Homogeneous Ag Particle Formation Confirmed by Real-time In Situ Surface-enhanced Raman Scattering Measurements under Microwave Irradiation

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In situ surface-enhanced Raman scattering (SERS) was applied to observe the early stage of the formation of Ag nanoparticles in solution under microwave (MW) irradiation. Rise of SERS successfully observed for Rhodamine 6G confirmed homogeneous particle formation due to homogeneous and rapid heating under MW irradiation.

Metal nanoparticles have been attracting attention of many researchers because of wide applications for electric, magnetic, and nonlinear optical devices.[1–3] The process of generation of the nanoparticles in heated solutions consists of the two steps: generation of nuclei and growth of particles.[4,5] When solutions are heated by conventional heating appliances using an electric heating wire, e.g., an oil bath or a mantle heater, the wall of the vessel is first heated and the solution having the contact with the inside wall is next heated. Then, the whole solution is gradually heated by the convection, resulting in the heterogeneity in the temperature distribution in the solution. Therefore, when the nanoparticles are prepared in the solution under conventional heating, the nuclei are generated at the wall of the reaction vessel, and then the particles grow randomly during the convection. This heterogeneity in the temperature distribution gives rise to a serious problem in preparing the precisely size-controlled nanoparticles with narrow distribution.

Recently, our group has reported preparation of monodispersed metal nanoparticles using long-chain alcohols as a solvent under heating by MW irradiation. We have succeeded in preparing monodispersed Ag and Cu nanoparticles with narrow size distribution.[6,7] A MW-assisted alcohol reduction process using silver long-chain carboxylates as a precursor gives precisely size-controlled Ag nanoparticles.[6] This process should be suitable for comparing heating modes affecting the controllability in the size distribution between MW heating and conventional heating in the wide range of temperature.

We have considered that uniformly and rapidly heating by MW irradiation should result in the preparation of monodispersed metal particles due to homogeneous generation of nuclei and growth of particles. For preparation of precisely size-controlled nanoparticles, the uniform heating of MW irradiation is ideal. This idea has led us to the next step, i.e., in situ observation of the particle formation depending on the local temperatures under MW irradiation and conventional heating.

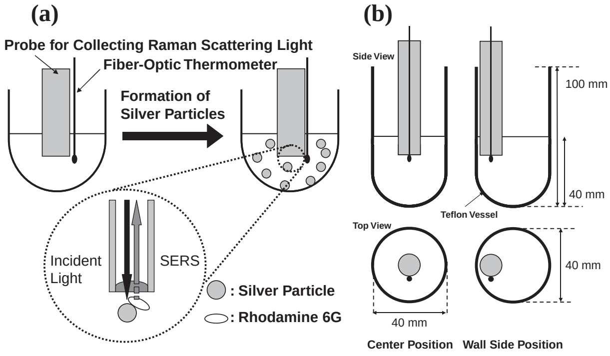
We selected Raman scattering measurement[8] as the most suitable method for in situ and direct observation of the phenomena occurring under MW irradiation. SERS should enable us to obtain information on the particle formation due to its high sensitivity obtained only for the sensor molecules interacting with metal particles.[9–11] This is the first report on in situ and direct observation of Ag nanoparticle formation under MW irradiation in comparison with conventional heating.

A Raman spectroscope consisted of a spectrograph equipped with a probe and a personal computer. A single mode diode laser (785 nm, 120 mW) was used for excitation. We developed a new probe in order to place a probe top at the desired temperature-measuring positions in the reaction solution (see Scheme 1a, Supporting Information Scheme S1).[12]

Rhodamine 6G (R6G) was used as a sensor molecule for the SERS observations.[13] R6G has strong peaks of Raman scattering at 1314, 1364, 1512, and 1651 cm^{-1}. Additionally, these peaks do not overlap Raman peaks of 1-hexanol. Consequently, SERS spectra of R6G were collected in the solutions as preparing Ag nanoparticles in 1-hexanol under MW irradiation and conventional heating (Scheme 1a).

Silver myristate (6.0×10^{-3} mmol) was dispersed in 1-heptanol (30 mL) including R6G (5.0×10^{-5} M) in a Teflon vessel ($40 \times 40 \times 100$ mm, Scheme 1b). The 1-hexanol solution was heated by MW irradiation using a MW apparatus MMG-213VP (Micro Denshi Co., Ltd., 150 W) for chemical synthesis equipped with a single-mode cavity or an oil bath. As oil bath heating, a Teflon vessel containing the 1-hexanol solution was immersed in silicon oil heated at 418 K. The spectra were collected in the range of 0–2000 cm^{-1} at 1-s intervals. The temperatures of the reaction solution were measured with a fiber-optic thermometer (AMOTH TM-5886, Anritsu Meter Co., Ltd.) directly inserted into the reaction solution.

