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Functional nanofibers in sensor applications

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Abstract: Over the last decade, the interest in electrospun nanomaterials and their applications has increased. The fascinating and unparalleled properties of electrospun nanomaterials, such as large surface-to-volume ratios and high open porosity, have opened new and unexpected fields of application, especially in ultrasensitive sensors. By exploiting the inherent physical, electrical and mechanical properties of nanomaterials, it is possible to improve the performance of conventional sensors by increasing their sensitivity, selectivity, portability and power efficiency. In this chapter, the recent progress in the development of electrospun nanomaterials is reviewed. In particular, applications in some predominant sensing approaches, such as acoustic wave, resistive, photoelectric, optical and biological, are discussed.

Key words: electrospinning, nanofibers, nanonets, nanostructures, sensing materials, sensors.

11.1 Introduction: modern electrospinning technology

Electrospinning is a highly versatile technique to process solutions or melts, mainly of polymers, into continuous fibers with diameters ranging from several micrometers down to a few nanometers by applying a high voltage on a polymer solution or melt ejected from a micro-syringe pump. In 1934, Formhals described the operation of electrospinning in a US patent for the first time; but only since the 1990s has it gained substantial attention. Since that time, the process has attracted rapidly growing interest triggered by potential applications of nanofibers in nanoscience and nanotechnology. Several research groups, especially the Reneker group, revived interest in this technology and have demonstrated a possibility to electrospin a wide variety of polymeric fibers (Doshi and Reneker, 1995; Reneker and Chun, 1996; Fong *et al.*, 1999). A number of review articles have been published recently which provide an insight into the most prominent aspects of electrospinning (Huang *et al.*, 2003; Li and Xia, 2004; Ramakrishna *et al.*, 2006;

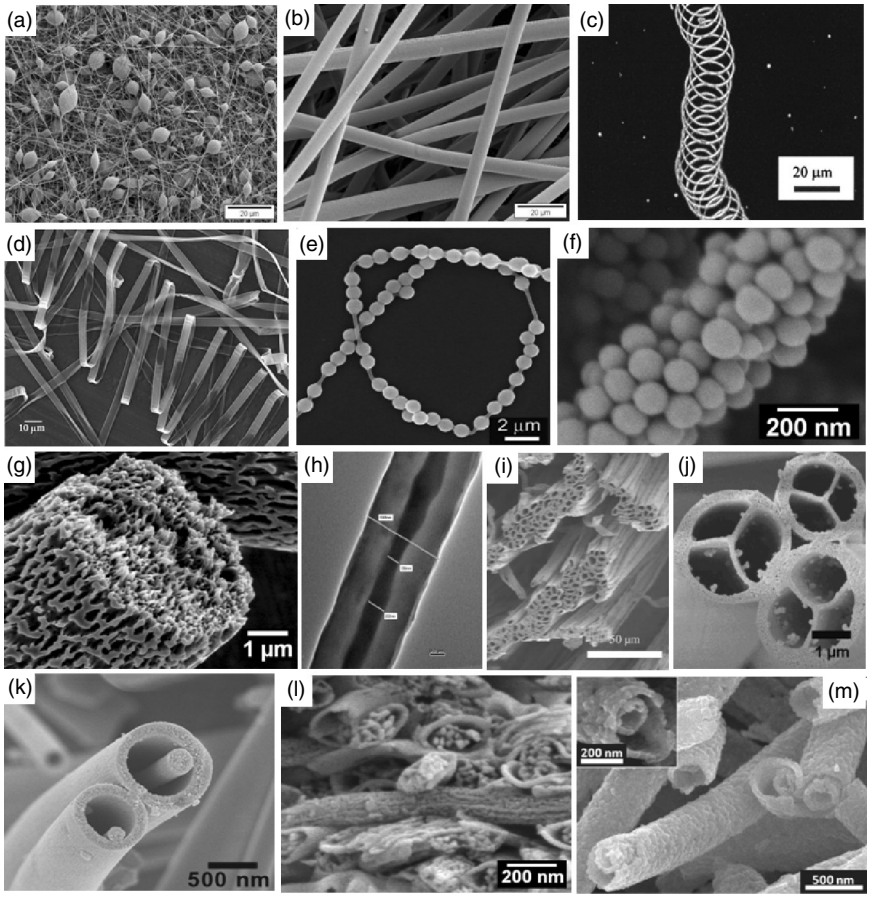
Teo and Ramakrishna, 2006; Greiner and Wendorff, 2007; Agarwal *et al.*, 2009). To date, over 100 synthetic and natural polymers have been successfully electrospun into fibers with a broad range of applications owing to their low dimensions and large surface areas.

Generally, electrospun fibers are collected as nonwoven membranes with randomly arranged structures, which have greatly limited their applications in electronic devices or biomedical applications (Teo and Ramakrishna, 2006; Agbenyega, 2008; Zhang and Chang, 2008; Liu *et al.*, 2010). In order to fully realize the potential of electrospun fibers, it is important to fabricate fibrous assemblies with controllable microstructures. Recently, several groups have demonstrated that electrospun nanofibers could be collected as uniaxially aligned arrays by using specially designed collectors. For example, Li and coworkers (2003) have demonstrated that nanofibers can be uniaxially aligned by introducing insulating gaps into conductive collectors. Matthews *et al.* (2002) have demonstrated that aligned fibers could be obtained by using a rotating collector at high speed; the mandrel rotation speed and fiber orientation strongly influence the properties of the electrospun nanofibers. Zussman *et al.* (2003) have demonstrated the use of a wheel-like bobbin as the collector to position and align individual polymer nanofibers into parallel arrays. However, because the edge of such a bobbin has to be relatively sharp, this technique does not seem to be feasible for forming well-aligned nanofibers over large areas. In addition, it was possible to obtain various patterned architectures of the electrospun nanofibers by varying the design of electrode pattern (Li *et al.*, 2005). One of the most interesting features associated with this approach is that this technique enables direct integration of nanofibers with controllable configurations into an electrode system such that the nanofibers can be fabricated and aligned simultaneously, which will significantly simplify the production of nanofiber-based devices.

11.1.1 Nanofibers

Different nanofiber morphologies can be obtained via control of the processing conditions, enabling one to produce smooth as well as beaded (Lin *et al.*, 2010) and helical (Kessick and Tepper, 2004) structures (see Fig. 11.1a–c). Recent demonstrations from a number of groups indicate that this technique is also capable of generating nanofibers with ribbon (Koombhongse *et al.*, 2001), necklace-like (Jin *et al.*, 2010), porous (Kanehata *et al.*, 2007; Ding *et al.*, 2008a), core-shell (Sun *et al.*, 2003), hollow (Dror *et al.*, 2007), multichannel tubular (Zhao *et al.*, 2007), nanowire-in-microtube (Chen *et al.*, 2010), multicore cable-like (Kokubo *et al.*, 2007) and tube-in-tube (Mou *et al.*, 2010) structures (see Fig. 11.1d–m).

