Supporting Information

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

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Figure S1. Characterization of C UME. (a) Microscopic image of C UME. (b) Cyclic Voltammetry of C UME in 0.9 mM ferrocenylmethanol solution at a scan rate of 100 mV s$^{-1}$.

A disk UME surface was observed from the microscopic image of C UME (Figure S1a). Furthermore, we estimated the radius of the C UME ($r$), using the limiting current by the equation S1:

$$i = 4nFDCr$$  \hspace{1cm} (S1)

Where $k_B$ is the Boltzmann constant (1.38×10$^{-23}$ J·K$^{-1}$), $i$ is the 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 × 10$^4$ C·mol$^{-1}$), $D$ is the diffusion coefficient of ferrocenemethanol as a reacting species (7.6 × 10$^{-6}$ cm$^2$ 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 (Figure S1b).
Figure S2. TEM characterization of PtNPs. (a) TEM image of monodispersed PtNPs and (b) the size distribution derived from TEM image, in term of the particle diameters with mean value of 3.0 ± 0.1 nm.
Figure S3. Amperometric current-time curves 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 2 mM H₂O₂.
Figure S4. Electrochemical behaviors of individual PtNPs for the catalytic reduction of protons in 50 mM HClO₄ solution. Current responses of individual (a) untreated PtNPs and (b) pretreated PtNPs with 5 mM H₂O₂ at -500 mV vs. Ag/AgCl at C UME. Inset: Close-ups of the representative time-resolved current traces, corresponding to the spikes. Histograms showing the distributions of the durations and the current amplitude of PtNPs. Black curves show Gaussian fits. The data were obtained from a large population of proton reduction events of individual PtNPs (more than 1000 events).

Furthermore, we also examined the proton reduction behaviors of single PtNPs after pretreatment with 5 mM H₂O₂ solution for 10 min. Compared to untreated PtNPs, similar collision events were observed for the pretreated PtNPs in 50 mM HClO₄ solution with a current amplitude of 46.62 ± 0.28 pA and a duration of 0.15 ± 0.01 ms, indicating that PtNPs in 5 mM H₂O₂ solution did not produce the Pt oxide or reaction intermediate adsorption that inhibits the proton reduction kinetics.
Figure S5. Contact angles of glass carbon plates. Droplet contact angles of deionized water on the (a) untreated and (b) the H$_2$SO$_4$/HNO$_3$ pretreated glass carbon thin slices. A 2 μL of liquid droplet was used in the contact angle measurement.

To confirm whether the dynamic interaction of NP-electrode affects the current responses, we further investigated the electrochemical behaviors of individual PtNPs at a C UME with the hydrophilic pretreatment. The hydrophilic pretreatments of the glass carbon thin slice or carbon fibers were carried out in a round-bottom flask with 3:1 (v/v) mixture of concentrated H$_2$SO$_4$/HNO$_3$ solution for 15 min sonication at 60 °C.$^{1,2}$ Figure S5 showed that the contact angle decreased from 77° to 42° after the glass carbon thin slices were treated with H$_2$SO$_4$/HNO$_3$ solution. The contact angle measurements indicated that a pretreated carbon surface with superior hydrophilicity was obtained. This is because that the oxygenated groups were introduced after the pretreatment with the concentrated H$_2$SO$_4$/HNO$_3$ solution, resulting in the local hydrophilicity of the carbon surface.
Figure S6. Electrochemical behaviors of individual PtNPs collide at a H$_2$SO$_4$/HNO$_3$ pretreated C UME (hydrophilic carbon surface) for the catalytic reduction reaction of protons. (a) Current responses of individual 3 nm PtNPs collisions at a hydrophilic C UME in 50 mM HClO$_4$ solution with 2 mM H$_2$O$_2$. (b) Close-ups of the representative time-resolved current traces, corresponding to the spikes. (c) Histograms showing the distributions of the durations and current amplitude of individual PtNPs. Black curves show Gaussian fits. The data were obtained from a large population of proton reduction events of individual PtNPs (more than 1000 events).

