**Supporting Information**

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# Verification of Radicals Formation in Ethanol–Water Mixture Based Solution Plasma and Their Relation to the Rate of Reaction

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**Reaction rate of reduction reaction of trivalent gold ions**

In order to clarify the dependence of reaction rate for reducing trivalent gold ions as a precursor of gold nanoparticles on ethanol concentration, the period when initial concentration of gold ions decrease to half value ($t_{1/2}$) was investigated as previously reported. $t_{1/2}$ value at respective ethanol mole fraction ($\chi_{ethanol}$) is listed in Table S1.

**Table S1.** The pseudo-first order rate constant ($k_{obs}$) for the reduction of gold chloride ions to AuNPs as a function of ethanol mole fraction ($\chi_{ethanol}$) in the ethanol-water mixture.

| $\chi_{ethanol}$ | $t_{1/2}$ (s) |
|---|---|
| 0 | 1480 |
| 0.042 | 84 |
| 0.065 | 58 |
| 0.089 | 44 |
| 0.14 | 64 |
| 0.21 | 97 |
| 0.37 | 185 |
| 0.61 | 235 |

$$\frac{t_{1/2} \text{ at } \chi_{ethanol}\ 0}{t_{1/2} \text{ at } \chi_{ethanol}\ 0.089} = 35.2$$

**Detailed information about the effect of added KBr**

**Table S2.** Concentration of the added KBr and electrical conductivity of the ethanol-water mixtures before and after the plasma discharge, as a function of ethanol mole fractions ($\chi_{ethanol}$).

| $\chi_{ethanol}$ | concentration of the added KBr (mM) | electrical conductivity (μS $cm^{-1}$) | |
|---|---|---|---|
| | | before SPP | after SPP |
| 0 | 0.8 | 150 | 153 |
| 0.042 | 0.9 | 149 | 152 |
| 0.065 | 1.1 | 151 | 154 |
| 0.089 | 1.2 | 147 | 150 |
| 0.14 | 1.35 | 149 | 152 |
| 0.21 | 1.42 | 150 | 152 |
| 0.37 | 1.57 | 151 | 153 |
| 0.61 | 1.68 | 149 | 150 |

**Table S3.** The dependence of integral intensity of ESR spectra of DMPO-H, DMPO-OH, and DMPO-CH($CH_3$)OH on added KBr concentration (~3 mM) in ethanol-water mixture at $\chi_{ethanol}$ of 0 and 0.089, respectively.

| concentration of the added KBr (mM) | $\chi_{ethanol}$: 0 | | | $\chi_{ethanol}$: 0.089 | | |
|---|---|---|---|---|---|---|
| | DMPO-H | DMPO-OH | DMPO-CH($CH_3$)OH | DMPO-H | DMPO-OH | DMPO-CH($CH_3$)OH |
| 1 mM | 403 | 526 | 0 | 176 | 124 | 743 |
| 2 mM | 411 | 523 | 0 | 159 | 127 | 755 |
| 3 mM | 412 | 514 | 0 | 183 | 132 | 738 |

