SUPPORTING INFORMATION

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

Alex L. Suherman[1], Giorgia Zampardi[1], Hatem M. A. Amin[1], Neil P. Young[2], Richard G. Compton[1,*]

[1]Department of Chemistry, Physical and Theoretical Chemistry Laboratory, Oxford University, South Parks Road, Oxford OX1 3QZ, UK.

[2]Department of Materials, Oxford University, Parks Road, OX1 3PH, UK.

1. Calculation Details

Concentration of AuNPs@TA suspension = 2.2 x 10^{10} particles ml^{-1}

Surface area of glassy carbon electrode (πr_e^2), r_e 1.48 $\pm$ 0.02 mm, = ca. 6.9 x 10^{-6} m^2

Radius of core AuNP, r_p, 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:

$$N = 0.91 * \frac{Surface\ area\ of\ GCE}{Surface\ area\ of\ AuNPs@TA} = 0.91\ \frac{\pi r_e^2}{\pi r_p^2} = \text{ca. } 2.0 \times 10^9 \text{ particles}$$

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

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

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)[23]

N_{TA} = $\frac{1.07\ x\ 10^{-22}\ m^3}{8.6\ x\ 10^{-28}\ m^3}$ = **ca. 1.2 x 10^5 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 x 10^{-5} m^2 is total surface area of one-monolayer of AuNPs@TA drop casted onto GCE surface) calculated as follow:

  = $\frac{Q}{zFA}$

  = $\frac{17.2\ x\ 10^{-6}\ C}{(2).(96485.33\ C\ mol^{-1}).(0.24\ cm^2)}$

  = ca. 3.7 x 10^{-10} mol cm^{-2}

  = **ca. 2.2 x 10^{14} atoms cm^{-2}**

2. Supporting Figures

2.1. Characterisation of AuNPs@TA

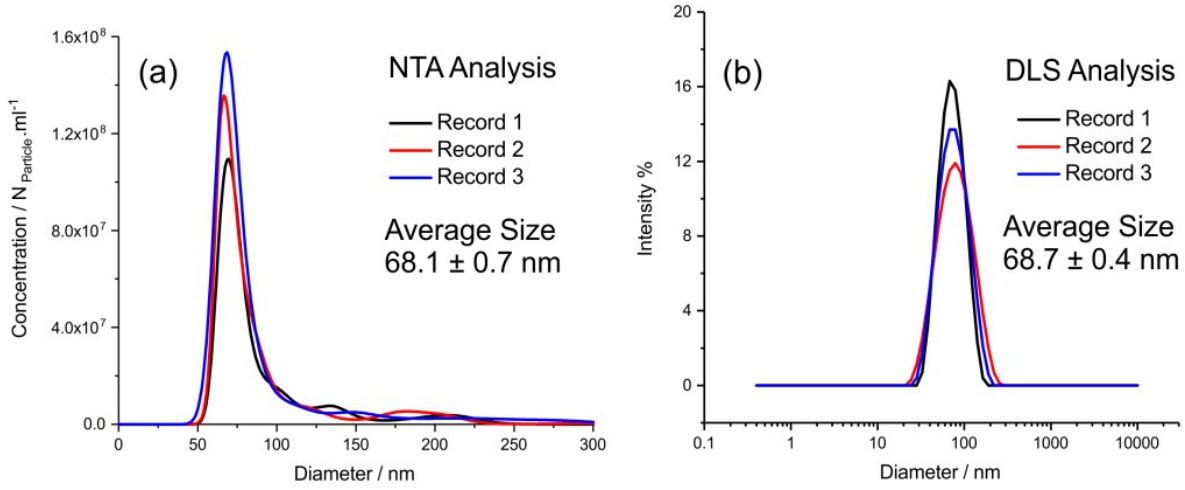

Figure SI.1. Characterization of the AuNPs@TA using (a) NTA and (b) DLS analysis

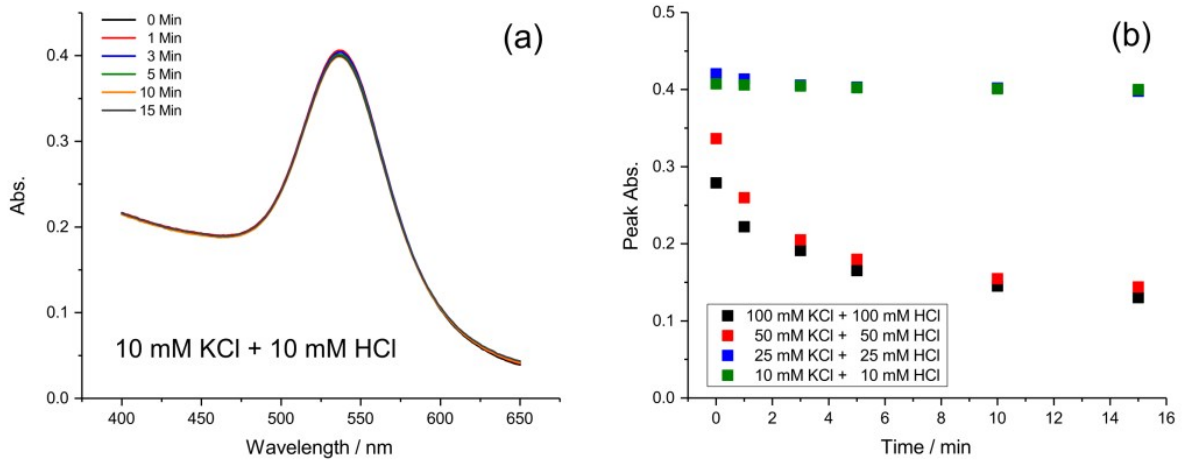

Figure SI.2. UV-vis analysis of AuNPs@TA. (a) UV-vis spectra of ca. 10 pM AuNPs@TA in a solution of 10 mM KCl + 10 mM HCl, (b) Plot of peak absorbance of AuNPs@TA in various electrolyte concentrations during 15 mins.

