Electronic Supplementary Material for PCCP

Electronic Supporting Information

Investigation of interparticle interactions of larger (4.63 nm) monolayer protected gold clusters during quantized double layer charging

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Table ESI 1 Peak positions and corresponding charge states for the DPV response shown in Fig. 3. (Columns have been named according to the individual DPV graphs as shown in Fig. 3).

Charge State	Fig. 3. a. (i) (V)	Fig. 3. a. (ii) (V)	Fig. 3. a. (iii) (V)
11/12	0.93	---	---
10/11	0.85	---	0.93
9/10	0.77	0.91	0.86
8/9	0.70	0.81	0.78
7/8	0.62	0.71	0.67
6/7	0.55	0.62	0.58
5/6	0.47	0.52	0.50
4/5	0.39	0.42	0.41
3/4	0.30	0.32	0.33
2/3	0.27	0.22	0.26
1/2	0.15	0.13	0.16
0/1	0.06	0.04	0.07
-1/0	-0.02	-0.06	-0.07
-2/-1	-0.09	-0.15	-0.02
-3/-2	-0.18	-0.25	-0.11
-4/-3	-0.26	-0.34	-0.20
-5/-4	-0.33	-0.44	-0.28
-6/-5	-0.41	-0.54	-0.37
-7/-6	-0.49	-0.64	-0.46
-8/-7	-0.57	-0.75	-0.55
-9/-8	-0.65	-0.84	-0.63
-10/-9	-0.74	-0.94	-0.7
-11/-10	-0.80	---	-0.81
-12/-11	-0.88	---	-0.91
-13/-12	-0.96	---	---

Chronoamperometric Analysis

The diffusion coefficients (D_C) of Au MPCs have been calculated by chronoamperometry using Cottrell equation assuming that linear semi-infinite diffusion is applicable for freely diffusing MPCs in solution, the current (I) - time (t) response can be written as follows:

$$I_d\,(t) = n\,F\,A\,C\,D_C^{\,1/2}\,\pi^{-1/2}\,t^{-1/2}$$

where, *n* is the change in core charge state, *C* is the MPC concentration in the solution (9.5×10^{-7} mol.cm^{-3})**,** *A* is the area of the electrode (0.5 mm diameter = 1.96×10^{-3} cm^2), *F* is the Faraday constant**,** *t* ($0.2\text{ s} \leq t \leq 20\text{ s}$) is the duration for the measurement of current after applying the respective constant potential corresponding to individual charge step in DPV response (i) shown in Fig. 3. (a) and D_C is the diffusion coefficient of the charged clusters in the electrolyte solution under applied potential. Various parameters are summarized in Table ESI 2.

Table ESI 2 Various parameters and calculated diffusion coefficient values at different charge steps of Au MPCs from chronoamperometry data (Fig. 4)

Charge State (DPV)	Applied Potential (V)	Slope μA.s$^{1/2}$	Number of Transferred Electron	D_C Cm^2.s^{-1}	From Stokes-Einstein equation (x 10^{-7} cm^2.s^{-1})
+1	0.19	0.06	1	3.50×10^{-7}	
+2	0.27	0.09	2	1.98×10^{-7}	
+3	0.35	0.13	3	1.74×10^{-7}	
+4	0.43	0.17	4	1.80×10^{-7}	
+6	0.59	0.32	6	2.84×10^{-7}	14.7
-1	0.02	0.003	1	1.40×10^{-9}	
-2	-0.09	0.04	2	3.10×10^{-8}	
-3	-0.16	0.07	3	4.60×10^{-8}	
-4	-0.23	0.10	4	6.00×10^{-8}	
-6	-0.48	0.36	6	3.50×10^{-7}	

