Surface Tension Driven Self-Assembly of Bundles and Networks of 200 nm Diameter Rods Using a Polymerizable Adhesive

Zhiyong Gu,[†] Yiming Chen,[†] and David H. Gracias*,[†,‡]

Department of Chemical and Biomolecular Engineering, and Department of Chemistry,
The Johns Hopkins University, Baltimore, Maryland 21218

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This letter demonstrates the first utilization of surface tension based self-assembly on the 200 nm scale to form mechanically stable aggregates comprised of metallic rods. The self-assembly occurs as a result of the minimization of interfacial tension of liquid layers of a hydrophobic polymerizable adhesive that is precipitated on the rods. After the assembly, the adhesive is polymerized to form permanently bonded aggregates. Depending on the patterning of the rods and the chemical functionalization used, either closed 3D bundles or open 2D networks can be formed.

In recent years, aggressive scaling of micromechanical structures to the nanoscale has challenged the limits of conventional microfabrication methodologies.[1] It is expensive to pattern structures below the wavelength of UV light (~250 nm) and virtually impossible to manipulate structures on the 200 nm length scale using pick-and-place tools used in conventional microfabrication. It is also very difficult to fabricate three-dimensional (3D) structures using conventional microfabrication. The inherent two-dimensionality of current microfabrication is a limitation since 3D structures have advantages such as high packing density, high interconnectivity, and small form factors. To facilitate a cost-effective, parallel approach to nanofabrication, it is necessary to develop new fabrication methodologies. One such approach that is being researched extensively in recent years is fluidic self-assembly.

Fluidic self-assembly involves tumbling chemically patterned components in a fluidic medium so that they can interact with each other and form stable structures with precise function. Several groups have described strategies for the 3D self-assembly of nanoparticulates such as gold/semiconductor nanocrystals or silica/polymer nanospheres using molecular linkers based on protein[2] or DNA recognition,[3] antibody−antigen recognition,[4] chemical bonding,[5] hydrogen bonding,[6] and metallic complexation.[7] Other groups have demonstrated the self-assembly of inorganic media on size scales ranging from nanometer to millimeter, using continuum forces such as magnetic[8] or electrostatic.[9] Although several approaches have been used in the fluidic assembly of nanocomponents, the assembled structures formed in many cases are not strongly bonded to each other, i.e., the assemblies cannot be easily manipulated outside the fluidic medium or even survive mild sonication.[10] For components with sizes on the 200 nm scale, the interfacial roughness of the components can be significant. When molecules including those with ligands[11] are used to bond components on the 200 nm length scale, it is difficult to form strong bonds and integrate a large number of components in the assembled structure since the interfacial contact area is small (contact occurs only at asperities).

In this letter, we demonstrate a strategy to form mechanically stable aggregates using surface tension based self-assembly. The work is based on the strategy used by Whitesides et al.[12] to form millimeter and microscale aggregates in two and three dimensions. Examples of surface tension based self-assembly include the formation of functional microsystems using solder and epoxy.[13−15] Although both solder and epoxy based self-assembly result in mechanically stable aggregates, the challenges associated with patterning components with solder and epoxy and the characteristics of the joints formed using the two strategies are very different. For example, solder joints formed on self-assembly are electrically conductive,[16] while epoxy joints formed are electrically insulating. The results presented in this paper demonstrate that surface tension based self-assembly can be extended to the 200 nm scale to form stable 3D structures and two-dimensional (2D) networks. Surface tension based self-assembly involves modification of the surface energy of components using molecules (hydro-

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[*] To whom correspondence should be addressed. E-mail: dgracias@jhu.edu.

[†] Department of Chemical and Biomolecular Engineering.

[‡] Department of Chemistry.

