



Conducting polymer 1-dimensional nanostructures for FET sensors

Mangesh A. Bangar, Wilfred Chen, Nosang V. Myung, Ashok Mulchandani*

Chemical and Environmental Engineering Department, University of California, Riverside, CA 92521, USA

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ABSTRACT

In this review we have highlighted advantages of 1-dimensional nanostructures for field effect transistor (FET)/chemiresistor based sensors and advantages of conducting polymer as material of construction over other nanomaterials. Here we have ensembled different techniques used for the fabrication, assembly/alignment, functionalization and sensing applications of conducting polymer nanowire/tube/junction based FET sensors for gas and biomolecule detection. The advantages and disadvantages of various fabrication, functionalization, and assembling techniques are discussed. We evaluate how such devices have enabled the achievement of improved sensor performance in terms of high sensitivity, selectivity and low detection limits. Finally, we conclude by highlighting overall merits of different techniques and challenges researchers face in the field of conducting polymer 1-dimensional nanostructures-based sensors and also predict the future direction in which research efforts are likely to flourish.

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1. Introduction

Miniaturization of device dimensions and improvement of their performance have pushed the scientists to develop synthetic routes to fabricate materials at a scale just above the atomic scale. This new class of materials called nanomaterials are building blocks of nanotechnological innovations. Nanoscale materials such as nanowires, nanotubes, nanoparticles, nanoribbons, nanosprings, etc., have gained tremendous interest because of their interesting electrical and optical properties and quantum confinement effect. As the smallest dimension of these nanostructures (<100 nm) is comparable to the wavelength of visible/UV radiations and also due to the electrical conduction almost approaching ballistic limits, these nanostructures exhibit excellent optical and electrical properties, respectively. As a result, they are being studied for their potential applications in electronics, optoelectronics, sensors, actuators, thermoelectrics, etc.

Particularly, one-dimensional nanostructures such as nanowires and nanotubes are very attractive for their integration as a sensing or transducing element of a sensor. Due to higher surface area to volume ratio, these nanostructures are very sensitive to even slight perturbations in their environment. Upon binding of charged analyte or change in pH on the surface, these nanostructures show changes in their electrical, physical or optical properties. Of particular interest, changes in electrical properties can be measured by simply measuring the change in the resistance of the nanostructure by passing the electric current. Such sensors utilize

simple chemiresistive or field-effect transistor (FET) architecture that offers simple, real-time and label-free detection. Compared to 2-dimensional thin films where charge addition or depletion takes place upon binding of a charged species on the surface which leads to current shunting due to larger cross-sectional area of the film, almost the entire cross-sectional area of the nanowire shows modulation of space charge region leading to larger changes in the electrical properties. This simple sensing mechanism combined with no lateral current shunting due to its small cross-sectional area, nanowires/nanotubes offers label-free, direct, real-time detection at very low concentrations, potentially down to a single molecule [1]. Due to their potential in label-free biosensing and integration into a high density nanosensor arrays enabling multiplex sensing for the detection of biomolecules at very low concentrations, one-dimensional nanostructures are receiving increasing attention for applications in proteomics, disease diagnosis, pharmaceutical drug screening and biowarfare agents detection. Recently, silicon nanowire (SiNW) [2–5] and carbon nanotube [6–8] based FET sensing applications have been developed. Even though these nanostructures have been shown to hold great promise in development of nanodevices, they suffer through an inherent disadvantage in terms of harsh conditions required for their fabrication. Both of these nanostructures are fabricated at elevated temperatures using techniques such as vapor–liquid–solid (VLS) processes, chemical vapor deposition (CVD) or laser ablation, which are very tedious and are expensive [9–12]. On the other hand, conducting polymers have shown great promise in the form of nanomaterials.

- 1) Their fabrication can be carried out using well established electrochemical [13,14] or chemical [15,16] synthesis routes at ambient conditions.

* Corresponding author.

E-mail address: adani@engr.ucr.edu (A. Mulchandani).

- 2) They exhibit tunable electrical, magnetic and optical properties [17–19].
- 3) Their conductivity can be modulated over 15 orders of magnitude.
- 4) They have excellent biocompatibility [20], which is a great advantage over other nanomaterials in fabrication of novel biosensors.

Recently, a couple of review papers [1,21] has documented utilities of various nanostructures including silicon nanowires, carbon nanotubes, conducting polymer nanowires/tubes for biosensing applications. Also, the conducting polymer nanostructure fabrication and their various applications have been reported in recently published reviews [22–25]. However, the focus of this review is on the applications involving conducting polymer nanowires/nanotubes as a transducer of a chemiresistive/FET sensor. Starting from their fabrication to alignment/assembly into functional device, we will discuss few specific sensing applications for these fascinating nanostructures.

2. Conducting polymer nanowire/nanotube synthesis

2.1. Template-free synthesis

Template-free synthesis method relies on preferential growth of conducting polymer nanowires in the presence of a driving force applied using a probe, self-assembly process or molecular/structural ordering. Self-assembly, Langmuir–Blodgett (L–B) film, dip-pen lithography (DPN), mechanical stretching, electrospinning and electrochemical synthesis are the examples of template-free synthesis methods for conducting polymer nanostructures.

A self-assembly route to synthesize nanoribbons of a polydisperse, soluble, end-functionalized poly(para-phenyleneethynylene) (PPE) derivative was reported by Samori et al. [26]. By simple solution casting, a drop of solution containing PPE derivative at a very low concentration was allowed to evaporate on mica to assemble nanoribbons (Fig. 1 (A)). Lengths of these nanoribbons spanned several microns whereas the width and height of the ribbons were dependent upon the solvent composition. Similar self-assembly of polyaniline nanotubes in a solution of poly(methylvinyl ether-alt-maleic acid) (PMVEA) by oxidative polymerization using ammonium persulfate as the oxidant has also been reported [27]. Nanotubes with outer diameter of 65 to 160 nm were fabricated depending upon the reaction solution composition. Another solution phase synthesis of nanowires using L–B films has been shown for polythiophene nanowires [28]. L–B films of amphiphilic polythiophenes, which were substituted by alternating hydrophilic and hydrophobic side groups, were compressed beyond the collapse point to form micron long nanowires. Upon doping with iodine vapors these nanowires showed very high conductivity (40 S/cm). Even though these methods offer a simple solution phase synthesis of conducting polymer nanostructures, they need extensive processing or alignment and assembly techniques for post-synthesis assembly into a functional device.

Amongst the methods employing probes to guide nanowire synthesis, DPN technique utilizes an AFM tip with polymerized conducting polymer as the ink for writing on oppositely charged substrate (Fig. 1 (B)). Doped polyaniline and polypyrrole lines of 310 and 290 nm widths, respectively, were written on silicon substrates [29]. Similarly, 30 nm wide poly 3,4-ethylenedioxythiophene was written using DPN technique [30]. This technique can be adopted to fabricate aligned conducting polymer nanostructures on prefabricated microelectrodes to form functional devices.

In mechanical stretching method, conducting polymer (polyaniline) was deposited in the gap (20–100 nm) between a scanning tunnelling microscope (STM) tip and gold (Au) electrode to form a nanowire of ~20 nm diameter. STM tip was subsequently moved

away from the electrode to reduce the diameter of the nanowire to ~6 nm. Stretching process resulted in better alignment of the polymer chains in the nanowire and very high conductivity (~5 S/cm) (Fig. 1 (C)) [31]. Such method even though useful for understanding the properties of conducting polymer at very low dimensions as the in-built electrode and STM tip can be used to probe the nanowire, has practical limitations in terms of yield/number of devices fabricated and complex fabrication. Fabrication using electrospinning technique utilizes microfabricated scanning tip. The tip is first dipped in a polymer solution, which forms a droplet of solution around the tip. A voltage is applied on the tip, which results in formation of a Taylor cone and at sufficiently high voltage a polymer jet is formed from the droplet. By rotating the substrate with pre-microfabricated contact electrodes on it, oriented polyaniline nanofibres integrated in electrical device was fabricated [32].

