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Rolling up graphene oxide sheets into micro/nanoscrolls by nanoparticle aggregation†

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We demonstrate an efficient and controllable way to roll up graphene oxide sheets into micro/nanoscrolls, where the rolling process is highly enhanced by nanoparticle aggregation. Nanoparticles like Ag and Fe₃O₄ attached onto graphene oxide sheets can help the rolling process, which may be expected to expand into other inorganic nanoparticles.

Owing to its excellent electrical, optical, mechanical and thermal properties, graphene is a research hot spot in current nanoscience and nanotechnology.^{1–4} To date, various synthetic methods to obtain high-quality and mass-scalable graphene and its derivatives have been achieved.^{4,5} On the other hand, functional inorganic nanostructures including metals and their oxides were also well developed in the last few decades.⁶ They exhibit excellent material characteristics, such as surface plasmon resonance, high carrier mobility, radiative recombination rate, and long-term stability, *etc.*⁶ It is anticipated that incorporating graphene or its derivatives, graphene oxide (GO) into inorganic nanostructures, may give rise to some enhanced performances for potential applications of high-performance supercapacitors,⁷ dye sensitized solar cells,⁸ drug carriers^{9–12} and magnetic resonance imaging,¹³ biosensors,^{14–16} photocatalysts,¹⁷ electrode materials,^{18,19} *etc.* To this end, the synthesis of some hybrid heterostructures of graphene and zero-dimensional inorganic nanoparticles, one-dimensional nanorods, and two-dimensional nanowalls has been actively explored in recent years.^{6,20,21} However, graphene or GO was in the original form of a 2D sheet in these hybrid architectures which might hinder the exploration of some novel properties and applications. Therefore, it is necessary to change the host's topological structure (graphene or GO) in hybrids to obtain enhanced properties and even introduce some novel performances. Carbon nanoscroll (CNS), as an emerging family member of carbon nanomaterials, is a

spirally wrapped 2D graphene sheet with a 1D tubular structure resembling that of a multi-walled carbon nanotube.²² Due to its unique topological structure, CNS not only shares the remarkable mechanical and electronic properties exhibited by carbon nanotubes (CNTs) and graphene but is also expected to exhibit novel features.²³ Meanwhile, theoretical calculations also predicted some unusual electronic and optical properties of CNS.^{24,25} Currently, there are several methods including microwave spark assistance,²⁶ high-energy ball milling,²⁷ and chemical routes to fabricate CNS.²⁸ Among these methods, sonication chemistry is preferred due to the advantages of simple operation, high yield and low energy consumption for the synthesis of CNS.²⁸ With the aid of sonication, Viculis *et al.* firstly reported the production of CNS using a donor-type graphite intercalation compound (KC₈).²⁸ Later, Savoskin *et al.* proved that acceptor-type graphite intercalation compounds could also be used to produce CNS under sonication effects.²⁹ Recently, Loh *et al.* transformed 2D GO nanosheets into carbon nanotubes by sonicating GO in 70% nitric acid.³⁰ The fact that the graphene sheet could roll itself into a scroll structure under sonication effect inspired us to extend the current work towards graphene–inorganic nanocomposites.^{31,32} To the best of our knowledge, there are few reports on the synthesis of graphene–inorganic composite scrolls under sonication irradiation.

Here we demonstrate an efficient and controllable way to roll up GO sheets into micro/nanoscrolls, where the rolling process is highly enhanced by nanoparticle aggregation. Nanoparticles like Ag and Fe₃O₄ attached on GO sheets can help the rolling process, which could be further applied to roll the sheets in a controllable way. The overall strategy of rolling an inorganic nanoparticle-decorated GO sheet is schematically displayed in Fig. 1, and the details can be found in the Experimental section.

