

Supplementary Information

Selective Interaction of As (III) and Luminol for the Development of Electrochemiluminescence-Based Arsenic (III) Sensors

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Experimental Section

Materials

Analytical-grade reagents were used throughout without further purification. Luminol was purchased from Tokyo Chemical Industry, while sodium arsenite (NaAsO_2), hydrogen peroxide (H_2O_2), sulfuric acid (H_2SO_4), potassium ferrocyanide(II) ($\text{K}_4[\text{Fe}(\text{CN})_6]$), and other chemicals were obtained from Sigma-Aldrich. All solutions were prepared with Milli-Q water ($18.2 \text{ M}\Omega\cdot\text{cm}$), and 0.1 M PBS was used as the supporting electrolyte. Screen-printed gold electrodes (SPGE; DropSens 250 AT) and screen-printed carbon electrodes (SPCE; DropSens 110) were supplied by Metrohm.

Preparation of Boron-Doped Diamond Electrode (BDD) and Its Modification

BDD films were synthesized on Si (111) wafers using a microwave plasma-assisted chemical vapor deposition system (MPACVD, AX-5400, CORNES Technology Corp.) for 6 h. Methane and trimethoxyborane were used as the carbon and boron precursors, respectively, at a B/C ratio of 1:100. The detail of the fabrication process is described in the previous study.¹ The screen-printed boron-doped diamond electrode (BDD) was prepared by inserting the BDD film in a commercial SPCE platform^{1,2} and then designed as the working electrode in the ECL systems with silver (Ag) and carbon (C) applied as pseudo-reference and counter electrodes, respectively.

Since the gold-based electrode provides better sensitivity than the carbon-based electrodes, the BDD electrode was then modified with gold nanoparticles (Au/BDD). The Au/BDD electrode was fabricated electrochemically by chronoamperometric deposition in a solution containing 1 mM HauCl_4 and 10 mM H_2SO_4 mixed at a 1:1 (v/v) ratio. The deposition was performed at an applied potential of -0.4 V for 400 s. The characterizations were shown in Supplementary Figures.

The measurements of ECL systems

Electrochemical responses and ECL signals were recorded simultaneously in a light-tight chamber. Electrochemical measurements were performed using a potentiostat electrochemical workstation (PGSTAT204, Metrohm) controlled by Nova 2.1 software, while

ECL emission was detected using a photomultiplier tube (H11902-20) positioned 1 cm above the electrochemical cell. Before ECL measurements, the working electrode was activated by cyclic voltammetry in 0.1 M H₂SO₄ from 0 to +1.0 V at 100 mV s⁻¹ for 10 cycles. The electrochemically active surface area (ECSA) was calculated using the Randles–Ševčík equation from cyclic voltammograms of 1 mM K₄[Fe(CN)₆] in 1 M KCl, recorded over 0.0 V to 0.4 V at scan rates of 10 mV s⁻¹ to 300 mV s⁻¹, as shown in the following Figure. Furthermore, cyclic voltammetry (CV) was employed as the electrochemical technique for the proposed ECL measurements with a scan rate of 100 mV s⁻¹ and a sample volume of 50 μL. The electrochemical and ECL behaviors of the luminol/As(III) system were investigated in a mixed solution of 1 mM luminol, 0.1 mM As(III), and 0.1 M PBS at a volume ratio of 1:1:1. All measurements were performed at room temperature.

