

Supporting Information

Revealing the heterogeneous catalytic kinetics of PtRu nanocatalysts at single particle level

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Experimental section

Materials and reagents

All chemical reagents were used as received without further purification. Chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) was purchased from Aladdin and ruthenium chloride anhydrous (RuCl_3) purchased from innochem. Citric acid and sodium borohydride (NaBH_4) were purchased from Xilong Scientific Co., Ltd. Hydrochloric acid (HCl , 0.1 M) and sodium hydroxide solution (NaOH , 0.1 M) were used for adjusting pH of the solution. Ultrapure water (18.2 $\text{M}\Omega$ cm) was used as the solvent throughout.

Preparation of the PtRu nanoparticles, Pt nanoparticles and Ru nanoparticles

A mixed solution comprising H_2PtCl_6 , RuCl_3 and citric acid was prepared. The concentration of metal ion was fixed at 0.36 mM. Preparation of different ratios of nanoparticles by adjusting the amounts of H_2PtCl_6 and RuCl_3 . The ratio of the concentration of citric acid to the concentration of all metal ions was 0.42. The pH of the solution was adjusted to 5.8 using HCl and NaOH . Subsequently, freshly prepared NaBH_4 was added to the solution under stirring at room temperature. The theoretical value of NaBH_4 was calculated based on four and three times the concentration of Pt and Ru ion, respectively. The quantity of NaBH_4 employed was 1.4 times the theoretical value. Upon the addition of NaBH_4 , the color of the solution changed to brown, indicative of the formation of nanoparticles. The solution was stirred overnight to complete the reaction.

Single particle reaction experiments

Single particle measurements were performed on a homebuilt prism-type TIRFM based on an Olympus IX71 inverted microscope. A continuous wave circularly polarized 532 nm laser beam (CrystaLaser, GCL-025-L-0.5%) of 4 – 5 mW was focused onto an area of $\sim 5000 \mu\text{m}^2$ on the sample to directly excite the fluorescence of resorufin. The fluorescence of resorufin was collected by a $60 \times \text{NA}1.2$ water-immersion objective (UPLSAPO60XW, Olympus), filtered by two filters (HQ550LP, HQ580m60), and projected onto a camera (AndoriXon EMCCD, DU-897U-CS0-#BV), which is controlled by an Andor IQ software. All optical filters are from Chroma Technology Corp. For each movie, it was taken on a fresh flow cell with constant substrate concentrations. PBS solution ($\text{pH} = 7.4$) was bubbled with H_2 for 30 min to produce the H_2 -saturated solution, and then different amounts of resazurin were added into this solution to prepare the final reaction solution. By varying the substrate concentration of resazurin, we finally got a series of movies. The movies are analyzed using a home-written IDL program, which extracts the fluorescence intensity trajectories from localized fluorescence spots individually across the entire movie. The intensity of each bright spot in an image is obtained by integrating the signal counts over an area of $\sim 1 \times 1 \mu\text{m}^2$.

All single particle measurements were performed in a home-made flow cell ($100\mu\text{m}(\text{height}) \times 2\text{cm}(\text{width}) \times 5\text{mm}(\text{length})$) consisting of double-sided tape (3M) between a quartz slide (Technical Glass) and a borosilicate coverslip (Gold Seal). The gap between the quartz glass slide and the borosilicate coverslip was sealed with epoxy resin (Devcon). Two holes were drilled in the quartz slide with a 1 mm diamond-coated

drill bit and connected to polyethylene tubing (Instech Laboratories, 0.76 mm ID) and a syringe pump for continuous flow of solution at $10 \mu\text{L min}^{-1}$. Before assembling the home-made flow cell, $50 \mu\text{L}$ of the nanoparticle solution was spin-coated onto a quartz glass slide using a spin coater (Schwan Technology, E24 SPIN COATER). After 60 minutes, the slide was rinsed with ultrapure water and then blown dry with N_2 . In this way, the nanoparticles were dispersed on the quartz glass slide at a very dilute concentration.