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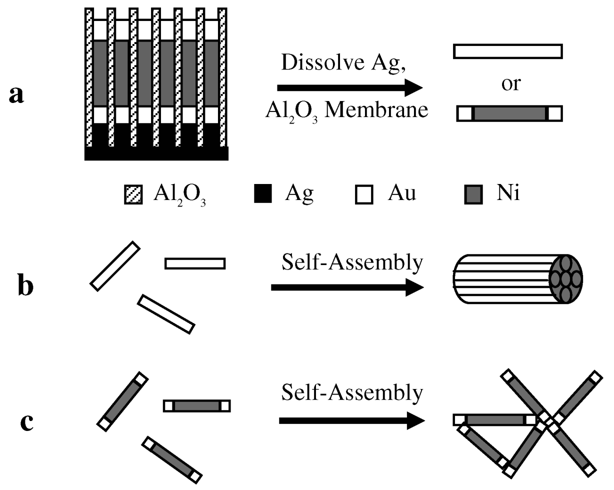

Figure 1. (a) A schematic diagram of the process used to fabricate rods consisting of all Au or Au−Ni−Au segments by electrodeposition in a nanoporous alumina template. (b) Self-assembly of Au rods results in the formation of 3D bundles. (c) Self-assembly of Au−Ni−Au rods results in the formation of 2D networks.

philic/hydrophobic), precipitation of a liquid layer on the components, and subsequent agitation of the components in a fluidic medium. The agitation causes the components to collide, and if the system is engineered right, there is a driving force for self-assembly due to the minimization of the interfacial free energy of liquid layers on the surfaces of the components. Since attachment occurs between liquid drops that extend out several nanometers from the components, interfacial roughness is not a big issue. As opposed to amphiphilic aggregation[10] based on hydrophobic and hydrophilic interactions, surface tension based assembly with polymerizable liquid adhesives results in stable mechanical attachment.

In our experiments (see the Supporting Information for additional details), we fabricated multicomponent rods composed of either all Au or Au−Ni−Au segments by electrodeposition in nanoporous templates[17] with a nominal pore size of 200 nm (Figure 1). The rods were approximately 150−250 nm in diameter and 2−6 microns in length. To facilitate an electrical contact for electrodeposition, a thin Ag seed layer was evaporated on one face of the alumina membrane. Multicomponent nanorods composed of Au or Ni segments were formed using an electrolytic solution containing the appropriate metal ions, and the length of the segments was restricted by controlling the current density and the duration of electrodeposition. Our choice of metals was motivated by the fact that it is easy to functionalize Au segments using self-assembled thiol monolayers, whereas these monolayers did not adhere well to the Ni segments due to the formation of an oxide layer during processing.[18] This allowed us to selectively pattern different parts of the rods to be either hydrophobic or hydrophilic. After electrodeposition, the evaporated Ag seed layer and the alumina template were dissolved to release the metallic rods. The rods were functionalized by immersion in a dilute solution of hexadecane thiol (HDT) for 24 hours that rendered the gold segments very hydrophobic as compared to the nickel segments, due to the formation of a self-assembled monolayer. The rods were then repeatedly rinsed with ethanol and dispersed by sonication. To facilitate self-assembly, we coated the rods with a curable adhesive. This adhesive comprised a monomer (LM, lauryl methacrylate), a cross-linker (HDD, 1,6-hexanediol diacrylate), and a polymerization initiator (either a thermal initiator, BP (benzoyl peroxide), or a photoinitiator, BIE (benzoin isobutyl ether)). We experimented with different concentrations of the constituents in the adhesive. LM was very hydrophobic as compared to HDD; hence increasing the ratio of LM to HDD resulted in a more hydrophobic adhesive, but consequently the low concentration of HDD to LM resulted in reduced cross-linking on curing (softer joint). Photoinitiation polymerization of the adhesive using BIE was faster than thermal initiation using BP; consequently the photoinitiator BIE was used in the assembly of open 2D networks. For closed 3D bundles formed on assembly, it was necessary to use thermal initiation, since light cannot penetrate the interior of the structure. In our experiments, we determined that a composition of 90:9:1 v/v (LM/HDD/initiator) gave best results for self-assembly and cure.

