Highly Efficient Synthesis of Neat Graphene Nanoscrolls from Graphene Oxide by Well-Controlled Lyophilization

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ABSTRACT: Graphene nanoscroll (GNS) is an important one-dimensional tubular form of graphitic carbon with characteristic open topology. It has been predicted to possess extraordinary properties that are significantly different from the analogical multiwalled carbon nanotubes. However, comprehensive experimental investigations on its properties and applications are still hindered by the lack of its reliable synthesis in high yield. To efficiently transform the scalable graphene oxide sheets into GNSs, here, we proposed a well-controlled lyophilization that comprises four sequential steps: chemical reduction of giant GO, freezing isolation of reduced graphene sheets, freeze-drying, and thermal annealing. The combined method has an extremely high efficiency, up to the record 92%. Systemic control experiments and cryo-SEM inspections revealed that the topological transformation from 2D sheet to 1D scroll is the sublimation-induced scrolling of individually confined graphene sheets in ice, which was controlled by chemical reduction, feed concentration, and freezing rate. GNSs exhibited high structural integration and were solution-processed into macroscopic forms. We also revealed the spontaneous swelling behavior of GNS in a reversible manner for the first time, verifying the featured open topology of GNS. Through this combined protocol, GNS can be scalably synthesized from massive graphene oxide with high efficiency, which should promote comprehensive research and massive applications in the real world.

INTRODUCTION

Graphene nanoscroll (GNS), or known as carbon nanoscroll, is an increasingly important carbonaceous nanomaterial with one-dimensional topology.1−11 Theoretically, GNS consists of a tubular graphene sheet and possesses topological open structure. It can be regarded as the resultant 1D form that is shaped by rolling graphene sheet in a continuous manner, which is distinct from the seamless concentric structure of multiwalled carbon nanotubes (MWNTs).3 The specific topology of GNS together with the merits of constituent graphene renders its considerable attractive properties and promising applications.4−7,11−20 First, foreign molecules can easily diffuse into the interlayer galleries of GNS, and its open topology also facilitates the radial expansion to accommodate the increasing volume during the intercalation process without any breakage of tubular walls. This feature is significant to storage-related uses, such as hydrogen storage, supercapacitors, and batteries.4−6,16,19 Second, GNS inherits many favorable properties of constituent graphene, such as high mechanical strength, outstanding electrical and thermal conductivities, and high carrier mobility.5,9,11 These eminent attributes of GNS will find wide use in advanced composites with high performance and multifunctionalities, sensors, and electronic devices. Third, GNS performs some different properties from CNT or graphene, especially in the electronic aspect. For example, π electrons in GNS are continuous, but π electrons of MWNTs are interrupted by the interlayer spacing between their concentric walls.5 As a result, GNS overwhelms MWNT in the capability to afford current density (i.e., ampacity), which promises preferable applications as wires or cables to transport extremely heavy current.7

To reliably synthesize GNS in high yield is the prerequisite for both comprehensive studies on its properties and extensive applications. The emerged methods to synthesize GNS are concluded in Supporting Information Figure S1. Chemical vapor deposition (CVD) and pyrolysis of polymers have been long employed to prepare CNS (or GNS), whereas, the complicated fabrication process, high energy-consumption, and abundant impurities (mainly including graphite and amorphous carbon) in products of these two methods urged us to find new paths to prepare GNS.5,9 Until 2003, Viculis et al. developed a low-temperature chemical exfoliation of potassium-intercalated graphite for GNS and attained a considerably high efficiency above 80%.2 The recent discovery of graphene21,22 has promoted new experimental strategies to transform 2D graphene into 1D GNS,11,12,16,20,23−27 Except for investigations of the transformative mechanism in the microscale,11,17,18 exfoliation of graphite with the aid of chemical intercalation,20

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sonication, or microwave, ultrasonication-driven assembly from dispersed graphene chemical derivatives, and templated assembly are three possible methods hitherto to synthesize GNS in large scale. However, their efficiencies of the topological transformation are below the high expectations.

