

Area-selective growth of amorphous carbon nanofibers *via* catalytic decomposition of polyimide thin film†

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A dense layer of amorphous carbon nanofibers was fabricated by pyrolyzing a thin film of polyimide using a monolayer of gold nanoparticles as a catalyst.

Although carbon nanotubes (CNTs) have become one of the most important nanoscale materials due to their technological importance in microelectronics,¹ carbon nanofibers (CNFs) with diameters of ~100 nm have attracted considerable interest. Envisioned applications for CNFs range from field emission devices,² biosensors and bioprobes,³ and optical antennas,⁴ to filter media.⁵ CNFs with different morphology and structure have been fabricated by several different methods: arc discharge, laser ablation, pyrolysis, and catalytic decomposition of hydrocarbons.⁶

In this study, we propose a unique method of fabricating CNFs without complicated equipment and in large quantity based on decomposition of a polyimide (PI) in thin film form with a monolayer of Au nanoparticles as a catalyst. Although Au nanoparticles have been previously utilized in the synthesis of CNTs, Au nanoparticles were chemically prepared in a separate process and loaded onto the substrate,⁷ which makes the process difficult to reproduce on a large scale. In our previous research, a well-dispersed monolayer of Au nanoparticles was produced on a PI thin film during imidization of the PI precursor.⁸ The proposed method involves a heat treatment of the Au particles/PI stack at 1000 °C, making the proposed process simple and cost-effective. Moreover, this process also allows growth of CNFs over a large area with high spatial selectivity by lithographing the initially deposited Au film.

A monolayer of Au nanoparticles dispersed on a PI film was produced by thermally imidizing the PI precursor with a thin layer of Au deposited on its top surface. The PI precursor was *p*-phenylene biphenyltetracarboximide type polyamic acid (Dupont, PI2610D) dissolved in *N*-methyl-2-pyrrolidinone (NMP). The polyamic acid solution was spin coated onto the Si substrate at 3000 rpm. The final cured PI thickness was controlled by varying the PI precursor/solvent ratio. The fully cured PI thickness was 7 nm on adjusting the precursor/solvent ratio to 1 : 15 by weight. The spin coated PI precursor was soft-baked at 135 °C for 30 min in order to evaporate the solvent. A 4 nm-thick Au layer was deposited onto the PI precursor-coated substrate using a thermal evaporator. The Au/PI/Si sample was fully cured at 400 °C for 1 h in vacuum (~10⁻³ Pa). The imidized film stack

was further treated by thermal annealing at 800 °C for 1 h under vacuum (<10⁻³ Pa), followed by another heat-treatment step at 1000 °C for 1 h under Ar atmosphere. Transmission and scanning electron microscopy (TEM and SEM) were used to characterize the CNF morphology. Raman spectroscopy was carried out using the 514.5 nm line of an Ar⁺ laser as the excitation source.

The formation mechanism for the monolayer of Au nanoparticles on top of a PI film is expected to be similar to that of the embedded sample described earlier.⁸ The as-deposited Au layer formed an island-like structure due to the limited wettability of Au on the PI precursor surface. During thermal imidization, the Au islands rearranged to form uniform-sized Au nanoparticles (average size = 7.2 ± 3.1 nm, areal density = 39.2%), uniformly dispersed on the PI film while maintaining the monolayer configuration. Then the Au nanoparticle/PI film was further heat-treated at 800 °C. Fig. 1 shows a typical plan view TEM image of the Au nanoparticles after annealing in two steps: 400 °C and 800 °C. After annealing at 800 °C, the average particle size slightly increased to 7.9 ± 2.0 nm due to coarsening, but the size distribution, on the other hand, further tightened due to the consumption of smaller-sized particles. However, the particle shape and areal density (38.8%) remained more or less unchanged. This limited change in particle size and shape after annealing at an elevated temperature was confined to the Au particles. When Co or Fe (typical catalysts for growth of CNT and CNF) was used in place of Au on the PI film, we observed large irregular shaped islands of Co or Fe which no longer maintained the monolayer configuration when annealed at 800 °C. The widely discrepant post-annealed microstructure could be attributed to the minimal chemical reactivity of inert Au with the PI film. In contrast to inert Au, Co or Fe catalyzed decomposition of the PI film even at 700 °C and led to local graphitization of the PI film around highly coarsened catalyst particles without developing any fiber-like structures.^{9,10} The intermediate annealing step at 800 °C prior to

