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Accelerated Nanoparticles Synthesis in Alcohol-Water Mixture Based Solution Plasma

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Extraordinary high-speed synthesis of gold nanoparticles (AuNPs), was discovered by synthesizing the AuNPs in ethanol-water mixtures using solution plasma process (SPP). Influence of the ethanol mole fraction (χ_{ethanol}) in the ethanol-water mixtures on the reduction rate of gold chloride ions to AuNPs under the SPP system was studied. Results indicated that reaction rate of the AuNPs synthesis exhibited a maximum value (*i.e.*, 35.2 times faster than in pure water system) at the significant point where partial molar volume of ethanol and water changed drastically.

There has been growing interests in utilizing metal nanoparticles for a wide range of applications such as catalyst, semiconductor, and biosensor.^{1–4} Many synthesis methods have therefore been developed to synthesize the metal nanoparticles.^{5–8} Among numerous methods, SPP—a non-equilibrium plasma in a solution under atmospheric condition—has been accepted as a potent method. It is like a glow discharge which results in a less increase in solution temperature. Fig. 1 illustrates the SPP system. The plasma is formed inside a stably-positioned bubble (gas phase) surrounded by liquid phase, between electrodes. Various reactive species such as electrons and radicals are generated and react with solutes and solvent molecules. Accordingly, extremely rapid chemical reaction occurs. In the case of water-based SPP system, among several radicals formed, hydrogen radicals are identified to be significant for the formation of metal nanoparticles.¹⁵ The size-controlled synthesis of several

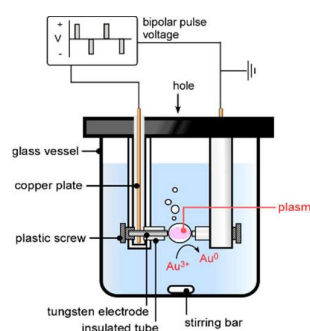


Fig. 1 Experimental setup of solution plasma process (SPP).

types of metal nanoparticles such as gold, platinum, and silver, in the water-based SPP system have been developed.^{9–15} By regulating temperature and pH, single nanoparticles can be successfully obtained.^{12,13}

In the present study, we discovered that the formation rate of AuNPs surprisingly increased by adding a small amount of ethanol in water. As is generally known, water and alcohol can dissolve each other due to the presence of hydroxyl group in both molecules. Furthermore, the alcohol content displays great influences on properties of the alcohol-water mixtures.^{16,17} Specifically, for ethanol-water mixture, when the ethanol mole fraction (χ_{ethanol}) is in the range of 0.08–0.1, partial molar volume of water exhibits maximum value while that of ethanol exhibits minimum value.¹⁸ At this composition, hydrogen bond networks among water molecules, therefore, show most stable structure. This lead to the specific behavior in physicochemical liquid properties (*e.g.* viscosity and density), liquid-vapor equilibrium, and surface properties of gas/liquid interface.^{16–19}

The plasma is generated in bubbles formed between electrodes which are submerged in a solution, it is expected that reaction in the SPP is significantly influenced by the solution properties. We assumed, therefore, that specific properties of the solution might affect the nanoparticles synthesis by the SPP. In this point of view, the AuNPs synthesis was selected as “a model” for the above described

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Electronic Supplementary Information (ESI) available: Experimental details, UV-vis spectra of synthesized gold nanoparticles and its temporal change in various ethanol compositions, the investigation of volatile reaction products, and the effect of UV-light, pH, and reaction products as well as physical conditions of plasma on reduction reaction of gold ions.

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investigation. Herein, we investigated effect of the ethanol-water composition on the SPP-based AuNPs synthesis.

