

Potential-Controlled Current Responses from Staircase to Blip in Single Pt Nanoparticle Collisions on a Ni Ultramicroelectrode

A Ram Jung, Sangmin Lee, Jin Woo Joo, Changhwan Shin, Hyeonhu Bae, Sun Gyu Moon, and Seong Jung Kwon*

Department of Chemistry, Konkuk University, 120 Neungdong-ro, Gwangjin-gu, Seoul 143-701, Korea

S Supporting Information

ABSTRACT: Collisions of electrocatalytic platinum (Pt) single nanoparticles (NPs) with a less electrocatalytic nickel (Ni) ultramicroelectrode (UME) surface were detected by amplification of the current by electrocatalysis of NPs. Two typical types of current responses, a current staircase or blip (or spike), in single NP collision experiments were observed at a time with a new system consisting of Pt NP/Ni UME/hydrazine oxidation. The staircase current response was obtained when the collided NPs were attached to the electrode and continued to produce electrocatalytic current. On the other hand, the blip current response was believed to be obtained when the NP attached but was deactivated. The different current responses depend on the different electrocatalytic reaction mechanism, characteristics of the NP, or the electrode material. How the deactivation of the electrocatalytic process affects on the current response of NP collision was investigated using the Ni UME. The current response of a single Pt NP collision is controllable from staircase to blip by changing the applied potential. The current response of the Pt NP was observed as a staircase response with 0 V (vs Ag/AgCl) and as a blip response with 0.1 V (vs Ag/AgCl) applied to the Ni UME.

Studying the electrocatalytic or other properties of nanoparticles (NPs) in a single NP level is very challenging due to the difficulty of identifying the small signal among the noise. The electrocatalytic ability or reaction mechanism of a single NP can be interpreted using a recently developed electrocatalytic amplification method by the Allen J. Bard group, using single metal or metal oxide NP collision on an ultramicroelectrode (UME) with electrocatalytic signal amplification.¹ The Compton group^{2–4} and many other groups^{5–7} are developing this technique with various NPs, UMEs, and reactions.

For the first time, an electrocatalytic current increase was observed when single platinum (Pt) NP collided with gold (Au) UME to electrocatalyze a hydrazine oxidation reaction.^{1,8,9} The current response of NP collision for this system was staircase-shaped, and the Pt NPs are considered to be attached to the Au UME, with continued catalysis of the hydrazine oxidation reaction resulting in a stepwise current increase. Later, iridium oxide (IrO_x) NP collision on a Pt or Au UME was also observed by the same method toward a water oxidation reaction.^{10–12} In this case, a blip current response was obtained whenever the NP collided with the UME surface. Discussions regarding the cause

of the blip response of the IrO_x NP system have led to the understanding that the deactivation of the struck NP is responsible for the current decay of the blip response.^{11,12} An oxygen, a product of the electrocatalytic water oxidation reaction by IrO_x NP, is believed to be a cause of the deactivation of IrO_x NP's electrocatalytic reaction in this system.¹² The oxygen on the surface of NP can induce a blockage of mass transfer that is responsible for the electrocatalytic current decay.^{13,14}

Recently, there was a report for the observation of a blip response from a Pt NP system by the Stevenson group.^{15,16} However, it was obtained using a specially employed mercury (Hg) electrode on which the NP can be sunk or amalgamated, so the Pt NP loses their contact with the reactant or activity. When the Pt NP strikes on the solid UME, except the above liquid electrode, the Pt NP is still understood to maintain electrocatalysis of the hydrazine oxidation reaction on solid electrode surface, resulting in a staircase response.

The current responses of single NP collision event depend on many variables: mechanism, reactant, or product of electrocatalytic reaction, interaction between NP and UME, surfactant of NP, electrolyte, or applied potential, etc. So it is interesting to investigate the origin of the frequency, amplitude, or shape of the current response of single NP collision and how to control that. We focus on the reaction product among them. The hydrazine oxidation by Pt NPs produces a gas phase product, nitrogen, similar to the oxygen gas that is produced by the IrO_x NP system mentioned above. So we thought that if the gas phase product plays an important role in deactivation, then the Pt NP system also could be considered a blip response, basically as the IrO_x NP system. Therefore, the staircase response observed in Pt NP system can be explained as a kind of blip response accompanying slow current decay. Then, the kinetics of production of gas phase product from the NP surface should be related to the chronological electrocatalytic current decay, and the kinetics of current decay will determine the type (staircase or blip) of current transient.

