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Surfactant mediated assembly of gold nanowires on surfaces

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The potential of surfactant interactions to direct both the placement and orientation of gold nanowires onto surfaces from solution has been investigated. Gold nanowires were synthesized by template electrodeposition in porous aluminum oxide membranes. Their assembly onto surfaces was controlled by functionalizing the nanowires and surfaces with self-assembled monolayers of thiol based surfactants. Nanowires were assembled from solution onto patterned functional surfaces, and after excess solvent had evaporated the arrangement of nanowires on the surface was observed. A variety of assembly techniques, based upon wettability, electrostatic, or chemical interactions have been studied. Nanowire assembly onto surfaces with patterned wettability resulted in the placement of nanowires on hydrophilic regions with a specific orientation. Hydrogen bonding and carboxylate salt attachment of mercaptoundecanoic acid functionalized nanowires to reactive regions of patterned surfaces has been demonstrated, with unbound wires removed by washing. Similarly, electrostatic interactions between charged nanowires and surfaces have been demonstrated to preferentially assemble nanowires onto oppositely charged surface regions. Although selective attachment of nanowires to reactive surface regions was achieved by both chemical and electrostatic assembly techniques, these methods did not control the orientation of assembled nanowires.

Keywords: Nanowire; Self-assembly; Nanorod; SAM; Assembly

1. Introduction

Commercial nanoscale circuit and device fabrication is currently dominated by ‘top-down’ lithographic techniques. Such fabrication employs procedures that directly manipulate components and/or substrates to construct architecture and devices. Future miniaturization using ‘top-down’ techniques is limited by experimental barriers that are, as yet, unresolved. Historically, such problems have been solved and lithographic techniques have proved capable of maintaining Moore’s Law [1].

In contrast, the ‘bottom-up’ approach exploits self-assembly such that component parts spontaneously assemble into functional arrangements, without the individual manipulation of each component. The promise of these techniques is reduced complexity and cost. Substantial research in the pursuit of viable bottom-up fabrication

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procedures has been concentrated in several strategic areas; development of assembly techniques, surface patterning techniques [2–4], nanoscale component fabrication [5–9], alternative circuit architectures [10–12], and molecular electronics [11, 13–16]. One of the long-term goals is to self-assemble an interconnected high density array of elements [4, 12, 17]. Such arrays could form the basis of logic or memory circuits, and other integrated nanosystems such as chemical/biological sensors [18, 19] or photonic devices [20].

The first demonstrations of nanoparticle self-assembly on surfaces used colloidal particles [21, 22]. Subsequent research has led to a diverse range of assembly techniques [23] that can be split (for descriptive purposes) into four key mechanisms:

1.1. Fluidic assembly

Interactions between the surface, solvent and colloid direct assembly. Examples include assembly due to solvent evaporation [24–26], assembly at fluid interfaces [27, 28], and directed assembly due to the trapping of solution at specific locations on patterned or textured surfaces [29–31].

1.2. Chemical assembly

Chemical interactions between the colloid and a patterned surface cause attachment at specific reactive sites. Interactions may be either covalent [32–35], or due to hydrogen bonding [36, 37]. Hydrogen bonded systems include biochemical processes, where attachment is due to the presence of biological components such as DNA [38], or avidin/streptavidin [39, 40].

1.3. Electrostatic assembly

Electrostatic interactions between charged colloids and surfaces direct assembly [41–44].

1.4. Field mediated assembly

Where interactions between the colloids and an external magnetic [45] or electric [46] field define their assembly.

The directed assembly of non-spherical particles has allowed more complex arrangements and structures to be self-assembled [47]. Nanorods possess several advantages over spherical colloids as components for nanoscale circuitry; they are better suited to replicating wire-based structures [4], forming nanoscale interconnects [48], and can be used to assemble complex devices themselves [5, 8, 49–51]. New complications are also introduced when manipulating anisotropic components, including the requirement to control both their placement and orientation. The directed assembly of carbon nanotubes has received considerable attention with examples in all of the categories defined above; fluidic assembly [52, 53], electrostatic assembly [54, 55], chemical assembly in presence of biological components [56, 57], and assembly controlled by magnetic [58] or electric [59, 60] fields. Similarly, successful assembly of supramolecular nanotubes [61–67] and metallic nanowires [68–70]

has been demonstrated. The assembly of nanowires has also been demonstrated in all of the above categories; fluidic assembly [71–76], chemical assembly [77], biochemical assembly [78–80], electrostatic assembly [71, 81–83], and assembly with magnetic [80] or electric [9, 84–86] fields. However, amongst these examples only two studies facilitate attachment onto surfaces at specific locations with a defined orientation [71, 80]. These studies have used complementary surfactant based interactions to bind nanowires at selected regions of a patterned surface, in addition to either fluid flow [71], or an external magnetic fields [80], to control their alignment. The capability to assemble anisotropic colloids, with control over both their placement and orientation, is critical to the directed assembly of basic circuit architectures.

