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Rolling up two-dimensional sheets into nanoscrolls

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ABSTRACT

Since discovery of graphene, various structures of two-dimensional (2D) sheets, such as nanoribbon, wrinkles, and folded layers, have been studied due to their unprecedented properties. Among them, a helical tube structure, which is called a nanoscroll, has been reported in naturally scrolled form of a graphene sheet. It has been expected that graphene nanoscrolls (GNSs) have exceptional properties, which are totally different from those of its constituent graphene sheet and multiwall carbon nanotubes (MWCNTs). Here we report a straightforward and controllable way to fabricate nanoscrolls of two dimensional sheets, such as graphene and molybdenum disulfide (MoS_2). We rolled up graphene sheets into nanoscrolls by sweeping them up with vigorously generated bubbles in a solution. It was verified that there is no formation of significant defects after scrolling process and the graphene layers in a nanoscroll are decoupled. GNSs behave like randomly stacked monolayers without any coupling between the adjacent layers and show p-type electrical conductance, which is distinct from graphene's electrical properties. In contrast, the stiffer MoS_2 was folded, not scrolled during scrolling process. Raman shift and photoluminescence (PL) of folded MoS_2 showed strong interlayer coupling between the stacked layers, which is opposite for the case of GNSs. To prevent this coupling effect, thin layer of lipids was deposited on the surface of MoS_2 before scrolling process. Inserted lipid layers between MoS_2 monolayers suppressed interlayer interactions, leading to enhanced PL intensity. Our work provides a novel way to fabricate various forms of 2D sheets, such as scrolled and folded structures, which are highly intriguing due to high possibility to seek for new physics in the scrolled structures of one-atom thick 2D sheets.

1. Introduction

2D materials, such as Graphene, transition metal dichalcogenides (TMDs), and hexagonal boron nitride (hBN), have been attracted extensive attention because of unique and remarkable electrical, mechanical, and chemical properties [1–4]. Previous researches have mainly focused on 2D form of these van der Waals materials. However, researchers have been interested in fabricating three-dimensional (3D) nanostructures by deforming the 2D material sheets and studying unprecedented properties of these 3D forms. For example, there have been studies on self-folding of graphene [5], graphene origami [6] and GNSs [7]. Graphene sheets can be rolled up in specific conditions, resulting in helical tube structures, called GNSs. The GNSs have been expected to show exceptional properties different from those of graphene and MWCNTs [8]. It was reported that accidently-formed GNSs have interesting properties valuable to be investigated [9]. The unique structure of nanoscrolls enables us to observe exceptional properties in them compared with MWCNTs, which consist of several coaxial carbon cylinders and is topologically closed [10]. In GNSs, it was speculated that electric current flows within a single scrolled graphene layer rather than through several coaxially nested graphene cylinders as in the case of MWCNTs. Moreover, theoretical calculations indeed predicted several unusual electronic and optical properties of nanoscrolls because of its unique topology [8]. However, methods for intentional formation of GNSs have been little known. Even though a few researchers have tried to fabricate the GNSs from graphene for decades, there is no controlled method for production of well-defined nanoscrolls. To date, GNSs have been produced by using arc-discharge method, high energy ball milling, sonication of intercalated graphite, cold quenching in liquid nitrogen, and Langmuir-Blodgett method [11–13]. However, these fabrication processes have difficulties in control of the shape and location of nanoscrolls, which makes it difficult to systematically investigate their properties and fabricate electronic devices. In addition, most of the studies on GNSs used graphene oxide (GO) rather than pristine graphene [14–16]. Because the nanoscrolls of GO and reduced graphene oxide (rGO) have high density of defects and functional groups, quality of these

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nanoscrolls are not good enough for study electrical properties of GNS devices.

Here we report a straightforward and controllable way toward production of GNSs and folded forms of graphene and MoS_2 by using bubble-induced scrolling process. We rolled up graphene sheets into nanoscrolls by sweeping them up with vigorously generated bubbles in a solution. It was found that GNSs behave like randomly stacked monolayers without any coupling between the adjacent layers with p-type electrical conductance. In contrast, the stiffer MoS_2 was folded, not scrolled during scrolling process, leading to quenching in PL intensity due to strong interlayer coupling. When lipid layers are inserted between stacked MoS_2 monolayers, interlayer interactions were suppressed, resulting in enhanced PL intensity.

2. Experimental

2.1. Fabrication of nanoscrolls

Graphene and MoS_2 were mechanically exfoliated onto hydrophilic 285 nm-thick SiO_2/Si substrates pre-treated by oxygen plasma (Femto Science, Covance-1MPQ) at power of 100 W, pressure of 340 mTorr, and oxygen flow rate of 20 sccm for 5 min. After numbers of layers in exfoliated graphene and MoS_2 were confirmed using Raman spectroscopy, the samples were vertically immersed into a beaker filled with sodium hydrogen carbonate ($NaHCO_3$) solution (0.075 g/ml) and kept at 50 °C for 1 min. Sodium hydrogen carbonate composed of sodium ions and bicarbonate ions is easily dissolved in DI-water at 50 °C, generating a large amount of carbon dioxide (CO_2) bubbles. After bubble-induced scrolling process, the sample was rinsed by DI-water. For direct comparison of scrolled graphene with as-exfoliated graphene, monolayer graphene was transferred onto hBN using Poly(methyl methacrylate) (PMMA) transfer method.[17]

