

# Supporting Information

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## **Synthesis of Au Nanoparticles in Natural Matrices by Liquid-Phase Plasma: Effects on Cytotoxic Activity against Normal and Cancer Cell Lines**

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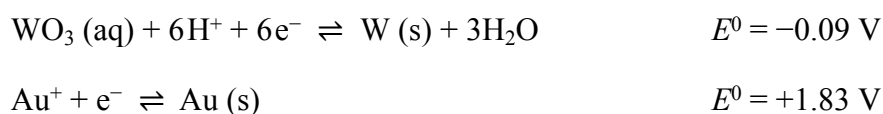
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### The reasons for selecting tungsten (W) as an electrode

In this study, we select tungsten as an electrode to prevent the electrode from erosion. Tungsten is a hard metal in which, among all discovered elements, it has the highest melting point (3,422 °C). As a result, it is a popular type of electrode used for welding.

In our study, the same metal electrode is used as both cathode and anode, *i.e.*, two gold-wire electrodes [1] or two tungsten-wire electrodes (this study).

As electrodes in an electrolytic cell, standard electrode potential ( $E^0$ ) values of the half-reactions of tungsten (W) and gold (Au) are as follows [2]:

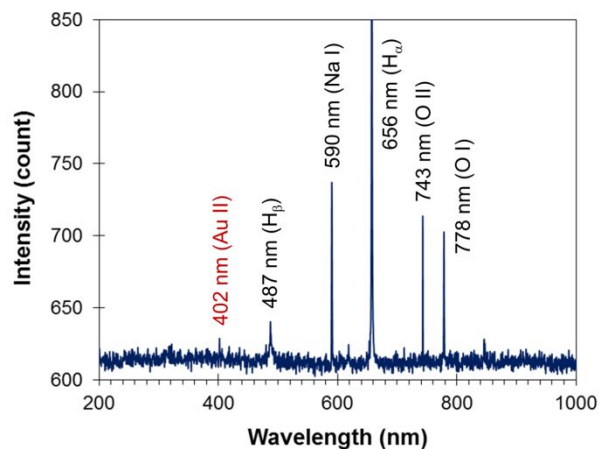


The  $E^0$  value of tungsten which is closer to zero than that of gold implies that the tungsten electrode is more inert than the gold electrode for erosion. Furthermore, the environments involving in the reaction for synthesizing AuNPs from (i) gold-wire electrodes and (ii)  $\text{HAuCl}_4$  precursor with tungsten-wires electrodes, are different. The components in both systems are as follows:

<b>System i:</b>	water + gold-wire electrodes
<b>System ii:</b>	water + $[\text{AuCl}_4]^-$ ions + tungsten-wires electrodes

For **System ii**, since  $[\text{AuCl}_4]^-$  ions exist in the solution (where the electrodes are immersed in), reactive species formed after the plasma generation prefer to react with the  $[\text{AuCl}_4]^-$  ions than bombard on the electrode surface. This could also prevent tungsten electrodes from erosion.

Optical emission spectrum (OES) of the plasma generated through a pair of tungsten electrodes in alginate aqueous solution containing gold (III) chloride trihydrate is shown in Figure S1. This result evidences that peaks of tungsten are absence. Generally, peaks of the W radicals appear at wavelengths 522 and 551 nm [3].

**Figure S1**

**Figure S1.** Optical emission spectrum (OES) of the plasma generated through a pair of tungsten electrodes in alginate aqueous solution containing gold (III) chloride trihydrate.

All of the above-mentioned reasons indicate that tungsten nanoparticles are not formed in this experiment.

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- [1] Watthanaphanit, A.; Panomsuwan, G.; Saito, N. A Novel One-step Synthesis of Gold Nanoparticles in an Alginate Gel Matrix by Solution Plasma Sputtering. *RSC Adv.* **2014**, *4*, 1622–1629.
  - [2] Bard, A. J., Parsons, R., and Jordan, J. (1985). *Standard Potentials in Aqueous Solutions* (Marcel Dekker, New York).
  - [3] Kim, D. W.; Li, O. L.; Pootawang, P.; Saito, N. Solution Plasma Synthesis Process of Tungsten Carbide on N-Doped Carbon Nanocomposite with Enhanced Catalytic ORR Activity and Durability. *RSC Adv.* **2014**, *4*, 16813–16819.

