Separation and Study of the Optical Properties of Silver Nanocubes by Capillary Electrophoresis

Fu-Ken Liu* and Fu-Hsiang Ko
National Nano Device Laboratory, 1001-1 Ta Hsueh Road Hsinchu, Taiwan

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This paper demonstrates the feasibility of employing capillary electrophoresis (CE) to separate silver nanoparticles and nanocubes. We monitored the efficiency of these separations by obtaining electropherograms, employing a diode-array detection (DAD) system, as well as by analyzing scanning electron microscope (SEM) images of fractional collection of particles. Our results demonstrate not only the potential for separating silver nanoparticles and nanocubes by CE with DAD but also the ability to use such a technique to investigate the spectroscopic properties of silver nanoparticles having different shapes.

Nanoparticles continue to attract widespread attention in many scientific fields.[1] The size and shape of such particles are two important factors that determine their physical and chemical properties.[2] It is well known that silver nanoparticles have superior properties relative to other nanostructured metal particles, such as their beneficial electrical conductivities,[3] antimicrobial effects,[4] optical properties,[5] and applications in oxidative catalysis.[6] Methods for the preparation of silver nanoparticles are discussed in a number of publications.[7]

In addition to discovering new approaches for their synthesis, there is also a requirement for new tools for characterizing and determining the size of nanoparticles. Recently, CE emerged as one of the most powerful separation techniques.[8] The CE technique has been used successfully to separate a number of differently sized materials, including inorganic oxide particles, latex particles, polystyrenes, silicates, and gold particles.[9] These particulate materials separate during CE because they possess surface charges and, therefore, they behave in a manner similar to that of small, soluble, charged species in CE. For example, the charge of a nanoparticle arises from the sorption of ions onto the nanoparticle's surface during the preparation process, which results in the subsequent forming an electric double layer.[9] The electric potential associated with this double layer not only stabilizes the nanoparticles but also prevents them from agglomerating. Differently sized particles have different values of their charge-to-size ratios and, therefore, they have specific mobilities in a capillary column under the influence of an external applied voltage. Consequently, CE can be used to provide characterization based on particles' sizes.

To the best of our knowledge, there have been no reports that discuss the use of CE to separate differently shaped silver nanoparticles, especially for a mixture of nanoparticles and nanocubes. If such a size- or shape-based separation of silver nanoparticles could be established, the prevalence of modern electropherometers in laboratories could make this method particularly attractive for their routine characterization. Also, since the optical properties of silver nanoparticles are dependent on their size and shape, CE systems equipped with DADs, which allow on-line monitoring of the spectra of separated samples, should be applicable for the characterization of the separated silver nanoparticles. In this paper, we demonstrate that CE, which is an approach used traditionally to separate molecules, can indeed be used to analyze nanoparticles with respect to both their size and shape. Such analyses can be performed on a single sample using volumes as small as several nL, with rapid analysis times of ca. 10 min.

We performed CE separations using an Agilent capillary electrophoresis system. Uncoated fused-silica capillaries of 75 micron m i.d. and 48.5-cm length were obtained from Polymicro Technologies. A detection window around 8.5 cm from capillary outlet was fabricated. Pressure injections for 1 s at 50 psi were employed throughout. Positive polarity was applied at the capillary inlet. The values of pH of the electrolytes were measured using an Orion model 420A pH meter. All electrolytes were prepared freshly each day and filtered through a 0.2-mm membrane filter before use. The capillary was pretreated before use as follows: the capillary was flushed sequentially with 1 N NaOH, 0.1 N NaOH, water, and buffer, each for 3 min. The capillary was also rinsed with running buffer for 3 min between

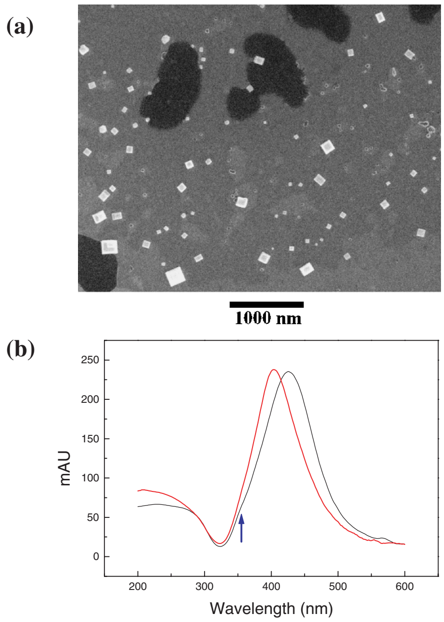

Figure 1. (a) SEM image of a mixture of silver nanoparticles and nanocubes obtained after heating a mixture of $AgNO_3$, SDS, and citrate under microwave irradiation at 100 °C for 10 min. (b) UV–vis absorption spectra of silver nanoparticles prepared as in Figure 1a. Red curve represents the absorption spectra of silver nanoparticles; Black curve represents the absorption spectra of mixtures of silver nanoparticles and nanocubes.

each run. All CE experiments were performed at temperature of ca. 15 °C.

