Direct Growth of Hollow Carbon Nanorods on Porous Graphenic Carbon film without Catalysts

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Abstract

A method is developed for growing three-dimensional hierarchic structures of porous graphenic carbon film/ hollow carbon nanorods where porous graphenic carbon film is first synthesized followed by, growth of carbon nanorods. By annealing an amorphous carbon layer deposited underneath a nickel thin film at elevated temperatures, the porous graphenic carbon film forms on top via carbon diffusion and precipitation from the grain boundaries of the nickel film. The porosity of the graphenic carbon film is determined by the surface voids of the nickel film resulting from grain coalescence during annealing. Hollow carbon nanorods can then be grown on the pore edges of the porous graphenic carbon film by chemical vapor deposition without catalysts. It is speculated that the dangling bonds of the carbon atoms on the pore edges of the graphene layers might be responsible for the nucleation of the hollow carbon nanorods. The microstructures and growth mechanisms of both porous graphenic carbon film and hollow carbon nanorods are characterized and discussed in detail.

Keywords: Porous hollow carbon nano-rods, graphene layers, hollow carbon nano-rods, catalyst-free, three-dimensional nanostructure

Introduction

Since its discovery in 2004 [1], graphene has attracted increasing attention due to its prominent properties, such as high carrier mobility ($\sim 200,000 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$) [2], excellent thermal and electrical conductivity [3], great mechanical strength [4], as well as high surface area [5]. The sp^2 -hybridized carbon atoms in two-dimensional (2D) honeycomb lattices are capable of storing and shuttling electrons. Thereby, graphene has been considered for many applications. Carbon nanotubes (CNTs), one-dimensional (1D) graphene-derived materials, have similar properties. Therefore, combining 1D carbon nanotubes with 2D graphene into hybrid composites extends these properties to three dimensions. Three-dimensional (3D) carbon hierarchical nanostructures can be made with multiple functions for application in lithium batteries [6], hydrogen storage [7], and supercapacitors [8]. However, previously reported growth methods for 3D carbon nanostructures incorporating CNTs on graphene catalysts, which are contaminants that are difficult to remove, causing difficulties in further device applications [9, 10]. Besides, Niu et al. have been reported that the CNT-graphene composites jointed with metal catalysts will degrade mechanical properties by simulation, and thus, it is highly desirable to synthesize the composites with seamless junctions, only composed of C-C sp^2 hybrid bonds [11].

CNTs have been grown on other carbon derivatives without catalysts. For Takagi et al. grew CNTs on nanodiamond particles, which acted as growth seeds [12]. They proposed a vapor-solid surface-solid (VSSS) growth mechanism, analogous to homoepitaxial diamond growth, in which hydrogen-terminated carbon atoms with sp^3 bonds are inhibited and changed to sp^2 bonds for the growth of CNTs. It has also been reported that multi-walled carbon nanotubes (MWCNTs) can be grown directly on defective graphite surfaces when subjected to oxidation, acid treatment, and laser ablation [13]. These studies prove that catalysts, either metallic or nonmetallic, are unnecessary for CNT growth. Therefore, the present study shows the viability of growing MWCNTs directly from the pore edges of porous graphene to form a MWCNTs/porous graphene 3D hybrid nanostructure without catalysts.

The synthesis of porous graphene has been achieved using polymer building plasma, electron bombardment, photo-etching, the template method, and chemical etching [14]. These methods usually involve a series of complicated but trivial processes. For example, porous graphene can be synthesized by preparing a template by etching, placing the template on top of graphene, and then applying oxygen. In contrast, the present study develops a facile synthesis method for growing porous

graphene with tunable porosity in one step.

In this work, we attempted to grow MWCNTs on multilayer graphene without catalysts. The results show successful growth of hollow carbon nanorods (HCNs) on porous graphenic carbon film to form a 3D hierarchic nanostructure, where the porous graphenic carbon film is so called because the as-grown product is characterized by more than 10 graphene layers in an extended 2D form with porous features with reference to [15]. The porous graphenic carbon film is made of multilayers to enhance mechanical strength (a single layer of porous graphene tends to break apart). The porous graphenic carbon film and hollow carbon nanorods are both characterized with their growth mechanisms discussed in detail. The obtained clean 3D all-carbon nanostructures have a large effective surface area, making them attractive for many applications.