Electrochemical template-free routes for conducting polymer nanowires synthesis have been reported. Polypyrrole nanowires with 50 nm diameter were deposited on a glassy carbon electrode (GCE) at a constant potential from a solution containing dopant, monomer and carbonate (Fig. 1 (A)) [14,33]. In another approach, electrochemical polymerization of conducting polymer on prefabricated platinum microelectrodes was adopted to form conducting polymer nanowire electrode junctions (CPNEJs) [34–36]. Three constant current density steps were used to nucleate and grow nanowires to bridge the gap between microelectrodes. Polyaniline, polypyrrole and poly(ethylenedioxythiophene) (PEDOT) nanowires with diameters in the range of 40–80, 60–120, 80–150 nm, respectively, have been fabricated. These template-free electrochemical nanowire fabrication methods are site-specific, but lack the precise control on nanowire dimensions and could potentially result in sensor to sensor variations due to varying number of conducting polymer nanowires electrically connected between the electrodes and/or varying dimensions of the nanowires. To achieve single nanowire connection a modified approach using microfabricated electrodes was taken. Microfabricated electrodes were fabricated using standard lithographic technique. The gap between a pair of electrodes was then reduced to few nanometers either by electrodeposition of metal [37] or by focused ion beam (FIB) deposition [38]. These gaps were subsequently filled with conducting polymer such as polyaniline to fabricate single nanowire connection between the electrodes. Again these techniques lack precise control on the nanowire diameter and result in low aspect ratio nanostructures, however these nanogap deposition techniques are particularly attractive for conducting polymers with very limited electrical conductivity.

2.2. Templated conducting polymer nanowire synthesis

2.2.1. Soft-templates

The use of liquid crystals and micelles as soft templates for nanowire synthesis has been studied. Using reverse hexagonal liquidnanowirecrystalline phase of surfactant sodium bis(2-ethylhexyl) sulfosuccinate (AOT) Huang L. et al. reported the synthesis of 50–70 nm diameter polyaniline nanowires [15]. Yoon et al. recently reported a technique to synthesize acid functionalized polypyrrole nanotubes inside cylindrical micelle templates in a water-in-oil emulsion [16]. The nanotube synthesis involved copolymerization of acid functionalized pyrrole and pyrrole inside cylindrical micelles. Nanotubes of 200–250 nm diameter and 30–40 nm wall thickness were obtained.

2.2.2. Hard template synthesis

This is the most widely used method of synthesizing conducting polymer nanowires. Substrate with a particular morphology or structure is utilized for one directional growth of polymer chains. First reported by Martin [13,39], anodized aluminum oxide (AAO) and track-etched polycarbonate (PC) membranes were used as

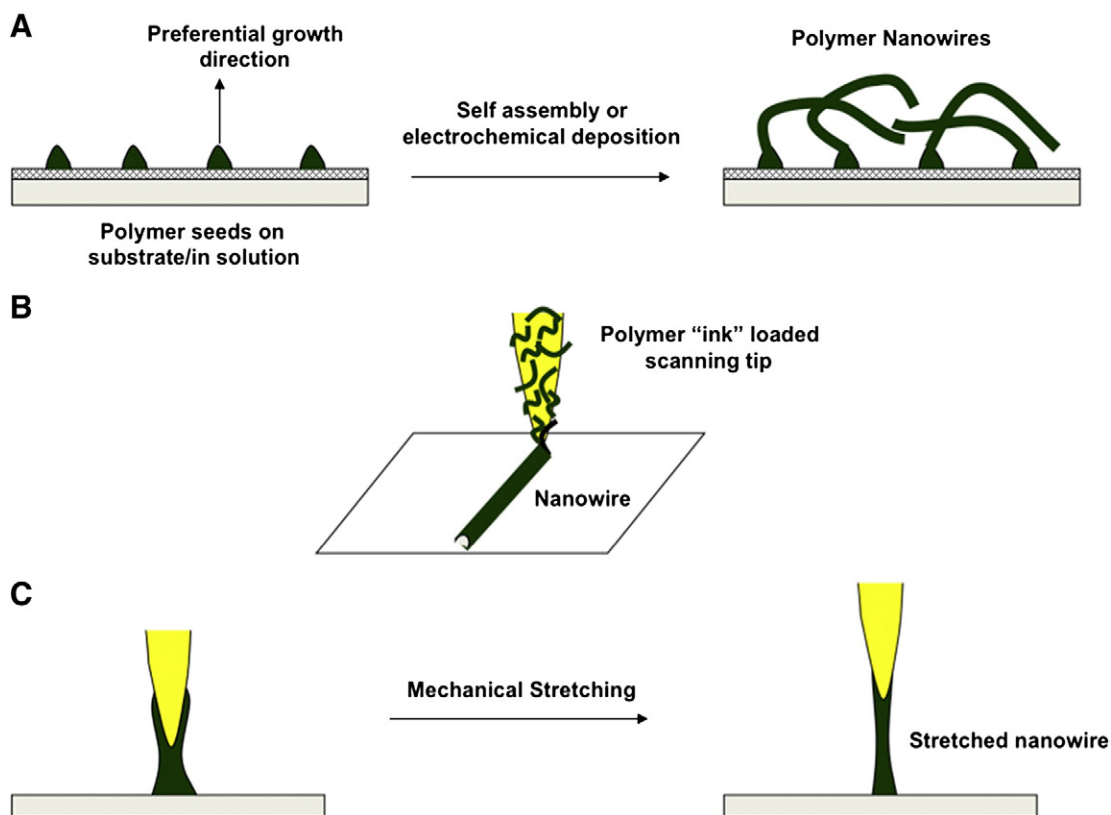


Fig. 1. Schematic representation of template-free conducting polymer nanowire fabrication. (A) Self-assembly process initiated from nuclei formation on the substrate followed by preferential 1-D growth. (B) DPN conducting polymer nanowire fabrication using polymer 'ink' loaded scanning probe tip on a substrate. (C) Mechanical stretching of conducting polymer deposit between a scanning tunnelling microscope tip and a substrate followed by stretching of the polymer to form a nanowire with highly aligned polymer chains.

scaffolds. Electrochemically conducting polymer was deposited in the pores of these membranes. For electrodeposition, one face of the template was coated with conductive metal (e.g. gold, silver), which acts as an anode. The length of the conducting polymer nanowire deposited inside the pores was determined by current density and deposition time. Novel multi-layered nanowire structures using such template electrodeposition with few modifications have been reported. By simply replacing the electrolyte to deposit different layers of the nanowire in the template, multisegmented gold-polyppyrrrole, gold-polyppyrrrole-gold, [40] and nickel-gold-polyaniline multisegmented nanowires [41] have been fabricated. For better adhesion between the polymer and metal layers an electroless deposition step followed by normal electrodeposition [20] or use of self-assembled monolayer has been adopted [41]. Our group has recently demonstrated an all electrochemical fabrication of gold-polyppyrrrole-nickel-gold multisegmented nanowires [42]. As a slight modification to the multisegmented nanowire synthesis method, core-shell nanostructure of polyaniline core and gold shell has been synthesized. The process was started with the deposition of polyaniline nanotubes inside an alumina template followed by drying and electrodeposition of gold shell from a pH 10 electrolyte bath. While the drying shrank the polyaniline nanotubes diameter, the basic pH made the polyaniline less conducting as well as partially etched the alumina template leaving an annular space between the polyaniline and the alumina for the electrodeposition of gold shell [41]. In chemical synthesis route, the template is immersed in a solution of monomer and oxidizing agent [43]. During chemical synthesis the polymer growth is initiated on the template walls due to hydrophobic interactions to form nanotubes and continue to advance towards the center eventually forming nanowires. Similar phenomenon was also observed with PC membrane [44,45]. A new melt-assisted template wetting method was adopted to form polyfluorene (PFO) nanowires wherein PFO was

melted on top of an AAO membrane which facilitated pore filling [46]. Upon subsequent cooling, polymer nanowires were formed inside the pores of the template. Fig. 2 schematically summarizes different synthesis approaches and the resultant conducting polymer nanostructures using template approach. After the deposition, the conducting metal layer used for electrochemical deposition and the template are etched using appropriate etchant, acid or base for alumina and organic solvent for PC, to free the nanowires. The diameter of the nanowires/nanotubes obtained is dictated by the pore size of the template. These nanostructures have shown improved conductivity than their bulk counterparts [47]. Other porous materials such as zeolites [48], and porous silicon have also been used as template. The fabrication of devices using these approaches faces serious drawbacks in terms of the following:

1. The use of harsh chemicals (acid/base or organic solvent for alumina and polycarbonate templates, respectively) to etch the template.
2. Post-synthesis alignment and assembly into functional device are necessary.
3. Functionalization of nanostructure can only be performed post-synthesis.