High-speed synthesis of the AuNPs in ethanol-water mixtures containing gold (III) chloride ions (AuCl_4^-) was achieved by adjusting the mixture compositions. The formation of AuNPs was confirmed with ultraviolet and visible (UV-Vis) spectroscopy (Fig. 2). The absorption spectra lying around the wavelength of 530–550 nm, indicating surface plasmon resonance (SPR) of the AuNPs, were observed (Fig. 2a). However, the absorbance of the SPR at this wavelength sometimes has inaccurate relationship with concentration of the nanoparticles due to their flocculation and surface area change, especially in longer processing time (Fig. S1 and S2)²⁰. For quantitative analysis of the synthesis rate, the temporal change of the concentration of AuCl_4^- was analyzed. During the AuNPs synthesis, reaction solution was collected with 3 mL at several reaction times and absorption spectra of the respective aliquot was analyzed by UV-vis. The absorption spectra of the gold (III) chloride ions appearing at around 285 nm (Fig. 2b) is shifted to longer wavelength and interfered by the peak of the SPR with increasing reaction time. This is the reason why we have to convert AuCl_4^- to AuBr_4^- by adding potassium bromide immediately into the collected aliquot. Adding the excess amount of Br^- causes the displacement of AuCl_4^- with AuBr_4^- perfectly (Fig. 2b).²¹ Absorption spectra of the gold bromide ions (AuBr_4^-) in water, having a wavelength of maximum absorbance (λ_{max}) at 380 nm, was detected and shown in Fig. 2b. The absorbance of AuBr_4^- was used for quantitative analysis.

Clearly, the absorbance at 380 nm decreased

monotonically when the processing time was increased (Fig. 2c). Profiles of A/A_0 versus processing time at various χ_{ethanol} are shown in Fig. 2d–f, where A_0 indicates initial concentration of AuCl_4^- (translated from concentration of AuBr_4^-) and A indicates temporal concentration of AuCl_4^- . As can be seen from Fig. 2d, the A/A_0 values in water ($\chi_{\text{ethanol}} = 0$) decreased slowly at the early state of the processing time (plateau period: ~0–700 s). After that, it suddenly decreased when the time was greater than 700 s. In this reaction routes, there was two important steps for the gold ion reduction: (i) a primary step of the precursor ions followed by (ii) the autocatalytic step.²² In the primary step, the Au(III) ions was reduced to Au(0) slowly and nucleation occurred. It has been reported that XANES and SAXS analysis reveal that nucleation started during this plateau period²³. After the concentration and size of nuclei increase, the precursor ions were reduced mainly on the surface of nuclei.^{24,25}

Fig. 2e–f show effect of ethanol concentration in ethanol-water mixtures on the reaction rate. Considering the ethanol-water mixtures, the plateau period seen in primary step in the case of the pure water system suddenly shortened with the addition of ethanol (Fig. 2e and 2f). Furthermore, apparent change in decreasing rate of A/A_0 value at various ethanol mole fractions (χ_{ethanol}) was observed. In order to clarify the dependence of these change on ethanol concentration, the period when concentration of gold ions (A) decrease to half value of initial concentration (A_0): $t_{1/2}$ was plotted against χ_{ethanol} in Fig. 3. This result revealed that the fastest reaction rate was observed at $\chi_{\text{ethanol}} = 0.089$, where partial molar volumes of ethanol and water were minimum and maximum, respectively.¹⁸ Notably, while the $t_{1/2}$ in pure water ($\chi_{\text{ethanol}} = 0$) was 1480 s the value at χ_{ethanol} of 0.089 was equal to 42 s which was approximately 35.2 times faster than that in pure water ($\chi_{\text{ethanol}} = 0$).

We additionally found that this specific correspondence was observed in other short-chain alcohols, *i.e.*, methanol and 2-propanol, as well. In order to identify the alcohol concentration dependence of reaction rate, $t_{1/2}$ values against alcohol concentration were plotted. Results are shown in Fig. 4. The inclusion of alcohol in the water-based SPP possibly gives rise to the drastic change in the radical formation.

The final sizes of nanoparticles depend on the number of nuclei, that is, the larger number of nuclei leads to the formation of nanoparticles with smaller size. The number of nuclei depends on reduction rate of precursor ions to form neutral atoms. The observed TEM images of the AuNPs synthesized at various χ_{ethanol} , along with their mean diameters are shown in Fig. 5a–c. The smallest size of the AuNPs at χ_{ethanol} of 0.089 (see Fig. 5d) is confirmed, where the highest rate of reducing gold ions occurs.

In solution plasma process in water, the following reactions occurs in plasma²⁶.



Adding the ethanol lead to the following reactions.