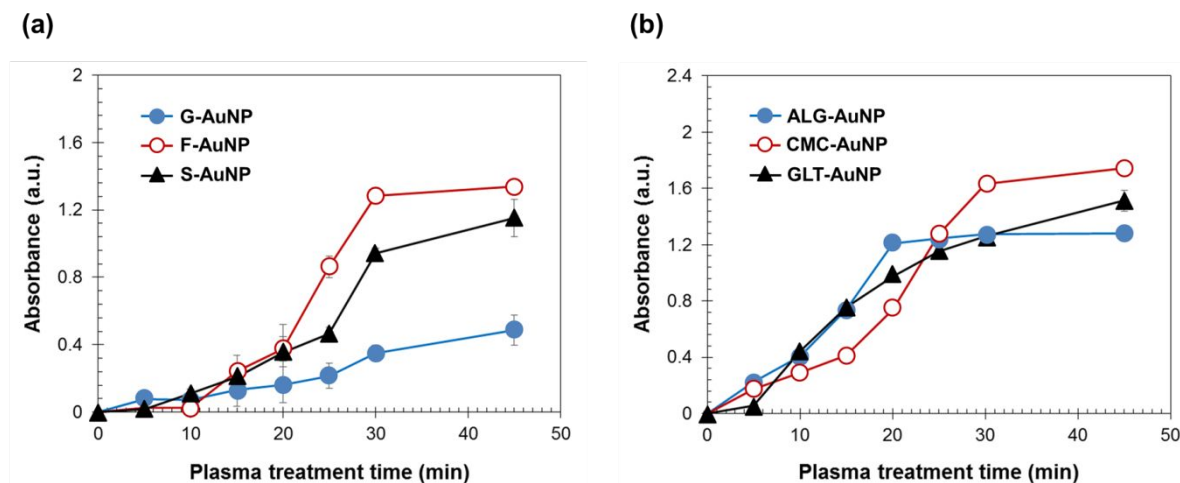
**Why were two concentrations (0.5 and 1.0 %w/v) of natural matrices used?**

In our previous work about the synthesis of AuNPs in sodium alginate by the SPP [4]; we found that 0.5 and 1.0 %w/v were suitable for plasma generation. Particularly, it was more difficult to generate plasma in a polymer solution with a low concentration ( $<0.5$  %w/v) because of the conductivity issue. On the other hand, a high concentration of the polymer solution ( $>1.0$  %w/v) led to high solution viscosity that can store much capacity of heat and has poor heat transferability. As a result, burning around electrodes occurred when the plasma discharge time was prolonged. These are the reasons why we choose 0.5 and 1.0 %w/v as concentrations of natural matrices. Besides, results from another former work indicated that the AuNP colloids synthesized in these concentrations exhibited good colloidal stability [5].

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[4] Watthanaphanit, A.; Saito, N. Effect of Polymer Concentration on the Depolymerization of Sodium Alginate by the Solution Plasma Process. *Polym. Degrad. Stabil.* **2013**, *98*, 1072–1080.

[5] Watthanaphanit, A.; Heo, Y.K.; Saito, N. Influence of the Discharge Time of Solution Plasma Process on the Formation of Gold Nanoparticles in Alginate Matrix. *J. Taiwan Inst. Chem. Eng.* **2014**, *45*, 3099–3103.