Here, we proposed a highly efficient route to synthesize neat GNS in high yield from the scalable graphene oxide sheets, through a well-controlled lyophilization that consists of chemical reduction, fast freezing, freeze-drying, and thermal annealing. The efficiency of our method is as high as 92%. Detailed investigations showed that two important factors, including van der Waals (vdW) interaction and the isolation of graphene sheets, dominated their spontaneous scrolling behavior. Using cryo-SEM characterizations together with systematic control experiments, we revealed that the topological transformation conforms to the mechanism of sublimation-induced sclicing of isolated reduced graphene sheets. The prepared GNSs exhibited high structural stability even under sonication and had solution processability for their macroscopic applications. We also observed the spontaneous intercalation behavior of organic solvents into the open interlayer gallery of GNS, which allows its potential applications for storage and versatile GNS hybrids with tunable functionalities.

![Figure 1](image)

**Figure 1.** (A) Photograph of GGO aqueous dispersion with the concentration of 0.5 mg/mL (left) and typical SEM image of GGO single layers with giant lateral size up to ~40 μm. (B) Photograph of CRG aqueous dispersion obtained from chemical reduction of GGO dispersion in (A) by N\textsubscript{2}H\textsubscript{4}H\textsubscript{2}O at 60 °C for 30 min (left). The right panel in B is the typical SEM image of single-layered CRG sheets deposited on the silica substrate from their diluted aqueous dispersion. (C) XRD patterns of CRG and GO filtered films. (D) TGA curves of CRG and GO powders.

Starting from GGO, the whole controllable process to fabricate GNS encompassed four steps: (1) chemical reduction of GGO to get single-layered chemical reduced graphene (CRG); (2) fast freezing CRG aqueous dispersions, (3) freeze-drying to remove ice; and (4) further thermal annealing to obtain GNS. Through these optimal steps, GGO sheets were transformed to GNS at a high efficiency up to 92%. To the best of our knowledge, the efficiency in this study is the highest as compared with other methods in previous reports.

In the course of making GNS, we found that three experimental factors, including the enhanced vdW interaction by chemical reduction, the low concentration of CRG sheets, and the high freezing rate, were critical to attain the high transformation efficiency.

**Chemical Reduction of GO.** Theoretical analysis predicted that the topological transformation from planar graphene to tubular GNS is dominated by the competition between elastic bending energy and free energy. Particularly, the decrease of free energy originated from the vdW interaction of overlapping domains of graphene sheet should overweigh the increase of elastic energy caused by rolling and distorting graphene sheets, promoting the spontaneous formation and stabilization of GNS. In the case of GO, its vdW interactions are greatly weakened by the pendant oxygen containing functional groups, which is the reason for its excellent dispersibility in water and solvents. To overcome the energy barrier of rolling, we turned GGO to chemical reduced graphene (CRG) to enhance the vdW interaction, through chemical reduction of hydrazine hydrate at 60 °C for 30 min. Compared with other previous reports on severe reduction of GO at higher temperature for longer time (such as 90 °C for 1 h), we employed this mild reduction to balance the conflict between the enhancement of interaction (higher reduction extent) and the dispersability as single layers with giant lateral width (less reduction extent) in a broad range of concentration from 0.05 to 1 mg/mL without any stabilizers. CRG aqueous dispersions kept homogeneous after reduction and CRG sheets remained in the single-layer dispersive state, as demonstrated by their SEM images (Figure 1B). Similar to the raw GGO, CRG had the average lateral size

**RESULTS AND DISCUSSIONS**

**Well-Controlled Process to GNS from GO.** As the important chemical precursor of graphene, graphene oxide (GO) can be prepared on a large scale from graphite by the oxidation process. With sophisticated control, GO sheets are uniform as single layers when dispersed in water and polar organic solvents. The uniform single layered merit of GO sheets helps the investigation of topological transformation behavior in the ultimate scale. In this study, we chose giant GO (GGO) as raw material to synthesize GNS. GGO was synthesized by modified Hummers’ method that was also employed in our previous reports. After severe oxidation, GGO still remained the planar morphology and possessed excellent dispersibility in water as single layers for its rich pendant functional groups.

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of ∼20 μm, and the highest size was up to ∼40 μm (Figure 1A). On the other hand, the chemical reduction eliminated the functional groups of GGO and restored the conjugated structure. This structural evolution was confirmed by characterizations of UV−vis, X-ray diffraction (XRD), thermogravimetric analysis (TGA), and X-ray photoelectron spectroscopy (XPS), as shown in Figure 1C,D and Supporting Information Figure S2. The enhancement of interaction was also evidenced by the appearance of fluffy precipitate in CRG dispersions after long-time standing (for example, one month in Supporting Information Figure S3), contrary to the outstanding stability of GGO for years without reduction.

