Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

# Supporting Information

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# Accelerated Nanoparticles Synthesis in Alcohol-Water Mixture Based Solution Plasma

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## Experimental sections

### Gold nanoparticles synthesis by solution plasma process (SPP)

The experimental setup used in our study is shown in Fig. 1. A 200 mL glass vessel was used as the reactor. A pair of 0.8 mm diameter tungsten electrodes (Nilaco Co., Ltd.) covered with insulating tubes having internal diameter of 0.8 mm and outside diameter of 1.2 mm (Nilaco Co., Ltd.) were inserted into the reaction vessel through rubber stoppers in parallel. The electrodes were kept 0.3 mm out from the tubes and distance between two electrodes was kept to be 0.5 mm. The bipolar pulse power supply (MPP-HV02, Kurita Co., Ltd.) was used to generate the plasma. The pulse frequency and pulse width were set to be 15 kHz and 1.3 μs, respectively. Ethanol-water mixtures were prepared by using ultrapure water (GSH-210, ADVANTEC) and alcohols: ethanol (>99.5%, Kanto Chemical Co., Inc.), methanol (>99.8%, Kanto Chemical Co., Inc.), and 2-propanol (>99.7%, Kanto Chemical Co., Inc.), with the respective alcohol mole fractions ($\chi_{\mathrm{ethanol}}$): 0, 0.042, 0.065, 0.089, 0.14, 0.21, 0.37, 0.61, and 1. Chloroauric acid ($HAuCl_4$, 99.0%, Kanto Chemical Co., Inc.), a precursor of AuNPs, was added into the solutions with the adjusted concentration of 0.3 mM. The prepared solution was then put into the reaction vessel. Before the plasma generation, $N_2$ gas was bubbled into the solution. Vigorous stirring was then carried out for 10 min to remove the dissolved $O_2$. The plasma generation was performed at the temperature of 22.5–24.0 °C under constant stirring at 250 rpm in the open air. The maximum applied pulse voltage was 4.2 kV.

### UV-vis

To measure the temporal change of absorbance with respect to surface plasmon resonance of AuNPs and of the concentration of $AuCl_4^-$, absorption spectra of the respective aliquot was analyzed by UV-3600 spectrometer (Shimadzu) operated in the spectral range from 250 to 800 nm, with a spectral resolution of 0.5 nm and an optical absorption path of 10 mm. Especially for the investigation of the concentration of $AuCl_4^-$, we have to convert $AuCl_4^-$ to $AuBr_4^-$ by adding potassium bromide (KBr, for IR spectroscopy, 99.0–100.2% purity, Sigma) into the collected aliquot. The reason of this is that absorbance of $AuCl_4^-$ has no quantitative relationship with its concentration while $AuBr_4^-$ exhibits this property.

### TEM observation

TEM observation was carried out with JEM-2500SE (JEOL Ltd.). Samples for TEM analysis were prepared on carbon coated Cu grids and the TEM analysis was operated at 200 kV.

## AuNPs synthesis

During the AuNPs synthesis, reaction solution was collected with 3 mL at various processing times and absorption spectra of the respective aliquot was analyzed by UV-vis. The absorption spectra lying around the wavelength of 530–550 nm, indicating surface plasmon resonance (SPR) of the AuNPs, were observed (Fig. S1). Profiles of absorbance of SPR versus processing time at various $\chi_{\text{ethanol}}$ are shown in Fig. S2a–c. In $\chi_{\text{ethanol}}$ of 0–0.089, rate of increasing absorbance increase with ethanol composition (Fig. S3a and b) and, on the other hand, it turned to decrease with further ethanol composition (Fig. S3c). Therefore, aforementioned decreasing final size of the nanoparticles might be induced via the accelerated formation of nuclei and following growth of AuNPs.

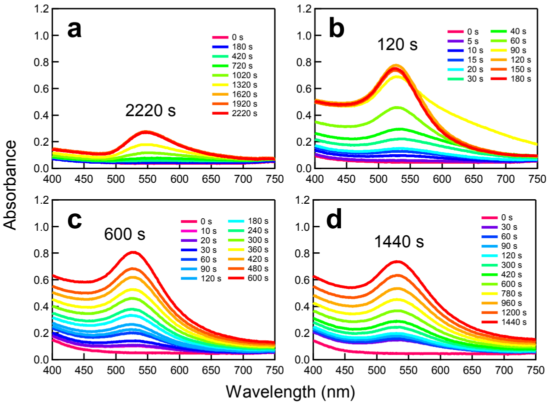

**Fig. S1** Absorption spectra of surface plasmon resonance of AuNPs synthesized at ethanol mole fraction ($\chi_{\text{ethanol}}$) of (a) 0, (b) 0.089, (c) 0.37, and (d) 0.61.