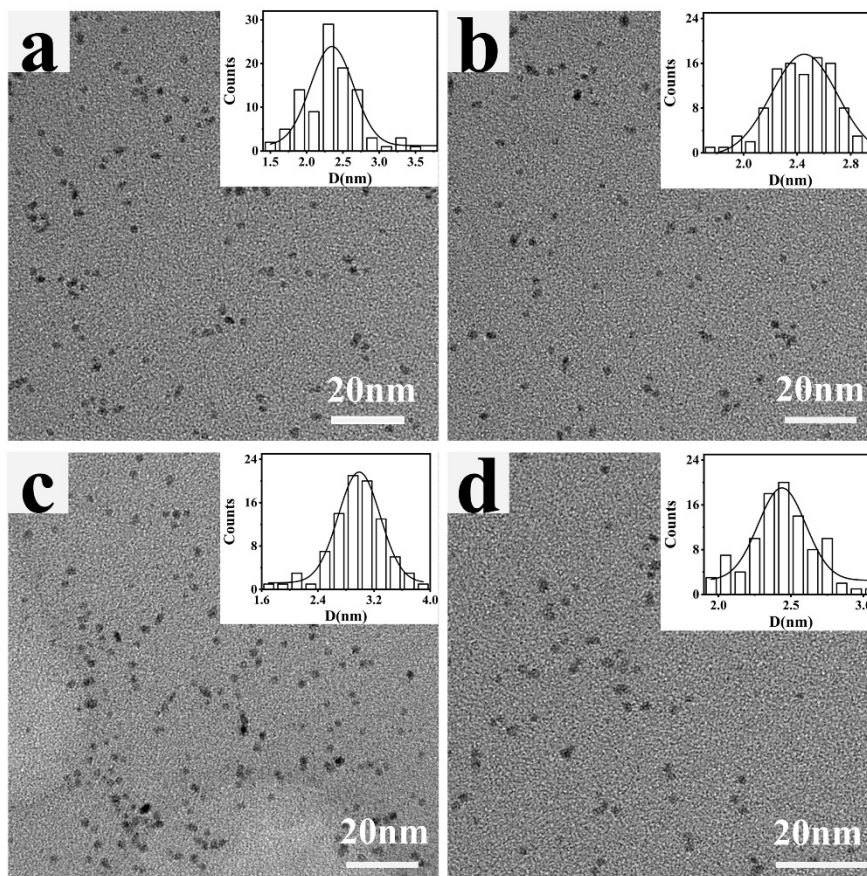


Figure S1. TEM image of (a) Pt₇₆Ru₂₄, (b) Pt₃₉Ru₆₁, (c) Pt and (d) Ru with sizes averaging about (a) 2.35 ± 0.05 nm, (b) 2.45 ± 0.02 nm, (c) 2.99 ± 0.01 nm and (d) 2.44 ± 0.02 nm.

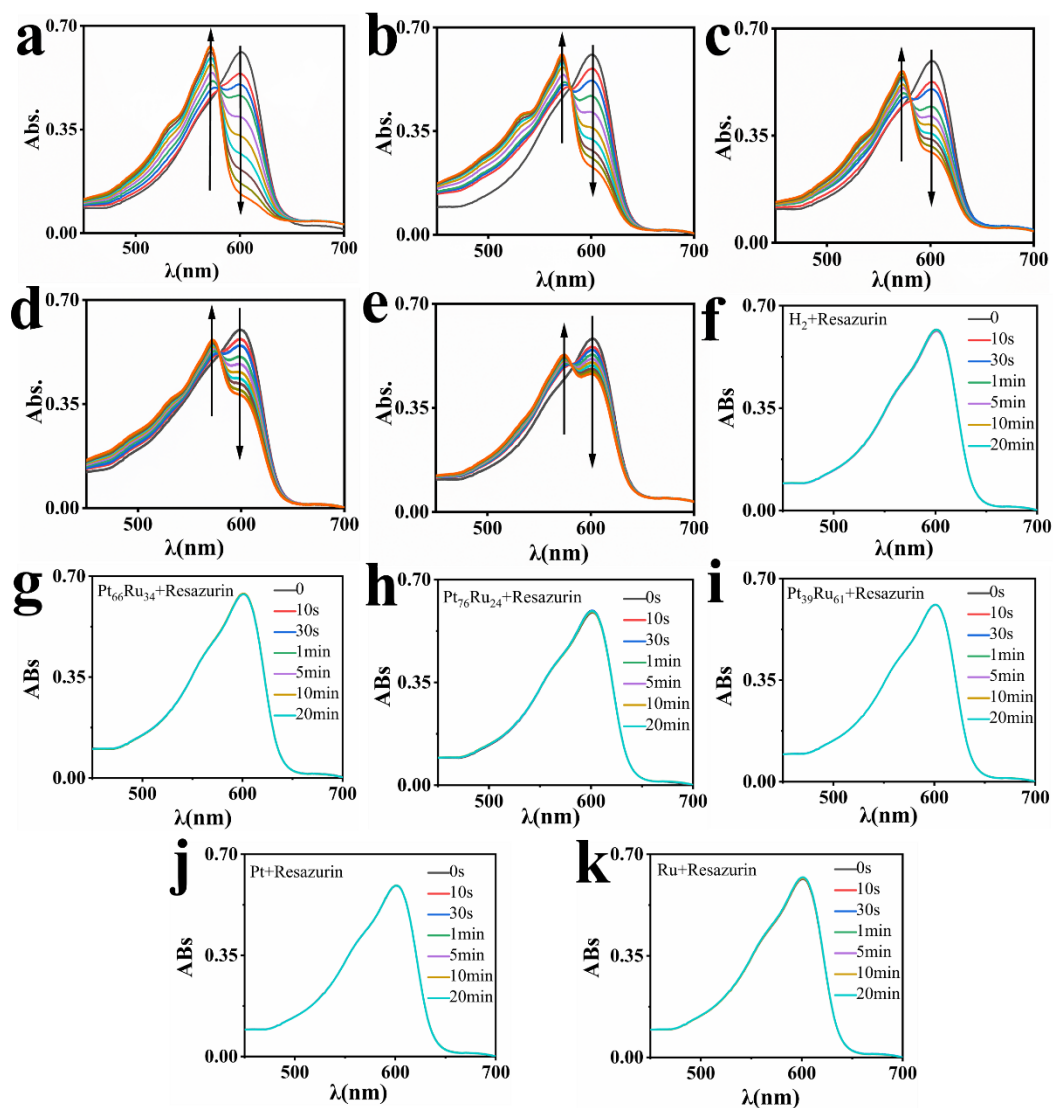


Figure S2 In situ absorption measurements of resazurin reduction by H_2 catalyzed by (a) $Pt_{66}Ru_{34}$ (b) $Pt_{76}Ru_{24}$, (c) $Pt_{39}Ru_{61}$, (d) Pt and (e) Ru in aqueous solution. (f-k) Control experiments without H_2 or nanoparticles. [resazurin] = 20 μ M.