To exclude the interaction effect between the NP and the electrode during the electrochemical measurements, we further examined the electrocatalytic proton reduction of individual PtNPs in a 50 mM HClO$_4$ solution containing 2 mM H$_2$O$_2$ at a H$_2$SO$_4$/HNO$_3$-pretreated C UME (Figure S5). We observed current traces with an amplitude of 18.41 ± 0.13 pA and a duration of 0.23 ± 0.01 ms (Figure S6), which were close to the experimentally measured results at an untreated C UME. This suggests that the hydrophilic pretreatment of C UME does not affect the current responses of PtNPs at the electrode interface, thus excluding the interaction effect of NP-electrode to the current signals.
Figure S7. Cyclic voltammograms of 5 μm Pt UME in argon-saturated 50 mM HClO₄ solution without (black) and with (red) 5 mM H₂O₂.

When PtNPs are dispersed in the solution, only decomposition of H₂O₂ occurred on PtNPs, resulting in the formation of oxygen bubble on the surface of PtNPs. As the particles approach the electrode surface, hydrogen evolution reaction takes place on the PtNPs. To study the competing effect of H₂O₂ decomposition on the current amplitude for hydrogen evolution reaction, we examined the voltammetric response of a 5 μm Pt UME in 50 mM HClO₄ solution with and without H₂O₂. In previously obtained results, the reduction reactions of O₂ and H₂O₂ on individual PtNPs were recently reported. S3-S5 However, experimentally, negligible differences were observed at a 5 μm Pt UME in 50 mM HClO₄ solution regardless of H₂O₂ or a lack thereof. As can be seen in Figure S7, a cathodic current can be observed at the 5 μm Pt UME at the potential from +0.40 V vs. Ag/AgCl wire, in which the reduction of H₂O₂ occurred. However, cyclic voltammograms performed in argon-saturated 50 mM HClO₄ solution without (black) and with (red) 5 mM H₂O₂ showed nearly perfect overlap in H⁺ reduction currents, indicating H₂O₂ reduction contributed negligibly to currents at potentials negative of -0.30 V vs. Ag/AgCl wire. This is because that electrochemical reduction of H₂O₂ was probably inhibited by H adsorption at Pt, which occurred before H₂ evolution. S6,S7 Therefore, the decomposition and reduction of H₂O₂ contributed negligibly to HER current at potentials more negative than the H-adsorption region (< -0.30 V vs. Ag/AgCl wire).
Figure S8. (a) Schematic illustration of microjet collision system. The current-time curves and the corresponding histograms of current amplitude (b) by injecting individual PtNPs into 50 mM HClO₄ solution, (c) by injecting individual bubble-PtNP agglomerations into 50 mM HClO₄ solution, and (d) by injecting individual bubble-PtNP agglomerations into 10 mM NaClO₄ solution.

To investigate the reduction of O₂ nanobubble on a single PtNP, we employed the microjet collision method during the electrochemical measurements. This method used a pressure-driven flow to transport PtNPs from a glass micropipette onto a detecting C UME placed ~10 μm away (Figure S8a). In brief, a glass micropipette with ~5 μm diameter orific (prepared by pulling borosilicate glass capillary tubes) was filled with PtNPs in target solution, connected to a Femtojet microinjector, and attached to a micropositioner so that the orifice was
dipped in the electrolyte solution. The C UME was then connected to a separate micropositioner directly opposite from the micropipette’s position. The positions of the micropipette and the C UME were adjusted until both were in focus using a 20× objective, and were approximately 10 μm apart facing each other.

Firstly, we attempted to transport PtNPs in 10 mM NaClO₄ solution from a glass micropipette onto a detecting C UME in 50 mM HClO₄ solution containing 10 mM NaClO₄. Rapid, consistent, and repeatable single-particle collision events in HClO₄ solution were observed for the proton reduction with a current height of 47.10 ± 0.24 pA (Figure S8b), which is closed to the current signals obtained from our free diffusion collision experiment. The similarity of these two current signals confirmed the feasibility of our microjet collision method. On this basis, we used the microjet collision method to transport PtNPs in 5 mM H₂O₂ solution from a glass micropipette onto a detecting C UME in 50 mM HClO₄ solution containing 10 mM NaClO₄. As expected, the current amplitude of electrochemical signals decreased to 19.83 ± 0.11 pA (Figure S8c). This is because that PtNPs in 5 mM H₂O₂ generated the oxygen nanobubbles which partially blocked the reactive area of PtNPs and consequently inhibited the reduction reaction of protons. In addition, the decreased current indicated that the formed bubble-particle agglomerations lasted long stability during the microjet process; that was, O₂ nanobubble still existed on the surface of PtNPs after the microinjection of bubble-particle agglomerations in 50 mM HClO₄ solution.