This paper explores the potential of surfactant based interactions to direct the assembly of gold nanowires at surfaces. The driving force for assembly arises from competition between nanowire-surface, nanowire-fluid and fluid-surface interactions. The potential to direct the assembly of metallic nanowires with an external field has been previously explored [86]. The specific examples investigated are: Nanowire assembly on patterned hydrophilic/hydrophobic surfaces, due to solvent affects, the attachment of nanowires to reactive regions of a patterned surface, by hydrogen bonding or carboxylate salt formation, assembly caused by electrostatic interactions between nanowires and patterned surfaces, where both are functionalized with charged carboxylic acid and/or amine surfactants.

2. Experimental methods

2.1. Nanowire fabrication

Gold nanowires were synthesized by template deposition [87] into commercially available ‘Whatman Anodisc’ porous aluminum oxide membranes, with 20 nm diameter pores and were 66 μm thick. The membrane is perforated by approximately cylindrical pores that propagate normal to surface and are not interconnected. The 20 nm diameter pores are only present at the filtration surface of the membrane, while the pore diameter through the majority of the membrane is 175 ± 25 nm, figure 1. Within approximately 1 μm of the filtration surface each pore splits to form a network of smaller pores.

Prior to nanowire growth, the filtration surface of the Anodisc membrane was coated with a 1 μm silver layer (Advent 99.99%) by thermal evaporation (Edwards Auto 306) to act as an electrode. Electrodeposition of gold was carried out in a PTFE cell containing an aqueous gold electrolyte, 0.02 M $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 1 M NaCl, with the pH adjusted to 1.5 using HCl solution. A 15 Hz, 1 V_{pp} , alternating potential was applied to the cell, in series with a 1 k Ω current limiting resistor, for 30 minutes. The reduction of gold within the pores results in the cumulative formation of metallic gold nanowires from the silver electrode. After deposition the silver electrode was removed from the membrane by etching in nitric acid (70 wt%). The nanowires were removed from the membrane by dissolving the aluminum oxide in 1 M aqueous sodium hydroxide. Sodium hydroxide was replaced with MilliQ 18.2 M Ω water by repeated centrifugation and dilution. Finally, the nanowires were transferred from water to HPLC grade methanol by the same procedure.

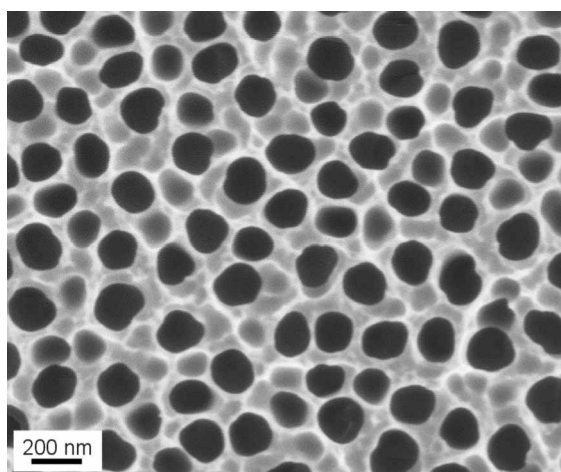


Figure 1. SEM image of the non-filtration surface of a 'Whatman Anodisc' membrane.

2.2. Nanowire functionalization

After release from the template and suspension in HPLC methanol, it is possible to functionalize gold nanowires with a variety of surfactants. During the course of this work three commercially available thiols have been used; mercapto-1-undecanol (HS-(CH₂)₁₁-OH) [OH], mercaptoundecanoic acid (HS-(CH₂)₁₀-COOH) [COOH], and dodecanethiol (HS-(CH₂)₁₁-CH₃) [CH₃], all obtained from Aldrich. Two further thiols, a fluorinated [CF₃] thiol (CF₃(CF₂)₉(CH₂)₆SH) and an amine [NH₂] terminated thiol (NH₂-(CH₂)₂(OCH₂CH₂)₈NHC=OCH₂CH₂SH), were supplied by the Seiko-Epson corporation. These materials shall be referred to henceforth by their terminal groups, shown in square brackets. The nanowires were functionalized by adding these materials at 1 mM concentrations to the methanol based nanowire solution. After leaving overnight to allow the formation of a Self-Assembled Monolayer (SAM), nanowires were filtered from the thiol solution and transferred to HPLC methanol.

2.3. Micro-contact printing of patterned SAMs

During the micro-contact printing technique [88] surfactant molecules absorbed onto a textured elastomeric stamp are transferred to the substrate upon contact. Finally, the bare regions of substrate are back-filled by incubating in a solution containing a different surfactant material.

Silicon substrates were cleaned in piranha solution and washed in MilliQ water (resistivity = 18.2 MΩcm⁻¹). A 100 nm gold film was evaporated onto the Si surfaces, bound with a 10 nm Cr adhesion layer. During microcontact printing a textured stamp (PDMS – Sylgard 184) was coated with one thiol material by immersion in a 7 mM methanol based thiol solution for 60 seconds, and dried under nitrogen. The textured PDMS surface was brought into conformal contact with the gold substrate for 10 seconds. Where the textured stamp touches the gold surface surfactant is transferred from the stamp to the gold surface. The remaining bare regions of the substrate were

'backfilled' by immersing the substrate in the second 3 mM methanol based thiol solution for 1 hour. Using this technique it has been possible to produce a variety of patterned surfaces with repeat lengths above 2 μm .

