Supporting Information for

**Enhanced Catalytic Activity of Gold@Polydopamine Nanoreactors with Multi-Compartment Structure under NIR Irradiation**

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**Supplementary Figures and Discussion**

**Fig. S1** Porous PS-P2VP particles with different swelling ratios. a $M_n$ (P2VP) = 50000 g mol⁻¹, $M_n$ (PS) = 16500 g mol⁻¹; b $M_n$ (P2VP) = 10400 g mol⁻¹, $M_n$ (PS) = 23600 g mol⁻¹; c $M_n$ (P2VP) = 4800 g mol⁻¹, $M_n$ (PS) = 26000 g mol⁻¹
**Fig. S2** a FTIR and b XRD spectra of the Au@PDA porous particles. c Nitrogen adsorption/desorption isotherms of the Au@PDA particles. d Pore size distribution curve

**Fig. S3** a PDA@PS-P2VP porous particles produced from reaction time less than 4h: A very thin layer of PDA formed on the surface of the templates; b The distorted PDA particles after removal of the PS-P2VP template

**Fig. S4** PDA particles obtained from reaction for 11 h. The PDA thickness is ~14 nm
**Fig. S5** a UV-vis spectra of the reduction of 4-nitrophenol by NaBH₄ using the Au@PDA particles as catalytic nanoreactors, b Conversion efficiency of the PDA@Au catalytic nanoreactors in 5 consecutive reaction cycles; TEM images of the PDA@Au particles before (c) and after (d) used in catalytic reduction reactions.

**Fig. S6** Au NPs measured for the total surface area in the catalytic reactions. a Size distribution of the Au nanoparticles; b TGA measurement of the Au@PDA particles shows that the Au content is ~71.4%

**Kinetic Analysis of the Catalytic Reduction of 4-Nitrophenol**

The Langmuir-Hinshelwood kinetics [S1-S4] has been used for the mechanistic analysis of the catalytic activity. As shown in **Fig. S7**, 4-nitrophenol (Nip) is first reduced to 4-nitrosophenol and then to 4-hydroxylaminophenol (Hx). In the final step, Hx is reduced to 4-aminophenol (Amp) [S2]. The kinetic study follows a system of two coupled differential equations which describe the two steps of the reduction [S2-S4]:

S3/S9
\[
- \frac{dc_{Nip}}{dt} = k_a S \frac{(K_{Nip})^n (c_{Nip})^n K_{BH4} c_{BH4}}{[1 + K_{Hx} c_{Hx} + (K_{Nip} c_{Nip})^n + K_{BH4} c_{BH4}]}^2 = \left( \frac{dc_{Hx}}{dt} \right)_{source} \quad (S1)
\]

\[
\frac{dc_{Hx}}{dt} = k_a S \frac{(K_{Nip})^n (c_{Nip})^n K_{BH4} c_{BH4}}{[1 + K_{Hx} c_{Hx} + (K_{Nip} c_{Nip})^n + K_{BH4} c_{BH4}]}^2 - k_b S \frac{K_{Hx} c_{Hx} K_{BH4} c_{BH4}}{[1 + K_{Hx} c_{Hx} + (K_{Nip} c_{Nip})^n + K_{BH4} c_{BH4}]}^2 \quad (S2)
\]

Here \( K_{Nip}, K_{Hx} \) and \( K_{BH4} \) are the Langmuir adsorption constants of the respective compounds, and \( k_a, k_b \) represent the reaction rate constants of step A and B, respectively. Equation (S1) describes the decay rate of 4-nitrophenol and the generation of Hx. Equation (S2) presents the generation and decay of the intermediate Hx. The concentration of 4-nitrophenol as the function of reaction time was then calculated by the numerical solution of Eqs. (S1) and (S2) as reported [S2-S4]

**Fig. S7** Mechanism of the reduction of 4-Nip by metallic nanoparticles on the direct route
Fig. S8 Fit of the concentration of 4-nitrophenol as the function of time by the numerical solution of Eqs. (S1) and (S2). The solid lines refer to the fits by the kinetic model. The concentration of 4-nitrophenol was normalized to the respective starting concentration $c_{Nip,0}$. The experimental data have been taken from reactions at 20 °C (data points with error bars)

As shown in Fig. S8, the concentration of 4-nitrophenol normalized by respective initial concentration $c_{Nip,0}$ was plotted as the function of time with different initial
concentrations of 4-nitrophenol and BH$_4^-$ The solid lines are the fits by theory. From Fig. S8 it can be seen that the experimental data can be well fitted even when the conversion reaches 70%. This is the first time that full kinetic study has been approved to be applied for catalytic nanoreactor with complex nanostructure.