To study the reduction of O₂ nanobubble on single PtNPs, we further examined the amperometric response of individual bubble-particle agglomerations by microjetting PtNPs in 5 mM H₂O₂ solution from a glass micropipette into 10 mM NaClO₄ solution. Significantly, a smooth curve was observed in the amperometric current–time curve at -500 mV vs. Ag/AgCl wire (Figure S8d). We speculated that the O₂ nanobubble may not be reduced on the PtNP at a submillisecond scale because the adhesion of nanobubble on PtNP caused an increase of interfacial ohmic drop and resulted in an impeded mass transfer inside nanobubble.⁸⁻¹⁰
Figure S9. Current responses of individual 3 nm PtNPs collisions at -500 mV vs. Ag/AgCl at C UME (diameter 7 μm) in 50 mM HClO₄ solution without (a) and with (b) 1.4 mg·mL⁻¹ PEG. Inset: Close-ups of the representative time-resolved current traces, corresponding to the labelled spikes with the same legend. Histograms showing the distributions of the duration and current amplitude of PtNPs. Black curves show Gaussian fits. The data were obtained from a large population of proton reduction events of individual PtNPs (more than 1000 events).

To probe the PEG effect to PtNPs, we investigated the electrochemical behaviors of individual PtNPs in 50 mM HClO₄ solution with and without 1.4 mg mL⁻¹ PEG in absence of H₂O₂. In a 50 mM HClO₄ solution, a characteristic single peak was observed with a duration of 0.15 ± 0.01 ms and a current amplitude of 46.32 ± 0.28 pA, corresponds to HER process of individual PtNPs (Figure S9a). When 1.4 mg/mL PEG was added into 50 mM HClO₄ solution, single peak still appeared, showing a duration of 0.15 ± 0.01 ms and a current amplitude of 46.36 ± 0.40 pA. It is worth noting that, almost the same electrochemical responses were observed for individual PtNPs in 50 mM HClO₄ solution with and without 1.4 mg mL⁻¹ PEG in absence of H₂O₂ (Figure S9b), indicating PtNPs were not affected by PEG during our electrochemical measurement process.
Figure S10. Zeta potential distributions of PtNPs (3 nm, 0.2 mM) in 50 mM HClO$_4$ solution without H$_2$O$_2$ (a), with 0.5 mM H$_2$O$_2$ (b), with 0.5 mM H$_2$O$_2$ and 1.4 mg·mL$^{-1}$ PEG (c), and with 0.5 mM H$_2$O$_2$ and 1 mg·mL$^{-1}$ TBP (d).

We performed Zeta potential measurement to reflect the magnitude of electrostatic interaction between dispersed PtNPs in different solution conditions. Figure S10a shows the Zeta potential value of around +11 mV for 0.2 mM PtNPs in 50 mM HClO$_4$ solution. The zeta potential of the PtNPs still was +12 mV after the further addition of H$_2$O$_2$ and remained on this level with PEG and TBP, respectively (Figure S10b-d). These results indicate that the PtNPs (3 nm, 100 pM) in the above solutions are monodispersed during single NP electrochemical measurement due to charge-induced colloidal stability.
Figure S11. DLS profiles of Pt NPs in 50 mM HClO$_4$ solution without H$_2$O$_2$ (a), with 0.5 mM H$_2$O$_2$ (b), with 0.5 mM H$_2$O$_2$ and 1.4 mg·mL$^{-1}$ PEG (c), and with 0.5 mM H$_2$O$_2$ and 1 mg·mL$^{-1}$ TBP (d).

The size distribution profiles of Pt NPs were measured by dynamic light scattering (DLS), obtaining monomodal curves with different additives. DLS result of Pt NPs in 50 mM HClO$_4$ solution shows a narrow size distribution with an average size of 4.5 nm (Figure S11a). The particle size calculated by DLS was always slightly higher than TEM due to the fact that DLS measures the hydrodynamic radius.$^{S11}$ And the size distribution was still around 4.5 nm after the further addition of H$_2$O$_2$ and remained on this level with the extra poly(ethylene glycol) (PEG) and tributyl phosphate (TBP), respectively (Figure S11b-d). DLS results indicate that the PtNPs in the above experimental conditions are monodispersed during single NP electrochemical measurement.
Figure S12. Collision frequencies of PtNPs (3 nm, 100 pM) in 50 mM HClO₄ solution without H₂O₂ (a), with 0.5 mM H₂O₂ (b), with 0.5 mM H₂O₂ and 1.4 mg·mL⁻¹ PEG (c), and with 0.5 mM H₂O₂ and 1 mg·mL⁻¹ TBP (d).

