Wireless Sensor Networks and Chemo-/Biosensing

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1. Introduction

The concept of 'wireless sensor networks' or WSNs is relatively new, probably less than 10 years old, and a logical extension of the greater 'networked world' through which a large proportion of the world's population is already connected, for example, through mobile phones and other digital communication platforms. It envisages a world in which the status of the real world is monitored by large numbers of distributed sensors, forming a sensor 'mesh', that continuously feeds data into integration hubs, where it is aggregated, correlations identified, information extracted, and feedback loops used to take appropriate action. The entire system, in its ultimate manifestation, will be composed of interlocking layers of sensors that can be characterized in terms of their fit into a hierarchical model based on complexity (and therefore dependability) with feedback equally divided into layers of complexity (e.g., local vs aggregated). University engineering groups and electronics companies such as INTEL have driven much of the early research in this area. Given the diversity of technologies and disciplines involved and the ubiquitous nature of its impact in a wide variety of application sectors, it is impossible to cover everything in appropriate detail, even in a comprehensive review such as this. We therefore apologize in advance to those readers whose work or area of interest is not included. Our particular emphasis in this review is to give a general overview of aspects of the area we feel are important to readers of *Chemical Reviews*, and hence, we will focus particularly on both the opportunities for researchers involved in chemo-/biosensing and the challenges that they must confront in order to ensure there is an appropriate fit between chemo-/biosensing and communications technologies.

Hence, the review is organized into several sections: (1) Developments in low-power wireless communications focusing on so-called 'motes' rather than mobile phone technologies as these have been designed specifically with wireless sensing in mind; applications of mote-based networks will focus on environmental deployments; (2) Wearable sensors and applications in personal health monitoring; (3) Futuristic concepts in chemo-/biosensing focused on control of surface binding and fluid movement.

2. Internet-Scale Sensing and Control

Early champions of the concept of Internet-scale control were the TJ Watson-based IBM researchers Alex Morrow and Ron Ambrosio.[1] According to their vision of 'Internet-Scale Control' the future world will operate on the basis of complex interlocking control loops that range from localized sensor−actuator systems to platforms that aggregate information from multiple heterogeneous sources. In the latter, specialized software routines trawl through huge information

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Dermot Diamond received his PhD from Queen's University Belfast (Chemical Sensors, 1987), and was vice president for Research at Dublin City University (DCU), Ireland, (2002–2004). He has ublished over 150 peer reviewed papers in international science journals, is a named inventor in 12 patents, and is coauthor and editor of two books, 'Spreadsheet Applications in Chemistry using Microsoft Excel' (1997) and 'Principles of Chemical and Biological Sensors', (1998) both published by Wiley. He is currently the Director of the National Centre for Sensor Research, one of the largest sensor research efforts worldwide (see www.ncsr.ie) and a Science Foundation Ireland Principle Investigator (Adaptive Information Cluster award, see www.adaptiveinformation.ie). He is a member of the editorial advisory boards of the international journals Talanta (Elsevier) and The Analyst (RCS). In 2002, he was awarded the Inaugural Silver Medal for Sensor Research by the Royal Society of Chemistry. He was awarded a DSc in July 2002 by Queen's University Belfast.

Shirley Coyle received her BEng in Electronic Engineering in 2000 from Dublin City University, Ireland. She then worked in the Information and Communications division in Siemens Ltd. for 2 years before commencing a PhD study in the field of Biomedical Engineering. The focus of this research was to develop a brain computer interface using optical brain imaging techniques. She received her PhD from the National University of Ireland Maynooth in 2005. Her research interests combine her biomedical engineering background with a longstanding interest in apparel design - wearable sensors and smart textiles for healthcare management. She has worked on the EU FP6 'Biotex' project, which is a European-wide multipartner research effort to merge sensing capabilities with fabrics and textiles. She is currently studying for a diploma in fashion design at the Grafton Academy of Dress Designing.

repositories searching for patterns and correlations, which can form the basis of responses to multiple action points. This is represented in a simplistic manner in Figure 1. Conventionally, the engineers who dominated this area over the past decade promote this as the merging of the 'real and digital' worlds. However, introducing chemo-/biosensing extends this vision to the merging of the 'molecular and digital' worlds, with chemical sensors, biosensors, and analytical devices providing a window between these worlds.[2]

Silvia Scarmagnani studied pharmaceutical chemistry in the University of Padua where in 2006 she received her Master Degree (Honors) in "Pharmaceutical's Chemistry and Tecnology". She carried out her master thesis (based on the synthesis of Antitumor Agents derived from Hydroxybenzaldehyde) in collaboration with Cardiff University, United Kingdom. In 2006 she started her PhD in Dublin City University, Ireland, where she is currently investigating the development of adaptive surfaces for optical sensing using molecular photoswitches under the supervision of Prof. Dermot Diamond.

Jer Hayes received a B.A. (Hons) in Psychology from University College Dublin in 1997 and completed an MSc. in Computer Science in 2003. He has researched Natural Language Processing, esp. in relation to semantics. More recently he worked on a project testing and further developing a wireless sensor network for monitoring the temperature of fish catches from ship to shore and onto the processing plant which was funded by Bord Iacaigh Mhara. He has also worked on wireless sensor networks as applied to water purification process monitoring and gas detection. He is currently involved in a desk-study for the Marine Institute investigating data management and communication issues for marine sensor systems.

In principle, if this vision is realized, it holds that the digital world can sense, interpret, and control the real world at the molecular level. Interestingly, it also means that the digital world approaches the complexity of the real world, and each can be regarded as a mirror of the other. This raises the interesting concept of 'soft-sensors' (i.e., software code whose function is to seek out specific patterns in data) which, in some ways, mimic the behavior of real sensors, for example, in terms of selectivity (detect a specific pattern) and transduction (generate a signal).

Hence, the real world will be mapped to the digital world by vast numbers of networked sensors of various levels of complexity and capability which are autonomic in nature in that they are self-sustaining for extended periods of deployment. However, the cost of reliable autonomous chemo-/biosensing is still far too great for massively scaled-up deployments, even for obvious applications in environmental

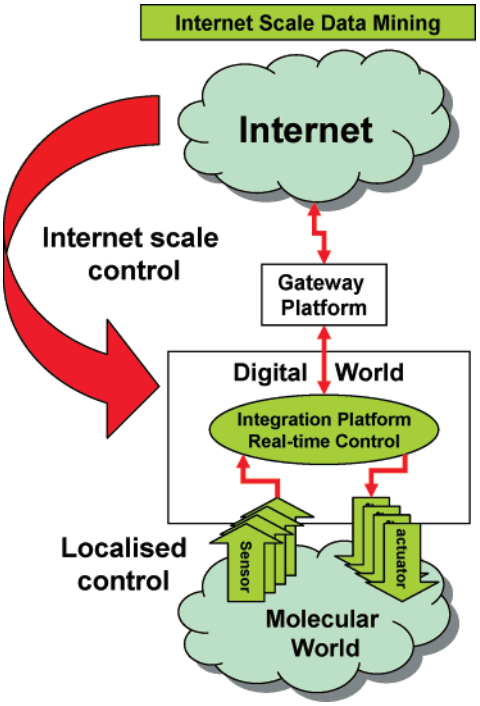

Figure 1. Concept of internet-scale control: conventionally control loops operate at a localized level with sensors monitoring one of more key parameters at one or more locations (bottom). Actuators are used to control the system being monitored on the basis of various algorithms. When the sensed information is passed through to the Internet, it is aggregated with other information streams emanating from a wide variety of sources. Specialized software seeks to identify patterns and correlations across the resulting hugely diverse data reservoirs which can be used to modify the system at the Internet scale.

monitoring or the rapid detection of bio-/chemowarfare agents. This cost base is due to the complexity of the processes that occur during chemo-/biosensing and particularly the need to include regular recalibration because of, for example, changes in the chemistry of the sensing surface that inevitably occur through exposure to the real world.[3] In this review, we will examine developments in wireless sensor platforms that are helping to drive the area forward and discuss how these platforms will stimulate demand for compatible approaches to chemo-/biosensing in areas like environmental monitoring and wearable sensing for vital signs monitoring. Potential routes to delivering reliable autonomous chemo-/biosensing platforms capable of some degree of scale up will be examined, like microfluidics. Finally, we will highlight the critical role of fundamental materials science research in bridging the very significant gap between what the chemo-/biosensor community can currently offer and what is needed to realize this vision.

3. WSN Platforms

3.1. Building Blocks of Autonomous Sensing Platforms

In engineering parlance, a sensor *node* is the smallest component of a sensor network that has integrated sensing and communication capabilities. It contains basic networking capabilities through wireless communications with other nodes as well as some data storage capacity and a microcontroller that performs basic processing operations. They usually come with several on-board transducers for temperature, light level, etc., and increasingly a sensor board that usually slots onto the controller board. This allows the user to interface other sensors, including chemo-/biosensors to the mote, provided the signal is presented in the appropriate form for the controller. They also include a power supply, usually provided by an on-board battery.

Ultimately, the goal is that WSNs will evolve into long-lived, open, ubiquitous, multipurpose networked systems that continuously feed sensed data into the networked world. However, in order for the required massive scale up in numbers to happen, these devices must be completely self-sustaining over extended periods of time (up to years). In recent years, there has been a focus on power consumption as the small lithium button batteries commonly employed have limited lifetime and regular manual replacement is unrealistic. The sensor nodes within a wireless sensor network are also commonly referred to as “motes”. Much of the early research into mote platforms happened in California, led by people like Deborah Estrin and David Culler at Berkeley and Kris Pister (originally at UCLA but now at Berkeley). The most widely used motes in recent years have been those provided by Crossbow Technologies Inc., based in San Jose, CA, which is a spin off from the Berkeley groups (www.xbow.com). The importance of this research was recognized by the establishment of the ‘Centre for Embedded Networked Sensors’ (CENs) in 2002 through the NSF Science and Technology Centre program.[4] Pister is also CTO of the company Dust Networks, which is making rapid headway in the commercialization of mote-based sensing. See the website www.dustnetworks.com for more information.

According to Wang et al., the hardware requirements for wireless sensors include robust radio technology, a low-cost and energy-efficient processor, flexible signal inputs/outputs for linking a variety of sensors, a long-lifetime energy source, and a flexible, open source development platform.[5] They also outline a number of software requirements for a wireless sensor node which include a small footprint capable of running on low-power processors, small memory requirement, and high modularity to aid software rescue. Thus, the basic components of a sensor node are a microcontroller, radio transceiver, set of transducers, and power source, and the software which runs on these nodes must be small and allow for efficient energy use.

With some motes, such as those provided by uParts,[6] a number of sensors are already built onto the mote and further sensors cannot easily be added. However, many motes have the capability to add specific expansion boards, which allow a wide variety of sensors to be attached. The motes listed in Table 1 share a number of common features such as the use of low-cost energy-efficient reduced instruction set computer (RISC) processors with a small program and data memory size (about 128 kb) and battery power supply. The typical interfaces are common on-board I/O buses and devices, e.g., the Universal Asynchronous Receiver-Transmitter (UART), timers, and analog-to-digital converters. A number of motes are displayed in Figure 2. In comparison to the current generation of laptops, motes have tiny amounts of memory and use low-powered processors, and they are therefore very challenged in terms of computational capability.

In the simplest case, motes are programmed before deployment to perform measurements at a particular sampling rate and return the captured data in a prearranged format. In more sophisticated deployments, the motes are programmed

Table 1. Comparison of Currently Available Motes and Motes in Real-World Applications

sensor platform	processor	memory	radio	interface	power supply
uNode	TI MSP430 at 4.6 MHz	10k RAM, 48k flash	868/915 MHz transceiver, 50kbs	12 bit ADCs (8), DACs (2), and GPIO (8)	coin cell
Tyndall25	ATmega128L	128 kB	2.4 GHz ISM band (nRF2401 from Nordic VLSI)	modular architecture	coin cell
uPart	PIC12F675 at 4 MHz	n/a	transmitter in 868, 914 MHz band communication or 433, 310/ 315 MHz band	on-board sensors: movement, light sensor, temperature, 1 LED, power regulation for unit	coin cell
Particle	PIC 18F6720 at 20 MHz	4 kB RAM, 1 kB EEPROM, 512 kB FLASH	rf communication through RFM TR1001, 125 kb bandwidth, 868.35 ISM band Europe	21 pin multipurpose connector with I2C, SPI, serial (625 kbps), parallel bus, analog input lines, interrupt input lines, digital I/O lines	1 AAA battery
Mica2	ATmega128L	flash memory 128 kB, measurement (serial) flash 512 kB, configuration EEPROM 4 kB	315, 433, or 868/916 MHz multichannel radio transceiver	10 bit ADC; other interfaces DIO, I2C, SPI	2 AA batteries
Mica2Dot	ATmega128L	flash memory 128 kB, measurement (serial) flash 512 kB, configuration EEPROM 4 kB	868/916, 433, or 315 MHz multichannel transceiver	10 bit ADC other interfaces DIO, 18 pin expansion board	3 V coin cell
Micaz	ATmega128L at 8mhz	flash memory 128 kB, measurement (serial) flash 512 kB, configuration EEPROM 4 kB	2.4 GHz IEEE 802.15.4	51 pin expansion connector supports analog inputs, digital I/O, I2C, SPI and UART interfaces	2 AA batteries
Imote2	Intel PXA271 Scale processor at 3−416 MHz	SRAM memory 256 kB, SDRAM memory 32 MB, flash memory 32 MB	CC2420 IEEE 802.15.4 radiotransceiver 2.4 GHz band	USB client mini-BB), SB host UART 3×, PIOs, 2 C, SDI0, SPI 2×, 2 S, AC97, camera	3 AAA batteries
Tmote Sky	8 MHz Texas Instruments MSP430 microcontroller	10k RAM, 48k flash	Chipcon wireless transceiver 2.4 GHz IEEE 802.15.4	integrated ADC, DAC, supply voltage supervisor, and DMA controller integrated humidity, temperature, and light sensors	2 AA batteries
Tmote Invent	8 MHz Texas Instruments MSP430 microcontroller	10k RAM, 48k flash	250 kbps 2.4 GHz IEEE 802.15.4 Chipcon wireless transceiver	integrated light, temperature, acceleration, and sound sensors	rechargeable lithium ion battery
BTnode(rev2)	ATmega128L.	128 kB flash 4 kB SRAM, 4 kB EEPROM	Ericsson Bluetooth module	10-bit analog-digital converter, I2C bus, and two hardware UART	3 cell battery pack

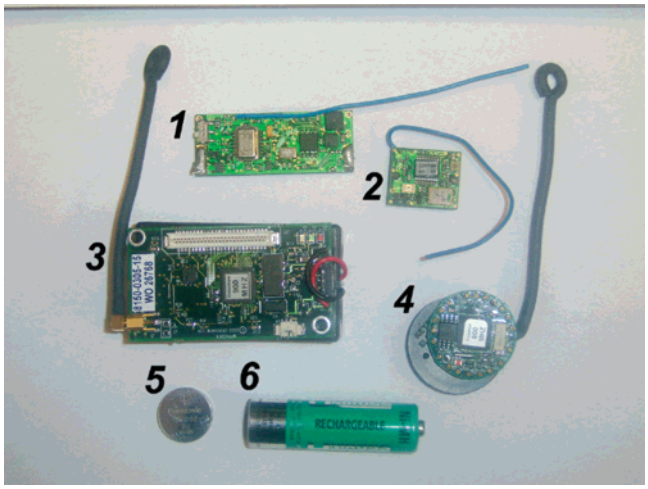

Figure 2. In the above image the following are displayed: (1) Teco Particle, (2) Teco uPart, (3) Micaz, (4) Mica2Dot, (5) coin cell battery, and (6) AA battery. The batteries offer a way to compare the relative size of the motes. Indeed, the actual size of a mote is generally constrained by the size of the power supply (the battery).

to facilitate sampling rates that adapt to external events and function cooperatively in terms of finding the optimum route for returning data to remote base stations. A new standard for smart sensors is also under development (IEEE 1451).[7] This "Smart Transducer Interface Standard" will enable Transducer Electronic Data Sheets (TEDS) to be attached to compatible transducers, which stores the following information: sensor identification (ID), calibration, measurement range, and manufacture-related information. While such data sheets are commonplace for transducers like thermistors (and include circuits for various specific applications), they tend to be less popular with chemo-/biosensors due to the increased complexity of their behavior and response characteristics.

3.2. Linking the Sensor into Communications Infrastructure

Due to the limited computing power of sensor motes, they often employ an operating system called TinyOS,[8] although more recently, products that are fully 'C' compliant have become available, and these are generally preferred by experienced programmers. TinyOS is an operating system written in the nesC programming language,[9] which is a dialect of C[10] specifically designed for restricted operating environments as exists on sensor motes where there is limited memory and processor power available. TinyOS has an extensive component library that includes network protocols, sensor drivers, and data acquisition tools, which can be used either as is or modified for custom applications. The operating system supports a large number of sensor boards and can be used with the most popular mote sensor platforms.

