

Selective Functionalization of Arbitrary Nanowires

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ABSTRACT

We report the selective functionalization of uniform and heterostructured nanowires with self-assembled monolayers (SAMs) of (3-mercaptopropyl)-trimethoxysilane (MPTMS). The wires were grown electrochemically in anodic aluminum oxide (AAO) templates. Selective deposition and removal of SAMs during nanowire growth permits the decoration of specific regions of the surface along the length of the nanowires. This technique presents a facile method for the tailored functionalization of nanowires, but does not rely on the intrinsic chemical properties of the nanowires as previous methods have.

The development and fabrication of DNA structured nanoscale scaffolds for the controlled placement of nanoscale devices and other molecules has received significant attention over the past few years. One technique permits full addressability at eight or 16 individual grid points,^{1,2} and others provide the possibility of attaching molecules such as Au nanoparticles to one or two possible hybridization sites.^{3,4} Recently, Rothmund has even devised a method for fabricating structures of arbitrary complexity.⁵ Although much-needed attention has been invested in the construction of these scaffolds, far less has been devoted toward providing similar levels of addressability for the devices and molecules that are envisioned to be connected to them. Comparable levels of addressability on both the scaffolds and the attached devices could conceivably present unprecedented levels of control and flexibility for future architectures.

In recent years, a large variety of nanoscale devices have emerged as candidates for fundamental elements in future nanoscale computational systems. Among these candidates are carbon nanotubes⁶ and nanowires constructed from various materials.^{7–9} Device construction schemes that make use of templates are particularly attractive as they not only provide control over the physical dimensions of the devices

but can also serve as masks for the subsequent selective functionalization of various regions of the devices fabricated within.¹⁰ In the past, templates composed of polycarbonate track-etched membranes or anodic aluminum oxide materials have been used for the construction of heterostructured nanowires composed of various materials. The nanowires constructed within the templates are obtained through the electrochemical reduction of metal ions from solution by either using multiple plating baths to deposit sequential segments of different metals¹¹ or a single plating solution containing multiple types of metallic ions with differing reduction potentials.¹² The selectivity that these multiple material structures have toward different chemical groups has been used to bind distinct molecular monolayers to specific regions of the nanowires.^{13,14} Other methods employ similar deposition routes and sacrificial layers to create pristine surfaces suitable for functionalization by other monolayers.

Herein we report a novel functionalization scheme that permits the selective deposition of molecular monolayers at arbitrary regions along the length of nanowires deposited within AAO templates, which is demonstrated for both heterostructured and single-material nanowires. Self-assembled monolayers of MPTMS are adsorbed to and removed from the inner pores of the AAO template during the deposition of the nanowires to define chemically modified (or unmodified) regions along the surfaces of the nanowires. The unmodified regions are available for subsequent functionalization, while the modified regions are protected with

