Mechanistic aspects of hydrazine-induced Pt colloid instability and monitoring aggregation kinetics with nanoparticle impact electroanalysis

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Here we investigate the mechanistic aspects of Pt nanoparticle (NP) aggregation in solutions typically used for detecting NP/electrode impacts by electrocatalytic amplification (ECA). We previously proposed a general mechanism for Pt colloid destabilization that involved the participation of both the hydrazine redox probe and the pH buffer species as coagulants. Herein the Pt NP coagulation and aggregation mechanisms were further investigated with microscopic kinetic NP concentration monitoring and zeta potential measurements using nanoparticle tracking analysis (NTA), as well as open circuit potential experiments with a citrate-treated polycrystalline Pt surface to assess electrical double layer potential. After considering the combined results of these experiments we propose that the colloidal stability of citrate-capped platinum nanoparticles involves much more than the typical physicochemical interactions predicted by DLVO theory. A structure based on intermolecular H-bonding in the citrate capping layer is the most plausible explanation for the exceptional stability of large Pt NPs in high ionic strength buffers. Thus, the mechanism of Pt NP aggregation includes specific reactive contributions from hydrazine. The catalytic decomposition of hydrazine, in particular, is thought to occur to some extent at the citrate-coated Pt surface while the citrate remains adsorbed. Evolved gases such as ammonia and possible surface bound intermediates from Pt-catalyzed decomposition of hydrazine may disrupt the stability of the citrate layer, causing colloidal instability and thus promoting Pt NP coagulation. In the closing section, we demonstrate nanoparticle impact electroanalysis by ECA detection as a method to quantify Pt NP concentration with adequate time resolution for monitoring the kinetics of Pt NP coagulation.

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Introduction

In a previous study, the colloidal stability of single particles during nanoparticle impact electroanalysis was examined.\textsuperscript{1} In this report we expand upon these findings and extend the investigation into the colloidal instability of citrate-capped Pt nanoparticles (NPs) and establish the conditions necessary for detection of single NP impacts \textit{via} electrocatalytic amplification (ECA). Almost a decade ago, Bard and coworkers pioneered the ECA strategy\textsuperscript{2} for detecting single NP electrocatalysts in solutions containing reactive molecules such as hydrazine (N$_2$H$_4$) as ECA detection probes.\textsuperscript{3} In amperometric ECA studies, an ultramicroelectrode (UME) is employed, and the best results are obtained when the UME substrate is electrochemically inert to the ECA probe molecules at the applied potential. A sharp burst in current is observed when the catalytic NP contacts the UME due to the resulting electrocatalytic oxidation or reduction of the reactive species in solution. For N$_2$H$_4$ oxidation, the characteristic shape of the ECA impact signal depends primarily on the composition and physical properties of the electrode material.

Among the various ECA detection strategies developed over the course of the past nine years, the most commonly employed scheme involves citrate-stabilized Pt NPs as the catalysts and hydrazine as the reactant species.\textsuperscript{3–16} Koper and coworkers reported the first evidence of Pt NP aggregation while conducting ECA experiments with hydrazine and phosphate buffer at pH 8 using 3–5 nm Pt NPs and Au UMEs.\textsuperscript{8} The authors showed that the Pt NPs were distributed as large branched aggregates on Au and pointed out large distributions of the measured current step ECA events which increase in polydispersity with increasing hydrazine concentration. Koper attributed the aggregation to specific interactions of hydrazine at the citrate/Pt interface and noted that the fractal dimension of the aggregates appeared to fit the growth model of diffusion-limited aggregation (DLA).\textsuperscript{8}

The DLA model was developed based on the experimental observations of Meakin and coworkers when studying polystyrene, SiO$_2$, and citrate-capped Au colloids.\textsuperscript{17} The authors experimentally established universal rate regimes for all three aggregating systems and correlated the kinetics to the observed fractal dimension of the resulting aggregates, which was common to all aggregated species regardless of chemical composition. The theory of universality for understanding colloid aggregation kinetics was then developed based on the fractal dimension of the aggregate structures as independent from the chemical nature of the colloid.\textsuperscript{18,19} Aggregation rates in these systems are typically measured with minute-scale time resolution by traditional light scattering methods, which do not include direct NP quantification in the measurements.

Shumaker-Parry and coworkers recently elucidated the surface structure of citrate adsorbed to single crystal Au surfaces and Au NPs by combined infrared and X-ray photoelectron spectroscopic methods. They proposed that citrate adopts a unique bilayer structure with “dangling” dihydrogen citrate ions (monovalent species) coordinated by hydrogen-bonds, which sits atop a neutral hydrogen-bonded network at the citrate/Au interface.\textsuperscript{20} The authors went on to suggest that the stability of this citrate/Au structure was crucial for Au NP growth during synthesis as well as the total stability of the colloid. In another recent
study, Johnston and coworkers reported conditions in which a citrate-stabilized Au colloid preferentially assembles into small chain-like clusters. The authors modeled their system based on Derjaguin–Landau–Verwey–Overbeek (DLVO) principles and proposed that attractive bridging interactions at the terminal ends of a small NP-chain directed the linear coagulation mechanism.