Experimental procedure

The methods for the synthesis of porous graphenic carbon film and HCNs/porous graphenic carbon film 3D hybrid nanostructures are shown in Fig. 1. First, 3-nm-thick carbon and 300-nm-thick nickel thin films were deposited sequentially on a SiO₂ substrate by sputtering (Fig. 1a). The SiO₂ layer (about 500 nm thick) was grown on a silicon wafer by thermal oxidation to act as a nickel diffusion barrier. Subsequently, the sample was loaded into a vacuum quartz (10⁻⁶ Torr) tube and heated rapidly to 950 °C for 10 minutes. Finally, the sample was placed in a low-temperature zone to quench it quickly to room temperature. During annealing, carbon atoms diffuse through the nickel thin film all the way to the surface, and then precipitate on the surface from the grains and grain boundaries of the nickel film as graphenic carbon film during quenching [16], as shown in Fig. 1b. The calculated diffusion rate of carbon atoms at 725 °C is about 1.2 μm per second [17], so the carbon atoms are redistributed over the entire 300-nm-thick nickel film and segregate on the surface through the grain boundaries, as shown in Fig. 1b. Upon annealing at high temperature, large grains grow at the expense of small grains, resulting from Ostwald ripening, leading to void formation in the nickel film, making the film porous. This porous nickel thin film can not only act as catalysts, but a template for the subsequent growth of porous graphenic carbon film. Therefore, the as-grown graphenic carbon film also exhibits porous characteristics (Fig. 1c). For microstructure characterization, the porous graphenic carbon film was transferred to a transmission electron microscopy (TEM) grid or SiO₂ substrate (Fig. 1d). The transfer process is as follows. The sample was first immersed in hydrogen chloride for one day to etch away the porous nickel thin film. Then, the hydrogen chloride was soaked out carefully to avoid graphenic carbon film damage, and the remaining hydrogen chloride was

1 diluted with distilled water several times. The graphenic carbon film was kept floating
 2 in water for half a day to minimize the residue of hydrogen chloride. The film was
 3 then lifted off with the target substrate. This method does not use a photoresist, which
 4 leaves behind some organic contaminations [18].

5 For the growth of HCNs, porous graphenic carbon film with the substrate was
 6 placed in a quartz tube and heated to 850 °C after the tube had been pumped down to
 7 a pressure of 10^{-2} Torr. Meanwhile, a mixed gas of ethylene and helium (9:1) was
 8 injected into the quartz tube at a rate of 40 ml/min. After growth for 30 minutes, the
 9 sample was cooled to room temperature by pure helium. The morphology, bonding
 10 configuration, and microstructure of samples were characterized by a scanning
 11 electron microscope (SEM, Hitachi SU-8000) equipped with a scanning transmission
 12 detector, a micro-Raman spectroscopy (Jobin Yvon, Labram HR) with a 514-nm
 13 wavelength laser, and TEM (JEOL 2100F), respectively.

14 **Results and discussion**

15 **1. Growth of porous graphene**

16 The structure evolution of the carbon/nickel thin film stack upon annealing was
 17 examined. The XRD patterns and Raman spectra are shown in Fig. 2a and 2b,
 18 respectively. After annealing, the (111) peak of face-centered cubic phase in Fig. 2a
 19 becomes prominent, suggesting that the nickel film transforms from probably
 20 nanocrystalline to textured crystalline. Figure 2b shows that the amorphous carbon
 21 transforms to crystalline graphenic carbon film, as evidenced by three characteristic
 22 peaks at ~ 1350 , ~ 1580 , and ~ 2700 cm^{-1} , corresponding to the D-, G-, and 2D-bands,
 23 respectively. The D-band indicates that there are some non-graphitic carbons and
 24 disordered structural defects, such as graphene edges and grain boundaries, and the
 25 G-band represents the in-plane vibrational mode of sp^2 hybridized carbon atoms. The
 26 2D-band results from the double resonance of hexagonal lattices in the Raman process,
 27 and its shape, width, and position are related to the stacking and number of graphene
 28 layers. In contrast, the Raman spectrum of amorphous carbon shows a broad band, a
 29 mixture of D- and G-band in the absence of 2D-band for not having long-range order.
 30 In addition, the as-synthesized porous graphenic carbon film is characterized by a
 31 domain size of approximately 25 nm [19], calculated as the ratio of D- to G-bands,
 32 and has multilayers, as evidenced by the intensity of the 2D-band being lower than
 33 that of the G-band and the full width at half maximum being larger than that of
 34 single-layer graphene. The porous graphenic carbon thim is turbostratic multilayer
 35 graphene stacking instead of single-layer graphene[20].