**Optical emission spectroscopy**

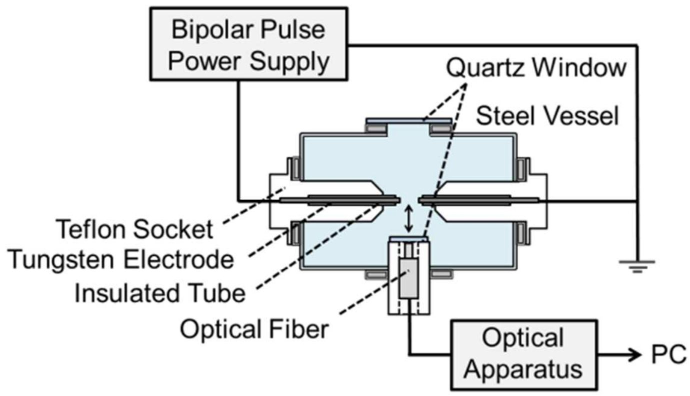


**Figure S1.** Experimental setup for OES measurement.

**Gas chromatography**

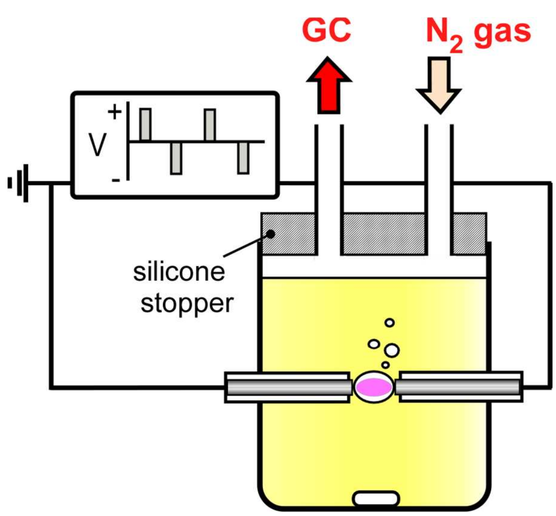


**Figure S2.** Experimental apparatus for gas chromatography (GC) measurement.

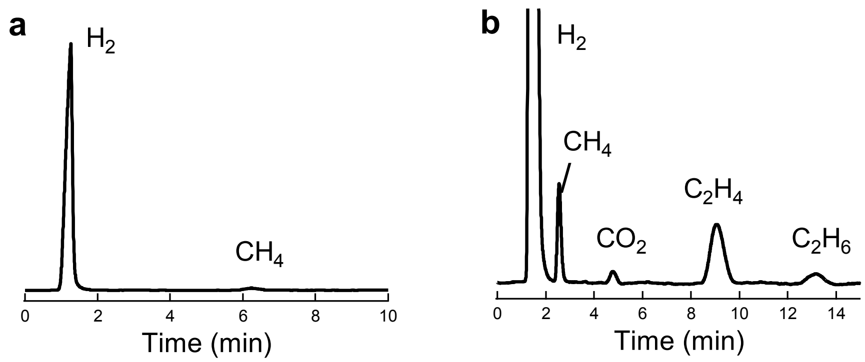


**Figure S3.** Chromatograms of the produced gases from solution plasma in ethanol-water mixture at $\chi_{ethanol}$ = 0.37 by using (a) molecular sieve 5A 60/80 and (b) Porapak Q 80/100 as analytical columns.

**Computer simulation of ESR spectra**

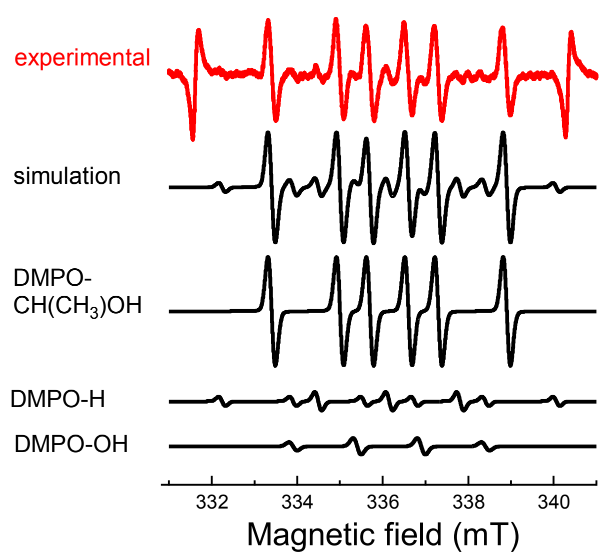


**Figure S4.** Computer-based simulations of the spin trap adduct spectra based upon the ethanol mole fraction ($\chi_{ethanol}$) of 0.042.

**Correlation between reaction rate of reducing gold ions and radicals detected by ESR measurement in present study**

Previously, overall reduction reaction of gold ions to AuNPs (from trivalent to zerovalent gold ions) by the SPP in water was reported.[R1] The equation is shown below, where hydrogen radicals (H·) play a crucial role as reducing agent.