Control Factor 1: Chemical Reduction. Figure 2A−C shows SEM inspections on the morphology of GGO after freezing (step 2) and lyophilization (step 3). In the resultant foams, GGO sheets kept their planar topology under the condition of high concentration (0.5 mg/mL) of the feed GO dispersions (Figure 2A). Even at low concentration down to 0.05 mg/mL, only scrolling morphology was seen at the fringe of GGO sheets and interconnecting parts. By contrast, almost all the CRG sheets were transformed to the rolling state (SEM images in Figure 2D,E), through the identical operations of steps 2 and 3 on the CRG dispersions (0.05 mg/mL). In consideration of both the single-layer dispersive state of GGO and CRG sheets before freeze, this distinct difference in morphology of their freeze-dried samples implied that the enhancement in vdW interaction promotes their scrolling behavior. In previous reports, mechanically exfoliated pristine graphene sheets on substrate exhibited the spontaneous rolling behavior with the aid of solvent evaporation, whereas some exterior forces were needed to roll GO sheets, such as nanoparticles-induced aggregation, 1D nanoparticle templating, and sonification.

Control Factor 2: Feed Concentration. Through examinations of freeze-dried samples of CRG with successively increasing concentrations, we found that the concentration of their feed dispersions also determined the efficiency of the topological transformation from planar to scrolling topology. Figure 2D−E (for more results see Supporting Information Figure S4) shows that the morphology evolved from planar sheets to scrolling fibers as the feed concentration decreased from 1.0 mg/mL to 0.05 mg/mL. To quantitatively assess the efficiency, we counted the number of CRG in the scrolling and planar states, respectively, in their SEM inspections, and took the proportion of scrolling CRG as the efficiency of topological transformation. The statistical counting results were demonstrated in Supporting Information Figures S5−S9. The efficiency of scrolling steadily increased from ∼6% at the concentration of 1 mg/mL to ∼92% at the concentration of 0.05 mg/mL. This highest efficiency in our study is even superior to the record value (80%) ever achieved in sonification-aided chemical exfoliation of potassium-intercalated graphite. 2

In order to understand the spontaneous scrolling behavior of CRG, we tracked the intermediate state of the freeze-drying process by cryo-SEM. The top-view image (Figure 3A,B) revealed two distinctive states of CRG in the freeze-drying process: scrolls floated in the vacuum (Figure 3C,D) and planar sheets confined in the ice (Figure 3E,F). Considering the high efficiency of the final freeze-dried samples (Figure 2D,E), we pondered that the topology transformation completed in the sublimation procedure, more specifically, occurred at the interfaces between ice and vacuum. Actually, we identified this transformation process on the ice surface under cryo-SEM, as shown in Figure 3E−J. As ice sublimated, the confined CRG exposed themselves in two ways: lying on (Figure 3G,H)
implanting into the ice (Figure 3E,F,I,J). The sublimation of ice made CRG sheets become freestanding, and these freestanding parts began to scroll. This tendency was exhibited by the rolling fringes of CRG sheets and GNS at the surface of ice. Previously, it is observed that graphene sheets on substrates scrolled into GNS by the evaporation of the choice solvents.11 By analogy with this phenomenon, we pondered that the scrolling of CRG sheets is driven by the sublimation of ice and free-standing of CRG sheets, similar to the evaporation of solvent.

