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Supporting Information

Catalytic ability characterization of *in situ* synthesized Pt NPs coated SBA-15 within a sub-micropipette

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1. Reagents and Materials. KCl was supplied by Tianjin Fuchen Chemical Reagents Co.; H_2O_2 (30 wt%), H_2SO_4 and AgNO₃ were provided by Guangzhou Chemical Reagent Factory; NaBH₄ was supported by Sigma Aldrich; NH₃·H₂O was obtained from Qiang Sheng Functional chemical Co.; hexadecyltrimethylammonium bromide (CTAB), tetraethyl orthosilicate (98%, TEOS), poly (ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (98% P123, Mn ~5800) and Pt(NH₃)₄Cl₂·xH₂O were provided from J&K. All of these reagents (except for TEOS and P123) were of analytical grade and used without further purification. In addition, all the chemicals were dissolved using deionized water with a resistivity of 18.2 M Ω cm produced by a Millipore purification system. Borosilicate capillaries with an outer diameter of 1.0 mm and an inner diameter of 0.5 mm were purchased from Sutter Instrument Co.

2. Synthesis of n-Pt/SBA-15 powder. The preparation of SBA-15 powder sample has been reported in the literature¹ and will not be repeated here. The fabrication of n-Pt/SBA-15 is briefly described below.² Firstly, Pt(NH₃)₄Cl₂ precursor with concentrations of 1, 5, 10 and 20 mM were prepared, 0.2 g SBA-15 powder sample was added to 20 mL Pt(NH₃)₄Cl₂. The pH of the mixture was adjusted to 9.0 with NH₃·H₂O to facilitate Pt(NH₃)₄²⁺ electrostatic adsorption in the negatively-charged SBA-15 nanochannels, which was kept stirred at room temperature for 4 h to allow the nanochannels of SBA-15 to be fully infiltrated. Next, the precipitate was centrifuged and washed three times to remove the excess solution, and 1 M AgNO₃ was used to check for no precipitate in the supernatant to ensure that the Cl⁻ was removed. The sample was dried under vacuum at 50 °C for 4 h. The sample obtained was still a white powder and added it into the fresh NaBH₄ solution (1 mM, 20 mL) and stirred at room temperature for 1 h. The white solution gradually turn grey. Finally, the sample was centrifuged and washed three times to obtain a grey n-Pt/SBA-15 (n is the concentration of the precursor Pt(NH₃)₄Cl₂, which can be 1, 5, 10 and 20 mM, the color of n-Pt/SBA-15 deepens with the increase of precursor concentration). Then, n-Pt/SBA-15 was vacuum dried at 50 ° C.

n-Pt/SBA-15 powder has been characterized by transmission electron microscope (TEM), X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) measurements, and

X-ray photoelectron spectroscopy (XPS).

3. Fabrication of n-Pt/GP-SBA-15. Before use, impurities inside and outside the borosilicate capillaries were completely decomposed through the piranha solution (98% $H_2SO_4/30 \text{ wt\%} H_2O_2, \text{v/v}=3/1$). The sub-micropipette with diameter of 500 nm is pulled using a P-2000 capillary puller (Sutter Instrument Co., America). The parameters used in this work are shown as follows: Heat 405, Fil 4, Vel 30, Del 200, Pul 0.

GP-SBA-15 was prepared using the same route as in the literature¹ and will not be repeated here. Then, the GP-SBA-15 was filled with an aqueous solution of $Pt(NH_3)_4Cl_2$ (pH 9.0), and the tip of GP-SBA-15 was also immersed in $Pt(NH_3)_4Cl_2$ for 12 h, so that the nanochannels of GP-SBA-15 were fully infiltrated and electrostatically adsorbed with $Pt(NH_3)_4^{2+}$. The solution inside the GP-SBA-15 was pumped off and rinsed with deionized water for three times, followed by vacuum drying at 50 °C for 4 h. The tip of the pretreated GP-SBA-15 was immersed in fresh 1 mM NaBH₄ for 1 h, and the aqueous NaBH₄ solution entered the nanochannels by siphoning as a result the $Pt(NH_3)_4^{2+}$ was reduced to Pt NPs. The above borosilicate pipette was rinsed and vacuum dried at 50 °C for 8 h to obtain n-Pt/GP-SBA-15 (where n represents the concentration of $Pt(NH_3)_4Cl_2$).