To identify the relation between kinetics of product production and current response of Pt NP collision experiment, more flexible experimental conditions especially in available potential window are required for the control of electrocatalytic reaction. Therefore, new electrode materials that are more available over various experimental conditions were investigated instead of the previously used Au UME to be restricted by the narrow potential windows available for the Pt NP collision

Received: November 19, 2014

Published: January 21, 2015

observation. Previously, carbon UME⁸ and boron-doped diamond (BDD) UME⁷ are substituted Au UME for applying higher potential due to the low electrocatalytic activity of carbon and BDD. On the carbon UME with higher applied potential, the current response of Pt NP for the hydrazine oxidation was still recorded as staircase without any special change. But the current response frequency was very sensitive to the hydrophobicity of carbon surface. In the use of BDD UME, the current event was intricately up and down. So the distinction of signal by each NP's collision was impossible for this case.

Therefore, Ni was chosen for this experiment due to its low electrocatalytic activity for the hydrazine oxidation^{17,18} and convenient preparation of the UME, though a Ni or Ni oxide electrode is not more widely used as a working electrode in general electrochemical experiments than a Au or Pt electrode due to its corrosive property in acid or alkaline aqueous solution or sensitivity toward chloride ions.¹⁹ One additional advantage of introducing Ni as an UME is the electrocatalytic effect of bimetallic property of the contact point between Pt NP and Ni UME. It is reported that Ni–Pt or Ni-based bimetallic nanocatalysts exhibit excellent catalytic activity to the decomposition of hydrazine.^{20–22} Therefore, it is expected additional signal amplification by the hot spot when the Pt NP collide on the Ni UME.

Here, the change of current response from staircase to blip in the single Pt NP collision was successfully recorded using Ni UME by controlling the reaction kinetics which depends on the applied potential.

For successive observation of Pt NP collision on Ni UME, an appropriate potential where the electrocatalytic reaction occurred more on the Pt NP than on the Ni UME should be chosen and applied to the UME. To determine the potential, the electrocatalytic availability of bare metal UMEs for the hydrazine oxidation was investigated by cyclic voltammetry (CV).

As shown in Figure 1, hydrazine electro-oxidation was much weaker in Ni UME than with Au or Pt UMEs. The onset

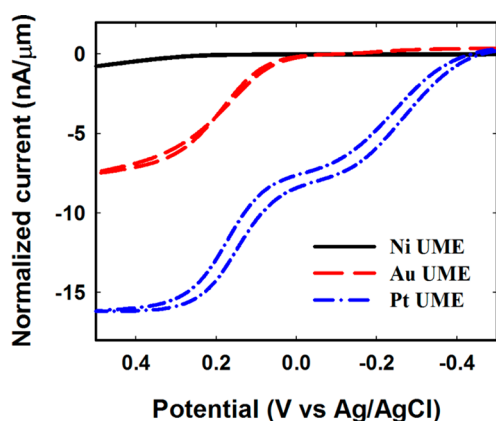


Figure 1. Cyclic voltammograms of hydrazine oxidation on Ni (black solid), Au (red dashed), or Pt (blue dash-dotted) UME (radius 12.5, 5, and 5 μm , respectively) in a 50 mM phosphate buffer (pH 7) containing 8.7 mM hydrazine. Normalized current means current divided by electrode radius.

potentials are -0.4 V (vs Ag/AgCl), 0 V, and 0.2 V for Pt, Au, and Ni UME, respectively. In previous studies, the Au UME was employed for the detection of Pt NP collision.^{1,8} The onset potential of hydrazine oxidation on Au UME was ~ 0 V; as a result, the applied potential window from -0.2 to 0 V was

practically available for the observation of a single Pt NP collision on the Au UME. Considering the two step electro-oxidation of hydrazine on the Pt UME, which is depicted in Figure 1, only the first process of hydrazine oxidation is available on the collided Pt NP in this potential window region.

