Supporting Information to:

Size Dependent Catalytic Activity and Dynamics of Gold Nanoparticles at the Single-Molecule Level

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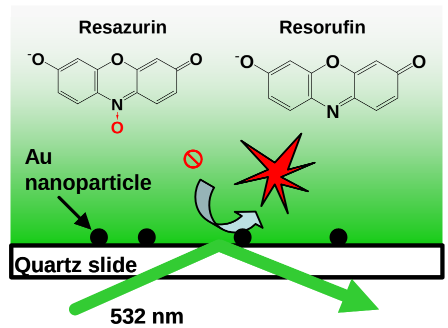
Supplementary Figures



Scheme S1. Experimental design and reaction scheme.

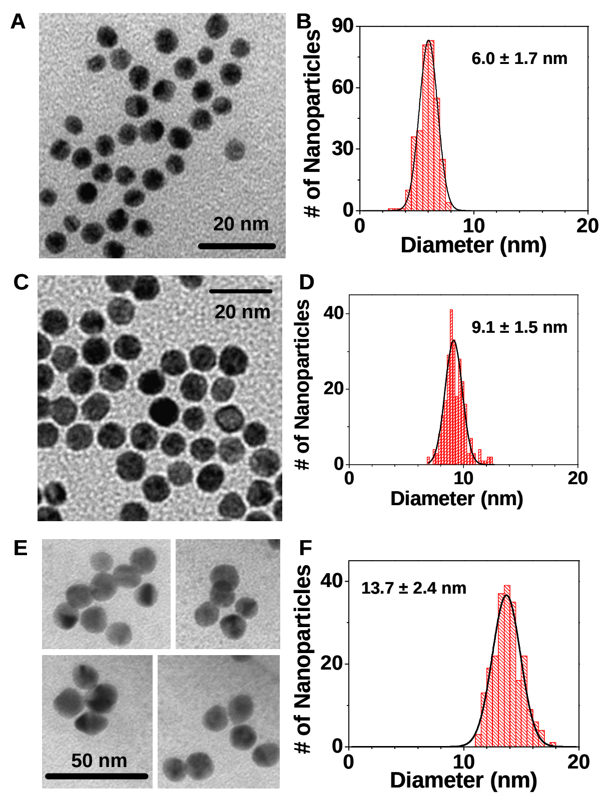


Figure S1. TEM images and diameter distributions of 6.0 nm (A, B), 9.1 nm (C, D), and 13.7 nm (E, F) Au-nanoparticles. Figures A and B taken from Xu et al, *Nat. Mater.* **2008**, *7*, 992.

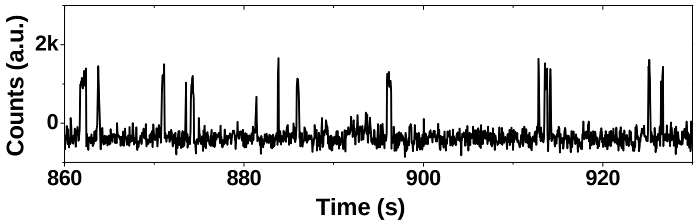


Figure S2. Segment of an exemplary fluorescence turnover trajectory of a single 13.7 nm Au-nanoparticle at 0.4 μM resazurin, 1 mM NH_2OH, and 50 ms imaging rate.

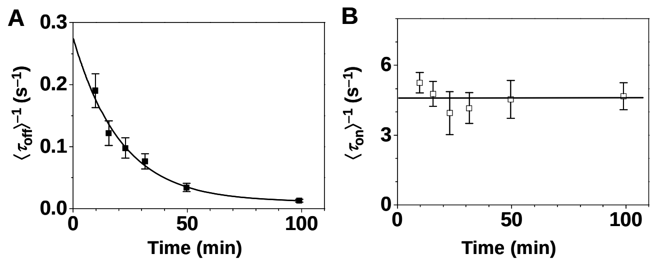


Figure S3. Exemplary time profiles of $\langle \tau_{off} \rangle^{-1}$ (A) and $\langle \tau_{on} \rangle^{-1}$ (B) from the turnover trajectory of a single 13.7 nm Au-nanoparticle at 0.6 μM resazurin and 1 mM NH_2OH. Each data point is an average of tens of turnovers, and the error bar is s.e.m. The solid line in (A) is a fit with exponential function $\langle \tau_{off} \rangle^{-1} = ae^{-t/c} + b$, and the fitted value at $t = 0$ is used as the initial value at this resazurin concentration for the titration curves in Figure 2B.