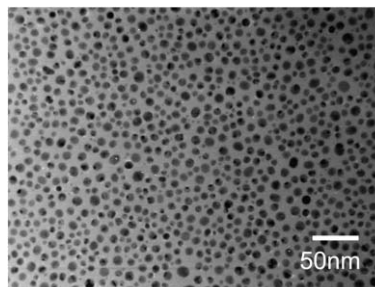


Fig. 1 Plan view TEM image of the Au nanoparticles after annealing in two steps: 400 °C and 800 °C.

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carbonization of the PI film was necessary to ensure uniform growth of the CNFs over the sample surface. Without the intermediate annealing step, non-uniform spatial distribution of the CNFs was observed for direct carbonization at 1000 °C due to excessive growth of Au particles and depletion of Au from the surrounding region.

Fig. 2(a) shows a SEM image of CNFs grown by treating the two-step annealed sample at 1000 °C for 1 h in Ar atmosphere. A dense layer of uniformly distributed CNFs was formed over the entire sample surface. The magnified SEM image in Fig. 2(b) indicates that the CNFs have diameters ranging from 20 nm to 80 nm. Although a thick PI film has been previously converted to a graphite film by heat-treatment at 1600 °C with Ni particles as catalyst,¹¹ growth of CNFs from pyrolysis of a PI thin film has not been previously observed to the best of our knowledge. We believe the monolayer configuration of nano-sized Au particles is essential in promoting the growth of the fiber structure. It is conjectured that carbonization occurred preferentially around the periphery of the Au nanoparticles which, in turn, acted as heterogeneous nucleation sites for further growth into a fiber, similar to the catalyst-assisted CVD growth model of a CNT.¹² In fact, the TEM image of the CNFs shown in Fig. 3(a) indicates that the ends of the CNF were terminated by Au nanoparticles as observed in CNTs.¹³ Among CNFs, we also observed growth of Au nanowires within a single CNF as shown in Fig. 3(b). In contrast to the previously reported CNFs,¹⁴ our CNFs grown using Au particles were amorphous, as evidenced by uniform contrast (*i.e.* no diffraction contrast) along the fiber as can be seen in Fig. 3(c), and confirmed by high-resolution TEM (HRTEM). Some degree of crystallinity was, however, observed from inverse Fourier transform of a HRTEM image, shown in Fig. 3(c) as an inset. The inverse Fourier indicates that the (002) planes are preferentially aligned along the fiber direction, suggesting that the CNFs are likely in a semi-crystalline state. A cross-sectional TEM image in Fig. 3(d) shows that the CNF layer extends up to ~1 μm from the Si substrate and the CNFs are well anchored onto the substrate. SEM images in Fig. 4(a) and (b) provide conclusive evidence that the presence of the Au nanoparticles is essential to the formation of CNFs during pyrolysis of the PI film. Using a metal shadow mask, patterns covered with Au nanoparticles were formed and heat-treated in steps to fabricate the CNFs. The region without the Au nanoparticles did not exhibit any growth of CNFs whereas the region with the Au nanoparticles was completely covered with CNFs. As can be seen from Fig. 4(b), the boundary between the masked and unmasked areas was quite sharp except from the fibers extending into the masked region. This high spatial

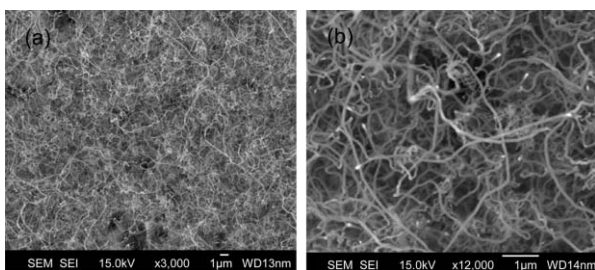


Fig. 2 (a) SEM image of the CNFs grown by heat-treating the sample at 1000 °C for 1 h in Ar; (b) magnified SEM image of sample in (a).