An available applied potential expands with Ni UME up to around 0.2 V where the second step process of hydrazine oxidation on Pt NP is possible due to the lower electrocatalytic activity of Ni than Au. Later, we will discuss how this second step process is related to the shape of current transient.

Consequently, much increased amplified current of the Pt NP with higher applied potential was expected by employing Ni UME and it makes the signal of Pt NP collision clear. The less electrocatalytic Ni UME is better than Au UME for clear distinction of the collision peak from noise, resulting in increased sensitivity in signal detection.

As shown in Figure 2, the current transient of a single Pt NP (diameter ~ 4 nm, see Figure S1) collision was investigated at

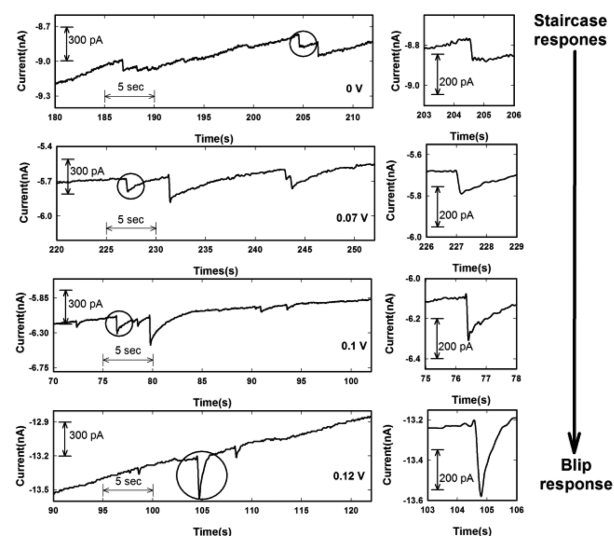


Figure 2. Chronoamperometric curves for single Pt NP collisions at different applied potentials (0, 0.07, 0.1, and 0.12 V) of Ni UME in a 50 mM phosphate buffer (pH 7) containing 8.7 mM hydrazine. The Pt NP concentration was 1.79 nM, and the data acquisition time was 50 ms.

various applied potentials using Ni UME (diameter 25 μm). A more amplified current was observed as expected at a higher applied potential. However, not only the current magnitude but also the shape of the current transient changed depending on the applied potential on the Ni UME. The shape of the current transient was a staircase shape at 0 V, similar to a typical current transient of the Pt NP system shown in previous studies using Au UME.^{1,8} However, the current transient changed to an unexpected blip response at a 0.12 V applied potential.

Whereas the staircase response is considered to result from the adhered NP continuing its electrocatalytic reaction, the blip response was obtained by the attached NP undergoing deactivation. Therefore, the blip/staircase responses are posited to be created by the same attachment process with/without accompanying deactivation. The change in current transient depending on the applied potential indicates that the deactivation process depends on the kinetic of electrochemical reaction. However, the obvious shape change of the current transient by the applied potential in the Pt NP/Au UME/hydrazine oxidation system was not previously reported because

the available potential window was limited by the magnitude of background current of the UME. In some previous Pt NP collision data using Au UME showed slight decay of the staircase response, but this seems that the staircase response laid on the sloped background.^{1,8,23}

By employing the less electrocatalytic Ni UME, the applied potential can vary more widely, so the Pt NP collision signal change obviously from staircase shape to blip response by increasing applied potential was observed, as shown in Figure 2. This observation is very interesting because the staircase and blip responses were previously believed to be caused by different mechanisms.^{2,10,15} The two different current responses had been obtained in different systems. However, in this work the two different responses were observed in one system by only changing the applied potential.

In a blip response system consisting of IrO_x NP/Pt UME/water oxidation, the slight current decay rate change was observed depending on the applied potential in a low electrolyte condition.¹² All blip responses at various applied potential had same order of charge transfer during a single transient, although the blip response was broader at a lower applied potential and narrower at a higher applied potential. It implies that the current decay, i.e., the deactivation of the NP, is related to the electrochemical reaction kinetics, and the deactivation process is completed after a certain amount of charge transfer. Thus, it indicated that the deactivation occurred by the reaction product, like the feedback in biology; when the electrochemical reaction is fast, the products are also produced rapidly and the deactivation becomes fast, too. The reaction product, oxygen, is assumed to be the reason for the electrocatalytic current decay by blocking the electrocatalytic reaction.