In the present work, GO sheets were produced by the modified Hummers method through acid oxidation of flake graphite and also by the method mentioned in our previous reports.^{33,34} The atomic force microscope (AFM) image in Fig. 2a shows the morphology of the as-prepared GO sheet. One can see GO sheets lying on the substrate with the size up to 10–20 μm, which is larger than the graphene formed by mechanical exfoliation, because small pieces can be filtered out during the fabrication process and therefore only large pieces are left for further characterization.

AFM results show that most of the GO sheets have a uniform thickness of ~1 nm, indicating that the GO sheets consist of only one single layer, proving that the current method is suitable for mass

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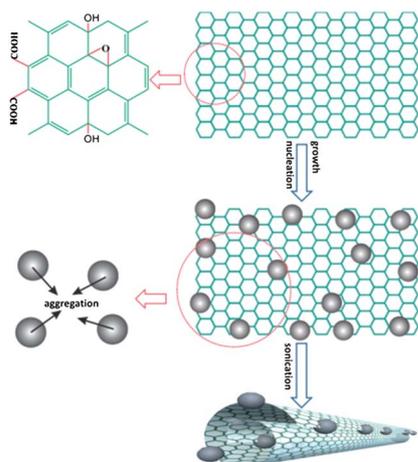


Fig. 1 Schematic diagram shows the rolling process of the inorganic particle-decorated GO sheet. The aggregation of inorganic nanoparticles leads to the formation of hybrid nanoscrolls.

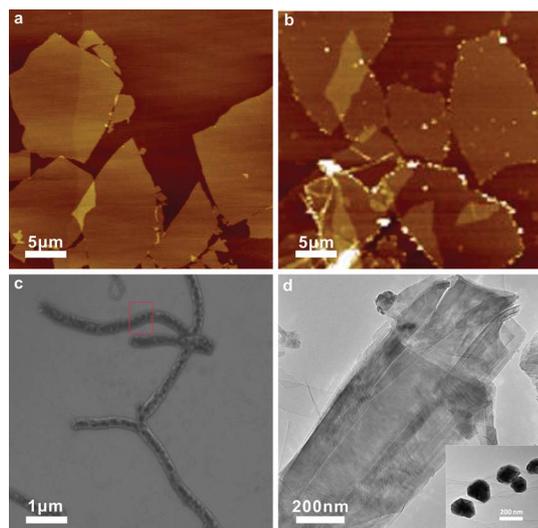


Fig. 2 (a) AFM image of as-prepared GO sheets. (b) AFM image of Ag nanoparticle-decorated GO sheets. Ag nanoparticles with sizes from 30 to 100 nm can be observed. (c) SEM image of rolled Ag-decorated GO sheets (Ag-GO hybrid nanoscrolls). (d) TEM image of the fabricated nanoscroll. The space between the rolls is obvious, indicating that the nanoscroll is from the rolling of 2D sheets. The TEM image in the inset shows that the nanoparticles are tightly wrapped by the rolled GO sheet. The inset is from (c), red square.

production of large-scale GO sheets with uniform thickness. It is well-accepted that the oxygen-containing functional groups (carboxyl, carbonyl, hydroxyl, and epoxide) exist on the surfaces of GO, which could act as the active sites for the trapping, stabilization, and nucleation of the metal ions.^{35,36} In the case of Ag nanoparticles, when the AgNO_3 solution was gradually added into the GO suspension, the Ag^+ ions could be trapped by the oxygen-containing functional groups and start to grow into clusters on the surface of the GO sheet. The size of the Ag clusters will grow with the reaction time and Ag nanoparticles can be observed after 48 h incubation. Fig. 2b exhibits the AFM image of the Ag nanoparticle-decorated GO sheet.

