Research Article

Using Size-Exclusion Chromatography to Monitor Variations in the Sizes of Microwave-Irradiated Gold Nanoparticles

Fu-Ken Liu

Department of Applied Chemistry, National University of Kaohsiung, No. 700 Kaohsiung University Road, Nan Tzu District, Kaohsiung 811, Taiwan

Correspondence should be addressed to Fu-Ken Liu, fkliu@nuk.edu.tw

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Size-exclusion chromatography (SEC) was used to evaluate gold nanoparticles (Au NPs) for variations in their sizes after microwave (MW) irradiation, with the eluted NPs monitored through diode array detection to reveal their surface plasmon absorptions. The sizes of citrate-capped Au NPs decreased upon increasing the MW irradiation temperature, consistent with digestive ripening of these NPs under the operating conditions. In contrast, Au NPs capped with sodium dodecyl sulfate increased in size upon increasing the MW irradiation temperature, consistent with Ostwald ripening. When the Au NPs were capped with 3A-amino-3A-deoxy-(2AS,3AS)- β -cyclodextrin (H_2N - β -CD), however, their dimensions were barely affected by the MW irradiation temperature, confirming that H_2N - β -CD is a good stabilizer against MW irradiation. Therefore, SEC—with its short analysis times, low operating costs, automated operation, and in situ analysis—has great potential for use in the rapid monitoring of NPs subjected to treatment under various MW irradiation conditions.

1. Introduction

Metal nanoparticles (NPs) are attracting a great deal of attention from practitioners in a wide variety of scientific fields [1–13] because their physical and chemical properties are related to their chemical compositions, sizes, and surface structural characteristics [14–17]. Among all metal NPs, Au NPs are especially attractive for research in nanotechnology [18], for example, in the detection of cancer [19], DNA [20], and even single molecules through surface-enhanced Raman spectroscopy [21, 22]. Because the chemical or physical properties of Au NPs are size dependent [9, 23, 24], monitoring the sizes of Au NPs is a critical step toward understanding how their functions are related to their dimensions [25, 26].

Several research articles have reported the reaction kinetics of Au NP formation using the citrate method [27–31]. Both Ostwald ripening [28, 29], whereby particles increase in size during the reaction, and digestive ripening, where the average particle size decreases, have been observed [30, 31]—with the latter being used to break colloids into smaller particles through the addition of ligands. As a result, many strategies have been developed for varying the sizes

of Au NPs [25]. Herein, we wished to establish a rapid and efficient strategy for determining the size-dependent chemical or physical properties of Au NPs prepared using a chosen treatment method.

Many methods are currently available for particle size analysis [32], including transmission electron microscopy (TEM), dynamic light scattering (DLS), analytical ultracentrifugation (AUC), asymmetric flow field flow fractionation (aF-FFF), X-ray diffraction (XRD), and UV-Vis spectroscopy. In addition, techniques that can be performed using a small volume of a single sample within a short analysis times and at a low operating cost are of interest for the separation NPs into their constituent sizes [33]. Relative to other separation techniques (e.g., centrifugation, high-performance liquid chromatography (HPLC) [9], capillary electrophoresis [34], diafiltration [35], and gel electrophoresis [36]), size-exclusion chromatography (SEC) has the advantageous features of short analysis times, low operating costs, and high reliability, with the potential for in situ analysis and in situ gathering of spectroscopic data of the individual separated NPs [37].

In previous studies, we demonstrated that SEC analysis could be applied as a stand-alone technique to determine the sizes of synthetic Au, Au/Pd core/shell, and Au/Pt core/shell NPs at room temperature [33, 38, 39]. In addition, we have recently employed SEC approaches to determine a suitable stabilizer for NPs under conditions mimicking the temperatures found in catalysis environments (ca. 100°C) [37] and to rapidly monitor the sizes of Au NPs in the presence of salt or organic environments to determine the effects of the stabilizers of Au NPs in these media [40]. Our results, combined with the prevalence of automated SEC systems, suggest that this approach is superior to other techniques (e.g., DLS and TEM) typically employed for the characterization of NPs [33].