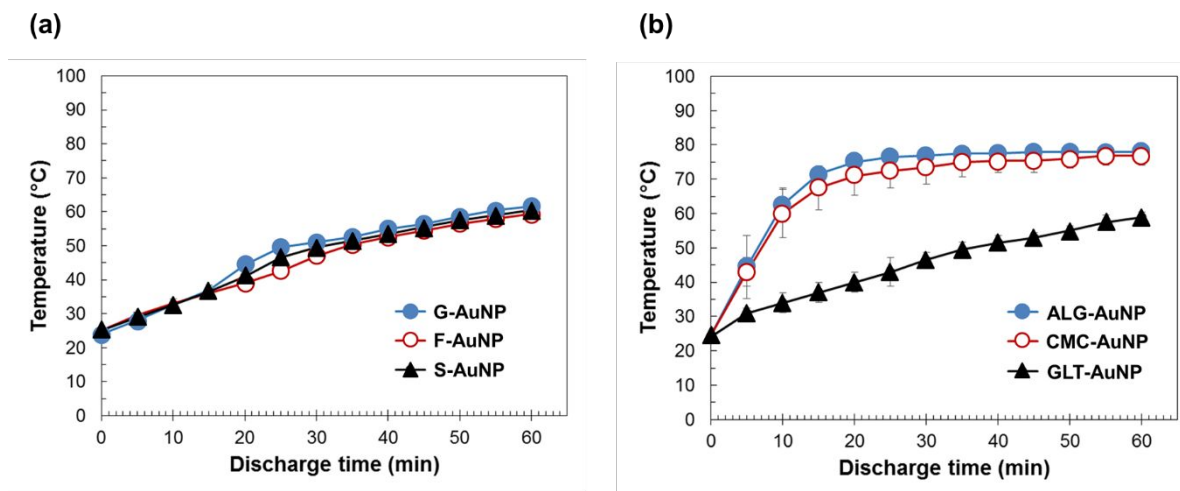
**Figure S2**

**Figure S2.** Maximum intensities of the UV-vis absorption spectra of the AuNP's SPR band ( $\lambda_{max} \sim 535\text{--}545\text{ nm}$ ) synthesized in (a) sugars and (b) biopolymers (concentration = 1.0 %w/v). Data were collected immediately after the treatment.

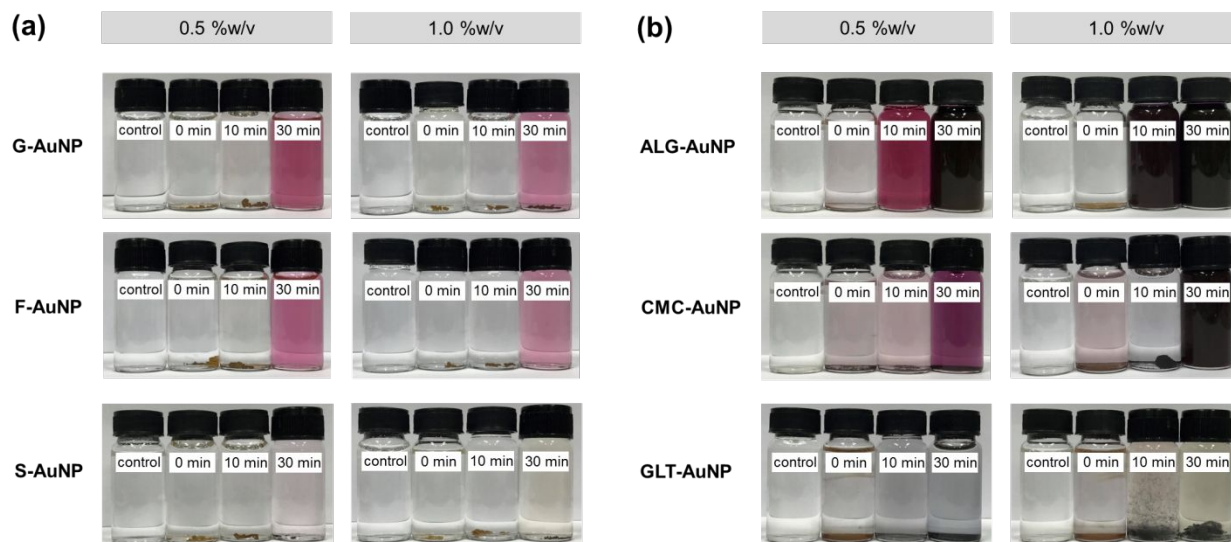
To select the plasma treatment time ( $t$ ), we conducted an experiment to find the intensity of the SPR band of the AuNPs ( $\lambda_{max} \sim 535\text{--}545\text{ nm}$ ) synthesized in all matrices (concentration = 1.0 %w/v) at  $t = 0, 5, 10, 15, 20, 25, 30$ , and 45 min. The UV-vis observation was performed immediately after the treatment at each time intervals.

We found that while the intensity increases rapidly from  $t = 0$  to 30 min, there is a slight increase from  $t = 30$  to 45 min. Generally, after the plasma is stopped, the remaining active species can drive a reaction forward for some amount. This is the reason why we select 30 min as maximum treatment time. Note that, the UV-vis spectra shown in the manuscript (Figure 3) are collected from samples leaving for one month after the synthesis.