With respect to WSN deployments, they can either be deterministic or self-organizing. In a self-organizing deployment the routes to pass information between the nodes are determined by the network itself. In theory, multihop routing is more desirable as the transmission power of a radio is theoretically proportional to the distance squared (or even higher orders in the presence of obstacles), and multihop routing will therefore consume less overall energy than direct communication to a remote base station. However, this must be balanced against the increased incidence of data corruption or loss of data packets, which tends to increase with the number of motes involved in relaying the information.

In practical terms, a random spatial deployment of sensor nodes without information on their location can be problematic as the time series data must be tied to a particular place to be of any real use. At present, locations are recorded manually in most deployments, which obviously inhibits large-scale deployments. Increasingly, GPS chips are being included on motes, but this comes with a cost and energy requirement that must be built into deployment considerations.

3.3. Wireless Communications Options

The communication standards for sensor networks in practice breakdown into general ISM band multichannel RF, the ZigBee protocol (IEEE 802.15.4), and the Bluetooth protocol (IEEE 802.15.1).[11] In addition to these low-power, relatively short distance platforms, other forms of wireless communication can be used such as short-range and point-to-point infrared (IrDA), wireless local area networks (i.e., 802.11 wireless LAN as embodied in Internet hotspots and laptop computers), and GSM mobile phone technology, with the latter being used over longer distances.

Deployments typically include a gateway node or base station that allows data transfer with other communications networks. In some scenarios the gateway node or base station is connected directly to a PC or laptop and the communication capabilities of the attached machine are used, for example, to transfer data to a web site. In other cases where WSNs are deployed in remote locations, a base station with built in communication capabilities such as GSM (where a signal is available) is used to simultaneously harvest the information from local motes (e.g., using Zigbee) and act as a gateway to the Internet.[12]

Briefly, both Bluetooth (802.15.1) and ZigBee (802.15.4) run in the 2.4 GHz unlicensed frequency band, use low power, and have a small form factor. The ZigBee standard is intended for consumer electronics, PC peripherals, medical monitoring, toys, and security and automation applications in buildings/homes. These applications require a technology with the ability to easily add or remove network nodes. ZigBee was developed largely for in-door use with rf signals being able to pass through most walls and ceilings,[13] while Bluetooth was initially oriented toward user mobility and replacement of short cables (e.g., between phone and headset). However, Bluetooth can also support ad-hoc networks over a short range. With the IEEE 802.15.4 protocol and the IEEE 802.15.1 protocol becoming more widespread there will be movements toward more interoperability between WSNs based on different physical sensor boards using the same communications protocol. Both Bluetooth and ZigBee have been designed for short range, although this range can be extended up to 75 m for ZigBee and 100 m for Bluetooth using more specialized chipsets and antennae. However, these are essentially short-range systems and will tend to be confined to situations that conform to this limitation such as within rooms or vehicles.

WSNs can be deployed using a number of network topologies such as 'star', 'tree', and 'mesh'. These network topologies determine the way in which nodes receive and transmit messages to each other. In a star topology there is a central hub to which all other nodes send and receive data. The hub needs to be more sophisticated than the other nodes to carry out message and data handling. In this type of network topology the central hub is a base station or gateway

node. In the tree topology, there again is a central root node but it communicates with only one level beneath it in the hierarchy and the nodes at this lower level in turn only communicate with a parent node and child nodes. This tree topology is less common than the mesh topology, where nodes in the network can communicate with any other node that lies within range (the nearest neighbors). As sensor nodes can be in contact with more than one neighbor there are usually multiple routing paths between nodes. The shortest distance is usually the favored route to the base station, but mesh networks can use alternative pathways where nodes fail and so are somewhat more robust. In reality a single network can be composed of several subnetworks which are composed of different topologies. For example, using Bluetooth a maximum of 8 nodes, out of a total of 256 devices, can actively communicate in a star-shaped cluster, called a piconet. In a piconet the central hub of the star topology is called a 'master', while the other nodes are called 'slaves'. However, piconets can also be interconnected via 'bridge nodes', and the resulting linked piconets together form a 'scatternet'. A bridge is a node which participates in more than one piconet on a time-sharing basis. The mesh network topology is appropriate for ad-hoc networks where nodes enter and leave the network at different times (e.g., when nodes are mobile).[14]

ZigBee can also support star topologies and mesh topologies. With ZigBee technology, the central hub is the coordinator and this node needs to store information about the network and act as a bridge to other networks. The other types of nodes in a ZigBee network are 'router nodes', which just pass data, and 'end-device nodes'. An end device can only communicate with its parent in the network. ZigBee operates in two main modes: nonbeacon mode and beacon mode. In the former, the router nodes periodically transmit beacons to each node, which wakes up each device and allows this device to return data if needed. This mode results in low power consumption as the end device can be maintained in a low-power sleep mode unless needed, and this can result in significant energy savings. In contrast, in nonbeacon mode any device can communicate with the coordinator and the coordinator must therefore always be awake to listen for communications. This requires more power for the coordinator device and may result in data loss, for example, when multiple end devices attempt to communicate with the coordinator at the same time.[11]

3.4. Examples of Mote-Based Environmental Sensing Deployments

In this section we will briefly examine six real-world deployments of mote-based wireless sensor networks for environmental sensing. We have chosen these deployments as they give a flavor of how current WSN technology is *actually* being used, as opposed to futuristic views on what WSNs *could* be used for, which at times can be misleading and over-optimistic. These deployments also highlight some advantages and some issues with deploying WSNs in the real world. The examples are (1) vineyard monitoring, (2) tree microclimate, (3) natural habitat monitoring, (4) intruder detection over a very wide area, (5) volcanic activity, and (6) soil moisture monitoring.

3.4.1. Example 1: Vineyard Monitoring

The vineyard deployment involved a sensor network comprising 64 Mica2 motes which were employed to monitor temperature over a hectare section of a vineyard for 30 days.[15,16] The motes were deployed in a grid and configured as a multihop network with a maximum depth of eight nodes. The sensor nodes were static (being placed 1 m off the ground), and the routing of messages across the network was determined before the network was deployed. Two pathways for upstreaming data were chosen. The network was composed of 16 backbone nodes, and associated with each backbone node were 3 sensor nodes. The backbone nodes could send packets up to 25 m, while the sensor nodes sent packets up to 15 m.

Data were recorded every 5 min, and during the deployment two arctic fronts moved across the vineyard. Between the sampling points, sensor nodes remained in sleep mode to conserve energy. All nodes had 43 amp hours of battery power, but the backbone nodes had to be changed every 6 weeks. However, one of the interesting aspects of the study was the difference in the expected success of data delivery and the actual data delivery in the field. Beckwith et al.[15] suggest that in-lab performance resulted in 99% of packets being delivered. The predicted performance for an eight-hop packet getting through was 92%, but over the course of the real deployment the actual success rate was 77%. This performance was based on sending the same data multiple times (five times from each sensor node), the performance deteriorating at higher transmission frequencies. Beckwith et al.[15] also reported that nodes would occasionally leave the network, i.e., they would lose contact with the rest of the network. If this happens to a backbone node then all the data from the associated sensor nodes can be lost. Despite these issues, the vineyard deployment allowed collection of dense information on the temperature of a vineyard over an extended period of time. They discovered that the regions of highest temperature changed from day-to-day throughout the vineyard. This type of information is important as it can identify regions within the vineyard that will be more susceptible to mildew attack and can therefore be used to determine a targeted and optimized spraying regime to minimize product loss and hence maximize yield.

3.4.2. Example 2: Tree Microclimate

In this case, a network of 33 Mica2Dot motes was deployed in a 70 m tall redwood tree to monitor the surrounding microclimate over a period of 44 days.[17] The sensor nodes monitored temperature, relative humidity, and photosynthetically active radiation, with the choice of phenomena measured guided by the biological research priorities. For example, data on temperature and relative humidity can be fed into transpiration models for redwood forests, and the photosynthetically active radiation data provides information about energy available for photosynthesis in redwood forests.

The sensor node was based on a Mica2Dot that had sensors for temperature, relative humidity, solar radiation (direct and ambient), and barometric pressure on board. The whole sensor node was encased in a specially designed housing to protect the components from physical damage during the deployment. To keep the WSN running for as long as possible without having to change batteries, the sensor nodes were activated for only 4 s to take measurements and data was transmitted at 5 min intervals for a period of 44 days. As the data was sampled every 5 min, large quantities of data were collected. Tolle et al.[17] suggest that each sensor

node acquired 50 450 data points and that 1.7 million data points in total should have been collected by the deployed network. However, only 820 700 data points were collected, meaning that only 49% of the possible data points were actually received. This suggests that WSNs should have a large degree of redundancy built in so that not every data point is required for decision making. Despite these losses in data gathering, Tolle et al.[17] were able generate rich information on the mesoclimate of the redwood tree that previously had not be accessible.

Arising from this study it was also apparent that some sensor nodes returned anomalous readings.[17] These sensors either never produced readings in the expected normal range or produced readings that did not tally with other sensors. It was found that battery failure correlated strongly with these anomalous findings.

3.4.3. Example 3: Habitat Monitoring

Szewczyk et al.[18] incrementally deployed two sensor networks of increasing scale and complexity in a wildlife preserve in order to monitor the distribution and abundance of sea birds on Great Duck Island (Maine). It was assumed that passive infrared (PIR) sensors could directly measure heat from a seabird in a burrow and that temperature and humidity sensors could measure variations in the ambient conditions of the burrow, which would indicate the length of occupancy.

Sensor nodes were deployed in various groupings referred to as 'patches' which involved either a line, a grid region, or a volume of nodes for 3-D monitoring. Each sensor patch had a gateway that sent data back via a transit network to a remote base station. The base station was located on a PC and provided database services and Internet connectivity. The sensor nodes were based on the Mica2Dot mote with two classes of sensor node deployed: a 'weather' mote and a 'burrow' mote. The weather mote was used to monitor the microclimate around a burrow and measured humidity, temperature, and atmospheric pressure. The sensors onboard the burrow mote measured temperature and humidity and had PIR sensors to detect burrow occupancy. This mote had to have a small form factor so it could be placed in a burrow.

Two network topologies were employed, namely, single hop and multihop. The single-hop network was deployed in an elliptic shape and covered 57 m. No routing was performed by the nodes, and data was passed straight through to the gateway system. The gateway system was composed of two motes with one in contact with the sensor nodes and other in contact with the base station. Data was sent every 5 min. The second sensor network was a multihop network which was kite-shaped, 221 m long, with a maximum width of 71 m, narrowing to 8 m. This network sampled data through to the gateway system every 20 min as a result of routing beacons transmitted by the gateway node to seed the network discovery process. Both networks operated on different radio frequencies with the single-hop network using the 433 MHz band and the multihop using the 435 MHz band. This was done to eliminate potential interference between the networks.

During the 115 day deployment, the networks produced in excess of 650 000 observations. It is difficult to judge the relative effectiveness of the two networks as a performance breakdown in relation to each network is not given, which is unfortunate. However, in relation to lab-based predictions compared against real-world applications, Szewczyk et al.[18] were able to accurately predict the lifetime of the single-hop network but not the multihop network. In particular, the impact of multihop traffic on power source consumption was underestimated. They also state that the quality of a mote's sensor readings was strongly dependent upon the mote power availability, which is in accordance with the previous case.[17] Consequently, it is vital to ensure that sensing motes have adequate power that can cope with extended periods of deployment.

3.4.4. Example 4: Intruder Detection over a Very Wide Area

Arora et al.[19] outlined the biggest current deployment of a WSN with respect to the number of sensor nodes and area covered. The central idea behind the project was to deploy a dense wireless sensor network that would be a virtual "tripwire" over a large area. The WSN would detect, track, and categorize "intruders" that enter the area covered by the network. The project involved two demonstrations with the first comprising 90 Mica2 motes that were deployed over a 25 m $\times$ 10 m grassy area. The second used over 1000 'XSM' motes as sensor nodes and 300 'XSS' gateway motes.

These XSM (extreme scale motes) do not appear to be publicly available and so are not listed in section 5.1, although they were commercially available previously under the trade name 'MSP410CA Mote Security Package'. They are based on an Atmel ATmega128L microcontroller, a Chipcon CC1000 radio operating at 433 MHz, and a 4 Mb serial flash memory. The mote has four PIR, two magnetometer and acoustic sensors, and the entire device is housed in a rugged weatherproof package.

The sensors nodes were deployed in such a way that more than one (up to five) would be triggered if an intruder (a person) entered the area covered by the WSN. More would be triggered if a larger object such as a vehicle entered the area. The coverage area was large compared to other WSN deployments—1.3 km by 300 m. This deployment involved two tiers, the 1000 sensor nodes and 300 gateway nodes. The PIR sensor surface charge varies in response to the received infrared radiation emitted from a body, giving an indication that someone is present. However, a polyethylene film was placed on the PIR windows to reduce the effect of sunlight and increase the robustness of the sensor. The raw data from the sensors also had to be analyzed in such a way as to isolate sensor signals from the slower background variations rising from temperature-based drift using a digital band-pass filter.

3.4.5. Example 5: Volcanic Activity

This network consisted of 16 nodes equipped with seismic and acoustic sensors deployed over a 3 km aperture on the Volcán Reventador in northern Ecuador.[20] The network was deployed for 3 weeks, and the data collected was routed over a multihop network and a long-distance radio link to a laptop sited at a remote observatory. The volcano is active, and at the time prior to deployment, seismic activity such as tremors and shallow rock fracturing had been recorded. The network consisted of 16 sensor nodes with each sensor node equipped with seismic and acoustic sensors. The nodes were built around the Moteiv TMote Sky wireless sensor network node and included a seismometer, microphone, and custom hardware interface board. These sensors draw a lot of power, and consequently, sensor nodes were powered by D cell batteries. Over the course of the 3 week trial, batteries were

Table 2. Summary of Real-World WSN Deployments

project	no. of motes	phenomena measured	sensor platform	types of sensors used	longevity
vineyard	64 (48 sensor nodes)	temperature	Mica2	thermistors	30 days
macroscopic forest	33	temperature, humidity, photosynthetically active radiation	Mica2dot	PIR	44 days
Exscal	1000*	PIR	XMS	PIR	
Great Duck Island	98 (62 burrow motes, 26 weather motes)	burrow motes: temperature and humidity sensors, infrared temperature sensor	Mica2dot	Sensirion SHT11, Intersema MS5534A barometer, TAOS TSL2550 light sensors, Hamamatsu S1087 photodiodes	burrow motes: 52 days
		weather motes: temperature, humidity, barometric pressure		Intersema MS5534A	weather motes: 120 days
soil moisture	9 (4 were sensor nodes)	soil moisture	Mica2	soil moisture sensor	28 days
volcano eruptions		seismic waves	Tmote Sky	seismometer	3 weeks

Table 3. Comparison of Commercially Available Batteries

type	typical lowest voltage output, V	typical highest voltage output, V	lowest capacity	highest capacity, Ah
alkaline	1.5	15	18 mAh	27
lithium	1.5	9	2.2 mAh	35
zinc carbon	1.5	9	405 mAh	16.5
lead acid	2	12	1 Ah	70
lithium rechargeable	3	15	1 mAh	6.8
nickel cadmium	1.2	24	1.25 mAh	4.5
nickel metal hydride	1.2	24	12 mAh	10

changed between 4 and 5 times. During the duration of the deployment, the network detected over 200 seismic events.

3.4.6. Example 6: Soil Moisture

Cardell-Oliver et al.[21] reported a wireless sensor network deployment that monitored soil moisture. The network also monitored rainfall and adjusted the frequency of measurements accordingly, i.e., when a heavy rainfall occurs the measurement frequency is increased. The purpose of the study was to monitor changes in the spatial distribution of soil moisture over time. The WSN was built around Mica2 motes as the sensor nodes and base station. Three motes had two soil moisture probes (the Echo20 soil moisture probe) attached as sensors. Another mote was connected to a tipping bucket rain gauge, while a fifth mote was used as a base station (which had GMS capabilities) and another four were used for routing. As the network needed to react to events such as a sudden rain fall, the network could not just sleep and wake up to sample at predetermined times over the course of the deployment. Rather the sensor nodes had to wake up and check regularly if an event had occurred. For this to happen every node on the network (base station, router nodes, and sensor nodes) had to be awake at the same time.[21]

The WSN was structured in such a way that the soil moisture readings from the sensor nodes were transmitted over five sensor network hops before reaching the base station. If any of these single-network hops failed then a reading would be lost. Over the first 13 days a total of 434 soil moisture messages were triggered but only 277 were logged, which is an overall delivery rate of 63.8%. However, Cardell-Oliver et al.[21] report that despite these losses, the deployment met the ultimate goal of providing useful data on dynamic responses of soil moisture to rainfall.

Table 2 compares these deployments in relation to how many sensors were used, what was "sensed", what type of sensors were used, and the longevity of deployment. The deployments vary in the number of motes deployed with the Exscal project having the largest scale,[19] while the period of the deployments ranges from 3 weeks to 120 days. Information on the loss of packets is also summarized where this is available. Glasgow et al.[22] in their discussion of real-time water quality monitoring describe a 92% data accuracy rate of one project as disappointing. From this perspective, the effectiveness of these WSN deployments is also disappointing but not unexpected. With wireless communications in the ISM bands used by these motes environmental factors will interfere with the signal. These performance rates of packet delivery are an indicator of problems that will affect WSNs in scaled-up deployments, as this will become much worse as the complexity and scale of the network increases.

