



Review

Conducting polymers for electrochemical DNA sensing

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ARTICLE INFO

Article history:

Received 30 September 2008

Accepted 24 December 2008

Available online 14 January 2009

Keywords:

Conducting polymers

Electrochemical DNA sensor

Electropolymerization

ABSTRACT

Conducting polymers (CPs) are a class of polymeric materials that have attracted considerable interest because of their unique electronic, chemical and biochemical properties, making them suitable for numerous applications such as energy storage, memory devices, chemical sensors, and in electrocatalysis. Conducting polymer-based electrochemical DNA sensors have shown applicability in a number of areas related to human health such as diagnosis of infectious diseases, genetic mutations, drug discovery, forensics and food technology due to their simplicity and high sensitivity. This review paper summarizes the advances in electrochemical DNA sensing based on conducting polymers as active substrates. The various conducting polymers used for DNA detection, along with different DNA immobilization and detection methodologies are presented. Current trends in this field and newly developed applications due to advances in nanotechnology are also discussed.

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1. Introduction

DNA analysis plays an ever-increasing role in a number of areas related to human health such as diagnosis of infectious diseases, genetic mutations, drug discovery, forensics and food technology. Conventional methods for the analysis of specific gene sequences are based on either direct sequencing or DNA hybridization. The sequencing technology was invented by Maxam and Gilbert [1] and Sanger et al. [2] in the 1970s. In the same period, solid-supported hybridization became a widespread method for DNA analysis using membrane-based blots [3,4]. However, these approaches have some disadvantages, such as the inability to use a large number of DNA samples, low selectivity between closely related sequences and they are often time consuming. In the early 90s, gene array technologies which relied on the anchoring of multiple specific probe DNA fragments or oligonucleotides (ODNs) onto solid surfaces and detection of fluorescently or radioactively tagged analyte oligonucleotides appeared as promising tools for the simultaneous analysis of multiple DNA sequences [5–7]. These array technologies have had a huge impact on genomics and proteomics applications, although they have shortcomings arising from, for example, limited tagging efficiency, hazardous waste

disposal and complex multi-step analysis. In order to seek faster, sensitive and label-free DNA detection, a number of approaches have been suggested based on optical [8–11], acoustic [12] and electrochemical [13–15] techniques.

Electrochemical DNA sensors are regarded as particularly suitable for direct and fast biosensing since they can convert the hybridization event into a direct electrical signal [16–18]. This means that there is no need for complex signal transduction equipment and the detection can be accomplished with an inexpensive electrochemical analyzer. Electrochemical DNA sensing approaches include the intrinsic electroactivity of DNA [19–22], electrochemistry of DNA-specific redox reporters [23,24], electrochemistry of nanoparticles [25–27] and conducting polymers (CPs) [18,28].

Conducting polymers (CPs) are polyconjugated polymers with electronic properties resembling those of metals, while retaining properties of conventional organic polymers. Since the observation of the remarkably high electrical conductivity of a halogen-treated polyacetylene [29], a number of other conjugated polymers have been transformed from an insulating into a highly conductive state. The most widely investigated conducting polymers include polyaniline, poly(phenylenevinylene), polypyrrole and polythiophene (Fig. 1). The award of the Nobel Prize in Chemistry in 2000 to H. Shirakawa, A. MacDiarmid and A. Heeger for their pioneering work on conducting polymers widely recognized the importance of these materials and has prompted even more vigorous research in the field. Compared to saturated polymers, CPs have a unique electronic structure which is responsible for their electrical conductivity, low ionization potentials and high electron affinity. For CPs in

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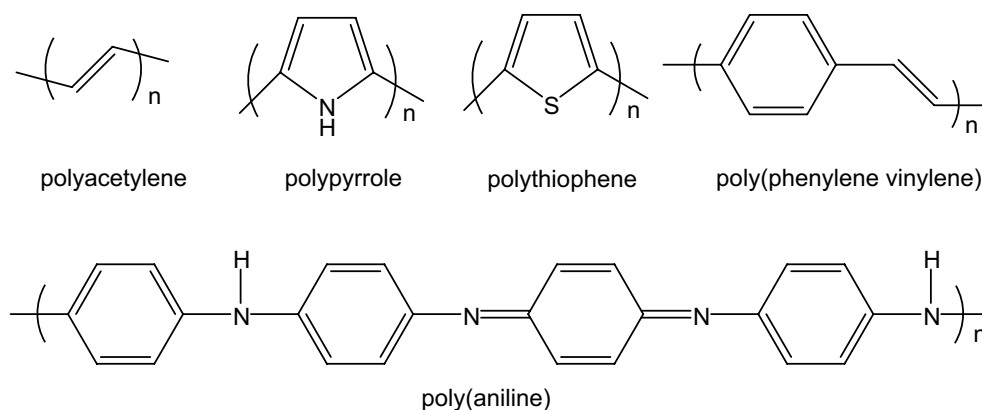