To overcome these drawbacks our group has demonstrated an electrochemical deposition technique of in-situ single-step conducting polymer nanowire fabrication using electron beam lithographically patterned nanochannels between two photoresist coated metal electrodes. Single or sequentially deposited array of individually addressable, dendrite-free and high aspect ratio nanowire/s can be fabricated in a single electrochemical deposition step [49]. Using this technique we have also demonstrated that ready to use biosensors can be fabricated by physically entrapping the biomolecule during electrochemical synthesis of the nanowire itself [50].

2.2.3. Nanostructures as templates

Other nanostructures have also been employed as templates for depositing conducting polymer nanowire structures. Recently, solution grafted film of polymer has been utilized in synthesizing different structures of polyaniline on organic polymer surface [51]. By controlling the conformation of the surface grafted polyacrylic acid (PAA) brushes as well as ratio of acrylic acid to aniline, the shape of polyaniline fabricated was varied from spherical particles to nanowires and nanoribbons. Nanowire and nanoribbon films thus formed on polypropylene film showed superhydrophobicity. Other researchers have utilized biomolecule templated growth of conducting polymer nanowire structures. DNA molecules were stretched and aligned on oxidized silicon substrate using molecular combing technique. Subsequently, these DNA templates were incubated in aniline solution to align aniline monomers along the DNA chains. Polymerization of aniline was achieved using horseradish peroxidase (HRP) and hydrogen peroxide [52]. In these methods, nanostructures used as template have to be assembled prior to the conducting polymer nanowire synthesis, which has not been completely mastered yet. Also carbon nanotubes have been electrochemically deposited with conducting polymer to form one-dimensional conducting polymer nanostructures for device applications [53]. However, the use of these nanostructures can increase the cost of fabrication substantially.

2.2.4. High density conducting polymer nanowire fabrication

High density large area conducting polymer nanostructure fabrication methods have also been developed. Using a silicon stamp with gratings fabricated by e-beam lithography, polymer gratings on silicon surface were replicated by technique called nanoimprint lithography (NIL). Subsequently, conducting polymer (Ppy) was deposited on the silicon substrate by immersing it in a monomer solution containing dopant and a substituted monomer (silanized derivative), which showed improved adhesion with silicon surface. Subsequent lift off left the conducting polymer nanowire with the desired diameter and pitch dictated by gratings on the silicon stamp (Fig. 3 (A)). Using this technique other high density nanostructures were also synthesized [54]. A modified approach of this technique employed embossing of silicon stamp into the conducting polymer thin film itself to produce nanowire pattern with desired dimensions and pitch as shown in Fig. 3 (B) [55]. Such

high density nanowire arrays fabrication requires deposition of metal electrodes for electrical connections to fabricate functional device and could result in possible thermal damage to the nanostructures during metal deposition.

Table 1 summarizes the merits and shortcomings of different conducting polymer nanowire/tube fabrication techniques described in the above section. However, appropriate nanowire fabrication method can be adopted depending upon the desired nanowire size, composition, conductivity, final device architecture and/or simplicity and cost of synthesis.

3. Alignment of conducting polymer nanowires

The most difficult step in realizing a conducting polymer nanowire based nanodevice is the assembly of pre-synthesized nanostructures onto a substrate with predefined architecture. In most fabrication techniques additional post-synthesis processing especially assembly is essential. Dispensing suspension of pre-synthesized nanowires onto prefabricated microelectrodes results in random orientation and number of nanowires connecting pair of contact electrodes making it an unreliable/inconsistent method for device assembly and could result in device to device variations [16]. In order to precisely control the orientation, placement and number of nanowires across pair of contact electrodes various methods have been used. A few of them are described in this section.

3.1. Magnetic alignment

Ferromagnetic materials such as cobalt or nickel nanowires display interesting magnetic properties, which are strongly influenced by their shape anisotropy. Due to their high aspect ratio these materials show preferential magnetization along the long axis of the nanowire and orient themselves in the direction of the applied external magnetic field. To align the conducting polymer nanowires by harnessing magnetic properties of ferromagnetic materials, multi-segmented nanowires with nickel–gold–polyaniline layers were fabricated and magnetically aligned between prefabricated contact electrodes [41]. Similarly, gold–polypyrrole–nickel–gold multi-segmented nanowires were aligned between prefabricated gold–nickel–gold multi-layered contact electrodes [42]. Multi-layered contact electrodes helped in concentrating the magnetic field in the electrode

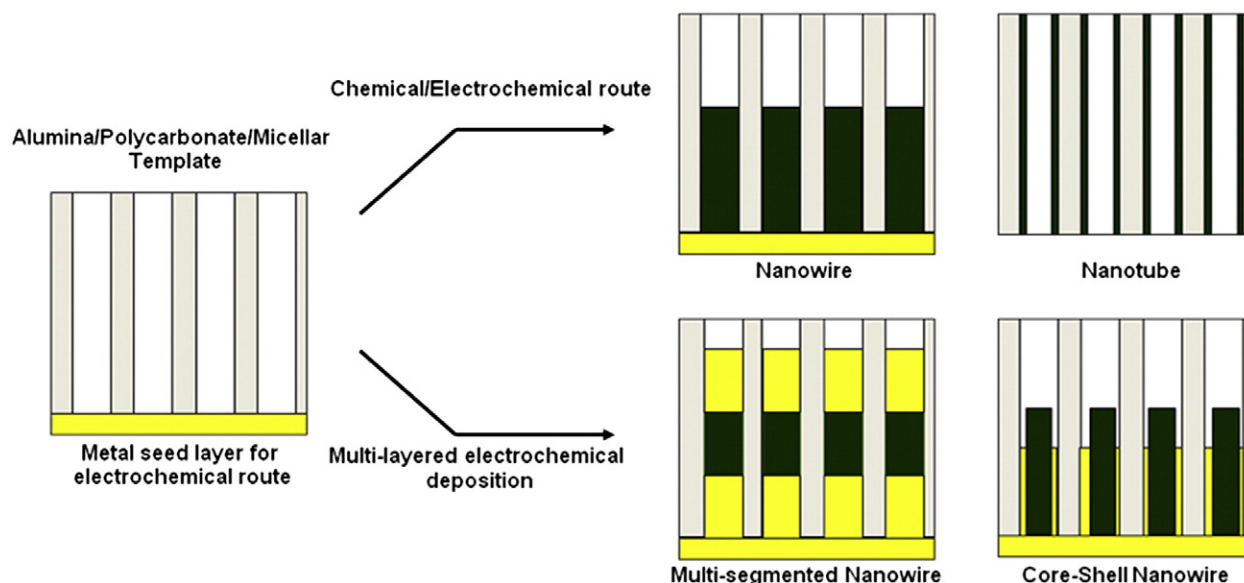


Fig. 2. Schematic representation of templated conducting polymer 1-D nanostructure formation. Chemical or electrochemical routes of nanowire fabrication resulting in nanowire or nanotube morphology (top). Electrochemical multi-layered deposition for segmented or core-shell 1-D nanostructure formation (bottom).

gap, whereas the magnetic nickel segment of the nanowire assisted in aligning and positioning the multisegmented nanowire precisely in the electrode gap in the direction of applied magnetic field (which was perpendicular to the electrode gap).