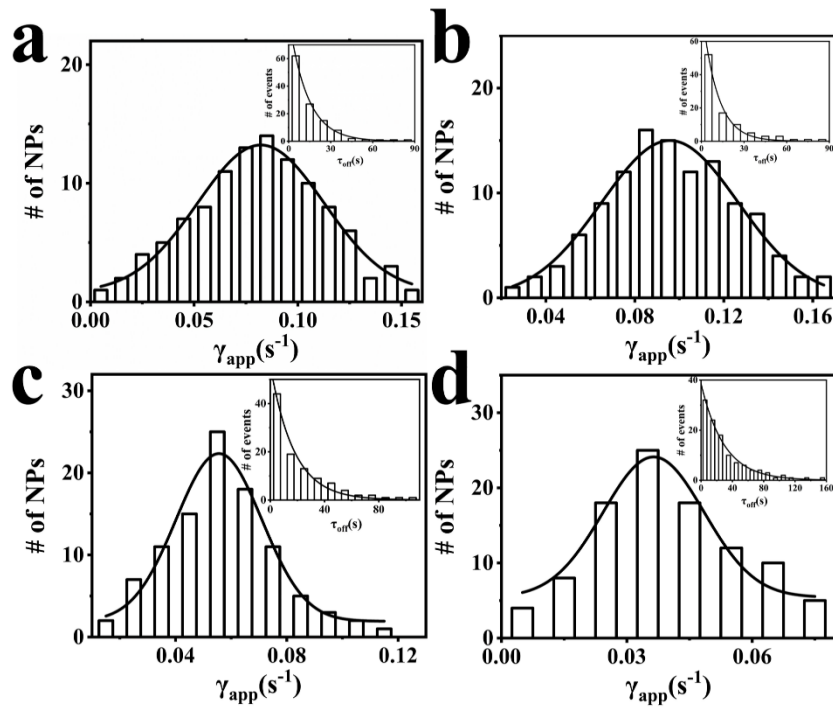


Figure S3 Distribution of γ_{app} of (a) Pt₇₆Ru₂₄, (b) Pt₃₉Ru₆₁, (c) Pt and (d) Ru at 10 nM resazurin. The solid lines are Gaussian fits. All experiments are in H₂-saturated solution. Insets: distributions of τ_{off} from a single trajectory. The solid line is single exponential fit and the decay constant is (a) $\gamma_{app} = 0.093 \pm 0.008$, (b) $\gamma_{app} = 0.075 \pm 0.003$, (c) $\gamma_{app} = 0.058 \pm 0.005$, (d) $\gamma_{app} = 0.034 \pm 0.001$.

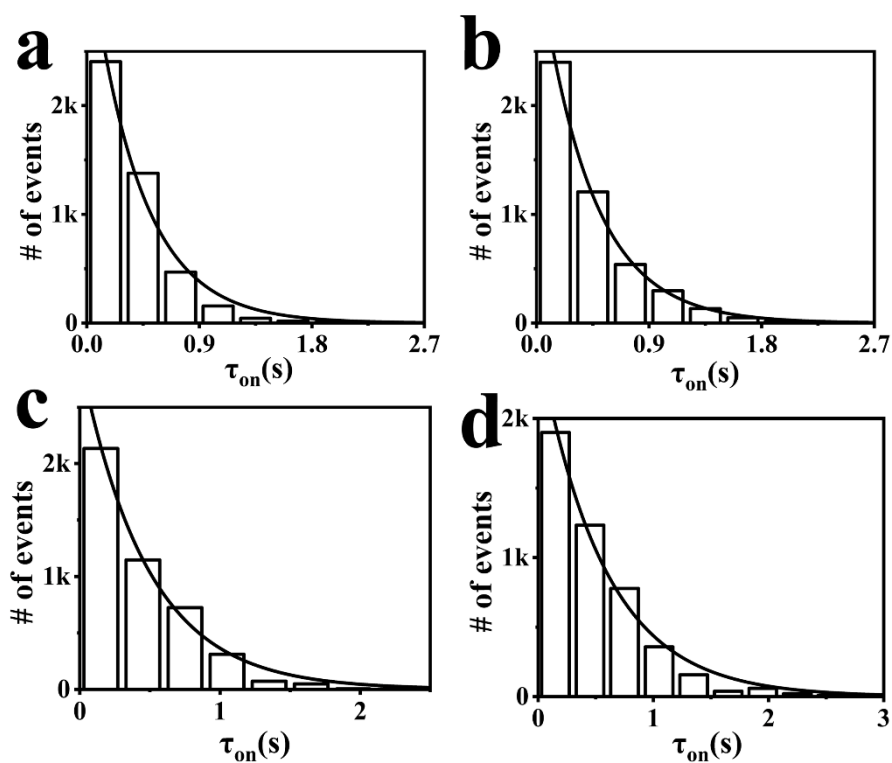


Figure S4 Distribution of τ_{on} from many trajectories of (a) Pt₇₆Ru₂₄, (b) Pt₃₉Ru₆₁, (c) Pt and (d) Ru at 10 nM resazurin; solid lines are single exponential fits. Fitting values are listed on Table 2 in main text.