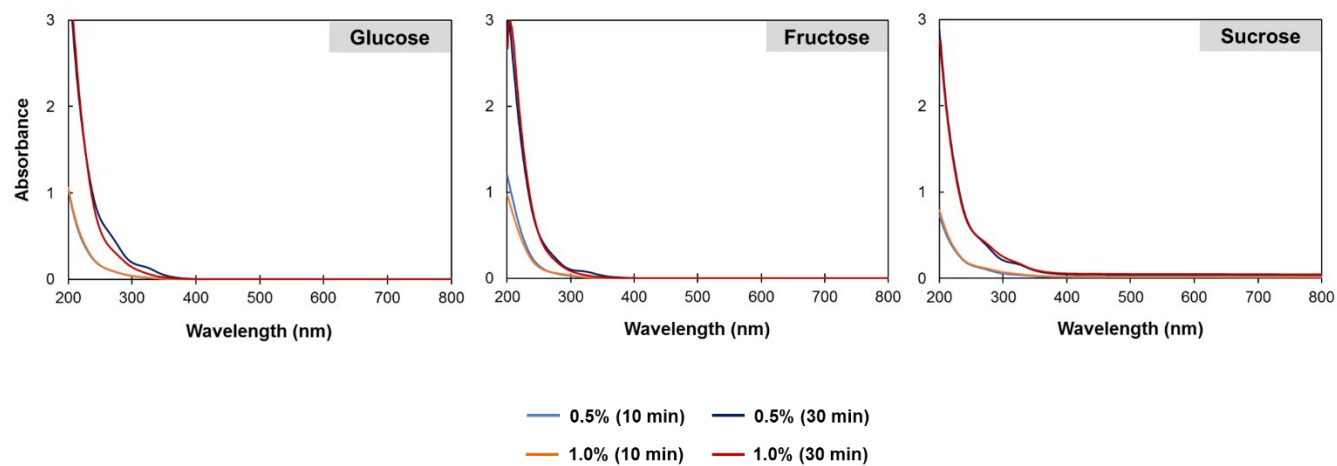
Moreover,  $t = 10$  min is selected for comparison as a representative of an incomplete reduction sample. As a result, the plasma treatment time is set at 10 and 30 min.

**Figure S3**

**Figure S3.** Temperature profiles of the solution during the synthesis of AuNP colloids by the SPP in (a) sugars and (b) biopolymers (concentration = 1.0 %w/v).