3.2. Electrophoretic alignment

By applying AC electric field using pair of contact electrodes, the conducting polymer nanowires in the suspension were polarized and attracted towards the contact electrodes where the electric field gradient was highest. Nanowires aligned themselves in the direction of the applied electric field and were placed in the gap between the contact electrodes. Using this method striped/multisegmented gold-poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate)(PEDOT/PSS)-gold nanowires were aligned between pair of electrodes with 8 μm gap with single nanowire connection yield of 35–50%. This self-terminating process showed a reduction in the nanowire alignment upon contact of first nanowire between the electrodes [56]. As an alternative, we have demonstrated that upon electrophoretic alignment of polypyrrole nanowires, multiple nanowire contact can be physically modulated using a simple gold microwire probe to obtain single nanowire contacts between pairs of electrodes in an array design [57].

3.3. Fluidic alignment

Using the hydrodynamic force applied during fluid motion on a nanowire suspension, nanowires were aligned in the direction of the flow on a silanized silicon surface. The authors found that nanowire alignment was greatly affected by hydrophilicity/hydrophobicity of the substrate. Hexamethyldisilazane (HMDS) treated surface exhibited more hydrophobicity which assisted in aligning nanowires in the preferred flow direction compared to untreated surface [58].

4. Sensing applications of conducting polymer nanowires

Conducting polymers due to their semiconducting and redox-active properties undergo changes in their electrical conductivity upon changes in the number of charge carriers by means of doping/dedoping, interactions of ions or charge transfer between molecules. This enables applying these novel materials for sensing applications as field effect transistors (FET). In this section we will review the use of conducting polymer nanowires based FET/chemiresistor sensors.

4.1. Gas sensing

Conducting polymers have shown high sensitivity towards polar gas molecules such as ammonia, NO_x , CO_x and VOCs. Ammonia is the most studied amongst the gaseous analytes and thus ammonia sensing can be taken as the basis for comparison between different sensors. Some of the examples coated here highlight the capability of conducting polymer in gas sensing arena.

4.1.1. Ammonia sensors

Due to its high toxicity rapid detection of ammonia at low concentration is desired in the areas of detecting leaks in the air for environmental analysis, explosives and fertilizer industries and medical diagnosis. Due to the availability of excess pair of electrons on nitrogen, ammonia acts as a Lewis base. Upon electronic interaction with ammonia, predominantly p-type conducting polymer shows loss in number of charge carriers due to dedoping, resulting in increase in its resistivity. This is a reversible reaction and sensor can be recovered back to its original conductivity by simply removing the analyte gas from the sensor. Poor diffusion of ammonia into the bulk of the polymer matrix forms the basis for investigating performance enhancement by use of nanostructures. A number of publications on ammonia sensing using conducting polymer nanowire sensors have recently been reported.

Wang et al. [36] reported an ammonia sensor based on network of high quality nanowires electrochemically fabricated as a CPNEJ (mentioned in Section 2.1). These sensors based on polypyrrole CPNEJs showed a very good reproducible response towards 1000 ppm of ammonia with change in the resistance ($\Delta R/R_0$) of about 350%. The sensor also showed very good recovery.

Similarly, an array of parallel polypyrrole nanowires connected using gold pads that were deposited with shadow mask method was used to detect ammonia gas. Very fast and reproducible responses of these sensors towards ammonia gas were reported [54]. For the same concentration, response of these sensors scaled inversely with the nanowire size. Smaller width (300 nm) nanowire showed about twice the response when compared to 5 μm wide nanowires at 240 ppm ammonia concentration, emphasizing the advantage of using nanostructures for improved sensor performance.

Kemp et al. [38] reported single polyaniline nanowire deposition between two platinum nanoelectrodes deposited using FIB technique. This device showed reversible response to different ammonia

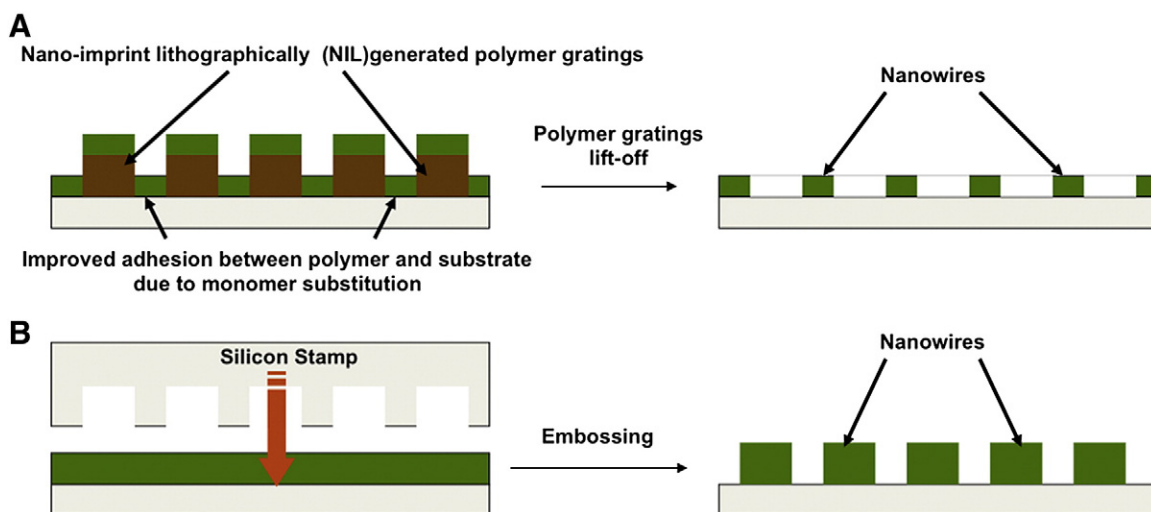


Fig. 3. Schematic representation of high density conducting polymer nanowire fabrication methods. (A) High density conducting polymer nanowire fabrication method employing NIL generated polymer gratings for predefined nanowire diameter and pitch. (B) Variation of method (A) for high density conducting polymer nanowire array fabrication by employing embossing of conducting polymer film using a silicon stamp with predefined features.

Table 1
Summary of various conducting polymer 1-D nanostructure fabrication techniques.

Category	Technique	Method/device	Nanostructure	Pros	Cons	References
Template-free	Solution phase synthesis	Solution casting and Langmuir–Blodgett	Nanoribbon or nanotube	Diameter easily controlled by solution composition	Extensive post-synthesis nanowire processing and alignment required	[26–28]
	Probe driven synthesis	DPN and electrospinning	Nanowire	Prepatterned electrodes offer aligned nanowires	Poor nanowire diameter and alignment control	[29,30,32]
		Mechanical stretching	Nanowire	Nanowire	Diameter of the nanowire can be stretched to few nm	1. Complex device geometry, 2. incompatible for high density array fabrication
	Electrochemical deposition	CPNEJ, FIB/ electrochemically fabricated nanogaps	Nanowire	Prefabricated electrodes are built in contacts for final device	Lack of precise control on nanowire diameter and no. of nanowires connected across the electrode gap or low aspect ratio nanostructures fabricated	[14,33–38]
Template-directed	Soft and hard template	Chemical, electrochemical and melt-assisted	Multi-or single-segmented or core-shell nanowire or nanotube	Diameter precisely controlled and dictated by template pores. Composition, morphology or aspect ratio of the nanostructure controlled by time and conditions of fabrication	1. Post-synthesis processing required, harsh chemicals used to remove the template can affect the electrical properties of the nanostructure, 2. alignment of the nanostructure is necessary to realize a functional device	[13,15,16,39–48]
	In-situ	Electrochemical deposition using nanochannel	Nanowire	One step nanowire fabrication and functionalization for individually addressable high density nanowire array based sensing applications	Nanochannel fabrication using e-beam lithography makes the process complex and expensive	[49,50]
	Nanostructure as template	Chemical or electrochemical deposition	Nanoparticle, nanowire or nanoribbon	Pre-aligned nanostructures allow spacial and dimensional control	1. Pre-alignment of nanostructures such as CNTs, DNAs is complex, 2. Use of other nanostructures add to the cost	[51–53]
	High density nanowire fabrication	NIL/embossing	Nanowire and other patterned nanostructures	Diameter and pitch of the nanowires in an array controlled using a prepatterned stamp	This bottom up approach requires metal electrode deposition on top of prepatterned conducting polymer nanowires which could suffer thermal damages resulting from high temperature physical metal deposition processes	[54,55]

concentration while at higher concentration it showed saturation with small irreversibility.

