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**Abstract:** We report a strategy to electrochemically detect individual conducting particles colliding with an ultra-microelectrode (UME). This method, called "electro-catalytic depression" (ECD), enables the detection of particles that are electrically conducting but catalytically inert, such as carbonaceous particles. The ECD method takes advantage of the intrinsic difference in heterogeneous kinetics of electron transfer for a given inner-sphere reaction to block the current at the surface of a particle made of a material having poor catalytic properties compared to the material of the electrode. We showcase this method with the detection of individual graphene nanoplatelets (GNPs) of few µm long and 15 nm thick. GNPs block the oxidation of hydrazine on a 5 µm radius Pt UME. We studied the influence of the potential on the current transient produced by individual GNP stochastically colliding on the UME. We evidence that, under 0.1 V vs AgAgCl 3.4 M KCl, electrically conducting GNPs produce discrete stair-shaped drops of current (negative steps) similar to the signal obtained with insulating particles like polystyrene beads. We show how the analysis of a "blocking-type" signal originally developed for insulating beads can be extended to the detection of conducting particles. However, at high potentials (> 0.1 V), where hydrazine oxidation occurs on the GNP, the kinetic difference between GNP and Pt decreases, leading to the decrease of both average and median current step size and the appearance of positive steps. The frequency of collision versus the concentration of GNP and the bias potential are discussed.

**Keywords:** analytical electrochemistry, single entity electrochemistry, graphene nanoplatelets, hydrazine oxidation

## 1. Introduction

Stochastic collision enables the detection of a wide variety of individual entities such as metal nanoparticles [1, 2], emulsion droplets [3, 4], vesicle [5, 6], micelles [7], proteins [8] and bacteria [9]. Depending on the nature of the entity (insulator, conductor, redox-active material), various electrochemical detection schemes can be used [10]. Insulating objects can be detected by "electrochemical blocking". This strategy, initially reported by Lemay and coworkers [11], relies on a "turn-off" type of response. A redox reporter is oxidized/reduced at a UME and a steady-state current is measured. Upon stochastic collision and subsequent irreversible adsorption of an individual insulating object, a portion of volume above the electrode is blocked and a discrete decrease of current (a "current step") is observed. The magnitude of the current step can be linked to the size of the object provided that the radial position of the object on the electrode is known [12]. We recently showed that using hemispherical UMEs instead of disk UMEs enables the quantitative

determination of the size without knowing the radial position [13]. The frequency of collision can be used to determine the concentration or charge of the objects in solution [13, 14].

Conducting nanoparticles require a different strategy to produce an electrochemical signal. Bard and coworkers developed a method called electro-catalytic amplification to detect particles made of a material that possesses, for a given inner-sphere reaction, "good" catalytic properties compared to the material of the electrode [1, 2]. Thus, the electrode does not produce any faradaic current by itself while the reaction is switched on when an individual catalytic nanoparticle is in contact with the underlying electrode. Catalytic amplification is extremely sensitive since it is a "turn-on" type of detector and the analysis of the frequency of collision can lead to the concentration of particle in solution. The analysis of the step size can, in principle, lead to the size of the particle. However, among eighteen examples of catalytic amplification [15, 16], only four cases show ideal step-like events [2, 17-19] while the others report spike-shaped current events. This peculiar shape is attributed to the deactivation of the particle and the shift of equilibrium potential during the collision [19, 20].

Redox-active objects such as silver nanoparticles or droplets and vesicles loaded with a redox molecule can be detected individually by electrolysis [3, 21-23]. Upon collision of a redox-active object on a UME, the redox content of the object is electrolyzed, generating a spike-shaped current event. The integration of each current event provides an amount of charge, directly related to the size of the object via Faraday's law of electrolysis. This correlation is possible when the particles undergo full oxidation [24-27].

