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Template-directed growth of nanostructures

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The controlled growth and alignment of carbon nanotubes and peptide nanoarrays offers new avenues for nanodevice fabrication.

Creating intricate nanoelectronic devices requires the precise patterning of carbon nanotube (CNT) arrays. However, creating such complex and carefully aligned structures at nanometer scales is a difficult challenge for researchers. One fabrication approach that has attracted tremendous interest is the use of templates to control the growth patterns of nanomaterials.^{1–3} These templates consist of substrates on which a catalyst has been carefully patterned. Synthesis of the nanostructures is then performed on the substrate, which directs their growth and alignment.

A number of techniques, including microcontact printing, photolithography, e-beam lithography, and dip-pen nanolithography (DPN), have been used to generate such templates at both micron and nanometer scales. Among these techniques, DPN^{4,5} can precisely deliver catalyst materials to a specifically designated location to form any desired pattern with feature sizes as small as 100nm. DPN is an atomic force microscopy (AFM)-based technique with high resolution and registration capabilities. More important, DPN is a maskless and single-step method that can be performed without the need for high-vacuum, high-energy ions, or electron beams. Taking advantage of these characteristics, our group has been exploring novel routes for controlled growth of single-walled CNTs (SWCNTs) and peptide arrays.

We have developed a simple, efficient, and uniform AFM tip-coating method called scanning-coating⁶ that enables us to pattern nanoparticle (NP) arrays over a large area without recoating the tip. The coated tip can be used to generate cobalt (Co) NP dots with feature sizes of less than 70nm. Dots, lines, and even sophisticated patterns of Co NPs can be routinely generated and used as templates for controlled growth of CNTs. Figure 1(A) shows SWCNTs successfully grown on DPN-patterned Co catalyst dots positioned on silicon/silicon oxide (Si/SiO₂) substrates. Furthermore, we were able to direct the growth of

Figure 1. (A) AFM topographic image of SWCNTs grown on DPN-patterned Co NP catalyst dots positioned on Si/SiO₂. (B) Scanning electron microscope image of SWCNTs grown on DPN-patterned Co NP catalyst lines positioned on quartz.

SWCNTs on stable temperature-cut single-crystal quartz substrates along the [100] crystallographic direction: see Figure 1(B). In addition, DPN is capable of delivering Co NPs precisely to the desired location without contaminating other regions. This offers a convenient approach for observing the growth of SWCNTs, which has provided direct proof of the base-growth mechanism for SWCNT formation observed in our experiments.⁶

Although peptide patterns have been previously generated using DPN on various substrates, including gold,⁷ nickel, Si/SiO₂, and gallium arsenide, to the best of our knowledge, the in situ growth of peptide nanoarrays with carefully controlled chain lengths has not been reported. We have developed a novel route based on the combination of DPN and ring-opening polymerization (ROP) of tryptophan-*N*-carboxyanhydrides (Trp-NCAs) to generate peptide patterns on the nanometer scale.⁸ The uniqueness of this method is that the DPN-generated amine-terminated polyamidoamine (PAMAM) dendrimer nanoarray serves as the anchoring scaffold for in situ growth of the peptide array. This is achieved by immersing the patterned substrate in a Trp-NCA solution. Figure 2(A) shows the DPN-generated PAMAM dendrimer dot array on a Si/SiO₂ substrate. After a

Continued on next page

Figure 2. AFM topography images of (A) DPN-generated PAMAM dot array on Si/SiO_x, and (B) peptide dot array subsequently grown on (A) after a 6h ROP reaction.

6h ROP reaction, the height of the patterned dots was dramatically increased, indicating that the peptides successfully grew on the PAMAM dendrimers: see Figure 2(B). Importantly, the height (i.e., chain length) of the synthesized peptides can be controlled by varying the ROP reaction time and concentration of the Trp-NCA in solution.

In summary, we have developed novel routes for generating CNT and peptide nanopatterns on DPN-fabricated templates. The controlled patterning of CNTs provides new possibilities for making CNT-based electronics, and the controlled growth of peptide nanoarrays offers new avenues for developing biology-based applications, including the study of cell behaviors, such as adhesion, growth, and migration. We are optimizing the DPN parameters and CNT growth conditions so as to get more precise control of the density and even conductivity of CNTs. The study of cell behaviors on designed nanoarrays is ongoing in our group.

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