36 The SEM images in Fig. 3 further explore the morphology evolution of the film
 37 stack after annealing. Figure 3a clearly shows numerous pores developing in the
 38

as-grown graphene, resulting from the diffusion of the 3-nm-thick carbon film through the 300-nm-thick nickel film followed by precipitation. The close-up image in Fig. 3b shows the crystallization of the nickel film with a grain size of $\sim 1.5 \mu\text{m}$. Although graphenic carbon film almost covers the porous nickel film, few areas lack film cover. Figure 3b shows an example of this, where the brighter area in the center region represents no graphenic carbon film cover. The porosity of graphenic carbon film is retained after the film is transferred onto a TEM lacy grid, as shown in Fig. 3c. By operating the transmission mode in SEM, it can be observed that the size of pores is less than $1 \mu\text{m}$ and that the thickness of graphenic carbon film is non-uniform, as evidenced by the varying contrast (Fig. 3d) [21, 22]. The number of graphene layers was confirmed by high-resolution TEM (HR-TEM). Figures 4a, b, and c, taken from three different sites, and their corresponding selected area electron diffraction (SAED) patterns in the insets reveal that the numbers of layers are 1, 2, and 16, respectively. The graphenic carbon film has turbostratic stacking instead of AB stacking since the diffraction spots arise from independent hexagons for both 16- and 2-layer graphene, which is consistent with the Raman spectra.

During annealing, the 3-nm-thick carbon film can almost dissolve into the 300-nm-thick nickel film since the carbon solubility in nickel at 1000°C is about ~ 1 at%, as obtained from the Ni-C phase diagram [17]. During quenching, some carbon becomes trapped inside the nickel film, making the thickness of the as-grown graphenic carbon film less than 9 layers on average, which is in accordance with the TEM results.

2. Growth of hybrid nanostructure of HCNs/porous graphenic carbon film

Figure 5a shows a SEM image of HCNs grown on porous graphenic carbon film being transferred onto a SiO_2 substrate. The HCNs emerge apparently in clusters distributed around pores, with some HCNs still discernible, such as the area marked by the white circle. However, this sample is impossible to be analyzed further by TEM to gain in depth characterization of the interfaces owing to the difficulty involved in transferring this hybrid nanostructure successfully. Therefore, on another run, HCNs were grown on porous graphenic carbon film being transferred onto a TEM grid. Figure 5b shows the obtained SEM image taken in transmission mode. Some areas were broken after HCNs growth resulting from the mismatch in the thermal expansion coefficient between the porous graphenic carbon film and the TEM Cu grid. Nevertheless, bundles of HCNs grown along pore edges, as indicated by the white ovals in Fig. 5b, are clearly visible, with much higher density than those grown elsewhere, as exemplified by the white square. Figure 5c is an enlarged image of the curved carbon nanorods growing out of the pore edges of graphene layers. Not only