The detection of non-redox active materials that are neither insulators nor good catalysts like carbonaceous materials remains a challenge. Detection of carbonaceous particles by electrochemical collision is reported for carbon nanotubes [28], graphene sheets [29], and graphene nanoplatelets (GNP) [30]. The detection of single-wall carbon nanotubes relies on area amplification [28]. The size of the nanotube should be larger than the size of the electrode. Upon collision of the carbon nanotube on a UME, a discrete increase of current can be evidenced by measuring the electrochemical response of a redox couple in solution. Note that ideal discrete increases of current were observed only for carbon nanotubes modified with gold nanoparticles but not for bare carbon nanotubes. The detection of a single graphene sheet was performed using a "tunneling" strategy consisting in adsorbing a conducting particle on an electrode passivated with an insulating layer thin enough to allow tunnelling [29]. Cyclic voltammetry on an individual graphene sheet enable the estimation of its size. The incubation of the electrode in the suspension of the graphene sheet was performed blindly (that is without monitoring the collisions) and thus the adsorption of individual graphene sheets was not observed in real-time and no analysis of the frequency of collision was performed. The third example relies on transient currents recorded upon collision of individual GNPs on a C-fiber UME [30]. Current transients were counted to estimate a concentration of GNP in solution. The authors proposed that current transients are generated by charging the capacitance of individual GNPs.

Here, we propose an alternative strategy, electro-catalytic depression (ECD), to detect carbonaceous particles. We study GNPs. These particles are used for a wide range of applications: dye-sensitized solar cells [31, 32], conducting support for loading catalysts [33, 34], supercapacitors [35], and sensors [36]. In this article, commercial GNPs with few microns in width and about 15 nm in thickness are used. We take advantage of the intrinsic difference in electron transfer kinetics for an inner-sphere reaction, hydrazine oxidation, to drive a current through a UME made of a good

catalyst (Pt), while kinetically blocking the current at the surface of a GNP. The frequency of collision versus the concentration of GNP and the potential is investigated. Also, we discuss the effect of the interplay between the distribution of the current step size, the kinetic difference between Pt and GNP and the potential.

## 2. Experimental Section

### 2.1 Chemicals and Reagents.

GNPs (≈ 5 µm particle size, 15 nm thickness, Sigma Aldrich), hydrazine monohydrate ($N_2H_4$ 64-65%, > 98%, Sigma Aldrich), ferrocene methanol (97%, Sigma Aldrich) and sodium hydroxide (0.1 M NaOH solution, Fluka) were used without further purification. Solutions were prepared with deionized water (Millipore Milli-Q, 18.2 MΩ·cm$^{-1}$).

### 2.2 Fabrication of Pt and C-fiber UMEs.

The 5 µm radius disk Pt UMEs are fabricated by heat-sealing a 5 µm radius Pt wire (hard tempered, Goodfellow) inside a borosilicate glass capillary (outer diameter: 2 mm, inner diameter: 1.16 mm, Sutter Instrument). A tungsten wire (250 µm diameter, Goodfellow) was glued on the Pt wire using conducting silver epoxy (Araldite). More details about the fabrication and polishing procedures can be found in the following reference [13]. C-fiber UMEs are fabricated by first gluing a c.a. 1 cm long 3.5 µm radius C-fiber (XAS quality, Goodfellow) on a tungsten wire with conducting Ag epoxy and then, casting the fiber and a portion of the tungsten wire into a hard epoxy (EpoHeat, Buehler) contained within a plastic pipette cone. The C-fiber UME is polished following the same procedure as the Pt UME.

### 2.3 Electrochemical measurements.

All electrochemical measurements were performed using a homemade two-electrode setup placed in a Faraday cage. Briefly, a USB-6212 acquisition card (National Instruments) is used to apply a potential at the working electrode and measure the current after its amplification with a trans-impedance current amplifier (DPPCA-300, Femto GmbH). The amplifier has a gain of $10^9$ V/A with a bandwidth of 150 Hz. Points are acquired every 6.7 ms and averaged to obtain a current value every 50 ms. Detailed information about the setup is provided in the following reference [13]. Chronoamperograms are recorded for 120 s or 900 s for each collision experiment. Before each collision experiment, chronoamperograms are recorded for 120 s in the absence of GNPs to ensure that no steps are observed (i.e., negative control). A 35 fM GNP suspension was prepared by adding 2 mg of GNPs to 200 ml of 10 µM NaOH electrolyte solution, assuming that GNP has a regular circular shape with a radius of 2.1 µm obtained from SEM (vide infra). Between experiments, the Pt UME is polished and then cleaned by dipping few tens of seconds in a Piranha solution (3:1v of 98% sulfuric acid and 30% $H_2O_2$) to remove the GNPs. A leakless miniature Ag/AgCl 3.4 M KCl electrode (ET072 from eDAQ) is used as both the reference and counter electrode. All potentials will be quoted against this reference electrode. The solutions are degassed by bubbling Ar for few minutes prior to the measurements.

