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A Novel Method for Large Area Graphene Transfer on the Polymer Optical Fiber

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We develop two simple methods—the dip coat stamping and lift-off methods—to transfer large area, high quality graphene films onto the top and side faces of the polymer optical fiber. The graphene films can be synthesized using chemical vapor deposition method on large Cu foils. After synthesis, the graphene films are characterized by scanning electron microscopy, atomic force microscopy and Raman spectroscopy. The polymer optical fiber probe with the transferred graphene film can be used as a chemical sensor for the detection of various organic aerosols.

Keywords: Graphene, Transfer, Polymer Optical Fiber, Sensor, Chemical Vapor Deposition.

1. INTRODUCTION

Carbon is one of the most abundant chemical elements and present in all known life forms. Carbon atoms bound in a two-dimensional honey-comb lattice built from benzene rings is known as graphene. Graphene is one of promising candidates for device and sensor applications because of its superior physical and chemical properties, which are often valid to bilayer and few-layer graphenes.¹ Graphene is a strong, stiff and impermeable to gas, transparent and suitable for food grade materials.² Two dimensional flat graphene has been investigated theoretically for more than 60 years.³ Since graphene is the basic material for three-dimensional graphites, one-dimensional carbon nanotubes and zero-dimensional bucky balls, its properties were predicted in theory for long before any experiments.

Fiber optic sensors (FOS) are very attractive in bio-chemical sensing applications due to their unique characteristics such as small size, light weight and high flexibility. FOS operation is based on either direct or indirect sensing mechanisms. In the first mechanism, the intrinsic optical properties of the analyte are measured, for example its refractive index, absorption, or emission; in the second mechanism, the color or fluorescence of an immobilized indicator, label, or any other optically detectable

bioprobe is monitored. Advanced methods, most notably evanescent wave,4-7 laser-assisted spectroscopy and surface plasmon resonance (SPR) are fascinating research fields in the modern sensor research and development.⁸⁻¹⁴ In some other cases FOS has an integrated biochemical transducer system, where FOS changes its optical properties upon interaction with the specific analyte. The transduction reagent can be immobilized directly on a membrane, which is held against the optical fiber. The other option is the reagent can be bonded directly to the optical fiber itself or a thin layer of a reagent containing polymer is bonded onto the fiber. In some other systems, a transducer reagent is placed on the fiber, where the reagent acts as the cladding or the core of the fiber optic device itself. Normally cladding is removed and replaced by a thin layer of the reagent phase which serves as an internal reflection element. The reagent interacts with the incident radiation through the evanescent wave which penetrates a small distance into the cladding. For fiber optic biosensors, various immobilization techniques have been applied to the fiber, including adsorption to solid supports, covalent attachment and entrapment in polymers but the promising one is the sol-gel technique.¹⁵⁻¹⁷ Due to the porous nature of the sol-gel network, entrapped species remains accessible and can interact with external chemical species or analytes.¹⁸ However, a sol-gel based sensor has a certain disadvantage; chemical and biological properties of

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the entrapped species may change in the sol-gel glass due to reduced degrees of freedom and interaction with the inner surface of the pores.^{19,20}

2. EXPERIMENTAL DETAILS

Described herein are simple methods for transferring single to multilayered CVD synthesized large area graphene onto various surfaces of the POF having core diameter of 980 µm for biological and chemical sensing applications. The large-area single and a few-layers of graphene sheets are synthesized by CVD of methane gas on Cu foils at 1000 °C, as described in Ref. [21] and consequently, and are deposited on a predefined location on the POF as a sensitive membrane. Figure 1 summarizes the steps of the graphene (GP) transfer process onto the deionized (DI) water surface. After the synthesis of GP on Cu by CVD, the polymethylmethacrylate (PMMA), 5 wt% in chlorobenzene, is spin-coated at 3000 rpm and incubated at 180 °C for a few minute. The underlying Cu foil is etched using 0.5 M aqueous ammonium peroxodisulfate. $((NH_4)_2 S_2O_8)$. Subsequently, the PMMA supported GP film is then transferred onto the DI water surface to facilitate the transfer of the GP film onto the POF.

