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Direct synthesis of highly conducting graphene nanoribbon thin films from graphene ridges and wrinkles

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ABSTRACT

We introduce a facile fabrication process for obtaining graphene nanoribbon (GNR) thin films on any substrate from solution-exfoliated graphene flakes with wrinkles or ridges. Copper nanoparticles (Cu-np's) grown on graphene films by radio-frequency sputtering adhere well on flat graphene surfaces, but not on graphene wrinkles and ridges. By etching the Cu-np's in nitric acid, we can remove the largest portions of flat graphene flakes, leaving behind only ridges and wrinkles as individual GNRs. The resulting GNRs are remarkably long and straight and, different from those obtained from graphene with other methods, are not oxidized. Two classes of GNRs are formed in our films: wide GNRs from planar ridges and narrow and straight GNRs from vertical wrinkles. Our GNR still retain the excellent electrical conductivity of pristine graphene.

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1. Introduction

The outstanding physical and electrical properties of graphene, including high electrical and thermal conductivity, high optical transparency, mechanical strength and flexibility [1] make graphene-based thin films, formed by patchworks of single- few- and multilayer graphene flakes, suitable for a large number of practical applications in electronics [1], thermal management [2] and micro-mechanics [3]. Although large-area, solution-processed, graphene-based thin films are more cost-effective than graphene layers directly grown by chemical vapour deposition (CVD) on specific substrates at high temperature, several of their properties are still reminiscent of the properties of single-layer graphene [4]. For these reasons, reproducible methods capable of providing high quantity of graphene-like materials for preparing large-area graphene thin films have been extensively investigated since the first reports on the discovery of graphene [5]. Additional properties and applications of graphene-based thin films can be envisaged if electron confinement can be attained in one of the two

dimensions of a graphene sheet and one-dimensional materials based on graphene can be obtained in large quantities and assembled in graphene-based thin films [6].

Graphene nanoribbons (GNRs) and graphene oxide nanoribbons (GONRs) are narrow sheets of graphene with lengths up to several tens of μm and 5–200 nm width [7]. GNRs have been fabricated using a large number of different methods [7–13]. However, most of these methods are highly sophisticated and are not capable of producing these graphene-like materials in large amounts [8,10,11], while other less costly and less sophisticated processes developed so far tend to always produce GONRs at low conductivity, low quality, and with large concentrations of defects [12,13]. Highly expensive, highly sophisticated methods to produce GNRs include electron-beam patterning of individual graphene sheets [8] or unzipping carbon nanotubes with plasma etching methods that require ultrahigh vacuum systems [10]. Unzipping carbon nanotubes in the presence of specific surfactants also lead to GNRs of relatively good quality, but with very low yield and large number of impurities in the by-products [11]. Conversely, exfoliating carbon nanotubes in highly oxidative environments (similar to the preparation of graphene oxide from graphene by the Hummer's method [12]) lead to potentially large amounts of GONRs and partially reduced GONRs, but at inferior quality [13]. Most of the methods proposed so far utilize carbon nanotubes as starting materials,

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which is disadvantageous due to their relatively high cost over graphite and the significant amount of metallic and amorphous carbon impurities associated with them.

Recently, a method leading to the preparation of nanoribbons from graphene sheets with ridges has been proposed by Zhou et al. [14]. However, even with this method, a plasma etching process is required, which oxidizes the residual material, leading to oxidized GONRs. Furthermore this technique requires coating the graphene sheets with relatively expensive silver nanoparticles, which poses stringent limits to the cost-effectiveness of the fabrication process over large areas. Another possible avenue for producing GNRs is by selectively etching graphene flakes [15–19]. There are numerous reports that ferromagnetic metal nanoparticles (e.g. Fe, Ni, Co) may etch graphene in the presence of hydrogen by means of oxidative processes [15–17,19]. However, in such works, nanoribbons are not necessarily produced and, in the few cases in which they are obtained [18], the as-formed material is oxidized and quite similar to GONRs due to the oxidation process undergone by the graphene layer, which is disadvantageous in terms of the electrical conductivity of the as-produced ribbons. The most facile and economical way of directly fabricating graphene nanoribbons of high quality from graphene or graphite is still a matter of debate.

Here we present a new alternative and cost-effective pathway for selectively etching graphene flakes and produce high-quality GNRs. Our method exploits the presence of ridges and wrinkles on few- and multi-layer graphene flakes. We find that ridges and wrinkles are very resistant to etching and oxidation, significantly more than the surrounding flat graphene regions. Removal of the graphene regions surrounding the ridges and wrinkles is carried out by us via deposition and etching of copper nanoparticles (Cu-np's). Cu-np's are found not to grow on graphene edges and wrinkles and are easily removed from the surrounding flat regions by nitric acid, a mild oxidizer, in a process that also removes the underlying graphene material. In this way the ridges and wrinkles are left behind, relatively non-oxidized, as highly conducting graphene nanoribbons. Our method is scalable over large areas and is general enough not to require single-layer graphene. It can be used on few- and multi-layer graphene flakes, which are normally forming large proportions of graphene-based thin films.