## 3. Results and Discussion

### 3.1 Kinetics of hydrazine oxidation on Pt UME vs. C-fiber UME

Hydrazine oxidation is a four-electron reaction:

$$N_2H_4 \rightarrow N_2 + 4\,H^+ + 4\,e^-$$

The pKa of hydrazine is 8.1 [37]. In the presence of 10 µM of NaOH in solution, hydrazine is deprotonated and the concentration of $N_2H_5^+$ is negligible (~30 µM) compared to the bulk concentration of hydrazine (1mM). Figure 1A shows typical cyclic voltammograms of hydrazine oxidation on a 3.5 µm radius C-fiber UME (black traces) and a 5 µm radius Pt UME (red traces), along with the corresponding blanks (dashed lines) recorded in the absence of hydrazine. The blanks do not show any faradaic current except the beginning of water oxidation at ca. 1.5 V on the C-fiber UME. In the presence of hydrazine, the current starting at -0.6 V for the Pt UME and 0.1 V for the C-fiber UME is caused by hydrazine oxidation. The cyclic voltammogram recorded with the Pt UME displays two plateaus of current ($i_{ss}^1$ = 4.5 nA and $i_{ss}^2$ = 10.8 nA). The plateau of current corresponding to the theoretical diffusion-limited current on a disk UME is given by equation 1 [38]:

$$i_{ss} = 4nFD_{\text{redox}}C_{\text{redox}}r_{\text{elec}} \qquad (1)$$

where $n$ is the number of electrons exchanged per molecule, $F$ is the Faraday's constant, $D_{\text{redox}}$ is the diffusion coefficient of the redox molecule, $C_{\text{redox}}$ is the bulk concentration of the redox molecule, and $r_{\text{elec}}$ is the radius of the electrode. Using our experimental parameters ($r_{\text{elec}}$ = 5.0 µm, $n$ = 4, $C_{\text{redox}}$ = 1 mM and $D_{\text{redox}}$ = 1.4 × $10^{-5}$ $cm^2 \cdot s^{-1}$) a theoretical limiting current of $i_{ss}$ = 10.8 nA is calculated [39, 40]. Thus, the second plateau at c.a. 10.8 nA on the red cyclic voltammogram in Figure 1A is attributed to the diffusion-limited current for hydrazine oxidation. The inflection point of the first and second sigmoids are around -0.4 V and 0.2 V, respectively. These values are close to the apparent standard potential reported for hydrazine oxidation in basic (pH ≈ 8) and acidic (pH ≈ 1-2) conditions, respectively [41, 42]. The first plateau (c.a. 4.5 nA) on the cyclic voltammogram of the Pt UME is attributed to a local change of pH at the surface of the electrode when hydrazine is oxidized. Indeed, the products of hydrazine oxidation are nitrogen and protons that will locally acidify the solution causing a shift of the apparent standard potential [43]. We verified this point by fixing the pH with increasing concentrations of NaOH and observing the complete disappearance of the intermediate plateau when the concentration of NaOH is about five times larger than the concentration of hydrazine (Figure S1 in SI). The cyclic voltammogram recorded with the C-fiber UME displays one plateau ($i_{ss}$ ≈ 3.8 nA) followed by an increase of the current above 1.5 V. The oxidation of water above 1.5 V masks the second plateau of hydrazine oxidation that should also be observed with the C-fiber UME.

Importantly, the oxidation of hydrazine on a C-fiber UME is extremely sluggish, as shown by the width (ca. 1 V) of the sigmoid (black trace in Figure 1A) and the onset potential 700 mV more positive on the Pt UME than the C-fiber UME. It is thus possible to find a potential window where the current of hydrazine oxidation is large on Pt while it remains extremely small on carbon. For example, at 0 V (blue arrow on Figure 1A) the current is hundreds of times larger on the C-fiber UME than on the Pt UME. At such potential, carbonaceous particles possessing kinetics of hydrazine oxidation similar to that of C-fiber can be considered as an inert surface and are expected to block the current when colliding on a Pt UME. In the following, we will assume that the overall shape of the CV of a GNP is similar to that of C-fiber presented in Figure 1A (solid black line) but with slower kinetics. This assumption is verified with collision experiments of GNP performed on a C-fiber UME (Figure S2 in SI). This assumption is also based on the potential dependent current step sizes of GNP on Pt that we observed (shown later in this paper).