To further demonstrate the monodispersed state of PtNPs in different solutions, we estimated the collision frequency of PtNPs based on the Shoup-Szabo equation. In this work, we counted the number of collision signals for 100 seconds to estimate the averaged experimental collision frequencies in different solutions. In theory, the number of collision events ($\tilde{N}_{\text{collision}}$) as a function of time (t) can be estimated by the integration of the diffusive flux towards a disc electrode with respect to t:

$$\tilde{N}_{\text{collision}}(t) = c^* r_d^3 F(\tau)$$

where $r_d$ is the disc radius of electrode (3.5 μm) and $c^*$ is the particle number concentration ($6.02 \times 10^{16}$ m⁻³). Using a Taylor expansion, $F(\tau)$ can be approximated to:

$$F(\tau) = \tau + 1.437\sqrt{\tau} + 6.567 \times 10^{-2} \ln \tau + \frac{3.425 \times 10^{-2}}{\sqrt{\tau}} - \frac{3.349 \times 10^{-3}}{\tau}$$

and $\tau$ is a dimensionless time parameter, which is defined as:

$$\tau = 4Dt/r_d^2$$

The diffusion coefficient of spherical PtNPs ($D_{np}$) can be calculated by the Stokes-Einstein equation as follows:
\[ D_{np} = \frac{k_B T}{6 \pi \eta r_{np}} \]  

(S5)

where \( k_B \) is the Boltzmann constant \((1.38 \times 10^{-23} \text{ J} \cdot \text{K}^{-1})\), \( T \) is the temperature \((298 \text{ K})\), \( \eta \) is the viscosity of the solution \((1 \text{ mPa} \cdot \text{s})\). As a result, the calculated frequencies are approximately 146 Hz and 145 Hz for the 100 pM PtNPs at a 7.0 \( \mu \text{m} \) diameter C UME in 50 mM HClO\(_4\) solution without H\(_2\)O\(_2\) and with 0.5 mM H\(_2\)O\(_2\) and 1 mg\( \cdot \text{mL}^{-1} \) TBP, respectively (Figure S12). For a dumbbell-like bubble-particle agglomeration, the diffusion coefficient \( (D_{B-p}) \) can be expressed in terms of the duration ratio of individual PtNPs before and after nanobubble formation as given in eq S6:

\[ D_{B-p} = \frac{D_{np} t_{c=0}}{t_{B-p}} \]  

(S6)

where \( t_{c=0} \) \((= 0.15 \text{ ms})\) is the duration of the current traces in 50 mM HClO\(_4\), \( t_{B-p} \) is the duration of the current traces of bubble-particle agglomeration in the presence of 0.5 mM H\(_2\)O\(_2\) without \((= 0.19 \text{ ms})\) and with 1.4 mg\( \cdot \text{mL}^{-1} \) PEG \((=0.23 \text{ ms})\). Correspondingly, the calculated frequencies ar approximately 106 Hz and 86 Hz (Figure S12). The experimentally observed current transient frequencies in above solution are close to the theoretical value in 100 pM PtNPs based on usual variation in the stochastic measurements, which suggests that the experimental conditions do not significantly influence the particle monodispersion.
Figure S13. TEM images and size distributions of the Pt NPs before (a) and after (b) the electrochemical experiments.