Nanoparticle tracking analysis (NTA) has recently been reported as a useful tool to characterize isosymmetric Au NPs and asymmetric nanorods in solution, with potential application to developing new immunoassay nanotechnologies that employ protein-conjugated Au NPs as detection probes. NTA has also been evaluated for the analysis of NPs in complex matrices such as food and environmental samples. Because NTA is a relatively new form of analytical instrumentation, many research groups have included it in multi-instrumental cross-correlative comparisons involving NP quantification and characterization. NTA simultaneously provides quantification of particle concentration and hydrodynamic diameters in a single acquisition, in contrast to more commonly employed ensemble-based methods such as dynamic light scattering.

Our group recently addressed the importance of using lower ionic strength buffers to prevent hydrazine-induced Pt NP aggregation and obtain reliable impact results for individual 50 nm citrate-capped Pt NPs, using Hg/Pt as the UME. In that study, we used kinetic NTA measurements to aid in the optimization of Pt colloids for single-NP detection by ECA nanoparticle impact analysis. We observed from the NP impact frequency that aggregating Pt NPs were found to collide with the Hg UME at a much slower rate than the optimized stable samples. The stable colloids, on the other hand, demonstrated the expected Langevin-derived diffusion-limited mass transport to the Hg UME, as correlated to NP hydrodynamic sizing by NTA and SEM measurements.

The general mechanism for coagulation was found to involve the participation of both the hydrazine (N₂H₄) redox probe and the pH buffer species as coagulants. Chemically-induced colloid instability was attributed to chemisorption or partial decomposition of N₂H₄ on the catalytically active Pt NP surface, in line with earlier findings by Koper and coworkers. However, we were able to stabilize the citrate-capped Pt NPs in the presence of N₂H₄ by simply decreasing the net ionic strength of the buffer. This NTA-guided systematic approach for optimizing colloid stability led to the discovery of solution conditions that were compatible for our single-NP sensing strategy based on the aforementioned ECA. The resulting NP impact rate analysis was found to correlate well with sizing by NTA and scanning electron microscopy (SEM), as evidenced by Pt NP diffusion coefficient (D₉₅₉) approximations based on the Stokes–Einstein–Sutherland relation. The experimentally determined Pt NP impact rate of the most stable sample, while giving an expected result according to Einstein’s kinetic relations, contradicts previous theoretical models of Pt NP impact rates in the N₂H₄ solutions. The earlier suggested model, reported by Bard and Zhang, was based on impact rate analysis of citrate-capped Pt NP samples that were detected by ECA in high ionic strength conditions. These experiments gave apparent diffusion coefficients that were two orders of magnitude slower than predicted based on diffusive transport to the UME. We suggested that the observed slow collision rates in earlier studies were attributed to hydrazine-induced particule coagulation, which is facilitated in high salt concentrations.
In this report, we examine the mechanistic aspects of Pt NP aggregation in ECA solutions based on microscopic kinetic Pt NP concentration studies and zeta potential measurements using nanoparticle tracking analysis (NTA).\textsuperscript{31,32} Zeta potential measurements were used to model the interparticle interaction energy based on DLVO theory and to study the effect of the citrate capping layer and Pt nanostructure on the colloidal stability. We evaluated citrate desorption from Pt with open-circuit potential (OCP) measurements and discovered evidence of preserved citrate–Pt stability in the presence of hydrazine undergoing Pt-catalyzed decomposition. Finally, we monitored the kinetics of Pt NP aggregation with NTA over longer time scales than previously reported. These NTA results revealed that the Pt NPs used in these experiments favor the aggregative assembly into linear chain structures as observed by scanning electron microscopy. This finding adds a new consideration to the overall discussion of “universality” in colloid aggregation,\textsuperscript{17} specifically the effect of Pt NP surface structure on aggregative assembly. We demonstrate in the final section the utility of NP impact electroanalysis (NIE) for quantifying NP concentration and monitoring Pt NP aggregation kinetics.

**Experimental**

**Materials**

Mercury(i) nitrate dihydrate (ACS reagent), chloroplatinic acid hydrate ($\text{H}_2\text{PtCl}_6$, $\geq 99.9\%$ trace metal basis), 64–65% hydrazine hydrate solution (reagent grade), and l-ascorbic acid (ACS reagent) were purchased from Sigma-Aldrich. ACS grade sodium phosphate buffer (SPB) salts, trisodium citrate, citric acid, concentrated sulfuric acid, and sodium borohydride were acquired from Fisher Scientific. All chemicals were used as received. Sulfuric acid was used to adjust the pH to 7.8 for each hydrazine-containing buffer. All water was purified to 18 MΩ cm resistivity with a Barnstead Epure System.