As the determinant factor, the concentration actually denotes the number density of the dispersive CRG sheets and correspondingly determines the interaction among them. For example, the increasing of concentration guides the formation of orientational ordering as liquid crystals in the case of GO37−39 and also facilitates the preparation of interconnected frameworks with good elasticity by freeze-drying.40 In this study, the decrease of concentration of CRG dispersions weakened the interaction among them and ultimately reached the isolation state. In the CRG sample with the lowest feed concentration down to 0.05 mg/mL we used, the isolated CRG sheets were identified as confined by ice, accompanying with the scrolling of the fringes of these CRG sheets without any contact with other sheets (Figure 3E,F). In the frame of conventional percolation theory, the excluded volume method predicted that the percolation threshold ($\phi_c$) of 2D platelets correlated with their aspect ratio ($\alpha$, $\alpha = w/t$, $w$ is the lateral size and $t$ is the thickness) and $\phi_c$ is in the range from $[1 - \exp(-3.6/\pi\alpha)]$ to $[1 - \exp(-5.6/\pi\alpha)]$.41 Referring to the lateral size of CRG as 20 $\mu$m and the thickness as 0.8 nm,33 the $\phi_c$ of CRG in aqueous dispersions (and confined ice) was calculated as $4.5 \times 10^{-5} \leq \phi_c \leq 6.9 \times 10^{-5}$. The low concentration (0.05 mg/mL, about $3.8 \times 10^{-5}$ of the volume concentration) that was employed to get the highest efficiency was near to the calculated range of the percolation threshold, which suggests that CRG sheets were isolated by water and ice at this low concentration. By contrast, the sample with higher concentration (0.5 mg/mL that exceeds the calculated percolating threshold about 5−7 times) showed connections between the trapped CRG sheets, which hampers their isolation and the complete scrolling (Supporting Information Figure S10). Thus, these interconnected CRG sheets mainly kept the planar morphology, either at interfaces or in vacuum.

Figure 3. (A) Schematic image to describe the immediate state in the freeze-drying of CRG aqueous dispersion, accompanied with the topological transformation from CRG sheets to GNSs. There are three regions: (1) completely transformed GNS in vacuum, (2) individual CRG sheets confined in ice that remain in a planar sheet topology, and (3) ice surface at which scrolling happens caused by the sublimation of ice. (B) Cryo-SEM full-view image of the topological transformation process by freeze-drying, which correlates the three regions described in (A). The magnified cryo-SEM images of the three regions: (1, C,D) GNS in vacuum, almost all the graphene took the scroll morphology in vacuum which means the accomplishment of topological transformation; (2, E,F) individual CRG sheets confined in ice without connection to each other. One CRG sheet has two morphologies, that is, free-standing scroll (without ice support) and laying planar sheet (implanted on ice surface); (3, G−J) the ice surface, immediate state of topological transformation, including laying planar sheets on the ice surface and free-standing scrolls, are seen, indicating the formation of GNS from CRG sheets is caused by the sublimation of ice.
Aside from the chemical reduction and the concentration, we noticed that the freezing rate influenced the topological transformation from sheets to scrolls as well. All the samples above that showed high efficiency were prepared at fast freezing rate by directly implanting dispersions into liquid nitrogen. We took another control experiment with low freezing rate by keeping dispersions in $-10$ °C surroundings (5 mL dispersion needed about 2 h to complete freezing). Slow freezing process caused the precipitation of CRG sheets, which was seen under optical microscopy even by naked eyes. After freeze-drying (step 3), these samples had thick planar bricks up to hundreds of micrometers (Figure 4), one magnitude larger than that of the feed CRG sheets, suggesting these platelets consist of multilayers of CRG sheets (about 15 at least) as a result of precipitation of CRG sheets in slow freezing. In contrast to (A–C), (D–F) show that the CRG freeze-dried sample by fast freezing in liquid nitrogen possesses scroll morphology. The length of GNS is around 20 μm that correlates to the average size of feed CRG sheets, indicating GNS formed by rolling individual CRG sheets into 1D nanofibers with radial size of $\sim$300 nm (the inset in F). The examined samples were prepared by dipping CRG dispersions (0.05 mg/mL) onto silica surface, fast or slow freezing, and freeze-drying.

**Mechanism of Topological Transformation.** From all these experiments on the synthesis of GNS from GO sheets, we concluded that the topological scrolling was dominated by three factors: the chemical reduction, concentration of feed CRG dispersions, and freezing rate. Thus, we can also conclude the underpinning mechanism of the topological transformation from 2D sheets to 1D nanoscrolls with high efficiency. Figure 5 gives the schematic procedure of the whole transformation. The chemical reduction enhances the vdW interaction of the CRG sheet to overcome the energy barrier of scrolling. The low concentration and fast freezing isolate CRG sheets in ice, keeping them free from contacting each other. In the following freeze-drying, the sublimation of ice induces the isolated CRG sheets to freely roll to scrolls. In fact, for the first time, we gave a mechanical answer to explain the intriguing scrolling behavior in the freeze-drying of chemical derivated graphene sheets.