3.5. Discussion and Conclusions

These deployments share a number of things in common. Generally in undertaking the deployment the researchers have to choose the wireless platform to use and the appropriate sensors to attach to these platforms. When the hardware has been chosen the researchers have to decide where the sensor nodes will be physically located and how they will operate cooperatively, e.g., single hop versus multihop. If a multihop architecture is chosen then the most appropriate routing algorithm must also be decided upon.

A number of issues become apparent from these deployments. For example, it is clear we are still a long way from the vision of large-scale deployments over wide geographical areas for long-term monitoring applications of any kind. It is also clear that massive scale up can only happen if the motes are essentially self-sustaining in all requirements. In terms of energy sources, at present, batteries are currently extensively employed in sensor networks. Table 3 compares the characteristics of a variety of available batteries. While battery performance has clearly improved in recent years and with power efficient sensors (like thermistors) it may be possible to achieve several years of autonomous operation, for chemo-/biosensing platforms battery power supply is at best only an interim solution as the power demand is much greater (see discussion below). For scale up, the inescapable conclusion is that each mote must incorporate a local energy

Table 4. Typical Power Consumption of Sensors and Sensor Components

sensor/sources	typical power consumption (mW)	examples
thermistors	<1	Radionics 813-806
light-dependent resistors (LDRs)	250	NORP12
LEDs	30	Standard
laser diodes	225	SIGMA/635/1
metal oxides	280	Figaro TGS2611
IR gas sensors	6000	KT sensor (PPM 4022H)
electrochemical: pH electrodes	50	Global water 407228 pH/mV

Table 5. Power Consumption of Components of an Autonomous Reagent-Based Analyzer

component	power consumption
photodiode	33 mW (10 mA, 3.3 V)
microprocessor (normal operation)	19.8 mW (6 mA, 3.3 V)
pump	3.6 W (300 mA, 12 V)
GSM: idle mode	300 mW (25 mA, 12 V),
TX burst mode	30,W (2500 mA, 12 V)

generation or scavenging capability that can provide enough power for the device to carry out all functions. Sources include small solar panels, wind/water turbines, and vibration energy, and it is not surprising that research to integrate appropriately scaled local energy sources to motes is rapidly gaining momentum.[23] Outdoor solar energy is a promising source with current technologies providing energy densities of ca. 7.5 mW/cm^2, a figure that is likely to increase significantly given the tremendous research activity in this area. For more background on the potential of local energy scavenging/harvesting to power autonomously deployed sensors, including wearable devices, the reader is referred to recent excellent reviews.[24,25]

In terms of distributed chemo-/biosensing, the energy demands and reliability *of the sensor* will be very significant limiting factors. Table 4 summarizes the power demand of some sensors and sensing components. Immediately, one can understand why temperature sensing is the first parameter that researchers focus on and why it is often built into sensing motes as a 'give away'. These are very low-cost (ca. $1−5), rugged, reliable, and consume virtually no power. Light detectors like LDRs are also popular, as they are also low-cost (ca. $2−5), rugged, and reliable, although they consume considerably more power. Chemosensors consume considerably more energy than thermistors and are much more expensive. For example, a single IR gas sensor (Table 4) will consume the same energy per unit time as several thousand thermistors, and the Figaro gas sensor range is priced from ca. $20 to $2000 per sensor. Interestingly, the cost of laser sources for optical sensing continues to drop. We use LEDs for many optical sensing applications because of their low cost, reliability, and relatively low power demand. However, for applications where sensitivity is an absolute requirement, laser diodes may be substituted for LEDs, bearing in mind that the power demand is increased by an order of magnitude.

With autonomous chemo-/biosensing platforms there are other demands on the power of the system beyond that of the sensor itself. In particular, incorporation of regular recalibration further increases the energy demand of autonomous chemo-/biosensing platforms beyond that normally encountered in physical sensing platforms. Table 5 compares the energy demand of various components used in an autonomous phosphate analyzer employing reagent-based chemistry in a microfluidic manifold that is typical of many devices of its kind.[26] From this it is clear that liquid pumping and GSM communications dominate the power demand. The wireless communications power issue is the subject of very considerable research activity worldwide, driven by huge commercial opportunities (e.g., personal communications, mobile computing, RFID, etc.), and it is likely that solutions will be found that will be employed in autonomous analytical devices. However, the issue of liquid handling is much more specific to analytical science, and this will be the key limiting factor inhibiting chemo-/biosensor network deployments for applications involving liquid-phase measurements (e.g., water quality monitoring). The solution is either to use communities of very simple (noncalibrated) devices that do not employ liquid handling or to develop completely new ways to move liquids around in fluidic manifolds, for example, through fundamental breakthroughs in materials science that will facilitate very low energy liquid movement within a microfluidic manifold. The importance of fundamental materials science to the future of chemo-/biosensor networks is discussed in more detail below.

Another factor that influences greatly the power demand of an instrument is the duty cycle (i.e., the time it is 'on' or in active mode compared to the time it is 'off' or in sleep mode). This in turn is related to how long it takes for the instrument to perform a complete measurement (including calibration and diagnostics) and how often this measurement must be performed. For more sophisticated and power-hungry instruments, the overall power demand can be reduced by maximizing the 'off' time relative to the 'on' time. This can be achieved by minimizing the number of measurements (a somewhat contradictory tactic as the function of the device is to perform measurements) and reducing the measurement time. This latter factor is determined by characteristics such as manifold dead volume, flow rate, and detector/electronics 'wake up' time. The employment of microfluidics is therefore an attractive option as this greatly reduces dead volume and analysis times, leading to a much more efficient system in terms of power demand. It is likely that power-hungry systems will be used to provide highly reliable validation measurements in future hierarchical deployments with the duty cycle linked to information provided from the sensor network (i.e., sampling frequency is increased at times when a dynamic event is predicted to be imminent by the network).

Considering the above discussion, it is understandable why mote-based deployments focus almost entirely on relatively simple transducers (thermistors, photodetectors, movement/vibration sensors, etc.) that require little power and are reliable over long periods of time. Another critical difference between chemo-/biosensors and these transducers is that transducers are invariably completely encased within a rugged encapsulant (e.g., epoxy) and yet continue to function, whereas chemo-/biosensors *must* be exposed directly to the real world (which in many cases can be a very hostile environment), and this constitutes a significant point of weakness for the entire device. One strategy to overcome this is to separate out the sensing and sampling functions using a fluidic manifold. For example, in water quality applications, water samples may be drawn in through an appropriate filter into the device where it is analyzed and stored for later disposal. However, for extended use, this means that all reagents must be stable in storage for at least

months (preferably several years) and the quantities used must be minimized, for example, using microfluidics (see below). This strategy allows the sensing to be performed within the relatively benign environment of the microfluidic manifold rather than in the sample.[27] Clearly, microanalytical instruments are much more sophisticated sensing devices than those employed in current WSN research, and despite the relatively small reagent consumption, they will have to be serviced or collected eventually, which acts against the realization of very large scale deployments. An alternative strategy that has great promise is to incorporate the chemical sensing film into RFID tags such that the response generated in the film modulates the response characteristics of the tag. In contrast to mote-based sensing, this platform has no inherent networking communications overhead, does not require a battery, and is very low cost and yet capable of very sensitive measurements to the parts per billion level of polar volatiles.[28] This type of imaginative approach to distributed chemical sensing is much more likely to lead to large-scale deployments than the current manifestations of mote platforms.

4. Body Sensor Networks

4.1. Wearable Sensors

Traditionally our clothes function as a protective layer, offer comfort and aesthetic appeal, and serve communication and cultural purposes. Moving beyond these functions, textiles provide a pervasive platform upon which to build sensor networks. Through integration of novel technologies our clothing will be equipped with information and power transmission capabilities, sensory functions, and an infrastructure for embedded microsystems.[29,30] This additional functionality has important applications in areas like personalized healthcare, athletic performance, threat detection, and future fashion trends. Given that most people these days are connected to digital communications via a mobile phone, the issue is focused on how to realize a body sensor network (BSN) that is linked to the external world via the mobile phone; for an excellent overview of this area, see ref 31. This means that the distances involved are much smaller and can be covered using a combination of low-power wireless communications and integrated conducting tracks embedded in the fabrics. There are major forcing driving this area forward, principally based around the concept of personal health or pHealth. This concept has arisen as a response to the unsustainable increase in healthcare costs worldwide due mainly to an epidemic of 'life-style' diseases arising from unhealthy diet and lack of exercise, such as obesity, cardiovascular disease, diabetes and chronic respiratory disease. There is a very significant focus on research related to pHealth in the European Union 7th Framework Programme, and an annual series of conferences in pHealth has recently commenced in an effort to structure this effort across many diverse disciplines (see, for example, the 4th pHealth conference, website 'pHealth 2007' at http://phealth2007.med.auth.gr/). Body sensor networks, or wearable sensors, is a major theme within pHealth as, in principle, it allows an individual's vital signs and physical activity to be tracked and monitored remotely. This is a technology that is certain to make a major impact on society within the next 5 years—the first commercial consumer products are beginning to appear, like the 'Nike-iPod sport kit' launched in May 2006 (see www.apple.com/pr/library/2006/may/23nike.html). At the annual MAC-World event earlier this year, it was announced that this product had realized sales of 500 000 units in the first 90 days since launch, which translates to a market of ca. $100 million for this product alone. The kit enables users to log activity through an accelerometer sensor embedded in an exercise trainer shoe that transmits data (such as number of steps, distance covered) wirelessly to an iPod (see www.apple.com/pr/library/2006/may/23nike.html). At the moment, this product is being used by joggers, but given the enormous impact of inactivity on healthcare costs, it is clear that its use will quickly be extended to encourage individuals at risk of obesity-linked diseases to exercise regularly. This in turn will create a framework within which demand for more specific information offered by chemo-/biosensors will rise rapidly, but once again, as for environmentally deployed mote-based sensing, the sensor configuration, form factor, and operating specifications will have to meet with the expectations of the users.

As an intermediary interface, wearable sensors have the potential to monitor and respond to both the wearer and his or her environment. Given the intimate connection with the wearer, garments may accommodate sensors placed in close proximity to the skin that look into the physiology of the body, e.g., breathing rate, body temperature, and heart rate. Conversely, clothes act as our protective shield, and sensors may be configured to look outward to the environment and identify any potential hazards that may endanger the wearer, e.g., the presence of toxic gases for emergency disaster workers.[32]

In order for the technology to be accessible it must remain innocuous and impose minimal intrusion on the daily activities of the wearer, and consequently, the sensors must monitor in a discreet manner that is easy to use. Therefore, wearable technologies should be soft, flexible, and washable to meet the expectations of normal clothing. Data transmission must be wireless to allow free movement of the wearer, and a means of feedback must be provided to the wearer through visual, tactile, or auditory means. The type and frequency of such feedback is largely application dependent and dynamic in nature, and context awareness is therefore a crucial feature in generating user feedback. Context awareness involves knowledge about the user (motion, activity, gestures, health status), the environment (weather, lighting, noise), and social influences (other people sharing information with an individual). Control systems are needed to perform data fusion from multiple sensors, data filtering, feature extraction, and classification approaches to take these factors into account in decision making.

Smart fabrics (in which sensing capabilities are integrated with the textile) are capable of sensing environmental conditions or stimuli arising from various sources (mechanical, thermal, photonic, chemical, electrical, or magnetic). They may also be able to respond to signals through actuators creating a fabric with inherent motor functionality. Conventional electronic components are hard and brittle, which lends to an inharmonious integration into the soft textile substrate. While electronic components are being continuously miniaturized, in order to preserve the inherent mechanical properties of clothing, the ultimate objective is to directly integrate the sensing capability into the textiles themselves, i.e. the fabric becomes the sensor.

4.2. Functionalized Fabrics

The first stages in wearable computing research involved adorning the wearer with conventional electronic devices. However, this resulted in problems related to washability, comfort, and flexibility.[33,34] For sensing technologies to be adopted by the clothing industry, aesthetic properties such as the handle, drape, and comfort of the fabric and garment must not be compromised. The cost factor is also a major challenge as the sensors must be priced appropriately in line with the application.

Conductive textiles (i.e., fabrics with integrated conductive polymer threads[35] or conductively plated fabrics and fabrics with embedded metallic fibers[36]), while originally developed for their antistatic behavior, can form the interconnection substructure required for wearable circuitry. Materials such as metallics, optical fibers, and conducting polymers may be integrated into the textile structure, thus supplying electrical conductivity and sensing and data transmission capabilities. The successful development of electronic textiles must take into account traditional textile manufacturing techniques in addition to the properties of the finished garment, e.g., metal threads tend to be heavier than most textile fibers, and their brittle characteristics can damage spinning machinery over time.[36] Woven optical fiber textiles must consider bending of the fiber during the manufacturing process and also with the end product, as bending and mechanical damage cause light to escape and hence signal loss.[37] Polymer electronic devices may provide a solution to overcome the stiffness of inorganic crystals such as silicon as they are light, elastic, resilient, mechanically flexible, inexpensive, and easy to process and have the potential to provide a variety of functions required for such systems including sensing, actuating, computation, and energy generation/storage.[38]

4.2.1. Metal Fibers

Metal threads are made up of metal fibers which are very thin metal filaments (diameters ranging from 1 to 80 μm). The fibers are produced either through a bundle-drawing process or shaved off the edge of thin metal sheeting.[39] Bekintex produces a range of yarns made of stainless steel blends for intelligent textile applications. These vary in composition from 100% continuous conductive steel fibers to feltings or composites of polyester with short steel fibers interspersed throughout. By varying the ratio of the two constituent fibers, different resistivity of the yarns may be achieved.

4.2.2. Conductive Inks

A conductive layout can be screen printed using conductive inks to add conductivity to specific areas of a garment. Carbon, copper, silver, nickel, and gold may be added to conventional printing inks to make them conductive. Printed areas can be subsequently used as switches or pressure pads for activation of circuits. This technique is supported by recent advances in digital printing, but further development is required for pre- and post-treatments, ink performance, agitation of the ink reservoir for an equal distribution of the conductive particles, and drying of the printed output.[36]

4.2.3. Inherently Conducting Polymers

Materials with inherent piezoresistive properties may be used as simple strain gauge or pressure-sensitive devices. Inherently conducting polymers (ICPs) are a class of polymers with multiple functions in sensing and actuation[40] with the electrical conductivity arising from their extended conjugated π-bond structure. Some commonly used ICPs are polyacetylene, polypyrrole, polyaniline, and polythiophene with polypyrrole (PPy) being popular due to its high mechanical strength coupled with high elasticity, general stability, and electroactivity in both organic and aqueous solvents. It has been used in the development of fabric-resistive sensors by depositing thin layers of PPy onto fabrics with high elasticity such as nylon Lycra using an in situ chemical polymerization process. Conductivity changes result from external deformation of the material, thereby creating a flexible strain gauge[41] that can be easily integrated with a wide variety of garments. The major advantage of this approach is that the sensors retain the natural characteristics of the underlying material. PPy-coated fabrics are reported to have an average gauge factor (GF) of -12 and temperature coefficient of resistance (TCR) of 0.018 $°C^{-1}$, making them suitable for strain gauge implementations. The gauge factor is a measure of the sensitivity to strain, i.e., the ratio of its relative change in resistance to the applied strain. Polyurethane foam coated with PPy has been used to produce a soft, compressible, conducting foam which may be used as a pressure sensor. When the foam is compressed under an external force, the degree of contact between regions coated with conducting PPy film increases. This results in a shortening of the overall conducting pathlength, which increases the bulk conductivity. However, these polymer sensors exhibit a variation in resistance over time and a relatively long response time.[38] Another approach to developing piezoresistive polymer sensors employs carbon-loaded elastomers.[42] The sensors are fabricated by coating with a conductive mixture of silicone and carbon black powder. The sensing component pattern is applied by masked smearing, and the same polymer/conductor composite is also used for the connection tracks between sensors and an acquisition electronic unit, thereby avoiding the stiffness of conventional metal wires.[38] They have been used to develop a number of sensorized garments in this way for high-performance sensing with a reported GF of 2.5, similar to metals, and TCR value of 0.08 $°C^{-1}$.