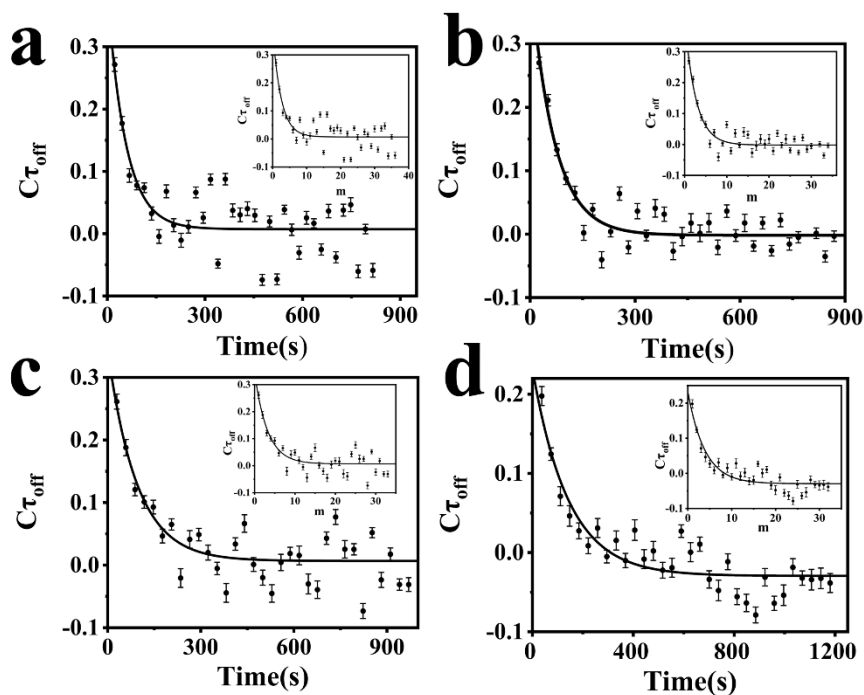


Figure S5 Autocorrelation function $C_{\tau_{\text{off}}}(t)$ of the microscopic reaction time τ from turnover trajectories of single (a) $\text{Pt}_{76}\text{Ru}_{24}$, (b) $\text{Pt}_{39}\text{Ru}_{61}$, (c) Pt and (d) Ru nanoparticles at 10 nM resazurin and in H_2 -saturated solution. The x-axis was converted from the turnover index m to real time using the average turnover time of each nanoparticle. Solid line is a single exponential fit, and the fluctuation correlation times are (a) 56 ± 16 s, (b) 68 ± 10 s, (c) 94 ± 20 s, and (d) 142 ± 28 s. Inset: autocorrelation function of the τ_{off} from the turnover trajectory of a single (a) $\text{Pt}_{76}\text{Ru}_{24}$, (b) $\text{Pt}_{39}\text{Ru}_{61}$, (c) Pt and (d) Ru nanoparticles. The solid line is a single exponential fit, and the decay constant are (a) 2.47 ± 0.69 , (b) 2.66 ± 0.36 , (c) 3.19 ± 0.7 , and (d) 3.85 ± 0.77 turnovers.