Moreover, TEM images show the narrow size distributions with the average diameters of 3.2 nm and 3.1 nm before and after the single entity electrochemical measurements, respectively, indicating the Pt NPs were well monodispersed during the entire electrochemical processes (Figure S13). These findings indicate that the above experimental conditions do not significantly influence the monodispersion of Pt NPs during the electrochemical measurements.
Figure S14. (a) TEM images of monodispersed AuNR@PtNPs and AuNRs. (b) DFM images of AuNR@PtNPs in 50 mM HClO₄ solution without (left) and with (right) 10 mM H₂O₂. (c) Scattering intensities of single AuNR@PtNPs in 50 mM HClO₄ solution without (black) and with (red) 10 mM H₂O₂. (d) DFM images of AuNRs in 50 mM HClO₄ solution without (left) and with (right) 10 mM H₂O₂. (e) Scattering intensities of single AuNR in 50 mM HClO₄ solution without (black) and with (red) 10 mM H₂O₂.
Despite considerable efforts have been devoted in a rich literature, small size and optical transparency make interfacial nanobubbles challenging to be probed with sufficient spatial and temporal resolution.\textsuperscript{S13} Micrometer- or submicrometer-sized bubbles can be probed by techniques, such as atomic force microscopy\textsuperscript{S14} and dark-field\textsuperscript{S15} or fluorescence microscopy.\textsuperscript{S16,S17} Recently, Xu \textit{et al.} reported the visualization of individual nanobubbles at hundreds of nanometers by observing the scattering intensity change of individual noble metal NPs via dark field microscopy (DFM).\textsuperscript{S18} However, due to the intrinsic weakness of plasmonic property in small size PtNPs, PtNPs less than 30 nm are invisible under DFM. Thus, it is challenging to directly visualize the nanobubble generated around 3 nm PtNPs in our work. In order to provide evidence of the nanobubble being attached to the PtNPs, we adopted a plasmonic antenna strategy to corroborate the generation of nanobubbles.\textsuperscript{S19,S20} Here, the gold nanorods (AuNRs) with excellent plasmonic property were served as the signal conduction unit and the platform for loading high catalytic components (small PtNPs). Hence, we employed the hybrid plasmonic antenna structure (AuNR@PtNPs) where 3 nm PtNPs modified on AuNR surface to monitor the nanobubble formation in H$_2$O$_2$ solution.

As shown in Figure S14a, the AuNRs had a cylindrical shape, and the length of these AuNRs was about 100 nm. Significantly, a fairly uniform morphology with highly-dispersed 3 nm PtNPs densely decorated on the surface of the AuNR. Firstly, we immobilized of AuNR@PtNPs on a cleaned indium tin oxide glass slide. A drop of 50 mM HClO$_4$ solution without or with 10 mM H$_2$O$_2$ was added to the ITO glass slide modified by AuNR@PtNPs. Compared with the scattering spectra in 50 mM HClO$_4$ solution, a brightness diming was significantly observed under the DFM after adding 10 mM H$_2$O$_2$ into 50 mM HClO$_4$ (Figure S14b). Meanwhile, when AuNR@PtNPs was in 50 mM HClO$_4$ solution, the measured scattering spectrum was found to peak at 690 nm. After adding 10 mM H$_2$O$_2$ into 50 mM HClO$_4$ for 5 min, the scattering spectrum exhibited a blueshift to 650 nm and an obviously decreased intensity (Figure S14c). This is because that when the O$_2$ nanobubbles were generated around PtNPs, it induced decreasing in refractive index of the medium around PtNPs from 1.33 to 1.00 and caused the blueshift of the scattering spectrum of AuNR@PtNPs.\textsuperscript{S21,S22} The observed blueshift of
40 nm was in good agreement with the blueshift obtained from a Mie theory for the same particle embedded in water compared with that in air.\textsuperscript{23} In addition, previous reports showed the formation of metal oxide on NPs, and that the scattering spectra of NPs would exhibit a redshift.\textsuperscript{24} Therefore, the blueshift of AuNR@PtNPs scattering spectra in 50 mM HClO\textsubscript{4} with 10 mM H\textsubscript{2}O\textsubscript{2} also excluded the formation of Pt oxide on PtNPs.

To verify that the brightness change in DFM and the scattering peak difference were due to O\textsubscript{2} nanobubbles surrounding the PtNPs, we further investigated DFM images and scattering spectra of individual AuNRs in 50 mM HClO\textsubscript{4} without and with 10 mM H\textsubscript{2}O\textsubscript{2} as control. Notably, DFM image and scattering peak were both unchanged regardless of 10 mM H\textsubscript{2}O\textsubscript{2} or a lack thereof (Figure S14d,e). All experimental results evidenced that nanobubble was attached to the PtNPs by H\textsubscript{2}O\textsubscript{2} decomposition.
Figure S15. The rate of H$_2$O$_2$ decomposition at PtNPs. (a) The absorbance spectra of H$_2$O$_2$ at various concentrations and (b) calibration curve for H$_2$O$_2$.

