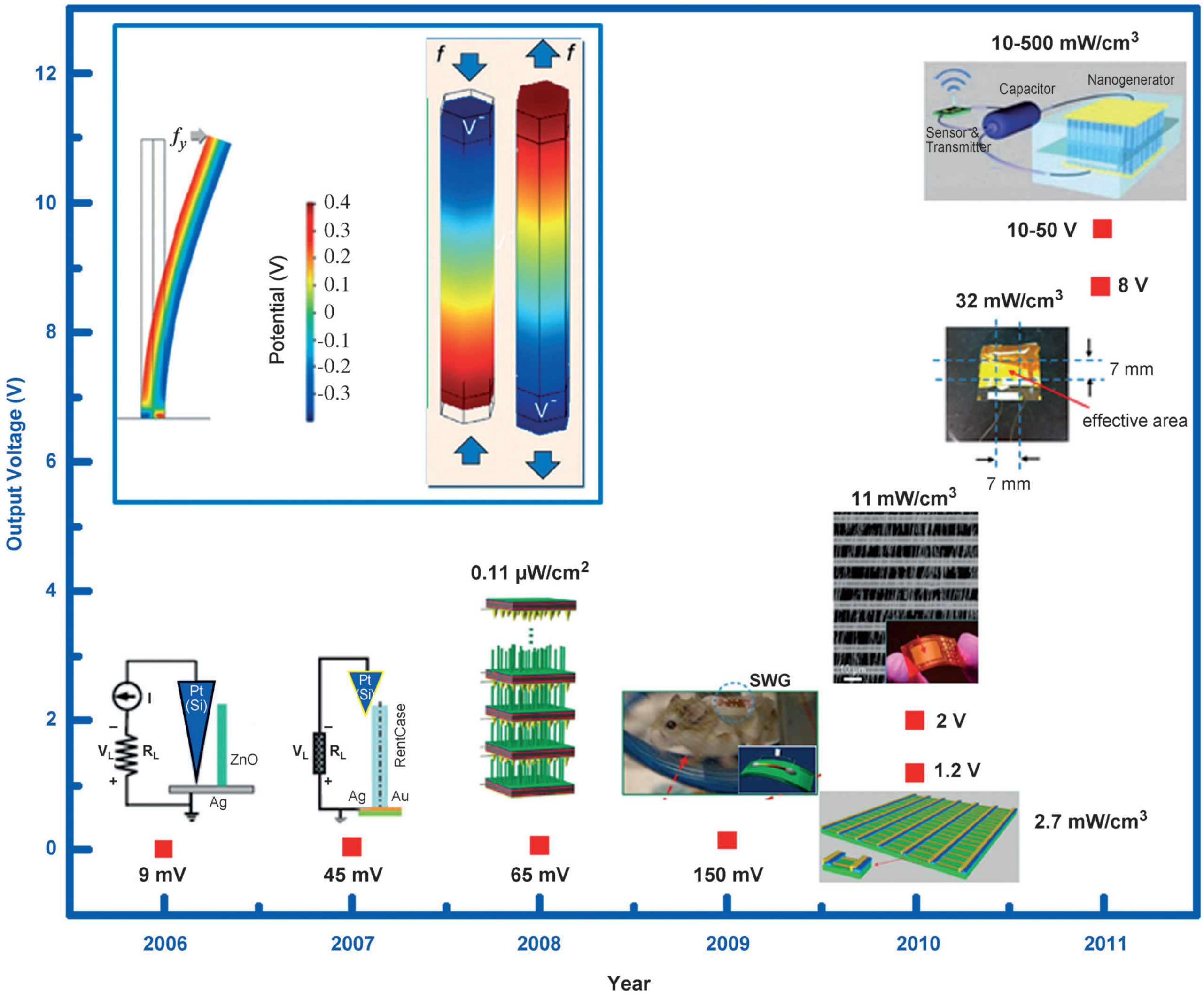

Figure 6. Improvement in the output voltage of nanogenerators based on ZnO nanowires in various configurations. The corresponding output power density is also indicated. The inset shows the simulated piezoelectric-potential distribution in the nanowires of the nanogenerator upon transverse and axial straining (from Ref. [104]). SWG = single wire generator.

expected that piezopotential can be increased significantly if carrier density in ZnO can be decreased by engineering methods.[14a,107] On the basis of these fundamental physical principles, the output of NGs has been improved dramatically in the last few years. Such devices are now suitable for driving commercial electronics. The plot in Figure 6 shows the technological progress we have made in NGs based on ZnO NWs in the last few years.

Strain-induced electricity generation from piezoelectric NWs was first demonstrated by atomic force microscopy (AFM) on vertically aligned ZnO NW arrays in the clamped–free configuration.[108] The Schottky contact formed between the AFM tip and the ZnO NW results in unipolar electrical output (Figure 7a). Similar experiments have been conducted subsequently on single ZnO wires with larger dimensions and NWs of other materials in the wurtzite family, such as CdS, InN, and GaN, with outputs ranging from several millivolts to 1 V.[109] These initial demonstrations of the harvesting of mechanical energy at the nanoscale inspired the development of the first prototype of integrated NGs for potential high-output applications, whereby the usage of AFM tips was extended to a platinum-coated serrated-electrode array, which converted ultrasonically induced vibrations of the vertically aligned ZnO NWs into electricity.[101a] Owing to the in situ rectifying effect of the Schottky contact formed between the top electrode and NWs, the output signal exhibited a direct-current (DC) characteristic with a typical operational power output of approximately 2.5 $\mathrm{nW\,cm^{-2}}$ (Figure 7b). This low power output was attributed to the large internal resistance of the device and the poor contact between NWs and the top electrode.[101a] Subsequent research significantly boosted the performance of DC NGs based on vertically aligned ZnO NWs to an output power density of 0.11 $\mathrm{\mu W\,cm^{-2}}$ at a voltage of 62 mV through pairing of the metal-coated ZnO-nanotip top electrodes with the active ZnO NW arrays in a multilayer stacking configuration[101e] (Figure 7c).