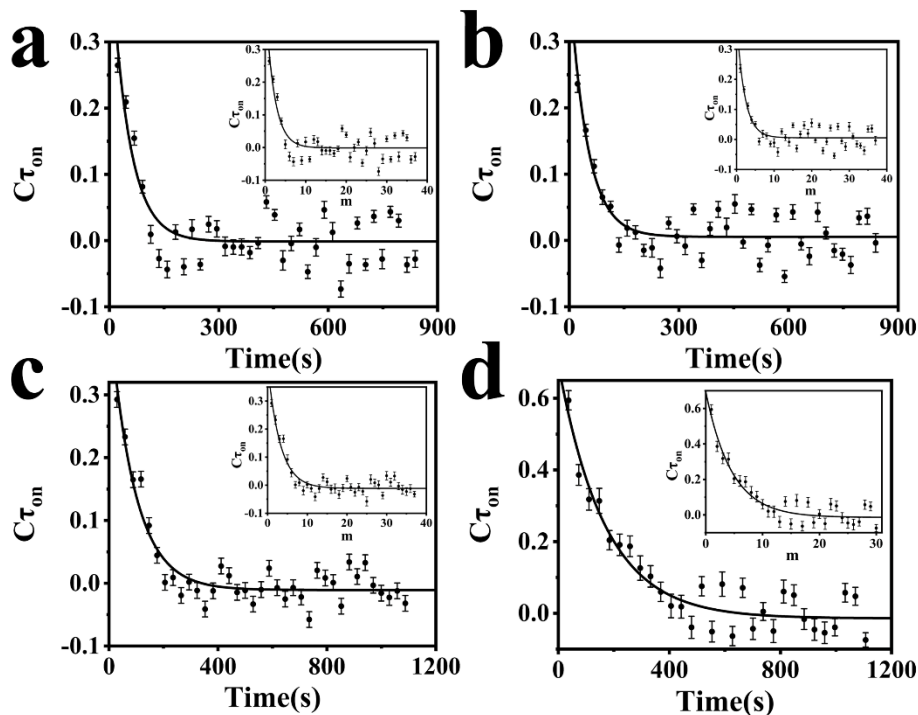


Figure S6 Autocorrelation function $C\tau_{on}(t)$ of the microscopic reaction time τ from turnover trajectories of single (a) Pt₇₆Ru₂₄, (b) Pt₃₉Ru₆₁, (c) Pt and (d) Ru nanoparticles at 10 nM resazurin and in H₂-saturated solution. The x-axis was converted from the turnover index m to real time using the average turnover time of each nanoparticle. Solid line is a single exponential fit, and the fluctuation correlation times are (a) 50 ± 11 s, (b) 56 ± 10 s, (c) 92 ± 11 s, and (d) 167 ± 23 s. Inset: autocorrelation function of the τ_{off} from the turnover trajectory of a single (a) Pt₇₆Ru₂₄, (b) Pt₃₉Ru₆₁, (c) Pt and (d) Ru nanoparticles. The solid line is a single exponential fit, and the decay constant are (a) 2.18 ± 0.46 , (b) 2.24 ± 0.46 , (c) 3.13 ± 0.37 , and (d) 4.53 ± 0.63 turnovers.

Schematic diagram of the kinetic mechanism of nanoparticles.

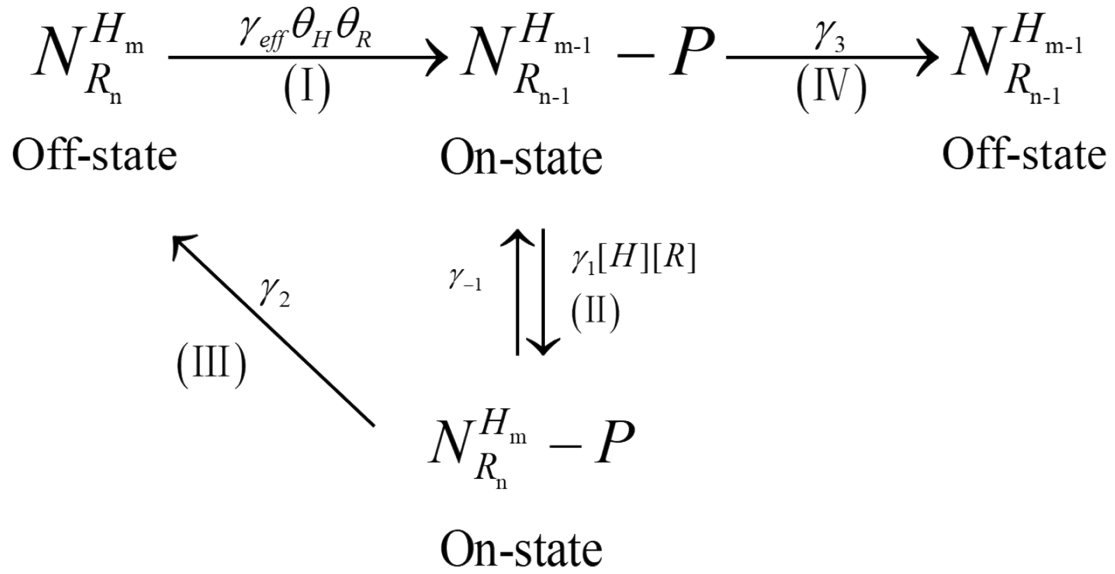
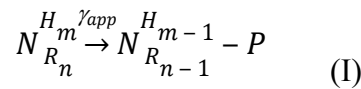


Figure S7 This reaction is based on the catalytic reaction kinetics mechanism of the Langmuir-Hinshelwood mechanism. In the schematic diagram, N stands for nanoparticles; H, R and P stands for hydrogen, Resazurin and Resorufin molecule; m and n represent the number of hydrogen and Resazurin molecules on a single nanoparticle when the adsorption reaction reaches equilibrium. γ_{eff} represent the rate constant of the reaction process; γ_1 and γ_{-1} represent the reaction rate constant of reversible reaction(II); θ_H and θ_R represent fraction of reaction sites occupied by hydrogen and Resazurin.