2.4. Contact angle measurements

Dynamic water contact angles were measured with a droplet of MilliQ 18.2 M Ω water. The water was dispensed onto the surface with the syringe until the contact point moves outwards. When movement occurs a video still image is captured enabling measurement of the advancing contact angle. The syringe is then used to withdraw water from the droplet until the contact point recedes, and the angle is measured by the same procedure.

3. Results

3.1. Nanowire growth

Nanowires grown in Anodisc membranes, under the conditions described above, have typical lengths and diameters of $4 \pm 2 \mu\text{m}$ and $175 \pm 25 \text{ nm}$ respectively. Evidence of growth from the split-pore region into larger pores shows how they replicate the template structure, figure 2.

3.2. Nanowire assembly on patterned hydrophobic/hydrophilic surfaces

In the following section we consider perhaps the simplest mechanism for the positioning of nanowires. The surface is patterned with stripes of contrasting hydrophobicity/hydrophilicity. Droplets containing the functionalized nanowires with hydrophobic or

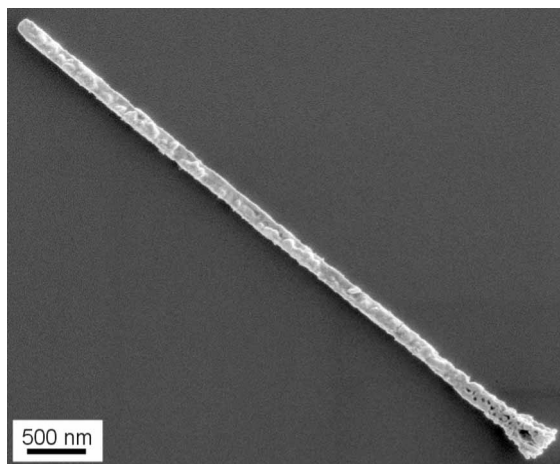


Figure 2. SEM image of a gold nanowire grown in a 'Whatman Anodisc' membrane.

hydrophilic terminal groups, are then allowed to recede over the surface leaving a 'deposit' of nanowires, figure 3.

Striped hydrophilic/hydrophobic surfaces were fabricated, by microcontact printing [3], with stripes 1, 2 and 5 μm wide. A range of assembly experiments have been conducted to assess the relative importance of solvent de-wetting and hydrophobic interactions.

Assembly of gold nanowires functionalized with mercapto-1-undecanol (OH terminated) from a methanol solution onto striped mercapto-1-undecanol/ CF_3 surfaces.

Assembly of gold nanowires functionalized with CF_3 from a methanol solution onto striped mercapto-1-undecanol/dodecanethiol (CH_3 terminated) surfaces.

Contact angle measurements were made to determine the relative wettability of the SAMs involved. Advancing and receding contact angles for a droplet of MilliQ 18.2 $\text{M}\Omega$ water on planar SAMs, on gold substrates, are shown in table 1.

The behavior of a water droplet receding across a patterned SAM with 10 μm stripes of mercapto-1-undecanol and CF_3 illustrates the effect of patterned wettability, figure 4.

As the droplet recedes across the patterned SAM it selectively de-wets the hydrophobic stripes leading to the expulsion of fluid and particulates to the hydrophilic regions. The fluid in these hydrophilic regions then beads into micro-droplets which subsequently evaporate.

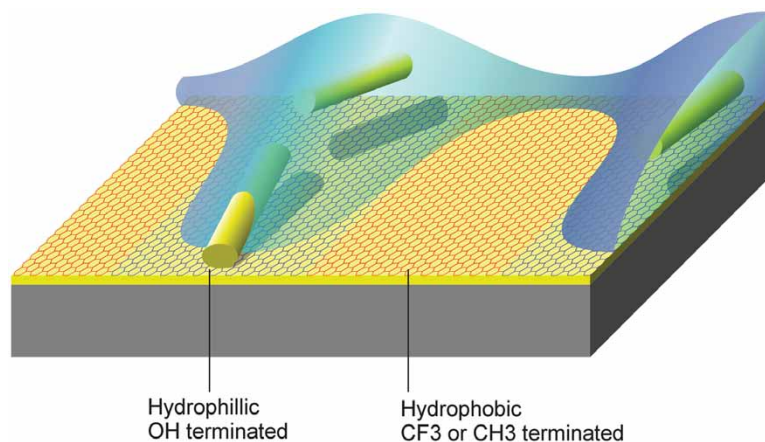


Figure 3. Schematic diagram of nanowire assembly on surfaces with patterned wettability. Solvent preferentially wets the hydrophilic regions of the surface, leaving nanowire deposits in these regions.

Table 1. Contact angle measurements of planar SAMs on gold.