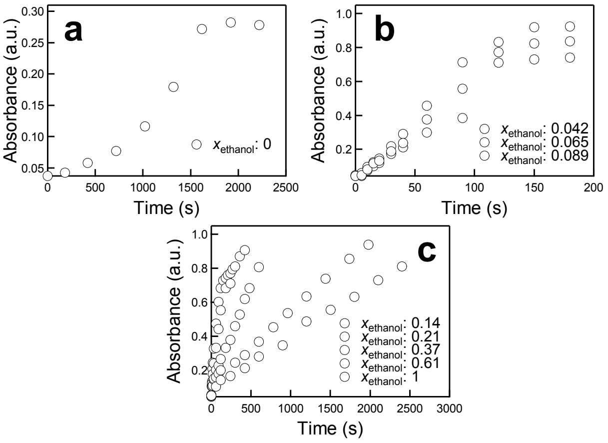

**Fig. S2** Temporal change in the absorbance of surface plasmon resonance (SPR) of AuNPs synthesized in ethanol-water based solution plasma at various ethanol mole fraction ($\chi_{\text{ethanol}}$): (a) 0, (b) 0.042–0.089, and (c) 0.14–1.

## Detection of volatile products

Volatile products formed from the reaction was investigated by gas chromatography-mass spectrometry (GC-MS, Agilent Technologies 7890A GC system) by auto injection method. The measurement was operated at an oven temperature ranged from 40 to 240 °C by using an analytical column: Agilent J&W GC Columns HP-5; length = 30 m, diameter = 0.320 mm, and film thickness = 0.25 μm. The solution plasma was generated at $\chi_{\mathrm{ethanol}}$ of 0, 0.089, and 1 without gold chloride ions for 3 min and the observed solution was collected during the process. Chromatograms of the products from a mixture of $\chi_{\mathrm{ethanol}} = 0.089$ are shown in Fig. S3a. Results indicated that three peaks at retention times of about 748, 772, and 785 s were observed and intensity of peaks increased with the extension of the processing time. The mass spectra attributed to products of the respective three peaks are shown in Fig. S3b. These spectra assigned to: (i) (E)-2,3-butanediol[R3], (ii) (Z)-2,3-butanediol[R3], and (iii) propylene glycol. These products were detected only at the $\chi_{\mathrm{ethanol}}$ of 0.089 and possibly formed from the following reactions[R4]. These results suggested that specific radicals derived from ethanol were generated in the ethanol-water mixture based SPP.

$$\mathrm{CH_3CH_2OH} + \mathrm{H}\cdot \rightarrow \mathrm{CH_3\dot{C}HOH} + \mathrm{H_2}$$ (reaction a)

$$\mathrm{CH_3CH_2OH} + \mathrm{e} \rightarrow \cdot\mathrm{CH_3} + \cdot\mathrm{CH_2OH}$$ (reaction b)

$$\mathrm{2CH_3\dot{C}HOH} \rightarrow \mathrm{CH_3CH_2(OH)CH_2(OH)CH_3}$$ (reaction c)

$$\mathrm{CH_3\dot{C}HOH} + \cdot\mathrm{CH_2OH} \rightarrow \mathrm{CH_3CH_2(OH)CH_2(OH)}$$ (reaction d)