The size and morphology of the GNPs were characterized by SEM (see inset in Figure 1B and Figure S3 in SI). The morphology of the GNP is relatively ill-defined, and thus we quantified their

size by averaging the longest and shortest axis of the platelets. Their size distribution is plotted in the histogram Figure 1B. The average length is about 4.2 ± 2.5 µm. The GNPs can be suspended at 35 fM to 70 fM in water in the presence of 10 µM NaOH. The presence of a base helps stabilizing carbonaceous particles in water [44]. Concentrations of NaOH larger than 10 µM or GNP concentrations larger than 140 fM induce sedimentation within few minutes. Although this issue could have been addressed by adding surfactants in solution, these latter were not used because of their adverse effect on the oxidation of hydrazine at the Pt surface.

### 3.2 Detection of individual GNPs by ECD

Figure **2**A shows two typical chronoamperograms obtained with a 5 µm radius Pt UME biased at 0 V in a 1 mM hydrazine and 10 µM NaOH solution in the presence (red trace) and the absence (black trace) of 35 fM GNPs. In the absence of GNP, the oxidation of hydrazine on the Pt UME leads to a quasi-steady-state current (the black trace in

Figure **2**B) of a few nA. Importantly, no abrupt change of current is observed. However, in the presence of GNPs, discrete stair-shaped current decays are observed on the red trace in

Figure **2**A. A zoom on typical current steps is shown in

Figure **2**B. Current steps were consistently observed in 19 individual experiments in the presence of GNPs but never in the blanks (i.e., in the absence of GNP). The observation of discrete decreases of current confirms that GNPs are kinetically blocking hydrazine oxidation on the Pt UME at a potential of 0 V. To prove this point, we also performed experiments with an outer-sphere redox couple (ferroceniummethanol/ferrocenemethanol), displaying fast kinetics of electron transfer on both Pt and carbon electrodes. A typical chronoamperogram is shown in Figure S4 in SI. No negative current steps are observed when the kinetics of electron transfer is as fast on Pt as on GNP.

Figure **2**C illustrates how this kinetic blocking takes place. Single GNPs collide on the Pt surface and partially cover this latter preventing locally the oxidation of hydrazine.

Apart from typical stair-shaped events (91% of all events), we also observe in rare occasions square-shaped events (5% of all events) as well as spike-shaped events (4% of all events). Examples of these events are shown in Supporting Information (Figure S5 in SI). The staircase-shaped events are attributed to GNPs irreversibly absorbing on the Pt surface. The square-shaped events are attributed to GNPs that are first adsorbing on the Pt surface and then leaving in solution. These two kinds of events are also observed for "blocking" type experiments with polystyrene beads [13]. The spike-shaped events are possibly caused by GNPs bouncing on the UME surface and thus displaying a short residence time (0.13 ± 0.04 s on average). Spike-shaped current events are also reported for gold nanoparticles bouncing at the surface of gold electrodes modified with self-assembled monolayers of alkanethiols [45]. In the following sections, we will focus on the "sticking" GNPs.

The ideal shape of the current events allows a precise measurement of $\Delta i/i_{ini}$. The histogram of the relative current step size is given in Figure S6 in SI. However, the quantitative analysis of the step-size is rendered difficult by the inhomogeneity of the shape and size of the GNPs as well as the edge effect always present on a disk-shaped electrode [12]. Numerical simulations of "ideal" GNPs having a disk shape and blocking the center and the edge of the UME were carried out. Details about the simulation can be found in Supporting Information. We found that GNPs between

0.5 and 3.5 µm in diameter could produce the minimum and maximum relative current steps observed in the chronoamperograms. This range of size is significantly lower than the size distribution obtained by SEM (c.a. 0.6 – 20 µm). In order to understand this discrepancy, we monitored optically (using bright field microscopy) the solution containing the GNPs directly after dispersion. We found that GNPs between 4 and 20 µm sediment within two minutes (time scale of our experiments) on the bottom of the cell (see Figure S9 in SI). Since our UME is facing downward, it is expected that the sedimentation of the large GNPs will hinder their collision.

