SUPPORTING INFORMATION

Tannic Acid Capped Gold Nanoparticles: Capping Agent Chemistry Controls the Redox Activity

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1. Calculation Details

Concentration of AuNPs@TA suspension = 2.2×10¹⁰ particles ml⁻¹

Surface area of glassy carbon electrode (πrₑ²), rₑ 1.48 ± 0.02 mm, = ca. 6.9×10⁻⁶ m²

Radius of core AuNP, rₚ, is 31.1 nm

1.1. Ensembles Particle Level

(a) Number of AuNPs@TA particles onto GCE surface for one-monolayer surface coverage, N, considering closest packing of equal sphere of 91%, calculated as follow:

$$N = 0.91 \times \frac{\pi r_c^2}{\pi r_p^2} = 0.91 \frac{\pi r_c^2}{\pi r_p^2} = ca. 2.0 \times 10^9 \text{ particles}$$

(b) Total surface area of AuNPs@TA drop-cast onto GCE surface, A, calculated as follow:

$$A = N \times (4\pi r_p^2) = 2.0 \times 10^9 \text{ particles} \times (1.2 \times 10^{-14} \text{ m}^2) = 2.4 \times 10^{-5} \text{ m}^2$$

1.2. Individual Particles Level (Nanoimpacts)

From the oxidative nanoimpacts experiment with the absence of the metal cations (oxidation of TA capping agent), the average spikes charge, Q, was found to be ca. 0.3 pC.

The number of moles, n, of TA involved in the reaction is calculated using Faraday’s first law:

$$n = \frac{Q}{zF}$$
where, $z$ is the number of electron transfer during oxidation of TA (assuming fully oxidised, $z = 20$) and $F$ is the Faraday’s constant (96485.33 C mol$^{-1}$). The number of moles TA was found to be ca. 1.6 x 10$^{19}$ or equal to ca. 1.0 x 10$^5$ molecules.

Meanwhile, the apparent number of TA molecules incorporated in a single AuNP core was calculated by dividing volume of AuNP core with known volume of a single TA molecule (8.6 x 10$^{-28}$ m$^3$)

\[
N_{TA} = \frac{1.07 \times 10^{-22} \text{ m}^3}{8.6 \times 10^{-28} \text{ m}^3} = \text{ca. 1.2 x 10}^5 \text{ molecules.}
\]

1.3. Underpotential Deposition (UPD) of Zinc onto Ensembles of AuNPs@TA

- From CV experiments, reductive charge of the Zn (UPD), $Q$, is ca. 17.2 μC.
- Surface coverage of 0.2 mM Zn$^{2+}$ UPD ($z = 2$, $F$ is Faraday constant 96485.33 C mol$^{-1}$ and $A = 2.4 \times 10^{-5}$ m$^2$ is total surface area of one-monolayer of AuNPs@TA drop casted onto GCE surface) calculated as follow:

\[
\frac{Q}{zFA} = \frac{17.2 \times 10^{-6} \text{ C}}{(2).(96485.33 \text{ C mol}^{-1}).(0.24 \text{ cm}^2)}
= \text{ca. 3.7 x 10}^{-10} \text{ mol cm}^{-2}
= \text{ca. 2.2 x 10}^{14} \text{ atoms cm}^{-2}
\]
2. Supporting Figures

2.1. Characterisation of AuNPs@TA

**Figure SI.1.** Characterization of the AuNPs@TA using (a) NTA and (b) DLS analysis

- **NTA Analysis**
  - Record 1
  - Record 2
  - Record 3
  - Average Size: $68.1 \pm 0.7$ nm

- **DLS Analysis**
  - Record 1
  - Record 2
  - Record 3
  - Average Size: $68.7 \pm 0.4$ nm

**Figure SI.2.** UV-vis analysis of AuNPs@TA. (a) UV-vis spectra of ca. 10 pM AuNPs@TA in a solution of 10 mM KCl + 10 mM HCl, (b) Plot of peak absorbance of AuNPs@TA in various electrolyte concentrations during 15 mins.
2.2. Electrochemical Analysis of AuNPs@TA

Figure SI.3. Oxidative particle impacts analysis. Representative chronoamperograms of microdisc electrode immersed in solution containing of 10 mM KCl + 10 mM HCl at potential of 0.4, 0.5, 0.6, 0.7 V vs SCE.

Figure SI.4. Reductive particle impacts analysis. Representative chronoamperograms of microdisc electrode immersed in solution containing of (a) blank and (b) AuNPs@TA + blank at potential of -0.3, -0.4, -0.5 V vs SCE.
2.3. Electrochemical Analysis of Ensembles of AuNPs@TA with Metal Cations

Figure SI.5 (a) Cyclic voltammograms of one-monolayer surface coverage of AuNPs@TA-GCE at various scan rates, (b) Linearity of peak current of the “peak 2” at various scan rates shown in (a).

Figure SI.6. (a) Cyclic voltammograms of one-monolayer surface coverage of AuNPs@TA-GCE at various concentrations of Zn$^{2+}$. (b) Plot of peak current of the “peak 2” at various concentrations of Zn$^{2+}$.

Figure SI.7. Underpotential deposition of Zn$^{2+}$ at the ensembles of AuNPs@TA, at a scan rate of 0.02 V s$^{-1}$.
2.4. Particle Impacts Analysis of Individual AuNPs@TA with Metal Cations

**Figure SI.8.** Linear relationship between average spikes: (a) charge, (b) current, (c) duration and (d) frequency with different potentials at various Zn\(^{2+}\) concentrations, resulting from oxidative and reductive particle impacts.

**Figure SI.9.** Reductive particle impacts. Linear relationship between average spikes: (a) charge, (b) current, (c) duration and (d) frequency with potentials at various Zn\(^{2+}\) concentrations (potential of -0.2, -0.3 and -0.5 V).
Figure SI.10. Linear relationship between average spikes: (a) charge, (b) current, (c) duration, (d) frequency at various Hg$^{2+}$ concentrations, resulting from oxidative and reductive particle impacts (potential of -0.2 to -0.6 V).

Figure SI.11. Langmuir plot of Zn$^{2+}$ on ensembles AuNPs@TA (before saturation) with $K = \text{ca. } 0.11 \text{ mM}^{-1}$.