In this study, we monitored the variations in size of Au NPs in the presence of different capping agents—citrate, sodium dodecyl sulfate (SDS), and 3A-amino-3A-deoxy-(2AS,3AS)- β -cyclodextrin (H_2N - β -CD)—under microwave (MW) irradiation treatment at desired temperatures. In contrast to our previous studies, all of the experiments described herein were based on MW irradiation treatment at temperatures greater than 100°C. We selected MW irradiation as a variable in this study because it is an efficient heating method that allows precise temperature control as a built-in function in commercial MW instruments. As a result, MW irradiation was a convenient tool for studying the relationship between thermal effects and the size of NPs, especially for reaction temperatures of greater than 100°C—difficult to achieve using conventional hot-plate heating methods [41]. To the best of our knowledge, no previous reports have described the feasibility of using SEC methods to monitor the sizes of Au NPs under MW irradiation conditions. Through this study, we have found that SEC is highly applicable to the rapid analysis of MW-treated Au NPs.

2. Materials and Methods

2.1. Materials. Hydrogen tetrachloroaurate ($HAuCl_4$) was purchased from Acros Organics (Geel, Belgium). Sodium citrate was obtained from Merck (Darmstadt, Germany). SDS and H_2N - β -CD were obtained from Tokyo Chemical Industry (Tokyo, Japan). All eluents were prepared afresh each day and filtered through a 0.45- μ m membrane filter (Alltech, Deerfield, IL, USA) prior to use. Deionized water ($>18\text{ M}\Omega\text{ cm}^{-1}$) was used throughout the experiments. Au NPs having a mean diameter of $11.5 \pm 0.6\text{ nm}$ were home-made; their fabrication is described in the following section. Standard Au NPs having a mean diameter of $21.3 \pm 1.3\text{ nm}$ were obtained from Sigma (St. Louis, MO, USA). Au NPs having mean diameters of 40.1 ± 3.2 and $59.9 \pm 4.8\text{ nm}$ were obtained from BBI International (Cardiff, UK).

2.2. Instrumentation. Different capping agents were placed in Au NP solutions that were then treated with an SP-D MW irradiation system (CEM, Matthews, NC, USA). The MW system was operated at powers in the range from 0 to 200 W; samples were treated with MW irradiation for 20 min with stirring at desired temperatures. An L-2000 liquid chromatograph (Hitachi, Tokyo, Japan) was used for SEC

separation of the Au NPs. The SEC apparatus was equipped with a diode array detection (DAD) system. A Nucleogel GFC 60-8 column (Macherey-Nagel, Duren, Germany; $300 \times 7.7\text{ mm}$; pore size: 4000 nm; particle size: $8\text{ }\mu\text{m}$) and a 0.5- μ m precolumn filter were employed for analytical separation; the flow rate was 1.0 mL min^{-1} , the detection wavelength was 520 nm, and the injection volume was $20\text{ }\mu\text{L}$. A JEOL JEM-2010 transmission electron microscope (Tokyo, Japan) was used to characterize the sizes of the Au NPs.

2.3. Synthesis of Au NPs. The synthetic procedure for the formation of Au NPs through citrate-mediated reduction of $HAuCl_4$ has been described elsewhere [42]. The sizes of the particles in the sample were determined through two-dimensional (2D) grain analysis after digitizing TEM images. The average particle diameter of the synthesized Au NPs was estimated to be $11.5 \pm 0.6\text{ nm}$.

3. Result and Discussion

3.1. Separation of NPs Using SEC. Au NPs of four different sizes (11.5 ± 0.6 , 21.3 ± 1.3 , 40.1 ± 3.2 , and $59.9 \pm 4.8\text{ nm}$) were separated in the presence of a mobile phase additive (10 mM SDS) at a flow rate of 1.0 mL min^{-1} . Accordingly, we found that the four differently sized Au NPs had different elution times; the sequence of elution times (increasing with decreasing Au NP size) paralleled the elution behavior described previously [37]. For SEC to be used practically for the routine analysis of NP sizes, it was necessary for us to validate the reproducibility of the elution times because it influences the precision of the size-characterization process. Thus, we measured the relative standard deviations of the elution times from five consecutive runs using the 11.5-, 21.3-, 40.1-, and 59.9-nm diameter Au NP standards; the calculated precisions were 0.10, 0.05, 0.13, and 0.28%, respectively; that is, the elution behavior of Au NPs through SEC was highly reproducible.

