Controllable Growth of Gold Nanowires for Photonics Applications

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We propose a one step method for growing high aspect ratio (6–300) gold nanowire (NW) segments from low aspect ratio (AR) gold nanorods by using the dielectrophoresis method between targeted points, copper electrodes in our case, one of which is stationary and the other movable to control the dimensions. The growth is obtained by applying low ac voltages of 0–4 V between the electrodes, unlike any other methods published. The gold nanowire structures are characterized by electron microscopy. This growth technique allows easy isolation from the solution, unlike chemical growth methods, at the single NW level. We have better control over the length and overall AR of the NW and growth of the NW can be stopped once we obtain the size we need, making the method useful for building optical nanocircuits. Wavelength tunability of surface plasmon resonance peaks, by varying the aspect ratio, makes this a promising tool for various optical applications over a wide range of frequencies.

Keywords: Nanowires, Nanorods, Dielectrophoresis, Nanophotonics, Microresonators.

Nanowires (NWs) are considered essential components towards building nanoscale devices and circuitry with increased performance and greater speed.[1–3] When we talk of shrinking processors or microchips, we talk about feature size being reduced from submicron to nanometer size. The chemically inert nature and relatively low resistivity of Au makes it a suitable candidate for growing wires. Gold nanomaterial can be grown by the wet chemical approach or the self-assembly method.[4–5] Other approaches require extensive secondary processing methods with less control over shape and size distribution. In the latest development in the area, chemically grown ultrathin NWs have been prepared with diameters of either 3 or 9 nm.[6] Gold nanoparticles provide unique and tunable optical properties resulting from their surface plasmon resonance effects[7–9] and can be used for various optical and sensing applications.[10–12]

NWs can be assembled or grown between targeted points in a circuit using the dielectrophoretic approach with a fixed dimensionality.[4,13,14] Gold NWs has been reported in many optical and sensing applications.[15–17] The dielectrophoresis (DEP) method of growing NWs is based on the mobility and interactions of nanoparticles (or nanorods (NRs), in our case) caused by gradient alternating electric fields. This electric field allows assembly and manipulation of the NRs used to grow NWs. The same approach is being used by us for growing NWs, with a different experimental setup—using a much simpler setup and having the capability to grow higher AR (ratio of width to its height) NWs. Proper choice of the electrode geometry, in our case copper electrodes, is important; their tips are made as sharp as possible to produce a sharp electric gradient in front of them. We can also grow NWs with other metal electrodes which do not oxidize, like gold. The NWs discussed in this paper were grown primarily from NRs of AR 3.5 ± 1 (Nanopartz). The NR solution is sonicated first and then centrifuged 2–3 times at 10,000 rpm to remove the majority of the cetyl trimethylammonium bromide (CTAB). CTAB present in the gold NR solution hinders the unidirectional growth of NWs. The dielectric force is given by the following equation:[4,13]

$$F_{DEP} = (m(t) \cdot \nabla E(t)) \tag{1}$$

where E is the electric field and m the induced dipole moment of the NR given by

$$m(t) = \varepsilon_m V_p K E(t) \tag{2}$$

where ε_m is the complex dielectric permittivity of the medium, ε_p is the complex dielectric permittivity of the particle and V_p is the volume of the particle and K is the complex polarization factor, which depends on the complex permittivity of the particle.

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The dielectrophoretic force shown above is caused due to the non-uniform electric field between the electrodes. This force causes the interaction between the dipoles in the NRs to be directed along the electric field, leading to single-step assembly of NWs between the electrodes.

The expression for dielectrophoretic using an ac electric field is given by[13]

$$F_{\text{DEP}} = (1/2)\pi r^2 \varepsilon_m l \text{Re}[K(\omega)]|\nabla|E|^2 \qquad (3)$$

where $K(\omega)$ is the real part of what is called the Clausius-Mosotti factor given by

$$K(\omega) = \text{Re}\left[\frac{\varepsilon_p^* - \varepsilon_m^*}{\varepsilon_p^* + \varepsilon_m^*}\right] \qquad (4)$$

l is the length of the particle and ∇E is the gradient of the electric field. The force due to DEP is oscillating in the direction of the electric field gradient. Here ε_p is the particle dielectric constant, in our case that of gold, and ε_m is the medium dielectric constant; note that the dielectric constants are complex quantities.

Electrode pairs are usually fabricated, using photolithography, onto a chip for growing wires in circuits.[2, 4] Here we use electrodes fabricated from copper wire. Figure 1 shows the experimental setup used for growing NWs. An arbitrary waveform function generator (Wavetek 395) is used to supply an alternating voltage at a variable frequency. We used a sinusoidal waveform. The region between the electrodes is observed using an optical microscope shown in Figure 1. To grow the NWs, 100 μl of gold NR solution was used. The weight concentration of the rods is 35.7 μg/ml, the pH was 3.1, and the molarity was 874 pM. The charge on the rods is usually determined from zeta potential measurements. The zeta potential of the NRs we used is 30 mV, indicating the NRs are positively charged.