SAM	Contact angle/degrees	
	Advancing	Receding
Mercaptoundecanoic acid	22	10
Mercapto-1-undecanol	38	15
Dodecanethiol	110	101
$\text{CF}_3(\text{CF}_2)_9(\text{CH}_2)_6\text{SH}$	122	115

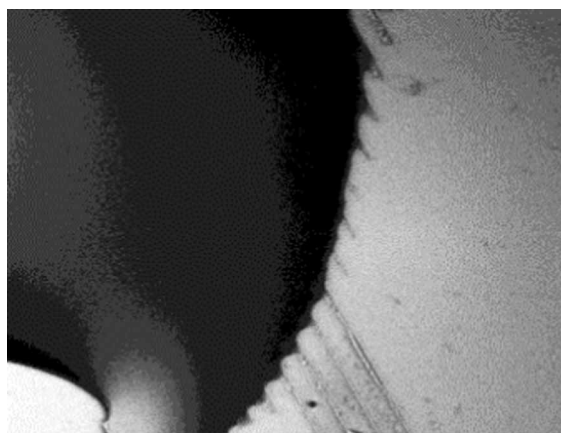


Figure 4. Optical image of a water droplet withdrawing from a patterned hydrophobic/hydrophilic region of the surface with $10\ \mu\text{m}$ wide stripes.

Scanning electron microscopy allowed observation of the patterned SAMs and nanowires assembled onto their surface [89]. The nanowires, functionalized with mercapto-1-undecanol, assembled selectively onto the hydrophilic regions of the $[\text{OH}/\text{CH}_3]$ surfaces, and were oriented with their long axis aligned with the striped pattern, figure 5a and b.

During microcontact printing of these surfaces, the CF_3 SAM was applied with a textured stamp, and unexposed regions were functionalized by immersion into 3 mM mercapto-1-undecanol solution. Different regions of the patterned SAMs were identified by their contrast at the edge of the stamped region, from figure 5a it can be determined that the darker colored areas are CF_3 functionalized.

The assembly of nanowires onto striped hydrophilic/hydrophobic surfaces is driven by the surface-fluid interactions. The coverage of nanowires remaining on the patterned region of the surface is of lower density than just outside the patterned region, figure 5a. Unstamped regions of the surface were more hydrophilic, and consequently the droplet containing nanowires flowed from the stamped to the unstamped regions. Nanowires suspended in the solution are thus drawn-off from the stamped region and precipitate in higher concentration at its edge as the solvent dries.

Nanowires predominantly align on a single stripe of the $1\ \mu\text{m}$ patterned surfaces, although those wires that are not aligned are positioned such that each end lies upon a hydrophilic region (not shown). Nanowires assembled onto $5\ \mu\text{m}$ striped surfaces, figure 5b, are positioned onto a single hydrophilic stripe, although the larger stripes allow a greater range or orientations. The forces orienting the wire are believed to be associated with the scale and geometry of the droplet at the point of assembly. This would explain the greater angular distribution observed for nanowires assembled onto the $5\ \mu\text{m}$ striped surface, figure 5b.

The assembly forces are believed to be primarily dependent on the patterned surface wettability, and to a lesser extent, its geometry. In the second experiment presented the surface-fluid interaction was altered by functionalizing the gold nanowires with

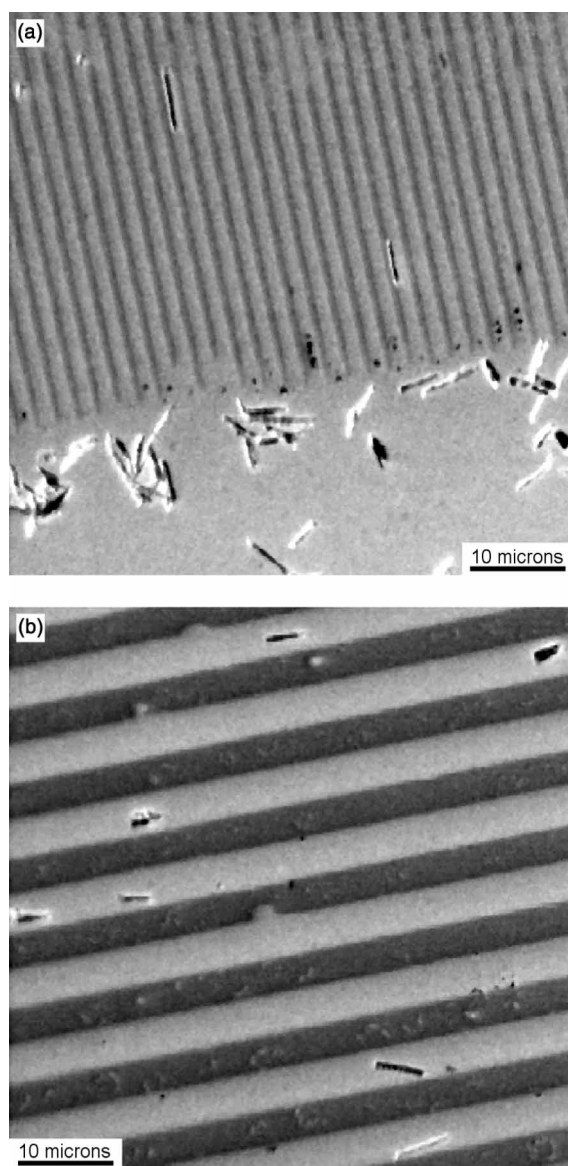


Figure 5. SEM image showing mercapto-1-undecanol functionalized nanowires assembled onto (a) 1 μm wide and (b) 5 μm wide mercapto-1-undecanol regions of a mercapto-1-undecanol (light)/CF₃ (dark) patterned surface.

a hydrophobic surfactant. Nanowires functionalized with CF₃ were assembled from methanol solutions onto CH₃/mercapto-1-undecanol patterned surfaces, figure 6.