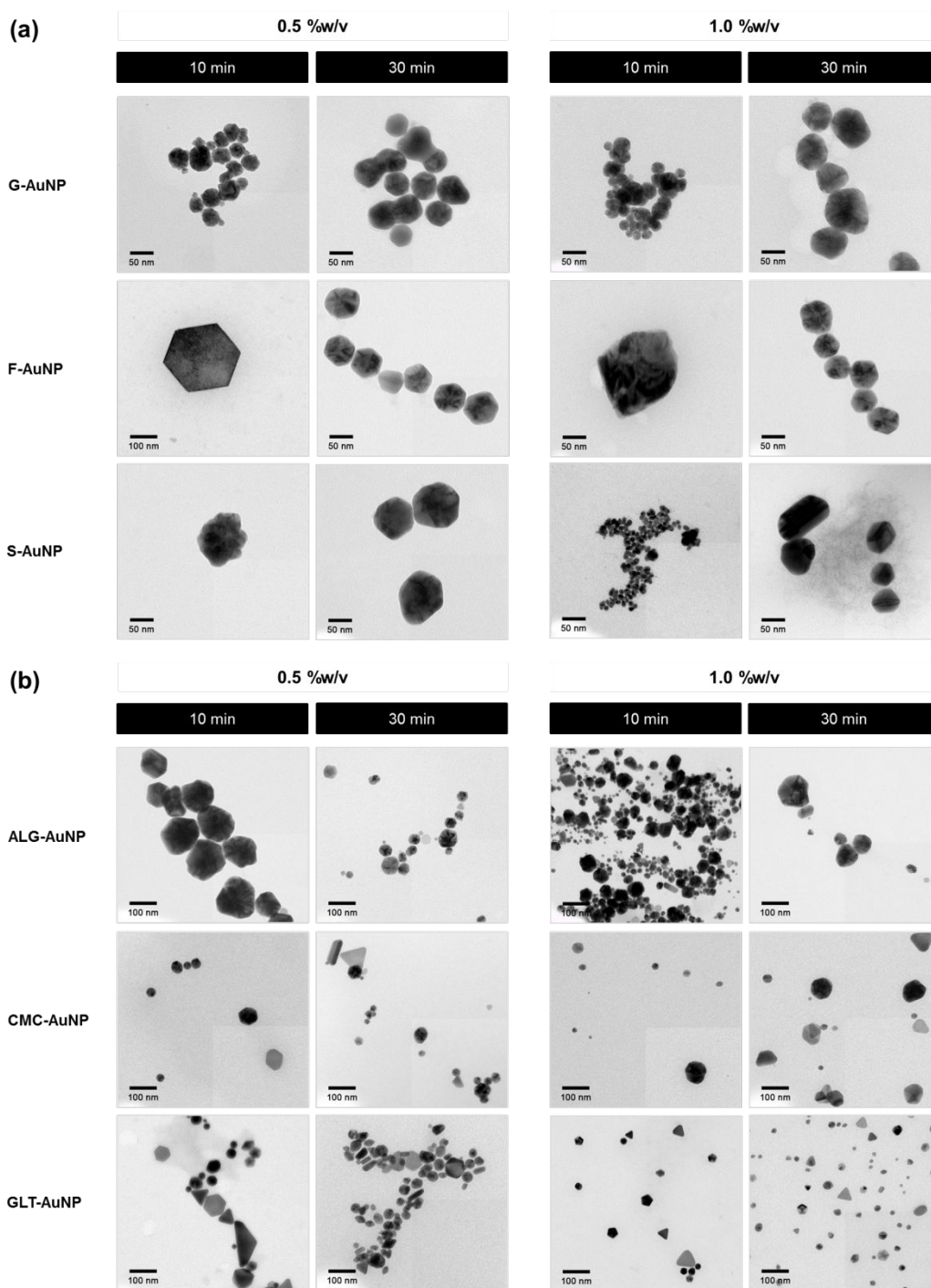
**Figure S4**

**Figure S4.** The appearance of the AuNP colloids synthesized by the SPP in (a) sugars and (b) biopolymers, with different concentrations of the matrices and plasma treatment times. “Control” refers to the matrices without the gold precursor. Pictures were taken after leaving the samples for 10 months.

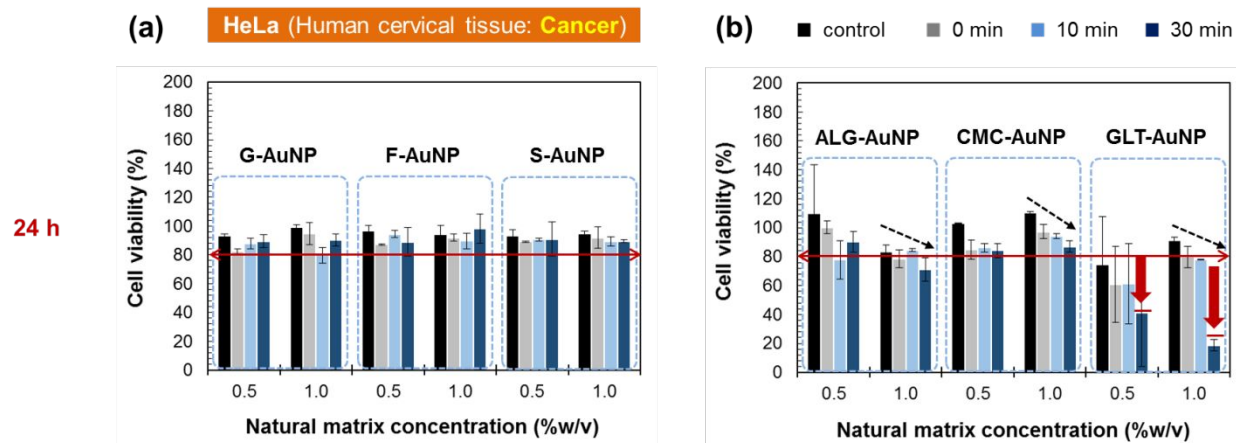
**Figure S5**

**Figure S5.** UV-vis absorption spectra of the aqueous solution of sugars: glucose, fructose, and sucrose (concentrations = 0.5 and 1.0 %w/v) after treated with the SPP for 10 and 30 min.



**Figure S6**

**Figure S6.** TEM images of the AuNPs synthesized in (a) sugars and (b) biopolymers, with different concentrations of the matrices, at plasma treatment times of 10 and 30 min. Note that, scale bars of the images synthesized in sugars are 50 nm while that of the images synthesized in biopolymers are 100 nm.

**Figure S7**

**Figure S7.** Cell viability of cancer cells (HeLa cells) after exposure to the AuNP colloids synthesized in (a) sugars and (b) biopolymers, for 24 h, determined by the MTT assay.