**Synthesis of Pt NPs**

The 50 nm Pt NPs used in this investigation were part of the same batch that was synthesized for a previous investigation.\textsuperscript{1}

**Nanoparticle tracking analysis**

Nanoparticle tracking analysis (NTA) was performed using the ns500 instrument from Nanosight, Ltd. The NTA method of optical single-NP detection is based on dark-field scattering microscopy; the light source is a blue 488 nm laser. The time resolved size measurements were performed following the experimental procedure as reported earlier.\textsuperscript{1} Zeta potential measurements were performed at an applied electrokinetic driving voltage of 24 V for samples in water, 8 V for 25 mM Tris sulfate and 10 mM sodium phosphate buffers,\textsuperscript{†} and 12 V for all other samples.

\textsuperscript{†} The zeta potential measurements performed in these high ion concentrations (>10 mM) are expected to be less reliable than those obtained in lower ionic strength because the electrokinetic driving voltage had to be reduced from 24 V (used for water and 10 mM ionic strength solutions) to 8 V in order to prevent a short circuit. The 8 V setting is the minimum recommended setting from the NTA manufacturer for obtaining reliable zeta measurements.
Open circuit potential measurements

All electrochemical experiments were performed with a two-electrode setup controlled by an electrochemical workstation (CH Instruments, Austin, TX, model 700). A saturated calomel electrode was used as reference. The OCP experiment is depicted schematically in Fig. 5.

Electron microscopy

Scanning transmission electron microscopy (STEM) was performed using a Hitachi-S5500 microscope operated at 30 kV equipped with a Bruker Quantax 4010 EDX detector. Samples were prepared for electron microscopy by dropping nanoparticle suspensions onto formvar-coated TEM grids and drying at 60 °C over the course of 3 days to fully evaporate water.

Scanning electron microscopy (SEM) was performed using a Hitachi-S5500 microscope operated at 5 kV. Samples were prepared by lowering a piece of stainless steel foil into two different ECA solutions (10 mM N2H4 and 5 mM SPB, pH 7.8 and 10 mM N2H4 and 50 mM SPB, pH 7.8) for two hours and allowing them to adsorb the Pt NP aggregates.

Nanoparticle impact electroanalysis

The NP impact data analyzed in this study along with the experimental protocol is reported in a previous publication. The NP frequency was calculated by applying a custom moving sum-average with an Excel spreadsheet. Specifically, the frequency for the first ten impacts was calculated by dividing the sum total by the elapsed time after Pt NP introduction. All other events after the 10th impact were counted as a total of 10 events divided by the time in between the first event of the set and first event of the next ten impacts. This data processing was also applied in the backward direction starting at the end time and the two forward/backward results were averaged together to construct the plot in Fig. 10a. The scatter data in Fig. 10a was fit to the Smoluchowski coagulation equation as a custom function in the Origin 2016 data analysis package to produce the plot in Fig. 10b.

Results and discussion

Time-resolved NTA: Pt NP concentration measurements

Pt NP concentrations were monitored over time by NTA for three different buffer species: sodium phosphate buffer (SPB), Tris sulfate buffer (TSB), and hydrazine sulfate buffer (HSB), as shown in Fig. 1. TSB was chosen as a relevant system of interest to hydrazine because the Tris amino base has the same pKₐ as hydrazine (8.1). It also works out that the ionic strength of both buffer species is equivalent to their respective formal concentrations at the pH maintained for these experiments. Therefore, the average valency of ions in solution is also equivalent for both buffers prepared at the same total ion concentration, so any difference in aggregation phenomena between the two conditions cannot be attributed to the relative degree of electrostatic charge-screening at the nanoparticle’s electrical double layer. The left panel shows that for 10 mM ionic strength, the Pt colloid maintains its initial concentration in the presence of all three buffering species. We also performed these experiments with 25 mM ionic strength (not shown) to obtain a similar result as that for the 10 mM condition. As shown in the right
panel of Fig. 1, the colloid also remains at a consistent concentration at 50 mM ionic strength for chemically inert SPB and TSB (Fig. 1b and d). In HSB, however, the Pt NP concentration does in fact decrease significantly over time (Fig. 1f), reducing to half of the initial concentration after 7–8 minutes. The aggregation rate is apparently linear at this time scale, and with an observed aggregation rate of $-4.3 \times 10^7$ NPs mL$^{-1}$ s$^{-1}$. The Pt colloid in 50 mM HSB therefore represents a unique experimental condition whereby aggregation is specifically induced by hydrazine, even when the ionic species for comparison (TSB) is a primary amine with similar basicity and assumedly comparable amine-Pt binding affinity. This result suggests that the reactivity of hydrazine at the Pt NP surface does indeed play a significant role in promoting aggregation.