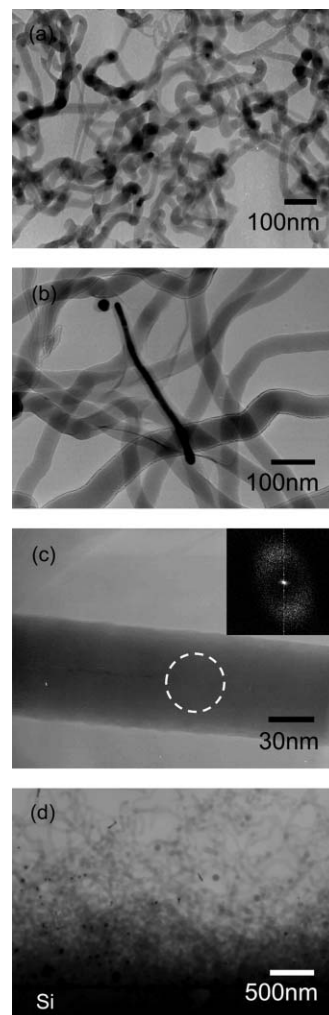


Fig. 3 (a) Plan view TEM image of the CNFs, (b) TEM image of a CNF containing a Au nanowire, (c) TEM image of a single CNF with inverse Fourier transform of the circled region in the inset, (d) cross-sectional TEM image of the CNF layer.

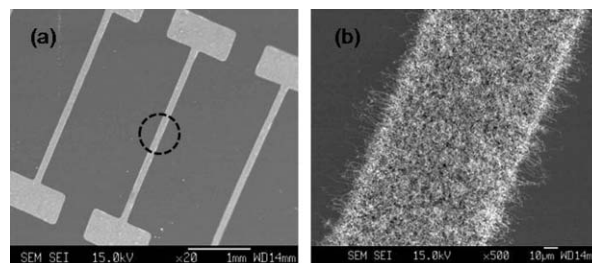


Fig. 4 (a) SEM image of the patterned CNF layer by selectively growing the Au nanoparticles on the PI film; (b) magnified SEM image of the circled region in (a).

selectivity would allow one to grow a dense layer of carbon fibers in a confined area by lithographing the initial Au layer.

Fig. 5 shows Raman spectra obtained from the samples pyrolyzed with and without the Au particles. The Raman spectrum from the CNFs exhibited two main peaks centered at 1350 cm^{-1} (D peak) and 1600 cm^{-1} (G peak), which are typically observed in carbon nanotubes and nanocrystalline graphite whereas the

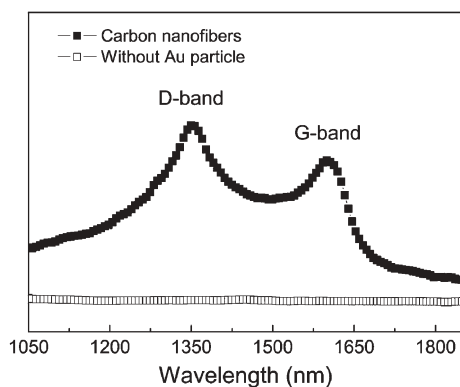


Fig. 5 Raman spectra obtained from the samples pyrolyzed with and without the Au particles.

spectrum from the sample annealed in Ar without the Au nanoparticles was nearly flat and no peaks related to carbon could be detected. Judging from the Raman spectra, it appears that when the PI film was annealed at 1000 °C in Ar atmosphere, the PI film was completely removed from the substrate. The Raman results lead to the conclusion that the Au nanoparticles promoted growth of a fiber structure while suppressing the burnout of the PI film in Ar.

It was demonstrated that a dense layer of CNFs can be fabricated by simply heat-treating a thin film of PI in Ar atmosphere, in presence of a well-dispersed monolayer of Au nanoparticles. The monolayer of Au particles acted as nucleation sites for growth of the CNFs while suppressing excessive burnout of the PI film during heat-treatment at 1000 °C. In addition, the CNF layer can be grown with high spatial selectivity by lithographing the initially deposited Au film. Potential applications

for the CNFs include nanocatalyst arrays and templates for synthesizing a variety of other nano-structures.

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