Compared with inorganic nanorods and carbon nanotubes, the electrospun nanofibers are continuous, which possess them with high axial strength combined with extreme flexibility. Yet, these assemblies would possess excellent

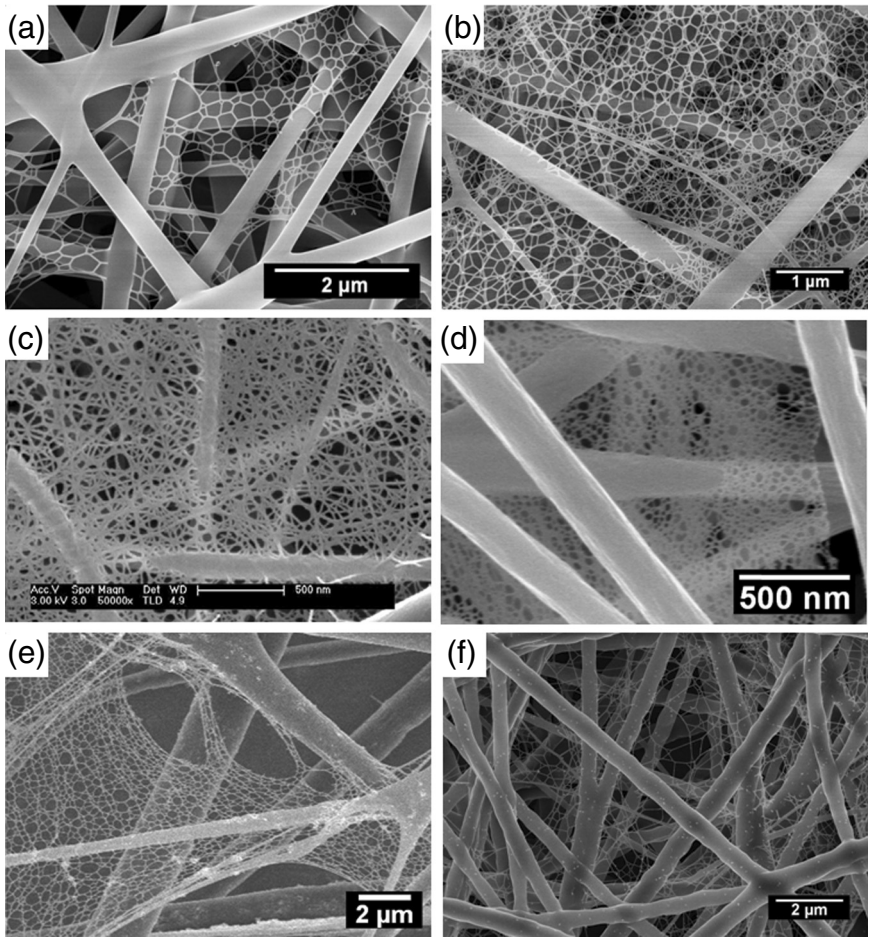


11.1 Different morphologies of electrospun fibers: (a) beaded, (b) smooth (Reprinted with permission from Lin *et al*. (2010). © 2010 American Chemical Society), (c) helical (Reprinted with permission from Kessick and Tepper (2004). © 2004 American Institute of Physics), (d) ribbon (Reprinted with permission from Koombhongse *et al*. (2001). © 2001 Wiley), (e) necklace-like (Reprinted with permission from (Jin *et al*., (2010). © 2010 American Chemical Society), (f, g) porous (From Ding *et al*. (2008a)), (h) core-shell (Reprinted with permission from Sun *et al*. (2003). © 2003 Wiley), (i) hollow (Reprinted with permission from Dror *et al*. (2007). © 2007 Wiley), (j) multichannel tubular (Reprinted with permission from Zhao *et al*. (2007). © 2007 American Chemical Society), (k) nanowire-in-microtube, (l) multi-core cable-like (Reprinted with permission from Kokubo *et al*. (2007). © 2007 IOP Publishing Ltd) and (m) tube-in-tube (Reprinted with permission from Mou *et al*. (2010). © 2010 American Chemical Society) structured fibers.

structural mechanical properties. Additionally, a multitude of functions can be incorporated into the fibers and an extremely broad range of potential applications exists in which electrospun nanofibers can make major contributions. These include not only textile, ultrafiltration, tissue engineering, catalysis and mechanical reinforcement applications, but also extend to the fabrication of sensors, batteries and other types of devices. It would be meaningful to combine the electrospinning technique with controllable nanofibers assembly for sensors fabrication, as this would provide a simple, rapid and cheap way to construct ultrasensitive devices. Although the use of nanofibers offers the prospect of high sensitivity and rapid detection, the ability to incorporate nanofibers into device architectures is limited by the difficulty in manipulating and locating the nanostructures with respect to the microelectrodes.

11.1.2 Nanonets

Electrospun fibrous membranes typically have fiber diameters in the range 100–500 nm, but properties such as surface area and porosity become more significant when the fiber diameter falls below 20 nm (Huang *et al*., 2006). The major challenge for developers is to come up with robust methods for manufacturing extremely small nanofibers in large quantities and with a uniform size. We have found a procedure for generating net-like structured nanowires with small diameters (~20 nm) in three-dimensional (3-D) fibrous mats by optimization of various processing parameters during electrospinning (Ding *et al*., 2006b). This novel process, termed 'electronetting', allows one-step fabrication of ultrathin 'nanonets' with large quantities and uniform size. The electrospun fibers act as a support for the soap-bubble-like structured nanonets comprising interlinked one-dimensional (1-D) nanowires (see Fig. 11.2). The major distribution region (over 70%) of nanowire diameters was in the range of 10–30 nm, which was one order of magnitude less than that of common electrospun nanofibers. The region of pore-width distribution of nanonets ranged from 20 to 550 nm, which was much less than that of pores among electrospun nanofibers. Therefore, nanonets possess great potential for application in filtration systems for the removal of particles or viruses with a size to nanometer ranges. To date, our group has successfully prepared various nanonets based on different polymer systems such as nylon-6 (Ding *et al*., 2006b), polyacrylic acid (PAA) (Ding *et al*., 2006b; Wang *et al*., 2010b), poly(vinyl alcohol) (PVA) (Ding *et al*., 2008b, 2010) and polyurethane (PU) (see Fig. 11.2). The formation of the nanonets is considered to be due to the electrically forced fast phase separation of the charged droplets which move at high speed between the capillary tip and the collector. The formation, morphology and area density of the nanonets in electrospun fibrous membranes are strongly affected by the solution properties and several parameters in the process of electrospinning.



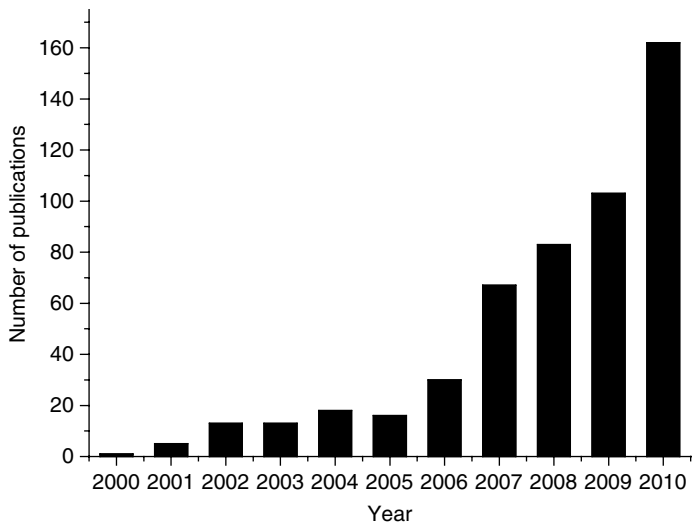
11.2 SEM images of various nanonets based on different polymer systems: (a) PAA (Reprinted with permission from Wang *et al.* (2010b). © 2010 IOP Publishing Ltd), (b) PAA/NaCl (Reprinted with permission from Wang *et al.* (2011). © 2011 Royal Society of Chemistry), (c) nylon-6 (Reprinted with permission from Ding *et al.* (2006b). © 2006 IOP Publishing Ltd), (d) PVA/ZnO (Reprinted with permission from Ding *et al.* (2008b). © 2008 Elsevier Ltd, (e) PVA/SiO_2 (Reprinted with permission from Ding *et al.* (2010). © 2010 Elsevier Ltd), (f) PU/NaCl.

