
Confined Electrochemical Behaviors of Single Platinum Nanoparticles Revealing Ultrahigh Density of Gas Molecules inside a Nanobubble

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Abstract: Understanding the basic physicochemical properties of gas molecules confined within nanobubbles is of fundamental importance for chemical and biological process. Here we successfully monitored the nanobubble-confined electrochemical behaviors of single platinum nanoparticles (PtNPs) at a carbon fiber ultramicroelectrode in HClO₄ and H₂O₂ solution. Owing to the catalytic decomposition of H₂O₂, a single oxygen nanobubble formed on individual PtNPs to block the active surface of particle for proton reduction and suppress their stochastic motion, resulting in significantly distinguished current traces. Furthermore, the combination of theoretical calculation and high-resolution electrochemical measurement allowed the size of nanobubble and the oxygen gas density inside a single nanobubble to be quantified. And the ultrahigh oxygen density inside (9286 kg/m³) was revealed, indicating gas molecules in a nanosized space existed with a high state of aggregation. Our approach sheds light on gas aggregation behaviors of nanoscale bubbles using single-entity electrochemical measurement.

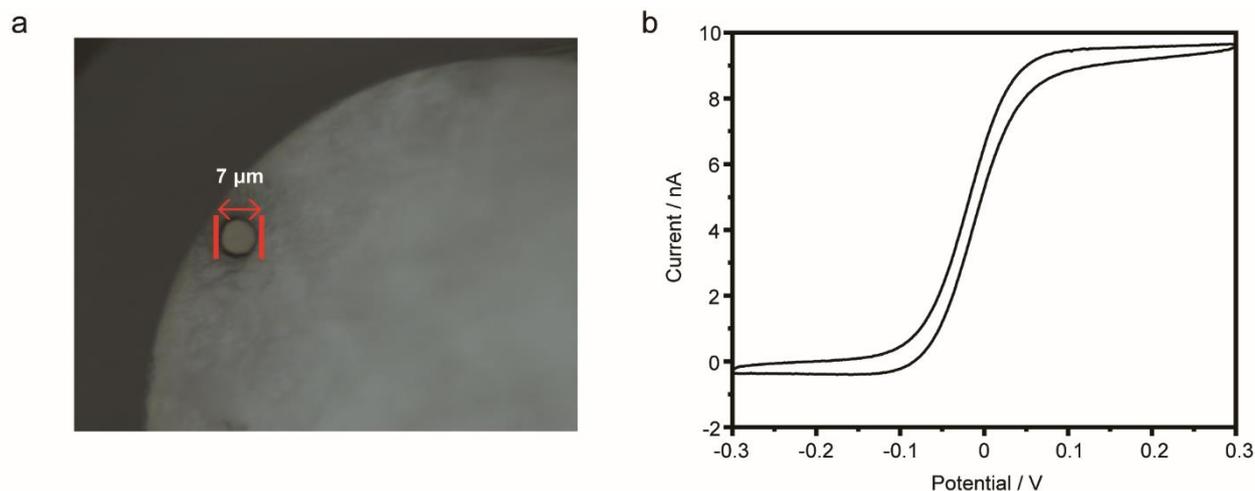
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Results and Discussion

1. Characterization

1.1 Characterization of Carbon Fiber Ultramicroelectrode (C UME):



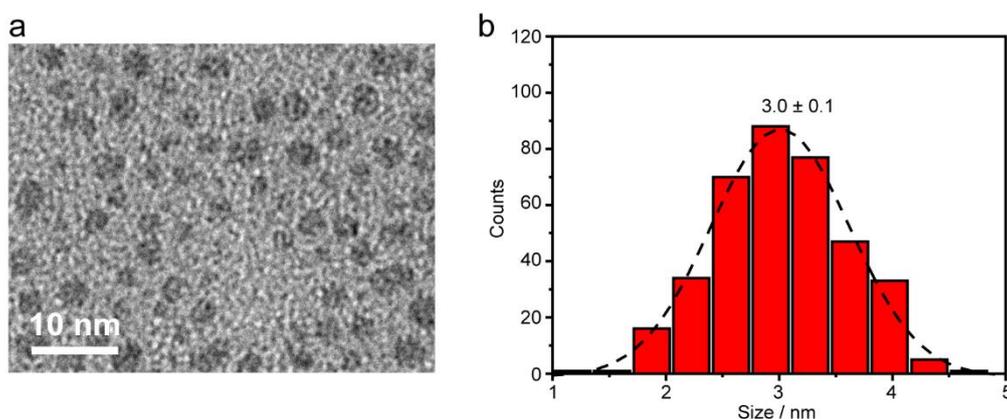
Supplementary Figure 1. Characterization of C UME. **a** Microscopic image of C UME. **b** Cyclic Voltammetry of Cn UME in 0.9 mM ferrocenylmethanol solution at a scan rate of 100 mV s⁻¹.