Nanowires functionalized with CF₃ are observed to assemble onto the lighter mercapto-1-undecanol regions of the mercapto-1-undecanol/dodecanethiol patterned surface. Whereas previously the driving force for assembly was solely due to the

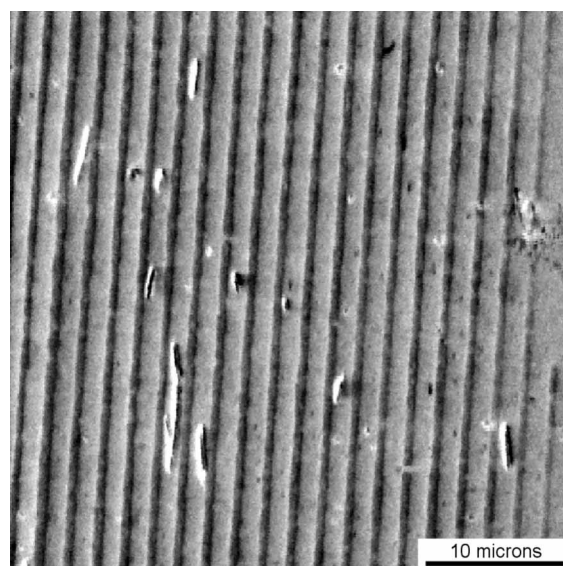


Figure 6. SEM image showing CF_3 functionalized nanowires assembled onto $1\ \mu\text{m}$ wide mercapto-1-undecanol terminated regions of a mercapto-1-undecanol (light)/dodecanethiol (dark) patterned surface.

surface wettability, assembly in figure 6 is complicated by the hydrophobic nanowires. Nanowires functionalized with CF_3 moieties introduce hydrophobic interactions between the surface and the nanowire and may be expected to lead to assembly onto the hydrophobic regions [90–93]. In addition, the behaviour of hydrophobic nanowire suspended in the solvent at the droplet-air interface will be altered. Despite these new factors, assembly forces drive these nanowires onto the hydrophilic regions of the surface.

3.3. Nanowire assembly due to hydrogen bonding

Using patterned SAMs comprised of mercaptoundecanoic acid (COOH terminated) and mercapto-1-undecanol, allows one to look at surfaces with similar wettability, table 1, but that interact with mercaptoundecanoic acid functionalized nanowires quite differently. The carboxylic acid terminal groups of mercaptoundecanoic acid can bind by hydrogen bonding [94, 95], and this process has been investigated as a mechanism for attaching the wires onto the mercaptoundecanoic acid regions of the surface. A similar process has also been investigated, where a carboxylate salt [96–98] was used to bind the nanowire to the surface, figure 7.

Patterned surfaces with alternate $[\text{OH}]/[\text{COOH}]$ $10\ \mu\text{m}$ stripes were prepared by microcontact printing on gold surfaces. Mercaptoundecanoic acid functionalized nanowires were then precipitated, from methanol, onto the surfaces which were subsequently washed with methanol, dried under nitrogen, and imaged with scanning electron microscopy. For assembly by carboxylate salt formation, the mercapto-undecanoic acid regions of the patterned surface were functionalized with Cd^{2+} by

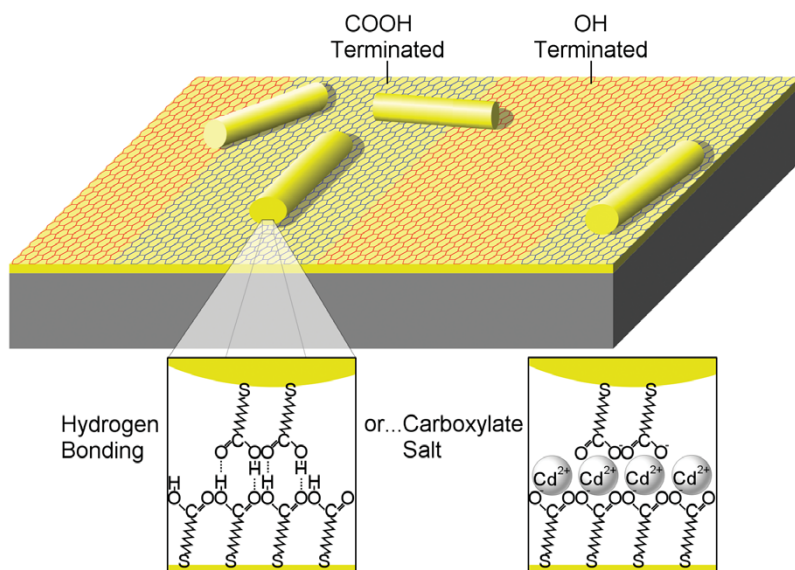


Figure 7. Schematic diagram showing chemical attachment of nanowires to reactive surface regions by either hydrogen, or carboxylate salt, bonding.

immersion into a 1 mM solution of CdCl_2 , in MilliQ 18.2 $\text{M}\Omega$ water. The salt formation was observed by X-ray photoelectron spectroscopy.