The electrodes are brought nearly into contact, without actually touching, before growing a NW. Using a translation stage shown in Figure 1, with one electrode fixed and by moving the second electrode, a gold NW can be drawn and its size controlled well. We typically used peak voltages of 2.5 ± 1 V and frequencies ranging from 1–10 Hz. The applied ac voltage was terminated manually when the desired wire size was obtained. As seen in Figure 1, one
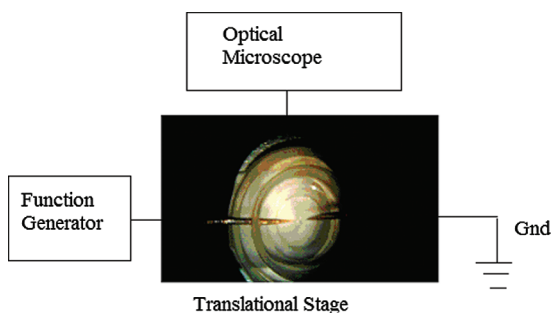
copper electrode is grounded and the other is connected to the function generator. The growth is monitored using an optical microscope (Leica). After the NWs are grown they are characterized using scanning electron microscopy (SEM). Transmission electron microscopy (TEM) has better resolution but it is difficult to load NWs onto a TEM grid without breaking them.

The chaining of nanoparticles or NRs in forming a NW depends strongly on the ability of the particle-field and particle–particle interactions to overcome Brownian motion.[4] The strength of the particle-field interaction is characterized by the unitless trapping parameter[4, 18]

$$\eta = \mu E/(k_B T) \qquad (5)$$

where μ is the magnitude of the induced dipole moment, E is the applied field magnitude, k_B is the Boltzmann constant and T is the temperature in Kelvin.

After the NW was grown between the electrodes, a high precision 3D stage was used to position the microsphere under the NW and then gently moved up through the electrode gap, breaking free the NW from the electrodes and positioning it on the surface of the microsphere. Figure 2 shows an SEM image of a NW after being deposited on a fused silica microresonator. The NWs can be grown long, from 5 μm to around 600 μm.

This is a novel method for growing long NWs, the length of which can be controlled well. The AR of the wires grown in the lab can be controlled to approximately 400 (as seen in Fig. 2) or more. Commercially available chemically grown NWs from Nanopartz have ARs from 150 to 200. Growth conditions such as electrode geometry and concentration of nanoparticle solution are kept identical, but the voltage amplitude and frequency are varied when we grow different NWs.
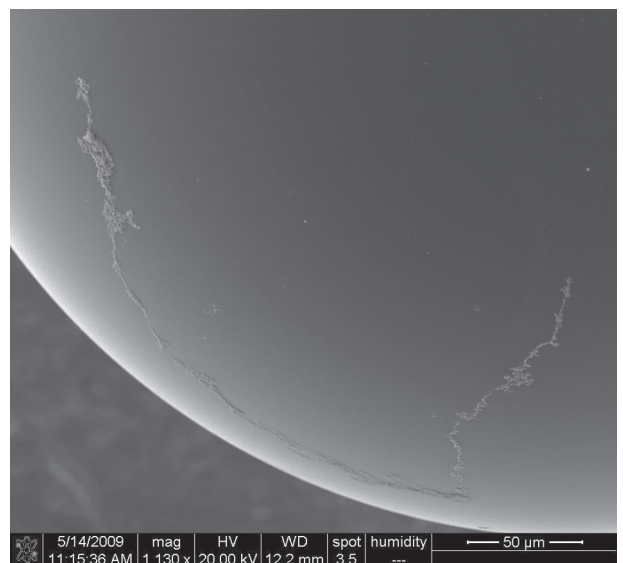

Fig. 1. Block diagram of the apparatus used for nanowire assembly.

Fig. 2. SEM image of a gold NW grown and then deposited on the surface of a fused-silica microresonator.

All the SEM images are taken at 20 kV. Figure 3 shows a TEM image of the gold NRs used for growing gold nanowires. Figures 4 and 5 show SEM images of various fragments of a NW with different ARs deposited on the fused-silica surface along with particles of gold.