2.2. Folding lipid-coated 2D sheets

To increase interlayer spacing of folded 2D sheets, a thin film of lipids was coated on as-exfoliated MoS_2 flakes before scrolling process. We prepared a lipid mixture by following the previously reported method. [18]The lipid solution was prepared by dissolving 1,2-dioleoylsn-glycerol-3-phosphocholine (DOPC) in chloroform (20 mg/ml). The lipid solution was coated on the surface of as-exfoliated MoS_2 by drop casting, followed by drying at room temperature for 5 min. Then scrolling process was conducted as aforementioned. Through this process, folded MoS_2 with the inserted lipid layers was fabricated.

2.2. Characterization

To analyze structures and optical properties of scrolled and folded forms of graphene and MoS_2, we used Raman spectroscopy (Renishaw, inVia) with a diode-pumped solid state laser of 532 nm wavelength and a spot size of 1 μm. AFM (Park systems, NX10) was utilized to observe the surface morphology and stiffnesses of GNSs.

2.3. Device fabrication

After bubble-induced scrolling process, GNS devices were fabricated using e-beam lithography, followed by deposition of Cr/Au (3 nm/50 nm) for metal electrodes. Electrical properties of GNS devices were measured by semiconductor parameter analyzer (Keithley 4200). The electrical currents of the devices were measured with a back gate voltage sweep from −40 V to 40 V at fixed source-drain voltage of 1 V.

3. Results and discussion

Fig. 1A shows the schematic illustration for scrolling process of a graphene sheet into nanoscrolls. Monolayer graphene exfoliated on a SiO_2/Si substrate are vertically immersed in $NaHCO_3$ solution at 50 °C. When the solution is heated on a hot plate, large amount of small CO_2 bubbles are generated as shown in Fig. 1B. These bubbles penetrate between graphene and the hydrophilic SiO_2 surface, and then pull up the edge of graphene, finally leading to a scrolled sheet as shown in the schematic of Fig. 1C. It was found that a monolayer graphene sitting on the more hydrophilic substrate is easily rolled up by bubbles because the smaller and more gas bubbles form on the more hydrophilic substrate as shown in Fig. 2A. The surfaces of five SiO_2 substrates were treated by oxygen plasma with different power and treatment time. It is clear that a larger amount of smaller bubbles are generated on the heavily-treated SiO_2 substrate, which is more hydrophilic. To confirm this, wetting angles of water droplets were measured by dropping the same amount of DI-water (100 μl) onto the oxygen plasma-treated SiO_2 substrates as shown in Fig. 2B. When the substrate was treated by harsh plasma condition, the wetting angle decreased from 49° for bare SiO_2 to 5° for plasma-treated SiO_2, indicating that plasma treatment results in hydrophilic surface. Position and configuration of the graphene samples are also critical factors in scrolling process. For successful scrolling, the sample should be placed vertically and thinner area of the flake should be positioned lower than thicker area as shown in Fig. 2C, because the generated bubbles scroll the flakes from bottom to top. When the SiO_2 substrate is placed horizontally or thinner region of the flake is located in higher position than thicker region, no scrolling of the graphene occurred. Additionally, we observed that scrolling of the flake starts only at the lower edge of the flake as depicted in Fig. 1A. These findings support that bubbling is the main reason for scrolling of graphene in our work. When graphene was too thick (>3 L), it was difficult to scroll the graphene due to high stiffness of thick flake.

The optical microscopic image of Fig. 3A shows a representative GNS sample before and after bubble-induced scrolling process. The structures of GNSs are dependent on the location, thickness, shape, and size of the as-exfoliated graphene flakes. However, It should be noted that monolayer graphene is transformed into GNS with high yield through our scrolling process. We infrequently observed folded graphene (FG) samples as shown in Fig. 3B. To analyze structures, we measured Raman spectra of as-exfoliated graphene, GNS, and FG in Fig. 3C. Absence of D peak in the as-exfoliated graphene and FG indicates that there is no defect. [19,20] Negligibly small D peak observed in GNS is due to two graphene edges of GNS. The Raman spectrum of the FG with specific alignment is analogous to that of bilayer graphene with AB stacking between the two layers. In contrast, Raman spectrum of a misoriented stack of two graphene monolayers is similar to that of monolayer graphene due to weak interaction between the two graphene layers [21–23]. Therefore, FG in our experiment might have the AB stacking order as bilayer graphene does. However, we cannot confirm this because FG is rarely formed through bubble-induced scrolling process. Interestingly, Raman spectrum of GNS looks similar to that of the as-exfoliated graphene as reported elsewhere [8,20]. However, it is worth noting that the overall Raman peak intensities increased, indicating that there is no interlayer coupling between graphene layers in GNS due to random stacking of graphene layers, and peak positions shifted, probably due to changes in doping and strain induced during scrolling process.

To quantitatively evaluate doping and strain in GNSs, we measured Raman spectra of more than 10 GNSs. The intensity ratio of 2D and G peaks (I_{2D}/I_G) has been used to estimate the number of

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