Uniform One-Dimensional Arrays of Tunable Gold Nanoparticles with Tunable Interparticle Distances

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Due to their intrinsic size-dependent properties, metal nanoparticles are excellent candidates for applications in electronic information storage,[1] in photonics,[2] in biological sensing devices,[3] and as catalysts for nanowire growth.[4] Although many preparation methods for gold nanoparticles have been described,[5] a challenge persists in being able to prepare well-defined, controlled assemblies in one-, two-, and three-dimensions.[1] 3-D and 2-D arrangements of metal nanoparticles have been extensively investigated, and some successful strategies have been reported.[1] 1-D assemblies are a "Holy Grail" in nanoparticle science because of their anticipated transport (optical and electrical) properties.[1,6] While quasi-1-D assemblies have been produced in several instances,[1,7,8] assemblies that are strictly 1-D in geometry are scarce. Among the few attempts of 1-D assemblies of gold nanocrystals, DNA−template[9] and polymer−template[10] methods have been described, but they have limitations arising from the specific scaffolds. Recently, combinations of STM-based chemistry and nanoparticle self-assembly have also been introduced.[11,12] Overall, the later techniques remain time-consuming and small-scale methods.

Here we describe a strategy for the 1-D assembly of gold nanoparticles on surfaces. An electron beam is used to write patterns in an ultrathin film of Au(I)−thiolate materials, and subsequent pyrolysis of the patterns allows for gold nanoparticle growth upon removal of the organic material. The Au(I)−thiolate precursor compounds are soluble, can readily be spin-coated on flat substrates at a desired thickness, and are stable enough to withstand the deposition, e-beam writing, and development processes without decomposition. The combination of such precursor materials with the electron beam lithography technique provides a flexible and rapid method for producing 1-D arrays of gold nanoparticles. This template-free technique allows one to (1) control and vary the nanoparticle size on a given sample, (2) control and vary the interparticle distances in the assemblies on a given sample, (3) precisely position the defect-free 1-D assemblies of monodisperse nanoparticles on the surface, and (4) prepare assemblies on a large scale.

Briefly, the Au(I)−thiolate complexes are synthesized using readily available precursors following an adaptation of a published route.[13] The thiols used to prepare the Au(I)−thiolates are thiocholesterol and polystyrenethiol (PS_{19}-SH; 19 units of styrene), yielding Au(I)−thiocholesterol and Au(I)-PS_{19}, respectively. Synthesis details are described in Supporting Information. Such Au(I)−thiolates were designed to be soluble materials that readily spread onto surfaces, due to the bulky thiol ligands used.[14] It is also necessary that the gold(I) precursors be sufficiently stable under the conditions of the experiment to be spread on a surface from solution and then manipulated. In our hands, less stable Au(I) complexes (such as gold(I) chlorotetrahydrothiophene) do not meet this condition and decompose when simply spread on a p-doped silicon substrate. The Au(I)−thiolates used here, however, have been stable for more than 2 yr when kept in the dark at 4 °C.

Once a thin film of a Au(I)−thiolate is deposited on a substrate such as Si or SiO_2/Si, a focused electron beam is used to write 1-D lines over a wide range of lengths and shapes (Supporting Information). A FEG-SEM microscope with an electron beam diameter of ca. 1 nm was used for this purpose. The writing process consists of a series of spot exposures to the e-beam, in which the dwell time over each spot, the distance between spots (center-to-center), and the position of the spots are controlled by computer to obtain the desired pattern. The samples are subsequently developed in suitable organic solvents (such as chloroform or toluene) for short periods of time (1 to 3 min) to remove unexposed Au(I) complex. After development, organometallic lines with widths as narrow as 15 nm are obtained (Figure 1A) when the center-to-center distance between two consecutive e-beam spots is small (e.g., 2.5 nm) and effective overlap of the