Fabrication of single conducting polymer nanowire based sensor utilizing chemically polymerized polypyrrole in the pores of alumina template was reported by our group. Highly doped nature of these polymer nanowires resulted in no response towards NO₂ gas as there were no electrons available for NO₂ to withdraw from the polymer. On the other hand, the sensor showed excellent response towards ammonia with detection limit of 40 ppm and sensitivity of 0.06% per ppm of ammonia up to 300 ppm concentration due to its behavior as a Lewis base [43].

The sensor sensitivity and detection limit are also influenced by the noise level in the measurement. One of the reasons for the noise lies in the inherent flaws of sensor architecture. Specifically contact resistance introduced due to sensor design plays important role in the sensor performance. By securing/anchoring polypyrrole nanowires using selective maskless metal electrodeposition on the contact pads, significant reduction in the noise level of single polypyrrole nanowire sensor was observed. A marked improvement in the sensitivity from about 0.14 to 0.63% per ppm of ammonia was observed by our group [59].

The use of carbon nanotubes as templates for electrochemical fabrication of polyaniline nanowires was demonstrated by Zang et al. [53] These thin nanowire (98 ± 5 nm) based sensors showed excellent sensitivity of 2.44% R/R₀ per ppm of ammonia with excellent detection limit of 50 ppb. Polyaniline deposited sensors showed marked improvement (~60 times) over bare carbon nanotubes sensors. These polyaniline nanowire sensors showed excellent sensitivity even at higher temperatures.

Comparison between few selective FET/chemiresistive ammonia sensors has been shown in Table 2, clearly indicating that the lower detection limit and higher sensitivity are contingent upon lower nanowire dimension/diameter and better electrical contact with the metal electrodes.

4.1.2. Detection of other gases

Detection of gases such as VOCs, alcohol vapors and other toxic gases plays an important role in environment monitoring. Novel nanowire based sensors can improve the detection capabilities towards these analyte gases for better response. The following are the examples of sensors developed by researchers emphasizing versatility of conducting polymer nanowire sensors.

Wang et al. [36] recently reported crystalline PEDOT and Ppy-based CPNEJs that were used as a sensor for ethanol detection. Both the sensors showed very good response towards saturated ethanol vapors. Ppy-based sensor showed non-selective response towards both ethanol as well as ammonia whereas PEDOT showed very selective response towards ethanol only. The mechanism of change in the resistance of the polymer nanowire is attributed to swelling of the polymer and reduction in the number of charge carriers on the polymer backbone.

Based on similar mechanism, dielectrophoretically aligned single gold-PEDOT/PSS-gold multisegmented nanowire based sensor was used to detect different gases viz. methanol, ethanol and acetone [56]. This single nanowire based sensor showed very good response to all three gases with linear responses towards methanol up to 50% of its saturation concentration and towards acetone up to about 80% of its saturation concentration with sensitivity of about 6% and 8% per % saturation, respectively. At concentrations higher than these, sensor showed irreversible resistance change. On the other hand response to ethanol showed saturation at higher concentration.

4.2. Biosensing

Conducting polymer by itself lacks the specificity/selectivity necessary to function as a biosensor. Biological recognition molecules such as antibodies, enzymes or oligonucleotides impart the desired selectivity and specificity to the biosensor based on conducting

polymer nanowires. Thus the first step in realizing successful biosensor application is immobilization of bio-recognition molecule on/in the polymer nanowire. The adaptation of appropriate biofunctionalization technique primarily depends on the fabrication conditions and/or the polymer composition, as discussed below.

4.2.1. Biofunctionalization

4.2.1.1. Covalent functionalization. The introduction of bio-recognition molecule on the conducting polymer nanostructure using covalent linking offers a very strong bonding between the two. This surface functionalization chemistry puts the recognition molecule on the surface making it completely accessible for sensing, resulting in faster sensing and higher sensitivity. The techniques used for thin films can be adopted for nanostructures as well. Functionality needed for covalent linking of recognition molecule can be introduced in/on the polymer before, during or after nanostructure synthesis.

4.2.1.1.1. Functional monomer. Synthesis and properties of conducting polymers fabricated from functional monomers have mostly been studied as thin films but their fabrication at nanoscale can be realized by adopting template fabrication methods used for nanowire synthesis. Biotin derivative of pyrrole was electrochemically deposited on metal electrodes using cyclic voltammetry. The electrode was further functionalized with avidin on the surface which was subsequently bound to biotinylated enzyme viz. glucose oxidase, GO_x [60]. Another example of functional monomer was demonstrated by electrodepositing thin films of poly(nitrilotriacetic acid) (NTA) derivative of pyrrole. Further functionalization of the polymer made use of metal chelating properties of NTA functional group to coordinates bivalent metal ions (Cu, Ni, Zn, and Co) leaving free coordination sites of the chelator–metal complex for the ligation of histidine-tagged proteins [61]. Using this technique our group has demonstrated fabrication of poly(pyrrole-NTA) nanotubes in the alumina template and application of these nanotubes for detection of histidine-tagged proteins via copper ion coordination [62]. Recently, carboxylic acid derivative of pyrrole was exploited for nanowire fabrication and its application for biomolecule conjugation through N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide (EDC) linking chemistry [63].

Alternatively, functional monomer has been copolymerized with its non-functional counterpart. Recently, fabrication of acid functionalized polypyrrole nanotubes was reported inside cylindrical micelle templates [16]. To express acid functional group on the surface of the nanotubes pyrrole-3-carboxylic acid (P3CA) as a co-monomer was polymerized along with pyrrole monomer. The acid functionality helped in not only attaching bio-recognition molecule on the top surface of nanotubes but also in assisting in the covalent attachment of nanotubes on amine terminated silanized silicon substrate from the bottom surface to form good contact with the metal electrodes. Amine terminated thrombin aptamer was selectively and covalently attached to the nanotube network as a recognition element.

4.2.1.1.2. Functional dopant. Dopants on the other hand can also be used as the sites for covalent attachment of the recognition molecule.

By incorporating dopant with appropriate functional group, surface functionalization can be achieved. For example, using poly(methyl vinyl ether-alt-maleic acid) (PMVEA) as a polymeric dopant, carboxylic acid functional groups were introduced in the PANI nanotubes. Subsequently, these nanowires were functionalized with amine terminated recognition molecules using well established surface functionalization chemistry using water soluble coupling agent N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDAC) [27].

Fig. 4 (A) depicts different sites on polypyrrole polymer where functional group/s can be introduced. These functional groups can be employed further as the immobilization site for bio-recognition molecules.

4.2.1.1.3. Surface functionalization using linker molecules. Prefabricated conducting polymer nanostructures or thin films can be functionalized with linker molecules to introduce certain functional group on the surface of the polymer which can subsequently be used for covalent attachment of recognition biomolecules. Fig. 4 (B) depicts a general route for functionalization of polypyrrole polymer using bi-functional linker molecule. Glutaraldehyde [64] and EDAC (as mentioned earlier) [65] are two most commonly used linker molecules for conducting polymer surface functionalization. Glutaraldehyde is a bi-functional linker molecule with aldehyde groups at both ends. One aldehyde group can be used to attach it to the primary or secondary amine group of the polymer while the other end can be attached to the amine group of the recognition molecule. EDAC on the other hand is a zero-length linking molecule used for attaching carboxylic group on the polymer/recognition molecule to the primary or secondary amine group on the recognition molecule/polymer, respectively, by forming an amide linkage. Many a time N-hydroxysuccinimide (NHS) is used as an activator to improve the yield of EDAC reaction through formation of stable amine reactive NHS-ester intermediate. Using EDC linking chemistry, our group has recently demonstrated biofunctionalization of single conducting polymer (polypyrrole) nanowire devices with antibodies for the fabrication of immunosensor [57].