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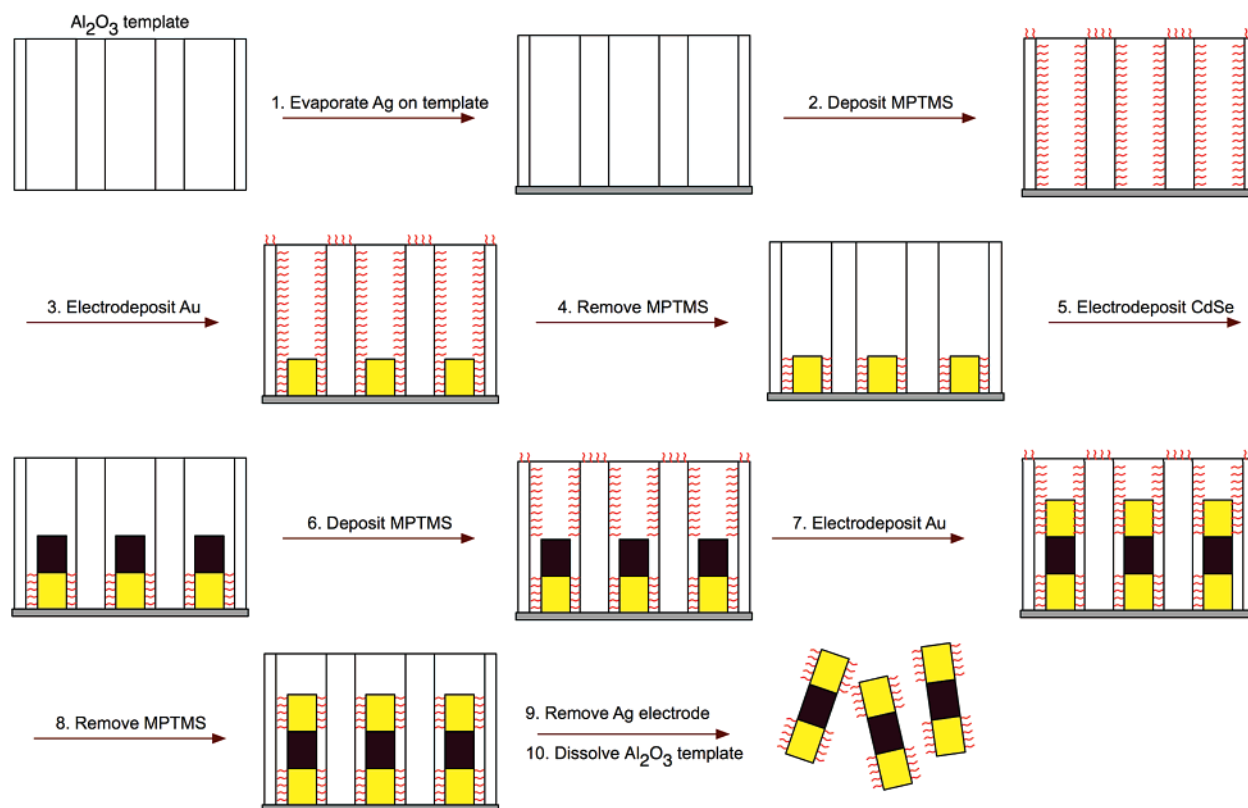


Figure 1. Preparation of selectively functionalized heterostructured nanowires. (1) Ag is evaporated onto the AAO template. (2) The template is coated with MPTMS through a vapor-phase reaction. (3) Au is electrodeposited into the AAO. (4) The template is placed into a plasma cleaner to remove MPTMS not bound to the surfaces of Au nanowire segments. (5) CdSe is electrodeposited into the AAO on top of the already-deposited Au segments. (6) MPTMS is deposited again through a vapor-phase reaction. (7) Au is electrodeposited into the AAO. (8) MPTMS is removed. (9) The evaporated Ag is removed with nitric acid. (10) The AAO template is dissolved with 0.05 M NaOH.

the MPTMS monolayer. We demonstrate this by functionalizing these regions with thiol-modified oligos. The locations of these molecules are confirmed by fluorescence microscopy of a fluorescent DNA-binding dye that is added to the nanowire solution.

Figure 1 represents the overall strategy of the functionalization scheme and a diagram of the resulting nanowire structure. AAO templates (Anodisc, Whatman, Inc.) with rated pore sizes of 200 nm are prepared based on a published procedure.¹⁴ Briefly, the templates are coated and sealed on one side via the thermal evaporation of Ag. Metal is then typically deposited via electrochemical reduction into these templates without any further preparation to form nanowires. We deviate from this method by using vapor deposition¹⁵ to coat both the pores and remaining face of the template with MPTMS. To achieve this, two AAO templates are placed metal side down into a large polystyrene (PS) dish. Next, 200 μL of distilled water and 100 μL of MPTMS are each placed into separate, smaller PS dishes and are then placed inside the larger PS dish with the prepared AAO template. The larger dish is sealed and then placed into an 80 $^{\circ}\text{C}$ oven for 90 min, which allows for the vapor deposition of MPTMS to proceed onto the surfaces of AAO templates.