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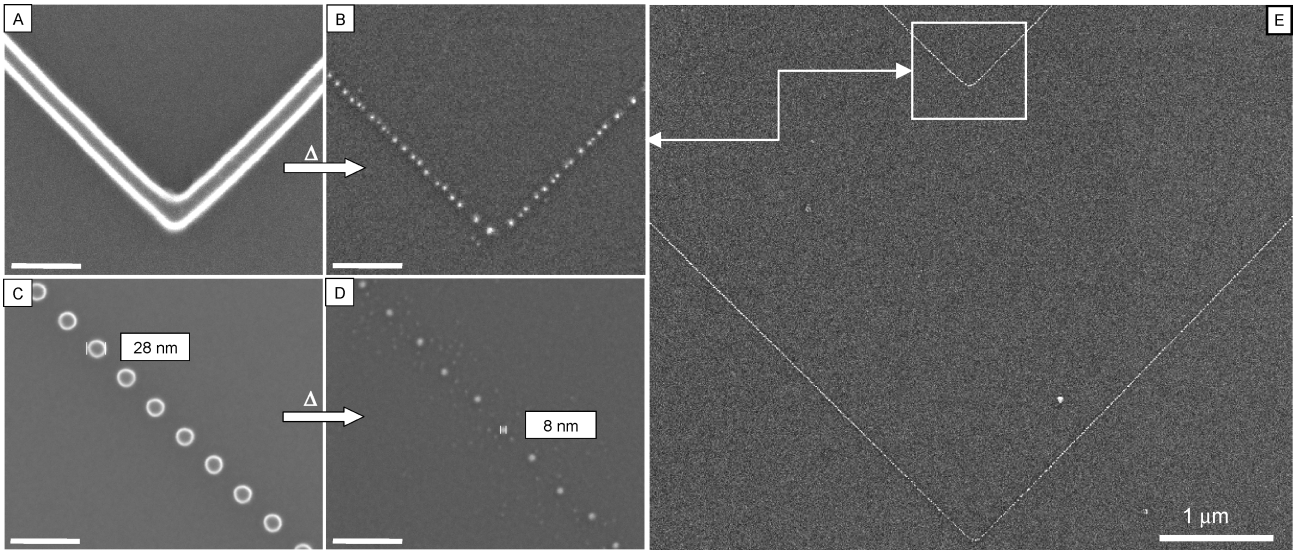

Figure 1. FEG-SEM images of Au(I)-PS_{19} patterns written with an e-beam spot center-to-center distance of 2.5 (A) and 60 nm (C), respectively, on p-doped Si, and of the corresponding gold nanoparticle arrays after pyrolysis (B) and (D). Scale bars in panels A−D = 100 nm. Panel E shows two larger scale 1-D arrays of 8 nm diameter gold nanoparticles prepared under the same experimental conditions as in panel B.

exposure spots is possible. Subsequent pyrolysis (450 °C) of this organometallic line in a mixed atmosphere of oxygen and nitrogen yields a 1-D line of single gold nanoparticles (Figure 1B). An initial 50 nm thick film of Au(I)-PS_{19} yields nanoparticles with diameters of ca. 8 nm. When the thickness of the Au(I)-PS_{19} film is doubled to 100 nm, the diameter of the gold nanoparticles increases to 10 nm. This change precisely corresponds to the doubling of the initial gold volume present in the organogold pattern, assuming that the final gold nanoparticles are pseudo-spherical (while we assume that the gold nanoparticles are spherical, other gold nanoparticle geometries cannot be excluded). When the center-to-center distance of the e-beam spot exposure is increased to larger values (for example to 60 nm), 1-D assemblies of cylinders of the organometallic material are obtained after the development step (Figure 1C). Following pyrolysis, 1-D lines of 8 nm diameter gold nanoparticles separated by 60 nm are observed (Figure 1D). Assuming a spherical shape of the nanoparticle, the nominal volume of gold present in a given organogold nanocylinder corresponds to the gold volume in a nanoparticle after pyrolysis of the nanocylinder. Figure 2 provides a schematic overview of the overall process.

X-ray photoelectron spectroscopy (XPS) analysis of a large 2-D array of the as-prepared gold nanoparticles (Figure 2D) reveals that they are composed solely of metallic gold (Figure S1, Supporting Information). Neither gold oxides[15] nor Au/Si alloys arise during the pyrolysis step, as only one gold species (Au^0) appears in high-resolution XPS measurements. There is neither trace of sulfur (thiol) nor unsaturated carbon (thiocholesterol or polystyrenethiol) species from the precursor complex remaining after pyrolysis. XPS data also confirm that the carbon/silicon ratio in the post-pyrolysis gold nanoparticle arrays is comparable to the carbon/silicon ratio on a clean, bare silicon wafer. This indicates that the gold