2. Methods

The process we developed for obtaining large quantities of highly conducting GNRs of good quality is summarized in Fig. 1. GNRs are synthesized by us via etching of large-area graphene thin films fabricated by vacuum filtration of suspensions of graphene flakes in water, which were obtained from exfoliation of graphite in the presence of a surfactant [20,21] (Fig. 1, steps a to e). Graphene flakes forming these films can be single- few- and multi-layer and always possess a significant amount of ridges and wrinkles that spontaneously form during the film's fabrication process [20,21]. Subsequently, films were coated with copper by radio-frequency sputtering using a method developed in Ref. [22] (Fig. 1, step f). Contrarily to iron–iron core–shell nanoparticles previously reported to adhere to edges and folds of graphene [20], copper sputtering is found to preferentially adhere on flat graphene regions, and can be annealed to nucleate Cu-np's [22] (Fig. 1, step g). Afterwards, the nanoparticles were etched in nitric acid without the presence of any specific oxidizing agents, in order to prevent their transformation into GONR (Fig. 1, step h). Etching away the copper nanoparticles also removed the underlying graphene flakes on which they are deposited, leaving behind the graphene ridges as individual GNRs.

The details of the fabrication of graphene-based thin films are as follows [21]: nanocrystalline graphite (Sigma–Aldrich, CAS 7782-

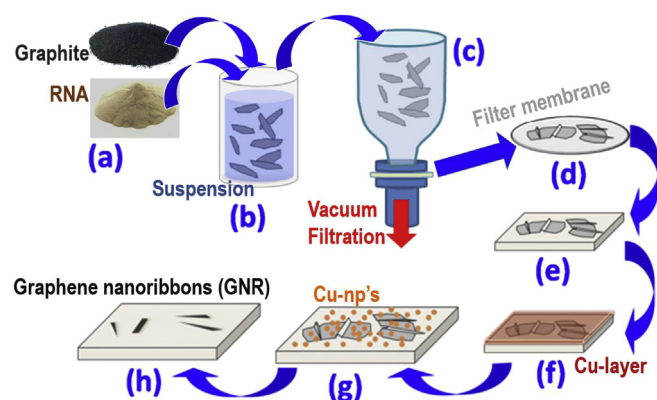


Fig. 1. Process for the fabrication of graphene nanoribbons from etching Cu nanoparticle-decorated graphene in nitric acid: starting materials are graphite and RNA (step a) which are dispersed in water by means of ultrasonication and centrifugation (step b). The supernatant is subsequently vacuum-filtrated on sacrificial membranes (step c) and resulting graphene flakes on filter membrane (step d) are transferred to the requisite substrate that is pre-annealed at 400 °C (step e). Afterwards a copper layer is deposited on the graphene film (step f), which nucleates into Cu-np's after a second annealing step (step g). Etching the Cu-np's in HNO₃ results in the removal of the underlying graphene layers, except for the ridges that remain in the form of GNRs (step h).

42–5) was exfoliated in water by using RNA as a non-ionic surfactant which leads to the stabilisation of single- few- and multi-layer graphene flakes [21]. 60 mg of RNA VI from *Torula utilis* yeast (Sigma–Aldrich, CAS 63231-63-0) were dissolved in 100 ml of distilled water and 6 mg of graphite were mixed with this RNA solution. The resulting RNA-based suspension of graphite was ultrasonicated for 4 h at room temperature (Branson DHA-1000 sonicator) for RNA to intercalate the grains of graphite and exfoliate them into thin sheets of graphene. Having the graphene-containing suspension left to sediment after sonication for 24 h at 2 °C in a beaker, the top three quarter of the beaker content was centrifuged at 6000 rpm for 1 h, which enriches the supernatant in thin graphene layers while separating it from thicker graphitic debris and particulate [21]. The centrifuged graphene suspension was filtrated through 0.2- μ m pore diameter nitrocellulose filter membranes (Millipore, HTPP02500) on which the graphene flakes are deposited. 20 mL of graphene suspension were filtrated in this way for depositing the films that were used to prepare graphene nanoribbons as described in this work. The filter membranes loaded with graphene flakes were transferred onto silicon and quartz substrates and the filter membrane was left in contact with the substrate and dried at 60 °C for 8 h. After drying, the nitrocellulose filter membranes were etched with multiple acetone and methanol baths leaving behind a thin graphene-based film on the desired substrate.

The details of the fabrication process of Cu-np's on graphene-based thin films are as follows [22]: the graphene-based thin films were pre-annealed at 400 °C for 2 h in nitrogen, which removes RNA from the surface and, possibly, forms some defects that are beneficial for nanoparticles to adhere and nucleate [23,24]. A 3-nm thick layer of copper was deposited on graphene thin films by 13.56 MHz radio-frequency sputtering. A SpinTron 2 magnetron sputtering source equipped with a 2' Cu target (Alfa Aesar, 99.99% purity) was placed in a high-vacuum chamber ($2 \cdot 10^{-7}$ mTorr base pressure). Argon was used as a sputtering gas at a 30 sccm flow rate, determined by an Omega FMA 5400 flow metre. The sputter source was operated at 90 W for 3 min and controlled using a RF-3 generator and PT–II–CE matching network (RF VII Inc.) and the temperature of the substrate was kept below 55 °C during the deposition of copper. In order to nucleate Cu-np's from the

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