Photos of GP-SBA-15 and n-Pt/GP-SBA-15 were taken by metallographic microscopy. **4. Characterization, electrical detection and data analysis.** TEM images were obtained from JEM-2100F (JEOL, Japan). XRD patterns were recorded on D8 ADVANCE X-ray polycrystalline diffractometer (Bruker, Germany, 20~80°) and Smartlab (Rigaku, Japan, 0.5~5°). BET was obtained using an ASAP 2460 (Micromeritics, America). Element valence states were analyzed on ESCALAB 250Xi (Thermo Scientific, America). The metallographic microscopy was provided by metalloscope (MJ33, mingmei, China).

The I-V response of linear sweep voltammetry was recorded using an electrochemistry workstation (CHI660E, Chenhua, China). A pair of Ag/AgCl electrodes were used as the working electrode (WE) in a glass pipette and the quasi-ground electrode in bulk solution, respectively. All voltages were with respect to a quasi-ground electrode in this work. The electrolyte was 100 mM KCl. Current-time (*i-t*) trace was recorded using a

home-made instrument. All translocation was conducted in the 100 mM KCl electrolyte containing H_2O_2 . The resistance pulse signals were obtained at negative applied voltages and 100 kHz sampling frequency. Besides, this measure was carried out in a Faraday cage to reduce electromagnetic interference. The data analysis is supported by MATLAB R2016b and Prism.

The relationship between peak current (ΔI) and O₂ nanobubble diameter (*d*) is calculated by Eq S1.³:

$$\frac{\Delta I}{I_0} = 8 \left(\frac{d}{D}\right)^3 \left(\frac{\Delta I}{I_0}\right) d/D = 0.5$$
(1)

where I_0 is the baseline current, *D* is the diameter of nanochannel, and $(\Delta I/I_0)_{d/D}=0.5$ is the current change at the ratio of d/D=0.5.



Figure S1. TEM images of (a) 1-Pt/GP-SBA-15, (b) 5-Pt/GP-SBA-15, (c) 10-Pt/GP-SBA-15 and (d) 20-Pt/GP-SBA-15. It is clear that SBA-15 still maintained a good channel structure after depositing Pt NPs. The number and size of Pt NPs deposited in the channel increase with the precursor $Pt(NH_3)_4Cl_2$ concentration, and the probability of containing multiple Pt NPs in a channel increases. Additionally, the corresponding Pt NPs sizes for 1-Pt/SBA-15, 5-Pt/SBA-15, 10-Pt/SBA-15, and 20-Pt/SBA-15 are (4.1±0.7), (5.4±0.6), (6.9±0.3), and (7.5±0.9) nm, respectively.



Figure S2. The characterization results of (a) BET, (b) pore size distribution from BJH, (c) XRD, (d) small angle XRD, (e) XPS, and (f) Pt 4f XPS spectra and the fitting curves.

The N_2 isotherm adsorption curves of 1-Pt/SBA-15, 5-Pt/SBA-15, 10-Pt/SBA-15, and 20-Pt/SBA-15 all exhibit typical Type IV isotherm characteristics, and the H1 hysteresis loops and reaching adsorption saturation platforms are observed from Figure S2a, indicating that these four samples maintain good pore structure. The pore size distribution from Figure S2b shows that there is no significant change in the aperture

after the deposition of Pt NPs. However, compared with SBA-15, the specific surface area of 1-Pt/SBA-15, 5-Pt/SBA-15, 10-Pt/SBA-15, and 20-Pt/SBA-15 show a significant decrease (the pore volume and pore size distribution calculated from BET are summarized in Table S1), indicating that the degree of Pt NPs blocking nanochannels is positively correlated with the concentration of $Pt(NH_3)_4Cl_2$, which is consistent with the results of TEM.