Assembly due to hydrogen bonding between carboxylic acid terminated nanowires and surfaces and causes selective placement, figure 8a, as does the formation of a carboxylate salt, figure 8b.

Darker stripes are mercaptoundecanoic acid regions whilst lighter areas are mercapto-1-undecanol. The wires assembled by hydrogen bonding onto the mercaptoundecanoic acid regions in figure 8a are circled, whilst those on the mercapto-1-undecanol regions are highlighted with a triangle. Nanowires assembled by hydrogen bonding constitute 66% of those sampled. Similarly, nanowires assembled by carboxylate salt formation onto mercaptoundecanoic acid regions in figure 8b are circled, whilst those on the mercapto-1-undecanol regions are highlighted with a triangle. Assembly was improved over hydrogen bonding, and the assembled wires in figure 8b constitute 75% of those sampled.

The chemical attachment of nanowires to reactive surfaces is a simple surface-nanowire binding process, without any long-range assembly forces. Nanowires precipitate at random onto the patterned surface and unbound or weakly bound wires are removed during the washing process. Those wires that remain attached to the reactive regions are said to be assembled. The results, figure 8a and b, suggest that carboxylic salt attachment provides better assembly than hydrogen bonding. However, the relative strength of the attachment process is unknown. This approach to assembly is not expected to align nanowires with any specific orientation. However, nanowires are generally aligned parallel to the pattern direction for the carboxylic salt binding experiment, figure 8b. Alignment may arise post adsorption, for example during the

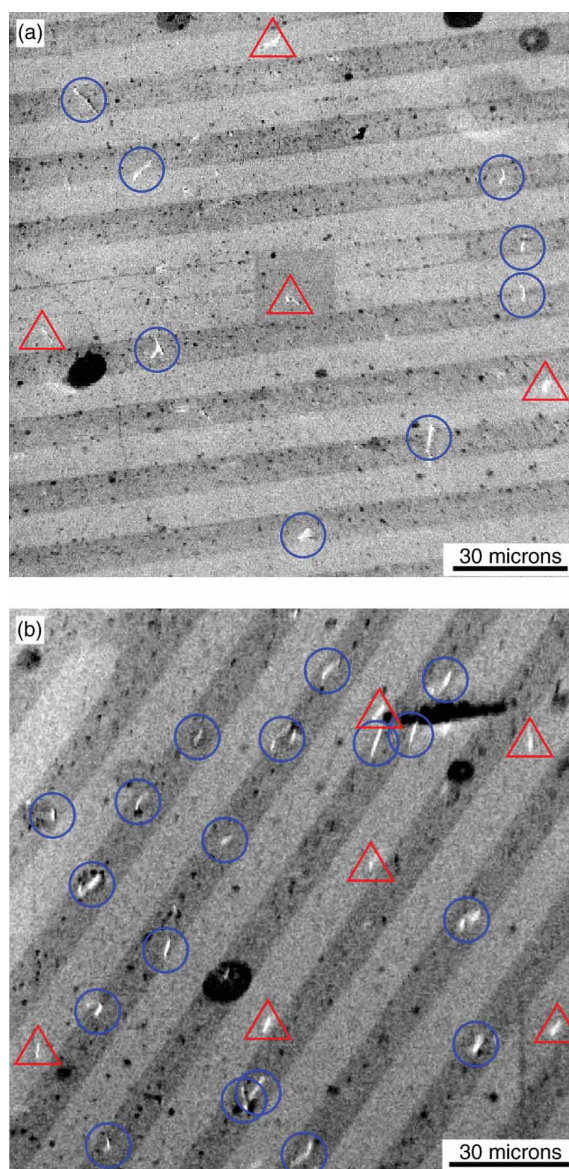


Figure 8. SEM image showing mercaptoundecanoic acid functionalized nanowires assembled onto 10 μm wide mercaptoundecanoic acid terminated regions of a mercaptoundecanoic acid (dark)/mercapto-1-undecanol (light) patterned surface attached by (a) hydrogen bonding and (b) a cadmium ion linker.

washing process, where nanowires appear to align perpendicular to the droplet edge as the sample is dried. It is possible that salt formation changes the wettability of mercaptoundecanoic regions of the surface, such that the surface will dewet similar to the striped hydrophobic/hydrophilic surfaces introducing alignment parallel to the pattern.

3.4. Nanowire assembly due to electrostatic interactions and charge transfer

Finally, the ability of electrostatic interactions, between nanowires and surfaces, to drive assembly has been investigated. Electrostatic forces are derived from the use of surfactants on both the nanowires and patterned surfaces that can be protonated or deprotonated by changing the pH of the solvent. The assembly forces are repulsive between like-charged surfaces and attractive between oppositely-charged surfaces. Two experiments have been performed; to assemble negatively charged nanowires onto neutral regions of patterned neutral/negatively charged surfaces, and to assemble negatively charged nanowires onto positively charged regions of patterned positively/negatively charged surfaces, figure 9.