4.2.4. Optical Fibers

Optical fibers may be used to transmit data signals, transmit light for optical sensing, detect deformations in fabrics due to stress and strain, and perform chemical sensing.[43] Optical fibers have the advantage of not generating heat and are insensitive to EM radiation. Bending of the fibers is a problem in the manufacturing process and also with the end product as mechanical damage causes signal loss. Therefore, the textile structure must be designed to minimize bending to prevent light from being lost.[37] For a good description of the integration process, see El-Sherif et al.[43] Commercially available Luminex fabric is a textile incorporating woven optical fibers capable of emitting light. While this has aesthetic appeal for the fashion industry, it is also used in safety vests and has the potential to be used for data transmission and a platform for building optical sensing capabilities.[44]

4.2.5. Coating with Nanoparticles

Nanotechnology is being widely applied within the textile industry to improve the performance and functionality of textiles. While conventional methods of imparting different properties to fabrics often do not lead to permanent effects,

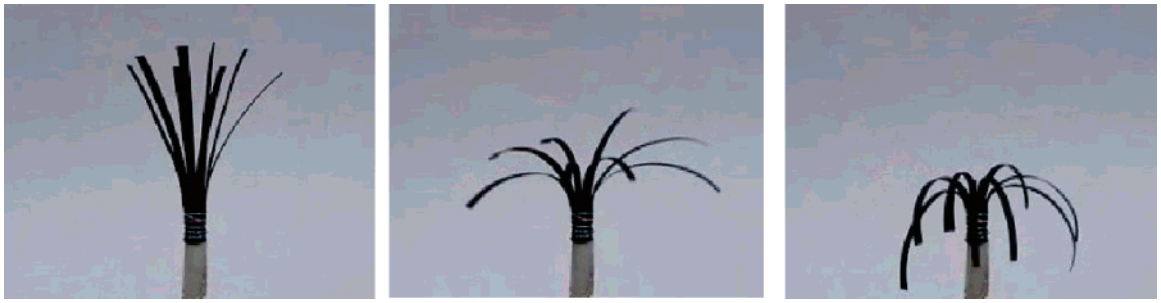

Figure 3. Strips of polypyrrole actuators are arranged in a flower structure. The actuators are shown to bend significantly, their bending direction depending on the voltage polarity (±1 V). The large displacement that can be obtained using low mass, low power, and low voltage polymer actuators makes them attractive in the development of biologically inspired robots. Photos courtesy of Y. Wu, Intelligent Polymer Research Institute, University of Wollongong.

nanotechnology can provide high durability for fabrics.[45] This is due to the large surface area to volume ratio and high surface energy of nanoparticles. Coating with nanoparticles can enhance the textiles with properties such as antibacterial, water repellence, UV protection, and self-cleaning while still maintaining breathability and tactile properties of the textile.[46] NanoTex has a range of products using such coatings to resist spills, repel and release stains, and resist static.[47] These textile enhancements are increasingly an inherent property of the fabric, improving the performance and durability of everyday apparel and interior furnishings.

4.2.6. Integrated Components

Organic semiconductors (polymers and oligomers) having the electrical properties of semiconductors and mechanical properties of plastics are good candidates for developing electronic and optoelectronic flexible components, e.g., transistors, LEDs, that are compatible with a flexible textile substrate.[38,48] For example, Bonfiglio et al. developed a structure for organic FETs (field effect transistors) based on thin film technology that is suitable for integration with flexible substrates. The approach employs an insulating film coated with gold on one side and a thin film of organic semiconductor on the opposite side. This was then glued to the textile ribbon with source and drain contacts created by simply crossing the ribbon with two parallel gold wires.[49] Another approach Bonfiglio's group has taken is to build organic field effect transistors in a fiber format rather than the conventional planar geometry, and they demonstrated that the resulting cylindrical organic thin film transistor could be used in a textile process such as weaving or knitting.[49]

Organic LEDs consist of multilayer structures where organic emitters are embedded between an evaporated metal electrode and a film of indium tin oxide coupled to a plastic or glass substrate. Philips recently released a light-emitting fabric, Lumalive, featuring flexible arrays of fully integrated colored LEDs. These light-emitting textiles can present dynamic messages, graphics, or multicolored surfaces[50] and could also provide a basic substrate for building wearable optical chemo-/biosensors.

4.2.7. Wearable Actuators

In order to create fabrics with motor functions flexible actuating devices are needed. One method of achieving this is through the use of shape memory fabrics. These are materials that are able to return to a preprogrammed shape under an external stimulus, normally temperature. Two approaches are used to make these materials, shape memory alloys (SMAs) or shape memory polymers (SMPs). In the case of shape memory alloys, at a low temperature the structure of the materials changes to a martensite phase, where they can be easily deformed. Upon heating, the structure changes to an austenite phase, and the programmed shape is recovered as the material "remembers" and restores its original shape. SMAs may be spun in combination with traditional fibers to create bicomponent yarns which can then be woven or knitted. SMPs on the other hand have higher extensibility, superior processability, lower weight, and a softer handle and therefore may be considered more suitable for the clothing industry. By coating a fabric with SMP it is possible to make "non-iron" garments that can return to the original shape when heated. Mitsubishi Heavy Industries have applied this technology to create a fabric, DiAPLEX, for the outerwear industry. DiAPLEX has an ultrathin nonporous SMP membrane that has the ability to open up its microstructure when the temperature increases, allowing heat and water vapor molecules to escape through the membrane. A similar approach has been taken by the Centre for Biomimetics at the University of Bath, where SMPs have been molded into biomimetic structures. A fabric surface mimicking the pine cone structure contains scales on the fabric surface that open and close in response to relative humidity or heat.[51] Another approach to thermoregulation has been demonstrated by Corpo Nove's shape memory shirt which incorporates SMAs to cause the sleeves to shorten when the temperature increases.[52]

Another technique is to use ICPs which have the ability to function in both sensing and actuation modes. The actuation property of ICPs results from a volume change of the polymer which accompanies oxidation and reduction (Figure 3). An applied positive potential leads to removal of electrons from the polymer backbone and incorporation of dopant ions to maintain electrical neutrality. The positive charges on the polymer backbone provide Coulombic repulsion forces between polymer chains, and this, together with the incorporation of dopant ions and associated water of hydration, leads to an increase in the polymer volume. This process can be reversed in a controlled fashion to produce usable mechanical work.[53] ICP-based mechanical actuators can achieve average stresses ~10−20 times those generated from natural muscle,[54] realize strains of over 20% comparable to that of natural muscle,[55] and achieve fast free-standing beam actuation with an operational frequency up to 40 Hz.[56] The most attractive feature of ICPs is their ability to emulate biological muscles with high toughness, large actuation strain, and inherent vibration damping.[53] This similarity has led to the term "Artificial Muscle" being applied to these materials, and in principle, they offer the potential of developing

biologically inspired robots.[57] While performance and long-term stability of these actuators still needs to be improved, there is potential to develop rehabilitation and orthotic devices.[57,58] Researchers at the Intelligent Polymer Research Institute in the University of Wollongong employ ICP actuators to assist the insertion of the Cochlear Implant electrode. In this application, a bilayer polypyrrole actuator is used to steer or bend the Cochlear Contour electrode in a controllable manner during surgery as it is being inserted into the ear.[58]

4.2.8. Interconnects and Infrastructure

The fundamental components within smart textiles are sensors, actuators, and control units. Obviously reliable links between the various components of a smart garment system are essential for wearable electronics, between the sensors and actuators incorporated in the garment, and also to external control and communication devices. In cases where conventional electronics are embedded into fabrics, interconnection strategies have included soldering, bonding, stapling, and joining.[33]

(i) Soldering: Surface-mount components have been soldered directly onto conductive fabric such as metallic organza. The problem with this technique is the toxicity of solder compounds, making them unsuitable for constant contact with a user's body. Aside from that, while it may give good electrical contact, the mechanical strength of the connection does not withhold typical strains exerted within a flexible garment.

(ii) Bonding: Components are bonded to a substrate using conductive adhesives. Adhesives are more suitable than solder, being nontoxic, highly conductive, highly durable, and moderately flexible

(iii) Stapling: Component leads grips a sewn conductive trace, within a conductive stitched circuit, by being pressed into shape around it. However, when the substrate flexes, it is likely to stretch open pins that have been formed into clasps and accelerate wear and tear of the fabric substrate.

(iv) Joining: Component leads are joined directly to a stitched fabric circuit, where components are formed with a single conductive thread per pin. The threads may be attached to the substrate by covering stitches of conductive threads, known as e-broidery.[33] Infineon used a similar approach to connect their components. They use narrow fabrics with woven copper threads that are coated with silver and polyester. Where electrical connections are made the coating of the thread is removed using a laser technique and soldered to bonding wires connected to a component or alternatively to a thin flexible PCB.[59] The electronic device is then encapsulated for protection and to allow laundering. This approach has been used to integrate an MP3 player into clothing using the conductive fabric bands to provide connections to headphones, battery power, and keypad.

Conductive textiles have been shown to be suitable for data transmission. Starlab Research Laboratories are working on fabric area networks (FANs). Magnetic induction with textile coils can effectively bridge distances less than 2 cm, allowing nodes of a communication network to be interspersed within the wearer's garments and accessories. Antennas are routed to the trouser pockets, shirt pockets, cuffs of the trousers, sleeves, back of the shirt, and other locations. These antennas can then be used to communicate with transponder chips that are embedded in the wallet, shoes, pens, watches, accessories, or personal items at the backpack, allowing intergarment communication within the body area network.[60]

Winterhalter et al. demonstrated the use of fine filament copper wires (<50um) within narrow woven fabrics to create a fabric version of the universal serial bus (USB) and also a radiating conductor for body-borne antenna applications. These devices were developed with military applications specifically in mind, where high performing and durable materials are needed. The fabric USB was tested before and after exposure to abrasion and cyclic loading and met selected test requirements of USB 2.0, while the fabric antenna demonstrated communication ranges compatible with military communications equipment.[61]

To accommodate communication using wireless technologies, flexible antennas need to be integrated into the textile material. The Wearable Computing Laboratory at ETH Zürich has developed textile patch antennas for Bluetooth applications in wearable computing using the frequency range around 2.4 GHz.[62] The antenna is a planar structure with a maximal thickness of 6 mm, based on the technology used to create printed microstrip antennas. The textile antennas use an electrically conductive fabric (metallic plated) for the ground planes as well as for the antenna patches. A fabric substrate, using wool/polyamide spacer fabric, is used as the dielectric between the antenna patch and the ground plane. Textile antennas have also been investigated at the University of Ghent to allow communication outside the garment, e.g., between the garment and a central control unit. A single-feed rectangular-ring textile antenna is proposed for wireless body LANs operating in the 2.4−2.483 GHz band. The conductive parts of the planar antenna consists of FlecTron fabric, which is a thin, flexible, and lightweight copper-plated nylon woven fabric, whereas fleece fabric is used as nonconductive antenna substrate.[63]

Power requirement is a critical issue for wearable sensor networks. Lithium ion batteries may be used, and in coin cell format they may be integrated relatively easily for many applications, but the ideal format is to use flexible batteries that are integrated into the garment. For example, Powerpaper is thin and flexible with zinc anode and manganese dioxide-based cathode layers. The cells are made of proprietary inks that can be printed or pasted onto virtually any substrate to create a battery that is thin and flexible.[64] Alternatively, fiber cells may be more suitable for textile integration. ITN energy systems are working with the U.S. agency DARPA to make batteries with fibers containing the anode, cathode, and electrolyte by coating a fiber with thin film layers, consisting of the same materials typically used in flat batteries, such as $LiCoO_2$ as the cathode, lithium as the anode, and LiPON as a solid electrolyte. To be more energy efficient and have the potential of an endless power supply, harvesting energy from various available energy sources would be of huge benefit. Starner summarized the harvesting of energy from the wearer's everyday actions, mainly leg motions and body heat;[65] see also an overview of energy scavenging by Yeatman and Mitcheson.[66] Piezoelectric transducers (converting mechanical energy), thermoelectric transducers (converting thermal gradients), and pyroelectric transducers (converting body heat) can provide power that is always available, thus removing the need for battery recharging. Solar cells may also be employed as garments have a relatively large surface area that can be employed for solar energy harvesting. Photovoltaic (PV) technology commonly

Table 6. Physiological Signals and Possible Sensing Platforms for Wearable Applications

physiological parameter	signal source	suitable sensors for wearable applications
ECG	electrical activity of the heart	woven/knitted metal electrodes[70,72]
EMG	electrical activity of a muscle	woven/knitted metal electrodes[91]
breathing rate	thoracic volume changes	electrical impedance plethysmography,[42,76] piezoresistive strain/pressure sensors[151]
blood pressure	force exerted by circulating blood on the walls of blood vessels	volume clamp method with finger cuff actuator,[152] measurement of pressure oscillations,[153] pulse transit time[91]
pulse oximetry	oxy-hemoglobin concentration in blood	optical sensors (LEDs and photodiode)[154] and optical fibers[82]
GSR	skin electrical conductivity	woven metal electrodes[75]
body motion	limb movements/gestures posture	piezoresistive strain/pressure sensors,[155] accelerometers, gyroscopes,[78] optical fiber sensors[70]

employs thin film materials based on amorphous silicon (A-Si) or copper indium gallium diselenide (CIGS). The former, which is the most common solar cell material for commercial application, suffers from being relatively heavy, fragile, rigid, and costly to ship and handle.[30] Recently CIGS thin film technology has been used in the development of a solar-powered jacket to connect and charge portable devices such as cell phones, PDAs, and MP3 players, thus providing power on demand.[67]

Wearable networks must also provide user input/output peripherals. Switches that are fabric based and fully washable and maintain the comfort and feel of textiles are being integrated into garments to control electronic devices such as MP3 players. Eleksen use capacitive pressure sensors to create control buttons on fabric and have even developed a fabric keyboard for PDAs that can be rolled out, easily stored, and transported. SOFT*switch* also manufacture fabric switches, keypads, and pressure sensors utilizing a quantum tunneling composite (QTC) provided by Peratech. QTC is a material that is normally a very good electrical insulator but turns into a conductor under compression, tension, or twisting. QTC contains tiny metal particles insulated within a polymer. When deformation occurs the metal particles are brought closer together and electrons pass through the insulation by a process called quantum tunneling. The transition from insulator to conductor follows a smooth and repeatable curve with the resistance dropping exponentially. In addition to providing user input through such textile peripherals, output display is another important aspect for the wearer and must be provided in a comfortable accessible format. On-garment visual feedback to the wearer can be provided via flexible displays based on liquid crystal technology or organic LEDs.[50,68]

4.3. Applications of Wearable Sensors

Monitoring vitals signs such as heart rate and breathing rates can give an insight to the wearer's health. By detecting limb movements it is possible to study body kinematics, an important physiology tool in sports applications to improve technique and performance, and also as a rehabilitation tool, e.g., post stroke patients. In sports science, wearable sensors enable coaches and athletes to understand how an athlete's body responds to exercise and track improvements in performance. In the healthcare sector wearable sensors allow continuous monitoring of a patient's condition, providing the opportunity to identify threats before an event happens, e.g., assessing cardiovascular disease. This is a rapidly growing research area with many new technologies and applications emerging.

Table 6 lists a number of physiological signals of valuable diagnostic importance that have been successfully monitored using wearable sensors. As part of any physiological assessment breathing rate is an important parameter as it is closely linked to our physiological and psychological state, even though we are often unaware of changes in our personal breathing pattern. For sports applications breathing rate is equally an important measure, giving a good indication of physical exertion or assessing metabolic capabilities. Further to breathing rate, respiration can be monitored by measuring changes in thoracic volume. This can be done using wearable strain gauge sensors or electrical impedance plethysmography. Electrical impedance plethysmography integrates two conductive wires into a garment, one around the ribcage and the other around the abdomen. Motions of the chest wall cause changes of the self-inductance of the two loops. Expansion of the thoracic cavity during inhalation causes an increase in conductivity of the material. This allows the rate and amplitude of breathing to be monitored, e.g., deep breathing manifests as a large change in signal amplitude and slow breathing rate.

Electrical signals such as electrocardiograph (ECG) and electromyography (EMG) may be measured by integrating textile-based electrodes into fabric. ECG typically uses silver chloride electrodes coupled to the skin with gel to measure electrical potentials. Flexible conductive yarns, fully metal yarns, or natural/synthetics blended with conductive fibers have been knitted into garments to develop textile electrodes, referred to as textrodes.[69,70] Carbon or conducting polymer-based yarns are not currently used as they are not conductive or sensitive enough for this application.[38]

Figure 4 shows a comparison of fabric electrodes against a standard system in a study by Paradiso et al.[69,70] and shows good correlation between the two systems. EMG uses surface electrodes to detect stimulation signals of the muscle fibers and has also been measured using metal-based yarn electrodes.[70] However, a major issue (particularly with ECG electrodes) is the need to use a gel to provide a good contact between the sensor and the skin. This restricts the ease of use, and in recent years, much effort has been focused on the development of 'dry' electrodes and the use of hygrogel membranes that can be integrated into a garment and used for ECG monitoring without having to manually apply a gel.[42,71,72]

While electrodes may be integrated as detectors, another possibility is to use the electrodes to stimulate muscles. Electrodes for functional electrical stimulation (FES) have been integrated into fabrics to provide actuation stimuli to muscles of spinal cord injured and stroke subjects in order to generate or improve lost motor function, e.g., for walking or hand gripping movements.[73]

Strain sensors made from piezoelectric materials may be used in biomechanical analysis to realize wearable kinesthetic

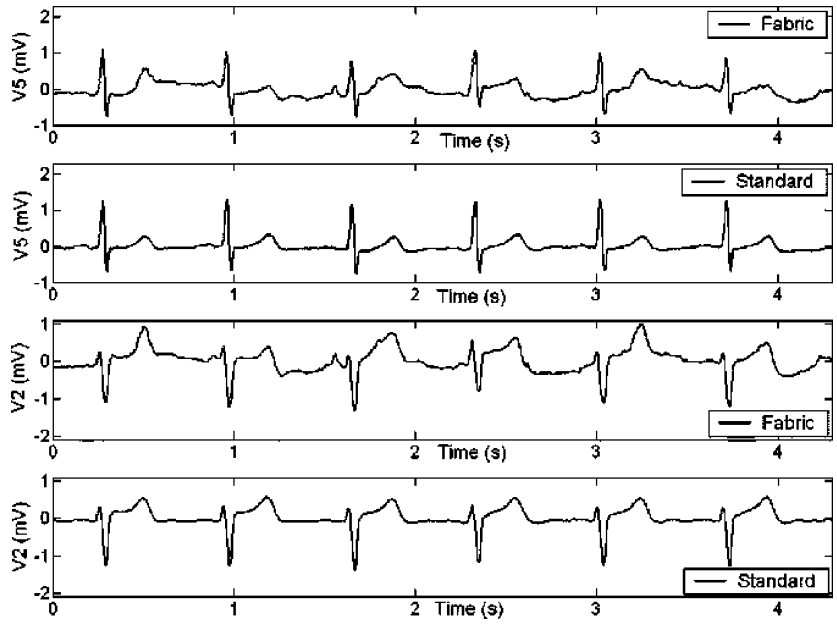

Figure 4. Comparison of ECG signals obtained with subject walking on the spot with standard and fabric electrodes. (Reprinted with permission from Paradiso, R.; Loriga, G.; Taccini, N. *IEEE J. Inf. Technol. B.* **2005**, *9*, xxxx. Copyright 2005 IEEE.)

