Preparation of Silver Nanorods by Rapid Microwave Heating

Fu-Ken Liu,* Yu-Cheng Chang,[†] Pei-Wen Huang,[†] Fu-Hsiang Ko, and Tieh-Chi Chu[††]
National Nano Device Laboratory, 1001-1 Ta Hsueh Road Hsinchu, Taiwan
[†]*Department of Nuclear Science, National Tsing Hua University, 101, Section 2 Kuang Fu Road, Hsinchu, Taiwan*
[††]*Department of Radiological Technology, Yuanpei University of Science and Technology, No. 306, Yuanpei St., Hsinchu, Taiwan*

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We report a method for preparing silver nanorods by a rapid heating process. The procedure we use is one in which a silver salt is reduced to silver metal by sodium citrate under the influence of microwave irradiation. The silver products were characterized by UV–vis absorption spectroscopy, transmission electron microscopy, energy-dispersive X-ray analysis, and X-ray diffractometry. Key aspects for the production of nanorods having high aspect ratios are rapid microwave heating and adequate reaction times.

Recently, one-dimensional nanostructured materials have been focus of much scientific research because of their unusual properties and potential for use in the development of nanodevices.[1] The synthesis of nanorods and the investigation of their properties have received considerable interest.[2] Finding novel synthetic routes that have control over both the nanocrystalline morphology and size is a challenge to chemists and materials scientists.[3]

Quite recently, thermal factors have been proven to affect the size and uniformity of nanoparticles.[4] Controlling a particle growth rate is possible through manipulation of the reaction time and temperature.[5] Microwave irradiation is an efficient heating method that has found a number of applications in chemical synthesis because the technique is quite fast, simple, and very energy efficient.[6,7] The programmable heating ramp is a built-in function of many commercial microwave instruments. This function makes such microwave systems good tools for observing the dependence of the morphology of nanoparticles on the rate of heating. In this paper, we demonstrate a unique phenomenon in controlling the synthesis of silver nanorods using a tunable heating ramp of a microwave system. This control is difficult to achieve when using a low-efficiency heating source, such as that of a conventional hot plate heat station.

To prepare silver nanoparticles, an aqueous solution (10 mL) of a mixture of 1.0 mM silver nitrate ($AgNO_3$) and 3.5 mM sodium citrate was placed in a microwave heating system (MARS-5, CEM Corporation) and reacted at a desired temperature. The microwave instrument was operated in the range from 0 to 100% of its full power (1200 W). An optical fiber was used to monitor and control the temperature by a feedback system to ensure the highest accuracy. The temperature sensor provides accuracy in-vessel readings for optimum control of reactions. After cooling to room temperature, the products were collected for further characterization.

UV–vis absorption spectroscopy (UV 2501PC, Shimadzu) is quite sensitive to the analysis of silver nanoparticles because the position of their plasma absorption peak depends on the particle size and shape.[8,9] Figure 1 presents the UV–vis absorption spectra taken for Ag colloid solutions. When the temperature was raised from 20 to 100 °C over a duration of 20 min, the appearance of a typical silver plasma peak at 440 nm indicates the formation of spherically shaped silver nanoparticles. Surprisingly, when the same rise in temperature occurred over a duration of 1 min, the surface plasma absorption of the silver nanoparticles presents three symbolic bands located at 350, 440, and 560 nm. We attribute the new peaks at 350 and 560 nm to the plasmon resonance peaks of silver with long nanowires and longitudinal plasma resonance of rod-shaped silver nanostructures, which is in contrast to the one absorbance maximum of colloidal spheres.[1]

When using a program in which the temperature is slowly raised (i.e., with the rise in temperature from 20 to 100 °C taking over 20 min), the transmission electron microscopic (TEM, H-7500, Hitachi) image, as presented in Figure 2a, reveals that only spherical silver particles were synthesized. The morphologies of these products are similar to those formed from syntheses using either a hot plate heating station or irradiation, which have been described previously.[10,11] In stark contrast, however, the TEM image obtained after extremely rapid microwave heating (from 20 to 100 °C in 1 min), which is shown in Figure 2b, demonstrates that highly anisotropic nanorods (aspect ratios >65 and lengths >1 micron m) were synthesized. The energy-dispersive X-ray analysis (Figure 2c) of a sample extracted from the mixture presented in Figure 2b provides further evidence that the product is silver. In addition, the X-ray diffraction pattern (X'Pert Pro X-ray diffractometer, Philips) of such a sample is displayed in Figure 2d. The diffraction peaks corresponding to the (111), (200), (220), and (311) planes of metallic silver are resolved. All of the peaks in this X-ray diffraction pattern suggest that the silver nanoparticles synthesized using this method exists as face-centered cubic structures.[12] The pattern suggests that this nanorod has a crystalline structure.