Nanonets exhibit several fascinating characteristics, such as extremely small fiber diameter and pore width, notable specific surface area and high porosity, superior mechanical performances, which make them attractive candidates for use in a range of applications including ultrasensitive sensors and ultrafiltration. Furthermore, nanonets have the potential to be used as ultrafine filters to intercept viruses and bacteria, such as influenza A (H1N1) virus, severe

acute respiratory syndrome (SARS) virus, *Escherichia coli*, etc. (Ding *et al.*, 2010). Clearly, there is growing interest in the process, but the results reported to date are primarily focused on the empirical production and the proposed uses of polymer nanofibers. At the same time, thorough understanding of the mechanisms of the breakup of liquid jet and subsequent nanonets formation is needed for the development of robust methods of process control.

11.1.3 Electrospinning and sensors

Development of electrospun nanomaterials, such as nanofibers and nanowebs, provided researchers with an opportunity to construct electronic interfaces with components whose sizes are comparable to the size of molecules, potentially leading to a much more efficient interface. Nanometer cross-sections of nanomaterials gives them enhanced surface sensitivity and allows them to utilize the benefits of size effects, such as quantization and single-molecule sensitivity. The comparatively large surface area and high porosity make electrospun nanomaterials highly attractive candidates for use in a range of devices, including ultrasensitive sensors. This is one of the most desirable properties for improving the sensitivity of sensors because a larger surface area will absorb more analytes and change the sensor's signal more significantly. A survey of open publications related to 'electrospinning and sensors' over the past ten years (at the time of writing) is given in Fig. 11.3.



11.3 Comparison of the annual number of scientific publications with the keyword 'electrospinning and sensor', as provided by the search engine of SciFinder Scholar.

The rapid rise in data clearly demonstrates that this subject has attracted increasing attention recently.

11.2 Formation of nanostructured sensing materials

The performance of a sensor is highly dependent on the configuration, morphology, thickness and the composite ratio of the sensing materials. There have been a vast number of methods developed to fabricate nanostructured sensing materials. Either single-component electrospinning or composite/doped electrospinning can be used to produce nanofiber functionalized sensing materials. Within each technique, the structure of the material may be random or ordered. However, up to now, preparation of electrospun sensing materials has always involved complicated polymer syntheses which make the fabrication time consuming; sometimes the leakage of sensing molecules affects the sensing performance. More available systems and new fabrication approaches need exploring. Recently, some research has focused on fibers with secondary porous structures. Moreover, it is a great challenge to immobilize the sensing elements onto the surface of the electrospun porous fibers. This section describes the design and fabrication processes that have been developed to realize electrospinning nanostructured sensing materials.

11.2.1 Single-component electrospinning

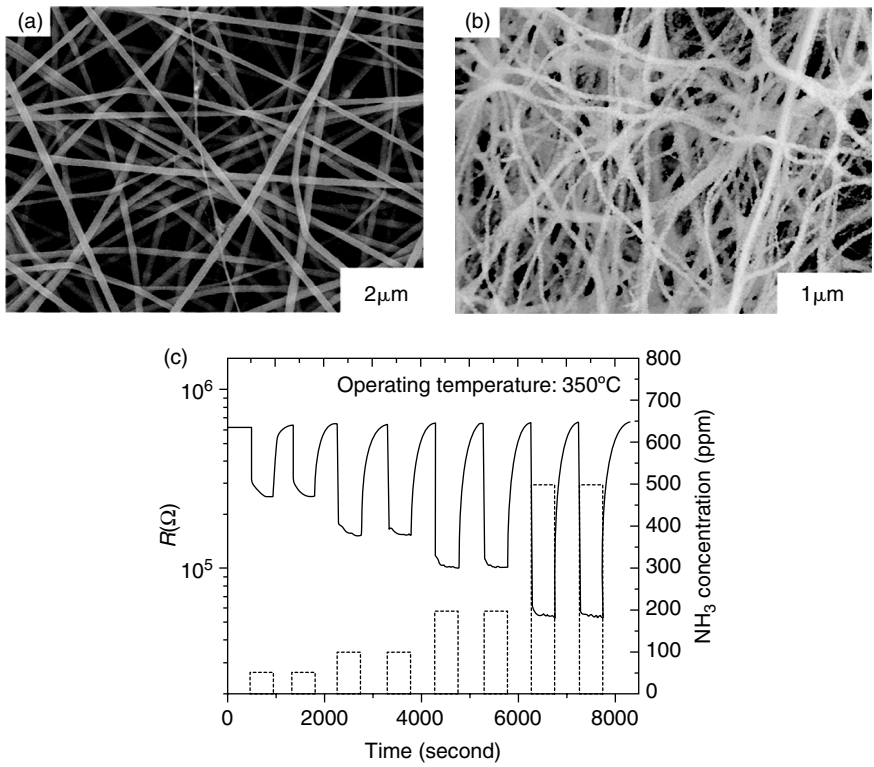
Single-component electrospinning can be used to produce nanofibers functionalized sensing materials. An interesting feature of this technique is that more sensing elements can be established on the surface of nanofibers, as well as more absorption sites exposed to analytes. To date, more than 100 types of natural and synthetic polymer have been electrospun into one-component nanofibers, such as poly(ethylene oxide), PVA, polystyrene (PS), polyacrylonitrile (PAN), polylactide, poly(ε-caprolactone), PU, polyamide, cellulose acetate (CA), poly(vinyl acetate) (PVAc) and many more (Huang *et al.*, 2003; Lu *et al.*, 2009); however, only few of them were used as sensing elements (Ding *et al.*, 2005b). Besides polymer-based sensing materials, nanostructured ceramics also have potential applications in nanoscale electronics, optical and sensing devices due to their notable electronic properties. The fabrication of sensing materials can be implemented over single-component electrospinning, but the remaining hindrance is that some polymers or ceramics cannot obtain nanostructured morphology via electrospinning directly (Wang *et al.*, 2010a). A promising approach to solve this problem is to use composite or doped electrospinning and even assemble these materials on the surface of nanomaterials.

11.2.2 Composite or doped electrospinning

Early work on electrospinning mainly dealt with conventional polymers that could be synthesized with sufficiently high molecular weights and could be dissolved in appropriate solvents. In an effort to greatly expand the functionality and thus the scope of applications associated with fibrous structures, composite and doped electrospinning have recently been developed to generate nanofibers with a range of chemical compositions, and therefore various electronic, magnetic, optical and biological properties.

In the past several decades, there have been many reports on the fabrication of composite nanofibers via electrospinning, including polymer/polymer, polymer/inorganic and inorganic/inorganic composites (Wang and Pan, 2008; Lu *et al.*, 2009). Recently, a large number of polymer/metal-oxide composite fibers have been produced by electrospinning in combination with sol-gel processes. In many cases, the composite fibers could be converted into metal-oxide fibers by subsequent calcination. Such composite fibers allow the fabrication of polymer fibers with special functionalities or of precursor fibers. For instance, Wang and coworkers (2006) obtained pure WO_3 nanofibers with controllable diameters of around 100 nm by electrospinning PVAc/tungsten isopropoxide solutions and subsequent calcinations (see Fig. 11.4a, b). The prepared WO_3 ceramic nanofibers have a quick response to ammonia in various concentrations, suggesting potential applications of the electrospun WO_3 nanofibers as a sensor material for gas detection (Fig. 11.4c).