Derivation of the mechanism of the off-time, $f_{\text{off}}(\tau)$ and of $\langle \tau_{\text{off}} \rangle^{-1}$

In the single-molecule catalytic reaction, time is divided into two parts, the time to wait for product generation $\langle \tau_{\text{off}} \rangle$ and the time to dissociate after product generation $\langle \tau_{\text{on}} \rangle$. To analyze the above timing, we consider the Langmuir-Hinshelwood mechanism in heterogeneous catalysis. Therefore, we consider that the two reactants are uniformly bound on the surface of the nanoparticles, conform to the Langmuir adsorption isotherm, and quickly reach the adsorption-desorption equilibrium. According to this mechanism, the kinetic reaction mechanism regarding OFF time is:



where γ_{app} is the apparent rate constant for forming one product on one nanoparticle

surface and takes the form^{1,2}:

$$\gamma_{app} = \gamma n_R n_H = \gamma n_T^2 \theta_H \theta_R = \gamma_{eff} \theta_H \theta_R \quad (S1)$$

where γ is the rate constant representing the intrinsic reactivity per catalytic site for the catalytic conversion reaction; n_H and n_R are the numbers of hydrogen and Resazurin molecule adsorbed at the catalytic site on one nanoparticle surface; n_T is the total number of the surface catalytic sites on one nanoparticle; θ_H , θ_R is the fraction of the occupied surface catalytic sites by substrates. Form the Langmuir adsorption isotherm:

$$n_H = n_T \theta_H = n_T \frac{\alpha_H [H]}{1 + \alpha_H [H] + \alpha_R [R]} \quad (S2)$$

$$n_R = n_T \theta_R = n_T \frac{\alpha_R [R]}{1 + \alpha_H [H] + \alpha_R [R]} \quad (S3)$$

Here α_H , α_R are the H_2 and resazurin adsorption-equilibrium constants, then we get

$$\gamma_{app} = \gamma n_T^2 \frac{\alpha_H [H] \alpha_R [R]}{(1 + \alpha_H [H] + \alpha_R [R])^2} \quad (S4)$$

In conventional ensemble measurements where the catalysis by a large of nanoparticles are measured in solution, and the kinetic rate equations are

$$\frac{d[N_{R_n}^{H_m}]}{dt} = -\gamma_{app} [N_{R_n}^{H_m}] \quad (S5)$$

$$\frac{d[N_{R_{n-1}}^{H_{m-1} - P}]}{dt} = \gamma_{app} [N_{R_n}^{H_m}] \quad (S6)$$

where $[N_{R_n}^{H_m}]$ is the concentration of nanoparticles carrying no product, and $[N_{R_{n-1}}^{H_{m-1} - P}]$ is the concentration of nanoparticles on which one product molecule is generated.

Under the condition of single-nanoparticle measurements, the concentration of one nanoparticle is meaningless, so we use the probability of a single nanoparticle instead.

So we get the following formula:

$$\frac{dP_{\left[\begin{smallmatrix} H_m \\ N_{R_n} \end{smallmatrix} \right]}(t)}{dt} = -\gamma_{app} P_{\left[\begin{smallmatrix} H_m \\ N_{R_n} \end{smallmatrix} \right]}(t) \quad (S7)$$

$$\frac{dP_{\left[\begin{smallmatrix} H_{m-1} - P \\ N_{R_{n-1}} \end{smallmatrix} \right]}(t)}{dt} = \gamma_{app} P_{\left[\begin{smallmatrix} H_m \\ N_{R_n} \end{smallmatrix} \right]}(t) \quad (S8)$$

where $P(t)$'s are the probabilities for finding the single nanoparticle in the site $N_{R_n}^{H_m}$ and $N_{R_{n-1}}^{H_{m-1}-P}$. When $t=0$, no product molecule has formed. So in the initial state, the

equation $P_{\left[\begin{smallmatrix} H_m \\ N_{R_n} \end{smallmatrix} \right]}(0)$, $P_{\left[\begin{smallmatrix} H_{m-1} \\ N_{R_{n-1}} \end{smallmatrix} \right]}(0)$. And at any time within τ_{off} , $P_{\left[\begin{smallmatrix} H_m \\ N_{R_n} \end{smallmatrix} \right]}(t) + P_{\left[\begin{smallmatrix} H_{m-1} \\ N_{R_{n-1}} \end{smallmatrix} \right]}(t) = 1$.

Therefore, we can then evaluate the probability density of the time $\Delta\tau$ needed to complete the off-time reaction, $f_{off}(\tau)$, that is, the probability density is τ_{off} . The probability for finding a particle τ is $f_{off}(\tau)\Delta\tau$, which is equal to the probability of switching from the $N_{R_n}^{H_m}$ state to the $N_{R_{n-1}}^{H_{m-1}-P}$ state for the nanoparticle between $t=\tau$ and $t = \tau + \Delta\tau$. In the limit of infinitesimal $\Delta\tau$, we obtain:

$$f_{off}(t) = \frac{dP_{\left[\begin{smallmatrix} H_{m-1} - P \\ N_{R_{n-1}} \end{smallmatrix} \right]}(t)}{dt} = \gamma_{app} P_{\left[\begin{smallmatrix} H_m \\ N_{R_n} \end{smallmatrix} \right]}(t) = \gamma n_T^2 \frac{\alpha_H[H]\alpha_R[R]}{(1 + \alpha_H[H] + \alpha_R[R])^2} P_{\left[\begin{smallmatrix} H_m \\ N_{R_n} \end{smallmatrix} \right]}(t) \quad (S9)$$