Impedance analysis

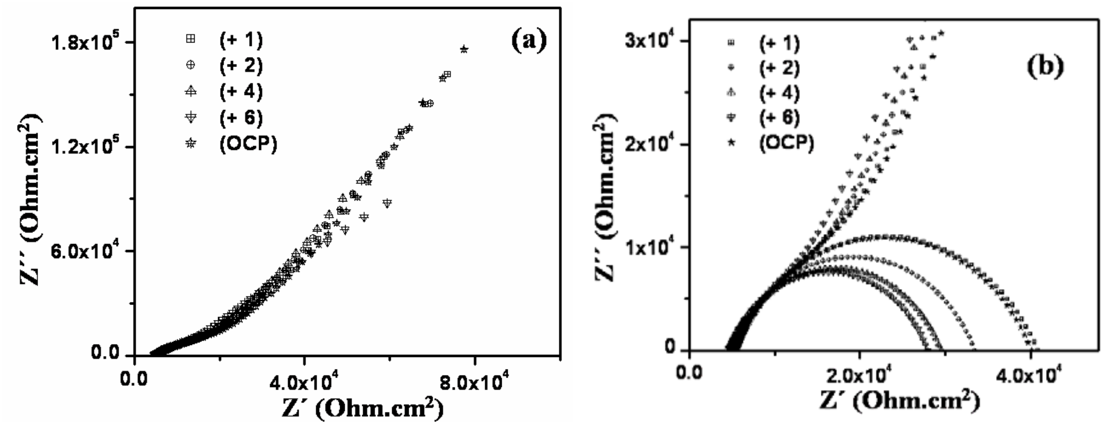


Fig. ESI 1 (a) Complex plane impedance plots of Au MPCs in CH_2Cl_2 on a Pt disc (0.5 mm diameter under OCP and various anodic dc bias corresponding to various charge steps (+1), (+2), (+4) and (+6); (b) the superimposed high frequency part of these plots, after fitting with Randles equivalent circuit.

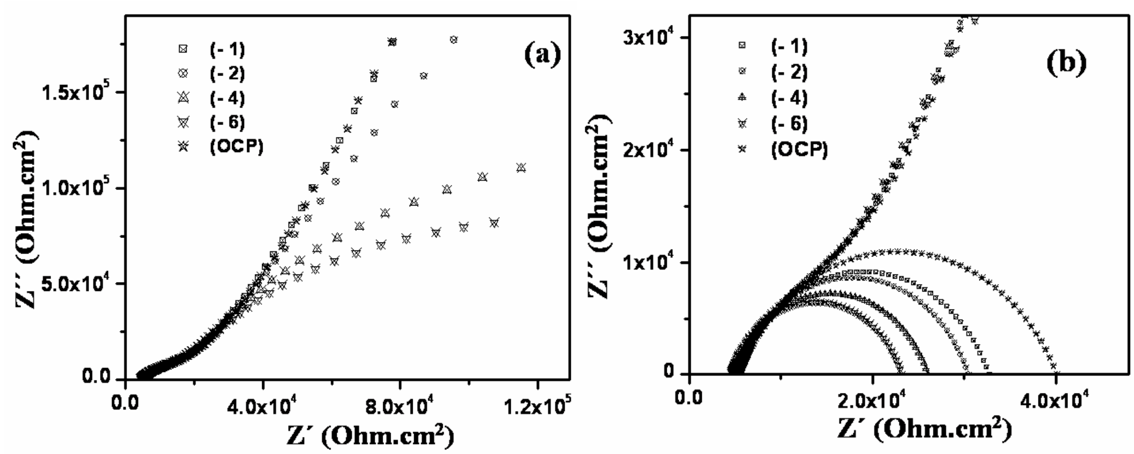
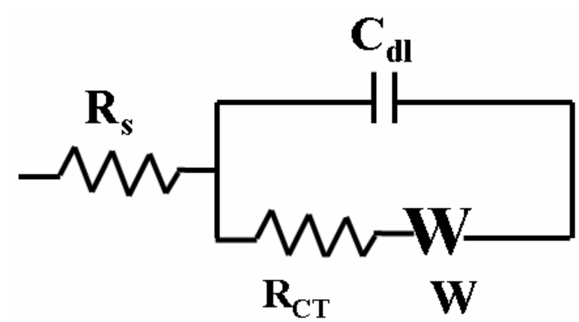


Fig. ESI 2 Complex plane impedance plots of Au MPCs in CH_2Cl_2 on a Pt disc (0.5 mm diameter under (a) OCP and various anodic dc bias corresponding to various charge steps (-1), (-2), (-4) and (-6); (b) the superimposed high frequency part of these plots, after fitting with Randles equivalent circuit.

