Supporting Information

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Single-Nanoparticle Coulometry Method with High Sensitivity and High Throughput to Study the Electrochemical Activity and Oscillation of Single Nanocatalysts

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Figure S1. Characterizations of PtTe Nanorods. (a) TEM images of PtTe nanorods. (b) The SEM image of PtTe nanorods on glass slide. (c) The statistical histogram of the length of single PtTe nanorods. (d) The TEM-EDX spectrum of PtTe nanorod.

Figure S1a and b demonstrate that PtTe nanorods have a fine dispersion, uniform size and morphology. Figure S1c shows that the length of most nanorods is mainly concentrated in 120–160 nm. Figure S1d shows that the atomic ratio of Pt to Te is approximately 1:2.
Figure S2. Crystal structure characterizations of the single PtTe nanorod. (a) TEM image of a nanorod. (b) The SAED pattern corresponding to the single nanorod in (a). (c)-(e) The TEM of the single nanorod with different scales.

As shown in Figure S2a, c and d, the single PtTe nanorod possesses nano-scale sponge rod structure with rough surface. Dark-colored areas may correspond to Pt sites with high catalytic activity. Figure S2b indicates polycrystalline structure of the single nanorod. Two diffraction rings can be related to two typical facets, Pt(111) with the interplanar spacing of 0.227 nm and hexagonal PtTe$_2$(011) with the interplanar spacing of 0.290 nm, that is confirmed in Figure S2e. Figure S2e also shows the discontinuous lattice fringes and lattice mismatch on the single nanorod surface. The red dotted line is the irregular facet boundaries due to the discontinuous lattice, while the lattice mismatch leads to the stepped atoms. These cause the presence of a large number of defects on the single nanorod surface.
Figure S3. Correlation of dark-field and SEM images of single nanorods. (a) The full dark-field image of the observation area before the reaction. (b) The schematic diagram of selected scattering spots (shown with red spots) in the full dark-field image. (c) The full dark-field image of the observation area after the reaction. (d) The corresponding full SEM image to (c) of the observation area after the reaction. (e) Zoom-in dark-field image of single nanorods immobilized on a glass slide, the area of (e) corresponds to the area within the red box in (c). (f) The corresponding zoom-in SEM image to (e) of single nanorods, the area of (f) corresponds to the area within the red box in (d). The insets are SEM images corresponding to the single nanorods within the red or blue box. The scale bars in the insets are 50 nm.
Figure S4. Control experiments of electrochemistry. (a) Cyclic voltammetry curves with/without supported PtTe nanorods, before and after adding AgNO₃. (b) Expand a part of a. (c) Chronoamperometry curves near the open circuit potential (OCP) after supporting PtTe nanorods. The solution used for the test is a mixture of 4 mM formic acid and 1 mM AgNO₃. (d) Cyclic voltammetry curves with/without supported Ag nanoplates in solutions with different formic acid concentrations (0.004 M (4 mM), 0.4 M and 4 M). The inset is the SEM image of Ag nanoplates.

Synthesis of Ag nanoplates. An aqueous solution of silver nitrate (Aladdin, 99.8%) (0.1 M, 4 mL) and trisodium citrate (Sinopharm Chemical Reagent Co., Ltd.) (75 mM, 80 mL) were added into 1920 mL of pure water with vigorous stirring at room temperature. Then, sodium borohydride (Sinopharm Chemical Reagent Co., Ltd., 96%) (NaBH₄, 0.1 M, 40 mL) was rapidly injected into the mixture, followed by injecting H₂O₂ (Sinopharm Chemical Reagent Co., Ltd.) (30 wt %, 14 mL) drop by drop. In the next several minutes, the solution color changed from yellow to blue, indicating that the morphology changed from sphere to nanoplate. The resulting solution was kept stirring for 4 h at room temperature.

As shown in Figure S4a, for different solutions that contain 1 mM AgNO₃, the Ag
reduction peak appears at 0.5 V (after PtTe supporting, the shoulder peak appears here for AgNO$_3$ + HCOOH mixed solution, as shown by the blue curve). The corresponding Ag oxidation peak appears near 0.6 V. After loading PtTe nanorods, Pt reduction peaks appears around 0.6 V in different solution systems, and oxidation peaks of formic acid appeared around 1.1 V. It shows that the addition of AgNO$_3$ slightly inhibits the catalytic activity of PtTe nanorods, but to a small extent. As shown in Figure S4c, for constant potential polarization currents corresponding to different potentials, the polarization current corresponding to 0.6 V is closest to 0, and the open circuit potential (OCP) can be considered to be near 0.6 V (vs. RHE).