### 3.3 Collision frequency vs. concentration of GNP

The average frequency of collision at 0 V is plotted as a function of the concentration of GNP in

Figure **3**. The frequency of collision was calculated from 11 individual chronoamperometric experiments and we only counted the first six collisions to minimize a possible effect of GNP stacking on the electrode. Representative chronoamperograms for different concentrations of GNP in solution are given in Figure S10 in SI. The collision frequency is in the range of 0.2 Hz to 0.8 Hz. It increases with the concentration of GNP and then seems to saturate at a concentration above 140 fM. The deviation from linearity (expected for diffusion-drift mass transport) could be caused by the aggregation and subsequent sedimentation of the GNP. Such deviation is also reported for the collision frequency of Pt nanoparticles on Hg UMEs [46, 47]. In that case, collision frequencies lower than expected were also explained by the poor stability of the particles [47]. In a nutshell, the stability of the colloidal suspension is of crucial importance to accurately determine the concentration.

The collision frequency is related to the origin of the GNP transport in the electrolyte. The arrival of the GNPs to the Pt surface cannot be ensured by diffusion because the estimated value of the collision frequency at 35 fM is of the order of 0.05 mHz at 0 V (see SI) which is lower by more than 3 orders of magnitude than the measured value (0.2 Hz). GNP migration should then play a major role. Indeed, GNPs are charged (the zeta-potential is $\zeta$-V = 32.5 ± 0.3 mV under our experimental conditions) and the ionic strength is kept extremely low (~40 µM). The expected value of the collision frequency induced by migration at 35 fM is 1.8 Hz (see SI). The theoretical frequency of collision is nine times higher than the experimental frequency of collision (0.2 Hz). As discussed previously, the suspension of GNP is unstable and thus the nominal concentration is larger than the concentration of GNP dispersed in solution. The collision frequency would be overestimated in proportion to the error on the concentration of GNP. Another factor to consider is the local ionic strength decreasing the contribution of migration to the collision frequency. Indeed, we evidenced a local decrease of the pH by several units of pH indicating an ionic strength significantly larger near the UME than in the bulk.

We also measured the average collision frequency (more than twenty individual measurements) at potentials of -0.3 V, 0 V, 0.7 V and 1.0 V. The corresponding steady-state currents / frequency of collision are c.a. 2 nA / 0.10 Hz, 4 nA / 0.20 Hz, 9 nA / 0.24 Hz and 11 nA / 0.24 Hz, respectively. We observe a clear increase of the collision frequency with potential, which seems to saturate at 0.7 V. In a migration dominated mass transport, the collision frequency is expected to increase proportionally with the current. The experimental trend significantly deviates from this linear dependence. In a similar way to what has been shown above, the saturation of the collision

frequency may be ascribed to the local increase of the ionic strength due to the release of protons during hydrazine oxidation.

### 3.4 Step size vs. potential

The histograms of the normalized size distribution of the relative current step (i.e., the current step, $\Delta i$, divided by the current right before the step, $i_{ini}$) are plotted in

Figure **4** for four different potentials. Typical chronoamperograms at different potentials are given in SI (Figure S11 and Figure S12). About 200 negative steps (for each potential) were recorded to provide a statistically significant description of the magnitude of the current steps and investigate the effects of the potential. Each experiment corresponds to a freshly polished Pt UME. In order to avoid the formation of multilayers, only the first six collisions are counted, considering that an "ideal" GNP is a disk with a diameter of 4.2 μm and has a surface area of 13.8 $\mu m^2$, around six times smaller than the Pt surface (78.5 $\mu m^2$).

The trend observed in

Figure **4** is the shift of the current distribution to lower values with increasing potentials, as indicated by the green dash arrow. This shift is small at 0.7 V (blue symbols) but significant at 1 V (orange symbols). We calculated the average, median, and distribution range obtained for each histogram (Table 1). The average (and median) step size is constant between 0.3 V and 0 V and then decreases by 15% (respectively 24%) as the potential increases from 0 V to 0.7 V (respectively 1 V).