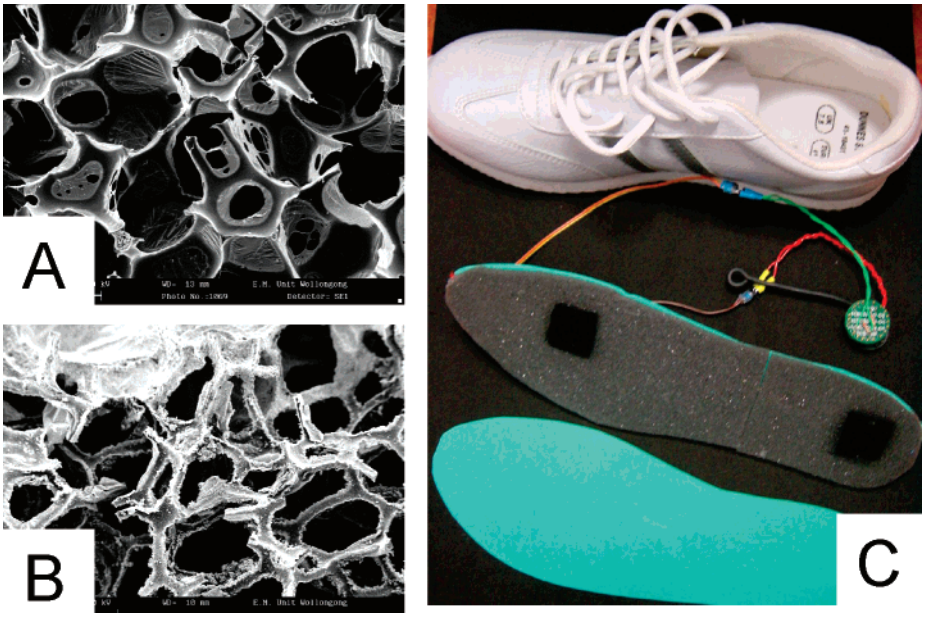

Figure 5. (a) SEM of uncoated polyurethane foam (×100). (b) SEM of polyurethane foam coated with polypyrrole (×100). (c) Foam-based polypyrrole pressure sensors integrated into an insole for gait analysis; the sensors are connected to a microprocessor and Crossbow wireless transmitter.

interfaces able to detect posture, improve movement performance, and reduce injuries.[42] Garments integrating piezoresistive electroactive polymers (EAPs) and conductor-loaded rubbers with strain-sensing capabilities have been demonstrated for continuous monitoring of body kinematics and vital signs.[38,74] Such devices may be used to teach athletes the correct way to perform movement skills by providing real-time feedback about limb orientation. For example, the Intelligent Knee Sleeve is a biofeedback device using PPy fabric sensors that monitor the wearer's knee joint motion during jumping and landing and uses an audible feedback signal to reinforce the correct landing technique signs.[38,74] Likewise, a foam-based PPy sensor has been used to detect joint movement and breathing function[75,76] and applied to examine pressure distribution within a shoe insole[77] (Figure 5). The insoles each have two sensors to monitor the difference between the heel strike and front foot lift off. An example of the measured response during walking is shown in Figure 6. This provides a way to characterize different movement activities, such as distinguishing normal walking steps from shuffling of the feet, which can help with the early diagnosis of conditions such as Parkinson's disease. Pressure-sensitive fabrics may also be used to prevent pressure sores which can lead to ulcers, which can happen if a person remains in the same position for long periods of time, or where sensation/feeling has been lost in a limb, which is a common problem for people suffering from diabetes.

The monitoring of body posture and gesture has been demonstrated using fabric strain gauges; another approach to measure posture has been demonstrated by Dunne et al., where a fiber-optic bend sensor has been integrated into a

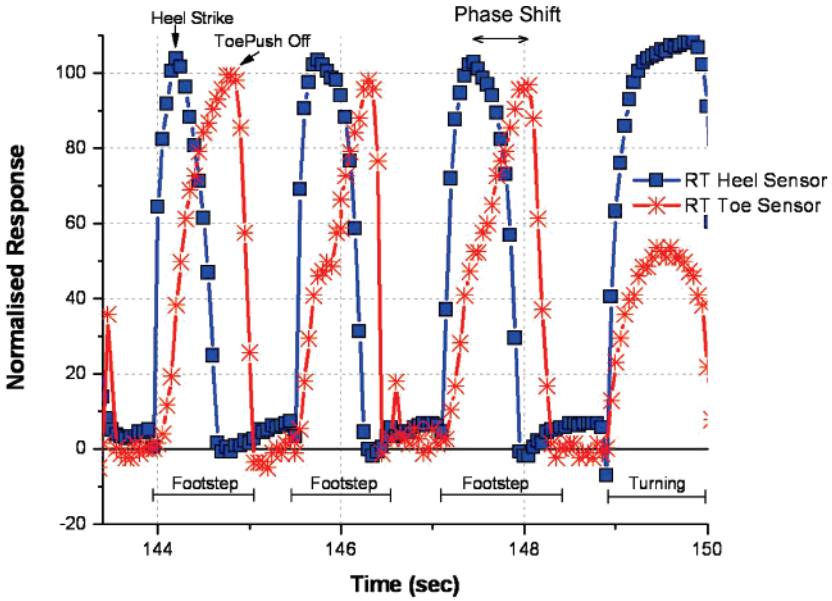

Figure 6. Normalized response for two PPy-coated foam sensors placed at the heel (RT Heel Sensor) and toe (RT Toe Sensor) position of an insole.[156] The time difference between heel strike and toe lift off is demonstrated during walking motion and may be used to analyze gait patterns for rehabilitation purposes or for the assessment of conditions such as Parkinson's disease.

garment for long-term monitoring of spinal posture in the working environment where poor seated posture is an increasingly significant source of back problems.[78] Another method to monitor body posture and motion is to use triaxial accelerometers mounted on different parts of the human body, as demonstrated by Farella et al., where the accelerometers form nodes of a wireless and wearable network for posture recognition.[79] Accelerometers have been widely used in body sensor networks for a wide range of applications, investigating aspects such as sleep−wake rhythm and hyperactivity disorder to locomotor activity rhythms in Alzheimer's disease.[29]

Optical components may be used to investigate blood oximetry. The absorption of light depends on oxy-hemeoglobin saturation. Tissue may be probed using LEDs and photodiodes that are coupled to the skin. Asada et al. demonstrated a reflectance prototype oximetry measurement system including a rf data transmission unit miniaturized in a finger-ring configuration.[80] The possibility of measuring blood pressure using photoplethysmography techniques has also been investigated.[81]

There is also potential for monitoring emotional, sensorial, and cognitive activities, as demonstrated by the MARSIAN smart glove. This monitors the autonomic nervous system, which is responsible for our body's involuntary vital functions, by measuring physiological parameters of the skin.[82,83]

4.4. Wearable Chemosensing

Most research to date in the field of wearable electronics has focused on physical transducers for reasons explained previously. These issues, including sampling procedures, calibration, safety, and power, also apply to wearable sensors with the added constraint that the sensors must not compromise the functionality or comfort of the garment. As for normal chemo-/biosensing, a sample must be delivered to an active surface on the sensor for a reaction to occur and the signal to be generated. If the wearable sensor is monitoring the external environment, the sample is likely to be volatile (e.g., presence of hazardous/toxic gas), whereas if the sensor is monitoring the body's physiology, a liquid sample must be delivered to the sensor. For wearable chemo-/biosensors, obtaining a sample is an issue as this ideally should happen naturally, and for this reason attention has focused on sweat rather than blood. In the case of body fluids, sample collection and delivery ideally should be incorporated within the layers of the garment, whereas external gaseous sampling requires the sensor to be positioned at the outer edge of the garment interface, where contact between the sensor and the sample will be optimal. The sensor itself must be robust, miniature, flexible, washable, and ideally textile based. The overall assembly of sensor must be safe for the wearer's health, and the use of toxic or hazardous reagents should obviously be avoided.

BioTex and ProeTex are two EU-funded projects that aim to develop textile-based sensors to be integrated within a garment for monitoring chemical and biological targets.[3,84] For Biotex, the goal is to place the sensor within a fluid handling platform that employs the inherent capillary action of certain fabrics. For example, polyamide Lycra has natural moisture-wicking properties and is used in conjunction with a super absorbent material to control fluid transport in the fabric. The configuration of the device is shown in Figure 7. It consists of a collection layer with a hydrophilic channel surrounded by hydrophobic silicone-coated regions. This channel contains an inlet for sweat, a pH-sensitive region, and an absorbent region. A cover is held 5 mm above the channel by moulded silicone, which prevents contamination, blocks stray light, and positions the optical sensing components. The color of the immobilized pH-sensitive dyes is monitored by reflectance colorimetry using LEDs with the measurements controlled by a Mica2dot mote which is also responsible for wireless transmission of the data to a remote base station.[84]

Much work has been carried out to develop wearable sensors for the management of diabetes. This condition requires the patient to monitor glucose levels closely and at regular intervals, typically using finger-pricking sequential blood tests. A wearable glucose sensor would be a real

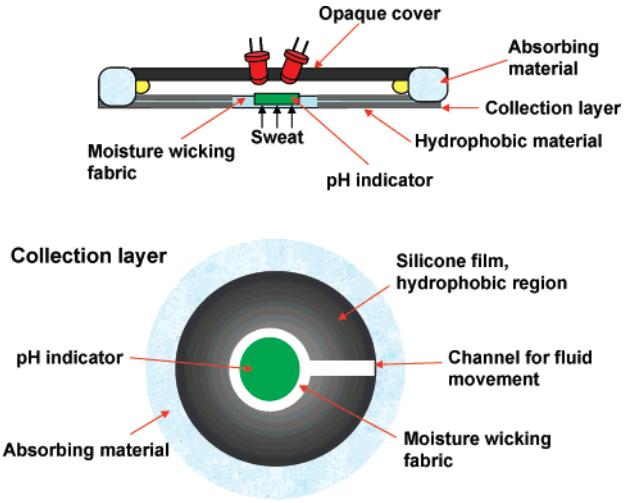

Figure 7. Textile-based device for collection and analysis of sweat. The device uses the inherent moisture wicking and absorbance properties of fabric to control fluid movement. A pH indicator is used to demonstrate colorimetric sensing capabilities using a paired LED configuration to perform reflectance measurements from the fabric surface.

benefit to the millions of people suffering from this disease provided it could meet the analytical requirements, provide hypo- and hyperglycaemic alarms, and meet the wearable sensor requirements summarized above. The Glucowatch (Figure 8) was one of the first approaches to noninvasive glucose monitoring and approved by the FDA in 2001. The device extracts glucose through intact skin via reverse iontophoresis, where it is detected by an amperometric biosensor. In a clinical evaluation study the device was reported to give accurate measurements continuously (3 per h) over a 24 h period.[83] Another approach developed by Badagu et al. is a disposable contact lens embedded with newly developed boronic acid-based fluorophores.[85] The contact lens changes color in relation to the amount of sugar in tears and can be monitored by the wearer simply looking into a mirror and comparing the color to a precalibrated color strip. Kudo et al. developed flexible biosensor for glucose measurement using functional polymers. The biosensor utilizes the physical and chemical functions of hydrophobic polydimethyl siloxane (PDMS) and hydrophilic 2-methacryloyloxyethyl phosphorylcholine (MPC) copolymerized with dodecyl methacrylate (DMA). The glucose sensor was constructed by immobilizing glucose oxidase (GOD) onto a flexible hydrogen peroxide electrode (Pt working electrode and Ag/AgCl counter/reference electrode). The electrodes were fabricated and integrated with the functional polymers using microelectromechanical systems (MEMS) techniques.[86]

SCRAM (secure continuous remote alcohol monitoring) is a tamper- and water-resistant bracelet containing an electrochemical sensor that is attached to the ankle using a durable strap. Targeted at drunk-driving offenders, the device captures transdermal alcohol readings from continuous samples of vaporous or insensible perspiration collected from the air above the skin. A correlation exists between the alcohol concentration in blood and perspiration, although there is a time difference in the response. The system contains a flash memory chip to store alcohol readings, a circumvention detection device to monitor body temperature and detect tampers, and uplink features that can transfer these readings via a wireless radiofrequency (rf) signal to the SCRAM modem. At scheduled times set by the court or probation agency, the anklet will transfer these data to the modem.

Fiber optic sensors with modified cladding materials have been shown to be suitable for detecting hazardous battlefield situations and may be easily integrated into soldiers' uniforms. The modified cladding materials are sensitive to different environmental conditions and cause a change in the refractive index, which affects the propagation of the transmitted light signal. El-Sherif et al. demonstrated this using a thermochromic agent, segmented polyurethane−diacetylene copolymer, and a photochemical polymer, PANi, as cladding agents.[37] This type of sensing has many uses in military applications to provide protection and advance warning to the troops regarding chemical and biological warfare threats or above-normal temperatures. Another chemosensor developed for military applications is Chameleon, developed by Morphix Technologies. It is a wearable armband integrating colorimetric sensing techniques to detect toxic gases like ammonia, basic gases, chlorine/fluorine, hydrogen sulfide, iodine, phosgene, phosphine, and sulfur dioxide via a range of disposable cassettes.[87]

Collins and Buckley demonstrated the chemical-sensing properties of conductive polymers coated onto woven fabric materials.[88] Thin films of conductive polymers, polypyrrole or polyaniline, were coated onto poly(ethylene terephthalate) or nylon threads woven into a fabric mesh. The conductive polymer overlayers were grown by chemical polymerization or oxidative coupling of the monomer, pyrroles, or aniline. These sensors were assessed for their ability to detect hazards that may endanger the health of the wearer. Low ppm detection limits were demonstrated for toxic gases such as ammonia and nitrogen dioxide as well as the chemical warfare simulant dimethyl methylphosphonate, DMMP. The chemical-sensing fabrics were reported to have the following advantages over the use of microelectronic devices: (i) potentially low cost and low operating power; (ii) commercial availability of the coated fabric; (iii) expected wide dynamic range due to the large surface area of a conductive polymer-coated piece of fabric; (iv) ease of measurement; and (v) demonstrated stability of the conductivities of coated fabrics. It was claimed that these electroactive polymer-coated fabrics could form the basis of future wearable, lightweight, clothing-integrated sensor systems to detect external hazardous environments.

4.5. Applications in Personalized (p)Health

The concept of personalized health, or pHealth, seeks to empower the individual with the ability to manage and assess their own state of health and healthcare needs. Wearable sensors enabling monitoring of long-term and short-term healthcare needs have a huge potential for disease prevention in medicine and early diagnosis. They facilitate assessment of the impact of clinical intervention by gathering data in the home and community setting. This can overcome the problem of infrequent clinical visits that may fail to detect transient events that may be of important diagnostic importance. Another problem with hospital-based healthcare is that it is impractical to measure physiological responses during normal periods of rest, activity, and sleep and monitor circadian variations in physiological signals without committing people to specialist facilities for days or weeks.[89] Early diagnosis through long-term trend analysis reduces the potential severity of an illness, and in the case of rehabilitation, a wearable sensing system could monitor the recovery process and detect complications as they arise.