The disk UME surface was observed from the microscopic image of C UME (Supplementary Figure 1a). Furthermore, we estimated the radius of the C UME (r), using the limiting current by the Equation:

$$i = 4nFDCr \quad (1)$$

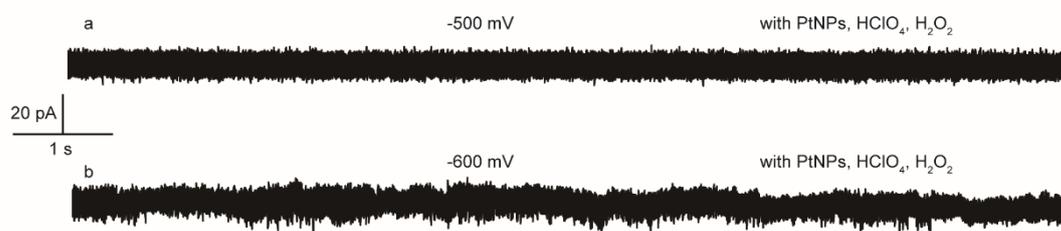
Where i is a mass transfer controlled limiting current, n is the number of electrons involved in the electrochemical reaction ($n = 1$ for oxidation of ferrocenylmethanol), F is the Faraday constant ($9.64853 \times 10^4 \text{ C mol}^{-1}$), D is the diffusion coefficient of ferrocenemethanol as a reacting species ($7.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) and C is the bulk concentration of the reacting ferrocenylmethanol solution (0.9 mM). From the limiting current, the radius of C UME was calculated to be 3.5 μm (Supplementary Figure 1b).

1.2 Characterization of PtNPs:

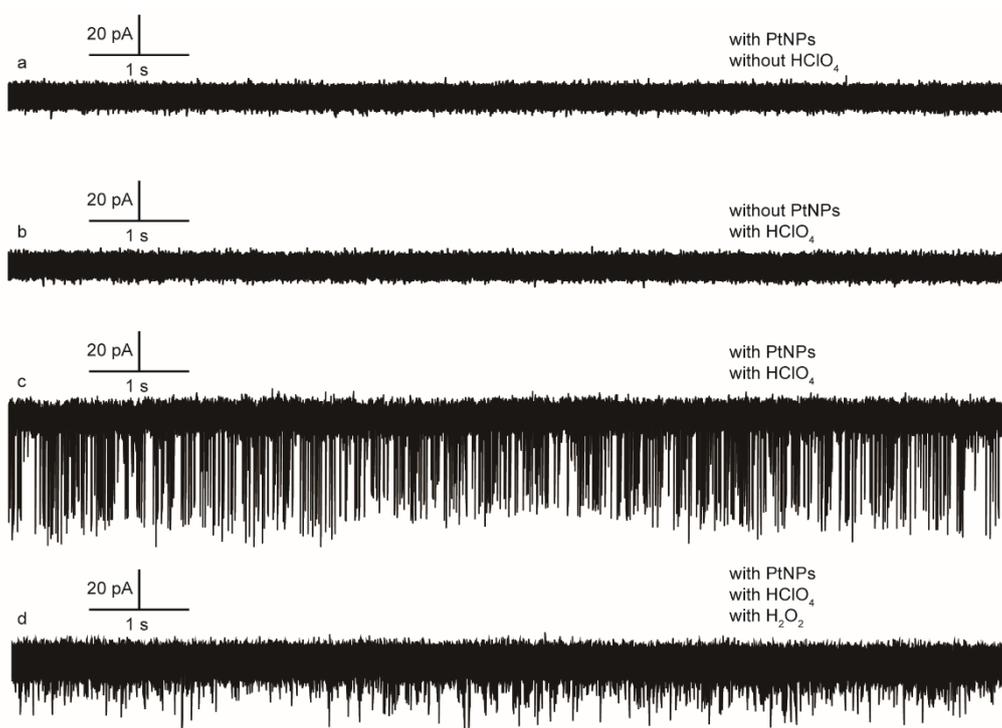


Supplementary Figure 2. TEM characterization of PtNPs. **a** TEM images of monodispersed PtNPs and **b** size distribution from the analysis of TEM images, in term of the particle diameters $3.0 \pm 0.1 \text{ nm}$.

2. Nanocollision Electrochemical Experiment of Single PtNPs



Supplementary Figure 3. Amperometric current-time curves of individual PtNPs at the applied potentials of **a** -500 mV and **b** -600 mV vs. Ag/AgCl wire in 50 mM HClO₄ and 2 mM H₂O₂ solution.