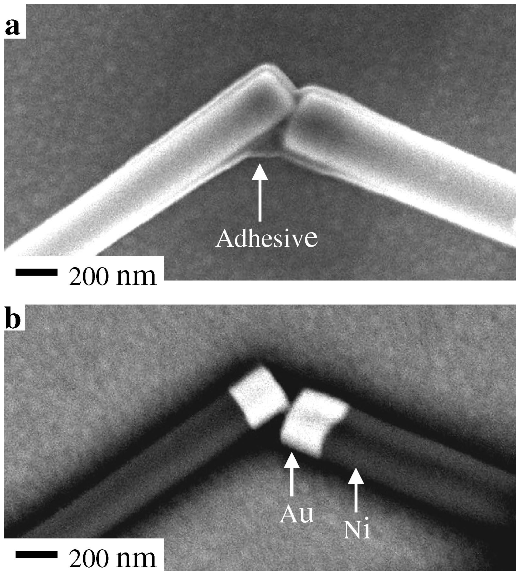

Figure 2. SEM images showing two rods held together by the polymerized adhesive. (a) Secondary electron image showing the polymeric adhesive and the rods. (b) Backscattered electron image (brighter regions correspond to materials with higher atomic numbers). The polymer is not visible; the Au segments appear brighter than the Ni ones.

In a typical experiment, a small amount of the adhesive solution was added to a few drops of a suspension of rods in ethanol. The glass vial was made hydrophilic by plasma treatment in air. This treatment was necessary to minimize sticking of the hydrophobic rods to the walls of the vial. After adding the adhesive to the rods, the vial was shaken well and allowed to sit for several minutes. Using a syringe, a few drops of water was added to the solution. Since the monomeric adhesive solution was hydrophobic, it precipitated preferentially on the hydrophobic Au−HDT segments on the rods. The adhesive coated rods immediately coalesced to form aggregates; this aggregation was very dramatic and could be observed with the naked eye. The excess ethanol adhesive solution was removed by the addition of an excess of water. The vial was then sealed and agitated to form self-assembled aggregates. After self-assembly, the aggregates were permanently bonded by curing the adhesive. Figure 2 shows a scanning electron microscopy (SEM) image of two multicomponent rods joined by an adhesive layer. By comparing the image obtained over the same region using

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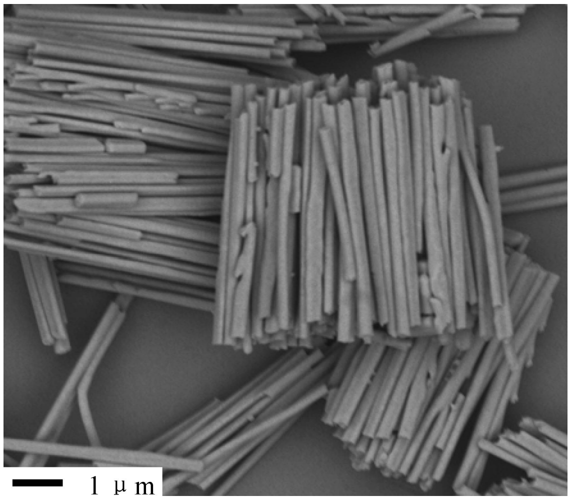

Figure 3. A backscattered SEM image of 3D bundles formed using rods composed entirely of Au.

two different detectors in the electron microscope (the backscatter and secondary electron detector), it was possible to discern the Au, Ni, and polymeric adhesive in the bonded structure.

To demonstrate the versatility of the methodology, we formed two structures with different topologies, (a) 3D bundles and (b) 2D open networks with end-to-end connectivity. The self-assembly of 3D bundles necessitated the use of rods composed entirely of Au, so that the whole rod was rendered hydrophobic by HDT. It was also necessary to keep the rods in the bulk during self-assembly, since there was a tendency of the hydrophobic rods to reside at the air−water interface to form 2D close-packed rafts. In our experiments, after the addition of the adhesive to the solution, the rods were allowed to settle at the bottom of the vial. Using a syringe, water was added extremely slowly at the bottom of the vial, making sure not to disrupt the solution thereby sending the rods to the air−water interface. The rods aggregated at the bottom of the vial as a result of the minimization of the surface free energy between the adhesive coated rods and water. Once aggregates were formed, their weight was sufficiently high that they did not migrate to the air−water interface. The excess adhesive was then removed, and the solution was agitated by rotating the vial overnight. The vial was then sonicated and sealed in a water bath that was purged with dry nitrogen gas. The nitrogen purge was used to remove oxygen, since the presence of oxygen inhibits polymerization. The water bath was heated to 80 °C for 10 hours to polymerize the adhesive. A few aggregates were transferred onto a silver coated silicon substrate by dip coating for SEM analysis. Figure 3 shows 3D bundles formed by self-assembly. The largest bundles contained hundreds of rods; the distribution of the number of rods in each bundle varied widely. We observed that the distribution was sensitive to the concentration of adhesive added, as well as the strength and duration of the agitation used.