There are broad diffuse peaks (22°) caused by amorphous silica in Figure S2c. In addition, two weak diffraction peaks around 39.5° and 45.5° are observed in 10-Pt/SBA-15 and 20-Pt/SBA-15, respectively, which are from the Pt (111) and Pt (200) crystal planes (corresponding to standard card Pt0 (PDF 01-087-0640)). However, no corresponding diffraction peaks are observed in 1-Pt/SBA-15 and 5-Pt/SBA-15 due to the small particle size and high dispersion of Pt NPs. Figure S2d shows the small angle XRD results, the strong diffraction peaks in 1-Pt/SBA-15 and 5-Pt/SBA-15 are recorded, corresponding to three crystal planes (100), (110), and (200), respectively. It is indicated that both 1-Pt/SBA-15 and 5-Pt/SBA-15 have a hexagonal ordered mesoporous structure and Pt NPs are encapsulated inside the mesoporous structure. As the Pt(NH₃)₄Cl₂ concentration further increases, the intensity of the three diffraction peaks in 10-Pt/SBA-15 and 20-Pt/SBA-15 decreases (especially in 20-Pt/SBA-15), which is due to the fact that the mesoporous organize surface partially blocked by larger size and higher content of Pt NPs. This possibility is not reflected in TEM due to n-Pt/SBA-15 powder was crushed and dispersed in an ethanol solution, the dispersion was sonicated and the supernatant was taken for TEM characterization, the sample taken may not reflect the surface coverage.

The surface chemical composition was characterized by XPS. Figure S2e and S2f show the full spectrum of XPS and the fine spectrum of Pt 4f, respectively. The binding energy around 71.0 and 74.3 eV corresponds to Pt 4f7/2 and Pt 4f5/2, respectively. In addition, the Pt 4f fine spectrum can be convolved into four peaks, corresponding to Pt⁰ and Pt²⁺, respectively. The binding energies of Pt⁰ and Pt²⁺, and the ratio of Pt⁰ are summarized in Table S2. It can be seen that except for 1-Pt/SBA-15, the Pt⁰ ratios of 5-Pt/SBA-15, 10-Pt/SBA-15, and 20-Pt/SBA-15 are similar.

| Sample | Specific surface/m ² ·g ⁻¹ | Pore volume/cm ³ ·g ⁻¹ | BJH pore diameter /nm |
|--------------|--|--|-----------------------|
| 1-Pt/SBA-15 | 470.0 | 0.85 | 9.3 |
| 5-Pt/SBA-15 | 420.9 | 0.88 | 9.2 |
| 10-Pt/SBA-15 | 345.0 | 0.89 | 9.1 |
| 20-Pt/SBA-15 | 318.6 | 0.75 | 9.1 |

Table S1. Summary table of BET data for n-Pt/SBA-15.

| Sampla | Binding Energy of Pt $4f_{5/2}$ | | Binding Energy of Pt $4f_{7/2}$ | | \mathbf{Pt}^0 ratio/% |
|--------------|---------------------------------|----------------------|---------------------------------|----------------------|-------------------------|
| Sample | Pt ⁰ /eV | Pt ²⁺ /eV | Pt ⁰ /eV | Pt ²⁺ /eV | 11 1410/70 |
| 1-Pt/SBA-15 | 73.49 | 74.35 | 70.14 | 71.00 | 55.8 |
| 5-Pt/SBA-15 | 73.61 | 74.50 | 70.26 | 71.15 | 62.6 |
| 10-Pt/SBA-15 | 74.34 | 75.25 | 70.99 | 71.90 | 63.7 |
| 20-Pt/SBA-15 | 74.11 | 75.48 | 70.76 | 71.83 | 62.3 |

Table S2. Summary table of XPS data for n-Pt/SBA-15.



Figure S3. Metallurgical microscope dark field photos of before and after *in situ* synthesis Pt NPs. There is no reflected light from the tip of GP-SBA-15 composed of silica, whereas reflected light from Pt NPs gradually appears at the tip of n-Pt/GP-SBA-15 with increasing concentrations of $Pt(NH_3)_4Cl_2$. In addition, the reflected light is concentrated at the tip of GP-SBA-15 and did not extend beyond 2.5 µm, indicating that the Pt NPs are synthesized in the nanochannels of GP-SBA-15.



Figure S4. *i-t* traces of (a) 5-Pt/GP-SBA-15 at positive applied voltages with 60 mM H_2O_2 in bath solution, (b) GP-SBA-15 and (c) 5-Pt/GP-SBA-15 at negative applied voltages with no H_2O_2 in bath solution. In (a-c), all *i-t* curves are smooth curves without any current modulation.



Figure S5. The percentage of dwell time at different negative applied voltages when H_2O_2 is 60 mM.



Figure S6. When the applied voltage is -0.05 V and the concentrations of H_2O_2 are 30 (yellow), 60 (light blue), 120 (green), 180 (light green) and 240 (purple) mM, (a) *i-t* traces, (b) scatter plot, (c) Gaussian distribution of signal peak, and (d) frequency histogram of dwell time.



