Preparation of Stable Water-Dispersible PEGylated Gold Nanoparticles Assisted by Nonequilibrium Atmospheric-Pressure Plasma Jets

Hitoshi Furusho[1], Katsuhisa Kitano[2,4], Satoshi Hamaguchi[2,4], and Yukio Nagasaki[1, 3 – 6*]

[1]Institute of Materials Science, Graduate School of Pure and Applied Science, University of Tsukuba, Ten-noudai 1-1-1, Tsukuba, Ibaraki 305-8573, Japan
[2] Center for Atomic and Molecular Technologies, Graduate School of Engineering, Osaka University, Yamada-oka 2-1, Suita, Osaka 565-0871, Japan
[3]Tsukuba Research Center for Interdisciplinary Materials Science, University of Tsukuba, Ten-noudai 1-1-1, Tsukuba, Ibaraki 305-8573, Japan,
[4]Center for Tsukuba Advanced Research Alliance, Ten-noudai, University of Tsukuba 1-1-1, Tsukuba, Ibaraki 305-8577, Japan,
[5]Master's School of Medical Sciences, Graduate School of Comprehensive Human Sciences, University of Tsukuba, Ten-noudai 1-1-1, University of Tsukuba, Ibaraki 305-8575, Japan,
[6]Satellite laboratory of International Center for Materials Nanoarchitectonics, University of Tsukuba, Ten-noudai 1-1-1, Tsukuba, Ibaraki 305-8575, Japan,

CORRESPONDING AUTHOR e-mail : yukio@nagalabo.jp

TITLE RUNNING HEAD: PEGylated Gold Nanoparticles

N6-PEG was prepared according to the synthetic route as shown in Figure S1. Synthetic conditions were described in the manuscript. ^{1}H NMR, size exclusion chromatography (SEC) and matrix-assisted laser-desorption ionization time-of-flight type mass spectroscopy (MALDI-tof-MS) were shown in Figures S2, S3(a) and (b), respectively.

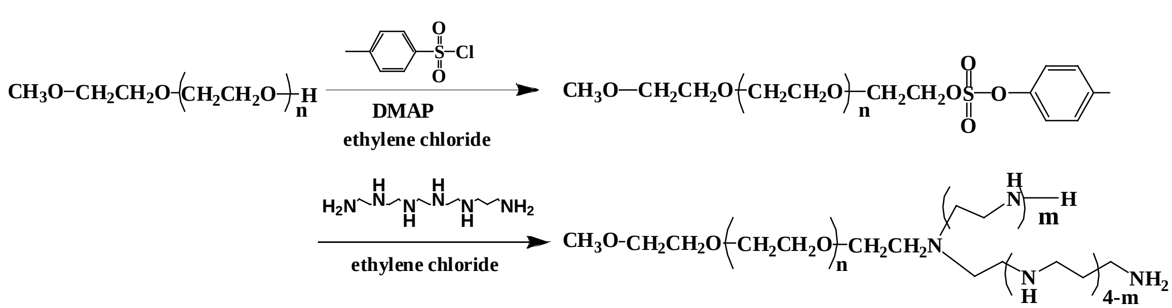

Figure S1. Synthetic route of N6-PEG.