![Graphs showing polarization currents](Image)

**Figure S5.** Control experiment in 1 mM AgNO$_3$ solution without HCOOH. (a)-(d) Four single PtTe nanocatalysts. There is no obvious deposition of Ag on single PtTe nanocatalysts. The sudden jump in the plots is due to the flying over of nanoparticles.
Figure S6. Calculation of instantaneous currents of single nanorods. (a) Schematic diagram of linear fitting of scattering intensity curve segments to calculate instantaneous current at a certain moment. (b) The correlation between the average current $i_{\text{average}}$ and $\Delta I / t$, the average rate of the scattering intensity variation during the reaction.

Calculation method of instantaneous currents of single nanorods. The black curve in Figure S6a is the single nanorod scattering intensity curve segment (1500 ~ 1550 s) recorded by the EMCCD camera, as shown by the blue dotted frame in Figure 1e. The blue curve in Figure S6a is the scattering intensity curve segment smoothed by the lowess algorithm, and the window width of the smoothing filter is 4999 points (249.95 s). The red curve in Figure S6a is the straight line obtained by linearly fitting the smoothed blue curve. The corresponding slope $k$ is $0.5696$ a.u./s, which is defined as the instantaneous reaction rate $k$ of a single nanorod at the initial time (1500 s).

Figure S6b reflects the conversion relationship between the instantaneous reaction rate $k$ and the instantaneous current $i$. The cross-sectional area $S$ of the deposited silver nanocluster can be obtained from the SEM image in Figure 1d. Assuming that the shape of the silver nanocluster is spherical, $S$ can be further converted into the average current $i_{\text{average}}$ during the reaction. The corresponding formulas are as follows:

\[
V = \frac{4S}{3\pi} \sqrt{\frac{S}{\pi}} \quad (S1)
\]

\[
N = \frac{\rho_{\text{Ag}} V N_A}{M t} \quad (S2)
\]

\[
i_{\text{average}} = N e \quad (S3)
\]
where $V$ is the volume of the deposited silver nanocluster, $N_A$ is the Avogadro constant, $r_{Ag}$ is the density of Ag, $M$ is the molar mass of Ag, $t$ is the total reaction time, and $N$ is the number of Ag atoms generated per second, $e$ is the amount of charge carried by a single electron.

The average rate of scattering intensity variation, $\Delta I / t$, can be identified as the average reaction rate $k_{\text{average}}$ of a single nanorod. For 121 single nanorod samples, the correlation between the average reaction rates $\Delta I / t$ and the corresponding average currents $i_{\text{average}}$ is shown in Figure S6b. From Figure S6b, when the used fitting equation is $\Delta I / t = m \ i_{\text{average}}$, the correlation between the two is high ($r = 0.961$), so it can be considered that the average reaction rate is proportional to the average current, and the conversion coefficient is the slope obtained by linear fitting ($m=4.2413$). This conversion factor is applied for the conversion between the instantaneous reaction rate $k$ and the instantaneous current $i$, there is:

$$i = 4.2413 \ k$$  \hspace{1cm} (S4)

Equation S4 can convert the instantaneous reaction rate of single PtTe nanorod into instantaneous current. According to this equation, the instantaneous current curve of a single nanorod with time during the reaction process is obtained, as shown in Figure 1f.
Figure S7. The noise value $\delta_i$ trajectory with the reaction time of a single nanorod.

As shown by the blue arrows in Figure S7, when the reaction time is 1500 s, the noise value $\delta_i$ at this time is 0.0713 fA.

According to Equation S4 and Equation 7, the signal-to-noise ratio at that time will be: $s = k/\delta = 4.2413k/\delta_i = 33.81$. Calculated signal-to-noise ratios at all moments are organized to obtain the signal-to-noise ratio trajectory with the reaction time as Figure 2b.
Figure S8. Statistical histograms of detect limits of single nanorods under different detect periods. The detect periods are (a) 20 s, (b) 100 s, (c) 200 s, and (d) 300 s.