Functionalized nanowire solutions were allowed to interact with mercapto-1-undecanol/mercaptoundecanoic acid and NH_2 /mercaptoundecanoic acid patterned SAMs under pH controlled aqueous solutions. Nanowires precipitate from solution onto patterned SAM surfaces. After assembly, surfaces were washed with 18.2 M Ω water and dried under nitrogen.

Electrostatic assembly of nanowires onto mercapto-1-undecanol/mercaptoundecanoic acid surfaces is reliant on repulsive interaction between the COO^- terminated regions of the surface and COO^- terminated surface of the nanowires. To ensure sufficient de-protonation of the carboxylic acid terminal groups the nanowire solution was adjusted to pH 8 by the addition of NaOH (the pKa value of a mercaptoundecanoic SAMs is ~ 5.5 [99, 100]). After nanowire assembly, the surface is imaged by the SEM, figure 10, which shows the mercapto-1-undecanol regions lighter, and mercaptoundecanoic acid regions darker.

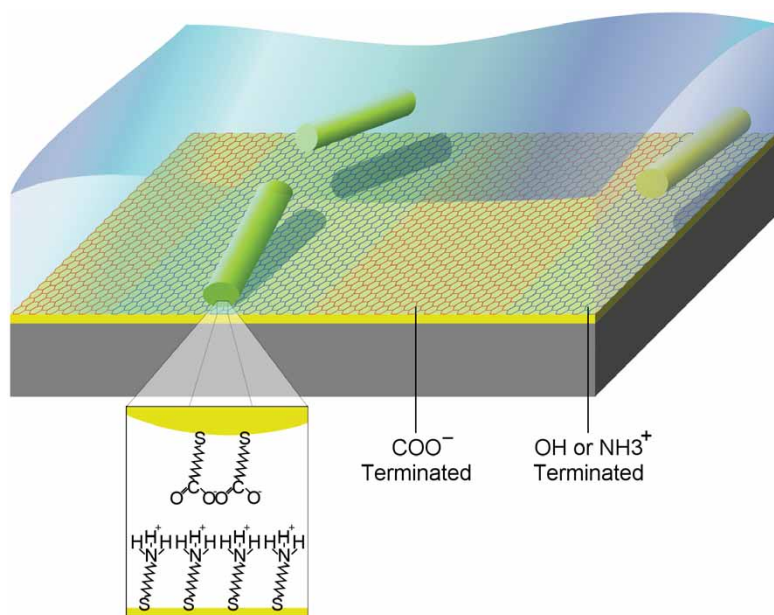


Figure 9. Schematic diagram of nanowire assembly due to electrostatic interactions between negatively charged nanowires and negative regions of a negatively/positively charged striped surface.

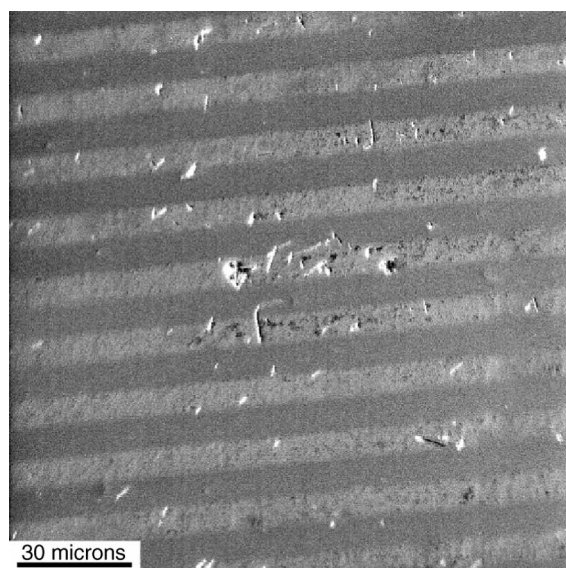


Figure 10. SEM image showing COO^- functionalized nanowires assembled onto $10\ \mu\text{m}$ wide mercapto-1-undecanol (light) terminated regions of a mercapto-1-undecanol/ COO^- (dark) patterned surface from pH 8 NaOH solution.

Electrostatic repulsion causes the nanowires to assemble onto the mercapto-1-undecanol (lighter) regions of the surface, where approximately 85% of the sampled nanowires are observed.

The assembly of mercaptoundecanoic acid functionalized nanowires onto mercapto-undecanoic acid/ NH_2 patterned surfaces is dependent on both repulsive and attractive electrostatic forces, and potentially amide bond formation [101]. It is possible to tailor the pH of the nanowire solution such that NH_2 regions protonate to NH_3^+ and have a net positive charge, whilst the mercapto-1-undecanol surfaces deprotonate to COO^- and have a net negative charge. The pKa of mercapto-1-undecanol and similar NH_2 terminated SAMs has been previously determined so that the range of pH where this applies is approximately 5.5–7.5 [99–102]. The solvent used was $18.2\ \text{M}\Omega$ water, with pH ~ 6.5 . After assembly the surface was imaged with a SEM, figure 11, which shows the mercapto-1-undecanol regions with a lighter coloration, and NH_2 regions as darker.