Compared to the smooth surface of as-prepared GO sheets, white dots can be observed in the AFM image, which represent the Ag nanoparticles formed during the incubation. The size of the Ag nanoparticles is distributed from 30 to 50 nm. Another interesting phenomenon is that most nanoparticles are attached to the edge of the GO sheet, and only a few nanoparticles are sparsely located in the basal surface of the GO sheet. This is reasonable because most of the oxygenated functional groups are located at the edge of the GO sheet for Ag nucleation. The AFM results in Fig. 2b thus clearly verify the fabrication of the Ag-decorated GO sheet in our experiment. After the Ag-decorated GO sheets were subjected to sonication (100 W) at 33 kHz for 2 h, the morphology characterization of the sample was carried out again (Fig. S1†) and the results show that structures are completely different from those smooth and flat sheets. The SEM image (Fig. 2c) exhibits the formation of wire-like structures rather than the flat sheet. The “wires” with lengths from 10 to 20 μm have a uniform diameter of about 400 nm (Fig. 2c). It is worth noting that the “wires” seem hollow and white dots with a size of 40 nm are observed to be embedded inside the “wire”. To clarify the nature of this wire-like structure, a transmission electron microscope (TEM) image with high magnification of the end of the “wire” is recorded and demonstrated in Fig. 2d. The image supports our presumption that it is a wire. In fact, these “wires” from sonication treatment are tubes, which originate from the rolling of the 2D GO sheet.^{22,37,38} The space between the adjacent rolls is obvious in the TEM image, suggesting that the spontaneous rolling with the assistance of sonication could not lead to tight rolling behavior. One could infer that the existence of Ag particles on the surface of the GO sheet may contribute to the separation between the rolls. However, the interval distance (more than 100 nm) is much larger than the size of Ag nanoparticles (~ 40 nm), indicating that the contribution should be quite limited.

To understand the key point in the rolling process, we carried out the control experiments. No such rolling behavior can be identified in the samples without inorganic nanoparticles attached or in those not subjected to post-sonication treatment. We note that the formation of carbon nanoscrolls was previously reported in sonicated graphene sheets, while it is not the case in our experiments with GO. A rational deduction may be from the different natures between graphene and GO or the power of the sonication used in the treatment. For instance, Viculis *et al.* used the high-energy (500 W) sonication to roll the graphene sheet while ours is as low as 100 W, which may not be able to directly roll the GO sheets.²⁸ Nevertheless, the control experiments suggest obviously a combined action from both inorganic nanoparticle attachment and sonication treatment. The rolling process can be therefore understood as follows: when the GO sheets attached with nanoparticles are subjected to the sonication treatment, the vibration causes the bending of the GO sheet and this effect can be further amplified by the nanoparticles because more energy is collected by the nanoparticles while their movements also drive the underneath GO sheet. There are several other factors that may also contribute to the rolling process. First, the van der Waals forces between the adjacent nanoparticles make them move towards each other, which is the energetically favorable state, and the GO sheets are rolled simultaneously. Second, the π - π interaction existing in the overlap region of the GO sheet decreases the total free energy,²² which offsets the increased energy from bending. Third, the nanoparticle at the edge of the bended part of the GO sheet may be attracted by the inner part of the GO sheet due to the sparsely distributed

oxygen-containing functional groups, proceeding the rolling. Thus, nanoparticles are observed to be tightly wrapped by the rolled GO sheet, as demonstrated in the inset of Fig. 2d. Such structure may combine the excellent performances of both inorganic nanoparticles and the GO sheet (*e.g.* flexibility) and thus promises many potential applications.

Since the pure GO sheets subjected to sonication do not roll or curl, the incorporation of inorganic nanoparticles should play an important role in the formation of the rolled structure during the sonication treatment. To disclose this process in more detail, we need to prove that the movement of the GO sheet can be driven by the force acted on the nanoparticles, which are chemically connected to the GO surface. As shown in Fig. 3a, an external magnetic field effectively attracts Fe_3O_4 nanoparticles in the solution, and meanwhile the decorated GO sheets are also pulled in the same direction as the solution becomes clear. This result demonstrates that the connection between nanoparticles and GO sheets is strong enough to transfer the effect of the external force exerted on the nanoparticles. Once the rolling process is completed, the aforementioned interaction effects can maintain the formed tubular structures, even if the nanoparticles are selectively removed by ammonia solution, as displayed in Fig. 3b. Obviously, this rolling behavior of the GO sheet is a nanoparticle-mediated, and the formed tubular (wire-like) structures normally wrap some nanoparticles in the tubular cavities or between the rolls. The amount of inorganic nanoparticles trapped therefore has an important influence on the final morphology after drying and electron-beam bombardment during electron microscopy imaging.

