

# Seedless, Surfactantless Wet Chemical Synthesis of Silver Nanowires

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## ABSTRACT

We report a method to make crystalline silver nanowires in water, in the absence of a surfactant or polymer to direct nanoparticle growth, and without externally added seed crystallites. The reaction is one in which silver salt is reduced to silver metal, at 100 °C, by sodium citrate, in the presence of NaOH. Hydroxide ion concentration is key to producing nanowires, which are up to 12 microns long, instead of nanospheres.

Metallic nanoparticles exhibit unusual optical, thermal, chemical and physical properties that are due to a combination of the large proportion of high-energy surface atoms compared to the bulk solid and to the nanometer-scale mean free path of an electron in a metal ( $\sim 10$ – $100$  nm for many metals at room temperature).<sup>1–4</sup> Silver is an especially attractive metal to examine on the nanoscale, due to its extremely high electrical conductivity in the bulk,<sup>5</sup> and its unusual optical properties that depend on nanoparticle size and shape.<sup>6–10</sup> Previous strategies to control the growth of anisotropic nanoparticles have involved either hard templates<sup>11–14</sup> or softer directing agents, including surfactants or polymers.<sup>15–21</sup> Although good control over nanoparticle dimensions can be realized in these syntheses, removal of the template or directing agent from the nanoparticle surface can require harsh conditions or multiple washings to remove unwanted materials. For sensing applications such as surface-enhanced Raman scattering that require analyte adsorption to the metallic nanoparticle surface, the presence of residue from the synthesis on the nanoparticle surface may be a significant interferent.<sup>22</sup> Linking metallic nanoscale objects together in a rational way requires knowledge of the exposed surface of the nanoparticle;<sup>4,23</sup> again, surface-bound residue from the synthesis increases the difficulty of doing chemistry at the surface. In this paper, we report a synthetic method to make silver nanowires in the absence of a surfactant or soft template, in an attempt to prepare metallic nanostructures with as “clean” surfaces as possible, in water.

A typical synthesis involves the combination of two silver solutions, A and B, prepared in glassware washed thoroughly

with soap (Alconox), deionized water, and aqua regia. Solution A consisted of 100 mL of deionized H<sub>2</sub>O, 1.5–2  $\mu$ L of 1 M NaOH (Fisher), and 40  $\mu$ L of 0.1 M AgNO<sub>3</sub> (Sigma). This solution, in an Erlenmeyer flask, was brought to a boil with rapid stirring. Quickly added to A was 5 mL of 0.01 M trisodium citrate (Fisher), and then the solution was allowed to boil for an additional 10 min. Concomitantly, solution B was made by mixing 150 mL of deionized H<sub>2</sub>O and 1.5–2  $\mu$ L of 1 M NaOH with 20  $\mu$ L of 0.1 M AgNO<sub>3</sub> and bringing this to a boil. Solution B was added to A, the neck of the flask was covered with an inverted 50 mL beaker, and the mixture was allowed to boil for 60 min while stirring rapidly. When the mixture evaporated to  $\sim 75$  mL, additional quantities ( $\sim 75$  mL) of boiling deionized water were added (this usually occurred at  $\sim 30$  min). The final volume was typically  $\sim 75$ – $100$  mL, and the final pH was  $\sim 7.0$ – $7.1$ .

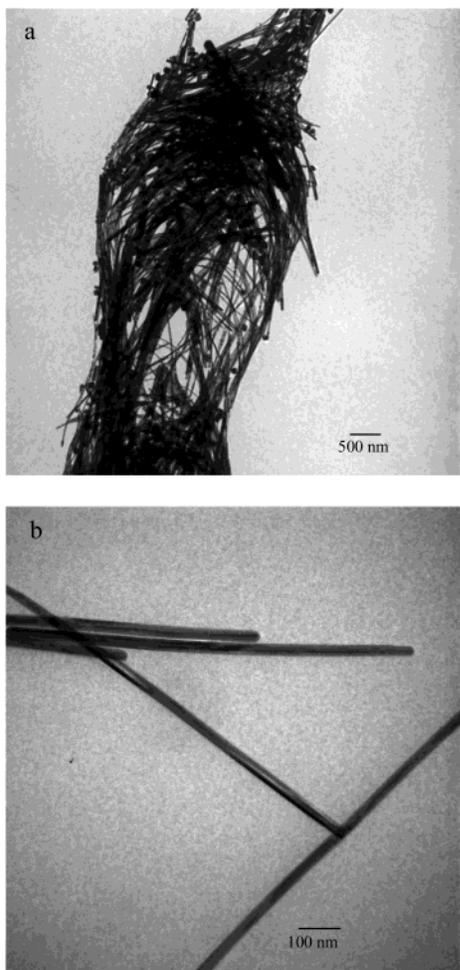
Transmission electron microscopy (TEM) was employed to visualize the size and shape of the resulting silver nanoparticles. Our results from this procedure show that the range of NaOH concentrations used in the synthesis ( $\sim 50$   $\mu$ M NaOH final concentration, compared to  $\sim 80$   $\mu$ M final Ag concentration) gave an abundance of nanowires of varying lengths, with relatively few spherical nanoparticles (Figure 1). A histogram of 400 nanowires shows the relative lengths of the wires measured, the shortest of which was 166 nm and the longest more than 12 microns (Figure 2). The width of the wires was, on average,  $35 \pm 6$  nm.