curved carbon nanorods but also straight ones grow on the edges of graphene layers, as indicated in Figure 5d, which shows that the curved carbon nanorods are solid. Two HCNs grown on pore edges were further analyzed by TEM, as shown in Fig. 6a and 6d, where no metal catalysts are observed on the tip or root of the HCNs. For the two HCNs in Fig. 6a and 6d, HR-TEM images showing the interface region are shown in Fig. 6b and 6e, and those of the top of the HCN body are shown in Fig. 6c and 6f, respectively. These images indicate that the HCNs have a diameter of 40 nm. Figures 6b and 6e reveal that the lattice fringes of the HCNs join directly with those of graphene layers. The SAED pattern of the HCN shown in the inset of Fig. 6c displays (0002) spots and (10-10) and (11-20) rings, indicating different chiralities among various shells of the HCN. Besides, the SAED pattern in the inset of Fig. 6d taken from the graphenic carbon film after the growth of HCNs nearby the pore edge displays the 10-10 and 11-20 rings, indicating the graphene layer has grown thicker with crystallinity deteriorated to be highly polycrystalline. We speculate that through the edges of pores of the porous graphenic carbon film, not only HCNs but also extra irregular carbon layers are deposited on top.

It is also worth mentioning that the major difference between this work and the work of Lin et al. is the type of the substrate. In the report of Lin et al. [13], they used chemical modified graphite and laser-damaged graphite as the substrate, by which more carboxyl and hydroxyl functional groups may form randomly on the substrate. Contrarily, since the substrate in this work as porous graphenic carbon film was synthesized by solid state diffusion in vacuum, carbon dangling bonds are possible to form at the edges of pores, which would become available as the nucleation sites in the subsequent growth for the growth of HCNs or CNTs at elevated temperature under reactive conditions. Furthermore, due to the presence of different types of carbon residues left on different typed substrate, the chemical-modified graphite tends to induce the growth of multi-walled carbon nanotubes, whereas the porous graphenic carbon film favors for the growth of crystalline hollow and solid carbon nanorods. Finally, the bulk graphite as the substrate in the report of Lin et al., is too thick to be analyzed by TEM. However, the thin film substrate employed in our work offers the opportunity to investigate the microstructure evolution of the substrate before and after the growth of HCNs by TEM.

Unlike the case in the report of Zhu et al., where defects such as seven-membered rings are required to grow MWCNTs on a plain graphene surface [9], the aromatic rings on the edges of graphene layers, characterized by many dangling bonds, allow for carbon atoms to attach directly to form HCNs without the assistance of catalysts or imperfect rings [23]. Even if the carbon atoms on the edges are hydrogen-terminated, they are still energetically favorable for the adhesion of carbon atoms, as mentioned in

the VSSS growth mechanism [12]. It has been reported that the hydrogen-terminated carbon atoms that form hydrocarbons can be decomposed thermocatalytically [24]. Accordingly, the growth mechanism of HCNs on porous graphenic carbon film sketched in Fig. 7 is proposed with a simplified model of less number of layers in graphene and walls in HCN for clarity. As shown in Fig. 7a, high-temperature growth might result in some aromatic rings with defects extruding on the pore edges or some graphene nanoribbons (GNRs) being split but still connected to the original graphene layers, which act as energetically favorable nucleation sites for the growth of HCNs. Upon further growth of HCNs, as shown in Fig. 7b, some radical species attach onto these sites to extend the length of graphene GNRs, allowing them to twist helically and transform into tubular structures. The radical species, such as carbon atoms, carbon dimers, and trimers, are decomposed thermally from ethylene gas at 850 °C. Afterwards, the radical species continue to attach onto the tubular structure and extend the length of HCNs, as shown in Fig. 7c. In addition, HCNs can be formed directly from multilayer graphene via this route, as shown on by left HCN in Fig. 7c for bi-layer graphene and double-walled HCN as an example. The HCNs may contain pentagon-heptagon defect pairs, which account for the bending of the HCNs [25] shown in Fig. 5. Without catalysts, the walls of the HCNs are likely to be composed of imperfect rings, such as pentagon-heptagon defect pairs and point defects, which act as the nucleation sites for the growth of extra walls, as illustrated by the right HCN in Fig. 7c. The walls of HCNs are thus thicker than the graphene layers, as evidenced by the HR-TEM images in Fig. 6.