**Table 1.** The statistical description of the magnitude of the negative steps at different bias potentials.

| Potential (V) | Counts | Average (‰) | Median (‰) | *Range (‰) |
|---|---|---|---|---|
| -0.3 | 201 | 8.0 | 5.3 | 1 to 55 |
| 0 | 198 | 8.0 | 5.4 | 1.1 to 54 |
| 0.7 | 202 | 6.8 | 4.5 | 0.7 to 42 |
| 1.0 | 210 | 6.1 | 3.7 | 0.6 to 39 |

* For 95% of the range (for all the potentials) the maximum step is about 21‰.

In order to understand the variation of the average step size, as a function of the potential we will examine the kinetics of hydrazine oxidation on Pt and carbon.

Figure **5**A shows the adimensional voltammograms (forward scan only) corresponding to hydrazine oxidation on Pt (black curve) and C-fiber (red curve), a proxy for the surface of the GNPs. The blue curve, $\Delta i$, represents the current difference between hydrazine oxidation on Pt and C-fiber. The trace corresponding to $\Delta i$ overlaps with the voltammogram of the Pt UME from the onset potential of hydrazine oxidation (-0.65 V) to the inflection point (0.25 V). As the potential rises above 0.25 V, this current difference decreases with increasing potentials. In principle, this difference should fall down to zero for sufficiently large potentials where the oxidation of hydrazine becomes limited by diffusion instead of electron transfer.

To correlate the kinetic difference between Pt and GNP with the change of the current step size as a function of potential, we plot in black in

Figure **5**B the ratio of $\Delta i$ and the current on Pt ($i_{Pt}$). The quantity $\Delta i/i_{Pt}$ would correspond to a situation where a 5 μm radius carbon disk completely covers our 5 μm radius Pt UME. From -0.8 V to -0.6 V the quantity $\Delta i/i_{Pt}$ varies abruptly with a discontinuity at -0.7 V caused by a crossing of

the X-axis. The variations observed at these potentials are caused by extremely small variations of the baseline current and will not be discussed further. Importantly, the quantity $\Delta i/i_{Pt}$ equals 1 up to 0 V and decreases with increasing potential due to the oxidation of hydrazine on the C fiber. The potential dependence of this curve is directly correlated with the kinetics of hydrazine oxidation on the C fibre since the hydrazine oxidation current on Pt is constant in this potential range (diffusion limited). The red points in

Figure **5**B represent the average relative step size corresponding to GNPs colliding on the Pt UME. They are associated with the right red scale chosen in a way that the average step size at 0 V and -0.3 V coincides with the value of 1 in the black curve, and that the relative range is identical to the left black scale. This choice of scale allows a comparison of the differences in kinetics independently of the difference in size between the UME and the GNPs. The red line is a logistic function adjusted on our experimental point in order to guide the eyes. The trend evidenced by collision (red points) is similar to the trend observed by cyclic voltammetry, that is first a plateau and then a decrease of the relative kinetic difference for large overpotentials. This trend is directly related to the kinetics of hydrazine oxidation on GNP since the current on Pt is constant in this potential range. Since the data points correspond to the average amplitude of the collision current step, the measured kinetics is an averaged value over the GNP size distribution and collision position on the Pt UME. The shift (~70 mV) between the red points ($\Delta i/i_{ini}$ for GNP collision) and the black curve indicates slower kinetics of hydrazine oxidation on GNP than on C fiber. This observation is in agreement with a separate set of experiments evidencing kinetic blocking of hydrazine oxidation by GNP colliding on C-fiber UMEs (see Figure S2 in SI).

As mentioned above, the estimated hydrazine oxidation kinetics on GNP is an average value. Obtaining such information on single GNP requires (i) to determine the size and the position on the Pt UME of the GNP, and (ii) to perform numerical simulations of the GNP with its size and position to determine the expected collision current step. This is out of the scope of this work.