The quantity of NaOH was an important factor in determining the morphology of the final product. Control reactions in which no NaOH was added gave products with very irregular surfaces, which often appeared as collections of sintered particles (Figure 3a). It was also observed that reactions with no NaOH plated out a large amount of the

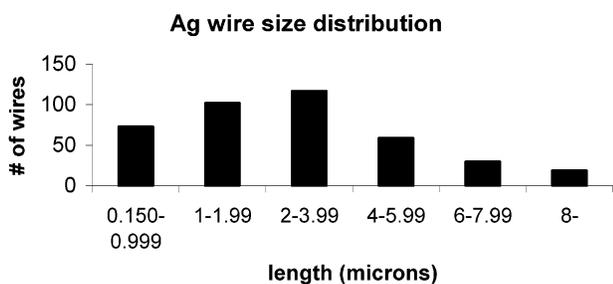
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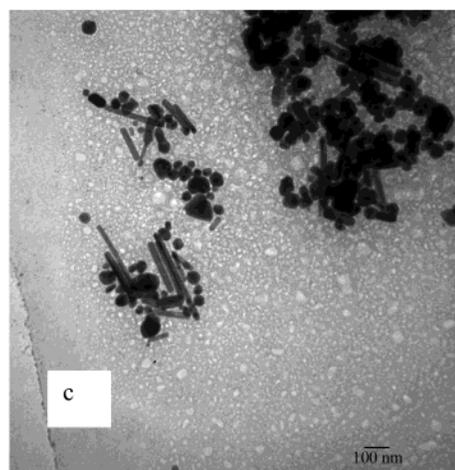
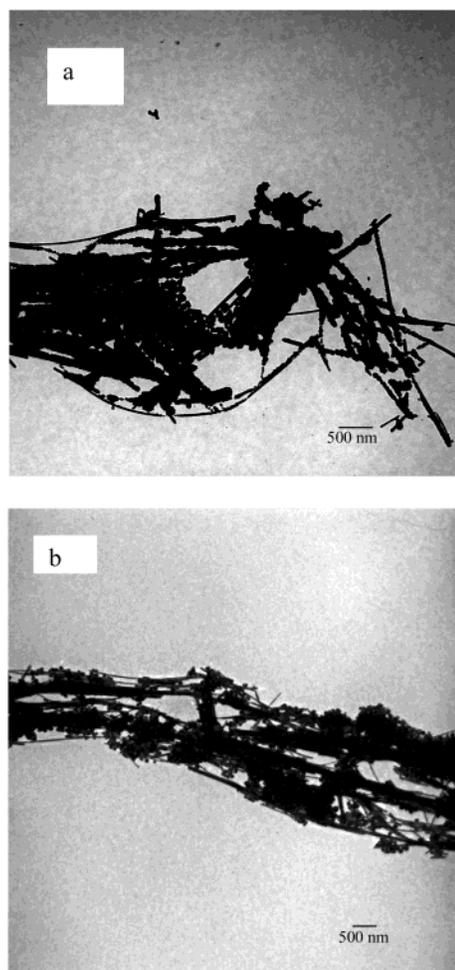
**Figure 1.** Transmission electron micrographs of Ag nanowires synthesized with 3  $\mu\text{L}$  of NaOH added: (a) 15 kX (b) 100 kX. Scale bar is (a) 500 nm, (b) 100 nm.



**Figure 2.** Histogram showing the distribution of nanowire lengths from a sample of 400 nanowires, counted in the transmission electron micrographs.

silver on the sides (and bottom) of the reaction vessel compared with the reactions in which NaOH was added. Also, other controls, including KOH and  $\text{NH}_4\text{OH}$  in lieu of NaOH, gave similar results to the NaOH experiments, and therefore we conclude that hydroxide, rather than sodium ion, is important in silver nanowire growth. Other workers have found that simple ions direct the growth of nanoparticles into different shapes, highlighting the importance of these species.<sup>24</sup>

Increasing the amount of NaOH in the reaction mixture leads to decreased nanowire yield. Reactions in which 6–8



**Figure 3.** Transmission electron micrographs of Ag nanoparticles from syntheses with (a) no NaOH, (b) 8  $\mu\text{L}$  NaOH, (c) 100  $\mu\text{L}$  NaOH. Scale bars are (a) 500 nm, (b) 500 nm, (c) 100 nm.