When the configuration of the vertically aligned ZnO NWs was changed from a clamped–free configuration to a clamped–clamped configuration, with both ends fixed by

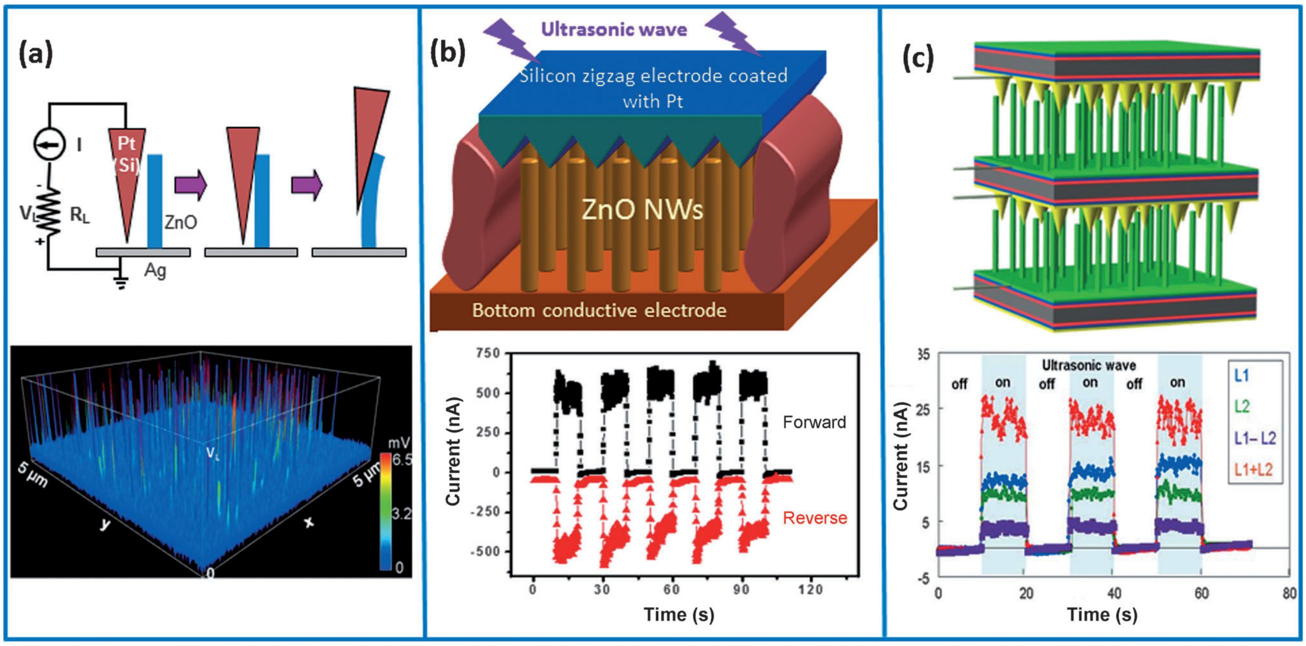

Figure 7. DC nanogenerators based on arrays of vertical nanowires. The three designs (a) from Ref. [108], b) from Ref. [101b], and c) from Ref. [101e]) function by transverse triggering of the ZnO nanowires by metal tips, which form Schottky contacts with the nanowires.

electrodes, the output current type of the NGs switched from DC to alternating current (AC; Figure 8a). More significantly, the performance of these AC NG prototypes was enhanced hugely to a peak power density of approximately 2.7 mW cm^{-3} with an output voltage of up to 0.243 V by three-layer integration. These NGs even outperformed conventional PZT cantilevers and exhibited the potential to power small electronic systems.[110]

Another AC NG prototype was created by the cyclic stretching/releasing of a single piezoelectric fine wire (PFW) that was laterally packaged on a flexible substrate with both ends firmly bound by metal electrodes.[101c] When the PFW was stretched by substrate bending, a piezopotential drop was created along the PFW; the flow of electrons was driven back and forth in the external circuit when the PFW was stretched and released (Figure 8b). Such single-wire AC NGs have been reported to be able to generate an AC output voltage of about 50 mV and to show an energy-conversion efficiency of 6.8% under 0.05–0.1% strain. Flexible AC NGs of this type have been implemented subsequently to harvest biomechanical energy both in vitro and in vivo.[111] The feasibility and potential of the use of flexible AC NGs for harvesting low-frequency mechanical energy from both the environment and a biological entity were thus demonstrated.

Although the use of such flexible AC NGs is a robust approach for harvesting low-frequency mechanical energy, applications of these systems are limited as a result of their low output power. In an effort to increase their power output to a level suitable for practical applications, the design of flexible AC NGs was scaled up to enable the collection of contributions from large NWs simultaneously and collectively, by integrating top-down microfabrication with bottom-up NW synthesis.[101d,110,112] A remarkably high output with an open-circuit voltage of up to 2.03 V and a peak output power density of around 11 mW cm^{-3} was reported for a flexible high-output NG fabricated by a scalable sweeping-printing method[101d] (Figure 8c). The electricity generated was stored and successfully utilized later to light up a commercial light-emitting diode (LED): a landmark step toward the construction of self-powered devices that harvest energy from the environment. Recent advances in the development of high-output AC NGs relax the contact requirement in fabrication. Cone-shaped ZnO NWs and a rational "composite" structure to induce the unipolar assembly of the conical NWs resulted in a macroscopic piezopotential to drive the flow of inductive charges between the top and bottom electrodes[101f] (Figure 8d). The output of such AC NGs, with voltages of about 2 V and a current of about 50 nA, is sufficient to continuously drive the operation of small electronic devices, such as liquid-crystal displays.