A commercial potentiostat (PST050, Radiometer Analytical) is used to electrochemically deposit the nanowires into the template with a platinum counter electrode and a Ag/AgCl (sat KCl) reference electrode. The MPTMS-function-

alized template is placed into a homemade electrochemical cell attached to this setup. The cell is then filled with Ag plating solution (Silver 1025, Technic Inc.), and a thin sacrificial layer of metal is plated at -900 mV into the pores of the AAO template for 30 min in order to fill the branched portion of the channels.¹⁶ Upon completion, the plating solution is removed and the cell is rinsed three times with distilled water. Next, the cell is filled with Au plating solution (Orotemp 24, Technic Inc.), and metallic Au is deposited potentiostatically at -1000 mV until -0.75 $^{\circ}\text{C}$ of charge has passed through the cell. The Au plating solution is removed and the cell is rinsed three times with distilled water before removing the AAO template from the cell and rinsing it with methanol (Fisher Scientific). By briefly placing the template into the chamber of an oxygen plasma cleaner set to 100 W, we can remove the immobilized molecular monolayers from the surfaces of the template into which metal has not already been deposited. This cleans the surface of any carbonaceous material and leaves a fresh metal oxide surface in its place, which can be later used for the attachment of another molecular monolayer that follows any of several standard attachment routes via silane chemistry.

After plasma cleaning is complete, the AAO template is removed from the chamber and placed into distilled water in an ultrasonicator for 30 s to aid in the removal of any nonspecifically bound residue material from the outer surfaces and inner pores of the template. The AAO template

is rinsed again in methanol and is then placed back into the electrochemical cell for the plating of the next material.

At this point, one of two routes is taken: either a semiconductor, CdSe, is deposited using the method devised by Kressin et al.¹⁷ for the formation of heterostructured nanowires, or more Au is deposited for single-material Au nanowires. For the heterostructured nanowires, the cell is rinsed three times with distilled water, and the AAO is removed in order to attach another layer of MPTMS before more Au is deposited into the AAO for the third and final segment of the nanowire. After the final Au segment has been deposited, the SAM removal step is repeated and the AAO is rinsed.

Upon completion of the nanowire deposition, the Ag attached to the AAO is removed by submerging the AAO into a solution of nitric acid (Fisher Scientific) in order to remove the thermally evaporated and electrochemically deposited Ag layers and is then rinsed with distilled water. The nanowires are released from their template by immersing the AAO in a 0.05 M solution of NaOH (Fisher Scientific) and is left overnight until the AAO is completely dissolved, producing free nanowires. Particulate matter resulting from dissolution of the AAO is removed by washing the nanowires three times in ethanol (Fisher Scientific) via centrifugation for 2 min at 8000 rpm.

Previous nanowire functionalization schemes have relied on nanowires that are composed of materials with vastly different chemical affinities toward different functional groups in order to attach different molecular monolayers.^{11,14} Nanowires composed of single materials or of single materials with similar chemical affinities cannot benefit from these schemes. This limitation applies to the heterostructured nanowires used in this report, as alkylthiols are known to be readily absorbed on both Au and CdSe surfaces.^{18–20} In this letter, we circumvent this limitation by forming a protective layer on selected surfaces of these nanowires as they are deposited into the template. This is achieved through the addition and removal of bifunctional surface modifiers that are attached first inside the pores of the template and then to the nanowires themselves as they are deposited into the pores through electrochemical reduction of metal ions. The addition and removal of these SAMs successfully define regions along the nanowires that prevent the absorption of other self-assembled monolayers during subsequent processing steps. This leaves only the nonfunctionalized regions available as potential sites for the attachment of other molecules, which can include other SAMs, DNA, or any other compatible molecule.

