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Carbon nanotubes and graphene nano field-effect transistor-based biosensors

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ABSTRACT

Graphene and carbon nanotubes (CNTs) have gained major research interests as signal transducing elements in electrical biosensors for applications in biosensing of a wide range of analytes. This is mostly due to the unique physical, chemical, and electrical properties of the carbon nanomaterials. This review discusses the integration and applications of these carbon allotropes into field-effect transistor-type (FET-type) nanobiosensors. We first discuss the various properties of CNTs and graphene that make them useful and attractive for FET-type sensing, followed by methods for synthesis of CNTs and graphene nanomaterials. Additionally, the underlying sensing mechanisms of CNT- and graphene-based FET-type biosensors and the methods for fabrication of these devices are discussed. Finally, recent reports on CNT- and graphene-based FET biosensors that employed a variety of novel device configurations, fabrication techniques, and assay strategies to achieve sensitive detection of small molecules, metal ions, proteins, and nucleic acids are examined.

Contents

1. Introduction

Serving as analytical devices that integrate biorecognition elements with signal transduction elements to convert molecular interactions to measureable signal, biosensors are important tools for myriad fields and applications [1]. Since the first carbon nanotube field-effect transistor (CNT-FET) devices reported in 1998, carbon nanomaterials, such as carbon nanotubes and graphene, have increasingly garnered considerable interest from the biosensor research community as they offer the potential for improved sensitivity, biocompatibility, portability, and most importantly the convenience of label-free sensing [2–4]. Due to the unique chemical, electrical, and

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physical properties of these carbon allotropes, these nanomaterials have been of particular interest in applications for field-effect transistor-based (FET) biosensors [2,5,6].

2. Carbon nanomaterials

2.1. Carbon nanotubes

2.1.1. Properties of CNTs

The carbon nanotube (CNT), which can be considered a 1-dimensional (1D) allotrope of carbon, can be described as a ribbon of graphene comprising sp^2 hybridized carbon atoms with a hexagonal lattice seamlessly rolled into a cylindrical tube [7,8]. CNTs can further be categorized based on the number of graphene layers forming the cylindrical tube. Single-walled carbon nanotubes (SWCNTs) have one single layer of sp^2 carbon atoms forming the nanotube (i.e. one graphene sheet), while multi-walled carbon nanotubes (MWCNTs) consist of two or more layers of graphene sheets that form concentric cylinders[7,9]. Depending on the synthesis method used, SWCNTs and MWCNTs have diameters that vary between 0.43-2.0 nm and up to more than 10 nm, respectively, with lengths ranging from hundreds of nanometers to hundreds of microns [10,11]. While MWCNTs have metallic electronic properties, SWCNTs can have either semiconducting or metallic electronic properties depending on their chirality and diameter [12]. Furthermore, SWCNT bandgap energies vary inversely with the diameter.

Despite sharing similar sp^2 chemical properties to 2D graphene sheets, the tube curvature of CNTs and quantum confinement in the circumferential direction result in unique electronic properties that are different from those of graphene sheets. Most relevant to FET-based biosensors are semiconducting SWCNTs which are inherently p-type semiconductors with holes as the main charge carriers. Semiconducting SWCNTs are consequently used as the semiconducting channel between the source (S) electrode and the drain (D) electrode [12,13].

2.1.2. Carbon nanotube synthesis

There are three major methods for CNT synthesis: arc-discharge [7], laser-ablation (vaporization) [14], and catalyst-assisted vapor chemical deposition (CVD) [11]. Arc discharge synthesis of CNTs requires the use of two graphite electrodes to produce a direct current electric arc discharge in an inert environment, where the CNTs are collected in the soot material [7]. SWCNT synthesis via this method further requires a metal catalyst such as cobalt, whereas MWCNT synthesis do not require a metal catalyst [15]. CNT growth by laser ablation uses intense laser pulses to ablate a carbon target, which contains 0.5 percent atomic concentration of cobalt and nickel, in a tube furnace at 1200°C under inert environment [11]. Both arc discharge and laser ablation methods yield high quantity and high quality CNTs. In CVD growth of CNTs, a catalyst material is heated to high temperatures in a tube furnace while the precursor hydrocarbon gas is flowed through the tube for a duration of time [16]. The hydrocarbons and catalyst material used, as well as the growth temperature are essential parameters to CVD synthesis of CNTs. Typical catalysts for this method are iron, nickel, or cobalt nanoparticles. The catalyst layer is typically patterned on a silicon substrate with an SiO_2 insulating layer [17].