NGs based on ZnO NWs can be fabricated on various substrates, including polymers, semiconductors, and metals, and even on unconventional nonplanar substrates, such as fibers. A textile-fiber-based NG has been developed for harvesting low-frequency energy created by vibration and friction,[101b] whereby sliding/deflection between two entangled fibers can result in the deflection of the uncoated ZnO NWs and hence produce a piezopotential for electrical output (Figure 9a). This prototype of a textile-fiber-based NG exmplifies the innovative advances that have been made in the fabrication of flexible, adaptable, wearable, and robust power sources in almost any shape. Moreover, the output can be dramatically increased by weaving bundles of such fibers into fabrics, potentially for applications such as smart clothes. Fiber NGs based on similar configurations were later implemented to harvest low-frequency vibrations induced by an air or liquid flow and by exhalation or the heartbeat of

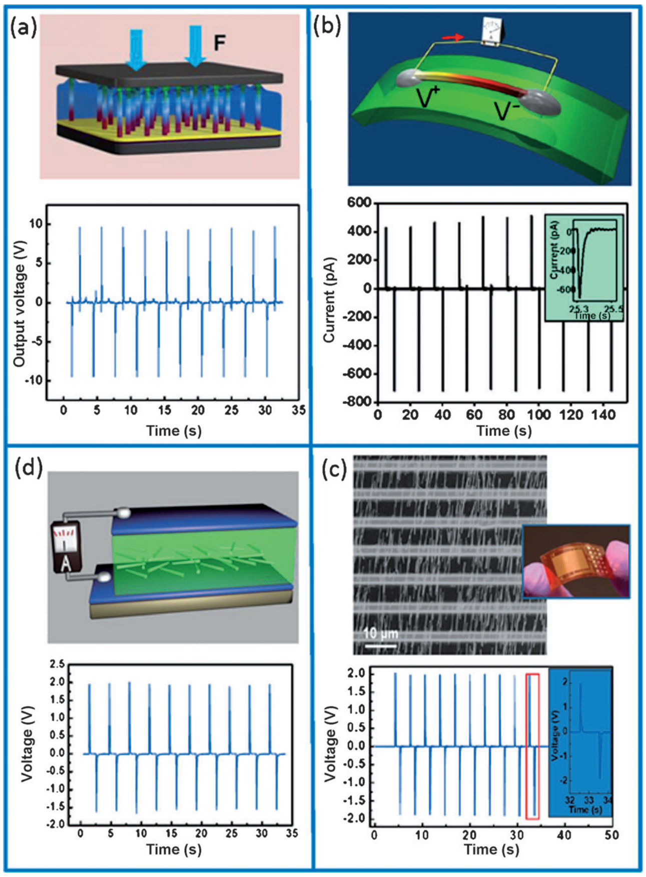

Figure 8. a–c) AC nanogenerators fabricated from vertical or horizontal nanowires that are bonded firmly at both ends to the two electrodes. In these three designs (a) from Ref. [110], b) from Ref. [101c], and c) from Ref. [101d]), one of the contacts has to be a Schottky contact or an insulator between the metal electrode and the nanowires. d) Nanogenerator with a composite structure of the nanowires and a matrix (from Ref. [101f]). This structure leads to macroscopic polarization perpendicular to the film.

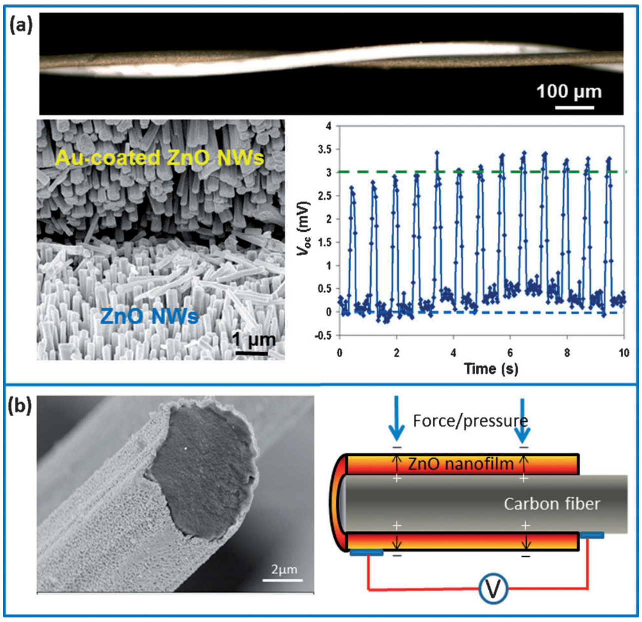

Figure 9. a) Fiber-based nanogenerator based on the principle described in Ref. [95b] (from Ref. [101b]). b) Fiber nanogenerator based on the use of a nanowire film formed on the surface of a carbon fiber (from Ref. [113]). The principle is shown on the right-hand side.

a human body for the generation of electricity or sensing applications (Figure 9b).[113]

ZnO NWs have been the dominant nanomaterial investigated for the development of NG applications. The biocompatibility of ZnO materials also enables potential applications of ZnO-NW NGs in the harvesting of mechanical energy generated by the human body. The human body contains an abundance of mechanical energy induced by continuous activities, such as breathing and the beating of the heart, and discontinuous motions, such as walking and muscle stretching, for powering future MNS-based biomedical devices, health-monitoring units, and even personal computers. Research on NGs for the harvesting of mechanical energy at the micro-/nanoscale has also been carried out with other materials, such as poly(vinylidene fluoride) (PVDF) fibers/belts, PZT nanoribbons, and other semiconductor materials.[112a,b,114] PZT nanoribbons and PVDF microfibers/belts exhibit potential for integration into functional systems as practical powering sources. Single-crystal perovskite materials, such as lead zirconate titanate (PZT), have conventionally been used in devices for piezoelectric energy conversion.[115] Although PZT has a much larger piezoelectric coefficient than other piezoelectric materials, such as PVDF or ZnO, its high permittivity reduces the energy-conversion efficiency, so that its performance is somewhat less than that of ZnO for this purpose. Furthermore, PZT is damaged by the high-temperature process and has limited possible applications owing to its brittleness and rigidity. Because of these characteristics, devices based on PZT can only be subjected to small strain deformations, and PZT can only be integrated with limited classes of substrates.[112b,114f] Thin membranes/ribbons of PZT with a thickness in the nanometer range, which have both a high piezoelectric coefficient and more importantly the flexibility to tolerate large strain deformations, can be transfer printed onto almost any substrate. In particular, deformable and stretchable substrates can be used for adaptive and flexible energy harvesting, although the issues of biocompatibility and environmental impact still need to be properly addressed. PVDF, on the other hand, exhibits good piezoelectric and mechanical properties.[112a,114a] Its chemical stability and biocompatibility also enable its application in sensing, actuation, and energy harvesting in biological systems. However, untreated PVDF can have several mixed crystalline phases. It has to be mechanically stretched and electrically poled to obtain the β phase for piezoelectric applications.[116]