Pure and doped metal-oxide semiconductors (MOS) nanostructured materials, such as ZnO, SnO_2 and other wide band gap metal oxides, have recently attracted considerable interest due to their unique physical properties and a wide range of possible applications (Andersson *et al.*, 1998; Li *et al.*, 2000; Schmidt-Mende and MacManus-Driscoll, 2007). However, most pure MOS are not stable in air and its electrical properties are significantly affected by adsorption of O_2, CO_2, hydrocarbons, S-containing compounds and water (Jimenez-Gonzalez, 1997). Therefore, it is highly desired to prepare 1-D MOS nanostructures doped with a selection of elements, such as Li, Ga, In, N, Al, Sn and P, to enhance and control their mechanical, electrical and optical performance. Electrospinning proved to be a simple, low-cost and reliable technique for dopant incorporation to attain modified structural, electrical and optical properties for these semiconducting nanofibers. Lotus and coworkers (2010) have investigated the effect of dopant addition on morphological, electrical and optical properties of semiconducting oxide nanofibers obtained by electrospinning. Pure SnO_2 and SnO_2 polycrystalline electrospun nanofibers doped with multiwall carbon nanotubes (MWCNTS) are synthesized by Yang *et al.* (2007). The SnO_2/MWCNTS composite nanofibers exhibited enhanced sensitivity compared

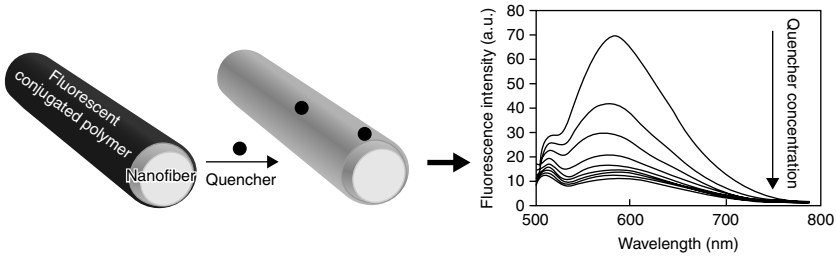


11.4 (a) SEM image of tungsten oxide/PVAc composite fibers, (b) SEM image of the same sample after it had been calcined in air at 500°C for 3 h and (c) response of WO3 nanofibers to ammonia (50–500 ppm). (Reprinted with permission from Wang *et al.* (2006). © 2006 American Chemical Society.)

to pure SnO_2 nanofibers. Doping with materials in the semiconductors may affect the electron transfer, which is considered in their investigation.

11.2.3 Surface assembly of sensing materials

Another area that has been explored for the parallel immobilization of sensing materials over large areas of electrospun nanomaterials is the use of surface assembly. With bifunctional molecules an efficient surface modification can be achieved. A further development of this idea resulted in self-assembled monolayers (SAMs). Between neighboring adsorbed molecules, both hydrogen bonding and weak van der Waals forces are active (Tsukruk *et al.*, 1997). The result is a densely packed layer of sensing molecules standing steeply at the surface. Interfaces functionalized by SAMs can be useful for electron transfer in the direct oxidation of organic



11.5 Assembling fluorescent probes on to electrospun CA nanofibers and fluorescence emission spectra of the sensing film with varying quencher concentration. (Reprinted with permission from Wang *et al.,* (2004). © 2004 American Chemical Society.)

substances, and they may also act as ion-selective surfaces. Assembly of sensing materials can also be driven by electrostatic interactions, resulting in layer-by-layer assembly (LBL) (Decher *et al*., 1992; Huang *et al*., 2001; Mamedov *et al*., 2002; Hammond, 2004). The LBL technique involves the alternate adsorption of anionic and cationic polyelectrolytes on a charged substrate by sequential dipping of the substrate into the appropriate aqueous polyelectrolyte solutions. This yields a highly tailored polymer thin film on the substrate. This technique effectively coated the individual electrospun fibers, thus leaving the inherent high surface area of the electrospun membrane intact (Ding *et al*., 2004a, 2005a; Ogawa *et al*., 2007). The LBL assembly technique has been successfully applied to sensor fabrication (Nohria *et al*., 2006). One of the amazing advantages of this technique is the versatility, in that a vast range of functional groups can be incorporated within the structure of the film. Furthermore, this technique is not limited to planar substrates and has been demonstrated in LBL assembly onto 2- and 3-D architectures (Kato *et al*., 2002). The combination of electrospinning and LBL assembly with different electrospun substrates and sensing layers or functionalities will afford new properties and tremendous flexibility for fabricating sensors. Wang *et al.* (2004) reported a sensitive optical sensor by assembling fluorescent probes onto electrospun CA nanofibers, which showed fluorescence quenching upon exposure to even an extremely low concentration (ppb) of methyl viologen cytochrome in aqueous solutions (see Fig. 11.5). There are also examples of self-assembling noble metal nanoparticles onto electrospun fibers (Formo *et al*., 2008; Huang *et al*., 2008). Li *et al.* (2006) have prepared silver nanoparticles deposited onto the surface of PAN nanofibers by photoreducing the desired metal salt directly. And, the solution route is also a generally simple and attractive approach for the fabrication of noble metal nanoparticles with a great level of control for both the size and dispersity onto the electrospun fibers.

11.3 Sensing mechanisms

11.3.1 Acoustic wave sensors

Quartz crystal microbalances (QCMs), one of a broad class of acoustic wave techniques, whose history dates back to 1880, when Pierre and Jacques Curie discovered the piezoelectric effect, where pressure exerted on a small piece of quartz causes an electrical potential difference between the deformed surfaces (Marx, 2003). The essence of QCM as an analytical tool lies in its ability to detect small mass changes of even smaller than nanogram order deposited on crystal surface and to act as a sensor. Interfacial mass changes can be related to changes in the QCM oscillation frequency by applying Sauerbrey's equation (Sauerbrey, 1959):

$$\Delta f = \frac{-2f_o^2 \Delta m}{a(\mu\rho)^{1/2}} \qquad [11.1]$$

where Δf is the measured frequency shift, f_o is the fundamental frequency of a bare QCM chip, Δm is the mass change per unit area, a is the electrode area, ρ is the density of quartz and μ is the shear modulus of quartz crystal.