2.2. Electrochemical Analysis of AuNPs@TA

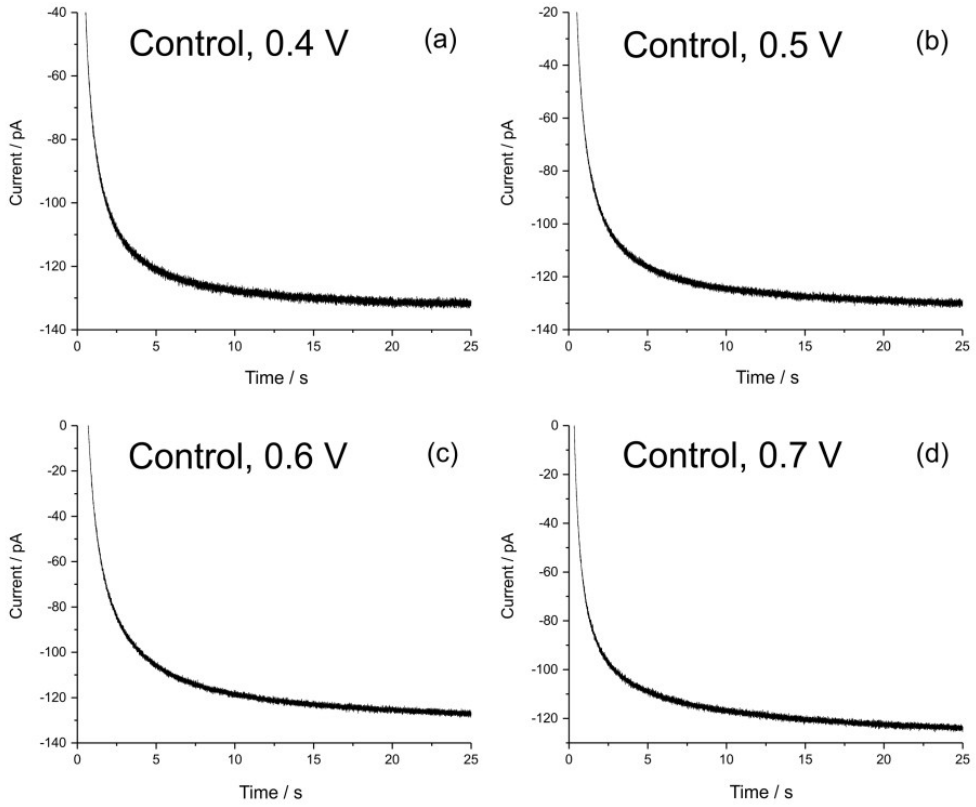

Figure SI.3. Oxidative particle impacts analysis. Representative chronoamperograms of microdisc electrode immersed in solution containing of 10 mM KCl + 10 mM HCl at potential of 0.4, 0.5, 0.6, 0.7 V vs SCE.

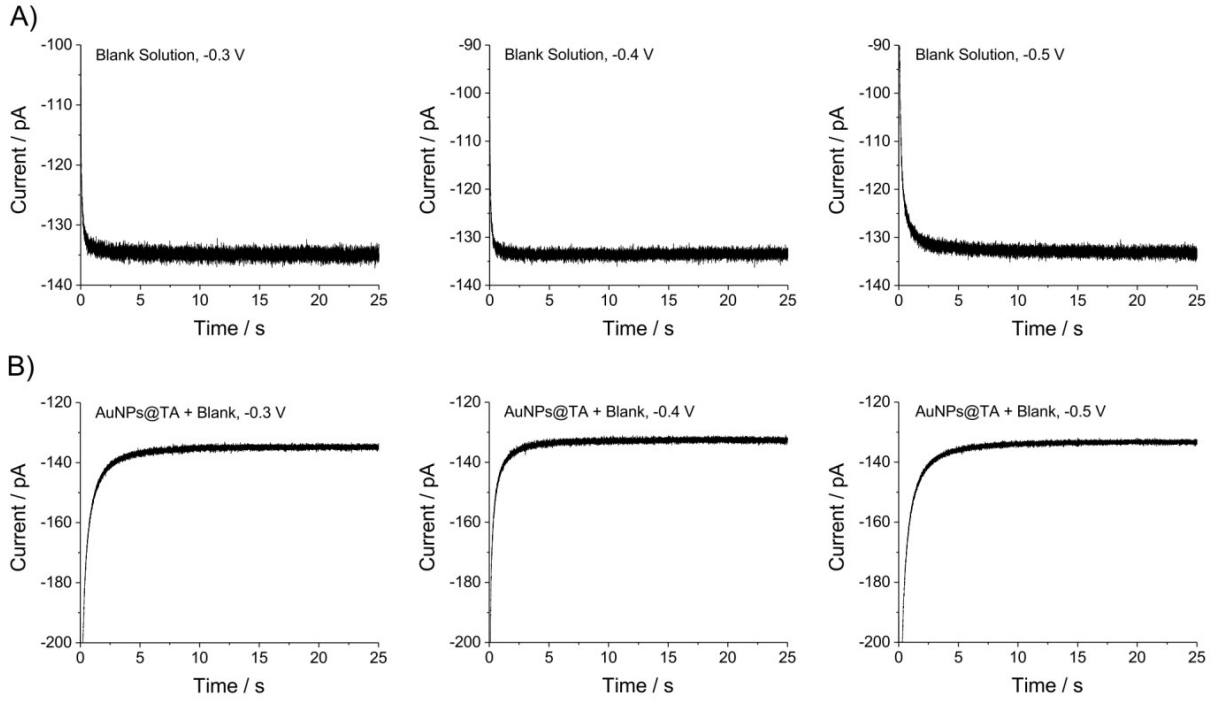

Figure SI.4. Reductive particle impacts analysis. Representative chronoamperograms of microdisc electrode immersed in solution containing of (a) blank and (b) AuNPs@TA + blank at potential of -0.3, -0.4, -0.5 V vs SCE.

