Plasma-assisted electrochemical synthesis of monodisperse Au and Au@Ag core–shell nanoparticles

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Abstract
The synthesis of well defined nanoparticles with green chemistry has been an area of intense investigation, but still requires development. In this study, we propose a novel approach for controlling the particle size and distribution through diffusion-controlled growth of plasma-assisted electrochemical synthesis. The continuous, controlled addition of an Au precursor with syringe pump successfully controls the particle size in the range of 50–300 nm with a monodisperse size distribution. Moreover, gold nanoparticles can be formed successfully without any stabilizer and reducing agent. Through optimization of the reaction parameters, including the reaction temperature, discharge current of the microplasma, pH, and concentration of D-(−)-fructose, we verify two distinct feature of diffusion-controlled growth that the particle growth is good agreement of theoretical growth rate \( r \sim t^{1/3} \) and the formed gold nanoparticles exhibit polyhedral or near-spherical shapes. This method has been applied to synthesize Au@Ag core–shell nanoparticles and control the Ag shell thickness.

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Metal nanoparticles (NPs) have widespread application, and controlling their size and shape with a monodisperse distribution is an important area of study, because the fundamental physical and chemical properties may be significantly affected [1, 2]. For example, gold (Au) and silver (Ag) NPs exhibit distinct surface plasmon resonance bands that vary with the size and shape, making them useful in a wide range of applications, from biotechnology to chemical catalysis [3, 4].

Thus far, substantial efforts have been devoted to the development of synthetic strategies (1) to synthesize size-controlled NPs with a highly narrow size distribution [5–7], and (2) to incorporate the principle of green chemistry into synthesis [8]. One promising approach is plasma-assisted electrochemical synthesis, in which the electrons in the plasma are transferred to the liquid, causing an electrochemical reaction at the plasma-liquid interface [9, 10]. This approach has been attractive in a variety of fields such as nanomaterial synthesis, hydrogen production, and polymerization [11]. Because it offers strong potential for providing a green (with non-toxic chemicals such as reducing agents) and facile process (with ambient conditions) [9], rapid reactions [12], and high purity and catalytic ability [13]. Nevertheless, to compete with the chemical approach [6], a key challenge is the precise control of sizes with a monodisperse size distribution. To date, several studies have
reported the control of the particle sizes and their distribution based on plasma-assisted electrochemical synthesis \([14–17]\); however, no studies on a controlled size with a monodispersed size distribution are available at present.

In this study, we propose a novel approach for diffusion-controlled growth by plasma-assisted electrochemical synthesis to control the size with a monodisperse size distribution precisely. This method involves the constant addition of an...
Au precursor and results in uniform, continuous growth of Au NPs with a monodisperse size distribution (figure 1(a)). We successfully controlled the Au NPs in the range of range 50–300 nm with a size distribution of less than 10% relative standard deviation (RSD) by optimizing the reaction parameters, including the infusion rate of the Au precursor, reaction temperature, discharge current of the microplasma, pH, and amount of stabilizer (namely D(-)-fructose). Moreover, we demonstrate that our approach enables the synthesis of Au@Ag core–shell NPs and control of the shell thickness.

Conventional plasma-assisted electrochemical synthesis normally exhibits a highly polydisperse size distribution. For example, when this synthesis was performed using an electrolyte containing 1 mM of HAuCl₄ and 10 mM of D(-)-fructose in a 100 ml total volume, the SEM characterization indicated the coexistence of large and small Au NPs (figure 1(b)). Moreover, we quantified the tendencies by statistically analyzing a population of more than 100 NPs, and the results demonstrate a bimodal distribution that were clearly distinguishable in the histogram. The first was a subpopulation of small Au NPs with an average diameter of approximately 40–50 nm. However, a considerable fraction of Au NPs with larger average diameters also existed, in the order of 120–180 nm. Furthermore, the ultraviolet-visible (UV–vis) absorbance peak was blue-shifted from 600 to 558 nm with increasing reaction time, which could be caused by the small Au NPs formed during the conventional plasma-assisted electrochemical synthesis (figure S1 available online at stacks.iop.org/NANO/31/165602/mmedia). We think that the tendency of average particle size is caused by the fraction change of the large particle size and the small particle size.