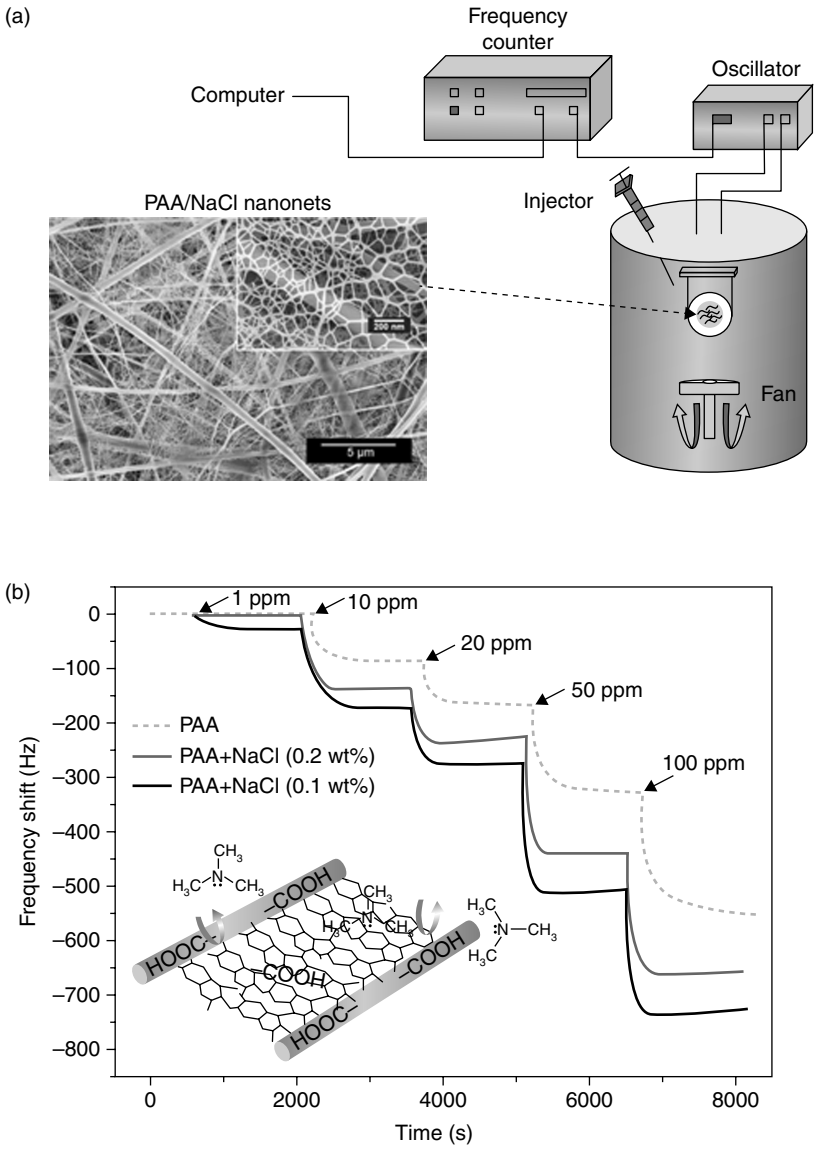
In the past decade, QCMs have been widely explored as sensors for the detection of biomarkers, drug targets, virus capsids, bacteria and living cells. Up to now, a variety of materials such as metals, ceramics, polymers, self-assembled monolayers, dendrimers, lipids and waxes (Ricco *et al.*, 1998, Grate, 2000) have been employed as sensitive coatings on QCM to improve the sensor sensitivity and selectivity for chemical analytes. It is widely accepted that the sensitivity of QCM sensors toward a specific analyte is enhanced by increasing the specific surface area of the sensing materials (Kolmakov and Moskovits, 2004). Recent efforts have been focused on the development of nanostructured coatings on QCM to improve the sensor sensitivity (Ding *et al.*, 2004b; Chao *et al.*, 2007). We have demonstrated the possibilities of fabricating novel QCM sensors by electrospinning deposition of nanofibrous membranes as sensitive coatings on the electrodes of QCM. Taking advantage of the large specific surface area, high porosity and good interconnectivity of these electrospun fibrous assemblies, we have successfully detected NH_3 (Ding *et al.*, 2004b, 2005b), H_2S (Ding *et al.*, 2006a), formaldehyde (Wang *et al.*, 2010a), moisture (Wang *et al.*, 2010b) and trimethylamine (TMA) (Wang *et al.*, 2011) with new detection limits at room temperature. Sensing experiments were carried out at room temperature in a flow-type gas testing system (Ding *et al.*, 2005b) and a static-type gas testing system (Fig. 11.6a) by measuring the resonance frequency shifts of QCM due to the additional mass loading. The experiments indicated that the sensitivity of the fibrous membrane-coated QCM sensors was several

times higher than that of the casting film-coated QCM sensors. Moreover, the fiber-coated QCM sensors with small average fiber diameter had a higher sensitivity. One exciting and challenging aspect of the work of our group lies in the fabrication of a novel TMA sensor by using an electronetting technique to deposit a PAA nanonets on a QCM (Wang *et al*., 2011). The versatile nanonets created enhanced interconnectivity and additional surface area, and facilitated the diffusion of analytes into the membranes, which significantly boosted the gas diffusion coefficient and sensing properties (Fig. 11.6b). These proof-of-principle experiments demonstrate the possibility of using electrospinning techniques to regulate the structure of membranes and hence obtain high surface activity and gas sensitivity; further experiments using more complex fiber arrangements and structures should expand the capabilities of this platform.

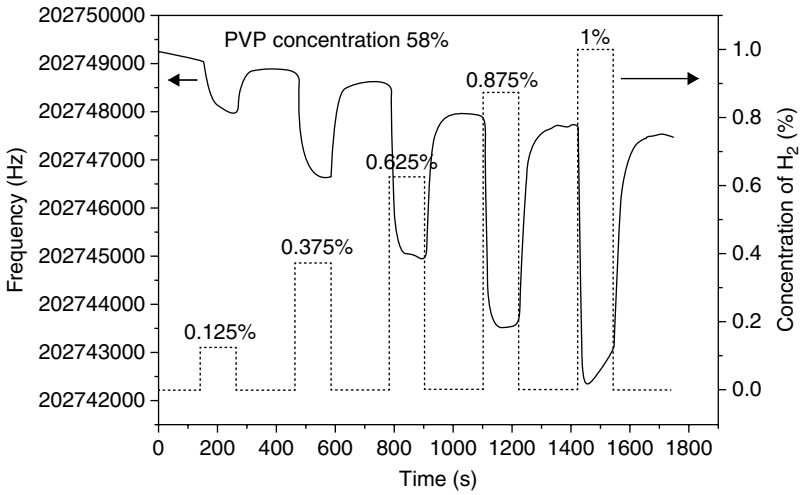
Surface acoustic wave (SAW) devices for gas detection have also attracted growing attention (Janata *et al*., 1994, Crooks and Ricco, 1998). The change in electrical conductivity or mass of the sensing layer perturbs the velocity of the propagating SAWs due to mechanical and piezoelectric effects. Concentrated efforts have been focused on depositing nanostructured coatings on SAWs via electrospray or electrospinning technique to improve the sensor sensitivity (Sarkar *et al*., 2006; He *et al*., 2010; Li *et al*., 2010). For example, He *et al.* (2010) demonstrated that a novel H_2 sensor could be prepared by electrospinning deposition of poly(vinylpyrrolidone) (PVP)/$LiTaO_3$ composite nanofiber on the electrodes of SAWs. Upon exposure to H_2, the PVP fibers adsorb H_2 molecules due to the hydrogen bond and the mass increase. Therefore, the frequency of the SAW device decreases as the adsorbed molecules reduce the acoustic wave velocity (Fig. 11.7). This indicates that the electrospinning technique can afford a simple approach for the fabrication of composite nanomaterials for sensing technology.