4.2.1.2. Non-covalent functionalization/physical entrapment. Due to benign synthesis conditions employed for fabrication of conducting polymer nanowire/nanotube structures, biomolecules can be physically deposited/trapped in the polymer matrix during the fabrication step itself. However, accessibility of these biomolecules for sensing purposes is a crucial issue in such functionalization schemes. Hernandez et al. has investigated optimum conditions for entrapping streptavidin in gold-capped polypyrrole nanowires from phosphate buffer saline solution [20]. Our group has demonstrated a single-step electrochemical biomolecule entrapped conducting polymer nanowire fabrication technique using e-beam lithographically patterned channels. This technique allowed us to fabricate ready to use sensors in a single fabrication step as mentioned earlier, without the need for any post-synthesis processing. Accessibility of the recognition molecule becomes a very important factor in case of physical entrapment as the biomolecule is buried in the polymer matrix. This could result in reduced sensitivity and longer response time. To

Table 2
Comparison between selective conducting polymer nanowire/s based ammonia FET/chemiresistive sensors.

Sensor configuration	Marked improvement	Detection limit	Sensitivity, $\Delta R/R_0$ (at NH_3 conc.)	Reference
CPNEJ fabricated nanowire network between two metal contact electrodes	Highly quality nanowires	10 ppm	350% (1000 ppm)	[36]
NIL and lift off generated array of parallel nanowire connected between shadow mask deposited metal electrodes	Well controlled nanowire diameter and pitch in an array	--	Up to 50% (240 ppm) for 300 nm dia. nanowire	[54]
Single Ppy nanowire connected between two gold electrodes		40 ppm	0.06%/ppm	[43]
Single Ppy nanowire connected between two gold electrodes anchored by maskless electrodeposition	Improved contact resistance and noise reduction	<10 ppm	0.63%/ppm	[59]
Carbon nanotube templated Ppy nanowire connected between gold electrodes	98 +/- 5 nm nanowire diameter	50 ppb	2.44%/ppm	[53]

address this issue, using atomic force microscopy technique we demonstrated that the biomolecules entrapped within the polymer are near the polymer surface and are accessible for analyte binding [50].

4.2.2. Sensing

Biosensors employing conducting polymer nanowires as the transducer and biomolecule as bio-recognition site can be configured as a simple chemiresistor or field-effect transistor (FET) sensor. Conducting polymer nanowire devices suffer from poor electric contact between the nanostructure and metal electrodes. Hence different approaches are taken to ensure good contact between conducting polymer nanostructures and metal electrodes. For such a biosensor, nanowire sites that are not functionalized with bio-recognition molecule can potentially participate in non-specific binding resulting in undesired noise in the signal. To avoid this problem a blocking agent is used to screen such interactions. Fig. 5 schematically depicts such a biosensor. Such a sensor upon selective binding of the target analyte to the receptor on nanowire surface shows change in the conductivity of the nanowire due to the following:

1. change in the number of charge carriers in the nanowire brought about by gating effect of the charged analyte or
2. change in the oxidation/reduction state of the conducting polymer.

Examples illustrating above phenomena are discussed in the following sections.

4.2.2.1. Protein sensors. The use of functional monomers for biosensing was demonstrated by using carboxylic acid derivative of pyrrole for conducting polymer nanowire fabrication. These nanowires were

functionalized with antibodies against human serum albumin (HSA) and drop deposited on to microfabricated gold electrodes to fabricate the sensor with multiple nanowires connected between pair of electrodes. To ensure good electrical contact between the ensemble of nanowires and the contact electrodes colloidal silver paste was applied to the ends of the nanowires. Selective detection of HSA at nanomolar concentration was demonstrated using liquid ion gated field-effect transistor (FET) sensor design wherein an Ag/AgCl reference electrode was employed as a gate electrode while the microfabricated gold electrodes were used as the source and the drain [63].

Another demonstration of use of functional monomer adopted copolymerization of acid functionalized pyrrole (P3CA) with pyrrole monomer to fabricate nanotube structures. By using a network of nanotubes functionalized with thrombin aptamer as a channel between a pair of contact electrodes as source and drain, a field-effect transistor (FET) with liquid-ion gate was constructed. Good electric contact between nanotube network and the metal electrodes was ensured by covalently anchoring the nanowires on the silane modified silicon oxide surface between the metal electrodes. To avoid non-specific adsorption, sensor surface was blocked by skim milk. Sensitivity of thrombin detection was found to be dependent upon the ratio of P3CA and pyrrole monomer used for electrodeposition as it affected density of carboxylic group on the nanotube surface. A detection limit of 50 nM of thrombin was achieved. This sensor showed measurable response towards 166 nM of thrombin in human blood serum exhibiting its importance in clinical diagnostics [16].

Using single surface functionalized polypyrrole nanowire-based immunosensor our group has recently demonstrated sensitive and selective detection of cancer biomarker. Single polypyrrole nanowire based devices were fabricated using electrophoretic alignment of

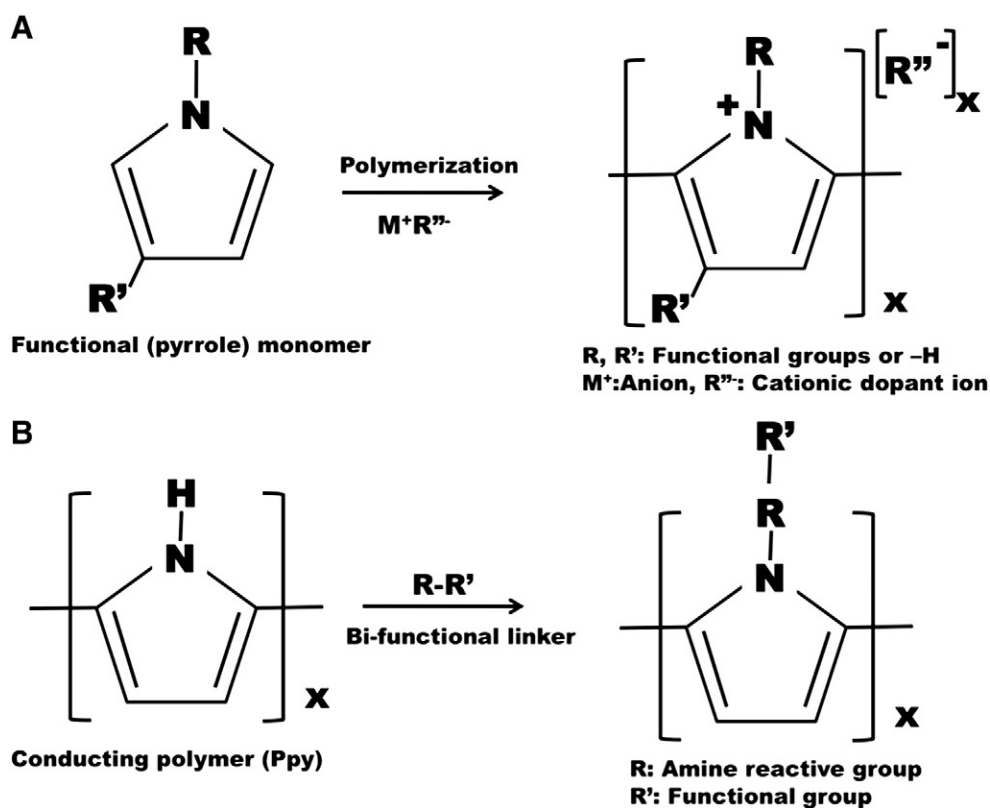


Fig. 4. Covalent biofunctionalization routes for conducting polymer (A) employing either functional monomer (e.g. either 1 or 3-substituted functional pyrrole) or functional dopant (e.g. PAA), which can further be linked to appropriate recognition molecule. (B) Alternatively non-functional conducting polymer can be surface functionalized with a bi-functional linker molecule which can bind to the conducting polymer at one end and to desired recognition molecule on the other end (e.g. glutaraldehyde can be used for surface functionalization of Ppy).