**NTA zeta potential and size measurements**

To further understand the specific role of hydrazine in Pt NP aggregation, we employed the electrokinetic tracking features of NTA to measure zeta potentials of the individual particles in solution. The zeta potential is the potential at the slipping plane of the electrical double layer (EDL) on an individual NP surface in accordance with the Gouy–Chapman–Stern model. The experimentally determined zeta potential values therefore serve as estimations for the activation...
energy of the pair interparticle interactions that are responsible for citrate-promoted charge stabilization of the Pt colloid. Fig. 2 shows the measured zeta potentials for a variety of solution conditions relevant to the ECA detection strategy, each plotted with respect to the approximated ionic strength. As expected, the Pt colloid in deionized water is the most stable sample, with a high average zeta potential of $-100$ mV. The Pt NP zeta potential decreases to less than half of this value for all other conditions tested in the range of ionic strength from 10 to 30 mM. The three buffer systems that were analyzed by NP concentration in the left panel of Fig. 1 (10 mM ionic strength) were also investigated. The average and standard deviation (measure of NP polydispersity and standard error) of the individual Pt NP zeta potential distributions for all three of these solution conditions are virtually identical ($-46 \pm 14$ mV). This zeta potential for citrate-capped Pt NPs is sufficient for colloid stabilization, as verified earlier in the concentration measurements from Fig. 1. At higher buffer ionic strength ($\sim 25$ mM; corresponding to 25 mM TSB and 10 mM SPB), the average zeta potential for the Pt NPs is decreased by $\sim 20$ mV with respect to the 10 mM ionic strength conditions and the zeta polydispersity increases as indicated by the vertical bars in Fig. 2.

The zeta result for the mixed hydrazine/buffer species condition of 5 mM SPB + 10 mM $\text{N}_2\text{H}_4$ is statistically similar to that of the three stable NP samples in 10 mM ionic strength (Fig. 2), which further supports our previously reported conclusions that the colloid is stable at this condition of important relevance to ECA detection of single Pt NPs. The measured mean NP diameters are quite similar for all conditions tested. However, a slightly higher degree of aggregation is indicated for the SPB supported colloids according to the 4 nm difference between 3.85 mM SPB and the monoprotic weak base buffers, HSB and TSB. The hydrazine-containing sample has the largest NP size overall despite the fact that its ionic strength is much lower than the 10 mM SPB sample. This finding further supports our hypothesis that hydrazine is promoting aggregation by chemically interacting with the Pt NPs in solution, but that these interactions can be regulated by tuning the pH buffer concentration.

![Fig. 2](image_url)  NT{{A-measured Pt NP zeta potentials plotted as a function of ionic strength. Various solution conditions were investigated as labeled in the legend. The corresponding mean Pt NP hydrodynamic diameters and standard deviations (standard error) are listed in the legend. Buffers were freshly prepared at pH 7.8 prior to acquisition.}
DLVO predictions and effect of Pt NP structure

The DLVO model of interparticle interactions is one of the most heavily applied theories to assess the stability of colloidal dispersions, and has been shown to correlate well with experimental measurements in various colloid systems. The DLVO approximation for the interaction energy between two approaching particles is based on the summation of the attractive van der Waals ($V_{VDW}$) and electrical double layer ($V_{EDL}$) contributions to obtain the pair interparticle potential ($V_T$) according to eqn (1).

\[ V_{VDW} + V_{EDL} = V_T \]  

(1)

The Derjaguin approximation\(^{34,35}\) serves as a simple model to estimate the van der Waals interaction energy as a function of interparticle separation distance ($H$) for hard spheres of equivalent radius ($r$) according to eqn (2),

\[ V_{VDW} = - \frac{A_{12}}{12h_1} \left[ \frac{1}{1 + h_2} + \frac{h_1}{1 + h_1 + h_3} + 2h_1 \ln \left( h_1 \left( \frac{1 + h_2}{1 + h_1 + h_3} \right) \right) \right] \]  

(2)

where $h_1 = \frac{H}{r}$; $h_2 = \frac{H}{4r}$; $h_3 = \frac{H^2}{4r^2}$ and $A_{12}$ is the Hamaker constant for the metal–water (1–2) interface.\(^ {36}\) One can also approximate the interaction energy of two overlapping double layers between two spherical NPs using eqn (3),

\[ V_{EDL} = 2\pi \varepsilon_{rel} \varepsilon_0 \zeta^2 r \ln[1 + \exp(-\kappa H)] \]  

(3)

where $\varepsilon_{rel}$ is the relative permittivity of the solvent, $\varepsilon_0$ is the permittivity of free space, $\zeta$ is the experimentally measured zeta potential from NTA, and $\kappa$ is the inverse Debye length, calculated by eqn (4).

\[ \kappa = \left[ \frac{1000\varepsilon^2 N (2I)}{\varepsilon_{rel} \varepsilon_0 k_B T} \right]^{\frac{1}{2}} \]  

(4)

Here $e$ is the elementary charge, $N$ is Avogadro’s number, and $I$ is the ionic strength. Eqn (3) is only valid when $\kappa r > 5$, such is the case for low potentials at high ionic strengths. At high zeta potentials, such as that observed for the 50 nm citrate-capped Pt NPs when dispersed in deionized water (Fig. 2), $\kappa r < 5$ and the expression for $V_{EDL}$ then becomes

\[ V_{EDL} = 4\pi \varepsilon_{rel} \varepsilon_0 \left( \frac{k_B T r Y}{e} \right)^2 \exp(-\kappa H) \]  