We prepared aqueous solutions of suspended silver nanoparticles and nanocubes using our newly developed microwave irradiation method. Briefly, an aqueous solution of a mixture of 1.0 mM $AgNO_3$, 20 mM sodium dodecylsulfate (SDS), and 3.5 mM sodium citrate (10 mL) was placed in microwave heating system (MARS-5, CEM Corporation) and was reacted at 100 °C. Figure 1a presents an SEM (JEOL JSM-6500F) image of a typical sample, which displays a mixture of silver nanoparticles and nanocubes. The silver nanoparticles have a mean diameter of 45 nm. In contrast, the silver nanocubes have edge lengths in the range from 60 to 220 nm (mean = 90 nm). Figure 1b provides a comparison between the UV–vis absorption spectra of the solution that was used for the SEM studies in Figure 1a (the black curve) and the absorption spectra of silver nanoparticles having a dimension of ca. 55 nm (the red curve). The spherical nanoparticles display a strong SPR band at ca. 405 nm, while the cubic nanoparticles exhibit two SPR bands (located at 355 and 430 nm), which are optical characteristics that are similar to those described in a previous article.[10] We believe that the spectrum of the mixture of nanoparticles and nanocubes presented in Figure 1b is the sum of the contributions of the spherical- and cube-shaped silver particles, because these particles, which have different sizes and shapes, could be separated from the mixture using CE. Although the electropherogram displayed in Figure 2a is not baseline-resolved, identification of the particles in each band can be obtained by examining the spectra provided by the DAD at a number of different times. Figure 2b presents the spectra obtained for the bands after 7.5, 8.1, and 8.7 min. It is interesting to note that the plasmon absorption peak of the first eluted peak occurs at a shorter wavelength than those of the later-eluting ones. Also, the full-width at half-maximum of each peak increases as the separation times increase. The absorption spectrum of peak that eluted at 7.5 min exhibits only one SPR band (located at 405 nm), which suggests the possibility that only the spherically shaped nanoparticles pass through the detector window of the capillary at this time. The absorption spectrum obtained at the 8.1 min mark exhibits two SPR bands (located at 352 and 416 nm), suggesting the possibility that the relatively small cube-shaped particles are being eluted. Finally, the absorption spectrum of the sample that elutes at 8.7 min exhibits two SPR bands (located at 355 and 432 nm); presumably the larger ones of the cube-shaped particles pass through the detector window at this time. To validate these hypotheses, we collected a sample at 8.7 min from the last-eluted peak; the SEM image presented in Figure 2c confirms that we have collected purely cube-shaped nanoparticles having a uniform diameter (mean = 175 nm). Because the sample solution from the fraction collection is highly dilute, only a few silver particles are presented here. It seems that the elution behavior of the particles presented in Figure 2b is based on the different sizes and shape of the particles, which, therefore, have various charge-to-size ratios. Consequently, the differently charged particles have specific mobilities in the capillary column and, therefore, separation of the nanoparticles and nanocubes is achieved in a capillary column under the influence of the externally applied voltage.

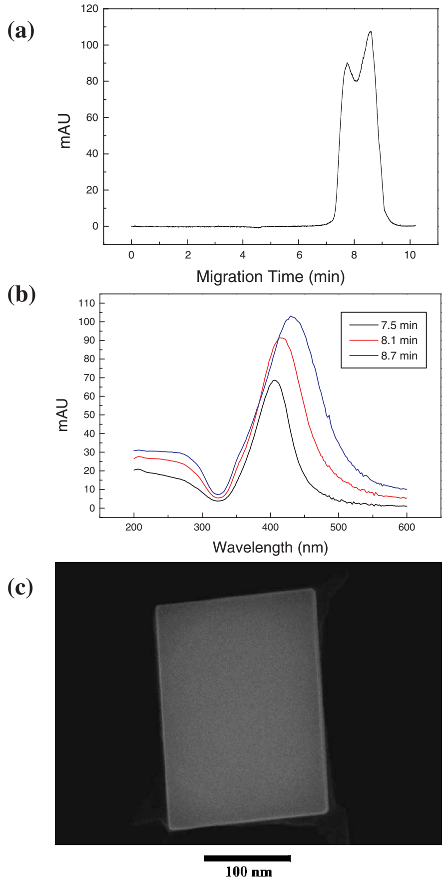

Figure 2. (a) Electropherogram of the mixture of silver nanoparticles and nanocubes prepared in Figure 1a. The separation was obtained using a running electrolyte of 20 mM SDS and 10 mM Tris-(hydroxymethyl)aminomethane (Tris) (pH 8.5) and an applied voltage of 30 kV. (b) UV–vis absorption spectra of silver nanoparticles obtained by the DAD at separation times of 7.5, 8.1, and 8.7 min. (c) SEM image of the silver nanoparticles collected at a separation time of 8.7 min.

In summary, we have demonstrated the potential of CE to be used for the separation of differently shaped silver nanoparticles. The spectra provided by the DAD system can be utilized to interpret the shapes of the silver nanoparticles. The combination of DAD and CE has the advantage of allowing an investigation of the spectroscopic properties of nanoparticles that have different shapes. We believe that this CE technique also will be applicable to the separation and characterization of size- and shape-dependent nanomaterials other than silver.

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