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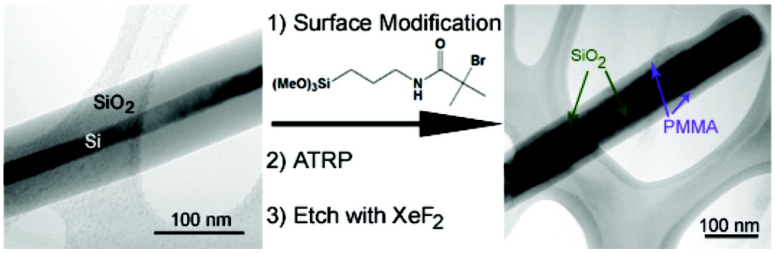

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Synthesis of Bifunctional Polymer Nanotubes from Silicon Nanowire Templates via Atom Transfer Radical Polymerization

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There currently exists an interest in nanostructured materials for various applications, including biotechnology,[1,2] battery technology,[3] and sensing technology,[2] each of which demands different chemical and physical properties. The realization of these devices will be dependent on the ability to modify and assemble nanoscale building blocks. Surface-initiated polymerization promises to be an important tool to further develop the chemical and physical properties of nanostructures, by providing a method to covalently attach polymer chains in a well-controlled fashion. Such modifications could tailor important properties, such as wetting and aggregation of the nanostructures. Controlled growth of polymer chains may also allow the addition of a dielectric layer of selectable thickness. Atom Transfer Radical Polymerization (ATRP) has been used to grow polymers from a variety of silica surfaces, including flat and spherical surfaces,[4,5] as well as in the pores of SBA-15.[6] Additionally, ATRP has been used to modify the surfaces of gold,[7] magnetic nanoparticles,[8] carbon nanotubes,[9] and CdS nanoparticles,[10] in each case, providing stability and/or other desirable surface properties.

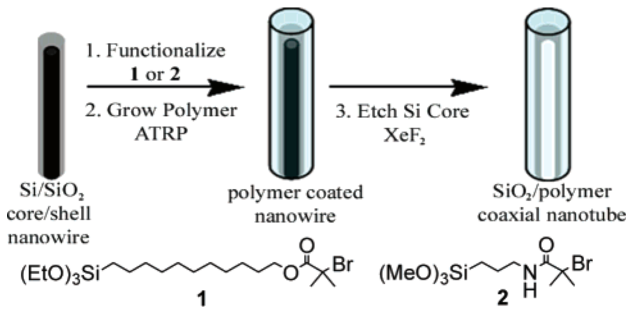
Here we present a method for obtaining a multifunctional material using procedures based on ATRP by growing polymers directly on silicon/silica core/shell nanowires. The template wires from these inorganic−organic hybrid structures can then be etched away to leave nanotubes which are open at one end and closed at the other.[11] As a result of our synthetic procedure, these nanotubes will have different functionality on the inner and outer surfaces, presenting a hydrophobic outer wall with a hydrophilic inner surface.

The synthesis of silicon[12] nanowire arrays was carried out using published procedures. Residual gold catalyst was removed by successive HF and KI/I$_2$ etching. A silica layer was then formed by thermally oxidizing the array under a flow of oxygen at 850 °C for 1−8 h. By varying the oxidation time, silica layers with different thicknesses can be obtained, thus providing a route to silica tubes with variable diameters.

Initiator **1** was synthesized from the condensation of 10-undecen-1-ol with 2-bromo-2-methyl-propionyl bromide, followed by hydrosilation with triethoxysilane and a platinum catalyst. While **1** is an effective surface initiator for ATRP, the hydrosilation reaction produced a mixture of compounds, which were separated distillation with a kugelrohr apparatus under vacuum at elevated temperatures. Initiator **2** was synthesized by the condensation of (3-aminopropyl)trimethoxysilane and 2-bromo-2-methyl-propionyl bromide. This one-step synthesis yields a clean product which can be used without purification.

Clean substrates were introduced to a 10 mM solution in toluene of surface initiator **1** or **2**. The reaction mixture was held at 80 °C overnight with gentle stirring, and the substrates were removed and rinsed thoroughly in toluene and 2-propanol. Modification of the surface was monitored using contact angle measurements. Before modification, the Si wire arrays have a contact angle of 60°; after modification with **1**, the array has a contact angle of 80°, while functionalization with **2** results in a contact angle of 85°. An even coating of initiator groups is assumed based on the conformal polymer layer obtained from these samples. Both cross-linked and non-cross-linked methacrylate polymers can be grown from the substrate surface. For example, using conditions similar to previous