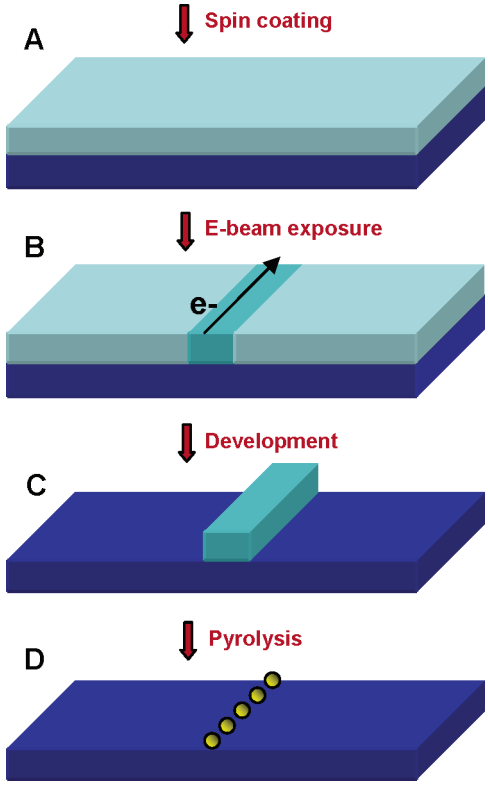

Figure 2. Schematic representation of the fabrication method. (A) A thin film of Au(I)−thiolate is spin-coated on a substrate. (B) The thin film is partially exposed to a focused electron beam. The resulting exposed region is outlined in darker blue. (C) Upon development in an organic solvent, the unexposed areas are dissolved away and only the beam-exposed organogold pattern remains on the substrate. (D) After pyrolysis, a 1-D gold nanoparticle array appears on the substrate.

nanoparticles are ligand-free. Undecorated gold nanoparticles can be readily functionalized with aurophilic ligands such as alkylthiols, alkylamines, or phosphines.

Transmission electron microscopy (TEM) was also used to characterize the gold nanoparticle arrays. Silicon nitride membrane windows (50 nm thick) are used as TEM substrates. After writing with the e-beam, the patterns were developed in toluene (chloroform breaks the thin silicon

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nitride membranes). After pyrolysis, TEM reveals the formation of faceted, crystalline gold nanoparticles (Figure S2, Supporting Information) similar to those described in a previous study.[16] TEM is also an effective tool to precisely determine the gold nanoparticle sizes; the sizes thus determined are in excellent agreement with those determined using FEG-SEM.

The TEM experiment was also used to understand the mechanism of the gold nanoparticle formation in the e-beam/pyrolysis procedure. To this end, the 50 nm thick lines formed in the e-beam on TEM grids were assessed by TEM before pyrolysis. Surprisingly, we were unable to detect any gold nanoparticles (i.e., larger than 5 Å) within the patterns. This suggests that the gold nanoparticle growth occurs during the pyrolysis step and not during the e-beam writing step. The e-beam step likely serves to cross-link the thiolates used,[17] allowing the organogold nanopatterns to resist dissolving during the development stage. It is likely that small gold clusters (diameter <5 Å) are formed under the reducing action of the electron beam. The growth of the gold clusters is probably limited by the highly viscous cross-linked polymer medium surrounding them. The existence of a uniform dispersion of gold nuclei within the organogold patterns is very probable given that the nanoparticles, after pyrolysis, are exactly positioned and aligned in the center of the pyrolyzed organogold nano-line. Also, pyrolysis of a thin Au(I)−thiolate film without previous e-beam exposure yields very polydisperse nanoparticle samples. In-situ pyrolysis of organogold nano-lines performed in a transmission electron microscope would reveal the details of such a nucleation and growth mechanism.

Contact-mode AFM was also employed to evaluate the nanoparticles. The gold nanoparticle heights are equivalent to their diameters. Heights determined from FEG-SEM images on the arrays of gold nanoparticles observed with the sample tilted at an 80° angle agree with the AFM-derived nanoparticle diameters (Figure S3, Supporting Information).

When Au(I)−thiocholesterol is used as a precursor film instead of Au(I)-PS_{19}, larger gold nanoparticles are obtained for the same initial film thickness. For example, when the Au(I)−thiocholesterol film thickness is 50 nm, gold nanoparticles of 13 nm diameter are obtained. This arises from the fact that the volume fraction of gold in Au(I)−thiocholesterol (2.6% volume gold in Au(I)−thiocholesterol) is five times higher than in Au(I)-PS_{19} (0.5% volume Au in Au(I)-PS_{19}).[18] Gold nanoparticles with diameters up to 24 nm have been obtained using Au(I)−thiocholesterol as a precursor (Figure 3). Access to different Au(I)−thiolates thus allows one to further "tune" the particle size.

