SUPPORTING INFORMATION

Understanding Gold Nanoparticle Dissolution in Cyanide-Containing Solution via Impact-chemistry

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SI.1 Calculation Detail

- Concentration of AuNPs suspension (indicated by manufacturer) = 2.61 x 10^{10} NPs ml^{-1}
- Average radius of AuNPs (indicated from TEM sizing), r_p = 31.45 ± 1.33 nm
  Surface area of single AuNP = 1.24 x 10^{-14} m^2
- Radius of GCE, r_e = 1.49 ± 0.01 mm
  Surface area of GCE 6.97 x 10^{-6} m^2
- Volume of single particle (V_p) = 1.30 x 10^{-22} m^3

Estimate number of AuNP in one-monolayer (considering closest packing of equal spheres 91%), n_p, is

$$n_p = 0.91 * \frac{6.97\ x\ 10^{-6}\ m^2}{1.24\ x\ 10^{-14}\ m^2}$$

= **ca**. **5 x 10^8 NPs**

Drop cast volume required for one-monolayer:

$$\text{Volume} = \frac{n_p}{[AuNP]}$$

$$= \frac{5.12\ x\ 10^8\ NPs}{2.61\ x\ 10^{10}\ NPs\ ml^{-1}} = 0.02 \text{ ml } (\textbf{\textit{ca}. 20 μL})$$

Expected Charge for a single AuNP

a) CV Experiments (*z* = 1, assuming 1*e*⁻ transfer)

$$Q = \frac{Density\ of\ Au\ \times\ Volume\ of\ AuNP}{Atomic\ Mass\ of\ Au}\ z.F = \frac{(1.93\ x\ 10^7\ g\ m^{-3})\ *\ (1.30\ x\ 10^{-22}\ m^3)}{(1.97\ x\ 10^2\ g\ mol^{-1})} * 1 *$$ 96485.3 C mol^{-1}

Q = 1.2 x 10^{-12} C per single AuNP

Expected charge for one-monolayer (contains 5 x 10^8 NPs):

$Q_{Expected}$ = (1.2 x 10^{-12} C NPs^{-1}) * (5 x 10^8 NPs)
= ***ca*. 600 μC**

[CN^-] / mM	Experimental Charge (Q_{Exp}) / μC	% Converted AuNP

1.0	9.6	*ca*. 1.6%
5.0	12.5	*ca*. 2.1%
15.0	28.7	*ca*. 4.8%
35.0	37.1	*ca*. 6.2%
50.0	47.0	*ca*. 7.8%

b) Nano-impact Experiments (assuming 1*e*$^-$ transfer)

Number of Au atom per particle = $\left(\frac{Density\ of\ Au\ *\ V_{AuNP}}{Atomic\ Mass\ of\ Au}\right)$ * Avogadro's number

= 7.6 x 10^6 atoms per particle

Number of Au particle added in the system = 0.7 ml * 2.61 x 10^{10} NPs.mL^{-1}

= 1.8 x 10^{10} NPs

Number of Au atoms (the number of species undergoing electrochemical process):

= 7.6 x 10^6 atoms per particle x (1.8 x 10^{10} NPs)

= 1.4 x 10^{17} atoms

Expected charge, $Q_{Expected}$, for 0.7 ml AuNPs suspension (each atom transfers 1.602 x 10^{-19} C):

= 1.4 x 10^{17} atoms * 1.602 x 10^{-19} C atom^{-1}

= 0.02 C (overall)

Expected charge, $Q_{Expected}$, for a single particle is

$$= \frac{0.02\ C}{1.8\ x\ 10^{10}\ particle}$$

= **1.1 x 10^{-12} C per single AuNP level**

[CN^-] / mM	Experimental Charge (Q_{Exp}) / pC	% Converted AuNP
1.0	0.29	*ca*. 26.4%
5.0	0.55	*ca*. 50.0%
15.0	0.76	*ca*. 69.1%
35.0	1.03	*ca*. 93.6%
50.0	1.04	*ca*. 94.2%

