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Low-temperature thermal reduction of suspended graphene oxide film for electrical sensing of DNA-hybridization

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ABSTRACT

A reduced graphene oxide (RGO) based capacitive real time bio-sensor was presented. Suspended graphene oxide (GO) film was assembled electrophoretically between the source and drain electrodes of a transistor and then reduced by annealing in hydrogen/nitrogen forming gas to optimize the surface functional groups and conductivity. The resonance frequency of the transmission coefficient (S_{21}) of the transistor was observed to shift with deoxyribonucleic acid (DNA)-hybridization, with a detecting limit of ~5 nM. The advantages of the bio-sensing approach include low-noise frequency output, solution based real time detection and capable of on-chip integration.

1. Introduction

Nanoelectromechanical sensor has attracted much attention in recent years as a label-free, real-time and highly sensitive approach to detect target molecules in solution. These devices measure the deflection of a cantilever or film caused by biomolecules binding to functional groups on the surface of the device, where the deflection of the micromechanical part was detected by optical [1–5], piezoresistive [6–8], piezoelectric [9–11], surface acoustic wave [12,13] or Metal-Oxide -Semiconductor Field Effect Transistor (MOSFET) [14–16], etc. In principle, the sensitivity of the nanoelectromechanical sensor is inversely proportional to the dimensions of the cantilever. Thus, micromechanical parts made up of nanotubes [17,18], nanowires [19,20] or graphene [21,22] are reported in recent. However, it is much more difficult to build a piezoresistive, piezoelectric or MOSFET sensor on nanomaterials than that on silicon. Thus, new deflection detection strategies based on nanomaterials for portable and in-situ applications are desirable.

Well-developed capacitive sensing technology could be used to detect the deflection of a film in the range of a few angstrom straightforwardly [23,24]. The structure of a capacitive deflection sensor is simple, too. For example, a suspended conductive nanomaterial cantilever or film and a solid underneath metal electrode can measure the deflection accurately.

In a previous work, we proposed a nanoelectromechanical biosensor with a suspended single walled carbon nanotubes (SWCNTs) film [25]. However, it is well known that SWCNTs have different sizes, types, chiralities and their orientations are hardly aligned perfectly in the film, which made the repeatability of the biosensor was not satisfied theoretically.

In this paper, we tried to replace the SWCNT film used in ref. 25 with suspended graphene film and investigated its potential applications on bio-sensing. Because Graphene oxide (GO) has good dispersity in water and could be better assembled in the same circumstance than graphene [26,27], the suspended graphene oxide (GO) film was firstly assembled to a transistor-like device with low parasitic capacitance [28]. However, the suspended GO film has low conductivity, which cannot act as a movable electrode of a capacitive sensor. Thus its electrical conductivity needs to be improved by reduction. Unfortunately, most of reported reduction processes of GO are performed at a high temperature or via complicated solution treatments [29–36], in which the device used in this work can be damaged. In that case, we proposed a low temperature and clean reduction process to reduce GO to RGO, while the RGO film could keep freestanding after the process.

As a proof-of-concept of this new biosensor, the hybridization of a single stranded DNA was real-time detected in solution. Comparing with many label-free DNA sensing approaches have been reported in literatures including electrical [37–43], electrochemical [44–48] and optical detection [49–54], the output of this device is based on frequency shift, which has better immunity to environmental interference than voltage or current output. Its driving circuit can also be integrated easily using the commercial CMOS technology with low cost. In addition, the proposed sensor is easy to be integrated to micro fluidic chips by simply coating polydimethylsiloxane (PDMS) channels on its top surface, implying a promising approach for portable, rapid and low cost biosensing.

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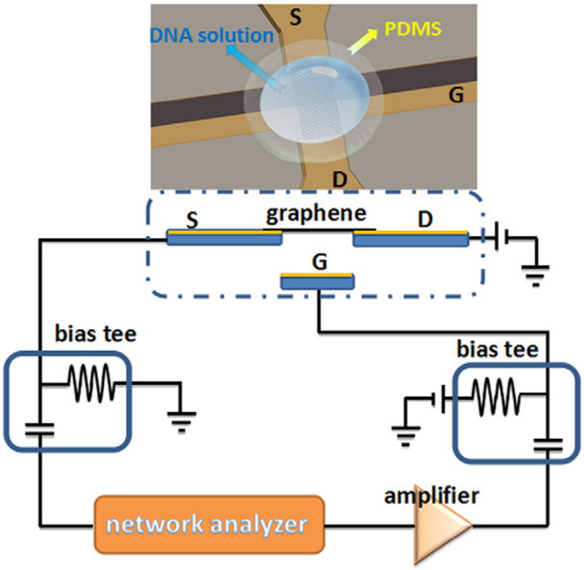

Fig. 1. Schematic of characterization of the proposed DNA sensor based on suspended RGO film.

