**Supporting Information**

**Enhancement of electrochemiluminescence by Au paste electrode for bipolar electroanalysis**

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S1. Luminescence by potential of cathodic ECL on AuPE surface

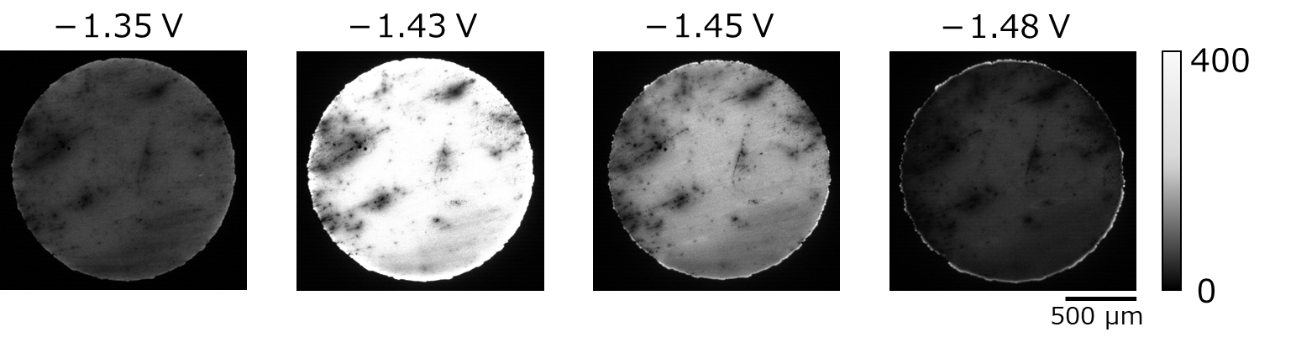


Figure S1. Images of AuPE surface at each potential.

S2.1. Surface analysis

CP, AuP, PDI-CP, and PDI-AuP were each filled into a 1.6 mm hole drilled on a brass sample stage. The surfaces were polished using the same procedure as that used to reproduce the paste electrodes. The Au disk was cut from a 0.1 mm-thick Au plate (99.99%, Tanaka Kikinzoku Kogyo K.K.) and utilized without further modification.

Surface morphology was examined through field-emission scanning electron microscopy (FE-SEM; JSM-IT700HR, JEOL Ltd.) conducted at an applied accelerating voltage of 15.0 kV. The samples underwent analysis without conducting the sputter coating process.

Absorption spectra in the UV-vis range were acquired using a micro-ultraviolet-visible-near-infrared spectrophotometer (micro-UV-vis-NIR, MSV-5200; JASCO Corporation, Japan). Measurements were conducted in the reflectance mode, suitable for both microscopic observations and photometry. The measurement parameters included a wavelength range of 300–700 nm, scanning speed of 1000 nm min-1, UV/vis bandwidth of 5 nm, and NIR bandwidth of 20 nm, with absorbance as the photometric mode. The spectrophotometer was outfitted with a 16× Cassegrain lens for the objective and eyepiece, a 100 µm aperture system, and an aluminum mirror serving as the reflective reference material. UV-vis absorption spectroscopy was conducted before SEM.

S2.2. Surface observation of paste electrodes by SEM

To confirm whether the ECL amplification effect of AuP was due to surface plasmon field enhancement, the surfaces of CP, AuP, PDI-CP (PDI-CH3/CP 1:1 weight ratio), and PDI-AuP (PDI-CH3/AuP 1:20 weight ratio) were observed using SEM. As shown in Figs. S2(a) and (b), the CP surface is rough, while the AuP surface is relatively smooth. The rough CP surface was due to the aggregation of acetylene carbon black in liquid paraffin. During SEM observation, liquid paraffin was volatilized in a vacuum, resulting in pore generation. On the AuP surface, the particles were bonded to each other; therefore, it could not be confirmed whether the particles were sufficiently particle-like to cause a surface plasmon field-enhancement effect. Gold particles in AuP are easy to fuse; therefore, fusion might have progressed because of polishing or leaving at room temperature until SEM observation. Figs. S2(c) and (d) show the PDI-CP and PDI-AuP surfaces, respectively, after polishing. Au particles were observed in PDI-AuP, confirming the possibility of a surface plasmon field-enhancement effect. However, given the SEM observations of AuP alone, it was not clear whether the surface plasmon field-enhancement effect of AuP caused an increase in the ECL intensity.

S2.3. UV-vis spectra

To gather additional evidence for the surface plasmon field-enhancement effect in AuP, absorption spectra in the UV-vis range for the surfaces of the gold disk, AuP, and PDI-AuP were collected and compared. As illustrated in Fig. S2(e), the spectra for both the gold disk and AuP display two absorption peaks at wavelengths of 350 and 500 nm. These peaks are also observed in AuP-PDI, signifying their origin via gold atom absorption. Although AuP does not show a clear spectrum corresponding to surface plasmons, which generally appeared at 550–600 nm for the particles with a diameter of 200–500 nm,1-3 the slope of the spectrum at 550–600 nm is smaller than that for the Au disk. This reduced steepness in the spectral slope at 550–600 nm is likely due to low absorbance levels, induced by the surface plasmon effect. This partial effect may be attributed to the fusion of most gold particles at the surface, as corroborated by Fig. S2(b). In stark contrast, PDI-AuP features a broad absorption spectrum with peaks at 350, 430, 500, and 600 nm. The peak at 600 nm is considered to be derived from the surface plasmons of Au nanoparticles with a particle size of 200–500 nm.1-3 This is supported by the SEM image (Fig. S2(d)), which shows that the particle nature of Au was maintained on the PDI-AuP surface. These findings imply that the surface plasmon field-enhancement effect plays a role in elevating the ECL of AuP. However, an enigmatic aspect remains, that is, in three-electrode measurements, the ECL enhancement of PDI-AuP (1.75-fold) closely aligns with that of the AuPE (1.4–1.7-fold). Conversely, in bipolar electrochemical measurements, the ECL enhancement for PDI-AuP is an order of magnitude greater than that for PDI-CP. One plausible explanation for this discrepancy is the alterations in the particle characteristics of AuP post-acquisition. Ongoing research aims to elucidate the correlation between the electrode surface conditions and ECL amplification.

写真, 立つ, 座る, 持つ が含まれている画像

自動的に生成された説明ケーキ, テーブル, 写真, 持つ が含まれている画像

自動的に生成された説明白い花が咲いている植物

中程度の精度で自動的に生成された説明白い花が咲いている植物

低い精度で自動的に生成された説明

(d)

(c)

(b)

(a)

(e)

グラフ, 折れ線グラフ

自動的に生成された説明

Figure S2. SEM images of paste electrode surfaces: (a) CPE; (b) AuPE; (c) PDI-CP (PDI-CH3/CP 1:1 in weight ratio); and (d) PDI-AuP (PDI-CH3/AuP 1:20 in weight ratio). (e) UV-vis absorbance spectra of the Au plate, AuP, and PDI-AuP (PDI-CH3/AuP 1:20 in weight ratio).

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