Solving Equation 7 and 8 for with the initial conditions, we have:

$$f_{off}(t) = \gamma n_T^2 \frac{\alpha_H[H]\alpha_R[R]}{(1 + \alpha_H[H] + \alpha_R[R])^2} \exp\left(-\gamma n_T^2 \frac{\alpha_H[H]\alpha_R[R]}{(1 + \alpha_H[H] + \alpha_R[R])^2} t\right) = \gamma_{app} \exp\left(-\gamma_{app} t\right) \quad (S10)$$

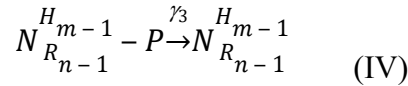
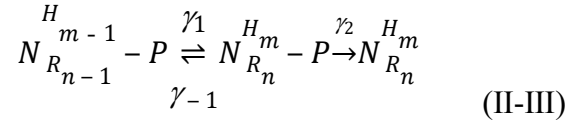
Then, $\langle\tau_{off}\rangle^{-1}$ represents the rate of product formation for a single nanoparticle:

$$\begin{aligned} \langle \tau_{off} \rangle^{-1} &= \frac{1}{\int_0^{\infty} \tau f_{off}(\tau) d\tau} = \gamma n_T^2 \frac{\alpha_H[H] \alpha_R[R]}{(1 + \alpha_H[H] + \alpha_R[R])^2} = \gamma_{eff} \frac{\alpha_H[H] \alpha_R[R]}{(1 + \alpha_H[H] + \alpha_R[R])^2} \end{aligned} \quad (S11)$$

Where $\gamma_{eff} = \gamma n_T^2$. In our experiments, the concentration of H_2 is fixed and the $[H]$ can be treated as a constant. From this equation, $\langle \tau_{off} \rangle^{-1}$ should increase initially and then decrease with increasing substrate concentration $[R]$.

Derivation of the distribution of the on-time, f_{on} , and of $\langle \tau_{on} \rangle^{-1}$

The on-time τ_{on} in the single-turnover trajectories spans from product formation to product dissociation, and it is the residence time of a product molecule on the nanoparticle surface after its formation. For product desorption, we considered two parallel desorption reaction pathways: one a substrate-assisted pathway (II-III) and the other a direct desorption pathway (IV):



Under the assumption of the mechanism where fast substrate adsorption equilibrium is established at all time, $N_{R_{n-1}}^{H_{m-1}}$ state will be quickly turned to the $N_{R_n}^{H_m}$ state, as substrate molecular in the solution will quickly bind to an available site to maintain the equilibrium. The conventional kinetic rate equations in concentration terms:

$$\frac{d[N_{R_{n-1}}^{H_{m-1}} - P]}{dt} = -(\gamma_1[H][R] + \gamma_3) [N_{R_{n-1}}^{H_{m-1}} - P] + \gamma_{-1} [N_{R_n}^{H_m} - P] \quad (S12)$$

$$\frac{d[N_{R_n}^{H_m} - P]}{dt} = \gamma_1[H][R] [N_{R_{n-1}}^{H_{m-1}} - P] - (\gamma_{-1} + \gamma_2) [N_{R_n}^{H_m} - P] \quad (S13)$$

$$\frac{d[N_{R_n}^{H_m}]}{dt} = \gamma_2 \left[N_{R_n}^{H_m} - P \right] \quad (\text{S14})$$

$$\frac{d[N_{R_{n-1}}^{H_{m-1}}]}{dt} = \gamma_3 \left[N_{R_{n-1}}^{H_{m-1}} - P \right] \quad (\text{S15})$$

In single-molecule measurements, the concentration terms of nanoparticles were replaced with their probabilities. We obtained:

$$\frac{dP \left[N_{R_{n-1}}^{H_{m-1}-P} \right] (t)}{dt} = -(\gamma_1[H][R] + \gamma_3)P \left[N_{R_{n-1}}^{H_{m-1}-P} \right] (t) + \gamma_{-1}P \left[N_{R_n}^{H_m-P} \right] (t) \quad (\text{S16})$$

$$\frac{dP \left[N_{R_n}^{H_m-P} \right] (t)}{dt} = \gamma_1[H][R]P \left[N_{R_{n-1}}^{H_{m-1}-P} \right] (t) - (\gamma_{-1} + \gamma_2)P \left[N_{R_n}^{H_m-P} \right] (t) \quad (\text{S17})$$

$$\frac{dP \left[N_{R_n}^{H_m} \right] (t)}{dt} = \gamma_2 P \left[N_{R_n}^{H_m-P} \right] (t) \quad (\text{S18})$$

$$\frac{dP \left[N_{R_{n-1}}^{H_{m-1}} \right] (t)}{dt} = \gamma_3 P \left[N_{R_{n-1}}^{H_{m-1}-P} \right] (t) \quad (\text{S19})$$

When $t = 0$, the Equations are $P \left[N_{R_{n-1}}^{H_{m-1}-P} \right] (0) = 1$, $P \left[N_{R_n}^{H_m-P} \right] (0) = 0$, $P \left[N_{R_n}^{H_m} \right] (0) = 0$, $P \left[N_{R_{n-1}}^{H_{m-1}} \right] (0) = 0$, and at any time,

$$P \left[N_{R_{n-1}}^{H_{m-1}-P} \right] (t) + P \left[N_{R_n}^{H_m-P} \right] (t) + P \left[N_{R_n}^{H_m} \right] (t) + P \left[N_{R_{n-1}}^{H_{m-1}} \right] (t) = 1$$