The use of piezoelectric nanomaterials for harvesting mechanical energy at the micro-/nanoscale has demonstrated the potential for applications in future self-powered MNSs. Despite current efforts in material processing and the optimization of NG design, however, the power density and energy-conversion efficiency have to be higher for real applications of NGs in the powering of small electronic devices and micro-/nanosystems to become viable. Moreover, a number of other aspects require proper attention, such as the mechanical properties of the materials at the nanoscale, modulation of the electrical properties of the materials, and the feasibility of manufacturing the materials on a large scale.

3.5. Biofuel Cells (BFCs) for the Harvesting of Chemical/Biochemical Energy

A fuel cell is an electrochemical-energy scavenger that converts the chemical energy of a fuel, such as hydrogen or methanol, into electricity through a chemical reaction with an oxidizing agent, such as oxygen or air.[117] In contrast to batteries, which chemically store electrical energy, fuel cells extract chemical energy from reactants and convert the extracted chemical energy into electricity as long as the reactants are available. Although it is a mature technology that finds numerous practical applications, mostly at the macroscale, conventional fuel-cell technology has several inherent disadvantages, such as the materials used, the fabrication cost, and size restrictions, for the cost-effective powering of MNSs in emerging applications, such as implanted biomedical sensors. A biofuel cell (BFC) is simply a fuel cell which uses biological enzymatic substances, rather than precious metals, to catalyze the anode and/or cathode reactions. BFCs have conventionally been classified into two categories: microbial fuel cells (MFCs) if the catalytic enzymes involved are in living cells, and enzymatic BFCs if the catalytic enzymes involved are located outside of living cells[118] (Figure 11 a). Chemical reactions in BFCs can occur by either direct electron transfer (DET), whereby the electrons transfer directly between enzymes and electrodes, or mediated electron transfer (MET), whereby mediators promote the transfer of electrons between enzymes and electrodes by reducing the kinetic barrier.[118a] In the case of DET, the enzyme needs to be strongly adsorbed onto the electrode surface through either physical or covalent bonding, and the redox center of the enzyme also has to be located adjacent to the electrode for efficient electron tunneling. Such a configuration is difficult to implement as well as detrimental to the enzyme activity. Furthermore, the transfer rate and hence the resultant current densities are low for DET. A direct path for electron transfer between the redox center of the enzyme and the electrode can be provided by immobilizing the redox species of the enzyme on the electrode through conducting linkers or nanostructured conducting paths to improve DET efficiency.[119] However, these methods are either expensive or unreliable for long-term applications. The rate of electron transfer between the active sites of the enzyme and the electrode, and hence the current densities, can be significantly improved by redox mediation in MET. However, the output voltage is lower in the MET process as a result of the mediated transfer, and the range of appropriate mediators is limited to those with redox potentials close to those of the enzymes used in the BFC.

As an emerging technology for the generation of electricity from renewable biomass, MFCs can convert biodegradable organic materials into electricity through microbial catalysis.[120] In contrast to conventional fuel-cell systems, MFCs employ live microbes to efficiently catalyze the degradation of organic substrates through metabolism under mild conditions. Hence, the materials used in MFCs are mostly abundant, nontoxic, and relatively inexpensive.[120b] Although the output power produced by MFCs is still insufficient to drive most electronic devices used nowadays, significant advances have been witnessed in MFC technology during the past decades, including enhanced power densities, improved reliability, and diversified functionality.[121] Recently, new platforms, such as microfluidics, have been introduced in the development of novel MFCs.[122] It has also been demonstrated that the electricity harvested in MFCs can be used in situ to drive other reactions integrated in the same system.[123] Moreover, MFCs can generate electricity renewably while treating waste water simultaneously;[124] they thus exhibit potential as a power source that could be used to drive self-powered sensors in environmental monitoring and possibly in vivo biomedical applications.

Although MFCs exhibit unique features unmatched by those of enzymatic BFCs, such as long-term stability and fuel efficiency, the power densities associated with MFCs are typically lower owing to inefficient mass transfer across cell membranes;[118a] for this reason the application of MFCs in miniaturized electronic devices might be limited. Unlike MFCs, enzymatic BFCs use isolated enzymes derived from living cells for the catalytic generation of electricity. These enzymes can be mass-produced readily and cheaply. Enzymes used in enzymatic BFCs can also process common inexpensive organic compounds that cannot be used in conventional fuel cells with metal catalysts owing to a poisoning effect.[125] In addition to simple BFC structures with enzymatic electrodes immersed in a buffer solution, enzymatic BFCs with more sophisticated designs to improve the conversion efficiency have also been reported, such as the integration of microfluidics[126] or an air-breathing cathode.[127] In enzymatic BFCs, higher catalyst concentrations are possible than in MFCs, and mass-transfer barriers can be readily removed to facilitate the production of higher current and power densities in the sub-$\mathrm{mW\,cm^{-2}}$ range. These fuel cells thus exhibit the potential to power miniaturized devices and systems.[118a] Enzymatic BFCs with a power density of $1.25\ \mathrm{mW\,cm^{-3}}$ were recently created through the use of multistacked structures and were demonstrated to be suitable for driving personal electronics.[127a] On one hand, the operation principle of enzymatic BFCs provides their potential as biocompatible and sustainable power sources for MNS-based in vivo biochemical/biomedical applications through the harvesting of biochemical energy directly from the human body. On the other hand, current BFCs normally suffer poor stability due to the limited lifetime of extracellular enzymes and their inability to fully oxidize fuels.