The bifunctional modifier MPTMS was used to functionalize the AAO template because it can form covalent bonds with silanes and metal oxide surfaces²¹ and because of the high affinity between surfaces of noble metals and thiolate groups.²² We anticipate that the silane group of MPTMS reacts with the surface of the AAO template and presents a thiolated surface inside the pores, as is observed with similar compounds.²³

Figure 2 compares bright-field and fluorescence images of selectively functionalized nanowires using this technique.

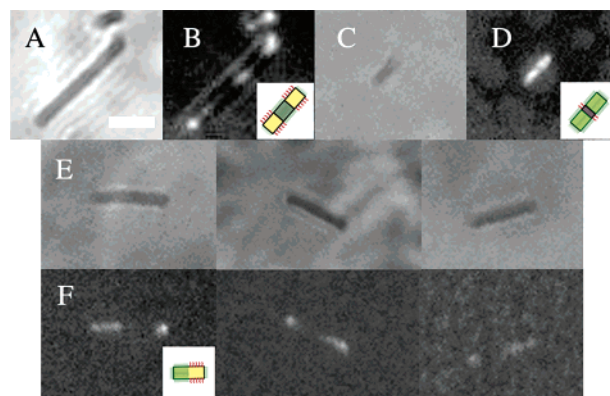


Figure 2. Optical and bright-field micrographs of nanowires protected at specific sites that have been subsequently functionalized with thiolated DNA and labeled with a fluorescent dye. Insets contain schematics of the designed fluorescence, where areas in green correspond to fluorescently labeled DNA bound to the nanowires and red lines denote the locations of the protective monolayer. (A) Bright-field micrograph of Au–CdSe–Au nanowires with Au protected sites. (B) Fluorescence micrograph denoting sites that have been functionalized with thiolated DNA. (C) A shorter Au–CdSe–Au nanowire with a protected CdSe region. (D) The resulting fluorescence micrograph. (E) Au nanowires, each with half of its length protected with MPTMS. (F) Fluorescence micrographs of the same nanowires showing where DNA has absorbed to the surface. An oil immersion 100 \times objective used for each micrograph. The scale bar is 3 μ m.

Parts A and B of Figure 2 show nanowires formed by depositing the semiconductor CdSe between two Au layers. MPTMS is deposited along the pores of the AAO template before the deposition of both segments of Au, and is removed before the deposition of the semiconductor segment by oxygen plasma cleaning the template. After the nanowires are released, we obtain nanowires functionalized with MPTMS along the Au segments, but not the intermediate CdSe segment. To demonstrate the selectivity of the functionalization process, thiolated single-stranded DNA (5'-GGGCGGCGACCT-3'-C6-disulphide oligonucleotide, UNC Pathology) is bound to the exposed Au surfaces of the nanowires through thiol linkages based on a previously published procedure.¹⁰ The oligos absorb only onto the unmasked regions of the nanowire, and the DNA is then tagged with a DNA-binding fluorescent dye, YOYO-1 (Molecular Probes). As is shown in the fluorescence images, the dye appears preferentially in the unmasked portions of the wires, leaving the masked portions dark. (We also note that DNA is bound to the extremities. This is due to the ends of the nanowires being exposed to either the Ag backing or the plating solution so that the masking SAMs are unable to absorb to the nanowires as the thiolate groups are either already absorbed to the Ag or are not present until after the nanowires have already been deposited into the pores. This artifact can be avoided if the electrode metal can be removed selectively after the nanowires are released.)