To form 2D open networks, we used rods with Au ends separated by a Ni segment. During processing of the rods, the Ni segments were oxidized and the monolayer HDT did not adhere well to these segments. As a consequence, the Au−HDT segments were much more hydrophobic than the Ni−HDT segments. We verified the difference in hydrophilicity of Au and Ni by measuring the contact angle of water on flat Au and Ni coated silicon substrates that were subjected to the same processing conditions as the metallic rods used in the self-assembly. The contact angles were 104° ± 3° for Au and 43° ± 10° for Ni. Aggregation occurred at the air−water interface on the addition of water to the adhesive coated rods. The solution was agitated using sonication to facilitate the formation of 2D networks. Since the 2D networks were formed at the air−water interface, it was possible to use photoinitiation to

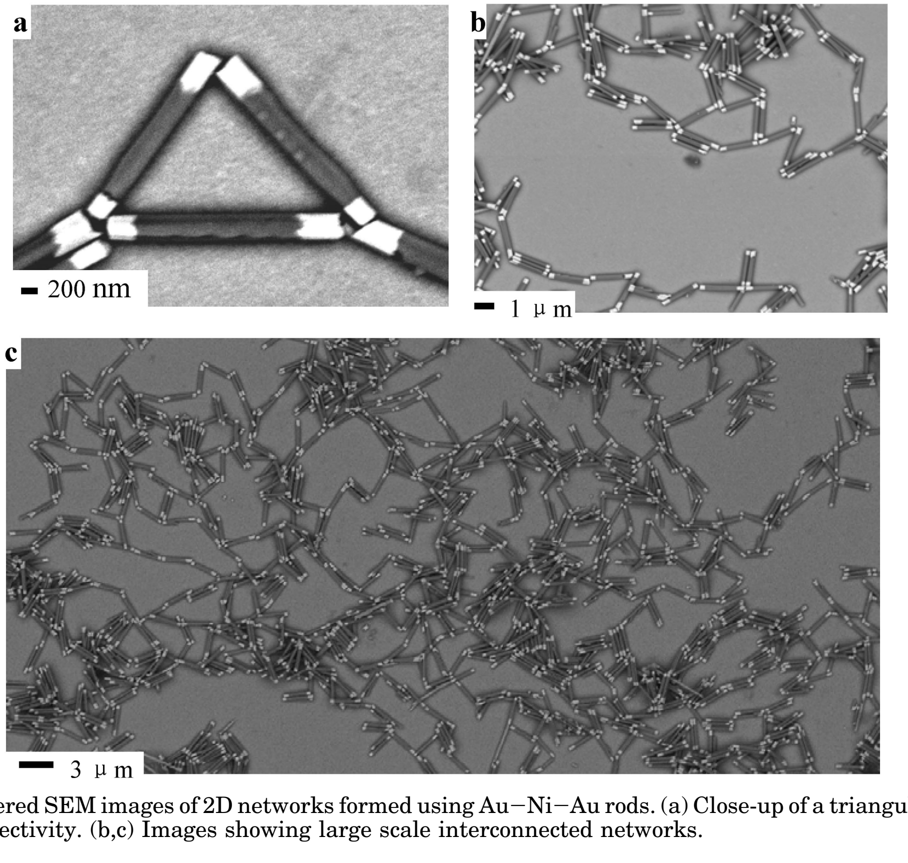

Figure 4. Backscattered SEM images of 2D networks formed using Au−Ni−Au rods. (a) Close-up of a triangular structure formed with end-to-end connectivity. (b,c) Images showing large scale interconnected networks.

