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Detection and classification of host–guest interactions using β-cyclodextrin-decorated carbon nanotube-based chemiresistors

Hari Krishna Salila Vijayalal Mohan [a, *], Jianing An [a], Kin Liao [b], Chee How Wong [a], Lianxi Zheng [a, b, **]

[a] School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore
[b] Department of Mechanical Engineering, Khalifa University of Science, Technology & Research (KUSTAR), P.O. Box 127788, Abu Dhabi, United Arab Emirates

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ABSTRACT

Carbon nanotubes (CNTs) in a chemiresistor setup have been widely explored in bio/chemical sensing. Detection of certain molecules with environmental and health related importance such as 9-anthracenecarboxylic acid, diclofenac sodium, and curcumin using electrochemical methods/unfunctionalized CNTs suffer from lack of response, high limit of detection (LOD) and poor selectivity. The key to overcome these issues is to decorate CNTs with host (receptor) molecules like β-cyclodextrin (β-CD) that interact with guest (target) molecules by host–guest complex formation. To improve guest recognition, and consequently, the sensor performance, effective immobilization of β-CD on the CNT surface using a non-covalent bridging molecule such as 3, 4, 9, 10-perylene tetracarboxylic acid (PTCA) is required. Furthermore, the selectivity can be assessed using the conductance correlation patterns of different host–guest systems in conjunction with a pattern classification tool. Our results indicate that PTCA linked β-CD-decorated CNT chemiresistors showed a good linear detection range (~100 pM–100 nM), sensitivity (~3×10^{-3}–9×10^{-2} nM^{-1}) and LOD (~62 pM–101 nM), compared to devices without PTCA, in the detection of the guest molecules. The distinction in correlation patterns of different host–guest systems was corroborated by pattern classification yielding a classification accuracy, sensitivity, and specificity of ~91.83%, ~90.13%, and ~85.39%, respectively.

1. Introduction

Molecules including 9-anthracenecarboxylic acid (9-ACA, polycyclic aromatic hydrocarbon derivative) [1], diclofenac sodium (DCFNa, a non-steroidal anti-inflammatory drug) [2] and curcumin (naturally occurring pigment in the plant curcuma longa) [3] have significant effects on the safety of environment and health, which necessitates their detection. Although electrochemical methods utilizing nanostructures have been employed to determine 9-ACA [4], DCFNa [5,6] and curcumin [7], they exhibited poor sensitivity and high limit of detection, in addition to the limited number of studies reporting their detection. This encourages the need to explore an electronic alternative utilizing nanostructures to detect these molecules.

A chemiresistor, is one such alternative, which is a simple electronic sensor that responds to the change in resistance introduced by the binding of analytes. Chemiresistors offer several potential advantages such as low cost, low power consumption, rapid and label-free detection of chemicals/biomolecules, and highly accurate resistance measurements [8–10]. Recently, there has been an escalation in the use of one-dimensional (1-D) nanostructures such as nanowires and nanotubes as transducing elements in chemiresistive sensors [11,12]. Such nanomaterials provide high sensitivity and selectivity, low limit of detection, rapid, low-cost, multiplexed, label-free, and point-of-care detection of various analytes.

Amongst the broad range of nanostructure materials, single-walled carbon nanotubes (SWCNTs), in particular, have garnered huge attention because of their excellent electrical properties and ultrahigh surface area to volume ratio, which makes their surface atoms highly sensitive to any surface adsorption/reaction events [13]. Specifically, the property of resistance/conductance change in

* Corresponding author.
** Corresponding author. Department of Mechanical Engineering, Khalifa University of Science, Technology & Research (KUSTAR), P.O. Box 127788, Abu Dhabi, United Arab Emirates.
E-mail addresses: hari1@e.ntu.edu.sg (H.K. Salila Vijayalal Mohan), Lianxi.zheng@kustar.ac.ae (L. Zheng).

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SWCNTs due to electrical perturbations on the surface following analyte binding forms the basis for electronic bio/chemical sensing [14,15]. However, when SWCNTs are used alone as a transducer element, they lack the sensitivity and selectivity as required in high-performance sensors. Nevertheless, the excellent chemical stability of SWCNTs allows sidewall functionalization [16,17], which improves the sensitivity and selectivity of target detection, and SWCNT-based chemiresistors in conjunction with chemical/bio-recognition molecules have detected various biomolecules and chemicals [18–20].

Of the numerous functionalization molecules available, cyclodextrin (CD) is widely used because of its ability to encapsulate a wide variety of guest molecules. CDs are oligosaccharides consisting of six, seven, or eight glucose units (named α-, β-, or γ-CD, respectively) giving it a truncated cone structure with a hydrophobic inner cavity and a hydrophilic exterior [21,22]. The hydrophilic outer surface of CD makes it water-soluble whereas its hydrophobic central cavity shows high molecular selectivity. This hydrophobic cavity creates a favorable environment for encapsulation of appropriately sized and/or nonpolar part of a wide variety of organic, inorganic, as well as biological guest molecules to form stable host–guest inclusion complexes or nanostructure supramolecular assemblies, based on physical fit and chemical affinity [22]. CDs are environmentally friendly and used widely in the field of chemical/biosensing [23–25]. The combination of the good electronic properties of SWCNT, the supramolecular recognition capability of CD cavity and the fast electrical readout of chemiresistor forms an excellent sensing platform for detecting host–guest interactions electrically. An important aspect of efficient electronic detection of host–guest interaction detection is the effective immobilization of the host receptor CD on the CNT surface. Using a non-covalent approach such as a pyrene derivative linker molecule like 3, 4, 9, 10-perylene tetracarboxylic acid (PTCA) [4], which interacts with SWCNT through stacking between the pyrene rings and with amine terminated CD through covalent bonding, could enhance the selectivity of receptor immobilization and host–guest interaction while preserving the intrinsic CNT properties. Very few investigations have pointed to the use of nanowire/nanotube based field-effect transistors (FETs)/chemiresistors to detect CD (host)–guest interactions [26–29].