(5)

with

\[ Y = \frac{8 \tanh \left( \frac{\varepsilon \zeta}{4k_B T} \right)}{1 + \left[ 1 - \frac{(2\kappa r + 1)}{(\kappa r - 1)} \right] \tanh^2 \left( \frac{\varepsilon \zeta}{4k_B T} \right)} \]  

(6)

Fig. 3 shows the calculated prediction for $V_T$ as a function of separation distance between two 50 nm Pt NPs at two different ionic strengths. The $V_{EDL}$ at $10^{-3}$ mM ionic strength (blue solid curve) was calculated using eqn (5) and (6) because the calculated $\kappa r$ value is 3. The inverse of $\kappa$ gives a Debye screening
length of 10 nm for this low electrolyte solution. $V_{\text{EDL}}$ for 10 mM ionic strength (blue dashed curve) was calculated using the expression for $k_r > 5$ (eqn (3)). As shown in Fig. 3, $V_T$ is predicted by DLVO theory to be a repulsive barrier at $10^{-3}$ mM ionic strength. For 10 mM ionic strength, however, the calculation predicts significant screening of the Pt surface charge to result in a net energy that is equivalent to $V_{\text{VDW}}$, essentially indicating that the 10 mM ion concentration is higher than the critical concentration of coagulation. Our experimental results do not fit the traditional DLVO prediction of rapid coagulation for these colloid species. Experimental disagreements with DLVO theory are well documented in the colloid literature, and the various factors that the approximation does not take into account continue to be a heated topic of discussion.

A more appropriate theoretical model must include another repulsive contribution to the $V_T$ equation to explain our observations. We reason that the key to stability enhancement most likely involves the structure of the absorbed citrate on the Pt surface. We suspect this structure involves a substantial degree of H-bonding, such as that determined by Shumaker-Parry for Au, with the addition of enhanced stability coming from Pt NP’s hydrophilicity and more favorable binding energetics with the OH group of citrate due to the presence of Pt surface oxides/hydroxides. The Pt NPs used in this study have a nanostructured surface roughness of $\sim$5 nm due to the aggregative growth mechanism during synthesis, which we expect to promote a higher relative surface coverage of Pt oxides/hydroxides with respect to bulk polycrystalline Pt due to stronger Pt–OH interactions at NPs $\leq$ 5 nm in diameter. Interestingly, Eychmüller and coworkers, who originally reported the synthesis of these Pt NPs, found it necessary to include a dielectric shell of 5 nm thickness in their computations of Pt NP
extinction spectra in order to fit their experimental results. If Pt nanostructure promotes H-bonded networks with citrate, then perhaps the thickness of this steric/charge stabilizing shell really is \( \sim 5 \text{ nm} \). The \(-100 \text{ mV}\) zeta value measured in pure water for our NPs is relatively high in comparison to citrate-capped Pt NPs of smaller size (\( \sim 5 \text{ nm}, \zeta = -40-50 \text{ mV} \)). The zeta potential is also larger than that observed for Au\(^{45}\) and Ag NPs\(^{46}\) of comparable size. The zeta potential of citrate-stabilized Ag NPs, for example, has been reported to range from \(-27\) to \(-53 \text{ mV}\) for monodispersed colloids with an average diameter between 5 and 100 nm.\(^{47}\) We suspect that Pt NP surface structure promotion of the H-bonding model with extended multi-citrate layer thickness accounts for this zeta potential discrepancy in relation to size, structure, and NP composition. The top panel of Fig. 4 shows an STEM image of two citrate NPs. The area of low contrast surrounding the NPs was observed to develop over time during image acquisition and was acquired after the layer had completed the thermally driven phase expansion caused by energetic losses to heat from the applied 30 kV accelerating voltage of the electron beam. We speculate that this shell is primarily composed of citrate and water that was trapped with the porous structure of the Pt NP during

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**Fig. 4** Scanning transmission electron micrographs of citrate-stabilized Pt spherical NPs. The top panel shows two Pt NPs at high magnification and the film that develops around the NPs over time under exposure of the electron beam. The bottom three panels show representative images of chain-like Pt NP aggregates.
the synthesis and later expelled upon swelling under the electron beam. The coating material may also include oxidation products from the reducing agents, such as polymeric borate species from sodium borohydride.