Characterization of Gold Nanoparticles

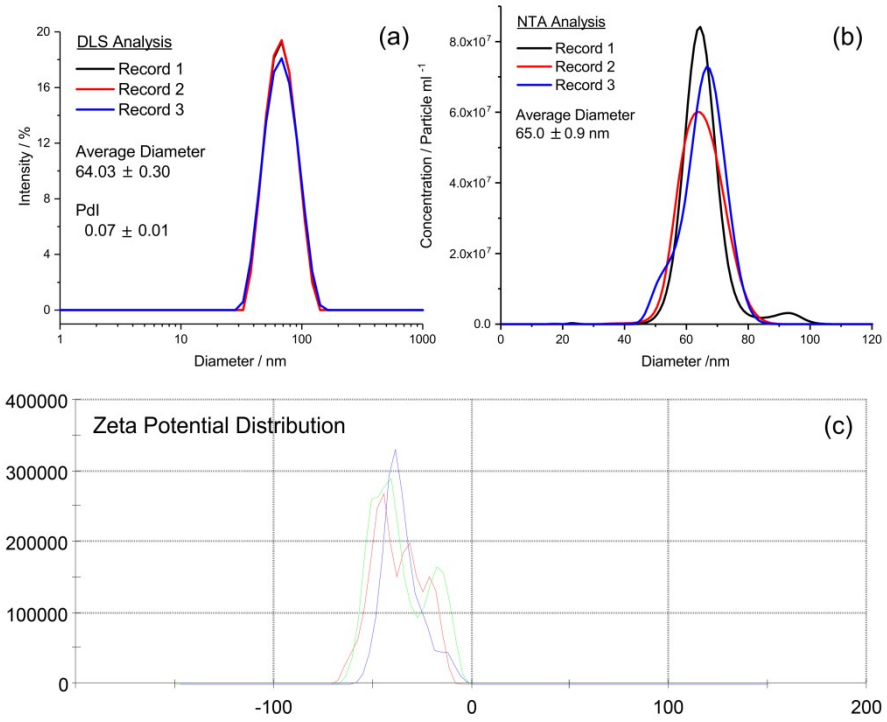

Figure SI.1. Characterization of the AuNP using (a) DLS, (b) NTA and (c) zeta potential.

Electrochemical Analysis of AuNPs-GCE by Cyclic Voltammetry: Study of Surface Coverages

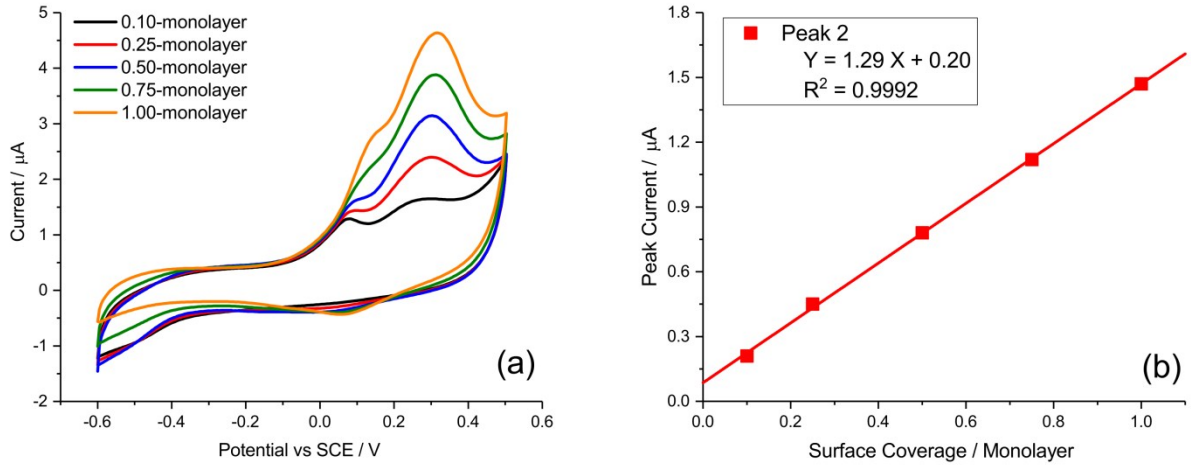

Figure SI.2. Surface concentration assessment of AuNPs-GCE immersed in 5.0 mM KCN + 10 mM NaOH at a scan rate of 0.1 V s^{-1}. (a) Voltammograms of AuNPs-GCE at various surface concentrations. (b) Linear peak current of peak 2 behaviour against surface concentration shown in (a).