We believe that the formation of silver rods occurs at the higher rate of heating for a couple of reasons. Firstly, the formation of silver nanoparticles from the reduction of metal ions in-

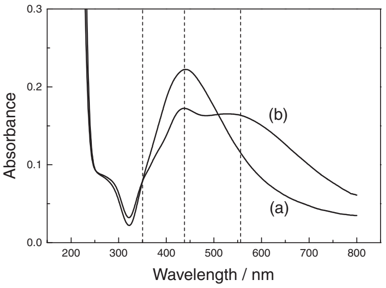
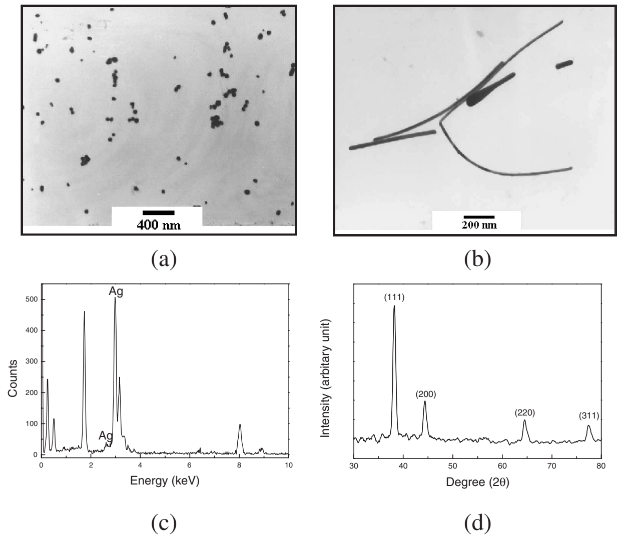


Figure 1. UV–vis spectra of silver nanoparticles obtained using heating ramps of (a) 4 °C/min and (b) 80 °C/min. The temperature was raised from 20 to 100 °C and kept for 10 min.



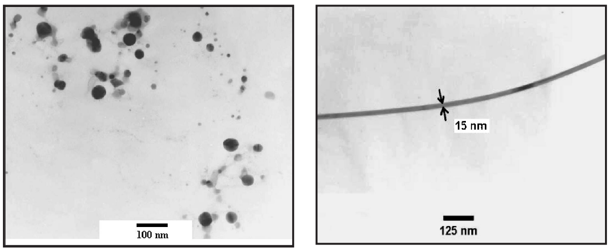
(a) (b)

(c) (d)

Figure 2. TEM images of silver nanoparticles obtained using heating ramps of (a) 4 °C/min and (b) 80 °C/min. (c) Energy-dispersive X-ray analysis and (d) X-ray diffraction pattern of silver nanorods prepared as in (b). The temperature was raised from 20 to 100 °C and kept for 10 min.

volves nucleation and then growth of the nuclei. There is competition between these processes. In general, particle nucleation is extremely sensitive to temperature.[13] Variation of temperature programs might have an important effect on the dynamics of particle growth, which, therefore, promotes the formation of this particular shape of silver rods. Secondly, the citrate ion performs multiple tasks during the synthesis: not only does it complex strongly with silver ions, but it is also responsible for their reduction, and then it acts as a capping agent on the silver metal.[14] At a relatively low rate of temperature increase (e.g., 4 °C/min), spherically shaped particles were produced. When the synthesis reaction was controlled with a heating rate of 80 °C/min, the rate constants for citrate binding at the different silver crystal faces are different. One function of the citrate ions is to kinetically control the growth rates of the various faces by interacting with these faces through adsorption and desorption.[14] The synthesis under the fast-ramp conditions might lead to a selective loss of citrate ions from certain crystal faces, which would allow the nanoparticle to grow along one of its axes.[14]

Figure 3 presents TEM images of two samples that were taken from a reaction mixture (from 20 to 100 °C in 1 min) after the silver and citrate ions had been heated for different periods of time: (a) 2 min and (b) 10 min. These images indicate that the silver nanostructures have different morphologies after different reaction times. When the silver ions underwent reduction by citrate, the initial products ($t = 2$ min) in the solution have spherical shapes (Figure 3a). The products consist of two sizes of spherically shaped particles (7 and 36 nm at average diameters). The smaller set of these silver nanoparticles (which have the larger surface activity) probably dissolve into the solution and grow onto the larger nanoparticles of silver via a process known as Ostwald ripening.[1] There is no significant difference in the morphologies of the particles at this initial stage of the synthesis. When the reaction proceeded for 10 min, the particles underwent an obvious change in morphology (Figure 3b): the silver nanoparticles had grown into high aspect ratio rod-shaped structures (the width of nanorod is 15 nm). At this reaction condition, the phenomenon of citrate-selective binding on certain crystal faces of silver becomes significant. Since the function of the citrate ions is, in part, to kinetically control the growth rates of the various faces of the particle by interacting with them through adsorption and desorption processes, under these conditions, the nanoparticle might grow along one of its axes to form some nanorods (Figure 3b). We note that no nanorods were synthesized unless the reaction time was sufficient; hence, the time of the microwave reaction, and not just the rate of heating, is also a key aspect for the growth of the silver nanorods.



(a) (b)

Figure 3. TEM images of silver nanoparticles obtained after reaction times of (a) 2 min and (b) 10 min. The temperature was raised from 20 to 100 °C using heating ramp of 80 °C/min.

In summary, these preliminary studies demonstrate that the successful microwave-assisted formation of silver nanorods is controlled mainly by two factors: (i) the use of a rapid heating ramp and (ii) the use of an adequate reaction time. This work clearly indicates the great potential and simplicity that rapid microwave heating techniques have for the synthesis of silver nanorods. The phenomena observed in this study would be difficult to monitor if using a hot plate heating station having low heating efficiency.

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