The concentration of H$_2$O$_2$ in the solution was determined by a spectrophotometric method based on Beer-Lambert law as previous work$^{S25}$:

\[ A = \varepsilon L C \]  

(S7)

where $A$ is the measured absorbance, $\varepsilon$ is the wavelength-dependent molar extinction coefficient ($\varepsilon_{H_2O_2} = 43.6$ M$^{-1}$·cm$^{-1}$ at 240 nm), $L$ is the pass length and $C$ is the concentration of H$_2$O$_2$. In order to obtain absorbance in an analytically meaningful range, H$_2$O$_2$ was diluted to in a range of 1 - 4 mM with ultrapure water. Figure S15a shows a broad absorbance peak at 240 nm in the UV spectra. The calibration curve with a good correlation coefficient ($R^2 = 0.99987$) indicates that the measured absorbance at 240 nm can be used for adequately converting the absorbance readings to the concentration of H$_2$O$_2$ (Figure S15b).
Figure S16. The formation time of nanobubble at PtNPs. Decomposition of H$_2$O$_2$ catalyzed by PtNPs. A plot of $\ln([\text{H}_2\text{O}_2]/[\text{H}_2\text{O}_2]_0)$ against decomposition time of H$_2$O$_2$ at various concentrations of 3 nm PtNPs.

The formation time of O$_2$ nanobubble was determined by monitoring the UV-Vis absorbance peak at 240 nm. As is shown in Figure S16, $\ln([\text{H}_2\text{O}_2]/[\text{H}_2\text{O}_2]_0)$ is linearly related to decomposition time before and after 300 s, indicating the decompositions of H$_2$O$_2$ at various concentrations 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 H$_2$O$_2$ significantly decreased. This is because that O$_2$ nanobubble formed on individual PtNPs blocks the active particle surface for catalytic chemically decomposition of H$_2$O$_2$. Therefore, O$_2$ molecules accumulated inside nanobubble can be obtained from integrating the produced O$_2$ molecule across 300 s.
Figure S17. (a) Amperometric current-time curves of individual PtNPs in 50 mM HClO₄ solution without and with addition of 2 mM H₂O₂ solution. (b) Close-ups of the representative time-resolved current traces.

We further investigated the formation time of the nanobubble on the PtNPs surface in H₂O₂ solution using single NP electrochemical experiment (Figure S17). Note that significant current transients of individual PtNPs were observed for proton reduction in 50 mM HClO₄ solution. After the addition of 2 mM H₂O₂ to the above solution, heavily fluctuating current signals appeared. After ~300 s, relatively uniform low current spikes were further clearly observed; the current amplitude of spike signals decreased, while the duration time increased. This is because that the formation of stable O₂ nanobubble on the PtNPs surface after ~300 s incubation in 2 mM H₂O₂ solution. That is, the formation time of the stable nanobubble from single NP electrochemical experiment is consistent with the measured result from UV-vis spectra (Figure S16), thus further confirming the reliability of stable nanobubble formation time in this work.
Figure S18. MD simulations of oxygen nanobubbles. (a) Snapshot of the initial configuration in the simulation. (b) The oxygen molecules in the aqueous solution adsorb on the surface of Pt after 1 ns. (c) Snapshot of an oxygen nanobubble stabilized on the PtNPs surface at 500 ps (front view). The green dots represent oxygen molecules, while red dots represent Pt atoms. (d) Mean square displacement (MSD) of oxygen atoms inside or outside of a nanobubble versus the calculated time.

In the study of Wang et al., the surface of a nanobubble was kinetically stable against high internal pressures and the gas-water interface had great diffusive resistance. According to Kim et al., the experimental diffusion coefficient of the gas inside 10 nm nanobubble was $0.5 \times 10^{-18}$ m$^2$/s, which was eight orders of magnitude smaller than the bulk diffusion coefficient. Therefore, the confined diffusion rate of O$_2$ molecules inside nanosized bubble (a curvature radius of 3.66 nm) should be considered in this case. Here, we used MD simulations to investigate the diffusion rate of O$_2$ molecules inside nanobubble with high laplace pressure. The catalytic generation of nanobubbles on a PtNP was simulated in this work. As shown in Figure S24.
S18a, the initial configuration of the model size was 6.0 nm*6.0 nm*6.0 nm, and the ratio of water molecules to oxygen molecules was 70:1. MD simulations were performed using the open source software LAMMPS (2020 version) in this work. All of the parameters and potential functions for bonded and nonbonded interactions during the simulations were given in Tables S1 and S2. The structure was optimized first, and then the relaxation time was 2 ns under the isobaric-isothermal (NPT) environment, temperature was set at 298 K, and pressure was 1 atm (atmospheric pressure). After 1 ns, the configuration of the simulation demonstrated that the O2 molecules in the aqueous solution will adsorb on the surface of PtNP (Figure S18b), indicating that O2 molecules can aggregate on the surface of PtNP.