**Theory for Surface Versus Diffusion Controlled Reactions**

The total catalytic reaction time in a pseudo-unimolecular reaction, $k^{-1}_{app}$, is the sum of the time for the reactant 4-nitrophenol to diffuse to the gold nanoparticles in the Au@PDA nanoreactors, $k^{-1}_D$, and the time to get reduced by sodium borohydride NaBH$_4$ adjacent to a nanoparticle, $k^{-1}_S$,

$$k^{-1}_{app} = k^{-1}_D + k^{-1}_S$$  \hspace{1cm} (S3)

Likewise, the diffusion time has two contributions: the diffusion from the bulk to the Au@PDA nanoreactor, $k^{-1}_{D0}$, and the diffusion from the outer surface of the PDA shell to the surface of a gold nanoparticle, $k^{-1}_{Dg}$, i.e. $k^{-1}_D = k^{-1}_{D0} + k^{-1}_{Dg}$. Since the density of gold nanoparticles in the nanoreactor is very large (e.g., as shown in Fig. 3), according to theoretical study for nanoreactors [S5] the rate limiting step in the diffusion approach (i.e. the slowest time) is the mean time to reach the nanoreactor from the bulk. Thus, in the case of a fully diffusion-controlled reaction, the macroscopically observable rate is given by the Smoluchowski rate [S5]

$$k_D \approx 4\pi D_0 R_0 c_{NR}$$  \hspace{1cm} (S4)

where $D_0 \sim 1$ nm$^2$ ns$^{-1}$ is the diffusion coefficient of 4-nitrophenol in water, $R_0 \sim (100-200)$ nm is the outer radius of the nanoreactor, and $c_{NR} = 0.025$ mg mL$^{-1}$ is the concentration of nanoreactors in solution. We estimate the molecular weight of our Au@PDA nanoreactors as:

$$MW_{NR} = V_{NR} \phi_{NR} \rho_{NR}$$  \hspace{1cm} (S5)

being $V_{NR} = (4\pi/3)R_0^3$ the nanoreactor volume, $\phi_{NR}$ the fraction of empty space in the porous hybrid nanoreactors, which we estimate to be 0.5 (based on analysis of tomography, Fig. 5 in the main manuscript), and $\rho_{NR} = 1.5$ g cm$^{-3}$ the mass density of the nanoreactor which we assume to be equal to the mass density of condensed PDA [S6]. Taking this into account, we find that the molar concentration of Au@PDA nanoreactors is $c_{NR} \sim 4 \cdot 10^{-12}$ M.

If we make an order of magnitude analysis, we conclude that $k^{-1}_D \sim 0.1 - 1$ s. From Fig. S9 and the other experimental data, we note that the apparent rate constant is, $k_{app} \sim 10^{-3} - 10^{-2}$ s$^{-1}$, which means that the total catalytic reaction time is
\( k_{\text{app}}^{-1} \sim 100 - 1000 \text{ s} \). Since the diffusion time is approximately at least 2-3 orders of magnitude smaller than the total catalytic reaction time, using Eq. (S3) we clearly conclude that the reaction is surface-controlled.

We express the surface reaction rate, \( k_s \), as

\[
k_s = K_{\text{vol}} c_{\text{Nip,}\text{g}}
\]  

(S6)

Where \( c_{\text{Nip,}\text{g}} \) is the 4-nitrophenol concentration in the nanoreactor next to the gold nanoparticles, and \( K_{\text{vol}} = k_{\text{vol}} \Delta V \), being \( k_{\text{vol}} \) the fraction per unit time of the 4-nitrophenol molecules that are reduced by NaBH\(_4\), and \( \Delta V \) the volume of the shell next to the gold nanoparticles where effectively the chemical reaction is happening. As a consequence, the surface reaction is directly proportional to the 4-nitrophenol and BH\(_4^-\) concentrations within the reactive volume. For large concentrations, a competition of both reactants for reactive sites on the metal surface would lead to a saturation and to a subsequent slowdown of the surface reaction rate.

We find such behavior in the total reaction rate, Fig. S9. The apparent rate, \( k_{\text{app}} \), increases linearly with increasing BH\(_4^-\) concentration. The diminution of \( k_{\text{app}} \) with increasing 4-nitrophenol concentration is due to the nearly full coverage of the nanoparticles surface by 4-nitrophenol, which as well slows down the injection of electrons to the metal surface. If the reaction would be diffusion-controlled, a modification of the BH\(_4^-\) concentration would not affect the total rate (since the concentration of BH\(_4^-\) is in large excess and the bimolecular reaction can be effectively considered as pseudo-unimolecular). This fact supports our conclusion about the surface-controlled nature of the catalytic reaction.
**Fig. S9** Dependence of the apparent rate constant, $k_{app}$, with the borohydrate concentration for different initial 4-nitrophenol concentrations. The solid lines refer to the fit of the experimental data obtained using, e.g., Eq. (3a) in Ref. [S7]

![Graph showing dependence of the apparent rate constant, $k_{app}$, with borohydrate concentration for different initial 4-nitrophenol concentrations.]

**Fig. S10** Control experiment with only reactants of 4-nitrophenol and BH$_4^-$ but without Au@PDA nanoreactors under NIR irradiation (808 nm, 3 W cm$^{-2}$, 500 S)

**Supplementary References**

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