Figure 1 indicates that a strong correlation ($R^2 = 0.996$) existed between the elution times and the diameters of the NPs; the error bars in the y - and x -dimensions represent the variations of the elution times and diameters, respectively, in terms of one standard deviation. This plot confirms that it is possible to employ SEC to characterize NPs having sizes in the nanometer regime.

3.2. Effect of MW Irradiation Treatment Temperature on Sizes of Citrate-Capped Au NPs. In these experiments, we obtained Au NP solutions after the addition of sodium citrate solution to a heated solution of Au precursor ions. During the synthesis of the Au NPs, the citrate ions performed several tasks; they complexed strongly to the Au metal ions, reduced them, and capped the resulting Au NPs. To examine the size variations of the citrate-capped Au NPs under MW irradiation treatment, we placed Au NPs (fabricated as described in Materials and Methods, 0.5 mL) into three MW reaction vials (10 mL), added deionized water (0.5 mL) to each vial, and then sealed the vials and treated them at 100, 120, or 140°C in a MW irradiation system with stirring for approximately 20 min. After cooling to room temperature, we performed SEC analysis of the Au NPs.

FIGURE 1: Calibration curve for the elution times of Au NPs plotted with respect to their diameters. The error bars in the y - and x -dimensions represent the variations of the elution times and diameters, respectively, in terms of one standard deviation. The separation conditions are described in Section 2.

Figure 2(a) displays chromatograms obtained from the solutions of the citrate-capped Au NPs that had been subjected to MW irradiation treatment at 100, 120, and 140°C. In each chromatogram, the intensity of the signal for the Au NPs decreased. In addition, the retention time lengthened slightly upon increasing the heating temperature—presumably a result of digestive ripening, which decreases the sizes of citrate-capped Au NPs [25, 37]. We used the calibration curve in Figure 1 to obtain the sizes of the fabricated NPs from the elution times in the SEC chromatograms of the NPs. Accordingly, the SEC chromatograms in Figure 2(a) revealed that the Au NPs that were eluted from the MW samples treated at 100, 120, and 140°C had diameters of 7.7, 7.5, and 4.1 nm, respectively. Thus, SEC analysis revealed that the sizes of the citrate-capped Au NPs decreased upon increasing the MW irradiation temperature, consistent with digestive ripening of the Au NPs occurring during the MW irradiation treatment processes. The phenomenon of digestive ripening of Au NPs has also been observed previously for citrate-capped Au NPs after prolonged photoirradiation [25].

Evidence for the digestive ripening of citrate-capped Au NPs after MW irradiation was also apparent from the eluted samples' surface plasmon (SP) absorptions in the UV-Vis absorption spectra obtained using the DAD system (Figure 2(b)). Link and El-Sayed reported that the sizes of Au NPs are related to the values of $\lambda_{\max}$ of their SP absorptions [43], which are blue shifted upon decreasing the sizes of Au NPs. Therefore, the use of SEC combined with a DAD system provides added value in terms of revealing the spectroscopic properties of the individual sets of separated Au NPs. Herein, we also used Au NPs' SP absorptions in Figure 2(b) to monitor their variations in particle diameters.

The corresponding values of $\lambda_{\max}$ of the SP absorptions of the Au NPs that had been subjected to MW irradiation treatment at 100, 120, and 140°C were 522, 521, and 520 nm, respectively, consistent with the sizes of the citrate-capped Au NPs having decreased slightly (i.e., digestive ripening occurred to form smaller particles) upon increasing the MW irradiation treatment temperature.

3.3. Effect of MW Heating Treatment Temperature on Sizes of SDS-Capped Au NPs. Surfactants can be employed as stabilizers in the size-selective preparation of metal particles [44, 45], with the ionic units surrounding the metal cores to prevent their agglomeration. Those previous studies, however, focused on the effects of surfactants in NP reaction media at temperatures lower than 40°C. In contrast, in this present study, we were interested in discovering whether the use of SDS as an additive anionic surfactant in the sample matrix would influence the sizes of Au NPs under MW irradiation treatment at high temperatures (>100°C). To examine the variations in size of SDS-capped Au NPs under MW irradiation, we placed Au NPs (fabricated as described in Materials and Methods, 0.5 mL) into three MW reaction vials (10 mL), added deionized water (0.4 mL) and SDS (100 mM, 0.1 mL) to each vial, and then sealed the vials and subjected them to MW irradiation treatment at 100, 120, or 140°C with stirring for approximately 20 min. After cooling to room temperature, we performed SEC analysis of the Au NPs.

