Introduction

Graphene, a promising material, has recently attracted considerable research interest for its unique thermal, electrical, and mechanical properties, and for its high potential in the field of nanoscale electronics. 1–5 Graphene films have been grown through chemical vapor deposition (CVD) 1,6,7 or thermal annealing 8 on transition metal thin films. Samples of as-grown graphene on metal substrates can be easily transferred to other substrates through chemical wet etching. 7–9 Among different transition metals, Ni and Cu substrates are useful, inexpensive, and potentially favorable for the large-scale production of graphene.4,10–12 The growth of metal-catalyzed graphene involves three separate processes: carbonization of metal catalysts, annealing, and etching treatment.13 Considerable attention has been given to graphene grown on planar substrates, and, furthermore, the formation of tubular graphene (TG) has recently been explored.14–16 In particular, the integration of individual graphene structures into mesoscopic or macroscopic architectures is imperative for practical applications.17,18

In the present study, we derived a strategy for fabricating freestanding, flexible TG architectures at the macroscopic scale on the basis of the rapid annealing of a solid carbon precursor on commercially available Ni mesh under low-vacuum conditions. This thermal annealing approach can avoid the hazards of using explosive gaseous materials (e.g. CH₄, H₂ in CVD) or toxic chemicals (e.g. N₂H₄, NaBH₄ in graphite exfoliation). During the annealing procedure, dissociated carbon atoms diffuse into the Ni template, and graphene precipitates onto the Ni substrate and cooling. TG can be obtained as woven tubes with diameters of approximately 50 μm after Ni etching and thermo-assisted removal of poly(methyl methacrylate) (PMMA). The fabricating parameters (such as annealing temperature, annealing time, and amount of CA), which strongly affect TG surfaces, number of TG layers, and other TG properties, were investigated. Our macroscopic, lightweight, and easily handled TG structures are useful as building blocks for multifunctional architectures. They are more convenient than those prepared using carbon nanotubes or fibers. Moreover, these TGs can be easily tailored into freestanding, highly flexible, and extremely conductive textiles that can be directly and effortlessly used without a support.
Experimental

Fabrication of macroscopic, freestanding, and tubular graphene mesh

All chemicals were of analytical grade and were used without further purification. A thermal annealing technique was used to prepare TG structures. Compared with other typical methods, the thermal annealing approach is safer because it does not require the use of explosive gaseous materials or toxic chemicals, it consumes little power, and it can be performed rapidly. Our method is based on the surface precipitation of carbon on Ni templates. First, a piece of Ni mesh (diameter, 50 μm) was cleaned and rolling-pressed with different amounts of cellulose acetate membrane (CA, C04S047A, Advantec) as a solid carbon precursor. Subsequently, the sample was placed in a quartz container in an infrared lamp annealing system. The sample was then heated to annealing temperatures at a heating rate of 15.0 °C/s; this temperature was maintained for 8 min at a vacuum level of 0.6–0.8 × 10⁻³ Torr. Subsequently, the sample was cooled to 500 °C at a cooling rate of approximately 5.6 °C/s; the sample reached room temperature within 10 min. A thin PMMA film was coated on the as-prepared sample by immersing the sample in a solution of PMMA (950 A9, MicroChem) diluted in acetone (V_PMMA/V_acetone = 1/2) for 60 min, followed by drying overnight at room temperature. The PMMA coating maintained the TG structure because its Ni core was completely removed by overnight immersion in an etching solution of FeCl₃/HCl (1 M/1 M). Note that the edges of the mesh were cut to promote the Ni etching reaction resulting from the anticorrosive behavior of graphene. The residues of the etchant were carefully washed out by immersing the sample several times in deionized water. Finally, the PMMA-coated TG sheath was heated to a temperature of 450 °C for 30 min under a pressure of approximately 0.6–0.8 × 10⁻¹ Torr to remove the PMMA. This yielded a woven TG structure.

We studied the effects of the fabrication parameters on the TG structures and their physical properties by adjusting the CA membrane amount (CA to Ni mesh area ratios of 1:1, 1:2, and 1:4 as illustrated in the insets of Fig. 4), annealing time, and annealing temperature.