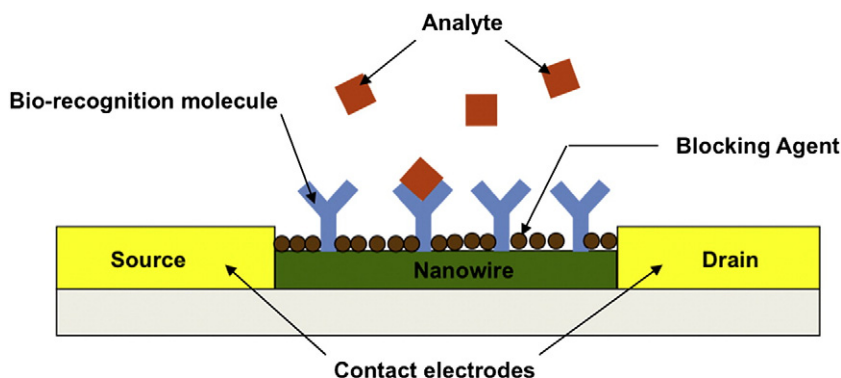


Fig. 5. Schematic representation of conducting polymer nanowire-based biosensor. Nanowire connected between the source and the drain electrodes is functionalized with appropriate bio-recognition molecule either on the surface or in the polymer matrix. Blocking agent is used to block sites which can result in non-specific interaction. When exposed to charged analyte, upon specific bio-interaction between recognition molecule and the analyte, modulation in the electrical properties (e.g. conductance) of the nanowire takes place, which is related to the sensing event.

prefabricated nanowires followed by physical modulation. To ensure good electric contact between the nanowire and contact electrodes, selective maskless electrodeposition of gold on the contact electrodes was carried out to anchor the ends of the nanowire in the metal. Functionalization of the nanowire surface with antibody against CA 125 was achieved using EDC linking chemistry followed by blocking of unfunctionalized sites using bovine serum albumin (BSA). Detection limit of single unit per ml of cancer antigen (CA 125) was achieved using these sensors. The sensor showed no loss of performance when sensing was carried out in human blood plasma demonstrating ability of these sensors to detect target analytes in real samples [57].

Using physical entrapment method, single-step electrochemical fabrication of avidin embedded polypyrrole (200 nm) nanowire biosensor was demonstrated by our group for detection of biotin tagged analytes. Built-in metal electrodes used for the electrodeposition of nanowire ensured a good electrical contact with the nanowire. Using this sensor biotin-single stranded DNA conjugate was detected at 1 nM concentration. Charge on the analyte molecule, which is necessary for the electrical detection was provided by the DNA in the analyte whereas avidin-biotin interaction was responsible for the binding of the analyte on the nanowire surface [50].

4.2.2.2. Glucose sensor. Forzani et al. fabricated glucose sensor using a nanojunction device. Glucose oxidase (GO_x) was physically trapped in polyaniline matrix, which oxidized glucose during sensing. On the other hand reduced GO_x underwent oxidation to produce H_2O_2 . H_2O_2 then oxidized polyaniline resulting in an increase in the current passing through the device [66].

Table 3 summarizes different biosensors as discussed earlier. From this table it can be seen that conducting polymer nanostructure based

biosensors are not only equally competent with other nanostructures but the sensitivity and the detection limit make them attractive for real world applications.

5. Conclusions and future perspectives

This review has summarized recent studies on the fabrication, assembly and sensing applications of conducting polymer 1-dimensional nanostructures for FET sensors. These novel nanostructures offer simple, benign fabrication conditions along with excellent and tunable electrical, mechanical and optical properties. Their simple functionalization routes and biocompatibility make them attractive alternative over other nanomaterials. However the use of conducting polymer nanomaterials has been limited due to their incompatibility with traditional microfabrication techniques owing to their possible thermal damages and unstable contact with metal electrodes in device architecture. However, from the examples shown in this review, it can be realized that the use of conducting polymer nanomaterials for FET sensors is on the rise with development of new fabrication, assembly and functionalization techniques. Also it can be realized that few techniques mentioned earlier have shown potential to demonstrate an array of conducting polymer nanowire with multi-functionality for the detection of multiple analytes/multi-plexing, which can further prove the utility of these novel nanomaterials.

However, most of the techniques utilizing conducting polymer nanomaterials for FET sensor fabrication are in early stage of their development. More improved methods for conducting polymer nanomaterial synthesis, assembly and functionalization are needed for better scalability, ease of operation and precise control on

Table 3
Summary of different conducting polymer 1-D nanostructure based FET/chemiresistive biosensors.

Sensor configuration	Monomer	Functionalization route/chemistry/agent	Recognition molecule	Detection limit	Reference
Multiple nanowires connected between gold electrodes and the ends secured with colloidal silver	Pyrrolepropyic acid (PPA) (functional monomer)	EDC cross linker	Anti-HSA	In the (<50) nM range of HSA concentration	[63]
Multiple nanowires connected between gold electrodes while anchored on to silicon oxide surface	P3CA (functional monomer) and pyrrole co-monomer	4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DMT-MM)	Thrombin aptamer	50 nM of thrombin	[16]
Single nanowire anchored between gold electrodes using maskless electrodeposition	Pyrrole	EDC (surface functionalization using linker molecule)	Anti-CA 125	1 unit/ml of CA 125	[57]
In-situ fabrication and functionalization of individually addressable nanowire	Pyrrole	Physical entrapment during nanowire synthesis	Avidin	1 nM of ssDNA–biotin conjugate	[50]
Nanojunction electrodeposited with conducting polymer nanostructure	Aniline (and poly(acrylic acid))	Physical entrapment post conducting polymer nanostructure synthesis	Glucose oxidase	In the μ M range of glucose concentration	[66]

nanowire dimension and assembly for mass production of these nanosensors. Also mechanical/thermal stability and durability of these polymers can limit the utility of nanosensors fabricated using these materials. However, with the invent of new functional conducting polymers with better electrical properties and durability, use of conducting polymer for nanosensor fabrication and application in real world can be realized.