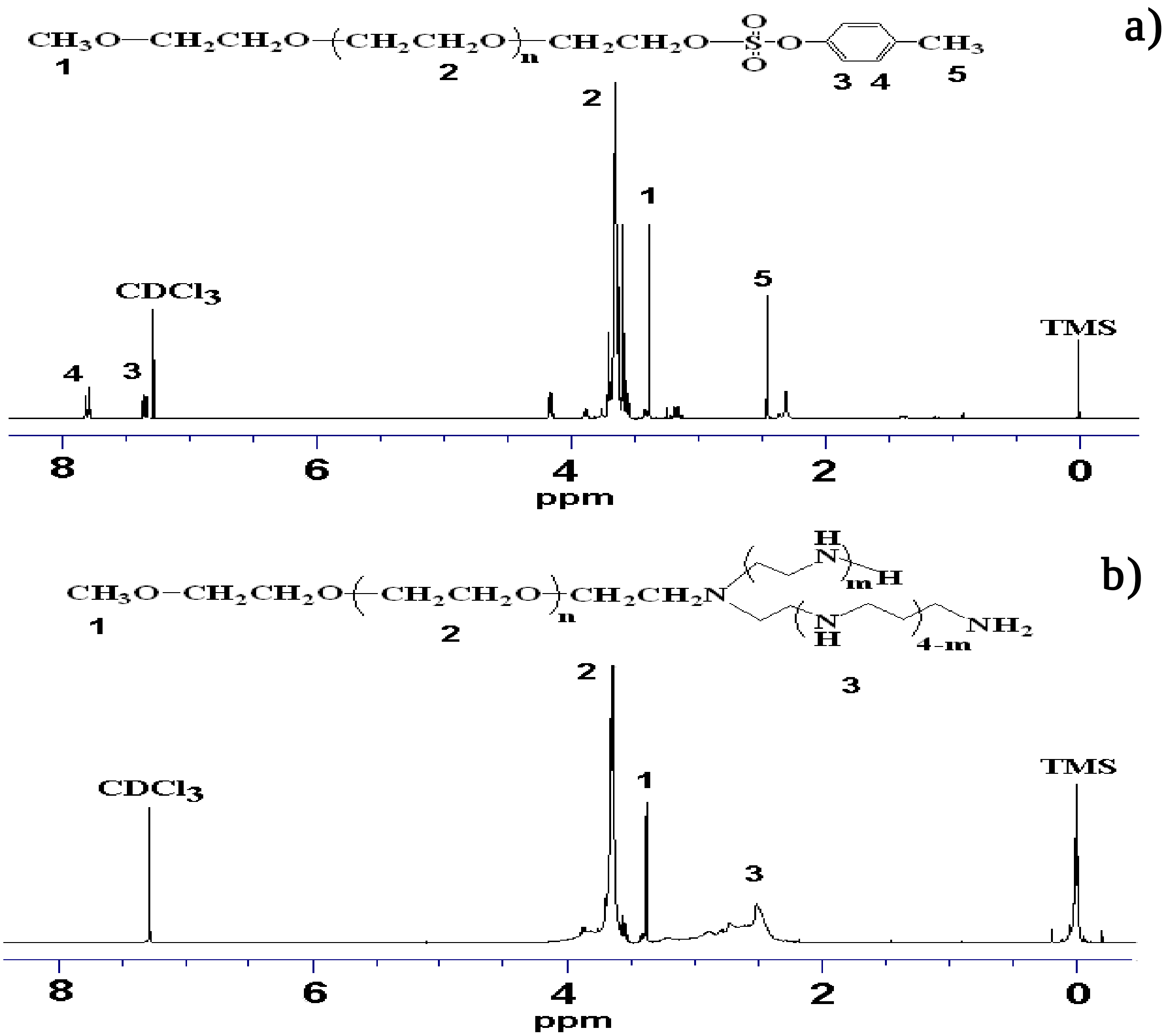

Figure S2. ^{1}H NMR (300 MHz) spectra at 25 ˚C in $CDCl_3$ of (a) the tosylated poly(ethylene glycol) and (b) N6-PEG.

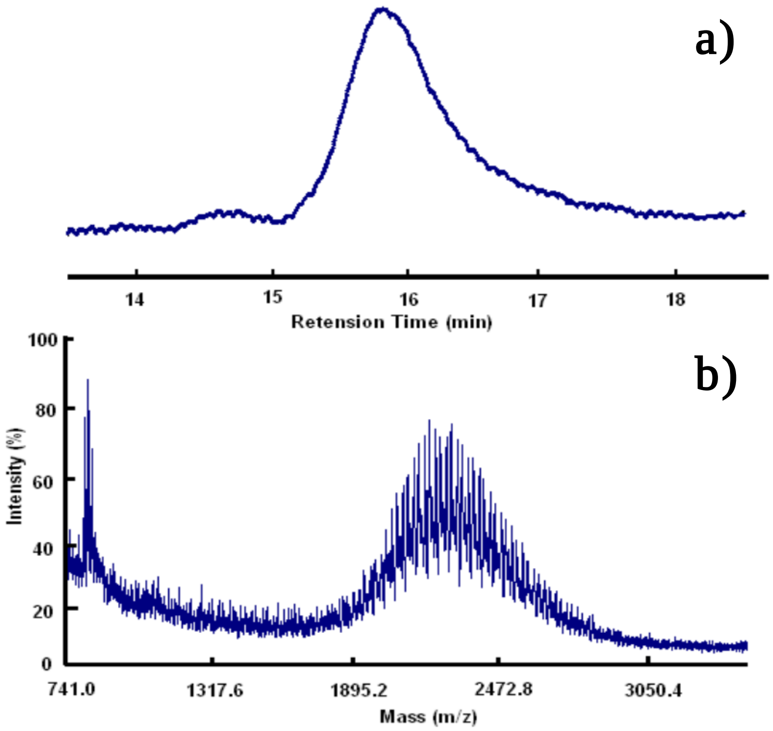

Figure S3. SEC and MALDI-TOF MS data of N6-PEG after purification. (a) SEC data, from which we obtain the molecular weight of N6-PEG as number-average molecular weight Mn = 2170 and the weight average molecular weight Mw = 2240, which makes the polydispersity index Mw/Mn = 1.03. (b) MALDI-TOF mass spectrum, where the peak of the mass-to-charge m/z ratio occurs at 2210.