3.6. Hybrid Cells for the Concurrent Harvesting of Multiple Energy Types

Rationally designed materials and technologies have been developed in the past decades for the conversion of various types of energy, such as solar, thermal, mechanical, and chemical energy, into electricity, as described above. These existing approaches, however, were investigated and developed on the basis of drastically different physical principles and diverse engineering approaches to specifically harvest a certain type of energy, while the other types of energy were wasted. Innovative approaches have to be developed for the conjunctional harvesting of multiple types of energy through the use of integrated structures/materials, so that all available energy resources can be effectively and complementarily utilized.[24] On a smaller scale, the temporal/spatial distribution and availability of energy sources for driving MNSs vary drastically. The concurrent harvesting of multiple energy types from the ambient environment by a single integral device has therefore emerged as a promising approach toward the sustainable and maintenance-free operation of MNSs. Ever since the first demonstration of a nanotechnology-enabled hybrid cell (HC) by the Wang research group for the simultaneous harvesting of multiple types of energy with a single device,[128] this technology has been advancing at an increasing pace.

3.6.1. *Hybrid Cells for the Harvesting of Solar and Mechanical Energy*

The first nanotechnology-enabled hybrid cell was developed by the Wang research group in 2009 for harvesting solar and mechanical energy with a single energy harvester. The device essentially integrates a DSSC and a piezoelectric NG, both of which are based on an array of ZnO NWs, on a common substrate.[128] The cathode of the NG and the anode of the DSSC were integrated on the same silicon substrate to form a serial connection between the DSSC and the NG. The DSSC and NG units in the HC can work independently when a source of either solar or mechanical energy is available. It has also been demonstrated that the HC can harvest both the solar and the mechanical energy simultaneously and synergistically. However, reliability issues imposed by solvent leakage and evaporation as a well as the low power output hinder the practical application of this HC. A prototype of a compact HC in which an NG based on a ZnO-NW array was integrated with a solid-state DSSC showed enhanced performance and durability owing to the introduction of a solid-state electrolyte and convolute structures formed between the NG and the DSSC[129] (Figure 10).

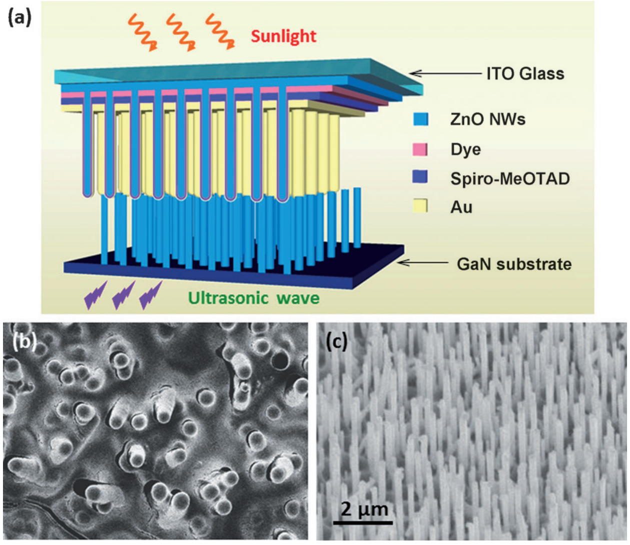

Figure 10. a) Compact hybrid-cell structure consisting of a solar cell and a nanogenerator. The hybrid cell is illuminated by sunlight from the top and excited by ultrasonic waves from the bottom. b,c) The fabricated top and bottom components of the hybrid cell. The hybrid cell simultaneously harvests solar and mechanical energy (from Ref. [129]). Spiro-MeOTAD = 2,2′,7,7′-tetrakis(*N*,*N*-di(4-methoxyphenyl)-amino)-9,9′-spirobifluorene.

Choi et al. later described a flexible HC based on a ZnO-NW array that overcomes the disadvantages of the above HC prototypes of cross-talk and additional assembly processes.[130] The ZnO-NW array in this flexible HC not only serves as the NG, but also acts simultaneously as the solar cell part of the device by integrating with an infiltrated organic polymer. One significant characteristic of this flexible HC is that the output signals from the solar-cell part take the form of a direct current, whereas the output signals from the NG originally occur as an alternating current. By controlling the mechanical straining process, the AC signals can be converted into DC-like signals. Owing to the controllability of the output behavior, the performance of the HC can be synergistically enhanced by the contribution of the NG part. Lee et al. demonstrated a conceptually similar HC prototype based on the integration of a ZnO-NW NG with infiltrated quantum dots (QDs), which surrounded the NWs. This HC was specifically developed for harvesting sound and solar energy simultaneously.[131] A further demonstration of the integration of multiple energy harvesters together with a storage device along a single fiber involved the use of ZnO nanowires (NWs) and graphene.[132] This approach allows simultaneous harvesting of solar and mechanical energy and in situ storage of this harvested energy for potential applications in flexible and wearable electronics.

3.6.2. *Hybrid Cells for the Harvesting of Biomechanical and Biochemical Energy*

There has been an increasing need for sustainably powered implantable wireless micro/nanodevices for in vivo biomedical applications, preferably without the incorporation of batteries. One viable approach is to concurrently harvest energy from multiple energy sources within the biological entity. Inherently, mechanical and biochemical energy due to body motion, muscle stretching, and metabolic processes abound in the biological entity. A prototype hybrid energy-scavenging device was developed to address the above application needs through the direct harvesting of mechanical and biochemical energies in a biofluid environment.[133] This hybrid energy scavenger consists of a piezoelectric PVDF-nanofiber NG for harvesting mechanical energy, such as from respiration and blood flow in the vessels, integrated with a flexible enzymatic BFC for harvesting the biochemical energy from the chemical processes between glucose and O_2 in biofluid. These two energy harvesting approaches, integrated within one single device, can work either individually or synergistically. This HC for harvesting biomechanical and biochemical energy has similar disadvantages to previous HCs: the separate arrangement of the two components on the substrate without sophisticated integration leads to engineering problems, such as cross-talk, and hence deteriorated overall performance. To solve this problem, a compact structure was developed by the integration of a ZnO-NW NG and a BFC on single carbon fiber.[134] The NG for harvesting mechanical energy is based on a textured ZnO-NW film and is grown radially on the carbon fiber, which serves as both the core electrode and the substrate for ZnO growth (Figure 11 b). The BFC for converting chemical energy from the ambient biofluid is fabricated at the other end of the same carbon fiber. Elimination of the separating membrane and mediator significantly reduced the size of the BFC relative to that of conventional BFCs. The integrated structure improves the performance as well as the adaptability of the HC for harvesting biomechanical and biochemical energy.