cure the adhesive. The vial was purged with nitrogen gas and exposed to ultraviolet light for 1 hour in order to achieve optimum cure of the adhesive. In the case of the 2D network assembly, in addition to removing oxygen during polymerization, the nitrogen purge also agitated the rods during polymerization and disrupted weakly adhered aggregates. Figure 4 shows SEM micrographs of the 2D networks formed using 2.5 micron long multicomponent rods. We observed two modes of attachment: the predominant mode of attachment was end-to-end, and a secondary mode of side-to-side attachment was seen with less frequency. The end-to-end attachment was due to the favorable interaction between hydrophobic Au−adhesive coated tips on two different rods during self-assembly in water. The side-to-side attachment occurred as a consequence of the alignment of hydrophobic Au tips and hydrophilic Ni tips on different rods.

The self-assembled aggregates formed on polymerization of the adhesive are mechanically bonded. This conclusion is based on the fact that the 2D networks survived considerable agitation during polymerization when N_2 gas was blown into the vial. We have also observed that the 3D bundles and 2D network aggregates survive mild sonication. We performed control experiments with rods that were not functionalized with HDT. In experiments in which the HDT functionalization step was skipped, we observed limited self-assembly using the hydrophobic adhesive. We attribute this limited assembly to the fact that the unfunctionalized Au surface was still relatively hydrophobic. However, HDT functionalization of the rods greatly improved the yield and quality of the assembled aggregates formed. We did not observe any aggregation of 2D networks or 3D bundles in experiments in which no adhesive was added (all other processing steps staying the same).

While dissolving the membrane to release the rods, we sometimes observed the formation of huge bundles or sheets, containing thousands of rods that were lined up, similar to that observed in the amphiphilic aggregation of Au−polymer rods observed in an earlier study.[10] However these aggregates disappeared after sonication in the NaOH solution that was used to dissolve the alumina membrane.

In our experiments, we were able to form 2D networks but did not observe any 3D networks; we believe this two-dimensionality was a result of the tendency of the rods and adhesive to reside at the air−water interface since air is hydrophobic. Once the rods aggregated at the interface, it was impossible to transport the networks back into the bulk. For the formation of 3D bundles, it was necessary to add water extremely slowly to the bottom of the vial to cause aggregation in the bulk. In the case of any disruption prior to assembly in the bulk, the rods formed 2D close-packed rafts. Once the 3D bundles aggregated in the bulk, the tendency to go to the interface was decreased. To extend this strategy to form 3D networks, it will be necessary to remove the hydrophobic air interface, using for example an airtight vial. The quantity of adhesive used in the experiments was also critical: the concentration of adhesive had to be small enough so that droplets of adhesive did not form and segregate in the water solution; the concentration however had to be large enough so that the rods were well coated with the adhesive. The surface area of each rod was extremely small; we estimated a concentration of approximately 10^{-10} μL/rod for a 10 nm coating on a 200 nm diameter Au rod of length 4 microns. When a larger quantity of adhesive was added, we observed some micron sized polymerized balls in SEM images. We did not observe a strong size dependence on the length of the rods used in the experiment; we believe this is due to the fact that the surface tension force is extremely large (as compared to other competing forces such as gravity) for 200 nm diameter rods with a length between 2 and 6 microns.

In summary, we have demonstrated a methodology for permanently bonding 200 nm scale rods using adhesive joints. This strategy can be extended to assembling other nanocomponents to form 2D and 3D integrated systems. Since the assembly of 3D bundles occurs because of a thin polymer sheath connecting the rods, it may be possible to fabricate insulated electrical wire bundles using this methodology. The attractive feature of this kind of assembly is that it is possible to form mechanically bonded structures that do not break apart easily; this rigidity is crucial in the fabrication of submicron and nanoscale 3D electromechanical structures of practical use. To form monodisperse bundles, it may be necessary to use surfactants such as block-copolymers to form cavities within the fluidic medium with well-defined sizes.[19] Finally, since the rods used contain Ni segments, it is possible to utilize orthogonal magnetic and surface tension based interactions to form more complex self-assembled structures.[20]

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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