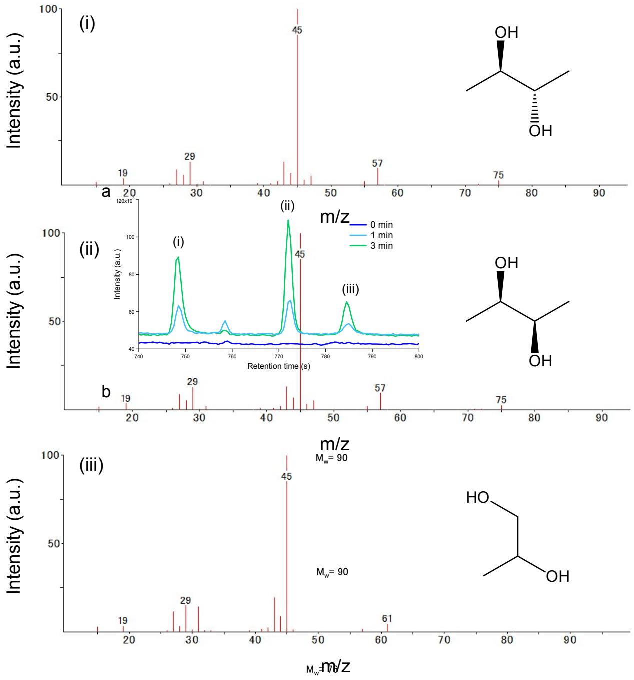

**Fig. S3** (a) Gas chromatography (GC) chromatogram of ethanol-water mixture with $\chi_{\text{ethanol}}$ of 0.089 after the plasma discharge for 0, 1, and 3 min. (b) Mass spectra of the related products derived from peaks (i), (ii), and (iii) in the GC chromatogram (a).

## Effect of UV-light, pH, and reaction products as well as physical conditions of plasma

### Effect of UV-light

Ethanol-water mixture at an ethanol mole fraction ($\chi_{ethanol}$) of 0.089 was added in the reaction vessel while the same mixture containing chloroauric acid—an AuNPs precursor—was added in quartz cell in Fig. S3. After 20 min of plasma discharge in the reaction vessel, the color change in the quartz cell was not observed. This result suggests that the effect of UV light is negligible for AuNPs synthesis in the ethanol-water mixture.

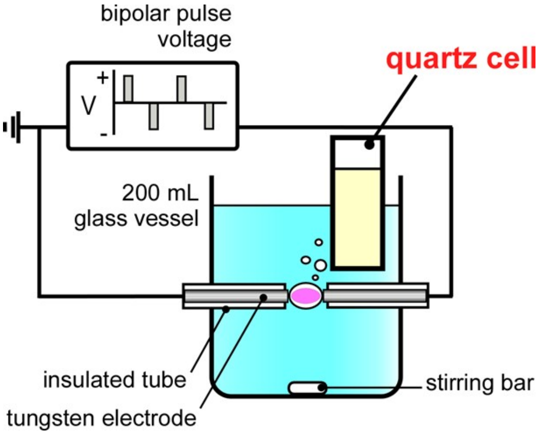

**Fig. S4** Experimental set up for the investigation of UV-light effect on the reduction reaction of gold ions.

### Solution pH before and after the SPP

The pH measurement was conducted using PC 6500, Eutech Instruments. From Table S1, it was found that pH of the solution reduced slightly after the SPP, so that, it is supposed not to influence the reactivity of the gold ions. In agreement with our opinion, Ji *et al.* mentioned that reactivity of gold ions changed drastically when the pH was in the range of 6.2 to 8.1 which was out from the range of our findings.[R6]

**Table S1.** The change in pH of reaction solution.

| $\chi_{\text{ethanol}}$ | before SPP | after SPP |
|---|---|---|
| 0 | 3.3 | 2.9 |
| 0.042 | 3.5 | 3.3 |
| 0.065 | 3.6 | 3.4 |
| 0.089 | 3.7 | 3.6 |
| 0.14 | 3.8 | 3.7 |
| 0.21 | 3.7 | 3.5 |
| 0.37 | 3.7 | 3.6 |
| 0.61 | 3.8 | 3.6 |
| 1 | 3.9 | 3.8 |

## Reaction products

In order to detect hydrogen peroxide formed in the SPP system, potassium permanganate titration was carried out. The plasma was generated in water and ethanol-water mixture ($\chi_{\text{ethanol}}$ = 0.042) with the inclusion of hydrogen chloride, instead of chloroauric acid, for 10 min. Then, 1 mL of the solution was collected. A volume of 1 mL of potassium permanganate aqueous solution (0.3 mM) acidified with dilute sulphuric acid was added in the collected solution before the mixture was well-shaken. After shaking we found that color of the solution did not change. This finding suggested that hydrogen peroxide might be formed but to a small extent that could not affect the AuNPs formation. Furthermore, formation of nitrogen-related compounds was investigated by using ion chromatography (850 Professional IC, Metrohm). TSKgel IC-Anion-PW$_{\text{XL}}$ with 4.6 mm I.D. × 3.5 cm length was used as analytical column. The discharge solutions were similar to that mentioned in the above experiment. Results indicated that nitrite ions with 0.003 mM and 0.024 mM were detected in water and ethanol-water mixture, respectively. These production yield was quite low comparing to concentration of chloroauric acid (*i.e.* 0.3 mM), the AuNPs precursor. We therefore concluded that reduction reaction in our system was mainly caused by the reaction with radicals as described in the main manuscript.

## References

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