2. Experimental

2.1. Materials

The well-dispersed solution of graphene oxide was synthesized via modified Hummers' method [55,56] and the concentration was about 20 μg/mL.

Single stranded probe and complementary DNAs were purchased from Invitrogen Biotechnology Co. Ltd. Their sequences and modifications are as follows: probe DNA: 5′-NH_2-$(CH_2)_6$-CGC CGA TTG GAC AAA ACT TAA A-3′; complementary DNA: 5′-FAM-T TTA AGT TTT GTC CAA TCG GCG-3′.

The single stranded probe DNA was dissolved into the immobilization buffer (1.5 mM NaCl + 0.1 mM $NaHCO_3$) to get probe DNA solution. Another single stranded complementary DNA was dissolved into the hybridization buffer (0.15 mM NaCl + 0.015 mM $C_6H_5Na_3O_7 \cdot 2H_2O$ + 2 mg/L SDS ($C_{12}H_{25}SO_4Na$)) to get D'FAM DNA solution.

2.2. Device fabrication

A bi-layer gate electrode (Cr/Au) was formed by sputtering and lift-off on a glass wafer. Next, a 2 μm thick photo resist layer (SU8-2002, MicroChem Corp. USA) was patterned by backside exposing using the gate electrode as photo mask. Another photo resist AZ4620 was then

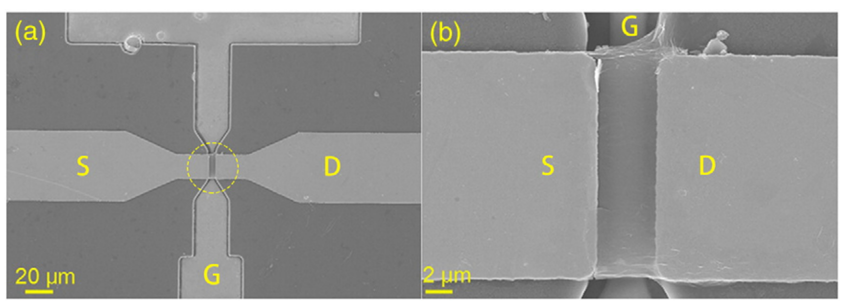

Fig. 2. SEM images of (a) as-assembled GO device; (b) annealed RGO device.

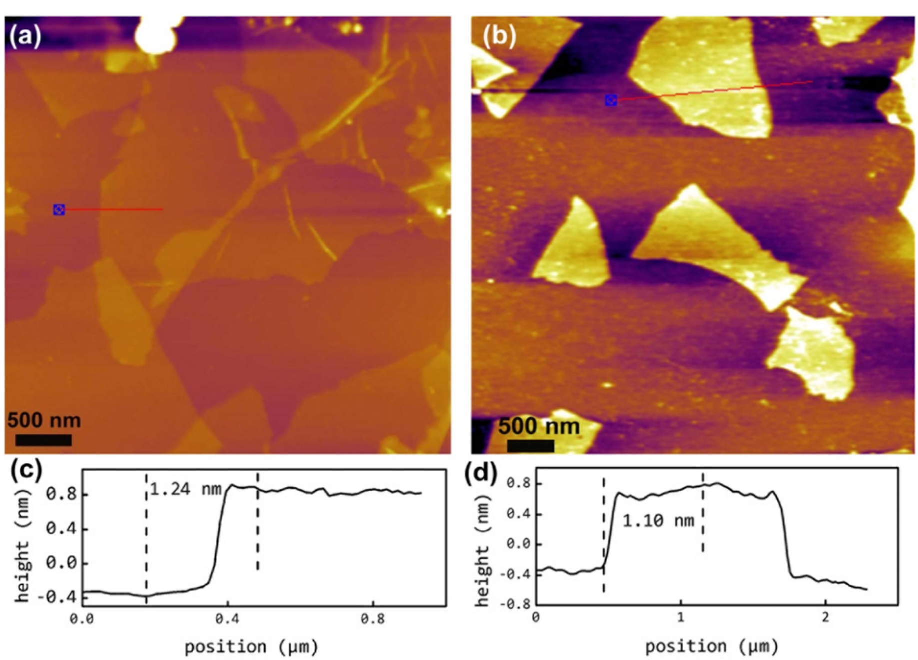

Fig. 3. AFM images of (a) GO and (b) RGO. The thicknesses of (c) GO and (d) RGO nanosheets were 1.24 nm and 1.10 nm, respectively.