Significant efforts have been underway to optimize these methods to yield defect-free crystalline CNTs and to control for the types of CNTs grown. Since these synthesis methods result in a mixture of metallic and semiconducting CNTs of varying dimensions, that have varying degrees of amorphous carbon contaminations, and may contain bundles of CNTs, isolation and purification of semiconducting SWCNTs are needed. Various purification methods have been developed as summarized by Ramnani et al. to yield the desired defect-free semiconducting SWCNTs [3]. Thanks to the development effort for scaled-up synthesis of CNTs, commercial sources for purified CNTs are readily available.

2.2. Graphene

2.2.1. Properties of graphene

Graphene is described as a planar 2-dimensional monolayer of sp^2 hybridized carbon atoms packed in a honeycomb lattice [6,18]. It is considered to be the building block for carbon structures of other dimensionalities [6]. Graphene can be wrapped up into zero-dimensional fullerenes, rolled up into 1D CNTs, and vertically stacked to obtain 3D graphite. Free-standing pristine graphene was first isolated and electrically characterized in 2004. Graphene is a zero-bandgap semiconductor that exhibits ambipolar electric field effect, where charge carriers are continuously tunable between holes and electrons in concentrations ranging up to 10^{13} cm^{-2} with mobilities above 15,000 $cm^2V^{-1}s^{-1}$ in ambient conditions [6,18,19]. This ambipolar characteristic suggests graphene's electrical sensitivity to both electron-donating and electron-withdrawing species. Furthermore, graphene's chemical stability allows the material to resist oxidation in solution under low voltage, eliminating the need for an electrical passivation layer. Graphene's high chemical stability, unique electrical characteristics, sub-nanoscale thickness, and large surface area suggests the nanomaterial's potential in FET-based biosensing [2].

2.2.2. Synthesis and variations in graphitic properties

Single layer graphene was first isolated from highly oriented pyrolytic graphite (HOPG) by Novoselov and Geim in 2004 via mechanical exfoliation [18]. This was achieved by repeated peeling of π-stacked graphene layers from the bulk graphite with scotch tape [18]. Mechanical exfoliation provides higher quality graphene with minimal chemical defects, but the method suffers from low yield and lacks scalability. An alternative method for mechanical exfoliation utilizes sonication of graphite in liquid phase (in organic solvent or water) while using ionic surfactants to maintain colloidal stability of the exfoliated graphene sheets to prevent aggregation [20,21]. Centrifugation of the dispersed graphene solution allows for further separation of single layer and few-layer graphene. Liquid phase mechanical exfoliation of graphite is scalable for higher yield of graphene that have minimal defects. Dispersed graphene solution can be conveniently used to deposit graphene flakes onto desired substrates via spray coating and drop-casting [22]. However, heat treatment of deposited graphene flakes may be required to ensure complete removal of chemical contaminants such as residual solvents or surfactants.

Epitaxial growth of graphene via thermal decomposition on the (0001) surface of single-crystal Si-6H substrate is another alternative for graphene synthesis that yields graphene with few defects [23,24]. Graphene synthesis via this method is carried out under ultrahigh vacuum and at high temperatures. Si atoms desorb from the surface of the SiC substrate while carbon atoms remain, undergoing surface rearrangement and rebounding to form graphene layers [25]. This method yields graphene on a semi-insulating SiC substrate, which eliminates the need for the transfer of graphene onto another insulating substrate, allowing for *in situ* use. However, the intrinsic thickness of the SiC substrate only allows for top-gating and liquid-gating – and not bottom-gating – of the graphene which will be discussed later in the review [26].

One popular synthesis method for graphene is chemical vapor deposition of carbon precursor gas on metal catalysts such as copper [27]or nickel [27,28]. CVD grown graphene enjoy minimal defects. In a tube-furnace, hydrocarbons are thermally decomposed to yield carbon atoms which undergo diffusion into the metal surface. Upon cooling of the metal-carbon solid solution the carbon atoms precipitate out and segregate on catalytic metal surfaces forming