Optical emission spectra of DBD plasma jet were analyzed by UV-vis spectrometer as a function of gas flow rate of helium gas as shown in Figure S4.

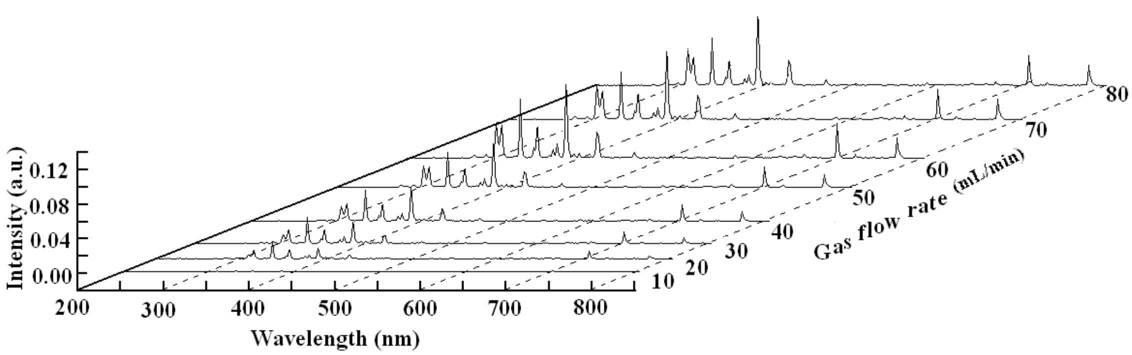

Figure S4. Optical emission spectra from DBD plasma jets as functions of the flow rate. The applied peak voltage and frequency were 8 kV and 10 kHz.

TEM photograph of the gold nanoparticles prepared under acidic conditions with P/A ratio of 5 is shown in Figure S5.

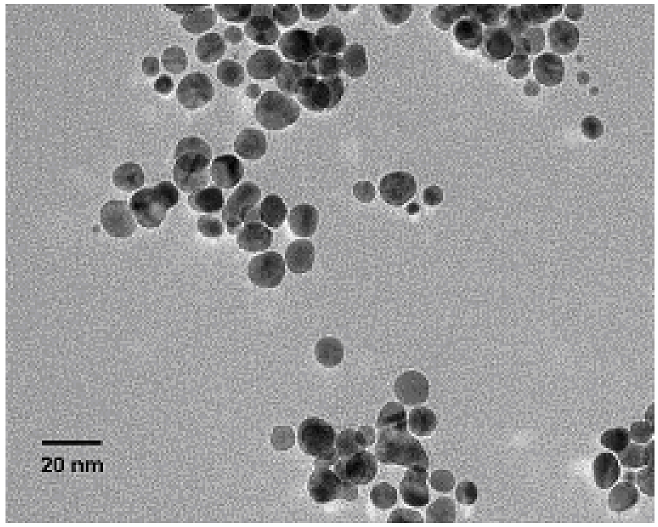

Figure S5. TEM images of gold nanoparticle prepared by plasma reduction at pH 3.9 condition: P/A ratio of 5.

The DLS measurements of the gold nanoparticles obtained with and without plasma irradiation under the acidic conditions in the presence of N6-PEG were carried out. Figure S6 shows the size distribution of the gold nanoparticle prepared with self-reduction (a) and plasma-induced reduction (b) under the acidic conditions with P/A ratios of 20 as a function of time.