Electrochemical Analysis of AuNPs-GCE by Cyclic Voltammetry: Study of Scan Rate Dependency

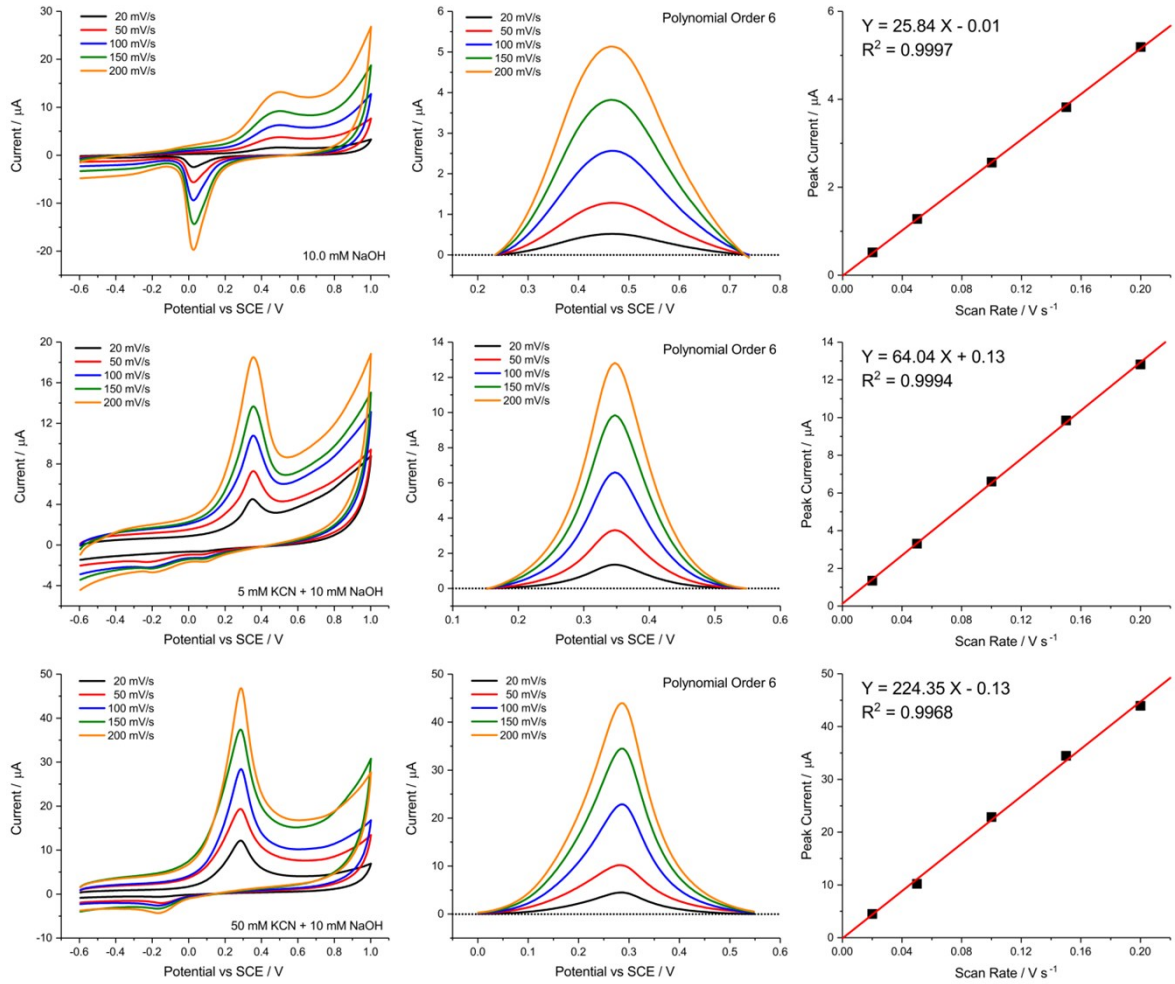

Figure SI.3. Representative voltammograms of one-monolayer AuNPs-GCE immersed in 10 mM NaOH, 5.0 mM and 50.0 mM KCN at a scan rate of 0.1 V s^{-1} (showing the original voltammograms, after polynomial (order-6) baseline correction and linear peak current behaviour against scan rates).