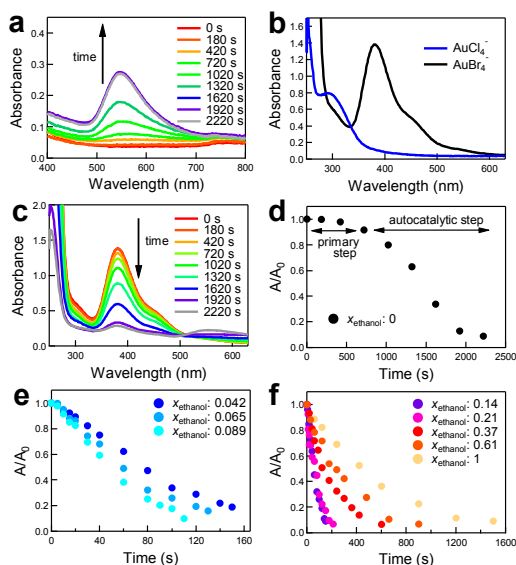
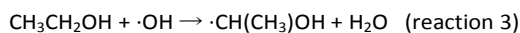
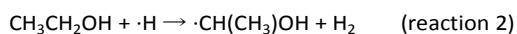
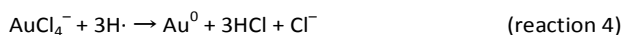


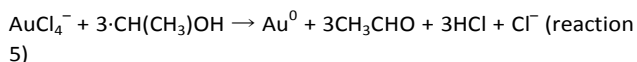
Fig. 2 (a) Absorption spectra of SPR in aqueous solution at different synthesis times, (b) Absorption spectra of AuCl_4^- and AuBr_4^- in aqueous solution, (c) Absorption spectra of as-prepared reaction solution in aqueous solution at different synthesis time, and (d–f) plot of A/A_0 value as a function of synthesis time at various ethanol mole fraction (χ_{ethanol}): (d) 0, (e) 0.042–0.089, and (f) 0.14–1.



Previously, overall reduction reaction of gold ions to AuNPs (from trivalent to zerovalent gold ions) by the SPP in water was reported.¹² The equation is shown below, where hydrogen radicals ($\text{H}\cdot$) play a crucial role as reducing agent.



In the case of adding ethanol, the following reaction is added.



Formation of the alcohol radicals was confirmed by gas chromatography-mass spectrometry (GC-MS) analysis. Results are shown in Fig. S3†.^{27,28} Ability of the alcohol radicals to reduce Au^{III} to Au^0 has previously been reported for radiation and sonication methods.^{20,25}

Hydrogen radicals are also accepted as strong reducing agent. In the present study, hydrogen radical should be generated in plasma (reaction 1) and reduce gold ions (reaction 4). But hydrogen radicals generated in plasma possibly react with alcohol molecules at gas/liquid interface and/or in bulk solution to form alcohol radicals immediately. Furthermore, hydrogen radical is extremely reactive. Therefore it can immediately react with solvent molecules and reaction products before disappearing easily. On the other hand, ethanol radical is more stable in the viewpoint of such reactivity.

Generally, alcohol itself is known to behave as a reducing agent and used for nanoparticles synthesis with reflux method^{29,30}. In this case, reduction rate of metal ions increases monotonically with increasing the alcohol

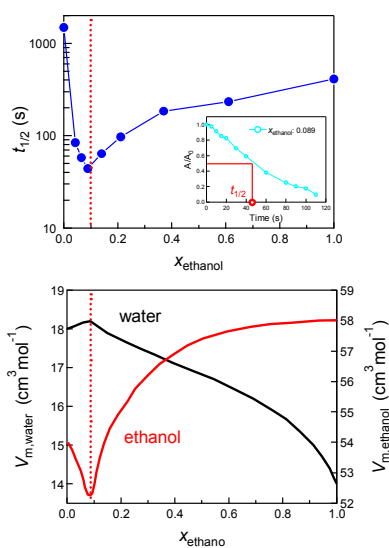


Fig. 3 The correlation between $t_{1/2}$ value and partial molar volume of water and ethanol, respectively in ethanol-water mixture as a function of the x_{ethanol} .

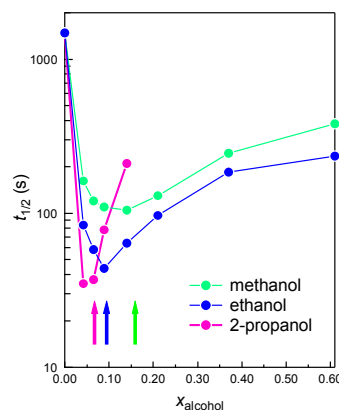


Fig. 4 The correlation between $t_{1/2}$ value and the position where partial molar volume of short-chain alcohols exhibits minimum value (respective colored vector indicates the position)³⁷; green line: methanol-water mixture, blue line: ethanol-water mixture, and pink line: 2-propanol-water mixture.

concentration and results in the formation of smaller nanoparticles. In the present study, the alcohol concentration dependence under the SPP system is not in accordance with the mentioned observation. It exhibits maxima value at low alcohol concentration, implying that, increment of the reduction rate of gold ions to AuNPs in the SPP is not mainly induced by the reduction reaction due to alcohol itself.