In this work, we demonstrate the detection of 9-ACA, DCFNa, and curcumin based on host–guest interaction with β-CD decorated on CNT chemiresistors. We also highlight the importance of using a bridging molecule on the senor performance. Using the conductance characteristics, we compute the autocorrelation and two-point correlation functions, and analyze the selectivity of the β-CD decorated CNT chemiresistor in discriminating the three host–guest systems. Moreover, we use these correlation functions as inputs to a pattern classification approach, namely, artificial neural network (ANN) [30,31], and classify the different host–guest interactions.

2. Materials and methods

2.1. CNT growth and chemiresistor fabrication

Random network SWCNTs were grown on n-type Si capped by 1 μm thermally grown SiO_2 using gas-flow-guided ethanol chemical vapor deposition (CVD) [32–34]. 0.1 M of $FeCl_3$ catalyst solution was applied using a dig-pen onto one end of Si/SiO_2, and placed in a horizontal 1-inch quartz tube furnace with the catalyst end directed toward the gas flow. Under ambient pressure, the furnace was heated to the desired temperature (960 °C) under a flow of 120 sccm argon (Ar) and 40 sccm hydrogen (H_2) to decompose and reduce the catalyst complex into Fe nanoparticles. After 20 min, the Ar and H_2 flow were reduced to 6 sccm and 4 sccm, respectively, and ethanol vapor was introduced into the furnace by bubbling Ar through ethanol (20 °C) at a controlled rate of 20 sccm to start the CNT growth. After a 50-min synthesis period, the ethanol supply was terminated, and the furnace was cooled to room temperature under ~120 sccm Ar. A 2 mm × 3.5 mm CNT network recording chamber area with source and drain electrodes at the two opposite edges of the CNT network was created using silver paint, and the two channel-electrode junctions were insulated using silicone rubber.

2.2. CNT functionalization

All chemicals and reagents were purchased from Sigma Aldrich, Singapore, unless otherwise stated. The as-fabricated chemiresistors were incubated with 2 mM of 3, 4, 9, 10-perylene tetracarboxylic acid (PTCA) dissolved in pure dimethylformamide (DMF) for 3 h at room temperature, followed by washing with DMF and de-ionized (DI) water. This was followed by incubation with 1 mM of mono-(6-ethanediamine-6-deoxy)-β-cyclodextrin (NH_2-β-CD, ATP Chems, Shanghai, China) dissolved in DMF for 3 h followed by washing with DMF and DI water. Finally, the PTCA-β-CD functionalized chemiresistors were exposed to increasing concentrations of 9-anthracenecarboxylic acid (9-ACA) (dissolved in DMF), diclofenac sodium (DCFNa) (dissolved in DI), and curcumin (dissolved in DMF), respectively. Fig. 1(a) and (b) show the chemical structures of NH_2-β-CD and PTCA, respectively. The chemiresistor setup using SWCNT for detecting different guest molecules is schematically shown in Fig. 1(c).

We used SEM (Jeol, JSM-7600F) with to observe the existence of CNTs over a large area. SEM was used to analyze the effect of PTCA linker and NH_2-β-CD decoration on the CNT morphology.

To characterize the surface-functionalized CNTs, Raman spectroscopy was performed using a Raman spectrometer (Renishaw inVia Raman Microscope). For the Raman measurements, the laser power used was kept below 1 mW with an excitation wavelength of 633 nm.

2.3. Electrical testing

All electrical recordings were made using Agilent 4156B semiconductor parameter analyzer at a constant drain bias (V_{DS}) of 1 V. The relative conductance is given by $(G - G_0)/G_0$, where G and G_0 are respectively the steady-state conductance after exposure to particular concentration of guest molecule and conductance after exposure to buffer only. The average of $(G - G_0)/G_0$ obtained from at least five devices for each guest molecule concentration gives the calibration curve i.e., $(G - G_0)/G_0$ vs. guest molecule concentration. The variation in relative conductance with time and guest molecule concentration was used to analyze the sensor performance. All the relative conductance plots given here show the variation in conductance after attaining the steady state base line value. The sensitivity is obtained from the slope of the linear region of the relative conductance $(G - G_0)/G_0$ vs. guest molecule concentration in the lower concentration range. The limit of detection (LOD) is given by $3\sigma/m$, where σ is the standard deviation of the blank measurement and m is the slope of the linear portion of the calibration curve. The correlation coefficient of determination (R^2) is obtained from a linear fit to the relative conductance vs. concentration plot. It gives the proportion of fluctuation of one variable (sensor response) that is predictable from the other variable (concentration). It is a measure of the extent of measure of how well the regression line represents the fitted data.