Parts C and D of Figure 2 show bright-field and fluorescence images of nanowires that are deposited in the presence of MPTMS under conditions complementary to the nanowires in Figure 2A,B and hence exhibits a small gap in the fluorescence micrograph in Figure 2D corresponding to the

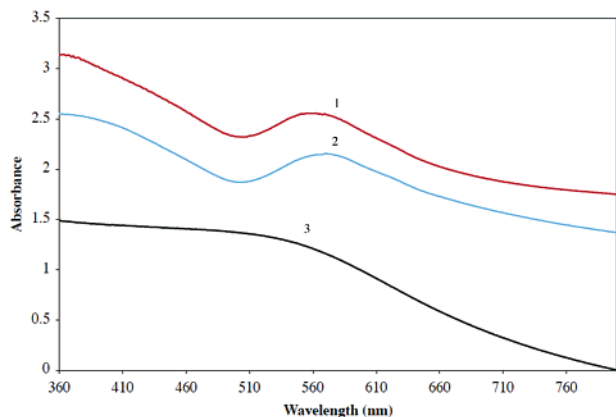


Figure 3. UV–visible spectra for Au nanowire/AAO composites and a blank AAO template. Curve 1, 200 nm Au nanowire/AAO composite functionalized with MPTMS; curve 2, 200 nm Au nanowire/AAO composite; curve 3, blank AAO template.

MPTMS-protected CdSe segment of the nanowire. The CdSe region here corresponds to 1000 cycles of CdSe deposition,¹⁷ which is about 700 nm under the conditions of our experimental setup. The size of the CdSe region can easily be reduced to the nanoscale, but this will require more sophisticated detection methods than what is applied in this work.

To demonstrate the robustness of this functionalization method, we have also applied our technique to nanowires composed solely of Au. Representative bright-field and fluorescence images of single-material (Au) nanowires with half of their total lengths functionalized with MPTMS are shown in Figure 2E. Nanowires of this form were constructed in the same manner as the heterostructured nanowires, except that the Au plating solution is not exchanged for the semiconductor solution between depositions. The same artifact discussed above is evident in Figure 2F.

The vapor-deposited MPTMS SAMs are believed to form an effective chemical resist on the surfaces of the pores inside the AAO. Thus, self-assembled monolayers that have not specifically bound to the surfaces of the nanowires are easily removed and leave the surfaces of the AAO in a near pristine condition, which permits subsequent layers to be attached. Methods other than oxygen plasma cleaning can be applied to remove the SAMs, e.g., a piranha solution (4:1 H₂SO₄/30% H₂O₂) may also be effective.

It is well-known that the surface plasmon absorption band of metal nanoparticles is sensitive not only to the size of the nanoparticles but also to the degree of aggregation between particles²⁴ as well as the presence of complexed surface molecules.²⁵ Figure 3 shows UV–visible absorption spectra of short (~1 μm) Au nanowires (still retained in AAO templates in order to avoid an observable broadening of the absorption peak maximum for nanowires with random orientations). Curve 3 shows the spectrum of a plain AAO template with 200 nm pores. Curve 2 is the spectrum of an AAO template filled Au nanowire that results in an absorption peak near 560 nm, and curve 1 is the spectrum of Au nanowires coated axially with a monolayer of MPTMS along its entire length. In our case, both the diameters of the pores

and the amount of Au deposited into the pores remains consistent from template to template. Thus, the relative intensity of the absorption peaks as well as the slight change in position of the peak in curve 1 can be attributed to the presence of MPTMS on the nanowires. This may correspond to a measurable difference in the local refractive index near the surfaces of the nanowires, although further work is needed in order to clarify the details of these observed differences and the relationship to the amount of material absorbed to the nanowires.

In conclusion, we have formed axially designed monolayers of MPTMS along the surface of heterostructured and single-material nanowires in a controllable manner. These SAMs can act as chemical resist masks that define regions for subsequent treatment with other molecular monolayers. The potential of this technique is demonstrated through the selective absorption of DNA onto patterned nanowires and can be analyzed by UV–visible spectroscopy and fluorescence microscopy. This technique allows for the assembly of molecular monolayers in a spatially patterned manner and may lead to applications in nanoelectronic and nanoscale self-assembled devices.

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