Due to the intrinsic defects of MD method (limitation of time and space scale), it was difficult to simulate the formation of hemispherical bubbles according to such irregular adsorption. Therefore, we simplified the simulation configuration and directly built a spherical cap-shaped oxygen nanobubble model formed at the PtNP surface (Figure S18c). The nanobubble was stabilized on the hemispherical surface constructed by hydrophobic Lennard–Jones particles; the basal diameter and height of the fitted spherical cap were about 3.0 and 7.0 nm. Then the positions of oxygen molecules inside the nanobubble and dispersed inside the surrounding water were recorded as a function of the simulation time. Specifically, we monitored every oxygen molecule in the last 1 ns to describe the stabilized configuration. The trajectory was saved completely in 100 frames. And the mean square displacements of oxygen molecules in nanobubble and in water were recorded for every frame and were shown in Figure S18d. The diffusion coefficients of the oxygen molecules were estimated in the linear region of 300–1000 ps. Accordingly, the diffusion coefficient of the oxygen molecules dispersed in water was estimated to be (3.37 ± 0.01) × 10^{-9} m^2/s, which is comparable to the result reported in bulk water (2.10 × 10^{-9} m^2/s) at 298 K. However, the diffusion coefficient of the oxygen molecules inside the nanobubble was estimated to be (0.055 ± 0.001) × 10^{-9} m^2/s; and the value is approximately 2 order of magnitude less than that for bulk water. These results suggested that the oxygen molecules inside the nanobubble remained in a very stable state and mainly moved inside the spherical cap.
According to the report of Lohse and Zhang about stable single surface nanobubbles\textsuperscript{28}, we can calculate the outflux rate \(v_{O_2, \text{flux}}\) of oxygen molecules from the mass change rate \((dM/dt)\) of the nanobubble mass \((M)\) as described by equations S8-S10:

\[
v_{O_2, \text{flux}} = \frac{dM}{dt} = -\frac{\pi}{2} L D \left( P_0 + \frac{4\sigma \sin \theta}{L} \right) \frac{c_s}{P_0} - c_\infty \right) f(\theta) \quad (S8)
\]

\[
f(\theta) = \frac{\sin \theta}{1 + \cos \theta} + 4 \int_0^\infty \frac{1 + \cosh 2\theta \xi}{\sinh 2\pi \xi} \tanh[(\pi - \theta)\xi] \, d\xi \quad (S9)
\]

\[
R = \frac{L}{(2 \sin \theta)} \quad (S10)
\]

where \(c_\infty\) is the gas concentration far away from the nanobubble, \(c_s\) is the gas solubility (= 8.38 mg/L), \(L\) is the basal diameter of nanobubble cap (= 2.97 nm), \(\sigma\) is the surface tension, \(P_0\) is the ambient pressure, \(\theta\) is the contact angle, and \(D\) is the diffusion coefficient of \(O_2\) molecules confined inside high density \(O_2\) nanobubbles. As a result, the calculated outflux rate \((v_{O_2, \text{flux}})\) was \(5.41 \times 10^{-21}\) g/s and the outflux of \(O_2\) molecules can be estimated as \(1.62 \times 10^{-18}\) g.
Table S1. Model parameters and potential functions of all non-bonded interactions.

| Non-Bonded Interactions |
|-------------------------|
| $V_{LJ}(r_{ij}) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$ |
| $\varepsilon_{ij} = \sqrt{\varepsilon_{i}\varepsilon_{j}}$ |
| $\sigma_{ij} = \frac{1}{2}(\sigma_{i} + \sigma_{j})$ |

| Molecules | Atom Types | $\sigma$(Å) | $\varepsilon$(kcal/mol) | $q$ (e) | Cut-off(nm) |
|-----------|------------|-------------|-------------------------|---------|-------------|
| O$_2$     | O          | 3.16        | 0.086                   | 0       | 1.0         |
| PtNPs     | Pt         | 2.53        | 7.800                   | 0       | 1.21        |

SPC/E water

| OW       | O          | 3.16        | 0.155                   | -0.8476 | 0.4238      |
| HW       | H          | 0           | 0                       |         |             |

Table S2. Model parameters and potential functions of all bonded interactions.