Figure S7. The percentage of dwell time at different concentration of H_2O_2 when the applied voltage is -0.05 V.

5. Finite element simulation

The COMSOL Multiphysics 5.4 software was employed for the finite element simulation. The Nernst-Plank (NP) equation is used to calculate ion mass transport, the Poisson equation provides electric potential, the Navier-Stokes (NS) equation gives the fluid motion.

The Nernst-Planck equation (Eq. S2) calculates the ion flux in the channel:

$$J_i = -D_i \nabla c_i - \frac{Fz_i}{RT} D_i c_i \nabla \Phi + c_i u$$
⁽²⁾

where J_i , D_i , c_i , z_i represent the flux, diffusion coefficient, concentration and charge of substance *i*, respectively. Φ is the local electric potential, *u* is the fluid velocity, F is the Faraday constant, R is the gas constant and T is the absolute temperature (298.15K). The three terms on the right-hand side of Eq. S2 represent diffusive, migrative, and convective fluxes, respectively.

The ion distribution and the applied potential are linked by the Poisson equation (Eq. S3):

$$\nabla^2 \Phi = -\frac{F}{\varepsilon} \Sigma_i z_i c_i \tag{3}$$

where ε is the dielectric constant of the electrolyte and is set as 78 F/m.

The Navier-Stokes equations (Eq. S4) is used to illustrate the flow distribution:

$$u\nabla u = \frac{1}{\rho}(-\nabla p + \eta\nabla^2 u - F(\Sigma_i \sigma_i)\nabla\Phi$$
(4)

where ρ is the density of medium and is set to 1×10^3 kg/m³, η is the viscosity and is set to 1×10^{-3} Pa·s, p is the pressure.

The simplified 2D model schematic of n-Pt/GP-SBA-15 is plotted in Figure S7, the model with an asymmetric nanochannel following our previous report¹, where the orifice is 9.3 nm and the length of channel is 20 nm. The boundary conditions are summarized in Table S3.



Figure S8. 2D model schematic of asymmetric nanochannel of n-Pt/GP-SBA-15, the red dashed line is the axis of symmetry. ($c_{\rm K}^+=0.1$ M, $D_{\rm K}^+=1.957\times10^{-9}$ m/s², $c_{\rm Cl}^-=0.1$ M, $D_{\rm Cl}^-=2.032\times10^{-9}$ m/s², and $D_{\rm H2O2}=1.5\times10^{-9}$ m/s² at T = 298.15 K).

| Segments | Nernst-Planck Eq | Poisson Eq | Navier-Stokes Eq | | | | |
|---------------|------------------------------|-----------------------------------|------------------|--|--|--|--|
| | $c_{\rm K}^+ = 0.1 {\rm M},$ | | | | | | |
| φ | $c_{\rm Cl} = 0.1 {\rm M}$ | $\mathbf{V} = 0$ | p = 0 | | | | |
| | $c_{\rm H2O2} = c$ | | | | | | |
| 2, 3, 6, 7, 8 | No flux | No charge | No slip | | | | |
| 4,5 | No flux | σ = -0.05 C/m ² | No slip | | | | |
| 0 | $c_{K}^{+} = 0.1 M,$ | $\mathbf{V} = \mathbf{V}$ | p = 0 | | | | |
| 9 | $c_{Cl} = 0.1 M$ | $\mathbf{v} = \mathbf{v}$ | | | | | |

 Table S3. Boundaries conditions of nanochannel.



Figure S9. (a) The migration direction of the fluid at ± 0.15 V. (b) Concentration distribution of H₂O₂ in nanochannel at ± 0.15 V. (c) Flow velocity on the *z*-axis at different voltages. (d) The H₂O₂ concentration distribution at the orifice under different applied voltages, when the bulk solution contains 60 mM H₂O₂.



Figure S10. *I-V* curves of GP-SBA-15 (black), 1-Pt/GP-SBA-15 (purple), 5-Pt/GP-SBA-15 (blue), 10-Pt/GP-SBA-15 (orange) and 20-Pt/GP-SBA-15 (pink).



Figure S11. *i-t* trajectories of 1-Pt/GP-SBA-15 (purple), 10-Pt/GP-SBA-15 (orange) and 20-Pt/GP-SBA-15 (pink) at -0.25 V (a) when there is no H_2O_2 in the bulk solution, (b) when H_2O_2 is 60 mM in the bulk solution. The inset in Figure S11b is the interval time between adjacent peaks.

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