Figure 3(a) displays SEC chromatograms of the SDS-capped Au NPs samples that had been subjected to MW irradiation treatment at temperatures of 100, 120, and 140°C for 20 min. The intensity of the signal for the Au NPs decreased upon increasing the heating temperature; in addition, the elution time for the Au NPs decreased accordingly—presumably as a result of Ostwald ripening, which increases the sizes of Au NPs [25, 37]. The elution times in the SEC chromatograms of the NPs in Figure 3(a) suggested that the eluted NPs from samples treated with MW irradiation at 100, 120, and 140°C had diameters of 10.5, 14.8, and 24.8 nm, respectively. These findings from SEC analysis revealed that the sizes of the SDS-capped Au NPs increased upon increasing the MW irradiation temperature, confirming that Ostwald ripening was occurring under these conditions. The presence of SDS in the reaction medium might be an important factor for nanomaterials to express Ostwald ripening phenomena; Wang et al. reported a similar SDS-induced Ostwald ripening in the formation of hollow CaWO_4 microspheres [46].

Evidence for Ostwald ripening of the SDS-capped Au NPs during the MW irradiation processes was also apparent from the SP absorptions of the eluted samples in the UV-Vis absorption spectra obtained using the DAD system (Figure 3(b)). Because the sizes of Au NPs can be monitored from their SP absorptions [43], we used the Au NPs' SP absorptions in Figure 3(b) to monitor the variations of their particle diameters.

The values of $\lambda_{\max}$ of the SP absorptions of the SDS-capped Au NPs that had been subjected to MW irradiation treatment at 100, 120, and 140°C were 522, 523, and 528 nm, respectively. These results follow the same trend obtained

FIGURE 2: (a) SEC chromatograms and (b) UV-Vis absorption spectra of citrate-capped Au NPs after MW irradiation at temperatures of (A) 100, (B) 120, and (C) 140°C. The separation conditions are described in Section 2.

FIGURE 3: (a) SEC chromatograms and (b) UV-Vis absorption spectra of SDS-capped Au NPs after MW irradiation at temperatures of (A) 100, (B) 120, and (C) 140°C. The separation conditions are described in Section 2.

in Figure 3(a); that is, the sizes of the SDS-capped Au NPs increased upon increasing the MW irradiation treatment temperature. Therefore, our findings confirmed that the SDS-capped Au NPs did increase slightly (i.e., Ostwald ripening occurred to form larger particles) upon increasing the MW irradiation treatment temperature.

3.4. Effect of MW Heating Treatment Temperature on Sizes of H_2N - β -CD-Capped Au NPs.

Employing cyclodextrins (CDs)

as capping agents for Au NPs, Liu et al. recently reported [47–49] that surface-attachment of CDs imparted Au NPs with excellent solubility in aqueous media. Furthermore, TEM analysis verified that these CD-capped Au NPs were well dispersed [49]; in addition, they exhibited excellent catalytic activity [50]. These features indicate that CDs have strong stabilizing effects on NPs, preventing them from aggregation, and, therefore, allowing them to function as usable materials for catalytic applications. In addition, we have also previously

FIGURE 4: (a) SEC chromatograms and (b) UV-Vis absorption spectra of $\text{H}_2\text{N-}\beta\text{-CD}$ -capped Au NPs after MW irradiation at temperatures of (A) 100, (B) 120, and (C) 140°C. The separation conditions are described in Section 2.

found that Au NPs capped with an amino derivative of $\beta\text{-CD}$ ($\text{H}_2\text{N-}\beta\text{-CD}$) have good thermal stability when treated in a thermal oven (ca. 100°C) [37]. In this present study, we wished to test whether $\text{H}_2\text{N-}\beta\text{-CD}$, as an additive in the Au NP medium, would result in any variation in size of Au NPs subjected to MW irradiation treatment at temperatures beyond 100°C.