To drive steady-state growth during the plasma-assisted electrochemical synthesis, our approach was the continuous, controlled addition of a precursor, which could lead to well-controlled particle growth with a narrow size distribution. To verify our concept, 5 mM of Au precursor and 50 mM of D(-)-fructose solution were added at an infusion rate of 3.33 ml h⁻¹ into 80 ml of DI water for 6 h. The final electrolyte concentration was expected to be the same as that of the conventional plasma-assisted electrochemical reaction (note that the expected total volume was 100 ml with 1 mM of HAuCl₄ and 10 mM of D(-)-fructose). Surprisingly, the SEM
images demonstrated that the Au NPs were grown as a function of the reaction time, with a uniform size distribution. Furthermore, the histogram exhibited a narrow size distribution without any tendency of a bimodal distribution (figure 1(c)). Moreover, it was observed that the UV–vis spectra were red-shifted as a consequence of the particle growth (figure S1) [18].

To gain further understanding of the growth of the Au NPs, we observed the growth kinetics and RSD as a function of time (figure 1(d) and (e)). While the conventional plasma-assisted synthesis did not exhibit any trends of the particle size depending on the reaction time and a broad size distribution of approximately 30%-50% RSD, the proposed plasma-assisted synthesis resulted in highly narrow size distribution of approximately 10%-15% RSD. Moreover, an average size increase of \( r \sim t^{0.305} \) \((R^2 > 0.992)\) is approaching the theoretical growth rate of \( r \sim t^{1/3} \) corresponding to diffusion-controlled growth [19-21].

To verify that the Au precursor concentration indeed led to diffusion-controlled growth, we varied the infusion rate from 3.33 to 20 ml h\(^{-1}\) and performed the reduction reaction for 1–3 h under 50 °C of reaction temperature (figures S2 and S3). The final concentration of the Au precursor was consistent with 1 mM of HAuCl\(_4\). As expected, the SEM images exhibited large and small Au NPs when increasing infusion rate of the Au precursor. Furthermore, the histogram indicated that the size distribution was broadened, and eventually, a bimodal distribution was observed in the histogram when the infusion rate of the Au precursor was increased. Therefore, we believe that controlling the infusion rate of the Au precursor, which is expected to adjust the Au precursor concentration in the electrolyte precisely, can effectively suppress the coexistence of large and small Au NPs and drive continuous diffusion-limited growth during plasma-assisted electrochemical synthesis.

To control the particle growth further, we also systematically studied the effects of the reaction parameters, including the reaction temperature, discharge current, pH, and D-(-)-fructose concentration. At the optimized infusion rate (namely 3.33 ml h\(^{-1}\)), the effects of the other parameters are illustrated in figure 2. Overall, the particle size of the formed Au NPs increased as a function of the reaction time, strongly matching the theoretical diffusion-controlled growth rate of \( r \sim t^{1/3} \). In particular, the reaction temperature had a significant influence on the particle size of the Au NPs, which increased when increasing the reaction temperature (figure 2(a)). However, at excessively low (for example, 20 °C) and excessively high (for example, 80 °C) reaction temperatures, triangle or hexagonal Au NPs were observed, and the dispersion degree was increased to approximately 40% RSD (figures S3–6). However, a higher discharge current of the microplasma and lower pH resulted in larger Au NPs (figures 2(b) and (c)). The size distribution also appeared to be slightly improved (figures S7–12). To
provide further insight into green synthesis without any stabilizer, we also investigated the effects of the stabilizer, namely the D-(-)-fructose concentration. It was found that the D-(-)-fructose concentration had an insignificant effect on the particle size and size distribution (figures 2(d) and S13–15).

Moreover, we observed that the Au NPs were stably dispersed in the solution, although it was synthesized without D-(-)-fructose. This could be owing to the formation of electrostatically stable Au NPs by means of the plasma-assisted electrochemical synthesis [14, 22].

Through intensive parametric studies, we attempted to obtain Au NPs of large sizes under the following conditions: (1) a moderate reaction temperature (50°C), (2) higher discharge current of the microplasma (8 mA), (3) higher pH (pH 3), and (4) 10 mM of D-(-)-fructose. As illustrated at figure 3, the Au NPs were grown up to 303.2 ± 29.9 nm with a monodispersed distribution. Moreover, the formed Au NPs exhibited polyhedral or near-spherical shapes, which is a distinct feature of diffusion-limited growth [23].