3.6.3. *Hybrid Cells for the Harvesting of Solar and Thermal Energy*

During the PV conversion process in solar cells, a big proportion of the wasted energy is converted into heat, which leads to a temperature rise in the solar cells. Furthermore, incident photons with longer wavelengths, which cannot participate in PV conversion, may also be converted into heat. To improve the conversion efficiency and fully utilize the solar spectrum, Guo et al. designed an HC to harvest solar energy as well as the concurrently generated heat.[135] The two-compartment hybrid tandem cell consists of a DSSC and a thermoelectric cell (TC). Solar energy is first converted into electricity in the DSSC, and the heat induced during this process is then transmitted to the TC for subsequent TE conversion. This HC is more efficient than a single harvester and fully utilizes the energy from the solar spectrum. Recently, a novel photovoltaic–thermoelectric (PV–TE) hybrid device composed of a series-connected DSSC, a solar-selective absorber (SSA), and a TE generator was reported with a significantly enhanced efficiency of 13 %.[136]

Although the concept of hybrid energy harvesting and the proposed approaches described above are promising, several practical issues need to be addressed before real applications of these prototypes are possible. One of the biggest issues is network matching between different energy harvesters. The power output from different harvesters differs significantly. Strategic approaches for matching and reconciling the different outputs should therefore be implemented. On the other hand, solutions to the current problems might also impart increased cost as well as difficulties in manufacturing. Overall, it can be anticipated that the concept of hybrid energy

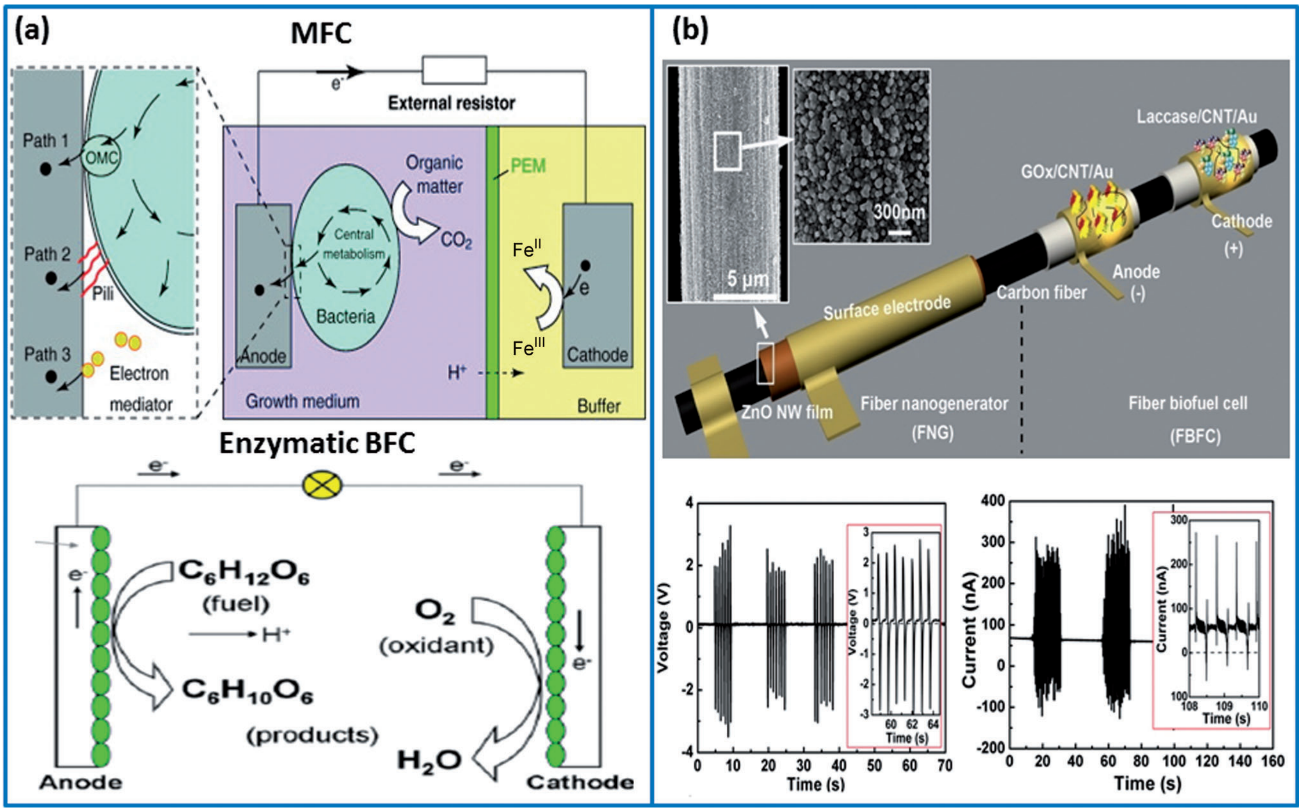

Figure 11. a) Operation principle of a microbial fuel cell (MFC; from Ref. [120b], Copyright 2011 Elsevier) and an enzymatic biofuel cell (BFC; from Ref. [118b], Copyright 2010 MDPI AG). b) A hybrid cell fabricated along a single carbon fiber. Part of the hybrid cell is the nanogenerator for mechanical-energy harvesting, and part is a biofuel cell for biochemical-energy conversion. The output corresponding to each part of the hybrid cell is shown below the structure (from Ref. [134]). CNT = carbon nanotube, GOx = glucose oxidase, OMC = ordered mesoporous carbon, PEM = proton-exchange membrane.

harvesting will play a critical role in the implementation of novel sustainable micro-/nanotechnology with more flexibility and adaptability. It can also be expected that more sophisticated hybrid energy-scavenging devices that are capable of concurrently harvesting even more types of energy may be developed.