As like the water oxidation by IrO_x NP, the hydrazine oxidation by Pt NP also produces a gaseous product, nitrogen. So, we first paid attention to this gas phase because if the gas bubble is formed on the surface of NP, then it can block the mass transfer or induce additional overpotential. Recently, the White group suggested that a bubble formation on the nanoscale electrode surface depends upon whether the concentration of the gaseous product near the surface of the NP exceeds a critical concentration at which supersaturated gas nucleates.^{24,25} According to this, the critical factor for the bubble formation, which is probably the reason for a blip response in our experiment, is the bulk concentration of reactant. When the bulk hydrazine concentration is high enough, the critical supersaturation concentration for the bubble formation is obtained and results in current decay. Therefore, control experiments at various concentrations of hydrazine were performed to investigate whether the nitrogen is responsible for the deactivation by bubbling. As shown in Figure S2, the staircase shape at 0 V in lower concentration of hydrazine is transformed to a blip shape in higher concentrations of hydrazine. However, it is unsure whether the deactivation is done by bubble or not.

Another control experiment was tried using a specially designed cell with inverted bare Pt disk electrode (radius ~250 μm) to analyze bubble production with the same potential was applied on the Pt disk electrode (see the SI for detail explanation). As shown in Figure S3, the blip-like current response was obtained only at 0.1 V applied Pt electrode, and it was synchronized to the bubble evolution.

The mechanism of hydrazine electro-oxidation on Pt is complex. Various adsorbed reactant and intermediates have been suggested depending on platinum facet and electrolyte composition/pH.^{26,27} Therefore, the special intermediate or

reaction condition is another consideration as a reason for the blip response. By employing Ni UME as a supporting electrode, the available applied potential to the Pt NP expands more than 0.05 V where the second step process of hydrazine oxidation in Figure 1 is possible. The second step process seems strongly related to the shape of current transient by considering experimental result. Therefore, the poisoning of Pt by the product or intermediate^{28–32} at the second step process may be the reason for deactivation of hydrazine oxidation on Pt NP. As shown in Figures S2, S4, and S5, the stepwise CV of hydrazine oxidation at Pt UME changed the form depending on the hydrazine concentration, buffer capacity, or pH. If the current at a certain potential (0 or 0.1 V) is decreased to the first steady-state current level by changing on a variable, the staircase response is obtained. The other way, if the current is increased to the second steady-state current level by changing a variable, the blip response is obtained. Also, Figure S8 shows the current decay in bare Pt UME was accelerated more in 0.1 V than in 0 V.

Therefore, we suggest the deactivation is possible by a special intermediate or product of the second step process or by the bubble formation at the potential above ~0.1 V.

The effect of the current transient shape on the collision frequency was also investigated. The frequencies of the single Pt NP collision at 0 (staircase response) or 0.1 V (blip response) applied to Ni UME were investigated as shown in Figure 3. Even though the current response was changed by the applied potential on UME, the collision frequency was independent of the applied potential (Figure S9). This means that both responses are based on the same collision behavior such as sticking collision. However, the collision frequency was ~4 orders of magnitude lower than the value calculated by the Fick's law:^{8,11}

$$f_p = 4K_{\text{ads}}r_{\text{UME}}D_{\text{NP}}C_{\text{NP}}$$

where K_{ads} is adsorption coefficient, r_{UME} is radius of UME, D_{NP} is diffusion coefficient of NP, and C_{NP} is concentration of NP. The lower frequency should be due to the aggregation of Pt NP in hydrazine solution³³ and lower adsorption coefficient between Pt NP and Ni UME.

The height of current transients with a bias of 0 or 0.1 V demonstrated in Figure S10. The calculated value^{8,11} for the single ~4 nm sized Pt NP is ~33 pA. The experimentally observed average height of current transients was ~166 pA. This can be explained by the aggregation of Pt NP or by the synergetic effect of bimetallic property of contact point of Pt NP collision on Ni UME.