References

- [1] A.K. Wanekaya, W. Chen, N.V. Myung, A. Mulchandani, *Electroanalytical* 18 (2006) 533.
- [2] G. Zheng, F. Patolsky, Y. Cui, W.U. Wang, C.M. Lieber, *Nat. Biotechnol.* 23 (2005) 1294.
- [3] W. Wang, C. Chen, K.-H. Lin, Y. Fang, C.M. Lieber, *PNAS* 102 (2005) 3208.
- [4] Z. Li, Y. Chen, X. Li, I. Kamins, K. Nauka, R.S. Williams, *Nano Lett.* 4 (2004) 245.
- [5] Y. Cui, Q. Wei, H. Park, C.M. Lieber, *Science* 293 (2001) 1289.
- [6] C. Li, M. Curreli, H. Lin, B. Lei, F.N. Ishikawa, R. Datar, R.J. Cote, M.E. Thompson, C. Zhou, *J. Am. Chem. Soc.* 127 (2005) 12484.
- [7] A. Star, J.-C.P. Gabriel, K. Bradley, G. Gruner, *Nano Lett.* 3 (2003) 459.
- [8] R.J. Chen, S. Bangsarunyip, K.A. Drouvalakis, N.W.S. Kam, M. Shim, L. Yiming, W. Kim, P.J. Utz, H. Dai, *PNAS* 100 (2003) 4984.
- [9] D.P. Yu, Z.G. Bai, Y. Ding, Q.L. Hang, H.Z. Zhang, J.J. Wang, Y.H. Zou, W. Qian, G.C. Xiong, H.T. Zhou, S.Q. Feng, *Appl. Phys. Lett.* 72 (1998) 3458.
- [10] M.K. Sunkara, S. Sharma, R. Miranda, G. Lian, E.C. Dickey, *Appl. Phys. Lett.* 79 (2001) 1546.
- [11] S. Iijima, *Nature* 354 (1991) 56.
- [12] Z.F. Ren, Z.P. Huang, J.W. Xu, D.Z. Wang, J.G. Wen, J.H. Wang, *Appl. Phys. Lett.* 75 (1999) 1086.
- [13] C.R. Martin, *Science* 266 (1994) 1961.
- [14] J. Li, X. Lin, *Biosens. Bioelectron.* 22 (2006) 2898.
- [15] L. Huang, Z. Wang, H. Wang, X. Cheng, A. Mitra, Y. Yan, *J. Mater. Chem.* 12 (2002) 388.
- [16] H. Yoon, J.-H. Kim, N. Lee, B.-G. Kim, J. Jang, *Chembiochem* 9 (2008) 634.
- [17] A.G. MacDiarmid, *Synth. Met.* 125 (2002) 11.
- [18] A.J. Heeger, *Synth. Met.* 125 (2002) 23.
- [19] H. Shirakawa, *Synth. Met.* 125 (2002) 3.
- [20] R.M. Hernandez, L. Richter, S. Semanick, S. Stranick, T.E. Mallouk, *Chem. Mater.* 16 (2004) 3431.
- [21] N. Chopra, V.G. Gavalas, B.J. Hinds, L.G. Bachas, *Anal. Lett.* 40 (2007) 2067.
- [22] S.I. Cho, S.B. Lee, in: J.A. Schwarz, C.I. Contescu (Eds.), *Dekker Encyclopedia of Nanoscience and Nanotechnology*, 2nd Edition, Taylor & Francis, New York, 2009, p. 965.
- [23] A.D.W. Carswell, B.P. Grady, in: J.A. Schwarz, C.I. Contescu (Eds.), *Dekker Encyclopedia of Nanoscience and Nanotechnology*, 2nd Edition, Taylor & Francis, New York, 2009, p. 3243.
- [24] H.D. Tran, D. Li, R.B. Kaner, *Adv. Mater.* 21 (2009) 1487.
- [25] L. Xia, Z. Wei, M. Wan, *J. Colloid Interface Sci.* 341 (2010) 1.
- [26] P. Samori, V. Francke, J.P. Rabe, *Thin Solid Films* 336 (1998) 13.
- [27] L. Zhang, H. Peng, P.A. Kilmartin, C. Soeller, J.T. Sejdic, *Electroanalytical* 19 (2007) 870.
- [28] T. Bjornhom, T. Hassenkam, D.R. Greve, R.D. McCullough, M. Jayaraman, S.M. Savoy, C.E. Jones, J.T. McDevitt, *Adv. Mater.* 11 (1999) 1218.
- [29] J.-H. Lim, C.A. Mirkin, *Adv. Mater.* 14 (2002) 1474.
- [30] B.W. Maynor, S.F. Filocamo, M.W. Grinstaff, J. Liu, *J. Am. Chem. Soc.* 124 (2002) 522.
- [31] H.X. He, C.Z. Li, N.J. Tao, *Appl. Phys. Lett.* 78 (2001) 811.
- [32] J. Kameoka, H.G. Craighead, *Appl. Phys. Lett.* 83 (2003) 371.
- [33] X.-L. Zhang, J.-X. Wang, Z. Wang, S.-C. Wang, *Sensors* 5 (2005) 580.
- [34] L. Liang, J. Liu, C.F. Windisch, G.J. Exarhos, Y.H. Lin, *Angew. Chem. Int. Ed.* 41 (2002) 3665.
- [35] M.M. Alam, J. Wang, Y. Guo, S.P. Lee, H.-R. Tseng, *J. Phys. Chem. B* 109 (2005) 12777.
- [36] Y. Wang, K.K. Coti, J. Wang, M.M. Alam, J.-J. Shyue, W. Lu, N. Padture, H.-R. Tseng, *Nanotechnology* 18 (2007) 424021.
- [37] E.S. Forzani, X. Li, N.J. Tao, *Anal. Chem.* 79 (2007) 5217.
- [38] N.T. Kemp, D. McGrouther, J.W. Cochrane, R. Newbury, *Adv. Mater.* 19 (2007) 2634.
- [39] J.C. Hulteen, C.R. Martin, *J. Mater. Chem.* 7 (1997) 1075.
- [40] S. Park, J.-H. Lim, S.-W. Chung, C.A. Mirkin, *Science* 303 (2004) 348.
- [41] M. Lahav, E.A. Weiss, Q. Xu, G.M. Whitesides, *Nano Lett.* 6 (2006) 2166.
- [42] M.A. Bangar, C.M. Hangarter, B. Yoo, Y. Rheem, W. Chen, A. Mulchandani, N.V. Myung, *Electroanalytical* 21 (2009) 61.
- [43] S.C. Hernandez, D. Chaudhari, W. Chen, N.V. Myung, A. Mulchandani, *Electroanalytical* 19 (2007) 2125.
- [44] C.R. Martin, *Chem. Mater.* 8 (1996) 1739.
- [45] R.V. Parthasarathy, C.R. Martin, *Chem. Mater.* 6 (1994) 1627.
- [46] D. O'Carroll, J. Irwin, D.A. Tanner, G. Redmond, *Mater. Sci. Eng., B* 147 (2008) 298.
- [47] J.P. Spatz, B. Lorenz, K. Weishaupt, H.D. Hochheimer, V.P. Menon, R.V. Parthasarathy, C.R. Martin, J. Bechtold, P.-H. Hor, *Phys. Rev. Lett.* 50 (1994) 14888.
- [48] M. Treuba, A.L. Montero, J. Rieumont, *Electrochim. Acta* 49 (2004) 4341.
- [49] K. Ramanathan, M.A. Bangar, M. Yun, W. Chen, A. Mulchandani, N.V. Myung, *Nano Lett.* 4 (2004) 1237.
- [50] K. Ramanathan, M.A. Bangar, M. Yun, W. Chen, N.V. Myung, A. Mulchandani, *J. Am. Chem. Soc.* 127 (2005) 496.
- [51] W. Zhong, Y. Wang, Y. Yan, Y. Sun, J. Deng, W. Yang, *J. Phys. Chem. B* 111 (2007) 3918.
- [52] P. Nickels, W.U. Dittmer, S. Beyer, J.P. Kotthaus, F.C. Simmel, *Nanotechnology* 15 (2004) 1524.
- [53] T. Zhang, M.B. Nix, B.-Y. Yoo, M.A. Deshusses, N.V. Myung, *Electroanalytical* 18 (2006) 1153.
- [54] B. Dong, N. Lu, M. Zelsmann, N. Kehagias, H. Fuchs, C.M.S. Torres, L. Chi, *Adv. Funct. Mater.* 16 (2006) 1937.
- [55] Z. Hu, B. Muls, L. Gence, D.A. Serban, J. Hofkens, S. Melinte, B. Nysten, S.D. Champagne, A.M. Jonas, *Nano Lett.* 7 (2007) 3639.
- [56] Y. Dan, Y. Cao, T.E. Mallouk, A.T. Johnson, S. Evoy, *Sens. Actuators, B* 125 (2007) 55.
- [57] M.A. Bangar, D.J. Shirale, W. Chen, N.V. Myung, A. Mulchandani, *Anal. Chem.* 81 (2009) 2168.
- [58] D. O'Carroll, A. O'Riordan, G. Redmond, *Mater. Res. Soc. Symp. Proc.* 948-B09-04 (2007).
- [59] C.M. Hangarter, M.A. Bangar, S.C. Hernandez, W. Chen, M.A. Deshusses, A. Mulchandani, N.V. Myung, *Appl. Phys. Lett.* 92 (2008) 73104.
- [60] S. Cosnier, B. Galland, C. Gondran, A.L. Pellec, *Electroanalytical* 10 (1998) 808.
- [61] N. Haddour, S. Cosnier, C. Gondran, *J. Am. Chem. Soc.* 127 (2005) 5752.
- [62] C.L. Aravinda, S. Cosnier, W. Chen, N.V. Myung, A. Mulchandani, *Biosens. Bioelectron.* 24 (2009) 1451.
- [63] S.B. Tolani, M. Craig, R.K. DeLong, K. Ghosh, A.K. Wanekaya, *Anal. Bioanal. Chem.* 393 (2009) 1225.
- [64] V.K. Gade, D.J. Shirale, P.D. Gaikwad, P.A. Savale, K.P. Kakde, H.J. Kharat, M.D. Shirsat, *React. Funct. Polym.* 66 (2006) 1420.
- [65] C. Dhand, S.P. Singh, S.K. Arya, M. Datta, B.D. Malhotra, *Anal. Chim. Acta* 602 (2007) 244.
- [66] E.S. Forzani, H. Zhang, L.A. Nagahara, I. Amlani, R. Tsui, N. Tao, *Nano Lett.* 4 (2004) 1785.