As displayed in Fig. 4a, the tubular structure is filled with Ag nanoparticles (white dots in the image) forming a “nanowire”, and the outer diameter of the Ag-GO hybrid nanowire is relatively uniform although small protuberances can still be observed. In contrast, the SEM image in Fig. 4b shows a completely different morphology because the inner cavity of the rolled GO sheet is not fully filled with Ag nanoparticles. The surface tension during drying and electron-beam bombardment leads to the shrinkage of the GO sheet which brings about a slight twist of the hybrid structure and the diameter of the tubular structure becomes smaller at the location where no nanoparticle inside supports the GO sheet. One can clearly see the remarkable fluctuation along the diameter of an individual hybrid in the regions with and without particles filling, as reflected in Fig. 4b. This phenomenon could be even obvious after the Ag nanoparticles are selectively removed and only the rolled GO sheet with little torsion is left (see the enlarged TEM image in Fig. 4c). We therefore believe that the structures of rolled GO sheets could be

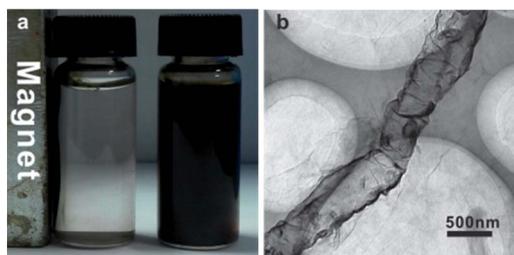


Fig. 3 (a) Photograph showing that Fe_3O_4 nanoparticle-decorated GO sheets in the water can be attracted by the external magnetic field. (b) TEM image of a rolled tubular structure from the GO sheet after removal of Fe_3O_4 inorganic nanoparticles.

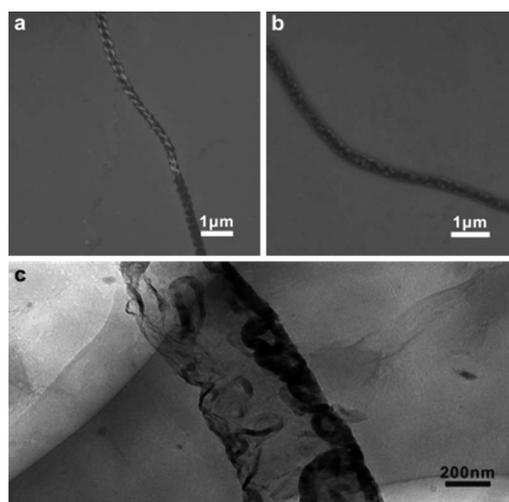


Fig. 4 SEM images of the rolled GO sheet (a) filled with Ag nanoparticles and (b) half-filled with Ag nanoparticles. (c) TEM image of a rolled GO sheet after the embedded Ag nanoparticles are selectively removed.

specifically tuned by decorating with nanoparticles of designed geometries, oriented to diverse applications.

In summary, we prepared GO sheets decorated with inorganic nanoparticles which can be further converted into rolled-up structures with the assistance of sonication post-treatment at room temperature. It is believed that the power of sonication is collected by the nanoparticles, which then drive the GO sheets to roll in the solution. The method is simple and energy efficient, and could be further extended to synthesize a range of inorganic-GO hybrid structures and even SWCNTs with well-defined geometry to open up new opportunities for the future development of functional materials for optical, electronic, magnetic, and catalytic applications.

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