Fig. 1. Structures of some of the most common conducting polymers.

the *ground state* (insulating or semiconducting state), π -bonds (π - π^*) are partially localized due to a phenomenon called the Peierls distortion [30]. During the *doping process*, the excitation across the π - π^* band gap creates *self-localized excitations* of conjugated polymers with localized electronic states in the gap region [30]. These self-localized excitations are called polarons, bipolarons and solitons and underlay electrical conduction in CPs. The unique properties of CPs have led to a variety of applications for these materials, such as light emitting diodes (LEDs) [31], electrochromic materials [32], anti-static coatings [33], solar cells [34], batteries [35], anti-corrosion coatings [36], chemical sensors and biosensors [37] and drug release systems [38–40].

Conducting polymers can be synthesized chemically [41,42] and electrochemically [43,44]. In terms of biological applications, electrochemical polymerization is widely used because of several advantages: (i) it is performed at ambient temperatures and microelectrodes or electrodes with a large surface area can be used; (ii) the polymer film formed is confined to the electrode and its shape can thus be controlled by electrode design, while the thickness can be controlled in the nanometer to micrometer range; (iii) the properties of the CP film can be widely modulated by varying electrochemical polymerization conditions. Electrochemical polymerization can be carried out potentiostatically, amperometrically or with potential scanning and the whole process may only take a few seconds [45]. During polymerization, the monomers are oxidized to form radical cations, followed by coupling reactions to form oligomers that eventually lead to deposition of the polymers on the electrode surface. More detailed descriptions of electrochemical polymerization can be found elsewhere [41,46].

The electronic structure of CPs is highly sensitive to changes in the polymeric chain environment and other perturbations in the chain conformation caused by, for example, a biological recognition event such as DNA hybridization. The changes in the delocalized electronic structure or in other CP properties are manifested in altered optical and electrical properties, and, when measured, can provide a signal for the presence of a target analyte molecule [47]. These advantages of CPs make them suitable materials for chemical sensors and biosensors. An excellent review on chemical sensors based on CPs by Swager and collaborators [47] outlines numerous synthetic approaches towards the specific recognition probes attached to a conjugated polymer backbone. More recently, Bai et al. reviewed the application of CPs as gas sensors [48].

This review paper focuses on the applications of conducting polymers specifically in DNA sensing, with a special attention paid to current trends and applications developed recently in the field due to advances in nanotechnology.

2. Immobilization of DNA probes

A typical configuration for DNA sensors based on CPs is shown in Fig. 2. Single-stranded DNA probes are immobilized on or within a conducting polymer layer. The target DNA is captured by base-pairing to generate a recognition signal, which is recorded through an electrode (gold, platinum, glassy carbon, etc.). Because the recognition event takes place at the CP/electrolyte interface and the recognition signal generated reaches the transducer through the CP layer, the properties of the CP and the orientation of the immobilized DNA probes on the CP are crucial to the sensor performance.

The procedure of DNA probe immobilization should retain the probe's affinity for complementary target DNA. Ideally, the orientation of probes should be predictable and readily accessible to the analyte DNA [49]. Generally, immobilization methods fall into the classes of electrochemical entrapment, covalent immobilization or affinity interactions.

The electrochemical entrapment method originates from the pioneering work on enzyme sensors by Umana and Waller [50]. It involves the electrochemical oxidation of a suitable monomer to the corresponding conducting polymer from a solution that contains oligonucleotide (ODN) probes. Wang et al. first illustrated that ODNs can act as the sole dopant during the growth of

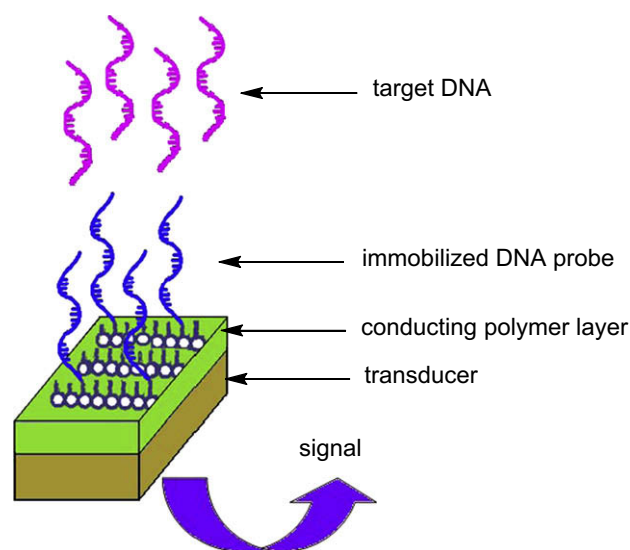


Fig. 2. General DNA sensor design based on CPs.

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