As an application of diffusion-controlled growth by plasma-assisted electrochemical synthesis, we employed the technique to synthesize Au@Ag core–shell NPs. Initially, we confirmed that the Ag NPs were also grown with diffusion-controlled growth by the plasma-electrochemical approach (figure S16 and S17). As expected, the Ag NPs were grown as a function of time, which also exhibited strong agreement with the theoretical diffusion-controlled growth corresponding to

![Figure 4.](image_url)

Figure 4. (a) Schematic for synthesizing Au@Ag core–shell NPs. (b) SEM images and histogram of Au@Ag core–shell NPs as function of time. (c) STEM-HAADF and EDS elemental mapping images of Au@Ag core–shell NPs as function of time. The microplasma was operated with an 8 mA discharge current and 30 sccm He gas flow rate. The reaction temperature was 50 °C and the solution was pH 3. 5 mM of HAuCl4 and 50 mM of D-(-)-fructose solution were added at a 3.33 ml h⁻¹ infusion rate into 80 ml of DI water for 15 min. The microplasma was operated at a 2 mA discharge current and a 30 sccm He gas flow rate. The reaction temperature and pH were 50 °C and pH 6.3, respectively. Afterward, to synthesize the Ag shell, 1.5 mM of NaOH was added to the electrolyte, and the AgNO3 was injected at 0.83 ml h⁻¹ for a further 6 h to control the outer layer thickness of the Ag shell.
r ∼ t^{1/3}. However, while the size distribution was less than 11% RSD for the initial 6 h, it was significantly increased up to 31% RSD with increasing reaction time. Therefore, we performed Ag shell growth up to 6 h in this study. Figure 4(a) presents a schematic illustrating the synthesis of the Au@Ag core–shell NPs by plasma-assisted electrochemical synthesis. The Au cores were synthesized for 15 min and 1.5 mM of NaOH was added to the electrolyte. Thereafter, AgNO₃ was injected at 0.83 ml h⁻¹ for a further 6 h to control the outer layer thickness of the Ag shell. Figure 4(b) presents the SEM images and histogram of the formed Au@Ag core–shell NPs. The particle size increased as a function of time and the size distribution was narrow (figures 4(b) and S18). Furthermore, the color of the colloidal solution changed from pink to yellow by the formation of the Ag shell (figure 4(b), inset), and the UV–vis absorbance peak was gradually shifted from 530–460 nm (figure S19), which indicated that the Au core was surrounded by the Ag shell [24]. To confirm the formation of the Au@Ag core–shell NPs further, we performed scanning TEM high-angle annular dark-field (STEM-HAADF) imaging and energy dispersive spectroscopy (EDS) elemental mapping (figure 4(c)). The representative STEM-HAADF image distinctively revealed NPs with a brighter inner area and relatively darker outer shell. Furthermore, the EDS mapping results indicated that the Au was in the center of the particle area as the core (in green), while the Ag was located on the outside as the shell (in red). EDS line scan confirmed again the distinct feature of the core–shell structure (figure S20) [25, 26].

To confirm the formation of AgCl in Au@Ag core–shell NPs, we performed XRD characterization (figure 5). The peaks of Au core exhibits clear peaks at 38.25°, 44.46°, 64.69°, and 81.88°, which are assigned to Au(111), Au(002), Au(022), Au(113), and Au(222), respectively (ICDD 98-016-1625). Moreover, there is no change of XRD peaks after adding 1.5 mM of NaOH into the electrolyte. However, the Au@Ag core–shell NPs exhibit peaks at 38.19°, 44.39°, 64.58°, 77.58°, and 81.73°, corresponding to Ag(111), Ag(002), Ag(022), Ag(113), and Ag(222), respectively (ICDD 96-901-2432). The results confirm that AgCl was not formed during the synthesis of Au@Ag core–shell nanoparticles. Furthermore, we could not observe any preferential growth of Ag at shell region [27, 28].

We also investigated the shell thickness and the particle size of Au core and Au@Ag core–shell as a function of the reaction time (figures 6 and S21). Whereas the particle size of Au core is not changed, the particle size of Au@Ag core–shell increased with increasing reaction time. We also observed that the shell thickness of Ag was grown up to 20.5 nm. These results demonstrate that the growth of Au@Ag core–shell NPs was caused by the shell thickness of Ag and we can control the shell thickness [29, 30].