Figure 1 shows Raman spectra continuously collected at the center position (CP) and the wall-side position (WP) of the sample solution heated by MW irradiation at 1-s intervals (Scheme 1b). Raman peaks of 1-hexanol were observed at 0 s (Figure S1). SERS of R6G arose up at approximately 100 s both



Scheme 1. Schematic illustration of the experimental set up for in situ observation of SERS (a) and collecting position of SERS (b).

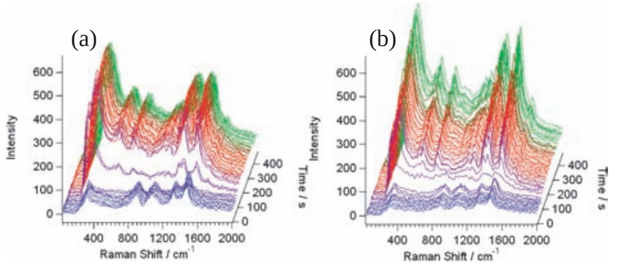


Figure 1. Time-depending Raman spectra observed at center position (a) and wall-side position (b) of the reaction solution heated under microwave irradiation.

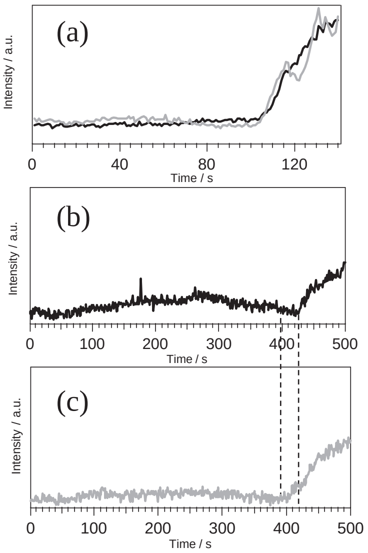


Figure 3. Raman scattering intensity at 1521 cm^{-1} with time observed at center position (black line) and wall-side position (gray line) of the reaction solution heated by microwave irradiation (a) and oil bath (b) and (c).

at the CP and the WP, and gradually grew up with the irradiation time. The Raman scattering intensities at 1521 cm^{-1} were plotted against the irradiation times for the two positions in Figure 3a. The rise of the SERS should demonstrate the formation of Ag nanoparticles above the size of 10–50 nm, because Khan et al. reported that Ag particles larger than 50 nm give strong SERS.[11] We have also preliminarily confirmed the formation of Ag nanoparticles of around 10–50 nm by TEM for the solution showing SERS. Both the temperatures at the CP and the WP were coincident and rose up in the same manner (Figure S2a).[12] Consequently, the solution was uniformly heated by MW irradiation.

Figure 2 shows Raman spectra continuously collected at the CP and the WP of the solution heated by an oil bath. The SERS of R6G measured at the CP arose at approximately 420 s, while that measured at the WP arose at approximately 400 s. The different times for the rises of the SERS between the two positions were demonstrated clearly in Figures 3b and 3c, in which the SERS intensities are plotted against the heating times. The delay of 20 s in the times corresponded to the temperature difference of 5 K (Figure S2b).[12] Consequently, the delay in the rise times in the SERS should be ascribed to the difference in the temperatures between the WP and the CP caused by the delay in the temperature rise at the CP compared to the WP as shown in Figure S2b.

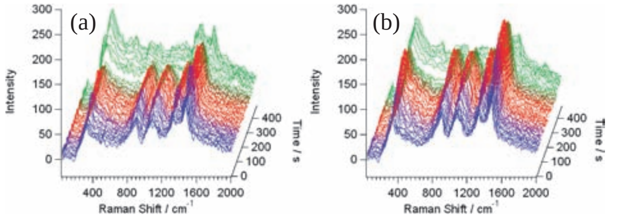


Figure 2. Time-depending Raman spectra observed at center position (a) and wall-side position (b) of the reaction solution heated by oil bath.

Figure 3 demonstrates that the intensities of SERS collected at the CP and the WP arose at the same time for MW heating, while the clear delay in the rise time of the CP was observed for the oil bath heating system. Now we have reached at a conclusion that uniform heating can be achieved by MW irradiation, resulting in uniform generation and growth of the Ag nanoparticles. A few reports on in situ measurements of chemical systems driven under MW irradiation have been reported.[14–16] However, this is the first one reporting the peculiarity of MW irradiation: homogeneous and rapid heating, functioning as a homogeneous trigger of chemical reactions in solutions.

One of the authors (T. Nakamura) thanks the financial support of the 21st COE of Osaka University. This work was supported by a Grant for Practical Application of University Research and Development Results under the Matching Fund Method of NEDO, Creation and Support Program for Start-ups from Universities of JST, and a Grant-in-Aid for Scientific Research on Priority Areas (417) (No. 17029038) from MEXT of the Japanese government.

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Published on the web (Advance View) November 11, 2006; doi:10.1246/cl.2006.1396