Fig. ESI 1 (a) shows the superimposed complex plane impedance plots of Au MPCs in CH_2Cl_2 on a Pt disc (0.5 mm diameter) working electrode under OCP and various anodic dc bias corresponding to various charge steps (+1), (+2), (+4) and (+6).

Subsequently, the impedance data have been divided into high and low frequency regions for the convenience of interpretation and analyzed using the Randles equivalent circuit (Scheme ESI 1), considering the electrode reaction to be a one-step, one electron process. The high frequency part of these plots has been fitted to semicircle using complex nonlinear least squares (CNLS) procedure and is superimposed in Fig. ESI 1 (b). Accordingly, Fig. ESI 2 (a) shows the superimposed complex plane impedance plots of these Au MPCs under OCP and various cathodic dc bias corresponding to various charge steps (-1), (-2), (-4) and (-6), whereas the semicircle fitted with the high frequency part has been indicated in Fig. ESI 2 (b). Various parameters calculated from these plots along with corresponding charge steps have been summarized in Table ESI 3.



Scheme ESI 1 Schematic representation of Randles equivalent circuit used for analyzed impedance data, where R_S is solution resistance, R_{CT} is charge transfer resistance, C_{dl} is double layer capacitance and W is Warburg impedance.

The standard rate constants of the one electron QDL charging process at various charge states have calculated using the following relationship,

$$k = RT / n^2 F^2 R_{CT} C$$

assuming n = 1, C= $C^*(O) = C^*(R) = (9.5 \times 10^{-7}$ mol.cm$^{-3})$, $\alpha = 0.5$, T = 273 K and the value of R_{CT} has been obtained from the fitted semicircle in the real axis as shown in Table ESI 3.

The diffusion coefficients are estimated for various charge state particles by analyzing the lower frequency part of the impedance plots (Warburg impedance), using the slope (σ)of the linearly fitted modulus of the real and imaginary part of the impedance data (3.76 Hz to 0.464 Hz) with $\omega^{-1/2}$ as shown in main text (Fig. 5), which can expressed as follows:

$$\sigma = \sqrt{2}\, RT / A\, n^2 F^2 D_C^{1/2} C$$

assuming n = 1, A = area of the electrode (1.96 x 10^{-3} cm^2), $D_O = D_R = D_C$, C = $C^*(O)$ = $C^*(R)$= (9.5 x 10^{-7} $mol.cm^{-3}$) and T = 273 K.

Table ESI 3 Various parameters such as solution resistance (R_S), charge transfer resistance (R_{CT}), double layer capacitance (C_{dl}), standard rate constant (*k*) and diffusion coefficient (D_C) at different charge steps of Au MPCs from the impedance measurement along with Stokes-Einstein equation. The diffusion coefficient values are comparable with values shown at Table 1 in the main text.

Charge State (DPV)	**Applied Potential**	**R_{CT} (Ohm. cm^{-2}) x 10^3**	**R_S (Ohm. cm^{-2}) x 10^3**	**C_{dl} (µF)**	***K* (cm. s^{-1}) X 10^{-5}**	**σ (Ohm. $cm^{-2}.s^{-1/2}$)**	**D_c ($cm^2.s^{-1}$) x 10^{-7}**	**From Stokes-Einstein equation (x 10^{-7} $cm^2.s^{-1}$)**
+6	0.70	23.35	4.63	2.82	1.10	277126.5	2.67	
+4	0.42	24.71	4.80	1.52	1.04	369729.0	1.84	
+2	0.28	28.52	5.00	1.32	0.90	428002.2	1.87	
+1	0.19	35.62	5.28	1.60	0.72	472642.4	1.53	
OCP	0.06	34.76	5.40	1.11	0.74	531373.4	1.21	14.7
-1	0.02	27.42	5.29	0.90	0.94	515216.0	1.29	
-2	-0.11	25.27	5.20	0.74	1.02	541246.0	1.16	
-4	-0.23	21.37	4.70	0.76	1.20	431390.0	1.84	
-6	-0.50	18.72	4.47	0.66	1.37	357823.8	2.67	