We can then consider the probability density $f_{\text{on}}(t)$ of the on-time τ_{on} . τ_{on} is the time required to finish reactions in eq 1c or the reaction eq 1d. The probability of finding a particular τ is $f_{\text{on}}(\tau)\Delta\tau$, which is equal to the sum of the probability for the nanoparticle

to switch from the $N_{R_{n-1}}^{H_{m-1}-P}$ states to the $N_{R_n}^{H_m}$ state between τ and $\tau + \Delta\tau$ and the probability for the nanoparticle to switch from the $N_{R_{n-1}}^{H_{m-1}-P}$ state to the $N_{R_{n-1}}^{H_{m-1}}$ state between τ and $\tau + \Delta\tau$. In the limit of infinitesimal $\Delta\tau$, we have

$$f_{on}(\tau) = \frac{dP_{\left[N_{R_n}^{H_m} \right]}(\tau)}{d\tau} + \frac{dP_{\left[N_{R_{n-1}}^{H_{m-1}} \right]}(\tau)}{d\tau} = \gamma_2 P_{\left[N_{R_n}^{H_m-P} \right]}(\tau) + \gamma_3 P_{\left[N_{R_{n-1}}^{H_{m-1}-P} \right]}(\tau) \quad (S20)$$

Solve the equation (S16-S19) based on initial, we get

$$f_{on}(\tau) = \frac{1}{2\alpha} [M e^{(\alpha+\beta)\tau} + N e^{(\beta-\alpha)\tau}] \quad (S21)$$

$$\alpha = \sqrt{(\gamma_1[H][R] + \gamma_{-1} + \gamma_2 + \gamma_3)^2/4 - (\gamma_1\gamma_2[H][R] + \gamma_{-1}\gamma_3 + \gamma_2\gamma_3)}$$

$$\beta = -(\gamma_1[H][R] + \gamma_{-1} + \gamma_2 + \gamma_3)/2$$

$$M = \gamma_1\gamma_2[H][R] + \gamma_3(\alpha + \beta + \gamma_{-1} + \gamma_2)$$

$$N = -\gamma_1\gamma_2[H][R] + \gamma_3(\alpha - \beta - \gamma_{-1} - \gamma_2)$$

For different substrate concentrations, $f_{on}(\tau)$ will exhibit different forms. When the resazurin concentration is extremely low and there is no path for substrate-assisted product desorption, that is $\gamma_{-1} = \gamma_1 = \gamma_2 = 0$. Formula (S21) simplifies to $f_{on}(\tau) = \gamma_3 e^{-\gamma_3\tau}$, this is an exponential decay function with γ_3 as the decay constant. When the concentration of resazurin is very high and product desorption is assisted by the substrate, the formula (S21) will be simplified to $f_{on}(\tau) = \gamma_2 e^{-\gamma_2\tau}$. High resazurin concentration causes product desorption to favor the substrate-assisted pathway, which makes the direct desorption pathway negligible.

Then $\langle \tau_{on} \rangle^{-1}$, which represents the time-averaged product desorption rate for a single nanoparticle, is

$$\langle \tau_{on} \rangle^{-1} = \frac{1}{\int_0^{\infty} \tau f_{on}(\tau) d\tau} = \frac{\gamma_2 K[H][R] + \gamma_3}{1 + K[H][R]} = \frac{\gamma_2 G[R] + \gamma_3}{1 + G[R]} \quad (S22)$$

Here, $K = \gamma_1/(\gamma_{-1} + \gamma_2)$. The concentration of [H] can be seen as a constant, $G=K[H]$.

When $[R] \rightarrow 0$, we get

$$\langle \tau_{on} \rangle^{-1} = \frac{\gamma_2 G[R] + \gamma_3}{1 + G[R]} = \gamma_3 \quad (\text{S23})$$

When $[R] \rightarrow \infty$, we can get

$$\langle \tau_{on} \rangle^{-1} = \frac{\gamma_2 G[R] + \gamma_3}{1 + G[R]} = \gamma_2 \quad (\text{S24})$$

To give a physical interpretation of [R] dependence of, $\langle \tau_{on} \rangle^{-1}$, when $[R] \rightarrow 0$, the tendency forward reaction III is extremely low, then the product desorption dominantly takes the direct desorption pathway (reaction IV) and the reaction rate constant is γ_3 . When $[R] \rightarrow \infty$, the product desorption will dominantly take the substrate-assisted pathway (reaction III) and the reaction rate constant is γ_2 .

- (1) Liu X, Ge X, Cao J, et al. Revealing the catalytic kinetics and dynamics of individual Pt atoms at the single-molecule level[J]. Proceedings of the National Academy of Sciences, 2022, 119(14): e2114639119.
- (2) Xu W, Kong J S, Chen P. Single-molecule kinetic theory of heterogeneous and enzyme catalysis[J]. The Journal of Physical Chemistry C, 2009, 113(6): 2393-2404.