| Bonded Interactions |
|---------------------|
| $V_{b}(r_{ij}) = \frac{1}{2}k_{ij}^b(r_{ij} - b_{ij})^2$ |

| Molecules | Bond   | b (nm) | $k^b$(kcal•mol$^{-1}$•Å$^{-2}$) |
|-----------|--------|--------|---------------------------------|
| O$_2$     | O-O    | 0.121  | 846.5                           |
| SPC/E water | O-H  | 0.100  | 540.6                           |

| $V_{\alpha}(\theta_{ijk}) = \frac{1}{2}k_{ijk}^\theta(\theta_{ijk} - \theta_{ijk}^0)^2$ |

| Molecules | Angle | $\theta^0$(deg) | $k^\theta$(kcal•mol$^{-1}$ rad$^{-2}$) |
|-----------|-------|-----------------|---------------------------------------|
| APC/E water | H-O-H| 109.47          | 50                                    |

Note: The optimized parameters of H$_2$O and O$_2$ are adopted from S29 and S30.
Supporting Note S1. Derivation the correction factors for the diffusion coefficient \((\alpha)\).  

In a system with random walks of particle with solvent molecules in bulk solution, the motion velocity of the diffusing particles is proportional to diffusion coefficient. Typically, the diffusion coefficient of spherical PtNPs \((D_{np})\) can be calculated by the Stokes-Einstein equation as follows:

\[
D_{np} = \frac{k_B T}{6 \pi \eta r_{np}}
\]  

(S11)

For a dumbbell-like bubble-particle agglomeration, the diffusion coefficients at the parallel \((D_{||})\) and perpendicular \((D_{\perp})\) directions\(^{31}\) are given by equations S12 and S13:

\[
D_{||} = \frac{k_B T}{8 \pi \eta a} \times \frac{(2-p^2)G(p)-1}{1-p^2}
\]  

(S12)

\[
D_{\perp} = \frac{k_B T}{16 \pi \eta a} \times \frac{(2-3p^2)G(p)+1}{1-p^2}
\]  

(S13)

\(G(p)\) is defined as the shape correction factors for the bubble-NP agglomerations. It follows \(G(p) = \log\left(\frac{1+\sqrt{1-p^2}}{p}\right)/\sqrt{1-p^2}\). Therefore, the orientation-averaged translational diffusion coefficient of bubble-NP agglomerations \((D_{B-P})\) can be expressed by equation S14:

\[
D_{B-P} = \frac{D_{||} + 2D_{\perp}}{3} = \frac{k_B T}{6 \pi \eta a} G(p)
\]  

(S14)

where \(k_B\) is the Boltzmann constant, \(T\) is the temperature (298 K), \(\eta\) is the viscosity of the solution (1 mPa·s), and \(p\) is the axial ratio. It follows \(p = b/a\), where \(a\) is the semi-axis along the axis of revolution and \(b\) is the equatorial semi-axis. As shown in Figure 4, \(a\) is the half length of the bubble-particle agglomerations along the y-axis \(a = \frac{1}{2}(h_B + 2r_{np})\), where \(h_B\) is the height of the nanobubbles and \(b\) is the radius of the PtNPs. As a result, we derived the correction factors for the diffusion coefficient \((\alpha)\) in equation S15:

\[
\alpha = \frac{D_{B-P}}{D_{np}} = \frac{r_{np}}{a} G(p) = \frac{r_{np}}{a} \log\left(\frac{1+\sqrt{1-p^2}}{p}\right)/\sqrt{1-p^2}
\]  

(S15)
Supporting Note S2. The lifetime of nanobubble with high inner density.

By assuming the diffusion of dissolved gas molecules away from a spherical gas bubble to determine the shrinkage rate, we can calculate the lifetime of a nanobubble, $t$, as a function of its density of gas molecules as described by Equation S16$^{32,33}$:

$$t = \frac{kr_B^3}{6D\gamma (1-\rho_g/\rho_l)^4}$$

where $k$ is the Henry law constant of O$_2$ gas, $\rho_g$ is the density of O$_2$ nanobubbles, $\rho_l$ is the density of liquid, $r_B$ is the radius of O$_2$ nanobubbles, $D$ is the diffusion coefficient of O$_2$ molecules inside the nanobubbles, and $\gamma$ is the surface tension. As is shown as the Equation S16, the lifetime of nanobubble is proportional to its density of O$_2$ gas inside a nanobubble. Therefore, the ultrahigh density of nanobubbles provides new insights to unveil the mysterious long-lived nanobubbles.
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