2.3. Electrochemical Analysis of Ensembles of AuNPs@TA with Metal Cations

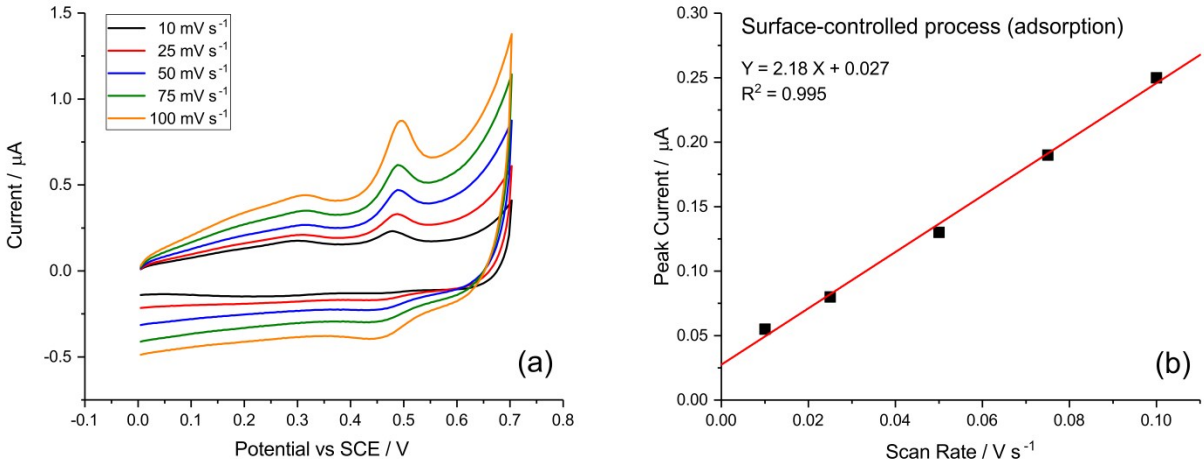

Figure SI.5 (a) Cyclic voltammograms of one-monolayer surface coverage of AuNPs@TA-GCE at various scan rates, (b) Linearity of peak current of the "peak 2" at various scan rates shown in (a).

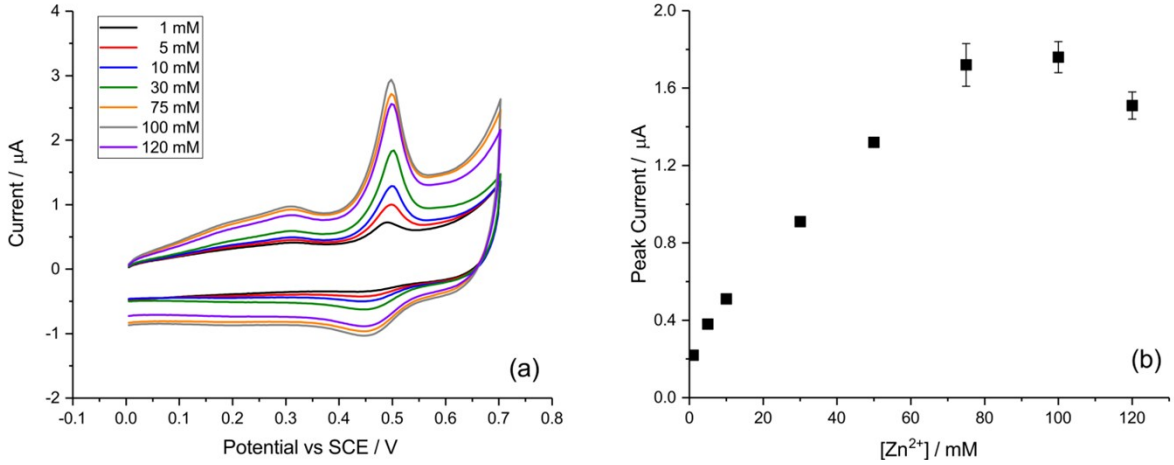

Figure SI.6. (a) Cyclic voltammograms of one-monolayer surface coverage of AuNPs@TA-GCE at various concentrations of Zn^{2+}. (b) Plot of peak current of the "peak 2" at various concentrations of Zn^{2+}