Providing feedback on health and well being through a body−sensor network in principle allows the patient to take

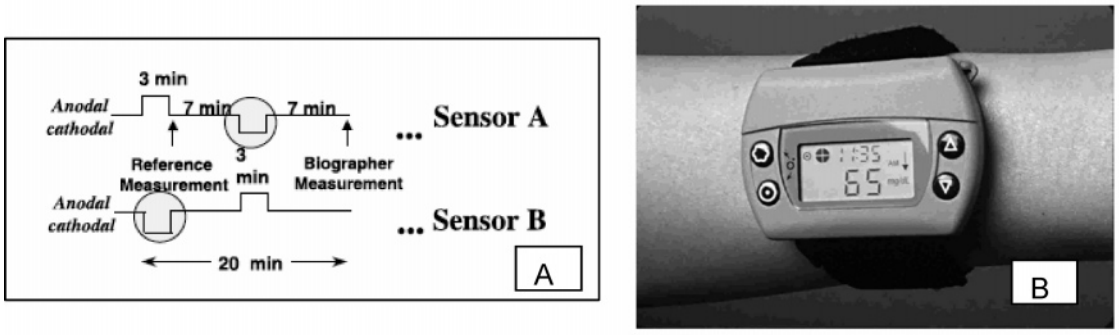

Figure 8. Glucowatch uses reverse iontophoresis to pull glucose through the skin into two gel collection discs (A). The glucose level is measured, and a reading is displayed to the user (B). (Reprinted with permission from ref 83. Copyright 2001 Elsevier.)

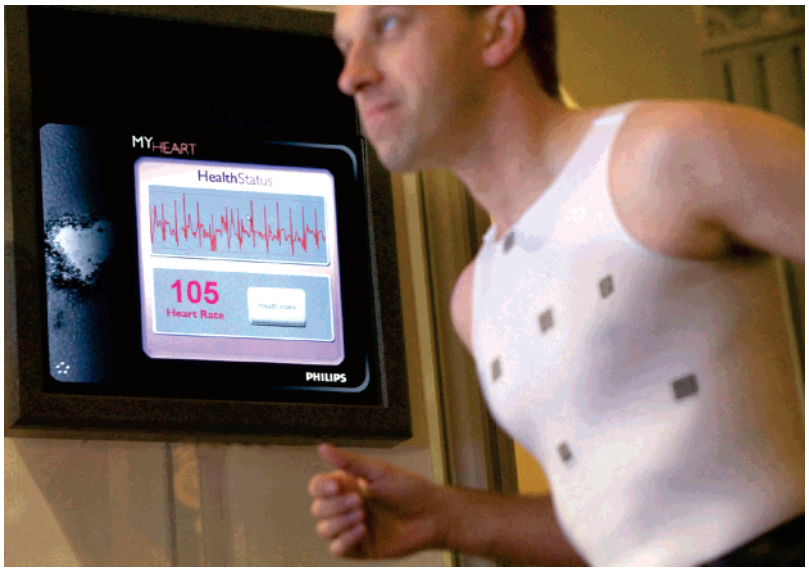

Figure 9. On-body sensors and electronics for monitoring vital body signs—a garment with textile ECG electrodes developed by the MyHeart project to prevent heart failure. (Permission to use this from Philips.)

care of his/her own health at home. For people at risk of disease, the system should facilitate responses to reduce individual risk factors, e.g., hypertension, obesity, diabetes, stress, and physical inactivity. In the occurrence of complications, the wearer may be alerted to contact their physician or a message can be sent automatically.[70] For those suffering from chronic illnesses, wearable sensors could facilitate self-management of the disease by facilitating personalized drug treatments and allowing self-administration of medications, e.g., in the case of Parkinson's disease, medication is often over- or underestimated based on population averages rather than individual statistics. Another potential application is epilepsy seizure detection by combining contextual activity regarding general activity with physiological measurements.[90] Depression is also another chronic illness where monitoring is needed to assess the effect of treatment. Overall the aim is to enable a personalized medication and rehabilitation schedule through continuous long-term monitoring and profiling of individuals.

There are a number of personalized healthcare systems that have reached or are nearing commercialization. Vivometrics developed the Lifeshirt which is a Lycra vest with sensors to detect respiration, ECG, posture, and movement. Textronics have released the NuMetrex heart-rate-monitoring sports bra that incorporates conductive knitted sensors that link wirelessly to a Polar heart-rate-monitoring watch. The Smartshirt by Sensatex, which evolved from the wearable motherboard shirt initially developed at Georgia Institute of Technology, integrates optical and conductive fibers with embedded sensing elements to monitor vital signs. The EU projects WEALTHY and MyHeart have developed sensorized cotton/Lycra shirts which integrate carbon-loaded elastomer strain sensors and fabric bioelectrodes, enabling the monitoring of respiration, electrocardiogram (ECG), electromyogram (EMG), and body posture and movement.[70,91] Figure 9 shows the system developed by MyHeart for on-line monitoring of vital signs. Foster-Miller Inc. is developing and commercializing an ambulatory physiological status monitoring system to monitor heart rate, respiration rate, posture, activity, and skin temperature.[92] BodyMedia are working on a body-monitoring system in the form of an armband as a physiological monitoring and calorie management system. The target users of all of these products include doctors, researchers, fitness professionals, nutritionists, and general consumers. As mentioned previously, the first mass consumer-wearable sensor product is the Nike-Apple iPod Sports kit in which a sensor placed in an exercise shoe relays information to an iPod. Given the market potential for wearable sensors evidenced by this product, it is clear that a series of new products will be launched in the next couple of years, and there are obvious opportunities for wearable chemo-/biosensors that can provide important health-related information within this scenario.

The Institute for Soldier Nanotechnologies (ISN, see http://web.mit.edu/ISN/) is an interdepartmental research center based at MIT whose research mission is to use nanotech-

nology to dramatically improve the survival of soldiers. Their vision of the battle suit of the future is a bulletproof jumpsuit no thicker than ordinary Spandex that monitors vital signs, eases injuries, communicates automatically, and allows medics to conduct a remote triage of combat casualties to help them respond more rapidly and safely.

The EU Framework project 'ProeTex' is developing textile- and fiber-based integrated smart wearables for emergency disaster intervention personnel in order to improve their safety and efficiency (see http://www.proetex.org/). By empowering them with wearable sensing and transmission systems, it is envisaged that vital signs, activity, position, and external environment can be monitored with the information and status indicators relayed to the individual and also to a central monitoring unit. The system monitors the vital signs of emergency disaster workers and warns of potential dangers, allowing communication between the individuals in the operations area and also with the support services outside the operations area. The aim is to provide active measures to prevent or reduce injury from burns, flashover, hyperthermia, explosion, burns by acids and corrosive substances, electrocution, and detection of NRBC (Nuclear, Radiological, Biological, Chemical) risks.

4.6. Conclusions

Wearable sensors provide the ability to enable innocuous sensing of the wearers and their environs. The challenge is to create sensors, driving electronics, and communication networks that are small, robust, reliable, and flexible so as not to impair the comfort of the wearer. While miniaturization of components has been of immense benefit in wearable sensing applications, the major problem of interconnections still remains, where conventional silicon and metal components are highly incompatible with the soft textile substrate. To help in overcoming this there has been much research and development of functionalized fabrics that can provide conductivity and sensing components to our clothing. Nanotechnology is making a huge impact within the textile industry and novel materials, such as conducting polymers, allow the fabrics to retain their natural flexible feel, which is imperative for "smart clothing" to become a realistic part of day to day life.

Body sensor networks allow the wearer to simultaneously monitor their personal health and status of their immediate environment and share this information with others via the Internet. Developments will be very rapid in the coming years, and as the user base expands, there will be a demand to integrate additional information from chemo-/biosensors, both in wearable formats and through small analytical kits or instruments (e.g., personal diagnostics). It is important therefore that the chemo-/biosensors research community is aware of these developments and emerging opportunities and focus on ensuring that technological barriers to this integration are overcome.

In the next section we shall examine the role of materials science in making this happen.

5. Materials Science—The Future

Materials science is a very broad interdisciplinary field that spans many areas of scientific research with recent exciting developments arising from our increasing ability to control the behavior of bulk materials through manipulation at the molecular level. The sections above have outlined developments in sensor networks in two main areas: environmentally-deployed mote-based sensor networks and wearable sensors. Both are linked in that they arise from the concept of pervasive computing, every person will be continuously linked to digital communications systems through wireless communications (infrastructure essentially already in place), and through this people will be increasingly linked to their environment, for example, to networks of objects and services, themselves (personal vital signs monitoring), and other people (for general background on this, see http://www.itu.int/osg/spu/publications/internetofthings/).

However, the real challenge is to link 'molecular' sensing through chemo-/biosensors to the networked world. From the previous sections it is clear that while certain building blocks for performing 'pervasive' sensing are being assembled, we are still a long way from the realization of large-scale sensor networks, even for relatively simple targets like temperature. The conclusion from those sections is clear: large-scale deployments of sensors can only happen when the sensor nodes are essentially self-sustaining in terms of all consumables (energy, reagents, etc.) for many years. Chemo-/biosensing is inherently much more complex than the type of sensing currently employed in these demonstration deployments and invariably involves liquid handling using conventional technologies (pumps, valves, etc.) which are very energy intensive. Furthermore, chemo-/biosensing requires intimate binding events or reactions to occur either in solution (e.g., with reagent-based systems) or at the surfaces of sensing devices. Thus, chemo-/biosensors are prone to degradation as they depend on active materials and surfaces that interact with the sample, and therefore, they must be regularly calibrated to compensate for changes in their operating characteristics over time. While considerable advances have been achieved, for example, with the move toward microfluidics and lab-on-a-chip devices (see below), the scale of the improvements required to meet the demands of pervasive sensing are such that a complete rethink of ways to perform chemo-/biosensing is probably needed. For the remainder of this review we shall focus on two critical areas where revolutionary breakthroughs could have a potentially revolutionary impact: liquid handling and control of surface interactions.

5.1. Microfluidics and Lab-on-a-Chip Devices

The concept of 'micro-total analysis systems' or μTAS was introduced by Manz et al. around 1990,[97] and it rapidly became known as lab-on-a-chip (LOAC). At its core the concept involved integrating multiple separate operations (sampling, sample processing, reagent addition, calibration, detection, etc.) into a compact, integrated, microfluidic manifold, which had channel dimensions typically in the range $10-500$ μm, to both speed up sample throughput and improve precision. This has become a huge area of research in its own right, and for general information the reader is referred to other recent excellent reviews.[98−100] In this section, we will restrict ourselves to the potential of LOAC devices for distributed sensor networks based on wearable and mote-based environmental platforms.

One of the main limitations of LOAC devices arises from difficulties in finding liquid handling/transport approaches that are truly compatible with scaled down microfluidic manifolds. Most published work involves the use of bench-scale pumps and external valves with emphasis being on the

improved sample-handling capabilities of the integrated microfluidics system and reduced reagent consumption/waste generation. Furthermore, attempts to produce integrated systems typically involve the use of scaled-down conventional pumps/valves produced by micromachining. While this has produced some very elegantly engineered systems, there is a growing realization that the next evolution of these devices requires completely new approaches to integration of liquid-handling functions and that the solution to this issue lies in fundamental materials science and new ways of thinking about microfluidics. For example, Whitesides and co-workers demonstrated valve effects using distortions in soft polymers,[101] while others propose more biomimetic solutions in which the microfluidic manifold is regarded as a primitive mimic of a biological circulation system, and biologically inspired routes to generating fluid circulation are employed, for example, using the 'artificial muscle' function exhibited by some redox-active soft polymers. Wallace et al. produced a pump based on the expansion/contraction cycle accompanying oxidation/reduction of polypyrrole deposited on a water-permeable tube. Application of an oxidizing potential at one end of the tube generated a peristalsis-type expansion wave that migrated along the surface, carrying water with it.[102] Recently, a biomimetic soft polymer pump was demonstrated based on polypyrrole Nafion actuators compressing a soft-walled polyurethane/polydimethylsiloxane chamber.[3] These pumps offer advantages in terms of relatively low energy requirements and are ultimately more compatible with microfluidics as their soft nature makes them much less prone to physical malfunction due to, for example, ingress of microparticulates, than conventional microengineered pumps and valves. For an introduction to biomimetics related to sensors, actuators, and artificial muscles, see ref 23 and the references therein.

LOAC devices, in principle, offer a route to incorporation of sophisticated chemo-/bioprocessing steps in a compact, low-power platform, which is attractive for remote sample processing (phase extraction, separation steps, reagent additions, calibration, etc.). Therefore, these devices offer a compromise between existing lab-based instruments and the vision of tiny, completely self-sustaining sensors capable of massive scale up. The limiting factor is now probably the need for reagents and waste storage/disposal. Ideally, these devices should be able to generate their own reagents on demand (e.g., electrochemical generation of protons or hydroxide ions to provide localized control of pH), but we are still a long way from this idealic vision of completely self-sustaining chemo-/biosensing devices.

5.2. Controlling Liquid Movement in Surfaces and on Channels

Providing the reagents within the LOAC device is only part of the story however. Reagents must be stable in long-term storage to be of any use (at least months, ideally years).[27] Furthermore, the manifold design must incorporate structures and features that control the flow characteristics by providing effective mixing regions to overcome the dominant laminar flow behavior. For example, a recent report described how efficient mixing can be achieved in LOAC manifolds converting the flowing liquid into discrete droplets that can be manipulated by electrowetting. The interfacial tension of droplets is controlled with the application of a voltage across an electrode array and the droplets behave as micromixing chambers while moving across the array.[98] Other approaches exploit colloidal particles[99] and flexible elastomers, that can open and close a microfluidic channel.[100] A hydrophilic microfluidic network with geometric valves that can slow down, stop, and accelerate liquid volumes within the microfluidic system has also been demonstrated.[103]

Clearly, a fundamental issue with all chemo-/biosensing platforms is how to control the movement of liquids in a way that is virtually energy free, so that functions like calibration can be incorporated. While considerable improvements can be obtained through downscaling analytical instruments using microfabrication approaches and this will lead to more widespread deployments of autonomous analytical instruments, for example, in environmental monitoring[104] or hazard/threat detection,[105,106] for truly pervasive chemo-/biosensing we need to go beyond downscaling of conventionally engineered devices like pumps and valves.

Control of the wetting properties of materials has been the focus of considerable research effort for many years, particularly by groups linked with the textile industry.[93,94] The ubiquitous presence of water in nature makes this study extremely relevant, yet despite the fact that many critical processes in nature, including sensing, occur at surface−aquo interfaces, the fundamental structure of water and its behavior at surface interfaces is still not fully understood.[95] Classically, materials are divided into two categories in terms of their degree of interaction with water: hydrophilic and hydrophobic.[96]

Surface tension can enable liquids to move spontaneously over surfaces without any application of external forces.[107] Wetting and adhesion properties between liquids and solids can be described by the measure of the contact angle between the two surfaces: the larger the wetting tendency, the smaller the contact angle or the surface tension. Surface tension changes, caused by evaporation of the alcohol, are responsible for formation of drops of wine on the surface of a glass.[108] This is generally known as the Marangoni effect,[109] and it describes the spontaneous movement of liquid from a low surface tension to a high surface tension environment. Unbalanced surface tension forces can drive liquid motion without any external intervention of any kind. It has been demonstrated that the speed of liquid flow driven by surface tension can be increased by a factor of hundreds or thousands times compared to the typical Marangoni effect by creating a radial surface tension gradient through the deposition of hydrophobic molecules in the center of a hydrophilic surface and subsequently forming water droplets by condensing steam on the hydrophobic region.[110] The drops driven by the gradient forces from one side and coalescence forces from the other side were found to move at speeds of up to 1.5 m/s. While the immediate applications of this effect are found in heat exchangers, it has an important role in clinical conditions such as in the treatment of respiratory distress syndrome (RDS), in which the lungs of prematurely born infants are not sufficiently developed to produce enough surfactant to control liquid distribution, and hence effective gas exchange is impaired.[111] These phenomena demonstrate that it is possible to use purpose-designed chemistries to control water behavior (including transport) across or even through surfaces. For example, by generating a spatial surface tension gradient on a surface the movement of a water droplet uphill without the assistance of any external energy has been demonstrated.[112] The gradient surface was created by diffusing decyltrichlorosilane vapor over a silicon wafer; evaporation of the silane vapor created a gradient of

concentration that decreased along the length of the surface. As a consequence, the edge of the wafer surface closest to the vapor source became hydrophobic and the farthest hydrophilic. When a water droplet is placed on the obliquely positioned silicon wafer, with the hydrophobic part lower than the hydrophilic part, the droplet begins to move spontaneously 'uphill' toward the hydrophilic end. This arises because of unbalanced forces acting on the liquid−solid contact line on the two opposite sides of the drop, driving the droplet upward against gravity toward the hydrophilic end.