Electrochemical Analysis of AuNPs-GCE by Cyclic Voltammetry: Study of Successive Scans

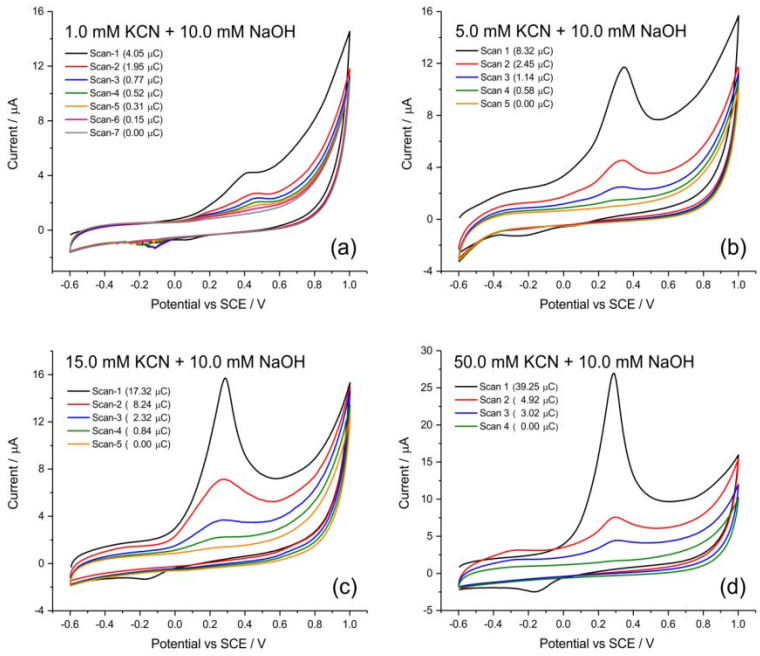

Figure SI.4. Representative successive scans of one-monolayer AuNPs-GCE immersed in (a) 1.0 mM KCN, (b) 5.0 mM, (c) 15.0 mM, (d) 50 mM KCN-containing 10 mM NaOH at a scan rate of 0.1 V s^{-1}.