To examine the behavior of $\text{H}_2\text{N-}\beta\text{-CD}$ -capped Au NPs under MW irradiation at different temperatures, we placed Au NPs (0.5 mL) into three MW reaction vials (10 mL), added deionized water (0.4 mL), and $\text{H}_2\text{N-}\beta\text{-CD}$ (100 mM, 0.1 mL) to each vial, and then sealed the vials and subjected them to MW irradiation treatment at 100, 120, or 140°C with stirring for approximately 20 min. After cooling to room temperature, we performed SEC analysis of the Au NPs.

Figure 4(a) displays the chromatograms obtained after MW irradiation of the $\text{H}_2\text{N-}\beta\text{-CD}$ -capped Au NPs. The elution times in the chromatograms of these three samples were very similar. From the calibration curve in Figure 1, the SEC chromatograms in Figure 4(a) sets A, B, and C indicate that the samples of $\text{H}_2\text{N-}\beta\text{-CD}$ -capped Au NPs all had an average diameter of 11.3 nm. Thus, SEC analysis revealed that the sizes of the $\text{H}_2\text{N-}\beta\text{-CD}$ -capped Au NPs were very similar after MW irradiation at different temperatures.

During the separations of the Au NPs, we also recorded the SP absorptions of the eluted samples. Figure 4(b) presents the corresponding SP absorptions of the $\text{H}_2\text{N-}\beta\text{-CD}$ -capped Au NPs after sampling the chromatograms in Figure 4(a) at their maximum signal intensities (each at an elution time of ca. 9.00 min). All of the SP absorption peaks had a value of λ_{max} of approximately 522 nm, indicating that the sizes of the Au NPs did not change significantly in this medium, regardless of the MW irradiation temperature. Taken

together, the results in Figures 4(a) and 4(b) suggest that $\text{H}_2\text{N-}\beta\text{-CD}$ is a good stabilizer for Au NPs against MW irradiation, even at treatment temperatures greater than 100°C; in addition, this stability is superior to that of Au NP suspensions in citrate or SDS (cf. Figures 2 and 3).

The mechanism through which $\text{H}_2\text{N-}\beta\text{-CD}$ stabilizes Au NPs most likely involves strong association of the Au NP surfaces with the amino groups [51], presumably through interactions that limit the size variation of the Au NPs [52]. Therefore, the $\text{H}_2\text{N-}\beta\text{-CD}$ -capped Au NPs were stable under MW irradiation.

Because the process of characterizing the analytes took less than 12 min (see Figures 2(a), 3(a), and 4(a)), SEC appears to be a good tool for rapidly determining suitable capping agents for varying the sizes of Au NPs under MW irradiation. We believe that the mechanisms through which the Au NPs associate with these and other protecting agents could be determined readily through the use of common, modern, automated SEC systems.

4. Conclusion

We have employed citrate-mediated reduction to produce Au NP solutions that we then subjected to MW irradiation at desired temperatures—using either the as-prepared medium (citrate capped) or SDS- or $\text{H}_2\text{N-}\beta\text{-CD}$ -capped Au NPs. We then monitored the resulting solutions through SEC analysis and UV-Vis absorption spectroscopy of the eluted Au NPs, noting that different capping agents affected the sizes of the Au NPs to different degrees. For the citrate-capped Au NPs, the average diameter decreased upon increasing the MW irradiation temperature, consistent with digestive ripening of the Au NPs under the operating conditions. The average

size of the SDS-capped Au NPs increased upon increasing the MW irradiation temperature, consistent with Ostwald ripening of the Au NPs. When the Au NPs were capped with H₂N- β -CD units, the average dimensions of the Au NPs were barely affected by the MW treatment, revealing that H₂N- β -CD is a good stabilizer for Au NPs against MW irradiation.

Our results suggest that SEC has some major benefits enabling the monitoring of Au NPs; for example, it might be useful for rapidly (<12 min) characterizing the size manipulation of Au NPs to ensure that they reach their optimal chemical or physical properties. SEC also aids in the search for new capping agents to control the sizes of Au NP products. In addition, when using SEC in conjunction with a DAD system, we can also obtain added value in terms of the spectroscopic properties of the individual sets of separated Au NPs.

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