Water repellency and in general material wettability are very important properties which depend on a material's surface free energy and surface roughness.[113] Control of these properties is important for many applications, such as variable focus liquid lens[114] or self-cleaning surfaces.[115] Using an electrode, droplet movement can be achieved using direct electrical control of the surface tension.[116,117] For example, it has been demonstrated that a droplet of a polarizable and conductive liquid can be moved when placed between two parallel plates, the upper consisting of a single continuous ground electrode and the bottom consisting of an array of independently controlled electrodes.[116] In another case, controlled droplet motion has been demonstrated on an open surface. A droplet placed on the surface between two dielectric-coated coplanar electrodes starts to move toward the more positive electrode when a sufficient voltage is applied. The greater positive polarity of one electrode relative to the other is responsible for the phenomenon, which is known as asymmetric electrowetting-on-dielectric oscillation (AEWOD). It is claimed that through this effect unidirectional and oscillatory transport of a droplet on an electrode surface can be performed.[117]

Another exciting possibility is light-driven liquid movement on a photoresponsive surface.[118] In one example, azobenzene derivatives were switched between the cis and trans isomers using light with corresponding changes from hydrophilic to hydrophobic surface characteristics. For a surface modified with an azobenzene derivative (*o*-carboxymethyllated calixresorcinarene), switching was achieved using UV irradiation to form the *cis*-azobenzene (hydrophilic) isomer and blue light to form the *trans*-azobenzene (hydrophobic) isomer.[119] When an olive oil droplet was placed on the surface, asymmetrical photoirradiation caused a gradient in the surface polarity that induced droplet motion, whose direction and velocity were found to be tunable by varying the light intensity (Figure 10).

In the examples reported above, external control of the surface wettability by means of light or electrochemical potential provides a mechanism for controlling liquid transport on surfaces at relatively high flow rates without the need for high voltages/currents and avoiding the use of conventional pumps, valves, or channels. Hence, changes in surface tension can provide a driving force to move liquids without application of an external mechanical force. Another consequence of surface tension is capillary movement. This depends on the diameter of the channel and the contact angle between the liquid and the channel. The smaller the radius of the channel and larger the contact angle, the more a liquid will be affected by capillary forces. When capillary forces become dominant, the flow regime is typically laminar, and the high ratio between area and volume makes the physical and chemical properties of the liquid−surface interface

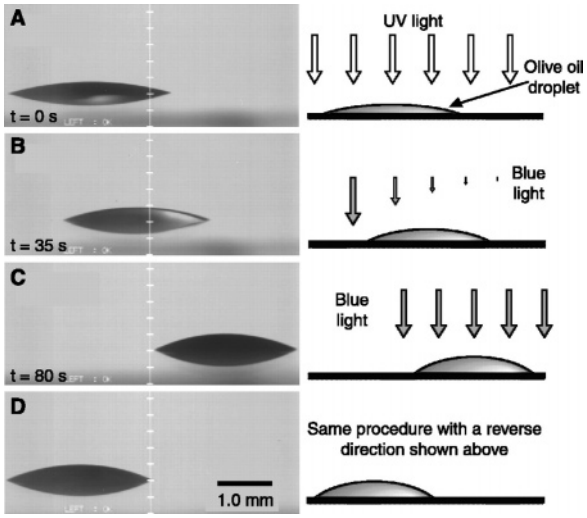

Figure 10. Photographs of light-driven motion of an olive oil droplet on a silica plate modified with an azobenzene derivative. The oil droplet moves because of a surface energy gradient generated by asymmetrical irradiation with 436 nm light perpendicular to the surface. (A−C) The sessile contact angles were changed from 18° (A) to 25° (C), confirming photonic modification of the surface polarity. (D) The direction of movement of the droplet could be controlled by varying the direction of the photoirradiation. (Reprinted with permission from ref 118. Copyright 2000 AAAS.)

critical for determining the overall characteristics of the system.

5.3. Controlling Binding Processes at Sensor Surfaces

For all chemo-/biosensors, control of surface structure at the molecular scale is the ultimate goal as this in turn determines all observable macroscale behavior, such as chemo-/bioactivity, selectivity, sensitivity, response time. In the past, materials science has focused on generation of surfaces that had a particular function, for example, very passive, protective surfaces such as Teflon, or very active surfaces generated by immobilization of specific binding sites such as synthetic ligands, or bioreceptors such as enzymes or antibodies. More recently, the concept of 'switchable' or 'adaptive' surfaces has emerged in which the surface typically can be switched between two or more modes that can have very distinctly different characteristics. Key to this developing area has been ways of immobilizing functional molecules on sensor substrates. In the following section, we shall examine strategies for producing functionalized surfaces that can be electrochemically, optically, or chemically switched between different modes of behavior (e.g., passive or nonbinding surface and active or binding surface), using external chemical, electrochemical, or photonic stimuli.

Control of binding behavior can be effected through molecules whose conformational, electron distribution (polarity), charge, wetting, and optical properties can be changed using light, electrostatic/magnetic field, electrochemical, or chemical stimuli.[120] For surfaces exhibiting such behavior, it raises the intriguing possibility of having a material that can be maintained in a passive mode that is relatively unaffected by exposure to the sample environment over time, switched to the active mode only when a measurement is needed, and subsequently switched back to passive mode. In principle, this could open the way to new types of chemo-/biosensors that can maintain their operating characteristics

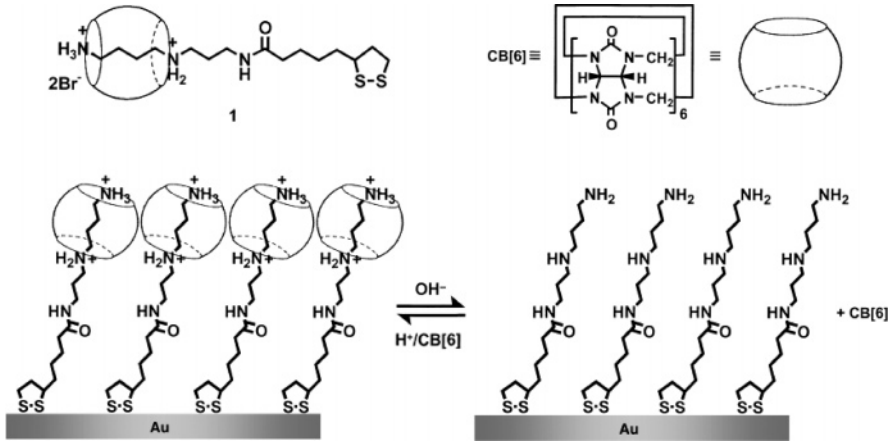

Figure 11. Self-assembled monolayer of pseudorotaxane on Au and dethreading and rethreading of the cucurbituril (CB(6)) macrocyclic cage on varying the pH. (Reprinted with permission from ref 122. Copyright 2003 Wiley-VCH Verlag GmbH & Co.)

for much longer times, hence reducing the need for complex calibration routines.

Electrochemical modulation of host−guest complexes at solid−liquid interfaces has been demonstrated using self-assembled monolayers (SAMs) based on pseudorotaxanes. Pseudorotaxanes are a class of supramolecular compounds composed of a molecular thread, encircled by a molecular bead, typically a macrocyclic cage, free to dissociate from the molecular thread[121,122] (Figure 11). pH-dependent, reversible dethreading and rethreading of the ring has been demonstrated when the thread component of the pseudorotaxanes is anchored to a gold surface by means of a disulfide pentacycle at the end of the chain and the macrocyclic cage is a cucurbituril (CB(6)), a compound comprising six glycoluril units. Under acidic conditions, the macrocyclic cage can bind an appropriate guest to form the pseudorotaxane supramolecular compound, while under alkaline conditions there is a dethreading of the macrocyclic guest and consequently dissociation of the pseudorotaxane complex. On the surface of an electrode, depending on the pH, the SAM can block or allow accessibility of electroactive species such as iron hexacyanate(III).[122] On the surface of an electrode the pseudorotaxane−SAM layer acts as an "ion gate", and its conductance can be changed under pH control. It has also been demonstrated that the complexation properties of a pseudorotaxane-functionalized self-assembled monolayer can be electrochemically controlled by adjusting the redox state of the guest species.[121] In this system the guest is a stable tetrathiafulvalene anchored to a gold electrode and the hosts are electron-deficient and electron-rich macrocyclic compounds. Electrochemical reduction of the tetrathiafulvalene leads to formation of a pseudorotaxane with the electron-rich macrocyclic host, while oxidation of the tetrathiafulvalene in the presence of the electron-deficient macrocyclic host leads to formation of a pseudorotaxane. Although reversibility is still an issue, this system offers the possibility of electrochemical- or pH-based control of interactions at the molecular scale. In a similar way, reversible control of the surface properties can be performed with electrical switching. Electrical potential stimulation can be used to control the surface properties of SAMs based on ionizable alkanethiolate on a gold surface.[123] They are low-density ionizable SAMs (LD-SAM) of (16-mercapto)hexadecanoic acid (MHA) where on one side of the long alkane chain the thiol groups anchor the molecule to a gold surface while on the other side the carboxylic function provides a hydrophilic cap over the hydrophobic chain. Upon applying a positive potential, the negatively charged carboxylate groups bend toward the gold surface, exposing the hydrophobic chain of the MHA to the surrounding medium. Otherwise, by applying a negative potential the negatively charged carboxylate groups undergo electronic repulsion toward the gold surface and the MHA adopts a straight conformation, exposing hydrophilic groups to the surrounding medium (Figure 12). A simple conformation change induced by electronic potential therefore can induce significant changes in the overall surface binding properties. In order to ensure that there is enough space for the MHA chains to bend and lift up, the assembling process of the SAM includes a wrapping−unwrapping step of the alkanethiolate with molecules that can provide a spacer function to maintain the MHA chains at a certain distance. The LD−SAM switchable surfaces have been demonstrated use to control protein assembly of two kinds of fluorescent avidin with two different isoelectric points, one positive and one neutral. This could open the way to controlled protein adsorption−release in capillaries, channels, or protein chips.[124]

Magnetic switching of surface orientation has been demonstrated with the development of a magnetic tunable electrochemical reactivity on catalytic nickel nanowires.[125] Considering the nickel's magnetic properties and electrocatalytic action toward carbohydrates and alcohols, it is possible to control its reactivity by magnetic modulation. Placing the nickel nanowire on the surface of a carbon electrode, a vertical orientation of the magnetic field induced a big increase of the current signal and full accessibility to the catalytic site, whereas with the opposite orientation, a decrease of the signal is detected and accessibility to the catalytic site is blocked.

Light-driven processes can also be used to induce reversible conformational transitions in molecules that can be used to produce surfaces with switchable behavior.[126] It commonly involves switching a leuco form to a colored form by exposure to UV radiation, accompanied by changes in the UV−vis spectrum and hence changes in the color of the material (photochromism). Organic photochromic compounds are molecules of considerable interest as they are expected to offer new functional materials such as erasable photomemories and photoresponsive devices that take advantage of polarity and geometrical changes induced by irradiation.[127] Among the class of the organic photochromic compounds, spiropyrans are some of the most attractive due to their high photosensitivity and very clear color change. Spiropyrans exist in a closed, uncharged, inactive, nonplanar, and

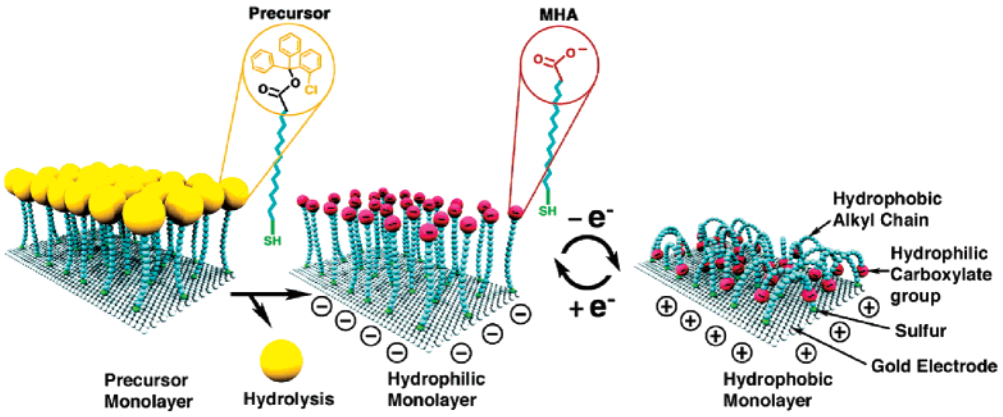

Figure 12. Representation of the wrapping−unwrapping step of the alkanethiolate with molecules that can provide a molecular event between to maintain the MHA chains at a certain distance and then the transition of the MHA chains between straight (hydrophilic) and bent (hydrophobic) molecular conformations. (Reprinted with permission from ref 123. Copyright 2003 AAAS.)

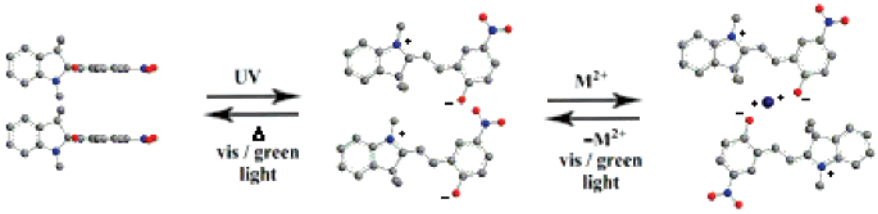

Figure 13. Spiropyrans reversible conversion between a closed, uncharged, inactive, nonplanar, and colorless "spiropyran" form (SP) by exposure to visible or green light and open, planar, active, highly conjugated, highly colored "merocyanine" form (MC) by exposure to ultraviolet (UV) light. The merocyanine form can bind metal ions through the phenolate anionic site and amino acids due to complementary zwitterionic association.[157] The guests can be subsequently expelled by irradiation with visible or green light, and the spiropyran reverts to the closed form. Light-modulated control of ion binding at spiropyran-modified surfaces is therefore possible.

colorless "spiropyran" form (SP) (leuco dye) which is converted by exposure to ultraviolet (UV) light to an open, planar, active, highly conjugated, highly colored "merocyanine" form (MC) (Figure 13). The SP closed form presents an absorption spectrum in the UV range with an actinic band situated near 320−380 nm. Absorption in this region leads to formation of the MC open form with a maximum absorbance wavelength between 560 and 570 nm (depending on the solvent used). The reverse process is stimulated by visible light (particularly in the green region, around 525 nm) or occurs slowly in the absence of light because the SP form is thermodynamically favored.

The exciting feature of this system is the ability of the merocyanine form to reversibly bind metal ions through the negatively charged phenolate group. On binding the metal ion the absorbance maximum shifts to around 430 nm and the absorbance at 560 nm decreases.[128] Hence, the system is inherently self-indicating as the color changes from deep purple (merocyanine form) to pink (metal ion complex). It has been demonstrated that when the spiropyran is covalently immobilized onto an optically transparent polymeric surface of PMMA (polymethylmethacrylate), it can be reversibly switched many times between the SP and MC forms using UV/green LEDs.[128] The negatively charged phenolate group of the MC form provides a weak and relatively nonselective binding site for a range of cations (Figure 14) that can be activated and deactivated at a user-selected location using the LEDs. As in the liquid-phase experiments mentioned above, ion-binding results in a shift in absorbance, which corresponds to a color change from purple to pink (λ_{max} ca. 430 nm). Then, upon irradiation of the complex with a green LED or visible light, the metal ion can be expelled and the MC reverted to the inactive SP form. This cycle can be repeated multiple times using UV and green LEDs to control the surface binding of a range of metal ions, including Co^{2+} and Cu^{2+}.[128,129] In principle, therefore, these are surfaces that can be switched reversibly between active and passive states. In the SP form no binding with metal ions occurs and the system is inherently self-indicating due to the color changes that accompany switching between SP and MC isomers and formation of the MC−metal ion complexes. Furthermore, the bound species can be reversibly expelled on demand simply by illumination of the surface with green or visible light, and the system once again indicates its status through return to the colorless SP form.