Impact-Chemistry of Single Gold Particle

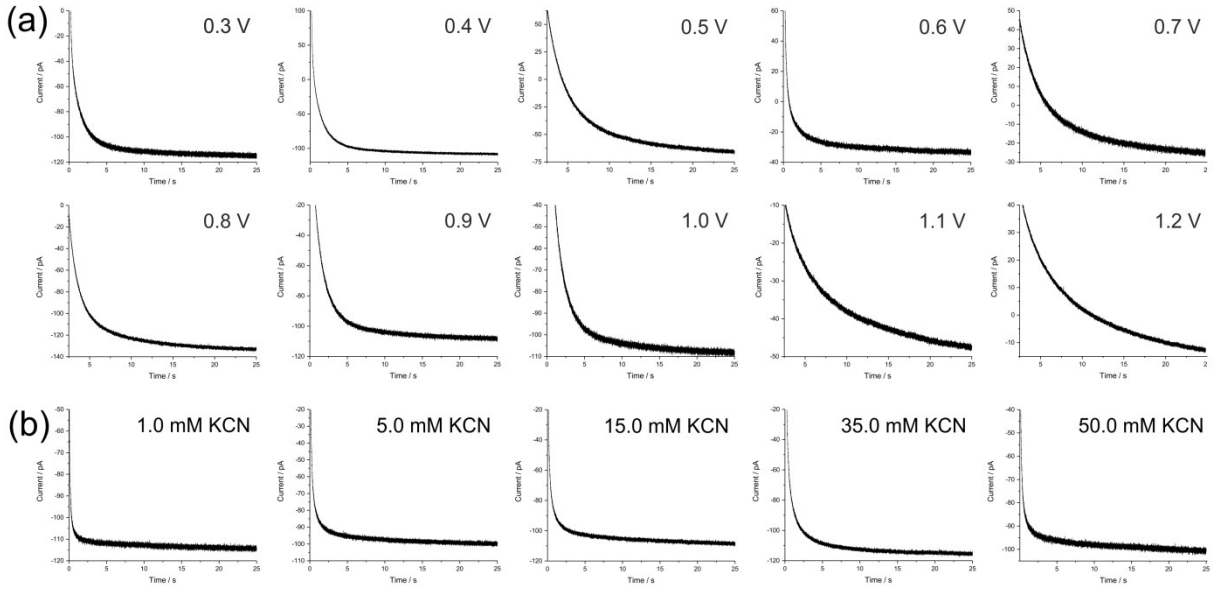

Figure SI.5. Representative chronoamperograms of 7.0 μm carbon microelectrode immersed in solution of (a) *ca*. 42.0 pM AuNP + 10 mM NaOH (without KCN) at varying potential of 0.3 V to 1.2 V. (b) 1.0 to 50.0 mM KCN + 10 mM NaOH (without AuNPs) at potential of 1.0 V.

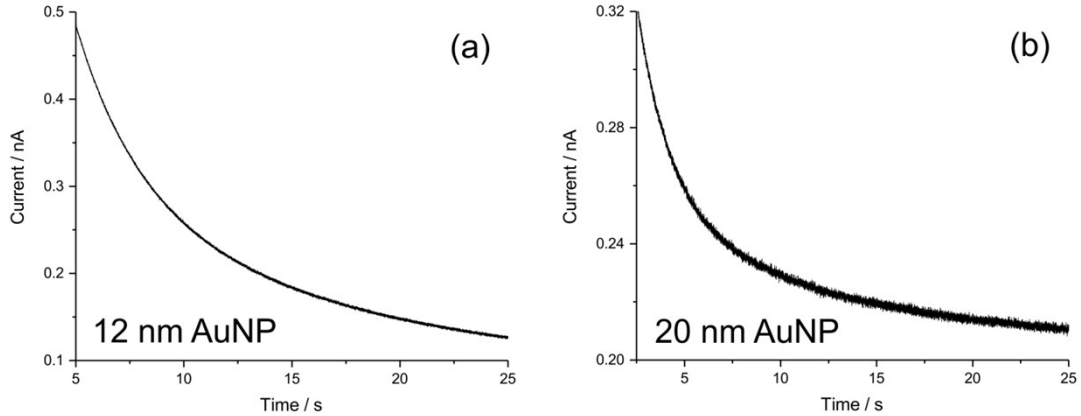

Figure SI.6. Representative chronoamperograms of *ca*. 42.0 pM AuNP immersed in 5.0 mM KCN + 10 mM NaOH at a potential of 1.0 V vs SCE. No spikes were observed both using (a) nominally 12 nm AuNPs and (b) nominally 20 nm AuNPs.

Table 1. Comparative result between nanoparticle ensemble (CV experiments) and single particle level (impact-chemistry experiments)

[CN^-] / mM	**CV Experiments**		**Nano-impact Experiments**				
	1st Scan (% Conv)	**Total Scan (% Conv)**	**% Conv.**	**Charge (pC)**	**Current (pA)**	**FWHM (ms)**	**Freq. (N_{Spike} s^{-1})**
1.0	0.6	1.6	26.4	0.29	3.05	50.12	0.09
5.0	1.3	2.2	50.0	0.55	4.50	31.05	0.15
15.0	2.7	4.8	69.1	0.76	6.22	20.22	0.17
35.0	4.6	6.2	93.6	1.01	8.95	13.33	0.22
50.0	6.2	7.8	94.2	1.02	10.05	11.05	0.24