## 4. Conclusion

We report a strategy, electro-catalytic depression, based on the intrinsic difference in electron transfer kinetics between materials to detect poorly catalytic particles such as GNPs. We show that our approach leads to the detection of individual GNPs of a few µm in length suspended at the concentration of 35 fM. More than 90% of the collisions lead to the irreversible adsorption of the GNP on the Pt surface. The current steps can be analyzed based on models already developed for insulating particles and the variation of their magnitude as a function of the potential can be rationalized with respect to the intrinsic difference in kinetics between the electrode and GNPs. We also show that despite measuring well-defined current signals (staircase-shape, low noise), a large dispersion of size and shape of the GNP, the poor stability of the GNP suspension, interactions between GNPs adsorbed on the electrode and the edge effect should be carefully considered before attempting any quantitative analysis of the data. The ECD method is expected to be applicable to a large variety of particles thanks to the diversity of electrocatalytic reactions.

## Associated Content

**Supporting Information.** The following elements can be found in Supporting Information: effect of pH on the oxidation of hydrazine, the kinetics of hydrazine oxidation on GNP versus C-fiber,

characterization of the GNP size by SEM, the shape of the current events, numerical simulations about a disk-shaped GNP blocking at a Pt UME, sedimentation of large GNPs, collision frequency vs. concentration of GNP and step size vs. potential.

## Author Contributions

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

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## Figure captions

**Figure 1.** (A) Cyclic voltammograms recorded on a 5 µm radius Pt UME (red traces) and a 3.5 µm radius C-fiber UME (black traces). The continuous and dashed lines correspond to cyclic voltammograms recorded in the absence and the presence of 1 mM hydrazine, respectively. [NaOH] = 10 µM, scan rate = 20 mV/s. (B) The size distribution of GNPs is obtained by SEM. The inset is a typical SEM picture of GNPs adsorbed on glassy carbon. Because GNPs do not have a well-defined geometry, the "size" of each GNP is estimated by averaging the longest and shortest axes. Total number of GNP = 702, bin size = 1 µm. The black line is the best fit of a Gaussian function. The center, standard deviation, and $R^2$ are 4.2 µm, 2.5 µm, and 0.98, respectively.

**Figure 2**. (A) Chronoamperograms recorded in the absence (black trace) and the presence (red trace) of 35 fM GNPs on a 5 µm radius Pt UME. The UME is biased at 0 V and the solution contains 1 mM hydrazine and 10 µM NaOH. (B) Zoom on typical current events recorded in the same condition as (A). (C) Scheme illustrating the collision of GNP on Pt UME.

**Figure 3**. Average frequency of collision (the error bars represent the standard deviation of eleven individual experiments) as a function of the concentration of GNP. Only the first six collisions are counted on each chronoamperogram. The 5 µm radius Pt UME is biased at 0 V and the solution contains 1 mM of hydrazine and 10 µM of NaOH.

**Figure 4**. Plots showing the normalized size distribution of the relative current steps caused by GNPs colliding on a 5 µm radius Pt UME under different potentials at an orange curve: 1.0 V, 210 counts, blue curve: 0.7 V, 202 counts, red curve: 0 V, 198 counts, black curve: -0.3 V, 201 counts, respectively. Bin size = 3.5, the points show the center of each bin and the maximum range is limited to 24.5‰ in order to better compare the data, accounting the majority of the data (over 96% of total counts). In each chronoamperogram, only the first 6 GNPs colliding on a bare UME are counted to avoid the effect of GNP stacking. [GNP] = 35 fM in 1 mM hydrazine and 10 µM NaOH.

**Figure 5**. (A) Difference between the adimensional linear voltammograms of Pt and C-fiber. Data is taken from Figure 1A, and normalized by the diffusion-limited steady-state current from Eq. 1. The black curve and the red curve correspond to the hydrazine oxidation occurring on a Pt UME and a C-fiber UME with the same radius as Pt. The Blue curve is the kinetic difference between the adimensional currents measured on Pt ($i_{Pt}$) and on C-fiber ($i_{C\text{-}fiber}$). (B) Left *y*-axis: The kinetic difference of hydrazine oxidation ($\Delta i$) on Pt versus C-fiber is divided by the current on Pt ($i_{Pt}$). The $\Delta i/i_{Pt}$ varies with the potential. The cross line close to -0.6 V is due to the intersection of non-faradaic currents on Pt and C-fiber. Right *y*-axis: the red points correspond to the relative current step size at different potentials given in Table 1, and the red curve is a fit of a logistic function performed only to guide the eyes.