Characterizations

The morphologies and dimensions of the TG structures were examined with a field emission scanning electron microscope (FESEM, JEOL, JSM-6500F) and scanning electron microscope (SEM, Hitachi, S-3000H). The crystallographic and layered structures of the TG samples were investigated using a Raman spectroscope (Horiba, XploRA ONE), atomic force microscope (AFM, XE70) and high-resolution transmission electron microscope (HRTEM, JEOL, JEM-2100). The elemental analysis of woven TG structures were conducted with the energy-dispersive X-ray (EDX) of the FESEM (JSM-6500F). The sheet resistance results of the samples were obtained using a four-point probe instrument at room temperature.

Electrochemical measurement

Electrochemical analysis of graphene/Ni and bare Ni samples were conducted in a three-electrode cell by using a Pt counter electrode and Ag/AgCl reference electrode. Potentiodynamic analysis was applied to determine the corrosion resistance of the samples in acidic and basic environments. Tafel plots were recorded in both 1 M HCl and 1 M KOH electrolytes. The scan potential ranged from −0.6 to 0.6 V with a scan rate of 10 mV/s. The electrochemical reaction of Ni was expected as follows:

\[
\text{Ni} \rightarrow \text{Ni}^{2+} + 2e^- \quad (1) \text{ anodic oxidation reaction}
\]

\[
\text{O}_2 + 2\text{H}_2\text{O} + 2e^- \rightarrow 4\text{OH}^- \quad (2) \text{ cathodic reduction reaction}
\]

Results and discussion

Characterization of the tubular graphene structure

We selected a typical sample processed at 950 °C, with a 1:1 area ratio of initial CA membrane to Ni mesh, for further characterization. After PMMA was coated on the graphene sheath and the Ni core was etched, the PMMA layer was thermally removed to form a TG architecture. The morphology of the TG grown on the Ni mesh at 950 °C was observed using the FESEM at different magnifications, as indicated in Fig. 1(a)–(d). Wrinkles were clearly visible on the TG surface, which demonstrated that it was constructed of interconnected graphene domains. The TG mesh retained the woven structure of its Ni template. The electron transparency of the TG structures displayed in Fig. 1(d) indicated that the walls of the tubes were thin. The ends of the tubes were effortlessly opened by cutting the edges of the graphene/Ni mesh, which produced TGs with extremely sharp wall edges. Small wires remained in the core of every graphene tube because of carbon impurities that formed during the annealing process, which were evidenced by the EDX results shown in Figs. 1(e) and S1. Furthermore, the EDX analysis results also reveal that the Ni core was completely removed after etching in the FeCl₃/HCl (1 M/1 M) solution. The TG mesh was composed of carbon (83.7 wt.%) and oxygen (16.3 wt.%) (see the inset in Fig. 1(e)). The presence of oxygen was probably induced by the low-vacuum annealing conditions.

A Raman spectroscope was employed to investigate the crystallinity of the TG sample. Figure 2(a) displays the Raman spectra with wave numbers ranging from 1000 to 3000 cm⁻¹ for the sample fabricated at the temperature of 950 °C. Three characteristic peaks (D peak at approximately 1351 cm⁻¹, G peak at approximately 1580.5 cm⁻¹, and 2D peak at 2714 cm⁻¹) were evident. The D peak, which represents defects or impurities in carbon materials, had an extremely weak intensity. This indicates a highly graphitic crystallinity of the sample. A Raman map that was acquired on 100 points of the TG surface (Fig. 2(b)) further confirmed its high crystallinity and extremely high uniformity. No notable change was observed in the intensities of the D, G, and 2D peaks, suggesting that the defects on the TG surface were negligible. The HRTEM image captured on the wall edge area revealed information regarding the layered structure (see Fig. 2(c) and its inset). The TG wall consisted of 12 graphene layers, as indicated. We also performed AFM measurements for additional evidence regarding the thickness of the TG sample. Because of the nature of hollow tubular structures, unzipped TG was first obtained for further observation,
as illustrated in Fig. S2(a). O₂ plasma was used to etch away the upper half of the TG sample while retaining bottom half. After being Ni-etched with a solution of FeCl₃ and HCl (1 M/1 M), the unzipped TG was formed and laid on a smooth substrate (silica). Figure S2(c) displays the morphology of the sample after O₂ plasma processing. The TG wall thickness determined by the AFM (Fig. S2(b)) was 5.9 nm (corresponding to approximately 16 layers), which approximated the value measured using the HRTEM. The effects of the fabrication parameters (e.g., annealing temperature, annealing time, and CA amount) on the TG layered structures were investigated to explain methods for controlling the thicknesses of tube walls.¹⁹