Due to the zwitterionic nature of MC, amino acids are potential guests through complementary two-point electrostatic binding. L-Tryptophan, L-tyrosine, and L-dopa have been demonstrated to bind reversibly with merocyanine zwitterions.[130] This raises the prospect of surfaces that can reversibly bind biomolecules on demand using light to control the system. Recently combining the photochromic behavior of spiropyrans and the swelling properties of hydrogel matrix it has been demonstrated that the volume of a hydrogel copolymer of spirobenzopyran and poly(*N*-isopropylacrylamide) (pNIPAAm) can be reversibly reduced and increased when the gel is alternatively exposed to blue light or kept in the dark.[131] In addition to switchable microrelief formation properties, the hydrogel exhibits changes in its electrostatic properties. When the hydrogel is placed in a slightly acidic bath the spiropyran moiety is neutral when irradiated with blue light (because of the prevalence of the closed form) and positively charged when kept in the dark (because of the prevalence of the open form in which both the phenolate and indoline nitrogen are protonated). After microrelief formation, negatively charged

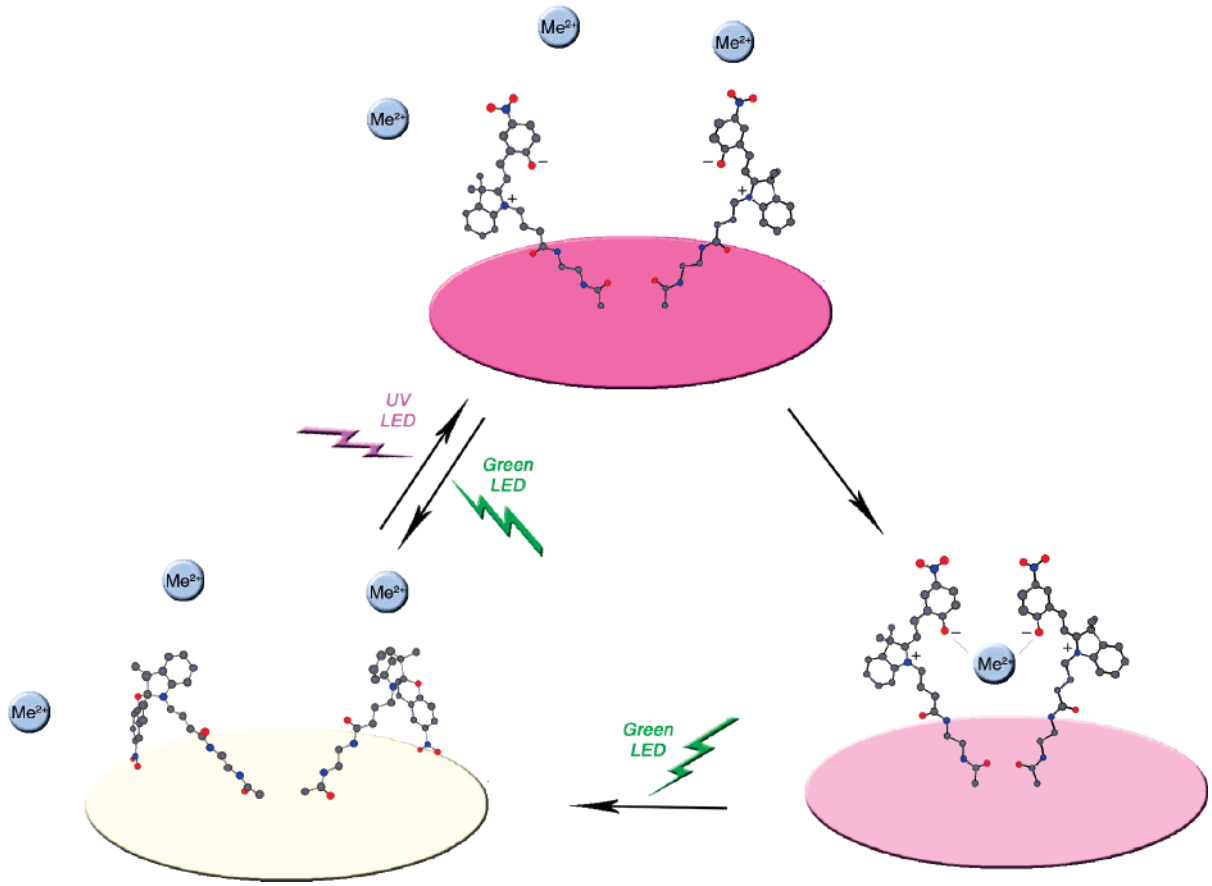

Figure 14. Schematic representation of a spiropyran derivative covalently immobilized onto an optically transparent polymeric surface of PMMA (polymethylmethacrylate). The colorless inactive SP form (top) can be reversibly switched using UV light/green LEDs to the pink zwitterionic MC active form (bottom). The negatively charged phenolate group of the MC form provides a binding site for a range of cations including Cu^{2+}, Cr^{3+}, and Co^{2+}.

fluorescent nanoparticles are adsorbed on the nonirradiated region because of the positive overall charge of the photochromic compound.

These are examples of materials whose function and properties can be radically changed and controlled using external stimuli. They will have important applications in microfluidics, separation science, controlled sampling and release, soft actuators, and sensing and could lead to development of radically different platforms for realizing autonomous analytical devices suitable for scaled-up sensor network deployments

5.4. Bead-Based Systems

Bead-based systems are a particular kind of biphase system in which solid particles in suspension can be moved as a fluid but easily separated from the liquid phase. Beads provide a higher surface area than flat surfaces for chemical reactions, and bead-based analytical approaches offer significant advantages for techniques that require reactions on surfaces.[122] The low density of the polymer matrix allows binding kinetics comparable to those of solution-based systems, and their large surface area and greater density permit rapid and highly efficient binding of target species.

Micro- or nanoparticles can be chemically derivatized with a wide range of specific ligands or specific recognition groups. General specificity particles are largely produced as substrates to attach a variety of affinity ligands which allow a broad range of direct applications, such as fluid flow-citometry analysis,[132] immunoassay-diagnostics,[133,134] cell biology,[135,136] and controlled release.[130] They are also generating increasing interest in the photonics community due to their high quality-factor (Q-factor) morphology-dependent resonances and sensitivity to refractive index and size changes. When biomolecules are adsorbed on their surface, a change on their effective size and refractive index occurs, and it is claimed that a biosensor based on this phenomenon can detect a single molecule.[137] Configured as optical microcavity resonators, applications include microlasers, narrow optical filters, optical switching, high-resolution spectroscopy,[137] and Raman sources.[138]

A variety of materials, including organic and inorganic polymers, have been used as substrates for micro- and nanospheres. Common organic substrates are polystyrene or polymethacrylate. Polystyrene microspheres are often used for protein binding due to the high degree of nonspecific protein adsorption (hydrophobic interaction is the most likely mechanism involved in adsorption of proteins). Inorganic substrates include metals, silica, or alumina. Silica microspheres are naturally hydrophilic, so relatively little nonspecific protein absorption should occur. Chromophore-modified microspheres are available in a wide variety of colors as are beads modified with fluorochromes, fluorophors, and scintillators. Superparamagnetic or radioactive microspheres are available with a range of different mean magnetic and radioactivities.

Bead-based approaches have been applied in fluidic systems in numerous ways, for separations, sample extraction, analyte detection, and controlled release. Silica beads

coated with octadecylsilane (ODS) packed in a microfluidic system enabled on-chip solid-phase electrochromatography for extraction of analytes with different polarity to be developed. The ODS-coated beads were mobilized in the cavity of a chromatography bed as part of a microfluidic system using electroosmotic flow. Two wires within a sample channel formed a cavity in which the beads were trapped. Beads were similarly packed in a chamber and reversed-phase capillary electrochromatography performed. A fluorescent nonpolar analyte and fluorescein were loaded on the chromatographic bed, and complete separation was achieved after 20 s.[139]

Bead-based techniques have been successfully adopted also for miniature biosamplers, such as filterless bioseparators, that allow separation of target biomolecules or bacteria from a liquid.[140] Superparamagnetic particles have been coated with antibodies and controlled in a microfluidic channel with a planar electromagnet. When the magnetic field is applied, beads are held in the channel, and when antigens are injected, the bound antigens are retained while others are washed out with the flow. Subsequently, magnetic beads are released to the sensing chamber for detection, and the filterless bioseparator is ready for another separation.

Immunoassay, thanks to its high specificity, is one of the most important detection methods for clinical diagnosis and biochemical studies. Employing mobile beads in an immunosorbent assay leads to a very flexible system with attractive characteristics compared to conventional approaches.[141] For example, a bead-based system provides simple and effective separation of the free and bound forms and allows heterogeneous immunosorbent assays to be performed within a microchannel. Polystyrene beads preabsorbed with s-IgA (antigen) were introduced in a microchannel, reacted with colloidal gold conjugated anti-s-IgA antibody, and detected by a thermal lens microscope. With this method the overall analysis time was reduced from 24 h for the conventional homogeneous liquid-phase immunoassay to 1 h, avoiding numerous washing and solution removal procedures.

A bead system has also been employed for gene expression analysis. A so-called 'nanobarcode'-based microbead assay has been developed to give an accurate and reproducible gene expression profile.[142] Four different quantum dot nanocrystal fluorescence emitters with different emission maxima were mixed with a polymer and coated in magnetic microbeads to generate nanobarcode beads called Qbeads. Gene-specific oligonucleotide probes were conjugated to the surface of each Qbead to create a panel which was able to decode an RNA target on the basis of the spectral profiles and intensity ratios of the four Qbeads. Unbound RNA can be easily washed out when the beads are exposed to a magnetic field. The gene expression data obtained with the beads was found to have a high correlation with reference Affymetrix Genechip microarray data. This nanobarcode system opens the way for a huge variety of applications in biology, chemistry, and medical diagnosis and can potentially code more than one million combinations.

Similarly, a bifunctional system based on mesoporous silica beads embedded with both semiconductor quantum dots for optical encoding and iron oxide for magnetic separation has been developed.[143] Quantum dots have attractive properties such as size-tunable light emission, resistance against photobleaching, and simultaneous excitation properties, while beads embedded with iron oxide have been used for biological separation, capture of rare cells,

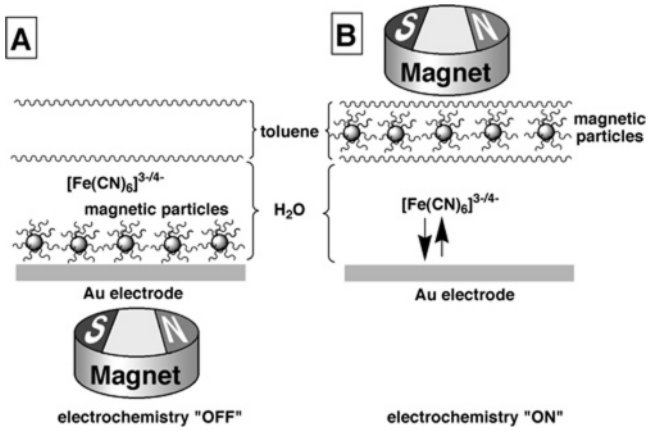

Figure 15. Magneto-controlled reversible translocation of the functionalized magnetic particles between the organic phase above the aqueous electrolyte and the electrode surface (A). The electrode surface is blocked with functionalized magnetic particles attracted to the electrode by the external magnet. (B) The magnetic particles are retracted from the electrode surface, and the electrode surface is electrochemically active. (Reprinted with permission from ref 144. Copyright 2004 American Chemical Society.)

proteins, and nucleic acids. Functionalized magnetic nanoparticles have also been successfully used to control and switch the hydrophilicity/hydrophobicity of an electrode surface.[144] A two-phase system, made up of water and toluene as the liquid phase and magnetic nanoparticles embedded with hydrophobic alkyl chains as a suspended solid phase, was placed in contact with an Au electrode. Applying an external magnetic field on the electrode surface induced physical attraction of the particles to the electrode surface turning the surface hydrophobic. On the other hand, applying a magnetic field to the upper toluene phase induces migration of the particles to this layer, generating a hydrophilic surface at the gold electrode (Figure 15). Electrochemical switching of the conductive support surface has been demonstrated by performing magnetoswitchable bioelectrocatalytic oxidation of glucose in the presence of glucose oxidase and ferrocene dicarboxylic acid. Removal of the magnetic particles from the electrode surface allows oxidation of ferrocene dicarboxylic acid at the electrode surface and bioelectrocatalyzed oxidation of glucose by glucose oxidase. This process is blocked by attraction of the particles to the electrode. Hence, by means of a physical change (bead movement) it is possible to control a reactive interface using the chemical and mobility properties of a bead-based system.

Light excitation is another mechanism for controlling the properties of microparticle systems. Light modulation of spiropyran-coated gold nanoparticles provides a potential system for the controlled release of amino acids.[130] A spiropyran-modified derivative with a thiol chain was self-assembled onto a gold nanoparticle surface, and the photoswitching of the Au−SP nanoparticle in the presence of various amino acid derivatives has been investigated. The spiropyran was excited with UV light and converted to the merocyanine form. Subsequently, it was demonstrated that the presence of certain amino acid derivatives stabilized the MC form due to formation of a stable complex between MC and the amino acid derivatives. Furthermore, irradiation of the complex with visible light triggers reversion of the MC to the SP form and release of the guest species. With this approach it may be possible to use light-modulated binding to control a localized amino acid concentration, which could

form the basis of new approaches to drug delivery or biological separations.

6. Overall Conclusions

Because of space limitations, this review has been largely restricted to two potential areas of application for wireless sensor networks: remote environmental monitoring and wearable sensors or body sensor networks. With respect to the environment, we focused on recent developments in mote-based wireless sensor networks and highlighted limitations with the current manifestations of these platforms, particularly with respect to integration of chemo-/biosensing capabilities and the essential requirement for these devices to be completely self-sustaining in all respects if the promised massive scale up to true pervasive sensing is to be realized.

However, in addition to the need for improvements in the engineering aspects of motes, there are very significant challenges for the chemo-/biosensor research community to deliver sensing platforms that are appropriate for integration into scaled-up deployments in terms of sustainability, cost, reliability, etc. While microfluidics offers a route to intermediate scale up in the short-to-medium term (5 years), particularly for autonomous environmental sensing, they still require reagents and generate waste and are still not sufficiently reliable for sustained use over many months/years. Consequently, examples of real deployments of chemo-/biosensor networks are few and far between. Consequently, we are only beginning to understand how signals obtained from groups or communities of simple, low-cost sensors may provide a higher degree of certainty in event detection (e.g., through tracking the dynamics of response patterns to validate a decision) and to what extent this may compensate for the lack of sophisticated calibration procedures.[145] In general, we can speculate that in the medium term (5 years) we will see a growth in the use of reagentless and 'noncontact' approaches that can generate molecular or chemical information about a sample. For example, methods such as UV−vis, IR, and Raman spectroscopies provide direct access to such information. While IR/Raman spectrometers are too expensive (typically $20K upward) to be considered for scaled-up deployments, IR detectors tuned to the specific absorbances of target gases are available commercially, and the cost of these is likely to decrease rapidly.[146,147] Direct UV measurement of nitrate in wastewater, lakes, rivers, and marine environments is a good example of a reagentless approach that has become increasingly employed for long-term monitoring applications.[148] Such nonselective measurements can be effective under very specific constraints (e.g., there are no coabsorbing species present in the sample) or where reagent-based approaches cannot be employed (e.g., time scale is very long, months/years between servicing).[149] Another approach is to employ noncontact ac conductance/impedance measurements. The advantage here is that the electrodes can be completely encased in a protective coating while still probing the local environment for changes in conductivity that are related to the ionic strength of liquid samples, which in turn is related to changes in the chemical composition. This approach does not provide the molecular selectivity accessible through more sophisticated chemo-/biosensors. In other words, it can detect that changes may be happening in the local chemical environment without being able to identify what species is causing the change. In the recent literature it has been combined with microcapillary electrophoresis as a detector, but it can function independently of a separation platform if general information about the gross chemical composition is the key operational requirement.[150]

Applications in wearable sensors/body sensor networks are certain to happen in the near future (2 years) as the first commercial products are already appearing and a very significant user base is rapidly emerging, initially through consumer exercise/fitness products, but these will quickly evolve into personal health applications and drive demand for chemo-/biosensing products capable of providing specific information on disease status that will complement the more generic health information available from wearable sensors.

However, the key to large-scale deployments of chemo-/biosensors lies in fundamental materials science. Radically new approaches to low-power transport of water across surfaces, through materials, and along microchannels are needed, for example, based on light- or electrochemical-mediated control of surface charge/polarity. In a similar manner, control of surface binding behavior is an exciting prospect as is control of surface docking and release of molecular targets or multifunctional beads. Biomimetics will gain popularity, leading to the development of microfluidic platforms with circulatory systems incorporating polymeric structures that provide the function of pumps and valves through muscle-like actuation behavior. Accordingly, there is a wonderful opportunity to link research in molecular materials with microsystems engineering and developing new platforms capable of performing reliable chemo-/biosensor measurements in scaled-up deployments that will have a major impact on individuals and society.

7. Abbreviations

AEWOD	asymmetric electrowetting-on-dielectric oscillation
Ag	silver
AgCl	silver chloride
A-Si	amorphous silicon
BSN	body sensor network
CB(6)	cucurbituril
CENs	Centre for Embedded Networked Sensors
CIGS	copper indium gallium diselenide
CTO	Chief Technology Officer
DARPA	defense advanced research projects agency
DMA	dodecyl methacrylate
DMMP	dimethyl methylphosphonate
EAPs	electroactive polymers
ECG	electrocardiograph
EM	electromagnetic (radiation)
EMG	electromyography
ETH	Eidgenössische Technische Hochschule (Zürich)
EU	European Union
FANs	fabric area networks
FDA	Food and Drug Administration
FETs	field effect transistors
GF	Gauge factor
GOD	glucose oxidase
GPS	global positioning system
GSM	global system for mobile communications
ICP	inherently conducting polymers
IEEE	Institute of Electrical and Electronics Engineers
ISM	Industrial, scientific, and medical (radio band)
ISN	Institute for Soldier Nanotechnologies
LAN	local area network
LD-SAM	low-density ionizable SAMs
LED	light-emitting diode
LDR	light-dependent resistor
LOAC	lab-on-a-chip
MC	merocyanine form

MEMS	microelectromechanical systems
MHA	(16-mercapto) hexadecanoic acid
MIT	Massachusetts Institute of Technology
MPC	hydrophilic 2-methacryloyloxyethyl phosphorylcholine
μTAS	micrototal analysis systems
NRBC	Nuclear, Radiological, Biological, Chemical
NSF	National Science Foundation
RFID	radiofrequency identification
ODS	octadecylsilane
PANi	polyaniline

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