

## Synthesis of Aligned Single-Walled Nanotubes Using Catalysts Defined by Nanosphere Lithography

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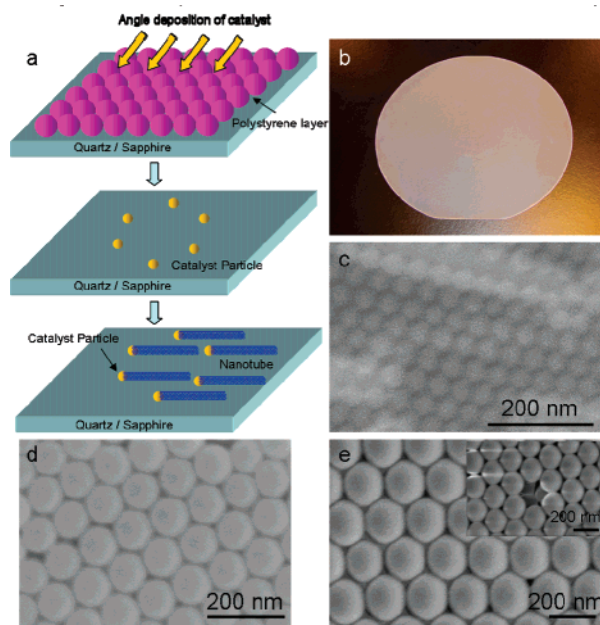
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Synthesis of highly aligned single-walled carbon nanotubes (SWNTs) with controlled positions is an important step toward manufacturable ultradense carbon nanotube integrated circuits. One of the most promising synthesis methods is chemical vapor deposition (CVD), in which small catalyst particles with diameters of approximately a few nanometers determine the position and diameter of SWNTs.<sup>1</sup> Significant advance has been made in the preparation of catalyst nanoparticles, including chemical synthesis and e-beam patterning.<sup>2</sup> In parallel, aligned nanotube growth has been achieved using sapphire<sup>3</sup> and quartz substrates<sup>4</sup> using randomly distributed ferritin or evaporated metal particles. Novel techniques that combine innovative catalyst preparation and aligned nanotube growth will be essential for further progress in the nanotube field.

Here we report the development of a nanosphere lithography (NSL) technique<sup>5</sup> for the preparation of catalyst nanoparticles for the synthesis of aligned single-walled carbon nanotubes on quartz. This technique, also known as colloidal crystal lithography for catalyst nanoparticles formation, uses close-packed monolayer or double layer of nanospheres as a shadow mask for metal evaporation, where the size and shape of resulting nanoparticles depend on (1) the size of template nanospheres, (2) incidence angle of metal evaporation, and (3) thickness of deposited metal layer. Previously, NSL utilized mostly large nanospheres (e.g., 895 nm in ref 6) and was shown to produce regular arrays of particles with uniform size (ca. several tens of nm) that have been successfully implemented to produce arrays of vertical nanowires<sup>6</sup> or multiwalled carbon nanotubes.<sup>7</sup> Packing of smaller nanospheres and synthesis of SWNTs has been achieved with the assistance of confinement defined by e-beam lithography,<sup>8</sup> which has the drawback of being a serial, slow, and expensive technique. In this paper we demonstrate that ordered arrays of nanospheres as small as 50, 100, and 200 nm can be obtained via a simple and reliable spin-coat technique, which subsequently led to highly ordered catalyst nanoparticles with narrow diameter distributions suitable for single-walled nanotube growth. In addition, we have combined photolithography and nanosphere lithography to gain simultaneous control over the packing and location of the nanospheres and catalysts. This technique has led to the successful synthesis of highly aligned and defect-free single-walled carbon nanotubes on quartz and sapphire, as revealed by scanning electron microscopy (SEM) and Raman characterization.