$AuCl_4^- + 3H\cdot \rightarrow Au^0 + 3HCl + Cl^-$ (reaction 1)

In the case of adding ethanol, the following reaction is added from the result of ESR measurement.

$AuCl_4^- + 3\cdot CH(CH_3)OH \rightarrow Au^0 + 3CH_3CHO + 3HCl + Cl^-$ (reaction 2)

We confirmed the hydroxyethyl radicals ($\cdot CH(CH_3)OH$) are a main reducing agent for the reduction rate of gold chloride ions by observing the correlation between $t_{1/2}$ value (see Table S1) and the integral intensity for ESR spectra of DMPO–$CH(CH_3)OH$ adducts (at $\chi_{ethanol}$ = 0.042–0.61).

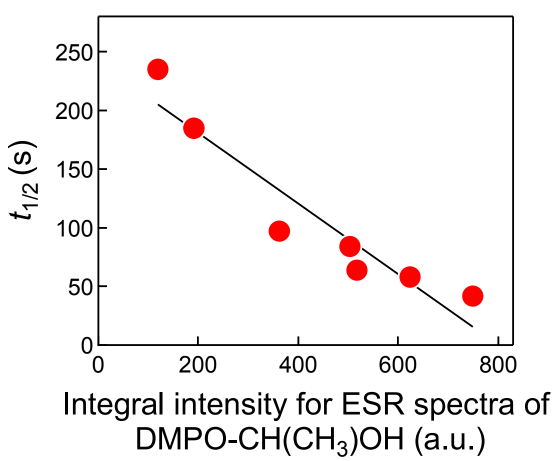


**Figure S5.** The correlation between $t_{1/2}$ value and integral intensity for ESR spectra of DMPO adducts with hydroxyethyl radical in ethanol-water mixture at $\chi_{ethanol}$ of 0.042–0.61.

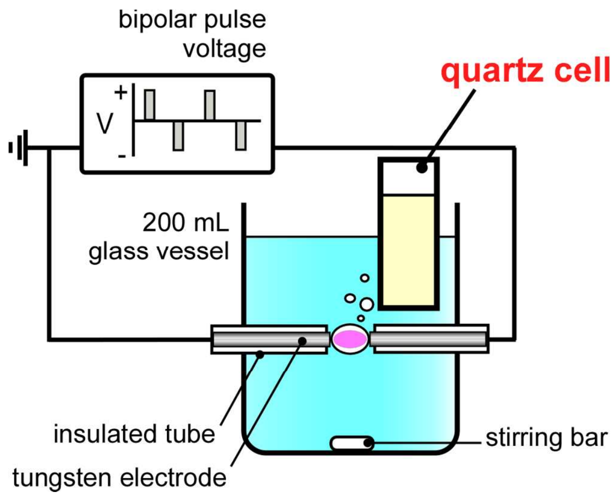


**Fig. S6** Experimental setup for the investigation of UV-light effect on the reduction reaction of gold ions.

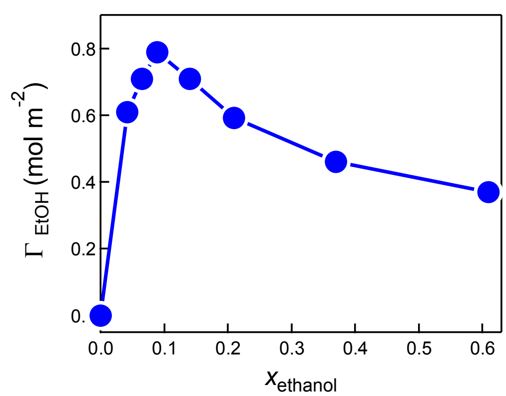


**Figure S7.** A profile of surface excess of ethanol as a function of ethanol mole fraction ($\chi_{ethanol}$) in ethanol-water mixture.

**Reference**

R1 Bratescu, M. A.; Cho, S. P.; Takai, O.; Saito, N. Size-Controlled Gold Nanoparticles Synthesized in Solution Plasma. *J. Phys. Chem. C* **2011**, *115*, 24569–24576.