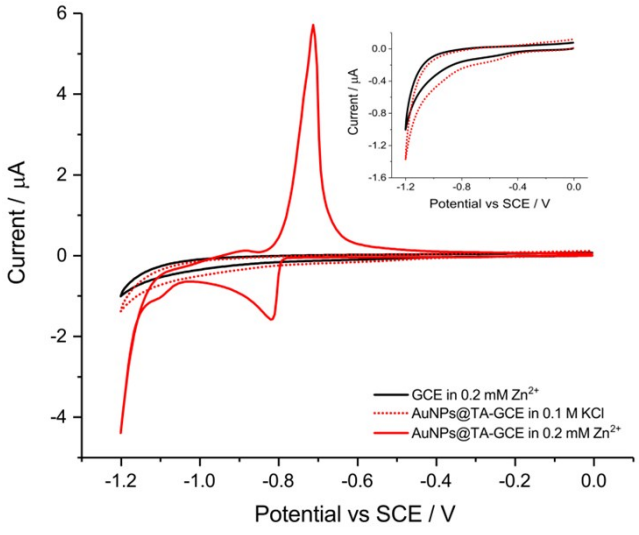

Figure SI.7. Underpotential deposition of Zn^{2+} at the ensembles of AuNPs@TA, at a scan rate of 0.02 V s^{-1}

2.4. Particle Impacts Analysis of Individual AuNPs@TA with Metal Cations

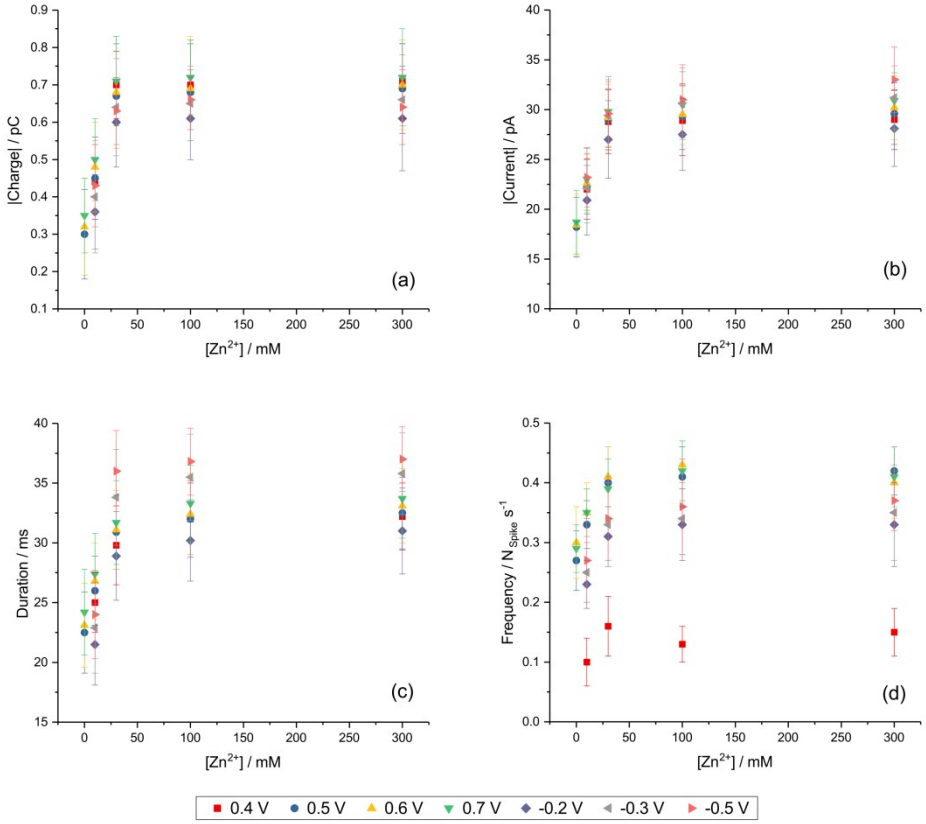

Figure SI.8. Linear relationship between average spikes: (a) charge, (b) current, (c) duration and (d) frequency with different potentials at various Zn^{2+} concentrations, resulting from oxidative and reductive particle impacts