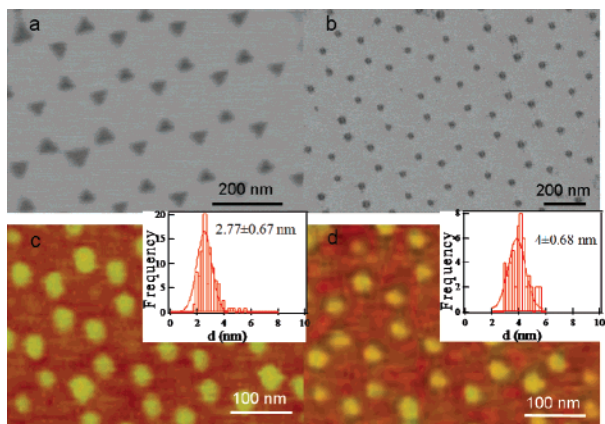
Figure 1a shows the schematic diagram of nanosphere lithography for aligned nanotube growth. Quartz or sapphire substrates were first cleaned in piranha ( $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2 = 3:1$ ) followed by base treatment ( $\text{H}_2\text{O}/\text{NH}_4\text{OH}/\text{H}_2\text{O}_2 = 5:1:1$ ) with sonication for 1 h to render the surface hydrophilic.<sup>5</sup> We subsequently optimized the recipe for the deposition and packing of polystyrene spheres by comparing different deposition techniques (spin-coat vs drop and drying), and using polystyrene from different vendors, of different sizes, and with different concentrations. The optimum packing has been achieved by spin coat of 200, 100, and 50 nm polystyrene



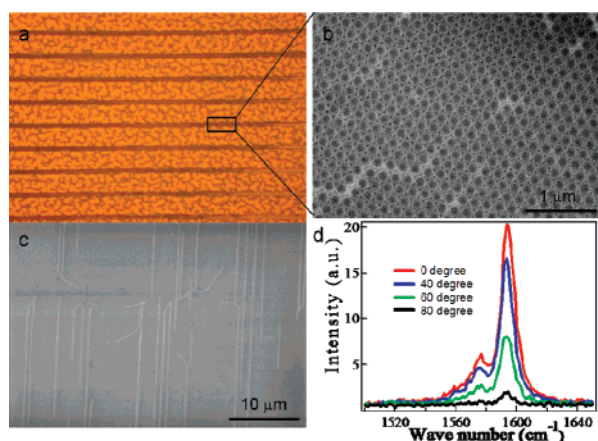
**Figure 1.** (a) Schematic diagram of nanosphere lithography for aligned nanotube growth; (b) photograph of a three-inch quartz wafer with spin-coated polystyrene nanospheres; (c–e) SEM images of ordered monolayers of 50, 100, and 200 nm polystyrene nanospheres, respectively; (e, inset) SEM image of an ordered bilayer of 200 nm nanospheres (The bottom layer is visible through the missing nanosphere in the top layer).

nanospheres (from Duke Scientific Co. and Alfa Aesar) at concentrations of 2%, 2%, and 1% and at spin rates of 4000, 4000, and 5000 rpm, respectively. This process resulted in the self-assembly of nanospheres into a close-packed monolayer or bilayer structures. Figure 1b shows the photograph of a three-inch quartz wafer with spin-coated 200 nm polystyrene nanospheres. Figure 1 panels c–e display the SEM images of highly ordered monolayers of 50, 100, and 200 nm, respectively, with domain size up to several  $\mu\text{m}^2$ . Figure 1e inset shows the SEM image of a 200 nm polystyrene bilayer structure. We note that our work represents significant extension of nanosphere lithography toward the deep submicrometer regime, as most previous work dealt with rather large nanospheres around several hundred nanometers.<sup>6–7</sup>

We subsequently deposited 5–10 Å of catalyst metal films made of Fe, Ni, or Co onto the substrates through the nanosphere shadow mask at either normal incidence or at controlled angles with respect to the substrate surface for fine-tuning of the catalyst size. The substrates coated with the catalyst metal films were then soaked into dichloromethane solution and sonicated for 3–5 min to remove nanospheres, leaving metal films deposited through the openings of the NSL mask on top of the substrate (Figure 2a). After annealing the substrates at 700–900 °C in  $\text{H}_2$  ambient for 10 min, the remaining metal films aggregated into spherical catalyst particles, as shown in Figure 2b. By assuming all volume of the metal film



**Figure 2.** (a, b) SEM images of catalyst arrays prepared using nanosphere lithography before and after annealing; (c, d) AFM images of catalyst arrays prepared with 3 and 5 Å Fe films deposited, respectively. Inset shows histograms of the catalyst particle size.