Mostly GP films are single- or bi-layers based on Raman spectra analysis, as depicted in Figure 2. However, an



Fig. 1. Transfer process flowchart of CVD synthesized large area graphene on to DI water surface.

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Fig. 2. Raman spectra of monolayer and bilayer graphenes. Inset shows AFM image of representative graphene.

AFM image in Figure 2 inset shows multilayer islands with few defects. As the GP layer is transferred two times, the intensities of the G mode peak and 2D band peak increase together, but their ratios do not change significantly because of random orientation of the hexagonal lattices of the upper and the lower layer. Hence, the original properties of each monolayer remains unchanged even after a few layers are stacked. The optical transmittance is usually reduced by approximately 2.2 to 2.3% for each additional transfer, implying that the average thickness is approximately that of a monolayer.

3. RESULTS AND DISCUSSION

The large area CVD synthesized graphene film floating on the DI water is ready for further transfer process on the POF. Two types of graphene transfer approaches are carried out for graphene deposition onto two different POF surfaces. For the first approach, the graphene film is ĽЫ transferred on the end face of the POF as shown in the Figure 3(a). Before transferring of the graphene film, the fiber end is cleaved with a precision cleaver and polished to obtain a uniform, plane cross section. Then, the POF is vertically immersed at a constant rate on the floating graphene film and slowly taken out of the water. When the POF core touches the floating graphene, the graphene film splits outside the core area and the graphene below the core attaches to the core due to the surface tension. The graphene remains attached on the POF even after the core is taken out from the water. Finally air is blown on the distal end of the POF to remove the excess water droplets on the POF and dried in the oven at 50 °C for 10 minutes. For bilayer graphene film deposition, this process is repeated. The AFM image of transferred graphene film is depicted in Figure 3(b) and the fabricated POF probe with graphene film at the end face can be used as fiber optic reflectance sensor (FORS) for biochemical sensor applications as shown in Figure 3(c). The actual SEM



Fig. 3. (a) Process for large area graphene film transfer on the POF end face, (b) the surface topology image of transferred graphene film acquired by AFM, (c) the application of transferred graphene on the end face of the POF for a reflectance probe, and (d) actual SEM image of graphene 4 film transferred on the end face of the POF. Sat, 14 Jul 2

image of graphene at the end face of the POF is shown in Figure 3(d).

For the second approach the optical fiber is configured in the evanescent wave type sensor, in which the transferred graphene film serves as a sensitive clad for the PMMA core of the POF. Before transferring or depositing the graphene layer on the POF core, the original clad was removed carefully shown in Figure 4. Subsequently, the removed clad portion of the POF is placed below the



Fig. 4. Process for large area graphene transfer on the POF as a sensitive clad fabrication with the actual microscopic image.

graphene floating on the DI water surface. Then the fiber is slowly lifted out of the water as the graphene transfers onto the unclad portion of the POF, as depicted in Figure 4. Then the POF with the transferred GP film was kept in the oven at 50 °C in order to remove the excess water. Diluted acetone treatment is applied to remove the thin PMMA layer on the GP film and the POF is ready to use as a biochemical sensor probe based on evanescent wave principle.

4. CONCLUSION

In the present study, we have demonstrated the large area synthesis of graphene film using CVD and alternative transfer processes of graphene onto the top and side faces of the POF. The fabricated sensor probes can be utilized in various chemical and bio sensor applications. For instances, the graphene transferred POF end face can serve as a reflectance probe which can detect organic vapor as a chemical sensor and the graphene transferred POF side face can act as a sensitive membrane which can detect various proteins as a bio sensor. The proposed method can help to extend exploration of graphene through optical interrogation of biochemical species.

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