A significant advantage of this method, over "bottom-up" self-assembly approaches, is that the patterns formed are highly regular and uniform, and the gold nanoparticles are placed in an exact and addressable fashion on the substrate. The process is very fast, since it takes only seconds to write

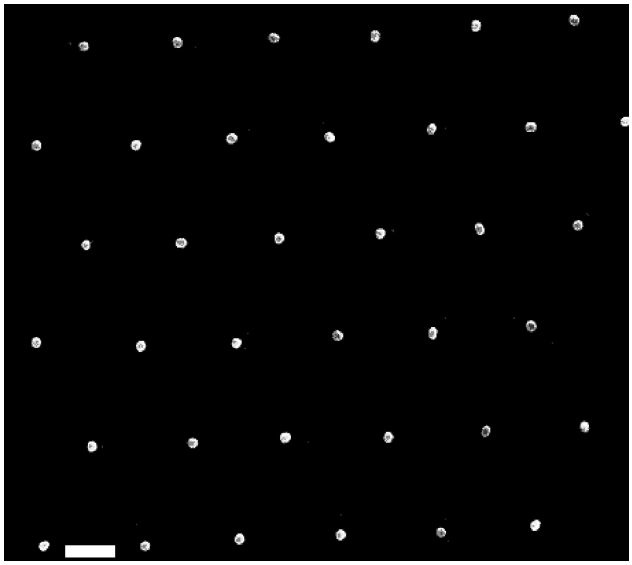

Figure 3. FEG-SEM image of 20 nm diameter gold nanoparticles, using Au(I)−thiocholesterol as a precursor. Scale bar = 100 nm.

patterns that are tens of micrometers long (Figure 1E). While a few other techniques[13] have been recently reported that also allow for the precise 1-D assembly of gold nanoparticles, they are currently only possible on a small scale and usually necessitate long fabrication times.

This method can also be used to prepare large 2-D assemblies of gold nanoparticles on surfaces. We have previously reported that a variation in electron beam dose allows one to vary the gold nanoparticle surface density in 2-D patterns.[8] The nanoparticle surface coverage ranges from $<1\%$ to 20% in the case of a 100 nm thick film of Au(I)-PS_{19} precursor. Thicker films and/or a Au(I) precursor having a higher gold content (such as Au(I)−thiocholesterol) result in an increased surface coverage.

Our new method combines both top-down (electron beam lithography) and bottom-up (nanoparticle nucleation and growth) approaches to simultaneously prepare and precisely assemble gold nanoparticles in true 1-D lines. The nanoparticle diameters (2−24 nm) are determined by varying the initial thickness of the Au(I)−thiolate films, by using thiolates whose ligands span a range of molecular weights, thereby providing control over the mass (or volume) fraction of Au in the precursor film, and by varying the electron beam exposure conditions. The interparticle distances, as well as the patterns composed of nanoparticles, are readily tunable on a given substrate by varying electron beam parameters. In addition to being direct, this fabrication method has the advantage that 'bare' nanoparticles are produced, thus allowing for their direct functionalization with molecules of interest. This is important for bio-sensing applications among others.[3]

We anticipate that the method reported here is a versatile technique that can be applied to many other organometallic systems, allowing one to produce a variety of metallic nanoparticles. Mixtures of different organometallic materials can also be used, resulting in alloyed metallic nanoparticles.[19]

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We are currently studying Au(I)−thiolates and mixtures of Ag(I) and Au(I) compounds as starting materials, and the nature of the nanoparticles produced. Larger Au or Ag nanoparticles on surfaces have been investigated as promising precursors for biosensors using techniques such as surface plasmon resonance spectroscopy[4] and surface-enhanced Raman scattering spectroscopy.[20] We expect that the Au (or Ag) nanoparticles described here will have different properties and sensitivities for such applications. Finally, plasmonics and electronics studies have not yet been performed on 1-D arrays of such small gold nanoparticles, due to the difficulty in making such arrays. The technique described here will enable some of these challenges to be overcome due to the ease and precision of formation of nanostructures from these novel precursors.

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Supporting Information Available: Experimental details and Figures S1 to S3. This material is available free of charge via the Internet at http://pubs.acs.org.

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