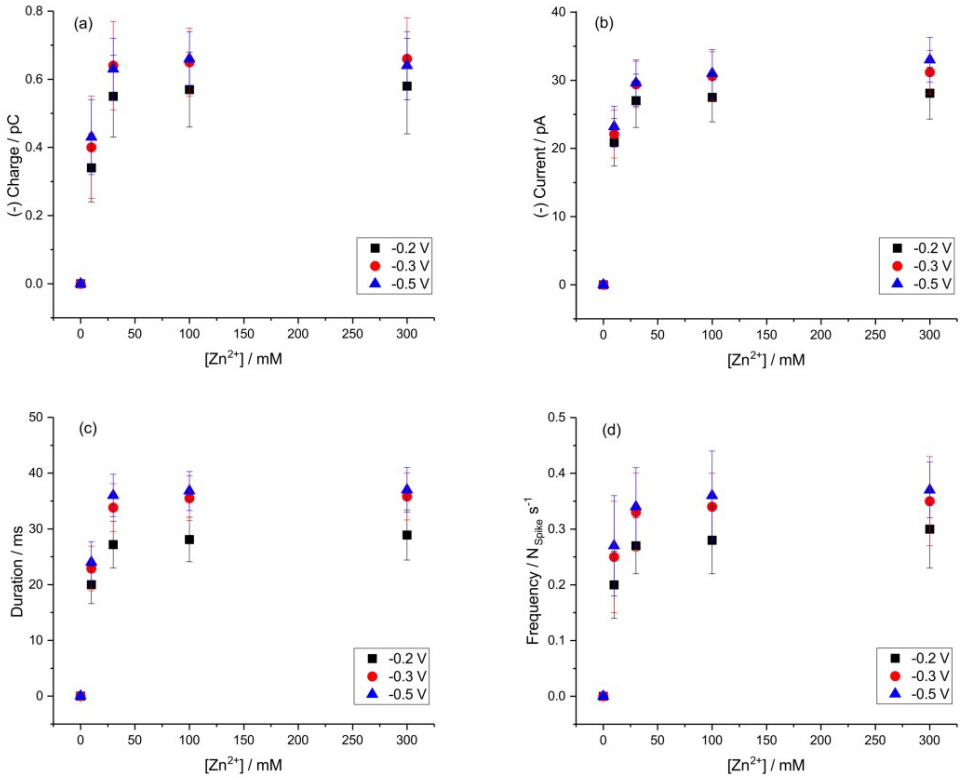

Figure SI.9. Reductive particle impacts. Linear relationship between average spikes: (a) charge, (b) current, (c) duration and (d) frequency with potentials at various Zn^{2+} concentrations (potential of -0.2, -0.3 and -0.5 V).