Effect of the fabrication parameters on the graphene structure

Effect of the annealing temperature

The dependence of TG graphitic quality on fabrication temperature was investigated by adjusting the annealing temperature within the range of 650–950 °C for samples with initial CA membrane-to-Ni mesh area ratios of 1:1, and annealing times of 8 min. The Raman spectra of the samples fabricated at different temperatures of 950 °C, 850 °C, 750 °C, and 650 °C are shown in Fig. 3. We thus labeled the samples as TG-950 °C, TG-850 °C, TG-750 °C, and TG-650 °C, respectively. The D peaks
annealing temperature at 950 °C and the annealing time for 8 min for all samples in the experiment. The samples are therefore denoted by TG-950 °C-1/1, TG-950 °C-1/2, TG-950 °C-1/4, respectively.

Figure 4(a)–(c) shows the Raman spectra obtained from the TG surfaces fabricated with different initial amounts of CA membrane. In these three spectra, the D peaks exhibited extremely weak intensities, representing very few defects or impurities. The I_D/I_G ratios of these spectra were calculated and are shown in Table 1. The TG-950 °C-1/1 sample had an I_D/I_G ratio of 0.37, lower than that of the TG-950 °C-1/2 (0.69) and TG-950 °C-1/4 (0.76) samples. This indicated an increasing trend in the I_D/I_G ratio that was inversely proportional to the amount of initial CA. Note that I_D/I_G ratio could be used as an index to evaluate the number of graphene layers. Higher I_D/I_G ratios indicate fewer layers of graphene. The number of graphene layers can be determined from the absorbance of monolayer graphene (an ideal monolayer of graphene has an absorbance of 2.3% in visible region). Thus, the number of layers in a TG structure (n) can be estimated as follows:

\[ n = \left( \frac{\text{I}_{\text{abs}}}{2 \times 2.3\%} \right) \]

To fulfill this purpose, a green laser beam size of 13 μm was vertically irradiated onto the TG surfaces. The laser power before and after the irradiation was recorded for enumerating the layers of TGs. As shown in Table 1, the wall-edge of the TG-950 °C-1/1 sample consisted of 10 or 11 graphene layers, which was consistent with the HRTEM results in Fig. 2(c). The morphologies of the TGs grown on Ni at different temperatures (650–950 °C) were characterized using an SEM; the results are shown in Fig. S3 and in the insets of Fig. 3. At an annealing temperature of 950 °C, the configuration of the TG mesh remained unchanged and preserved the woven structure of its template. The TG exhibited electron transparency, evidencing that the walls of the tubes were thin. The TG surfaces contained substantial defects for the samples annealed at 850 °C and 750 °C. In the sample annealed at 650 °C, the tubular structure of graphene was collapsed and broken. Accordingly, 950 °C was considered the optimal annealing temperature for fabricating high-quality TGs.

### Effect of the initial CA amount and thermal annealing time

We studied the effect of the CA amount on the graphene properties by adjusting the area ratio between the initial CA membrane and Ni mesh to 1:1, 1:2, and 1:4; we maintained the annealing temperature at 950 °C and the annealing time of 8 min for all samples in the experiment. The samples are therefore denoted by TG-950 °C-1/1, TG-950 °C-1/2, TG-950 °C-1/4, respectively.