**Structure of GNS.** After well-controlled lyophilization, the following thermal annealing turned scrolled CRG into GNS and stabilized the scrolling morphology further. Figure 6A shows macroscopic GNS framework and GNS cotton had an ultralow density of about 0.2 mg/cm³. Under SEM (Figure
GNS exhibited the typical scrolling morphology as filaments (short fibers) that interlaced with each other. Their length was measured as about dozens of micrometers (from ~20 to ~40 μm) and correlated the lateral size of raw GO sheets, which implies that GNSs were transformed from individually isolated CRG sheets. The radial size of GNS was measured as around 260 nm, larger than the calculated value (93 nm) of the ideally rolled graphene sheet with lateral width of 20 μm (for the detailed calculation see Supporting Information Figure S11). This comparison illustrated that the GNS we prepared were the bundles of scrolls instead of perfect ones. The theoretical calculation demonstrated that the radial size of GNS scales with the width of feed graphene sheets, offering a method to tune their radial size.

On the GNS surface, we identified the aligned wrinkles along the axis that were wrapped together to form these nanofibers (Figure 6B–D). Figure 6E and Supporting Information Figure S12 demonstrated some immediate state between sheets and scrolls. During freeze-drying, GNS connected to each other by diverse ways (Figure 6F–H), such as head-to-head, head-to-trunk, and trunk-to-trunk, to form 3D frameworks of GNS. By virtue of further examination of TEM, the structure of GNS can

Figure 6. (A) Photo of GNS cotton. Its density was measured to be about 0.2 mg/cm³. (B–D) SEM inspection of the structure of GNSs. (E) The immediate state of scrolling from sheet to scrolls. (F–H) The interconnection styles of GNSs in their free-standing framework as prepared. (I, J) TEM images of GNSs that are dispersed in hexane by sonication. (K) Photo of the GNS self-standing film reassembled from GNS cotton in A. (L) SEM image of the interfacing structure of GNS films.

Figure 7. (A) Evolution of interlayer spacing of GNS in one swelling–drying cycle by ethanol. (B) Schematic illustration of the reversible swelling behavior of GNS in good solvents. GNS can be spontaneously intercalated by solvent molecules into the interlayer gallery and also recovers its original state by simple evaporation, accompanied by the expanding (intercalation step) and shrinkage (evaporation step) of interlayer spacing between overlapped graphene sheets.
be described as bundles of scrolls that were wrapped by unrolled graphene sheets (Figure 6I,J). Since the dominated vdW interaction, GNS possessed high structural stability and kept their-scrolling morphology even under ultrasonications (Supporting Information Figure S13). Thus, GNSs were dispersed in solvents and solution-processed to thin films and papers for macroscopic uses (Figure 6K,L and Supporting Information Figure S14).

Reversible Swelling of GNS. Because of the open topology of GNS, its interlayer gallery between overlapped graphene is available to accept versatile solvents and other molecular guests, just by facile infiltration. This notion on this typical property of GNS has been merely predicted in theory, but never observed in experiments. In the GNS sample, we observed its spontaneous swelling (or breathing) behavior as soaked in organic solvents on XRD examinations (Figure 7A). Once soaked in ethanol, the deflection (002) peak of GNS at 26.2° decreased to 21.9°, which corresponds to the increasing interlayer spacing from 3.39 to 4.05 Å. Accompanied with this peak shift is the emergence of a new peak (001) centered at 11.0° (8.04 Å), indicating that the intercalation of ethanol molecules expands the interlayer spacing. As ethanol evaporated at room temperature during XRD test, the peak at 11.0° immediately faded away (Supporting Information Figure S15). After complete drying under vacuum at 150 °C, the peak at 21.9° shifted back to the original location at 26.2°, which denotes the recovery of interlayer spacing and the corresponding structure of GNS. The similar reversible behavior of GNS was also detected by XRD in other solvents such as DMF and toluene together with molecular fullerene (Supporting Information Figure S16). These XRD tracking experiments revealed the reversible breathing behavior of GNS in solvents (Figure 7B) and indicated its open topology that is in contrast to the concentric attribute of MWNs, which is promising for the in situ synthesis of nanoparticles-hybridized GNS with designed functionalities.42,43