It can be seen from Figure S8a, b, c and d that when the detect period is 10 s, the distribution range of instantaneous current detect limits of single nanorods is 0.47~0.73 fA. When the detect period is increased to 300 s, the distribution range of detect limits is 0.02~0.12 fA. With the extension of the detect period, the detect limits of single nanorods decrease significantly. Under different detect periods, all detect limits of single nanorods show a significant Gaussian distribution. Therefore, Gaussian fitting is performed for detect limits of single nanorods, and the obtained expected value is used as the overall detection limit of this detection method.
Figure S9. Activity of example single nanoparticle at different formic acid concentrations. (a) Trajectory for type-a. (b) Reaction rate for (a). (c) Trajectory for type-b. (d) Reaction rate for (c).
**Figure S10.** Correspondence between the turns of electrodeposition direction and the sudden rises of the instantaneous current. (a) Superimposition of the SEM image of a single nanorod and the scattering center trajectory during the reaction process. (b) The super-resolution coordinate curve with time along the x-axis direction. (c) The super-resolution coordinate curve with time along the x-axis direction. (d) The corresponding instantaneous current curve with time of a single nanorod.

The movie is decomposed into 2497 pictures to obtain the scattering center of each picture by two-dimensional gaussian fitting, and then the trajectory of the scattering emission centers of the single nanorod during the electrodeposition process, as shown in **Figure S10a**. The deposition growth direction on the single nanorod surface can be roughly determined (shown by the red arrow). The trajectory of the scattering emission centers is decomposed into the coordinates along the x-axis direction and the y-axis direction. The reference coordinates are shown by the blue dashed arrows in Figure S10a. The variation of coordinates along the x-axis is shown in Figure S10b, and the variation of the coordinates along the y-axis is shown in Figure S10c. From Figure S10b-c, the turn number of the scattering center trajectory during the process and the corresponding time domain (represented by black arrows) are obtained. Comparing the instantaneous current curve with time of a single nanorod, as shown in Figure S10d, the number and the time domain of sudden rises in the instantaneous current curve (represented by red arrows) correspond to the turns of the scattering center trajectory.
Figure S11. The curve of standard error of oscillation amplitudes with peak frequency.

It can be seen that the standard error generally decreases exponentially with the peak frequency. When the peak frequency is larger than 0.2 Hz, the decay of standard error is no longer significant. Two anomalous increases correspond to abnormal peak frequencies with rare occurrence, which are discussed as follows.

Figure S12. Correlation of frequency-amplitude graphs and SEM images of single nanorods with different abnormal peak frequencies. (a) 0.17 Hz. (b) 0.36 Hz. (c) 0.38 Hz. The insets are SEM images of corresponding single nanorods. The lengths of scale bars in the insets are 50 nm.
Figure S13. Correlation graph between the L-S transition type (0.05 Hz) oscillation amplitudes and average currents of single nanocatalysts.

Table S1. Comparison of the detect limitations of some nano-electrocatalytic current methods with the novel single nanoparticle coulometry method.

<table>
<thead>
<tr>
<th>Method</th>
<th>Probe</th>
<th>Detection Limit (S/N=3)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanoparticle Collision</td>
<td>Au Confined nanopore electrode</td>
<td>1.8±0.3 pA</td>
<td>[1]</td>
</tr>
<tr>
<td></td>
<td>Pt Tunneling ultramicroelectrode</td>
<td>&gt; 1.8 pA</td>
<td>[2]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ca. 150 fA (for photocurrent)</td>
<td></td>
</tr>
<tr>
<td>Single Nanoparticle Coulometry</td>
<td>Single PtTe nanorods</td>
<td>0.0396~0.5703 fA</td>
<td></td>
</tr>
</tbody>
</table>

We have defined that the detection limit is triple value of the background ground (that is to say, the signal-to-noise ratio (S/N) is fixed to 3). Usually, the detection limit is considered to be higher than the diffusion limiting current. The detection limit of most nano-electrocatalytic methods is limited to pA level. Only for some specific reaction system (such as photocurrent), the detection limit could reach sub-pA level. The detect limitation of the novel coulometry method is more than three orders of magnitude lower than other listed methods.
References