Figure 4(a)–(c) shows the Raman spectra obtained from the TG surfaces fabricated with different initial amounts of CA membrane. These three spectra, the D peaks exhibited extremely weak intensities, representing very few defects or impurities. The I_D/I_G ratios of these spectra were calculated and are shown in Table 1. The TG-950 °C-1/1 sample had an I_D/I_G ratio of 0.37, lower than that of the TG-950 °C-1/2 (0.69) and TG-950 °C-1/4 (0.76) samples. This indicated an increasing trend in the I_D/I_G ratio that was inversely proportional to the amount of initial CA. Note that I_D/I_G ratio could be used as an index to evaluate the number of graphene layers. Higher I_D/I_G ratios indicate fewer layers of graphene. The number of graphene layers can be determined from the absorbance of monolayer graphene (an ideal monolayer of graphene has an absorbance of 2.3% in visible region). Thus, the number of layers in a TG structure (n) can be estimated as follows:

\[ n = \left( \frac{\text{I}_{\text{abs}}}{2 \times 2.3\%} \right) \]
Corrosion behavior and electrochemical measurement

An active metal can be protected from corrosion if it is coated with an anticorrosion barrier that prevents contact between the electrolyte and the metal. Figure 5(a) shows SEM images of graphene/Ni and bare Ni samples after they had been corroded in FeCl₃/HCl (1 M/1 M) for 5 min. For such a short immersing time, little change was observed in the morphology of the graphene/Ni sample because of the anticorrosion ability of graphene toward metal, whereas the morphology of bare Ni sample was extremely damaged. The Ni diameter was drastically reduced from 50 μm to less than 10 μm, and its surface showed considerable roughness. The hydrophobic and electrical conducting properties of a TG mesh were demonstrated by integrating it with a three-blue LED lamp circuit (Fig. 5(b)). The inset shows a magnified image of the TG mesh with a water droplet on its surface. The lamps were lighted brightly under a low voltage of 3 V. The TG mesh here served as a hydrophobic and electrical interconnect, which has high potential as an underwater conductor.²²

Figure 5(c) and (d) shows the difference in the Tafel polarization curves between the graphene/Ni and bare Ni samples obtained in basic (1 M KOH) and acidic (1 M HCl) environments, respectively. In both cases, the corrosion potentials of the graphene/Ni shifted toward more positive values compared to bare Ni.

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**Table 1** TG structure properties

| Samples            | Absorbance (%) | # of Layers | \(I_{2D}/I_{G}\) | Resistance (Ω/□) |
|--------------------|----------------|-------------|-------------------|------------------|
| TG-950 °C-1/1      | 47.4           | 10–11       | 0.37              | 48.1             |
| TG-950 °C-1/2      | 36.8           | 8           | 0.69              | 68.8             |
| TG-950 °C-1/4      | 29.9           | 6–7         | 0.76              | 74.0             |

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In addition, we studied the effect of the annealing time on the woven TGs. As shown in Fig. 4(d), the electrical sheet resistance of the TG-950 °C-1/1 mesh was in the range of 21–58 Ω/□, slightly dependent on the annealing time. The longer the annealing time was, the more graphene layers formed, consequently decreasing the electrical resistance.¹⁶
with those of the bare Ni, implying that the graphene/Ni samples effectively resisted the HCl and KOH corrosive environments.23, 24 In a 1 M KOH solution, the corrosion current density of a grown graphene sample was smaller than that of bare Ni, indicating that graphene has superior corrosion resistance in a basic environment. The anticorrosion mechanism of the graphene/Ni sample may have been due to the impermeability of the graphene. This type of graphene can serve as an excellent barrier against corrosion and against the diffusion of ions such as H+, OH−, and Cl−.

Conclusions

In summary, we developed a fabrication process for macroscopic TG. The number of graphene layers can be controlled by adjusting the processing parameters such as the initial CA quantity or annealing time. The TG architectures fabricated at an annealing temperature of 950 °C exhibited high graphitic crystallinity, strong electrical conductivity, and high corrosion resistance. The graphene grown through the proposed method can be an excellent anticorrosion barrier for Ni in both acidic and basic environments. High-quality graphene with well-controlled number of layers can be obtained on the basis of the fabrication parameters investigation.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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Supplementary material

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