Scheme 1



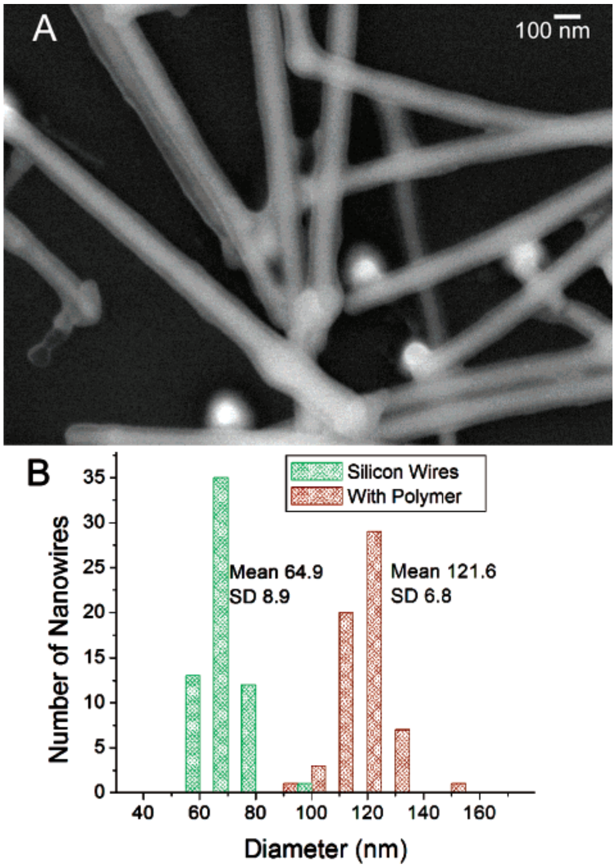


Figure 1. (A) SEM micrograph of silicon nanowires coated with PMMA. (B) Histogram of starting wire thickness compared with the thickness after polymerization. On average, the polymer thickness is 28 nm.

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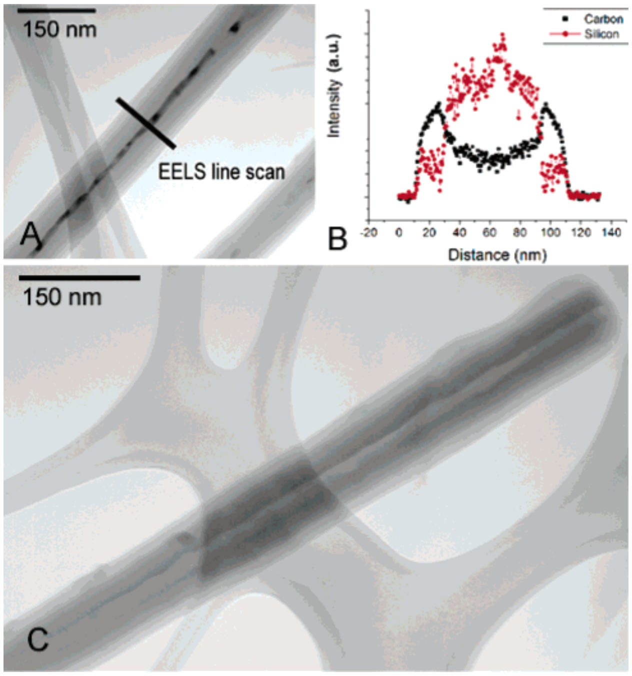

Figure 2. (A) TEM micrograph showing the modification of silicon/silica core/shell nanowires with PMMA. (B) Electron Energy Loss Spectrum taken using the nanoprobe scanning mode in a Philips CM200 TEM, showing the relative amounts of carbon and silicon present in the polymer-coated nanowire. (C) TEM micrograph of the resulting polymer-coated nanotubes after etching with XeF_2.

reports of surface initiated ATRP,[13−16] modified arrays of Si wires were immersed in a dioxane solution of CuBr, 4,4′-dinonylbipyridine, ethyl 2-bromo-2-methylpropionate, and methyl methacrylate under an inert atmosphere. The reaction was carried out for 48 h at 50 °C. The substrates were then soaked in acetone to remove any noncovalently attached polymer and any other contaminates. After polymerization, the contact angle increased to 100°. Size exclusion chromatography analysis of free polymer formed in the reaction solution indicated a well controlled polymerization (M_n = 217 713 g/mol, M_w = 232 331 g/mol, and PDI = 1.07).

SEM/TEM images show undamaged arrays, where 25−30 nm coating is visible on the surface of the wires. For methyl methacrylate, this layer is on average 28 nm thick (Figure 1). Initiators **1** and **2** gave indistinguishable results. Energy dispersive spectroscopy indicates the incorporation of carbon into the resulting structures. TEM analysis aids the determination of the polymer thickness and the visualization of the silicon core (Figure 2). This layer was further characterized by Electron Energy Loss Spectroscopy (EELS) to obtain line profiles of the polymer-coated structures. From the carbon trace, it is apparent that the polymer deposition has occurred selectively on the outside of the structure and is 25 nm thick (Figure 2).

Polymerizations were also performed in the absence of ethyl 2-bromo-2-methylpropionate, which served as a polymer initiator in the solution. By omitting the solution initiator, the use of cross-linking monomers becomes possible. Using the same catalyst, solvent, and temperature, the monomer ethylene glycol dimethacrylate yielded a 10 nm polymer coating in 12 h. Longer runs did not produce a thicker polymer layer. For comparison, methyl methacrylate was also polymerized in the absence of free initiator and was found to produce a 10 nm polymer layer in a similar amount of time. As previously demonstrated, presence of the free initiator in solution increases the concentration of deactivator, giving a more controlled polymerization.[4]

To obtain tubes, the Si cores were etched from samples with grafted poly(methyl methacrylate) using XeF_2 (20 cycles, 60 s/cycle) giving polymer nanotubes supported on silicon oxide. The polymer layer makes the outer surface of these tubes hydrophobic, while the SiO_2 on the inner surface is hydrophilic (Figure 2c).

In summary, we have demonstrated a simple method to produce coaxial polymer/silica tube structures. This general method is currently being extended to other polymers and other inorganic templates to realize a wide range of hybrid materials with controllable surface chemistry. Additionally, we have begun work to selectively functionalize the interior of these tube structures using the same silane chemistry used to anchor the ATRP initiators on the outside of the Si/SiO_2 structures. We expect this work to yield a wide variety of multifunctional nanostructures for nanofluidic applications.[17,18]

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Supporting Information Available: A copy of the experimental procedures used for the synthesis and characterization of all initiators, polymers, and hybrid structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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