**OCP experiments**

OCP experiments were performed on a Pt wire to assess the stability of the citrate surface structure upon exposure to hydrazine solutions. Fig. 5a depicts the scheme for surface pretreatment experiments and Table 1 lists the corresponding OCP measurements. First, the OCP of a clean, flame-annealed Pt wire was measured in 50 mM SPB under ambient conditions to obtain a value of 260 mV vs. SCE, which is estimated to be \( \sim 0.95 \text{ V vs. RHE} \) in pH 7.8 based on the Nernst equation (RHE = 0 V – 0.0591 \times \text{pH vs. NHE}). This potential is the expected value based on the onset of the oxygen reduction reaction on Pt. After cleaning the electrode again, it was then immersed in 100 mM HSB for 1000 s (step 1, Fig. 5a), giving an OCP of \(-510\) mV which is poised between the electrocatalytic onsets for O₂ reduction and N₂H₄ oxidation. Importantly, macroscopic bubbles were observed to form on the surface of the electrode during this time period, indicating Pt-catalyzed hydrazine decomposition. The N₂H₄ decomposition reaction can occur by two alternative pathways, the direct pathway to form hydrogen and nitrogen gas as shown in eqn (7), and the alternative pathway leading to the formation of nitrogen gas and ammonia (eqn (8)).

\[
\begin{align*}
\text{N}_2\text{H}_4 & \rightarrow \text{N}_2 + 2\text{H}_2 \\
3\text{N}_2\text{H}_4 & \rightarrow 4\text{NH}_3 + \text{N}_2
\end{align*}
\]

Hydrazine decomposition on polycrystalline Pt and Pt NPs has been shown to significantly favor the ammonia production pathway in both acidic and alkali...
conditions. So while Pt is an excellent catalytic surface for efficient \( N_2H_4 \) decomposition, the reaction follows the less desirable \( NH_3 \) path making Pt a poor choice of catalyst for the efficient production of \( H_2 \) from \( N_2H_4 \).\(^{51}\) We therefore assume that the observed bubbles are primarily composed of gaseous \( N_2 \) and \( NH_3 \). The catalytically evolved bubbles formed at a gradual rate and the OCP was not observed to fluctuate significantly over the course of a single measurement. In step 2 of Fig. 5a, the Pt wire from the \( N_2H_4 \) solution was quickly transferred to SPB to obtain a lower OCP than seen for the clean Pt surface. In this experiment, the potential vs. time was observed to fluctuate during the acquisition time and vary between trials. The cause of the observed fluctuation is unclear and could be due to several possible processes that are suggested to occur on deactivating Pt surfaces.\(^ {52}\)

Shown in Fig. 5b is the description of the citrate treatment method, the first step involving the saturation of the Pt wire surface with a Na citrate solution. After a gentle rinse, the electrode was transferred to 50 mM SPB to measure the effect of the citrate coating on the electrode potential (Table 1). We attribute the \(-178\) mV difference between the OCPs measured for the clean and the citrate-treated Pt wires to the influence of the charged citrate layer adsorbed on the electrode. The potential shift is higher than the measured zeta potential for the Pt NPs \((-100\) mV) because the OCP measurement represents the potential at the compact double layer, which is well known to be greater in value than the zeta potential. We then tested the effect of 100 mM HSB on the adsorbed citrate by the same method used for clean Pt. Bubbles also gradually formed for the citrate-coated Pt wire in the 100 mM HSB condition, so the wire was still catalytically active for \( N_2H_4 \) decomposition despite the citrate-saturated surface. The equilibrium potential was shifted \(-100\) mV positive of that observed for clean Pt, indicating that \( N_2H_4 \) oxidation on Pt is kinetically hindered by attached citrate. For the OCP result corresponding to step 2 of Fig. 5b, we observed a negative shift that is roughly comparable in value to what we saw for the clean Pt wire experiment \((\sim 100-200\) mV difference), so there is no apparent evidence from this experiment of citrate removal from the electrode after exposure to \( N_2H_4 \).

### Table 1

<table>
<thead>
<tr>
<th>Conditions</th>
<th>OCP (mV)</th>
</tr>
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<tbody>
<tr>
<td>Clean Pt</td>
<td></td>
</tr>
<tr>
<td>Initial</td>
<td>255 ± 7</td>
</tr>
<tr>
<td>100 mM HSB</td>
<td>-512 ± 6</td>
</tr>
<tr>
<td>Post-treatment</td>
<td>140 ± 40(^ a )</td>
</tr>
<tr>
<td>Citrate saturated Pt</td>
<td></td>
</tr>
<tr>
<td>Initial</td>
<td>87 ± 2</td>
</tr>
<tr>
<td>100 mM HSB</td>
<td>-416 ± 5</td>
</tr>
<tr>
<td>Post-treatment</td>
<td>-80 ± 50(^ a )</td>
</tr>
<tr>
<td>10 mM HSB</td>
<td>-490</td>
</tr>
<tr>
<td>Post-treatment</td>
<td>87</td>
</tr>
<tr>
<td>10 mM ( N_2H_4 ) + 50 mM SPB</td>
<td>-388</td>
</tr>
<tr>
<td>Post-treatment</td>
<td>92</td>
</tr>
</tbody>
</table>

\(^ a \) For the post-treatment experiments in 100 mM HSB, the standard deviation in the OCP over a 1000 s time period was propagated with the standard error.
These experiments were also performed for the 10 mM N₂H₄ solutions that were studied previously with NTA and NP impact experiments. Similar results are observed for both 10 mM N₂H₄ conditions with and without 50 mM SPB added, suggesting that ionic strength during the N₂H₄ pretreatment does not have an effect on the activity of citrate-coated Pt. There is no difference between the initial citrate-coated and post-treated Pt OCP values for the 10 mM N₂H₄ conditions, indicating that the citrate remains adsorbed to the electrode.