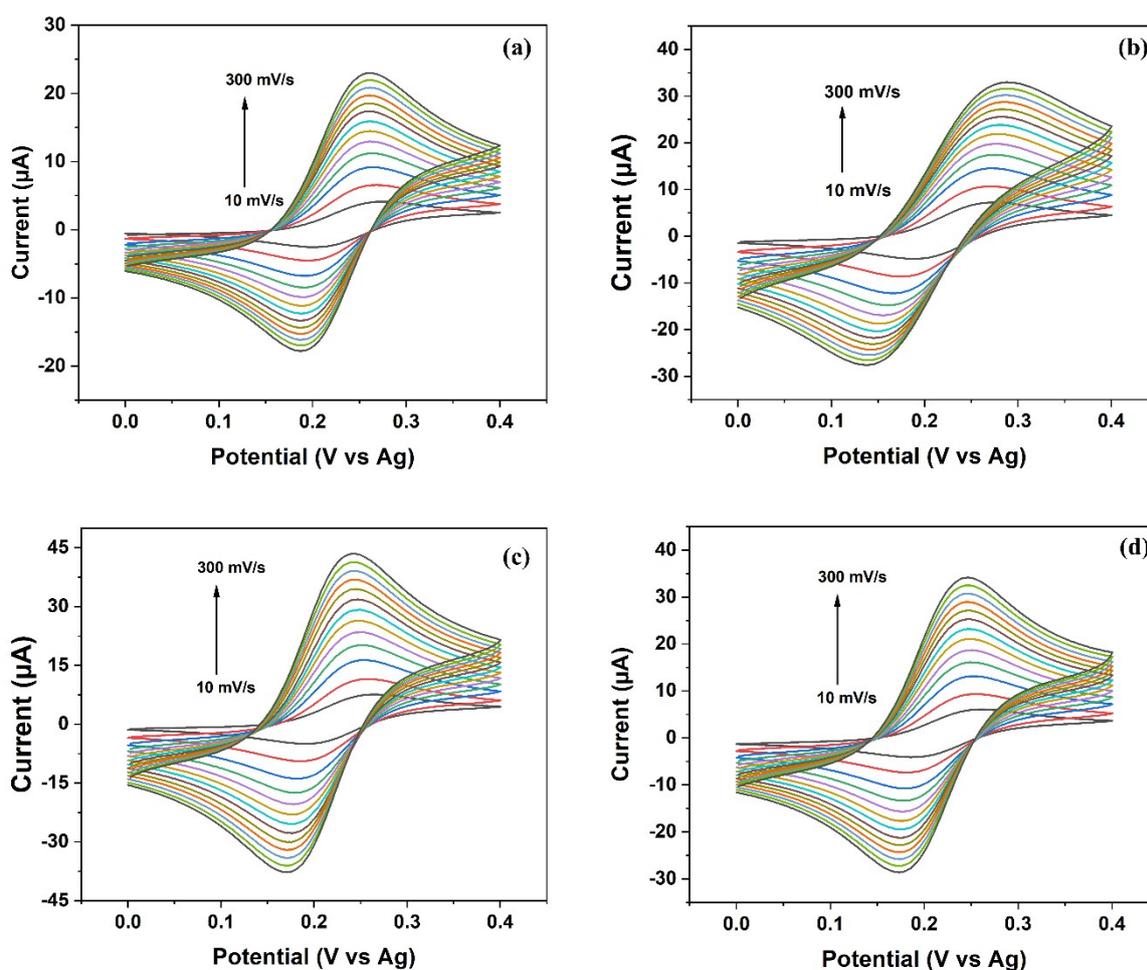


Figure. Cyclic voltammograms of 1 mM K₄[Fe(CN)₆] in 1 M KCl at various working electrodes: (a) BDD, (b) SPCE, (c) SPGE, and (d) Au/BDD