$\mu\text{L}$  of 1 M NaOH was added did show nanowire formation; however, more spherical nanoparticles were also present (Figure 3b). Reactions with relatively large quantities of NaOH (100  $\mu\text{L}$  of 1 M NaOH) were also run and showed no wires, few rods, and an abundance of small, irregularly shaped particles.

A 15 mL aliquot of the Ag wires produced by the addition of 3  $\mu\text{L}$  of 1 M NaOH was concentrated by centrifugation.

X-ray energy dispersive microanalysis of the Ag wires showed that the sample was essentially pure Ag. Traces of carbon, oxygen, and nitrogen (from citrate and nitrate) were not detected, though a small amount of sodium was present. Considering the concentration of sodium ions from trisodium citrate and sodium hydroxide, this is not unreasonable because the product was not washed before analysis.

Aqueous suspensions of Ag nanowires have a sharp peak at 370 nm in the UV-vis spectra, corresponding to the transverse plasmon band of the wires.<sup>25</sup> In contrast, the control solutions of silver nanoparticles made without NaOH has little absorbance in this region, which correlates well with the observed lack of nanowires in the TEM.

In this synthesis, the citrate is performing multiple tasks. It not only strongly complexes the silver ion ( $pK_1$  for the Ag-citrate complex is 7.1) but it is also responsible for the reduction to silver metal and acts as a capping agent to the silver metal. Although the ratio of silver/citrate is similar to that of other studies,<sup>26</sup> our synthesis resulted in anisotropic particle formation instead of nanospheres. The explanation for this probably involves Ostwald ripening<sup>25–27</sup> and the capping action of the citrate. As the reaction heats, the reduction of the silver ion will start producing small particles of silver metal, which will be capped with citrate due to the 8:1 ratio of citrate/Ag present. At room temperature, the layer of citrate would produce a uniformly stabilized particle, but at elevated temperatures the equilibrium constant for citrate binding to certain crystal faces of silver may begin to differ, leading to selective loss of citrate on certain crystal faces and allowing for the nanoparticle to grow along only one axis. Xia has observed that polymer-mediated silver nanowire growth produced nanowires twinned along the {111} faces.<sup>25</sup> Electron diffraction of our samples in the TEM revealed that the Ag wires were also twinned; the patterns resemble a superposition of a  $\langle 110 \rangle$  and  $\langle 111 \rangle$  zones as previously reported for gold nanorods.<sup>28</sup> This implies that the silver rods are not single crystals but twinned and likely to be twinned about a 5-fold axis, as the patterns look similar to gold and this twinning is well known for face-centered cubic silver.<sup>28</sup> More detailed analysis of the electron diffraction patterns is in progress.

There is a large difference among the morphologies of products in the control (no NaOH), a small amount of NaOH (3–4  $\mu\text{L}$  of 1 M), and a large amount of NaOH (100  $\mu\text{L}$  of 1 M) conditions. The pH of the control solutions before citrate is added is  $\sim 5.5$  compared with  $\sim 6.5$  for solutions containing small amounts of NaOH. Because the  $pK_{a3}$  of citrate is 6.4, more than half of the control solution citrate will be monoprotonated ( $\text{Hcit}^{2-}$ ). This leads to a weaker complexing agent and allows the nanoparticles produced to sinter together and form larger agglomerates of silver (Figure 3a). Alternatively, solutions with higher amounts of NaOH show products that form a few short rods but are dominated by irregularly shaped particles. Although nearly all of the citrate would be deprotonated and thus available for capping the silver, there may be competition from the hydroxide ion for the silver ion. Although hydroxide is only weakly

complexing with the silver ion ( $\log K_1$  is 2.3 and  $\log K_2$  is 1.9), in the reaction with 100  $\mu\text{L}$  of NaOH added there is a 2:1 ratio of hydroxide/citrate. The level of hydroxide could interfere with the capping ability of citrate and lead to the observations in the TEM (Figure 3c).

In summary, a method has been described to produce nanowires of silver in good yield, with relatively few spherical nanoparticle byproducts. The method is simple in that it does not require a surfactant or polymer template, or a “seed”, and the products shown are without purification.

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