The observed bubble formation and OCP shift for 100 mM N₂H₄ warrants a discussion on the possibility of nanobubbles forming from the products of catalytic N₂H₄ decomposition on these structured Pt NP surfaces. The properties of both the Pt surface and the encompassing citrate layer are expected to contribute to nanobubble stabilization, regardless of the decomposition product. We propose that a H-bonded citrate film allows the diffusion of most N₂H₄ to the NP surface and influences mass transport to some extent by electrostatic attraction of N₂H₅⁺. This electrostatic effect could either enhance or hinder hydrazine transport to the Pt active sites by electromigration (enhanced transport) and electrostatic trapping (hindered transport) of incoming N₂H₅⁺ at the charged carboxylate groups of citrate. The transport of hydrazine is therefore dependent on the porosity and thickness of the H-bonded polycitrate layer. We expect that most hydrazine molecules penetrate through the citrate “membrane” deep into the interstitial sites of the nanostructured Pt NP. The gaseous products that form, however, may become trapped in between the Pt surface and the H-bonded polymeric citrate coating layer. The nanobubble stabilizing mechanism is a working hypothesis at this juncture and beyond the scope of this study. However, we speculate that if nanobubbles are stabilized to some extent on these Pt NPs, they could very well influence the coagulation and direct it to occur at the most active Pt nanograins. Plausibly, the Pt catalyzed decomposition mechanism (eqn (8)) is the most likely explanation for the observed specific hydrazine-induced aggregation result from NTA in Fig. 1f.

### Aggregation kinetics

Fig. 6a shows Pt NP size distributions over time as monitored by NTA for the aggregation inducing 50 mM SPB + 10 mM N₂H₄ condition. Fig. 6b shows the corresponding mean NP diameters plotted over a time of one hour. After 30 minutes of aggregate growth, a linear growth region is observed corresponding to an average aggregation rate of 3.8 nm min⁻¹. Fig. 6c shows the natural log of the aggregate diameter divided by the initial 50 nm diameter, ln(d/d₀), as a function of ln(t/τ), where t is time and τ is the time constant for the rate of coagulation, determined to be roughly 240 s, which is the time when the NP concentration decreases to half its initial value (Fig. 6a). The ln–ln plot in Fig. 6c clearly shows two different rate regimes; the earlier one is slow followed by an abrupt transition to a faster rate regime after 30 minutes. The slow growth region indicates reversible coagulation. For the fast rate a fractal dimension (δ) of 1.0 from the inverse slope of the plot in Fig. 6c is obtained, indicating a linear structure of the Pt NP aggregates. The inset electron micrograph in Fig. 6b shows a small linear chain of four Pt NPs that aggregated naturally during solvent evaporation on the hydrophobic carbon film coated TEM grid. Other Pt NP chains are shown in Fig. 4. The SEM images in Fig. 7 and 8 show the aggregate structures.
formed in the presence of two ECA buffers that we’ve investigated previously with NTA and NP impact rate analysis. For these experiments, a piece of stainless steel foil was lowered into the ECA solution and left to adsorb the Pt NP aggregates that formed over the course of 2 hours. Fig. 7 shows a mixture of primary 50 nm Pt NPs and small aggregates containing no more than 5 primary NP units that adsorbed on the metal surface in 10 mM N₂H₄ + 5 mM SPB solution. In Fig. 8, we see larger aggregates that formed in the higher ionic strength 10 mM N₂H₄ + 50 mM SPB solution, as expected. Chain-like NP aggregates appeared in both figures along with some that adopted more closely packed arrangements.

We suggest that our NPs are directed to assemble in a linear fashion by stronger bridging interactions and large electrostatic repulsive contributions from the densely adsorbed citrate on the surface, in line with Johnston’s proposed mechanism. However, one must also consider the heterogeneity of the Pt nanograins on the NP surface. Some of these crystallites may be much more active than others for N₂H₄ decomposition. We are not sure exactly how this relates to aggregation. It could create pressure-driven repulsion if the rate of decomposition is sufficiently fast and bubbles are released at a continuous frequency. In this sense we are proposing that the Pt NPs may be behaving like nanomotors propelled by gas production. If the gas is building up from within the Pt NP, then this could eventually rupture the stabilizing citrate layer at a specific site and further promote linear assembly. An alternate explanation for the nanobubble hypothesis is that hydrazine is becoming a part of the H-bonded citrate network,
Fig. 7  SEM of Pt NPs adsorbed on stainless steel foil from a solution of 10 mM N₂H₄ + 5 mM SPB, pH 7.8 over the course of one hour at 1.1 pM Pt NP concentration.