**Figure 3.** (a) Photograph of a quartz substrate with polystyrene nanospheres packed in stripe-shaped trenches patterned in photoresist; (b) SEM image of an ordered array of nanospheres inside the trench; (c) SEM image of aligned nanotubes grown from the catalyst prepared using NSL; (d) polarization-dependent Raman spectrum of a nanotube.

deposited through a single opening aggregates into a spherical particle, the diameter of these round catalyst particles can be estimated as  $D = 2(3 \times S(\alpha, \varphi) \times a^2 h / 16\pi)^{1/3}$ , where  $h$  is the thickness of metal film,  $a$  is the diameter of nanospheres, and  $S(\alpha, \varphi)$  is a geometrical factor depending on the angle of metal deposition.<sup>5</sup> Detailed calculation of the catalyst particle size can be found in the online Supporting Information (S1).

We note that this method offers many means to fine-tune the catalyst size, as the catalyst size can be precisely controlled by tuning the nanosphere size, the deposited metal film thickness, and the deposition angle (S2). Figure 2 panels c and d display the AFM images of catalyst particles prepared using monolayers of 100 nm nanospheres with 3 and 5 Å Fe films deposited, respectively. Histograms of the catalyst size determined by AFM are displayed in Figure 2c–d insets, revealing distributions of  $2.77 \pm 0.67$  and  $4 \pm 0.68$  nm, respectively. We have also prepared catalyst nanoparticles using packed bilayer nanosphere arrays, showing 3-fold triangular arrays (S3). Our results clearly reveal the potential of using NSL to prepare a highly ordered array of catalyst nanoparticles with controlled diameters.

We have further combined nanosphere lithography, photolithography, and growth on quartz/sapphire substrates for simultaneous control of the nanotube orientation and position. Figure 3a shows a quartz substrate spin-coated with 200 nm nanospheres packed in

stripe-shaped trenches in photoresist patterned by photolithography. Nearly perfect packing of the nanospheres with large domains ca.  $5 \mu\text{m} \times 5 \mu\text{m}$  was observed, as shown in Figure 3b, as a result of the confinement of the photoresist trenches. Following the catalyst deposition and removal of photoresist and nanospheres, we used chemical vapor deposition for the growth of SWNTs at 900 °C for 10 min under gas flows of  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ , and  $\text{H}_2$  controlled at 2000, 17, and 600 sccm, respectively. As shown in Figure 3c, very well-aligned nanotubes arrays were produced from the catalysts prepared using NSL, with lengths up to 100–200  $\mu\text{m}$  and diameters of  $1.8 \pm 1.0$  nm. We note that the yield of nanotubes still needs to be improved. Figure 3d shows the Raman spectrum of a typical SWNT with the excitation laser polarization direction tuned to various angles relative to the nanotube array orientation. One can clearly see a monotonic decrease in Raman response when the laser polarization was adjusted from parallel to orthogonal to the nanotube array, indicating the well-aligned nature of the nanotubes. In addition, negligible D-band was observed in the Raman spectrum (S4), confirming very clean and defect-free nanotubes were grown.

In summary, we have extended nanolithography into deep submicrometer regime to obtain packing of 50, 100, and 200 nm polystyrene nanospheres, which were then successfully employed to produce highly ordered catalyst nanoparticles with narrow size distributions. We have further combined NSL and photolithography to grow highly aligned single-walled carbon nanotubes atop quartz and sapphire substrates. This method has great potential to produce carbon nanotube arrays with simultaneous control over the nanotube orientation, position, density, diameter, and even chirality, which may work as building blocks for future nanoelectronics and ultra-high-speed electronics.

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**Supporting Information Available:** Detailed calculation of geometrical factor (S1) and nanoparticle size (S2), AFM images of catalysts prepared using bilayer 100 nm nanospheres (S3), and Raman spectrum showing the negligible D-band of nanotube and RBM mode (S4). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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