CONCLUSIONS

In summary, we developed a well-controlled lyophilization method to transform scalable GGO sheets to neat GNSs in high efficiency up to the yield of 92%. Through cryo-SEM and systematic control experiments, we unveiled the mechanism of the topological transformation of GNS as the spontaneous rolling behavior of individual graphene sheets driven by the sublimation of ice. We also concluded that vdW interactions and the isolation of graphene sheets play a key role to dominate the formation of GNS, which was controlled by chemical reduction, concentration, and freezing rate in experiments. This efficient method to synthesize GNS from massive GO should promote comprehensive research and massive applications of GNSs. The structurally stable GNSs exhibited favorable solution processability for their macroscopic applications. For the first time, we found the spontaneous breathing behavior of GNS in organic solvents that correlates its characteristic open topology. This experimental observation will guide the wide use of GNS in storage-related areas and the preparation of GNS hybrids with tunable functionalities.

EXPERIMENTAL METHODS

Giant Graphene Oxide. The raw was synthesized from natural graphite platelets by modified Hummers’ method, as described in our previous papers at length.31–33 Graphite powder (~500 μm) was obtained from Qingdao Henglide Graphite Co., Ltd. Concentrated H2SO4 (98%), KMnO4, and N2H4·H2O were purchased from Sinopharm Chemical Reagent Co., Ltd. and used as received.

Well-Controlled Lyophilization for GNS. The whole method included four steps:

Step 1: GGO aqueous dispersions with a serial of concentrations (from 0.05 to 1 mg/mL) in flasks were kept at 60 °C in an oil bath for 5 min, and N2H4·H2O solution (85%) was added into GGO dispersions (the weight ratio of N2H4·H2O GGO was about 15:1) and kept at 60 °C for 30 min to get homogeneously dispersed CRG feed dispersions.

Step 2: To achieve the highest efficiency, CRG feed dispersions in glass beakers were directly immersed into liquid nitrogen at high freezing rate to freeze into solids. In the case of control experiment of low freezing rate, CRG feed dispersions were kept at −10 °C in the refrigerator to freeze.

Step 3: Freeze solids of CRG were placed into the lyophilizer, and the samples were kept at around −5 °C and under −1 Pa vacuum. After freeze-drying, samples were transferred to a vacuum oven and dried at 50 °C for 12 h to obtain GGO scrolls.

Step 4: GGO scrolls were sealed into the alundum tube and heated to 1300 °C at the rate of 5 °C/min and kept at 1300 °C for 2 h, under the atmosphere of the mixture of H2 (5%) and Ar. After cooling to room temperature, GNSs were obtained.

Cryo-SEM Inspections. Cryo-SEM images were taken on a Hitachi S4800 field-emission SEM system equipped with Gatan freeze specimen chamber. CRG dispersions were dipped into the aluminum alloy cell and directly immersed into liquid nitrogen. After complete freeze, samples were transferred into the Gatan specimen chamber that was maintained at −180 °C and cut by a blade to get a fresh observation fraction surface. The following steps included sublimation at −65 °C for 10 min to remove a thin layer of ice on the fraction surface and sputtering Au coating for examination. To avoid the possible variation of the structure, samples were kept at −180 °C during SEM observations.

Characterizations. SEM images were taken on a Hitachi S4800 field-emission SEM system. TEM images were taken on a JEM-12300 with the accelerating voltage of 80 kV. XPS was performed using the ESCALAB 250Xi System. All binding energies were referenced to the C 1s neutral carbon peak at 284.8 eV. TGA was carried out using a thermogravimetric analyzer (PerkinElmer Pyris 1) from room temperature to 800 °C at 10 °C/min heating rates under N2 atmosphere. XRD data were collected with an X’Pert Pro (PANalytical) diffractometer using monochromatic Cu Kr1 radiation (λ = 1.5406 Å) at 40 kV. UV–vis absorption and transmission spectra were obtained using a Varian UV9003 spectrophotometer.

ASSOCIATED CONTENT

Supporting Information

UV–vis, XPS spectra of GGO and CRG, detailed calculation of the efficiency, SEM images of controlled experiments, theoretical calculation of the function between the lateral width of graphene sheets and the radial size of scrolls, dispersed GNS and their assembled macroscopic form, and XRD curves of DMF-swelling GNS. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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