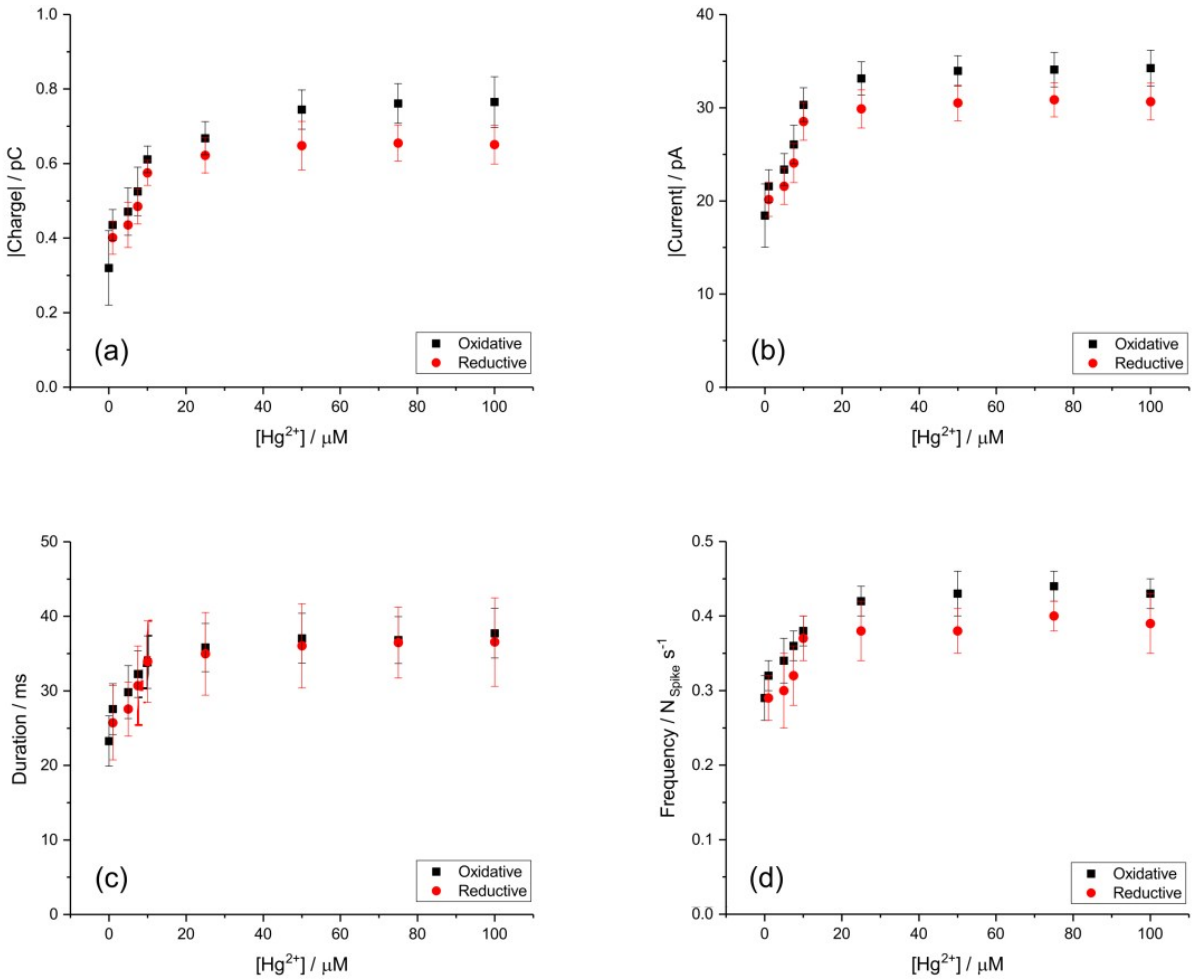

Figure SI.10. Linear relationship between average spikes: (a) charge, (b) current, (c) duration, (d) frequency at various Hg^{2+} concentrations, resulting from oxidative and reductive particle impacts (potential of -0.2 to -0.6 V)

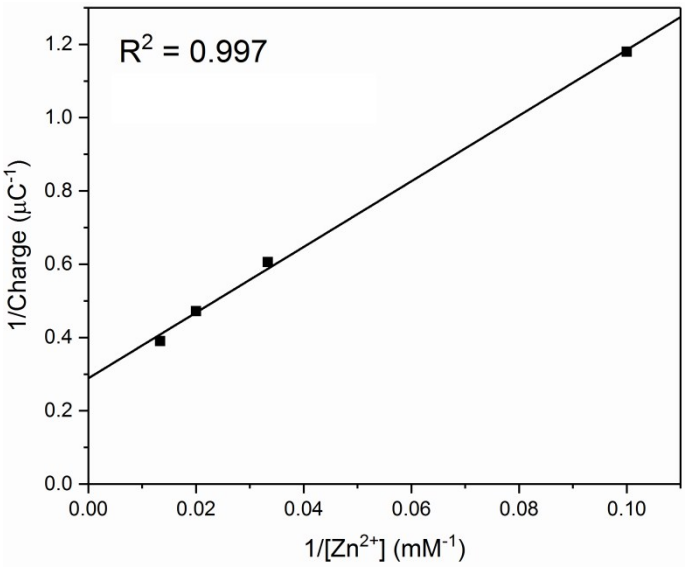

Figure SI.11. Langmuir plot of Zn^{2+} on ensembles AuNPs@TA (before saturation) with K = ca. 0.11 mM^{-1}