4. Self-Powered Micro-/Nanosystems

4.1. Concept of the Self-Powered MNS

The current rapid advancement of micro-/nanotechnology will gradually shift its focus from the development of discrete devices to the development of more complex integrated systems that are capable of performing multiple functions, such as sensing, actuating/responding, communicating, and controlling, by the integration of individual devices through state-of-the-art microfabrication technologies. Furthermore, it is highly desired for these multifunctional MNSs to operate wirelessly and self-sufficiently without the use of a battery, especially in applications such as remote sensing and implanted electronics. This operation scheme will not only extend the life span and enhance the adaptability of these MNSs while greatly reducing the footprint and cost of the entire system, but it will also increase the adaptability of these MNSs to the environment in which they are deployed. As the dimensions of individual devices shrink, the power consumption decreases accordingly to a reasonably low level, so that energy scavenged directly from the ambient is sufficient to drive the devices. The concept of self-powered nanotechnology was first proposed and developed by the Wang research group,[7b,c,25,108,137] with the aim of building a system that operates by harvesting energy from the ambient vicinity of the system and converting it into usable electrical power for wireless, self-sufficient, and independent operations. A typical self-powered MNS should consist of a low-power microcontroller unit, high-performance data-processing/storage components, a wireless signal transceiver, ultrasensitive sensors based on micro-/nanoelectromechancial systems (MEMSs/NEMSs), and most importantly the embedded powering/energy-storage units (Figure 12).

4.2. Examples of Self-Powered Sensors and Systems

Extending the initial concept of self-powered micro-/nanotechnology, the Wang research group demonstrated the first integrated self-powered nanosystem on a large scale without an external power supply. Within this system, the NW pH sensor and the UV sensor were driven by an integrated ZnO-NW NG.[110] Self-powered nanoelectronic systems based on discrete core/shell silicon-NW photovoltaic devices have also been demonstrated,[14c] and a DSSC based on high-density arrays of vertically aligned ZnO nanotubes has been investigated as the power source to drive a humidity sensor.[138]

Intensive research effort has since been invested in the development of self-powered MNSs, and various prototypes have been reported. A self-powered wireless transmission system composed of an NG for harvesting mechanical energy, a low-loss full-wave bridge rectifier with a capacitor for storing the energy, an infrared photodetector, and a wireless data transmitter was shown to transmit data wirelessly and

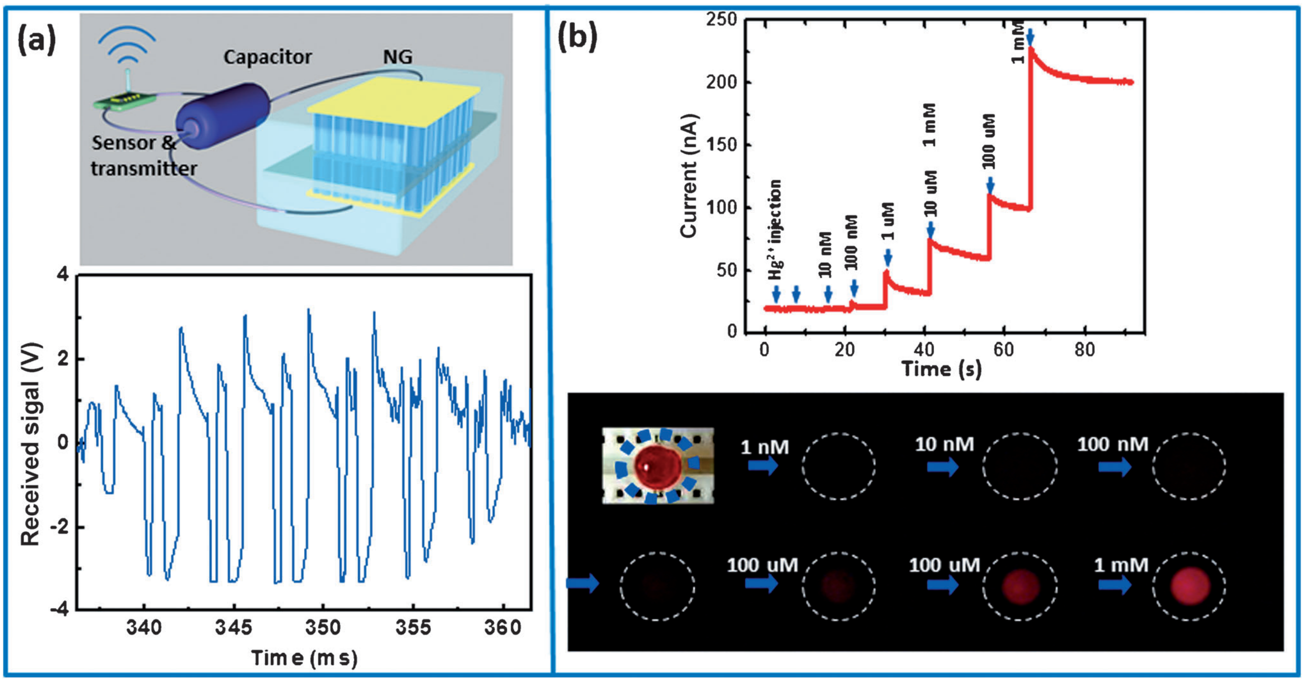

Figure 12. Self-powered nanosensor systems for a) optical sensing with wireless data transmission (from Ref. [13b]) and b) Hg^+ sensing with an indication signal (from Ref. [131]).