Conclusion

In this work, porous graphenic carbon film was synthesized by a facile method of annealing a carbon/nickel stacked thin film. The nickel thin film acts as a catalyst for the growth of graphene layers and as a template for the formation of porous graphenic carbon film due to the coalescence of nickel grains. The porous graphenic carbon film has multilayers with turbostratic stacking, where the layer number can range from 2 to 16. The domain size of the porous graphenic carbon film is about 25 nm. Furthermore, HCNs can be grown on the porous graphenic carbon film without catalysts to create hybrid nanostructures. The diameter of the HCNs is about 40 nm. The density of HCNs growing on the pore edges is higher than those growing on the plain surface of porous graphenic carbon film, implying that the pore edges of graphene layers can assist the growth of HCNs. The pore edges of porous graphene layers may have more dangling bonds for the growth of HCNs than those in the plain area. Because the growth occurs without catalysts, the imperfect walls of HCNs may contain pentagon-heptagon defect pairs and point defects, resulting in the bending and

broadening of HCNs. This 3D hybrid carbon-based nanostructure without catalysts may extend the application of 2D graphene-based devices.

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Figures:

Fig. 1. Synthesis scheme of porous graphenic carbon film and HCNs/porous graphenic carbon film. (a) Carbon/nickel thin film. (b) Diffusion of carbon atoms through grain boundaries in nickel thin film during annealing. (c) Formation of porous graphenic carbon film on top of nickel thin film. (d) Porous graphenic carbon film

- 1 lifted off nickel thin film. (e) Porous graphenic carbon film transfer onto SiO₂
- 2 substrate. (f) Growth of HCNs from pore edges of porous graphenic carbon film.

3
4 Fig. 2. (a) XRD patterns and (b) Raman spectra of carbon/nickel thin film before (blue
5 line) and after (red line) annealing, exhibiting grain growth of Ni film and formation
6 of graphenic carbon film, respectively.

Fig. 3. SEM images showing formation of porous graphenic carbon film upon annealing. (a) As-annealed thin film showing some pores in Ni film. (b) High-magnification image of as-annealed thin film revealing formation of graphenic carbon film on nickel film. (c) Graphenic carbon film transferred onto a lacy TEM grid showing pores. (d) SEM image in transmission mode of graphenic carbon film showing multilayer characteristics.

Fig. 4. TEM bright-field images of porous graphenic carbon film taken at three pore edges with corresponding SAED patterns shown in insets, showing (a) 1, (b) 2, and (c) 16 layers.

Fig. 5. SEM (a) secondary electron image and (b) transmission electron image of HCNs grown on porous graphenic carbon film transferred onto SiO_2 substrate. White

circle in (a) indicates example of HCNs grown on pore edge. Two white ovals in (b)
 indicate bunches of HCNs grown on pore edges. White square indicates no HCNs
 grown on plain area of graphene layers. (c) TEM image of curved carbon nanorods. (d)
TEM image at higher magnification showing curved solid carbon nanorods and
straight HCN, grown around pores of graphenic carbon layer.

Fig. 6. TEM analysis of two typical HCNs grown from pore edges of porous graphenic carbon film. (a) and (d) Bright field images of HCNs (b) and (e) HR-TEM images of roots of HCNs in (a) and (d), respectively, with inset in (d) showing the corresponding SAED pattern of the graphenic carbon film after the growth of HCNs. (c) and (f) HR-TEM images of tips of HCNs in (a) and (d), respectively, with inset in (c) showing corresponding SAED pattern.

Fig. 7. Schematic of proposed growth mechanism for HCNs growing on pore edges of graphene layers. (a) Atomic structure of pore edges comprising protruded hexagonal lattices with possibly dangling bonds and split graphene nanoribbon. (b) Carbon radicals decomposed from precursors attaching onto aforementioned features in (a), acting as nucleation sites. Hanging graphene nanoribbon might curl to form tubular structure. (c) Carbon radicals continue to attach onto graphene nanoribbon and extend length of tubular structure. Double-layer graphene film on left shows how HCNs can be formed by twisting multilayer graphene, where black arrows indicate pentagon-heptagon defect pairs, resulting in HCN bending. Red arrow on HCN on right side indicates dangling bonds on wall, which further widens HCN.