Fig. 8  SEM of Pt NPs that adsorbed on stainless steel foil from a solution of 10 mM N₂H₄ + 50 mM SPB, pH 7.8 over the course of one hour at 1.1 pM Pt NP concentration.
as proposed by Li and coworkers. Indeed, N₂H₄ could very well function as both H-bond donor and acceptor. The N₂H₄ may be donating H to the carboxyl groups of citrate and create a strong bridging interaction, thus cross-linking the Pt NPs by interparticle H-bonding to induce aggregation.

**Monitoring aggregation kinetics with nanoparticle impact electroanalysis**

Finally, utilizing our theory of Pt NP aggregation, we show that NP impact events detected by ECA can be calibrated to NP concentration, even for nonlinear fast coagulating conditions. The chronoamperometric trace in Fig. 9 shows the ECA impact events for a single measurement with 1.1 pM Pt NPs in 10 mM N₂H₄ + 50 mM SPB. As we pointed out previously, the NP impact frequency decreases significantly over time. This is shown graphically in Fig. 10a. For the spherical cap UME used in this study, the impact frequency is proportional to NP concentration according to eqn (9).

\[
R_{NP} = f_{NP}C^{-1} = 2\pi\beta N_A D a_{UME}
\]  

(9)

\(R_{NP}\) is the impact rate, \(f_{NP}\) is the frequency of NP impacts at a given NP concentration \(C\), \(N_A\) is Avogadro’s number, \(D\) is the NP diffusion coefficient, and \(a\) is the basal radius of the Hg cap (5 μm for Pt disk UME substrate). The term \(\beta\) is a size dependent constant based on the calculations by Alfred and Oldham. For our Hg UME, \(\beta = 1.35\).

Fig. 10a shows the NP impact frequency as a function of time for five replicate measurements. We estimated \(C_{NP}\) by rearranging eqn (9) using the measured impact frequency and an average diffusion coefficient of \(\sim 1 \times 10^{-7}\) cm² s⁻¹ (50 nm diameter) to calculate the scatter plot in Fig. 10a (blue), which is shown as relative concentration \(C/C_0\) with \(C_0 = 1.1\) pM, the experimentally determined value in water by NTA. The measured \(C/C_0\) values from NTA are included for comparison. The scatter plots were fitted using the general Smoluchowski coagulation function (eqn (10)).

![Fig. 9](image-url)  
**Fig. 9** Chronoamperometry of Pt NP impacts in 10 mM N₂H₄ and 50 mM SPB, pH 7.8. Pt NP concentration is 1.1 pM. The sharp current fluctuations at ca. \(t \sim 60\) s mark the time when Pt NPs were introduced into the hydrazine/buffer solution (4 mL) as a 20 μL injection caused by opening the door on the Faraday cage.
Here \(1/\tau\) represents the coagulation rate and \(\tau\) is the time when the total particle concentration, \(C\), is decreased to half of its initial value. As shown in Fig. 10b, both datasets match well to show the rate of coagulation, with NP impact electroanalysis giving a slightly slower coagulation rate and better fit with eqn (10) after averaging the raw data in Fig. 10a, as described in the Fig. 10 caption and Experimental section. These results demonstrate a proof-of-concept that by analyzing NP impact events, one can calculate the dynamic NP concentration during aggregation, even for nonlinear fast coagulating conditions.

\[
\frac{C}{C_0} = \frac{1}{1 + \frac{t}{\tau}}
\]

**Conclusions**

The combined results of these experiments support that the stability of citrate on Pt involves much more than just electrostatic interactions. A structure based on intermolecular H-bonding in the citrate capping layer appears to be the most likely explanation for the exceptional stability of these large Pt NPs in 50 mM ionic strength in the absence of hydrazine and the stability in hydrazine-containing solutions of lower ionic strength (<20 mM). The stability was evidenced by the range of reversible metastability (agglomeration) before linear directed assembly of Pt NP chains. The mechanism of Pt NP aggregation includes specific reactive contributions from hydrazine, as indicated by the observed hydrazine decomposition gaseous products on a citrate-coated Pt wire. According to the OCP measurements, the citrate remains adsorbed on the Pt surface even after treatment with 10 mM and 100 mM \(N_2H_4\). This is most likely true for the Pt NPs as well. Although citrate stays stuck to the Pt and does not undergo substantial ligand-exchange with hydrazine, we expect that the membrane-like structure is
disrupted by evolved gaseous decomposition products or adsorbed intermediates and then ruptures, causing instability and promoting coagulation. The heterogeneity of the nanostructured Pt NP surface is expected to influence the aggregation mechanism and induce polarity by bridging interactions, which we expect to involve both a higher degree of interparticle H-bonding at the terminal primary NPs of the chain in the presence of hydrazine and the physicochemical contributions from Pt-catalyzed hydrazine decomposition products. In the last section, we demonstrated a proof-of-concept using nanoparticle impact electroanalysis by electrocatalytic amplification as a method for quantifying Pt NPs with suitable time resolution for studying kinetics of Pt colloid aggregation.

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Notes and references