11.3.2 Resistive sensors

Commonly, resistance changes caused by the interaction between electrodes and analytical samples can be obtained by measuring the electrical conductivity (or resistivity) and evaluating to extract analytical results. Significant progress has been achieved in developing highly sensitive MOS resistive sensors using novel 1-D nanostructured architectures such as TiO_2, SnO_2, ZnO, In_2O_3, WO_3 and other wide band gap metal oxides. The fundamental principle of these devices is associated primarily with the adsorption of the chemisorbed species on the surface of the MOS inducing electric charge transport between the two materials, which changes the resistance of the oxide. 1-D sensing architectures provide unparalleled advantages in terms of facilitating fast mass transfer of the analyte



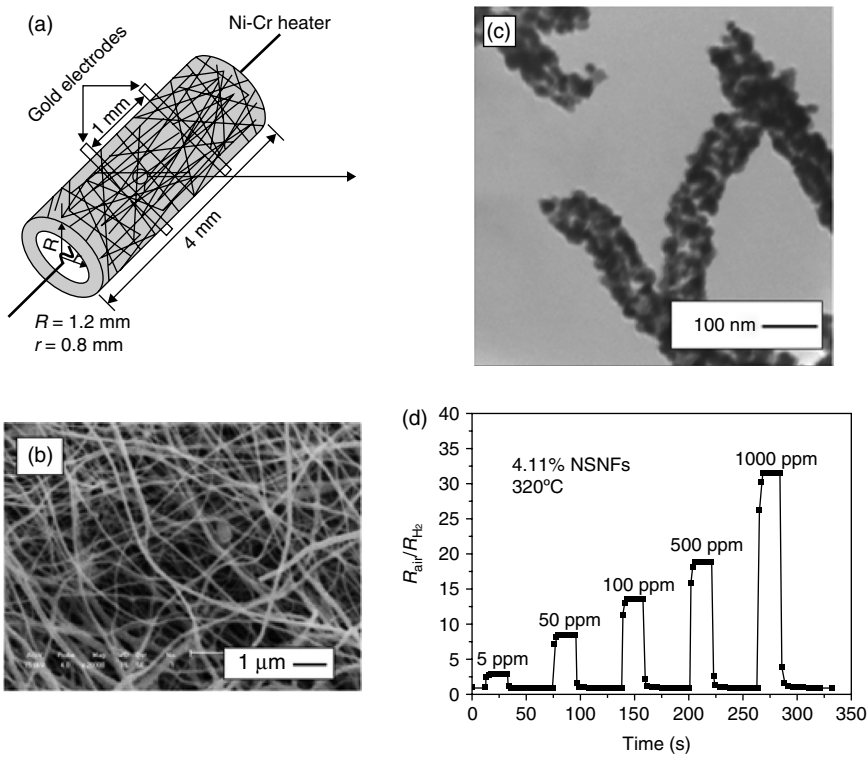
11.6 (a) Schematic of a gas testing system for TMA detection. (b) Response of sensors coated with PAA-NaCl nanonets containing different concentrations of NaCl (0 (dotted line), 0.1 (black line), and 0.2 wt% (gray line) and exposed to increasing TMA concentrations ranging from 1 to 100 ppm. The inset shows the schematic of gas-sensing mechanism between PAA nanonets and TMA. (Reprinted with permission from Wang *et al*. (2011). © 2011 Royal Society of Chemistry.)



11.7 Dynamic response of PVP/$LiTaO_3$ SAW device toward H_2 at room temperature. (Reprinted with permission from He *et al.* (2010). © 2010 Elsevier Ltd.)

molecules to and from the interaction region, as well as requiring charge carriers to traverse any barriers introduced by molecular recognition events along the entire wire. Among the variety of methods for the preparation of such nanostructured architectures, electrospinning is one of the most simple, versatile and cost-effective approaches, offering the ability to produce long, continuous organic or inorganic nanofibers with potential for alignment and spooling.

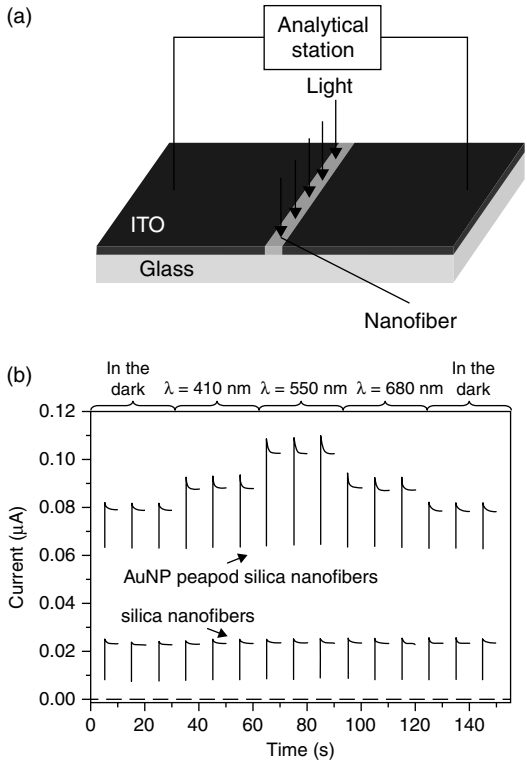
So far, many attempts are carried out to prepare ultrasensitive resistive sensors to detect NH_3, H_2S, CO, NO_2, O_2, CO_2, moisture and volatile organic compound (CH_3OH, C_2H_5OH, $C_5H_{10}Cl_2$, $C_6H_5CH_3$, C_4H_8O, $CHCl_3$, $C_2H_2Cl_2$, C_3H_6O, C_3H_7NO, C_2HCl_3, N_2H_4, $(C_2H_5)_3N$, C_6H_{14}, etc.) vapors with new detection limits using electrospun nanofiber functionalized MOS such as TiO_2, ZnO, WO_3, MoO_3, SnO_2, In_2O_3 and ITO (Choi *et al.*, 2009; Ding *et al.*, 2009; Qi *et al.*, 2009; Wang *et al.*, 2009; Zhang *et al.*, 2009). Wang *et al.* (2010c) studied the H_2 sensing properties of p-NiO/n-SnO_2 composite nanofibers (NSNFs) synthesized through an electrospinning method (Fig. 11.8). The sensor response was measured between 260°C and 380°C by comparing the resistance of the sensor in dry synthetic air with that in target gases. Extremely fast response-recovery behavior (~3s) has been obtained at the operable temperature of 320°C, based on the prepared sensor, with the detection limit of approximate 5 ppm H_2. Many applications of electrospun nanofibers could be greatly improved by increasing the surface area and porosity of the fibers.



11.8 (a) Schematic illustration of the fabricated device structure for the H_2 sensing measurement and the corresponding TEM image of the 4.11 mol % NSNFs. (b) SEM images of 4.11 mol % NiO–SnO_2 composite nanofibers. (c) Response and recovery characteristic curves of the sensor based on 4.11 mol % NSNFs to H_2 in the range of 5–1000 ppm at 320°C. (Reprinted with permission from Wang *et al.* (2010c). © 2010 American Chemical Society.)