In conclusion, Ni UME is employed as a new UME and is available in a wide potential window for single Pt NP collision observations. Interestingly, the current response of a single Pt NP collision changed from staircase shape to blip depending on the applied potential. The staircase current response was observed at 0 V applied to Ni UME, and the blip current response was observed at ~0.12 V applied to Ni UME. By analyzing the current decay as a function of the applied potential, the single NP collision systems produced a staircase-shaped or blip response caused by the same attached NPs on the UME, with the difference being the speed of the deactivation processes.

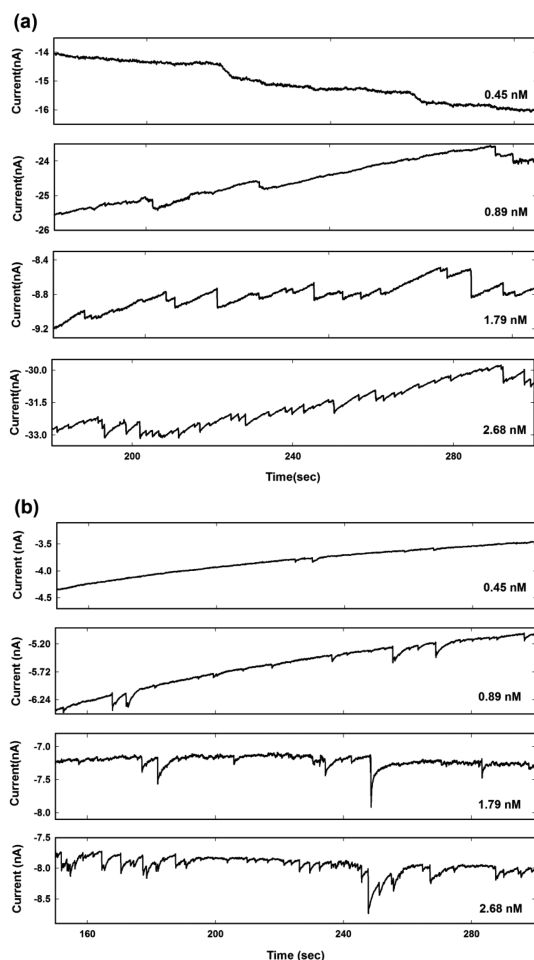


Figure 3. Chronoamperometric curves for single Pt NP collisions on Ni UME (radius $12.5 \mu\text{m}$) in 50 mM phosphate buffer (pH 7) containing 8.7 mM of hydrazine and different concentrations of Pt NPs from 0.45 to 2.68 nM. The applied potential is (a) 0 and (b) 0.1 V vs Ag/AgCl, and the data acquisition time is 50 ms.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental details and additional experimental data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*sjkwon@konkuk.ac.kr

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT and Future Planning (NRF-2012R1A1A1040285 and 2009-0082580) and by TJ Park Science Fellowship of POSCO TJ Park Foundation.

■ REFERENCES

- (1) Xiao, X.; Bard, A. J. *J. Am. Chem. Soc.* **2007**, *129*, 9610–9612.
- (2) Zhou, Y.-G.; Rees, N. V.; Compton, R. G. *Angew. Chem., Int. Ed.* **2011**, *50*, 4219–4221.