The most important parameters affecting growth are the field strength and NR concentration; they should exceed certain limits or thresholds in order to start seeing NW growth. As we increase the particle concentration beyond 0.13%, the growth rate and thickness of the wire increases.[13] If we switch over from ac voltage to dc voltage we have observed branching under nearly identical conditions. The conductive properties and other electronic characteristics of the high-AR wire still need to be investigated

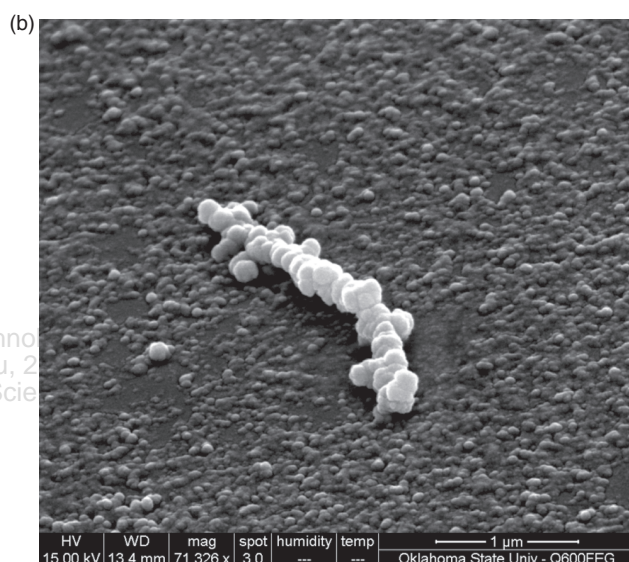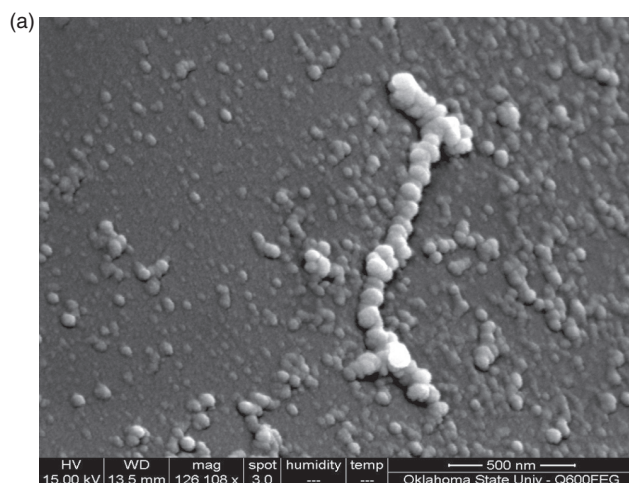**Fig. 3.** TEM image of gold NRs of AR 3.5 ± 1 used for the growth of gold nanowire; the scale bar is 100 nm.

Fig. 4. SEM image of a gold NW fragment deposited on a fused-silica substrate; the scale bar is 2 μm.

(a)

(b)

Fig. 5. SEM images of gold NW segments deposited on a fused silica substrate for imaging. (a) AR $\sim$ 17, scale bar is 500 nm. (b) AR $\sim$ 7, scale bar is 1 μm.

before it can be used for engineering applications to build circuits.

The novelty in our technique is that we can grow wires without having to amplify the voltage to 30 V or greater as has been reported earlier.[4, 13, 14] The frequency we used is also relatively low, 1–10 Hz, compared to 100–150 Hz or even a few MHz used by other groups.[4, 13] As we draw the wire the thickness of the wire reduces, perhaps due to the decrease in the influence of the electric field on the particles.

In conclusion, nanowire growth between targeted points, copper electrodes in our case, is obtained by using the DEP method. An alternating voltage is applied to the electrodes immersed in a gold growth solution containing low-AR gold NRs. By controlling various parameters we can grow needle-shaped or dendritic NWs of different AR. This is a novel method for controllable growth of high-AR (6–300) gold NWs from low-AR NRs. We have
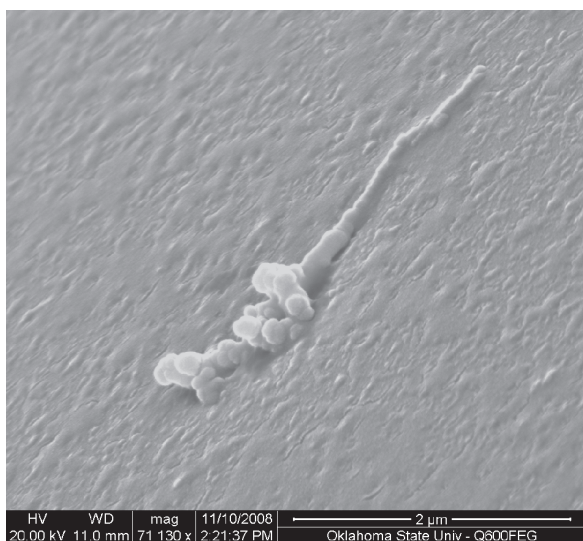
better control over the length of the NW and growth of the NW can be stopped once we obtain the size we need. This wire growth method can be applied to various other metals, alloys and pure semiconducting compounds. The wavelength tunability of the SPR peaks, achieved by varying the aspect ratios of nanowires, makes this a promising tool for various applications including surface-enhanced Raman scattering and optical sensors.

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