11.3.3 Photoelectric sensors

Recently, metallic nanoparticles encapsulated into dielectric matrices have been considered to have practical applications in photoelectric devices owing to their enhanced third-order nonlinear susceptibility (Haglund *et al.*, 1993). The enhancement of photoresponse behaviors arising from the excitation of the surface plasmon is attributed to the generation of hot electrons. The generated hot electrons drift or diffuse to the oxide barrier and tunnel to the counterelectrode. Generation of hot electrons and electron tunneling through the oxide nanowires may contribute to the enhanced photoresponse behavior in the hybrid nanowire (Hu *et al.*, 2006). Recently, Shi and coworkers (2009) have developed a method to fabricate Au nanoparticles (AuNPs) embedded in silica nanofibers via



11.9 (a) A schematic of the microreactor for photoelectric response measurements. (b) Photoelectric response measurements of the room-temperature current response as a function of time of light illumination for pure silica nanofibers and AuNPs peapod silica nanofibers. (Reprinted with permission from Shi *et al.* (2009). © 2009 Elsevier Ltd.)

electrospinning and thermal decomposition of hybrid nanofibers, which exhibited an obvious photoelectric response under illumination (Fig. 11.9a). Photoelectric response measurements were conducted under dark condition or under alternate light illuminations of different wavelengths (k = 410, 550 or 680 nm). Data were obtained by an electrochemical analyzer with applied constant voltage of 10 V every 5 min. Upon light illumination, the hybrid peapod nanofibers presented a wavelength-dependent photoelectric current response. Particularly, the current photoresponse reached a maximum value under illumination at a wavelength of 550 nm, which was close to the surface-plasmon-resonance absorption band of the AuNPs nanofibers (Fig. 11.9b). These results show the potential of using gold nanopeapodded silica nanowires as wavelength-controlled optical nanoswitches. The microreactor approach can be applied to the preparation of a range of hybrid metal-dielectric 1-D nanostructures that can be

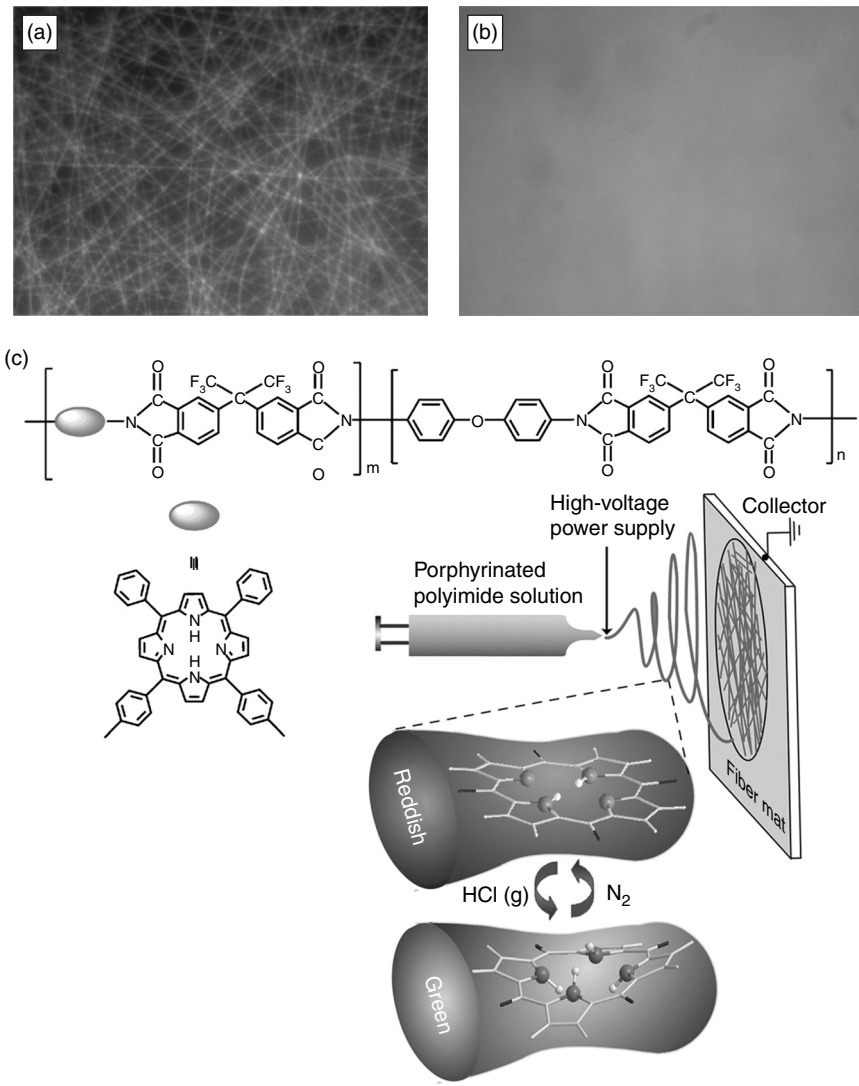
used as functional building blocks for nanoscale waveguiding devices, sensors and optoelectronics.

11.3.4 Optical sensors

Optical sensor-based electrospun nanomaterials can be grouped into three general types: (a) quenching-based fluorescent optical sensors; (b) colorimetric sensors; and (c) Fourier transform infrared (FTIR) spectroscopy optical sensors.

For quenching-based fluorescent optical sensors, utilizing the fluorescence quenching of the sensing material against the targeted chemical molecules, the sensitivity of the device can be dramatically affected by the accessibility of the sensing elements to the quencher or analyte. Electron-deficient metal cations such as Fe^{3+} or Hg^{2+} and nitro aromatic compounds such as 2,4-dinitrotoluene (DNT) and 2,4,6-trinitrotoluene can serve as quenchers for a fluorophore (Wang *et al*., 2002b, 2002c). The pyrene methanol (PM) (Wang *et al*., 2002a) and conjugated polymers (Long *et al*., 2009) were chosen as fluorescent indicators due to their large Stokes shift, high quantum yield, strong absorbance, excellent photostability and lifetime. Here the quenching of fluorescence is due to the interactions of an electron-rich indicator and electron-deficient quencher, and the degree of quenching depends on the amount of analyte. Electrospinning was used as a novel and simple method to fabricate fluorescent optical sensors. Wang and coworkers (2002b) have successfully developed nanofibrous PAA-PM membrane optical sensors for metal ion (Fe^{3+} or Hg^{2+}) and DNT detection using the electrospinning technique. Recently, electrospun nanofibrous PS film doped with a fluorescent conjugated polymer was developed as a sensory device for detection of the explosive DNT (Fig. 11.10a, b) (Long *et al*., 2009). Polymer acting as a fluorescence probe presented relatively large affinity for the nitroaromatic compound DNT, which is mainly based on photoinduced charge transfer and ϖ–ϖ stacking interaction and could provide a strong driving force for fast fluorescence quenching. Second, the electrospun nanofibrous sensing film possessed remarkable specific surface area, in which more recognition elements were located on the surface.

Lv *et al.* (2010) reported a method for the colorimetric visualization of trace amount of HCl gas using electrospun porphyrinated polyimide (PPI) nanofibrous membrane as schematically illustrated in Fig. 11.10c. The dual chromo- and fluorogenic responses of the nanofibrous membrane upon exposure to HCl gas are interpreted in terms of the out-of-plane distortion of porphyrin macrocycle, which ultimately affects its optical properties. Exposing the PPI nanofibrous membrane to HCl gas for only 10 s generates a fast color change (from reddish russet to green) on the sensor surface, which can be ascribed to the protonation of the neutral porphyrin moieties



11.10 Fluorescence images of polymer P-Doped PS nanofibrous sensing membranes (a) before and (b) after being exposed to DNT vapor for 30 min. (Reprinted with permission from Long *et al.* (2009). © 2009 American Chemical Society.) (c) Molecular structure of PPI used in this work and the schematic illustration for the whole colorimetric and fluorescent detection of HCl gas.

in PPI . It is notable that the intensity of green color increases with the concentration of HCl gas (5–100 ppm). Additionally, the reusability of this PPI nanofibrous membrane sensor is proved by color recovery after puffing with N_2 for a certain time.