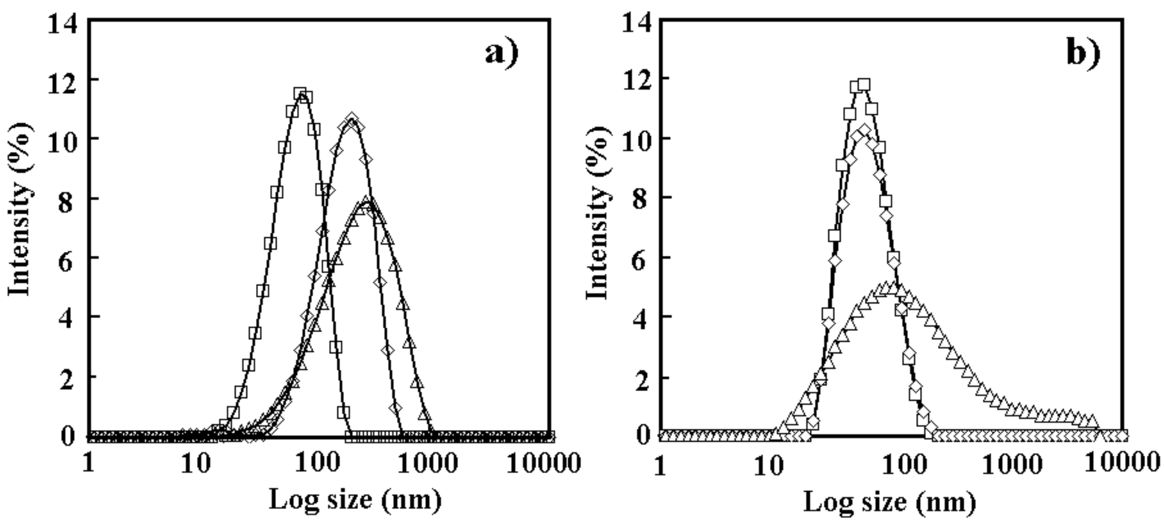

Figure S6. Dispersion stabilities under physiological conditions for gold nanoparticles prepared by different methods. In (a) gold nanoparticles prepared by N6-PEG self-reduction under acidic conditions, i.e., pH 3.9 with the P/A ratio being 20. The shapes of symbols indicate different standing periods; the square, diamond, and triangle represent 1 h, 6 h, and 15 h standing at room temperature, respectively. In (b), the gold nanoparticles were prepared by plasma-induced reduction under acidic conditions, i.e., pH 3.9 with the P/A ratio being 20. The shapes of symbols indicate different standing periods; the square, diamond, and triangle represent 1 h, 15 h, and 30 h standing at room temperature, respectively.

UV-vis measurements of surface plasmon band of the gold nanoparticles obtained under the acidic conditions were carried out. Figure S7 shows the time evolution of the surface plasmon band for gold nanoparticle prepared with (a) and without (b) plasma irradiation with P/A ratios of 20 under acidic conditions (pH 3.9).

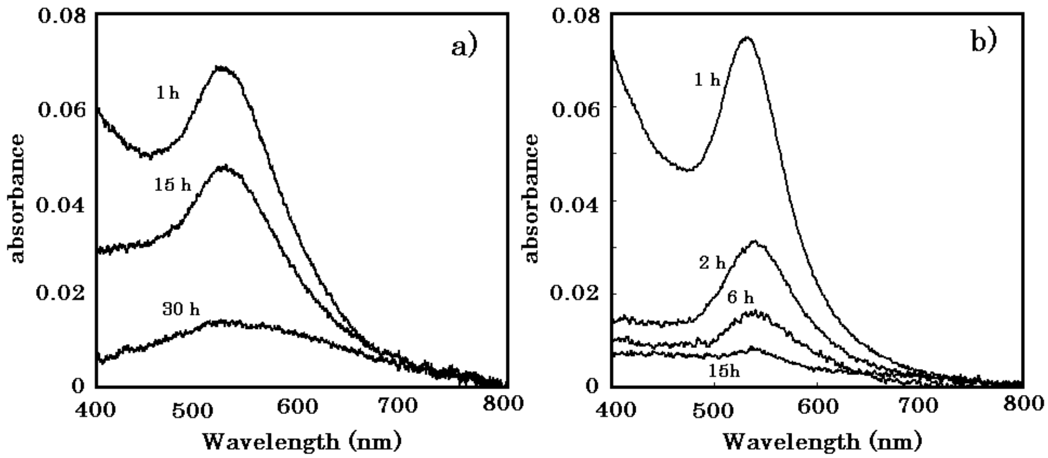

Figure S7. Change in the surface plasmon absorptions of the gold nanoparticles prepared at pH 3.9 with P/A ratios of 20 with 1.5 h plasma irradiation (a) and 120 h self-reduction by N6-PEG (b). Times inserted in figures were standing time after centrifugation purification as shown in experimental section in manuscript.

Hazards of DBD-plasma jet: During DBD-plasma jet irradiation with 10 kV, generation of ozone was observed. The user must be careful to ventilation.