self-sustainably (Figure 12a) and demonstrated the potential of ZnO-NW NGs in applications of wireless biosensing, environmental/infrastructure monitoring, and wireless sensor networks.[13b] In another example, a fully stand-alone, self-powered environmental sensor based on a single-walled-CNT (SWNT) field-effect transistor (FET) and a ZnO-NW NG was implemented for the detection of Hg^{2+} ions and evaluation of their concentration in water.[139] This application is of potential importance for the monitoring of water quality. The sensor array based on the SWNT network served as the Hg^{2+} sensor, and the ZnO-NW NG served as the energy-harvesting component (Figure 12b). In a recent study, a ZnO-NW NG was integrated onto the inner surface of a tire to scavenge mechanical energy from deformation of the tire during motion, and the harvested energy was used to power a liquid-crystal-display (LCD) screen.[107] A similar approach could be used to develop a self-powered tire-pressure sensor and speed detector for mobile vehicles. The feasibility of building self-powered nanodevices for in vivo biomedical applications has also been investigated, with the use of harvested biochemical energy[140] or a combination of biomechanical and biochemical energy[133,134] to power NW-based sensors. The seminal studies carried out by Wang and others have inspired rapid progress in the field of self-powered micro-/nanotechnology worldwide in applications ranging from corrosion monitoring to distributed sensing and environmental monitoring.[141]

4.3. Prospects and Challenges in the Development of Self-Powered MNSs

It can be anticipated that self-powered MNSs will play a critical role in the implementation of implantable electronics, remote and mobile environmental sensors, nanorobotics, intelligent MEMSs/NEMSs, and portable/wearable personal electronics. Self-powered MNSs are also key components of large-scale fault-tolerant sensor networks. When traditional discrete sensors are replaced by a large number of sensor nodes distributed in a field, the statistical analysis of signals collected through the network of distributed sensors can provide precise and reliable information for tracking and monitoring purposes. An internet of things which can correlate objects/products and devices with databases and networks is expected to revolutionize the future of health care, medical monitoring, infrastructure/environmental monitoring, logistics, and smart homes.[142]

One decisive factor for the implementation of self-powered MNSs is the successful development of energy-harvesting technologies to provide appropriate power sources that operate over a broad range of conditions for extended time periods with high reliability. For comparison, the major energy-harvesting techniques discussed herein and their prospects for application in self-powered MNSs are summarized in Table 1.

Despite the excellent progress that has been made in the emerging field of self-powered micro-/nanotechnology, several issues still need to be addressed appropriately for the promised potential of self-powered micro/nanotechnology to be fully realized. The design/fabrication flow for the development of future self-powered MNSs should be amenable to scaleup and, critically, be compatible with the microfabrication technology. Almost all prototypes demonstrated to date were fabricated at a level unsuitable for mass production. State-of-the-art microfabrication technologies were hardly used, which severely prohibits the broader implementation of current self-powered MNSs. Moreover, future self-powered MNSs should be implemented in such a way that multiple types of energy can be harvested synergistically by hybridized systems with sufficiently high outputs. Finally, to enable not only the self-sufficient but also the sustainable operation of the deployed devices/systems in applications such as wireless biomedical sensing, the development of self-powered MNSs from materials which are environmentally friendly, biocompatible, and biodegradable is essential. When these issues are addressed properly, sustainable self-sufficient micro-/nanosystems will play a critical role in the advancement of the important fields of sensing, medical science, infrastructure/

Table 1: Comparison of energy-harvesting techniques and their potential for self-powered MNSs.

Energy source	Harvesting principle	Approximate power density	Advantages	Disadvantages	Potential applications in self-powered MNSs
solar	photovoltaic	10–100 $mW\,cm^{-2}$	microfabrication compatible, mature technology, long lifetime, high power output	limited by environmental conditions, not applicable in biological entities	remote sensing and environmental monitoring
thermal	thermoelectric	10–100 $\mu W\,cm^{-2}$	no moving parts required, long lifetime, high reality, continuous output	low efficiency, large size, a large and sustained thermal gradient is required	structural-health monitoring for engines and machines, wearable biomedical devices
mechanical vibrations	piezoelectric	1–10 $mW\,cm^{-2}$	ubiquitous and abundant in the ambient, broad frequency and power ranges	low efficiency, discontinuous output	remote sensing and environmental monitoring, structural- health monitoring, wearable systems, in vivo applications
biochemical	biochemical reactions	0.1–1 $mW\,cm^{-2}$	biocompatible/degradable, clean energy, environmentally friendly, inexpensive, abundant in biological entities	low power output, poor reliability, limited lifetime	in vivo applications, environmental monitoring/sensing

environmental monitoring, defense technology, and even personal electronics.

Addendum

Triboelectric Nanogenerators

Recently, a triboelectric nanogenerator (TENG) has been fabricated by stacking two polymer sheets made of materials having distinctly different triboelectric characteristics with metal films deposited on the top and bottom of the assembled structure.[143] Once subjected to mechanical deformation, a friction between the two films, arising from the nanoscale surface roughness, generates equal amounts of charges of opposite signs at the two sides. Thus, a triboelectric potential layer is formed at the interface region if the generated triboelectric charges are separated by a small distance. The TENG gives an output voltage of up to 18 V at a current density of about 0.13 uA cm^{-2},[144] but recently an output voltage of approximately 200 V was reported.[145] TENGs have the potential to harvest energy from human activities, rotating tires, ocean waves, mechanical vibration, and more. They have great potential applications in self-powered systems for personal electronics, environmental monitoring, medical science, and even for large-scale power.

Pyroelectric Nanogenerator

Harvesting thermoelectric energy mainly relies on the Seebeck effect, which utilizes a temperature difference between two ends of the device to drive the diffusion of charge carriers. However, in an environment in which the temperature is spatially uniform without a gradient, the pyroelectric effect can be used, which is based on the spontaneous polarization in certain anisotropic solids as a result of a time-dependent temperature variation. By using this effect, we demonstrated the first application of pyroelectric ZnO nanowire arrays for converting heat energy into electricity.[146] The coupling of the pyroelectric and semiconducting properties of ZnO creates a polarization electric field and charge separation along the ZnO nanowire as a result of the time-dependent change in temperature. Pyroelectirc nanogenerators can also be fabricated by using a nanowire composite material or a thin film.[147]

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