Supplementary Figures

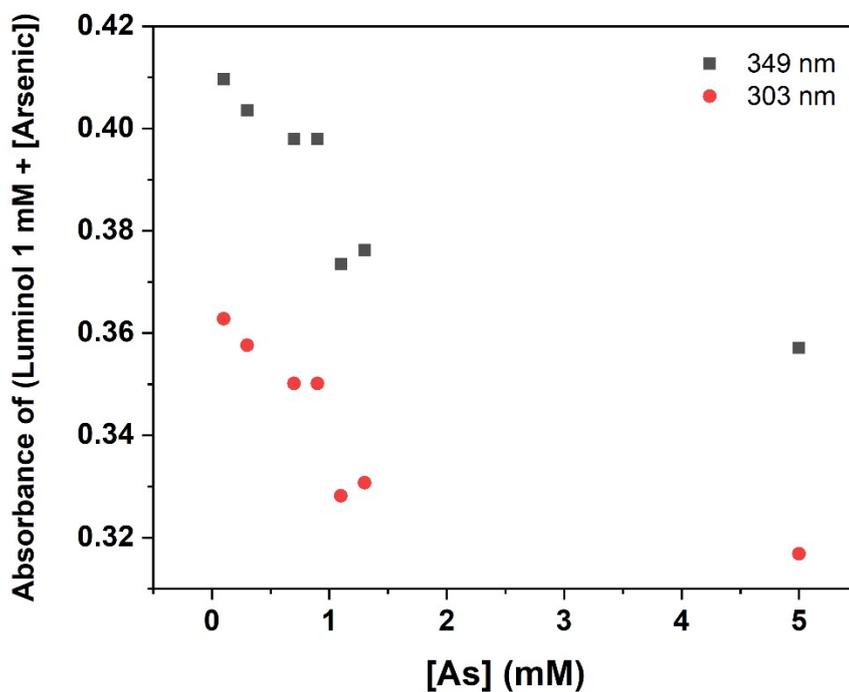


Fig S1. Absorbance of UV-Vis spectra for luminol/As(III) solution

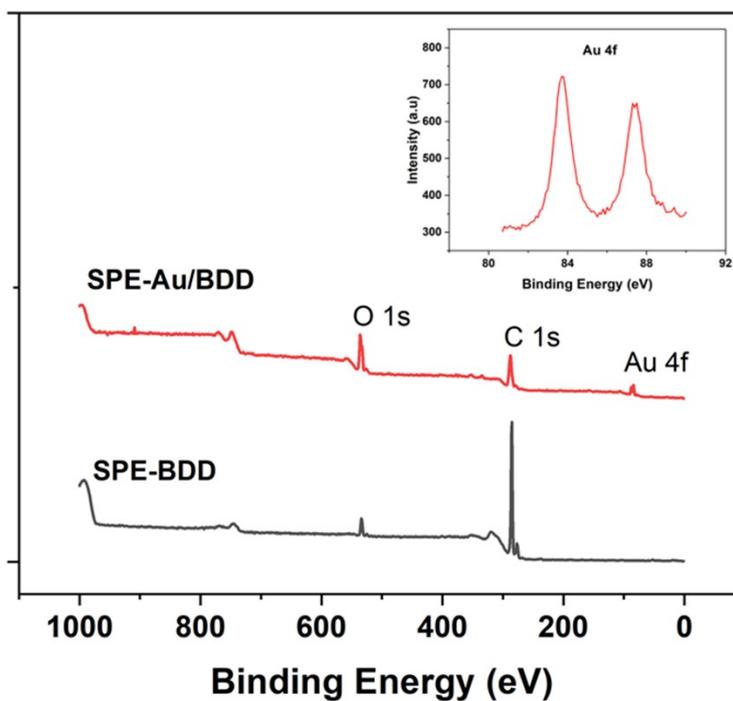


Fig S2. The XPS spectra of BDD and Au/BDD electrodes, and (c) SEM image of Au/BDD electrode

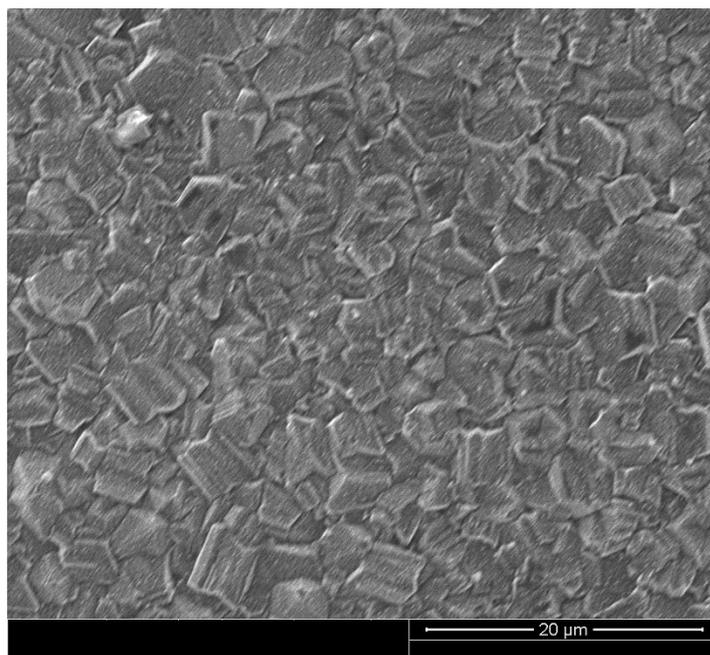


Fig S3. SEM image of Au/BDD electrode

References

- 1 H. Harmesa, A. Fiorani, Y. Einaga, A. Johan, A. Saefumillah and T. A. Ivandini, *Diam. Relat. Mater.*, 2025, **160**, 112956.
- 2 I. Rahmawati, E. Saepudin, A. Fiorani, Y. Einaga and T. A. Ivandini, *Analyst*, 2022, **147**, 2696–2702.