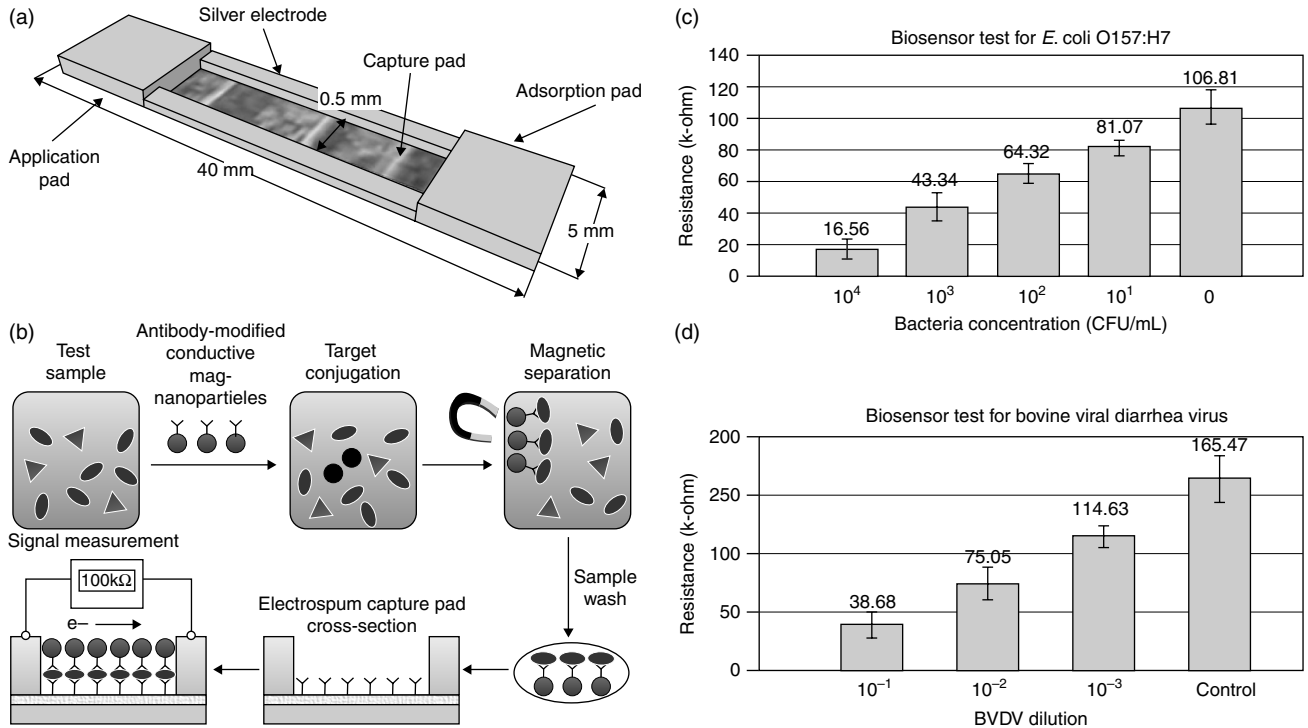
FTIR spectroscopy is another widely used optical method to study the interaction of electromagnetic radiation in the infrared region with chemical compounds. The mechanism of FTIR sensor is based on the fact that different functional groups within a compound absorb radiation at different frequencies and yield unique infrared absorbance spectra. The large band width (400–4500 cm^{-1}) and the distinct absorbance bands render FTIR technology suitable for sensor applications. Hahn *et al.* (Luoh and Hahn, 2006) first utilized the electrospun nanocomposite PAN/oxide fiber mats as optical sensors in conjunction with FTIR spectroscopy to detect CO_2 gas. The absorbance spectra showed a higher sensitivity with a fiber mat, regardless of its type, than without, indicating gas adsorption on the fiber mat.

11.3.5 Biological sensors

Biosensors are becoming essential in the fields of health care, chemical and biological analysis, environmental monitoring and good processing industries (Ahmad *et al.*, 2010). Electrospinning is a versatile method by which to fabricate biocompatible nanomaterials. The novel nanostructure increases the surface area and mass transfer rate, which significantly improves the biochemical binding effect and sensor signal to noise ratio. The past several decades have witnessed big progress on fabricating biological devices for fast and reliable monitoring of biological targets.

Up to now, most biological sensors-based electrospinning techniques were used to detect glucose. Among those devices, amperometric glucose biosensors, with glucose oxidase (GO_x) and without GO_x, have been an intensively investigated research area because a low detection limit can be achieved easily. Ren *et al.* (2006) have developed an amperometric biosensor by electrospinning deposition of nanofibrous GO_x/PVA membranes as sensitive coatings on the surface of the Au electrode. Chronoamperometric measurements demonstrated that electrospun fibrous enzymatic electrodes exhibited a rapid response (1 s) and a higher response current (l μA level) to glucose in the normal and diabetic level. The linear response range (from 1 to 10 mM) and the lower detection limit (0.05 mM) of the sensor are satisfying. The electrospun method makes it convenient and efficient to prepare the enzymatic electrode for biosensors.

Apart from glucose biosensors, Luo *et al.* (2010) utilized the surface functionalized electrospun nitrocellulose nanofibers as a direct-charge-transfer biosensor to detect *E. coli* O157:H7 and bovine viral diarrhea virus (BVDV) cells. The biosensor was assembled by attaching the three membrane pads (application pad, capture pad and absorption pad) onto the polyvinylidene chloride substrate as shown in Fig. 11.11a. Figure 11.11b shows the pathogen detection principle of the biosensor. The electrospun biosensor exhibits



11.11 (a) Schematic of the biosensor structure and membrane assembly consisting of cellulose application and absorption pads and electrospun cellulose nitrate capture pad. (b) Detection scheme of the lateral flow immunosensor based on the antibody functionalized electrospun capture membrane. (c) Biosensor test results for *Escherichia coli* O157:H7 bacteria demonstrate the linear sensor response and lower detection limit of 61 CFU/mL. (d) Biosensor test results for BVDV virus demonstrate the linear sensor response. (Reprinted with permission from Luo *et al.* (2010). © 2010 Elsevier Ltd.)

a linear response to both microbial samples, the *E. coli* O157:H7 and BVDV. The detection time of the biosensor is 8 min, and the detection limit is 61 CFU/mL and 103 CCID/mL for bacterial and viral samples, respectively (see Fig. 11.11c, d). With the advantage of efficient antibody functionalization, excellent capillary capability and relatively low cost, the electrospinning process and surface functionalization method can be implemented to produce nanofibrous capture membranes for different immunodetection applications.

11.4 Future trends and conclusions

Electrospinning is a versatile method of creating high-functional and high-performance nanofibers that can revolutionize the world of structural materials. It is obvious that the current research has focused on seeking the possible applications of these resultant nanofibers with broad functionalities. The utilization of electrospun nanofibers with a large specific surface as sensing materials has received great attention since 2004. The fine structure of electrospun fibers makes them excellent candidates to replace the current widely used solid flat membranes, promising to further increase sensor sensitivity; this opens a new way to fabricate ultrasensitive sensors (Ding *et al.*, 2009). It is important to note that the application of electrospun nanomaterials for sensors still faces many challenges. Preparation of sensing materials in the form of nanostructures may significantly improve their performances in the existing devices or open doors to new types of applications. However, integration of nanomaterials into sensors requires materials of well-controlled orientation, size and other target characteristics, as well as reproducibility locating them in specific positions and orientations. The ability to achieve this, however, remains a major challenge in the field (Frenot and Chronakis, 2003). Fortunately, several approaches have emerged that promise to bridge these gaps and realize the vision of upgraded nanosensors. Given the versatility of electrospinning for generating fibrous membranes with various nanostructures, it is likely that electrospinning will be one of the most significant nanotechnologies in the fabrication of more and more ultrasensitive and practical sensors.

11.5 Acknowledgments

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