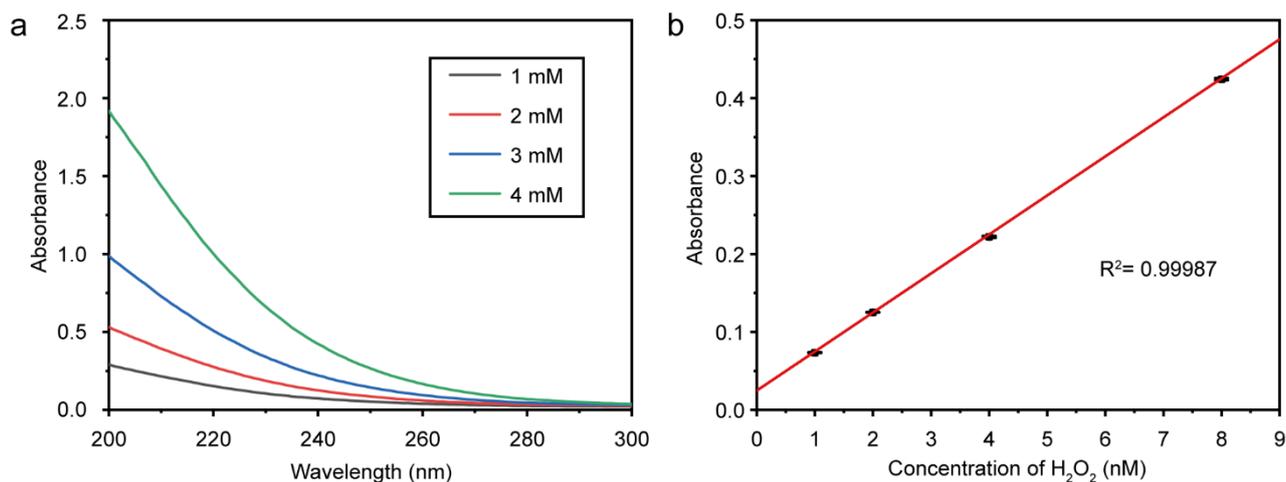
Supplementary Figure 4. Amperometric current-time curves of individual PtNPs at the applied potentials of -500 mV vs Ag/AgCl wire in 10 mM NaClO₄ solution **a** with PtNPs and without HClO₄, **b** without PtNPs and with 50 mM HClO₄, **c** with PtNPs and with 50 mM HClO₄, and **d** with PtNPs, 50 mM HClO₄ and 1 mM H₂O₂.

3. The rate of H₂O₂ decomposition at PtNPs

The concentration of H₂O₂ in the solution was determined by a spectrophotometric method based on Beer-Lambert law as previous work^[1]:

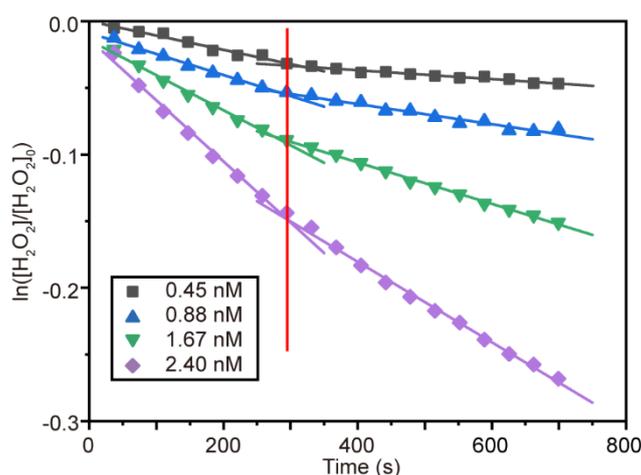
$$A = \epsilon LC \quad (2)$$

where A is the measured absorbance, ϵ is the wavelength-dependent molar extinction coefficient ($(\epsilon_{H_2O_2}) = 43.6 \text{ M}^{-1} \text{ cm}^{-1}$ at 240 nm), L is the path length and C is the concentration. In order to obtain absorbance in an analytically meaningful range of 1 - 4 mM. H₂O₂ showed a broad absorbance peak at 240 nm in the UV spectra (Supplementary Figure 5a). A calibration curve with good correlation coefficients ($R^2 = 0.99987$) indicated that the measured absorbance at 240 nm could be used for adequately converting the absorbance readings to the concentration of H₂O₂ (Supplementary Figure 5b).



Supplementary Figure 5. a The absorbance spectra of H₂O₂ at various concentrations and **b** calibration curve for H₂O₂.

4. The formation time of nanobubble at PtNPs



Supplementary Figure 6. Decomposition of H₂O₂ catalyzed by PtNPs. A plot of $\ln([\text{H}_2\text{O}_2]/[\text{H}_2\text{O}_2]_0)$ against decomposition time of H₂O₂ at various concentrations of 3 nm PtNPs.

The formation time of O₂ nanobubble was determined by monitoring the UV-vis absorbance peak at 240 nm. As is shown in fig. 6, $\ln([\text{H}_2\text{O}_2]/[\text{H}_2\text{O}_2]_0)$ is linearly related to decomposition time before and after 300 s, indicating the decomposition of H₂O₂ at various concentration of PtNPs were all fitted well based on the first-order kinetics. Before 300 s, the slopes of curves represents the decomposition rate constant on overall PtNPs surface at various concentrations of PtNPs. After 300 s, the decomposition rate of H₂O₂ significantly decreased. This is because that O₂ nanobubble formed on individual PtNPs blocked the active particle surface for catalytic chemical decomposition of H₂O₂. Therefore, O₂ molecules accumulated inside nanobubble can be obtained from integrating the produced O₂ molecule across 300 s.

References

[1] Yu, W., Batchelor-Mcauley, C., Chang, X., Young, N. P. & Compton, R. G. Porosity controls the catalytic activity of platinum nanoparticles. *Phys. Chem. Chem. Phys.* **21**, 20415–20421 (2019).