It is certainly true that UV-light, reaction products,^{31–33} and an alteration of the solution pH, as well as physical condition of the plasma could affect reducibility of the gold ions. Thus, we conducted additional experiments to confirm that these parameters were negligible in the present study. Data are shown as supplementary information in Fig. S4 and Table S1†.

Consequently, addition of ethanol causes the increasing ethanol radicals which lead to increasing reduction rate of gold ions. Subsequently, primary nucleation occurs quickly and autocatalytic process is promoted, resulting in the increasing reduction rate of gold ions.

Below, detailed reaction route is discussed. The reaction rate is increased at low concentration for all short-chain alcohols. Herein, we focused on hydrophobicity of alcohols. The degree of hydrophobicity was expressed as $\log P$ (higher $\log P$ value indicates higher hydrophobicity).³⁴ $\log P$ and $t_{1/2}$ values of methanol, ethanol, and 2-propanol at $x_{\text{alcohol}} = 0.042$ were compared and shown in Table 1. This result implies that

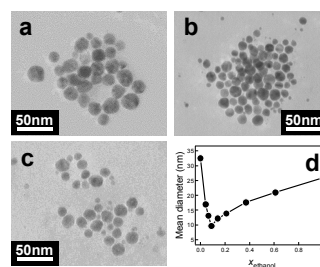


Fig. 5 Selected TEM images of AuNPs synthesized at various ethanol mole fraction (x_{ethanol}) of: (a) 0, (b) 0.089, and (c) 0.37. (d) Mean diameter of the AuNPs as a function of the x_{ethanol} .

the hydrophobicity correlate with the reaction rate. As the hydrophobicity of alcohol molecules increases, the larger number of alcohol molecules gather on gas/liquid interface for thermodynamic stability. Considering vapor-liquid equilibrium (VLE) diagrams¹⁷, on the other hand, gas phase should be mainly composed of water at low concentration of alcohol. Therefore, hydrogen radicals and hydroxyl radicals generate in plasma according to reaction 1. These radicals are supposed to react with alcohols in reactions 2 and 3 at the interface. Furthermore, it is reported that excess alcohol molecules exist at gas/liquid interface comparing bulk concentration,^{35,36} and this excess value reach maxima when partial molar volume of short-chain alcohols exhibits minimum value.³⁵ Based on this information, the amount of reduced gold ions relates well with alcohol concentration at the gas/liquid interface, which support the proposed interfacial reaction. At higher alcohol concentration, the physical condition of plasma changes and then the reduction rate decreases.

In summary, synthesis of AuNPs was carried out in ethanol-water mixture by discharging plasma in the mixture containing gold ions precursor. $t_{1/2}$ was investigated by observing intensity change of the UV-vis spectra. According to the observed results, the addition of ethanol in water for the SPP-based AuNPs synthesis has an important roles on an acceleration of the reaction. The reduction rate of trivalent (Au^{III}) gold ions exhibited maximum value at the $\chi_{\text{ethanol}} = 0.089$. At this point, the reduction rate was approximately 35.2 times faster than that in the pure water system ($\chi_{\text{ethanol}} = 0$). The most important fact is that this concentration corresponds to the significant point where microscopic structure of the ethanol-water mixture changes drastically. In addition, similar phenomenon was also observed in the mixtures of water and other short-chain alcohols, *i.e.*, methanol and 2-propanol. From the comparison with these alcohols, hydrophobicity and reaction at gas/liquid interface is proposed to be important. And in the case of short-chain alcohols, it is suggested that the change in microscopic structure significantly affect the interfacial reaction. The synthesis of nanoparticles in the SPP system can be designed by tuning the solution composition.

Table 1 Relationship between hydrophobicity of short-chain alcohols (log P) and $t_{1/2}$ value at $\chi_{\text{alcohol}} = 0.042$.

alcohol	log P	$t_{1/2}$
methanol	-0.77	162
ethanol	-0.31	84
2-propanol	0.25	35

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