We systematically designed the experiments to investigate the effects of core size to the core–shell NPs. To control the size of Au core, the reaction time was varied with 5, 15, and 60 min. As the results, we can prepare different sizes of Au core (23.2 ± 1.9, 41.4 ± 3.8, and 70.2 ± 5.4 nm) and subsequently synthesize Ag shell by adding AgNO₃ (figures S22 and S23). When the size of Au core is small (5 min of reaction temperature, 23.2 ± 1.9 nm), we observed the formation of Ag NPs with small fraction of Au@Ag core–shell NPs. On the other hand, Ag shell seemed to be slowly formed when at large Au core (60 min of reaction time, 70.2 ± 5.4 nm). For example, Ag shell at large Au core seemed to form after 360 min (figure S23(c)). Therefore, the uniform Au@Ag core–shell NPs forms around 41.4 ± 3.8 nm of Au core under the experimental conditions.

In summary, the proposed diffusion-controlled growth by plasma-assisted electrochemical synthesis via the continuous, controlled addition of Au precursor can precisely tune the particle size in the range of 50–300 nm with a monodisperse size distribution. The infusion rate of Au precursor is important to lead diffusion-controlled growth and the moderate reaction temperature (for example, 50 °C) is helpful to synthesize uniform Au NPs. The discharge current and pH affect to the particle size with a monodisperse size distribution. The proposed plasma-assisted electrochemical synthesis offers a promising green chemistry approach that it forms electrostatically stable Au NPs without any stabilizer. In addition, this approach enables the synthesis of Au@Ag core–shell NPs and control of the shell thickness.

**Experimental section**

**Materials**

Gold (III) chloride trihydrate (HAuCl₄·3H₂O, 99.9% purity), silver nitrate (AgNO₃, 99% purity), sodium hydroxide (NaOH, 98% purity), and D-(-)-fructose (99% purity) were purchased from Sigma-Aldrich, USA. Hydrochloric acid (HCl, 36.5–38%) was obtained from Duksan Pure Chemicals, Korea. A
formvar-carbon-coated copper transmission electron microscopy (TEM) grid with 200 mesh was purchased from Ted Pella Inc., USA. A platinum foil (0.025 mm thick, 99.9% purity) for the anode electrode of the plasma-electrochemical cell was purchased from Alfa Aesar, USA. High purity helium (He) gas (99.999%) was used for the generation of the atmospheric-pressure DC microplasma. Deionized (DI) water (18.2 MΩ cm) was used in all the experiments.

Characterizations

Field emission scanning electron microscopy (ZEISS, Germany) was used to characterize the surface morphology of the synthesized NPs. The samples were prepared by drop-casting 300 μl of Au colloidal solution on a Si wafer, and drying overnight under ambient conditions. The particle size and distribution were obtained by analyzing over 100 particles of the representative SEM image using Image J (NIH). The UV–vis absorption spectra were recorded using a Shimadzu UV-3600 spectrophotometer (Shimadzu Corporation, Japan) with a wavelength range from 300 to 800 nm. The samples were prepared by extracting 1 ml of the Au colloidal solution, which was diluted with 3 ml of DI water. STEM-HAADF imaging and EDS mapping were performed with a JEM-ARM200F (Jeol, Japan) operated at 200 kV. For the sample preparation, 10 μl of the Au colloidal solution was drop-casted onto the TEM grid, following which it was dried for 24 h under ambient conditions.

Plasma-assisted electrochemical synthesis of NPs

Atmospheric-pressure DC microplasma was formed as the cathode between a stainless steel capillary tube (outer diameter = 0.159 cm, inner diameter = 100 μm × 15 cm length, Restek, Inc., USA) and electrolyte, using a negatively biased high-voltage power supply (RR30-20N, GMMA High Voltage Inc., USA). A Pt electrode (Pt, 1 cm × 2.5 cm area) was employed as an anode and immersed in the electrolyte. He gas flowed into the stainless steel capillary tube at 30 scm, and a high voltage (~1.5 kV) was applied. The plasma was then stabilized at a constant current by means of a ballast resistor (R = 150 kΩ) and adjusting the power supply voltage. To control the reaction temperature, a 100 ml jacketed beaker was employed, in which the water was circulated using a chiller, and the temperature was controlled within the range of 20°C–80°C, which was monitored by a digital multimeter (87 IV, Fluke, USA). The conventional plasma-assisted electrochemical reaction was performed with the electrolyte containing a metal precursor, which was systematically controlled with syringe pump (Pump 11 Elite, Harvard Apparatus, USA) by adjusting the infusion rate.

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