Nanowires have assembled predominantly onto the amine regions, with relatively few wires occupying the acid regions despite the high overall nanowire density.

Electrostatic interactions between the nanowires and surfaces provide long-range assembly forces but weak attachment at the surfaces. Although assembly is observed on the mercapto-1-undecanol/mercaptoundecanoic acid surfaces, no nanowire alignment is observed. This result should be compared with nanowire attachment due to hydrogen bonding. Both experiments use identical surfaces and nanowires, whilst different assembly mechanisms are utilized by tailoring the solvent. With electrostatic interactions the nanowires assemble onto mercapto-1-undecanol regions of the surface, whilst hydrogen bonding causes the nanowires to attach to the

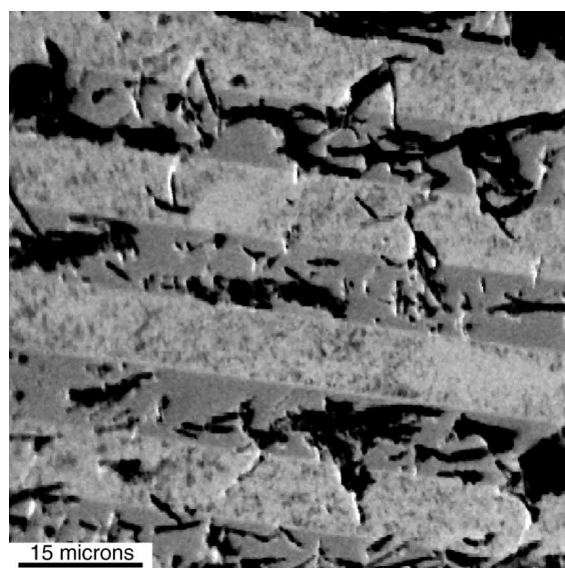


Figure 11. SEM image showing COO^- functionalized nanowires assembled onto $5\ \mu\text{m}$ wide NH_3^+ terminated regions of a COO^- (light)/ NH_3^+ (dark) patterned surface from water, pH 6.5.

mercaptoundecanoic acid regions. Assembly onto mercaptoundecanoic acid/ NH_2 surfaces also shows selective placement of nanowires, but with no defined orientation.

4. Conclusions

This study presents a systematic investigation of surfactant assisted assembly of nanowires onto surfaces. In comparison to studies of colloid or carbon nanotube self-assembly, there is relatively little published work on the assembly of metallic nanowires onto surfaces. These results represent the most comprehensive study to date of surfactant mediated assembly of metallic nanowires onto surfaces. By tailoring the functionality of the nanowires and surfaces, the effect of surface-nanowire, surface-fluid and fluid-nanowire interactions have been investigated.

Assembly of nanowires onto striped hydrophilic/hydrophobic surfaces is dependent on surface-fluid, and to a lesser extent fluid-nanowire interactions. The withdrawal of the solvent from patterned hydrophobic regions assembles and orients the nanowires onto the hydrophilic areas, due to fluid flow and surface tension. Nanowires are aligned parallel to the direction of the striped surface by the fluid-nanowire interaction, as the solvent recedes. Control over the assembly process may be achieved by adjusting the contrast between hydrophilic and hydrophobic regions, and adjusting the pattern's scale or geometry.

Chemical reactions between functionalized nanowires and surfaces are capable of selectively binding nanowires to reactive surface regions. Unbound or weakly bound may then be washed away. Two attachment processes, hydrogen bonding, and

carboxylate salt formation, between mercaptoundecanoic acid surfactants have been used to assemble nanowires. Although these assembly techniques are not expected to control nanowires orientation, nanowires bound to the surface by carboxylate salt formation have an average orientation parallel to the pattern direction. It has been suggested that this is a result of the washing procedure, and any wettability differences between the mercapto-1-undecanol and carboxylate surface regions.

Electrostatic assembly of negatively charged nanowires onto patterned charged surfaces has been demonstrated, controlled by adjusting the solvent pH. Negatively charged nanowires are repelled from similarly charged surface regions on COO^- /mercapto-1-undecanol surfaces, depositing on the uncharged mercapto-1-undecanol surface regions. Similarly, they are assembled onto oppositely charged amine regions of $\text{COO}^-/\text{NH}_3^+$ patterned surfaces by attractive and repulsive interactions. Although long-range electrostatic interactions may be expected to control nanowire alignment, no preferential orientation is observed.

Techniques for assembling nanowires into functional arrays must control both the location and orientation of component nanowires. Only one technique investigated here consistently demonstrated both these attributes, nanowire assembly onto patterned hydrophilic/hydrophobic surfaces. During the assembly mechanism both nanowire placement and alignment are derived solely from the surface-fluid interaction. The other techniques investigated demonstrate selective placement of nanowires onto complementary regions of the surfaces. These attachment techniques may be used in combination with external forces to constrain the nanowire alignment, as has been previously demonstrated with fluid flow [71] or external fields [80].

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