- (3) Zhou, Y.-G.; Rees, N. V.; Pillay, J.; Tshikhudo, R.; Vilakazi, S.; Compton, R. G. *Chem. Commun.* **2012**, *48*, 224–226.
- (4) Zhou, Y.-G.; Rees, N. V.; Compton, R. G. *Chem. Commun.* **2012**, *48*, 2510–2512.
- (5) Fosdick, S. E.; Anderson, M. J.; Nettleton, E. G.; Crooks, R. M. *J. Am. Chem. Soc.* **2013**, *135*, 5994–5997.
- (6) Kleijn, S. E. F.; Lai, S. C. S.; Miller, T. S.; Yanson, A. I.; Koper, M. T. M.; Unwin, P. R. *J. Am. Chem. Soc.* **2012**, *134*, 18558–18561.
- (7) Wakerley, D.; Guell, A. G.; Hutton, L. A.; Miller, T. S.; Bard, A. J.; Macpherson, J. V. *Chem. Commun.* **2013**, *49*, 5657–5659.
- (8) Xiao, X.; Fan, F.-R. F.; Zhou, J.; Bard, A. J. *J. Am. Chem. Soc.* **2008**, *130*, 16669–16677.
- (9) Xiao, X.; Pan, S.; Jang, J. S.; Fan, F.-R. F.; Bard, A. J. *J. Phys. Chem. C* **2009**, *113*, 14978–14982.
- (10) Kwon, S. J.; Fan, F. R. F.; Bard, A. J. *J. Am. Chem. Soc.* **2010**, *132*, 13165–13167.
- (11) Kwon, S. J.; Zhou, H.; Fan, F.-R. F.; Vorobyev, V.; Zhang, B.; Bard, A. J. *J. Phys. Chem. Chem. Phys.* **2011**, *13*, 5394–5402.
- (12) Kwon, S. J.; Bard, A. J. *J. Am. Chem. Soc.* **2012**, *134*, 7102–7108.
- (13) Gabrielli, C.; Huet, F.; Keddam, M.; Macias, M.; Sahar, A. J. *Appl. Electrochem.* **1989**, *19*, 617–629.
- (14) Dukovic, J.; Tobias, C. W. *J. Electrochem. Soc.* **1987**, *134*, 331–343.
- (15) Dasari, R.; Robinson, D. A.; Stevenson, K. J. *J. Am. Chem. Soc.* **2013**, *135*, 570–573.
- (16) Dasari, R.; Walther, B.; Robinson, D. A.; Stevenson, K. J. *Langmuir* **2013**, *29*, 15100–15106.
- (17) Asazawa, K.; Yamada, K.; Tanaka, H.; Taniguchi, M.; Oguro, K. *J. Power Sources* **2009**, *191*, 362–365.
- (18) Ayoub, H.; Griveau, S.; Lair, V.; Brunswick, P.; Cassir, M.; Bedioui, F. *Electroanalysis* **2010**, *22*, 2483–2490.
- (19) Suzuki, T.; Yamada, T.; Itaya, K. *J. Phys. Chem.* **1996**, *100*, 8954–8961.
- (20) Singh, S. K.; Xu, Q. *Inorg. Chem.* **2010**, *49*, 6148–6152.
- (21) Cao, N.; Yang, L.; Du, C.; Su, J.; Luo, W.; Cheng, G. *J. Mater. Chem. A* **2014**, *2*, 14344–14347.
- (22) Kuttiyiel, K. A.; Sasaki, K.; Choi, Y.; Su, D.; Liu, P.; Adzic, R. R. *Nano Lett.* **2012**, *12*, 6266–6271.
- (23) Park, J. H.; Boika, A.; Park, H. S.; Lee, H. C.; Bard, A. J. *J. Phys. Chem. C* **2013**, *117*, 6651–6657.
- (24) Luo, L.; White, H. S. *Langmuir* **2013**, *29*, 11169–11175.
- (25) Chen, Q.; Luo, L.; Faraji, H.; Feldberg, S. W.; White, H. S. *J. Phys. Chem. Lett.* **2014**, *5*, 3539–3544.
- (26) Rosca, V.; Duca, M.; de Groot, M. T.; Koper, M. T. M. *Chem. Rev.* **2009**, *109*, 2209–2244.
- (27) Rosca, V.; Koper, M. T. M. *Electrochim. Acta* **2008**, *53*, 5199–5205.
- (28) Aldous, L.; Compton, R. G. *J. Phys. Chem. Chem. Phys.* **2011**, *13*, 5279–5287.
- (29) Garcia, M. D.; Marcos, M. L.; Velasco, J. G. *Electroanalysis* **1996**, *8*, 267–273.
- (30) Bard, A. J. *Anal. Chem.* **1963**, *35*, 1602–1607.
- (31) Anan'ev, A. V.; Boltoeva, M. Yu.; Sukhov, N. L.; Bykov, G. L.; Ershov, B. G. *Radiochemistry* **2004**, *46*, 578–582.
- (32) Ranney, J. T.; Gland, J. L. *Surf. Sci.* **1996**, *360*, 112–120.
- (33) Kleijn, S. E. F.; Serrano-Bou, B.; Yanson, A. I.; Koper, M. T. M. *Langmuir* **2013**, *29*, 2054–2064.