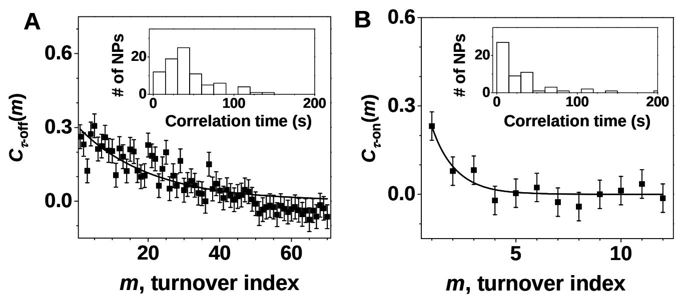


Figure S4. Autocorrelation functions of the τ_{off} (A) and τ_{on} (B) from the turnover trajectory of a single 13.7 nm Au-nanoparticle at 0.8 μM resazurin. The average turnover time of this trajectory is ~9.3 s. Solid lines are exponential fits with decay constants of m_{off} = 20.1 ± 0.1 and m_{on} = 1.1 ± 0.5 turnovers. Inset: Histograms of fluctuation correlation times for τ_{off} and τ_{on} reactions at 0.8 μM resazurin. NPs: nanoparticles.

Control experiments on possible effects of citrate on catalysis and surface restructuring.

The three colloidal Au-nanoparticles we studied here have citrate ions on their surfaces as stabilization ligands. Although these nanoparticles were extensively washed with water after immobilization on the quartz surface, residual citrate can still be present and may play roles in the catalysis and the dynamic surface restructuring. To probe the possible effects of citrate, we studied the Au-nanoparticle catalysis in the presence of varying citrate concentrations. First, we studied the effects of citrate on catalysis at the ensemble level, using UV-Vis absorption to follow consumption of resazurin and focusing on the smaller 6.0 nm and the larger 13.7 nm particles as representatives. With fixed initial concentrations of resazurin and NH_2OH and fixed amount of Au-nanoparticle catalysts, we measured how the initial reaction rate (i.e., the rate of resazurin consumption) depends on the citrate concentration. Up to 1 mM citrate, a concentration much larger than the possible residual citrate concentration in our nanoparticle samples, no significant effects are observed in the reaction rates (Figure S5). We thus conclude that citrate plays no significant roles in catalysis under our experimental conditions.

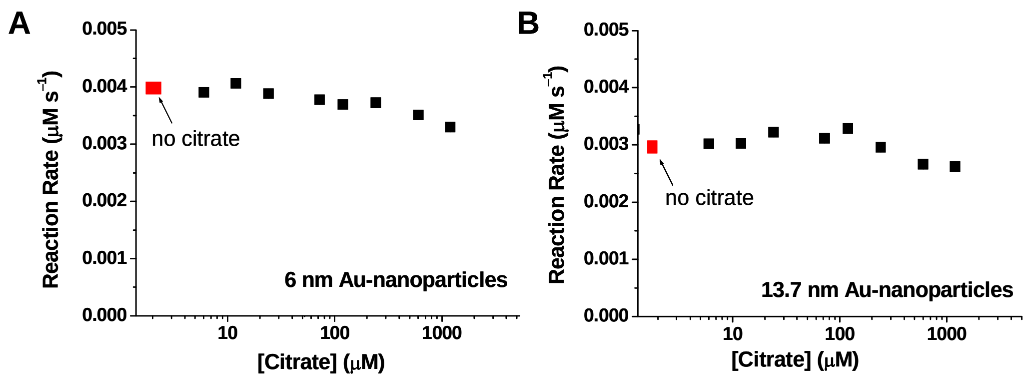


Figure S5. Titrations of the initial ensemble reaction rates of Au-nanoparticle catalyzed resazurin reduction to resorufin in the presence of increasing citrate concentrations. (A) For 6.0 nm Au-nanoparticles. [Au nanoparticles] ≈ 2.7 nM, [NH_2OH] = 1 mM, [S] = 6 μM, and pH 7.3. (B) For 13.7 nm Au-nanoparticles. [Au nanoparticles] ≈ 40 pM, [NH_2OH] = 1 mM, [S] = 6 μM, and pH 7.3. The reaction rates in the absence of citrate are also plotted on the figure (red squares) as references, but artificially displaced on the x-axis to be visible on the log-scale x-axes.

Second, we studied Au-nanoparticle catalysis at the single-molecule level in the presence of varying citrate concentrations, using 13.7 nm particles as representative. At fixed [resazurin] and [NH_2OH], $\langle \tau_{off} \rangle^{-1}$ and $\langle \tau_{on} \rangle^{-1}$, the single-particle rates of product formation and dissociation, show no significant dependence on the citrate concentration up to 2 μM, a concentration 20 times larger than the resazurin concentration (0.1 μM) (Figure S6). This further indicates that citrate plays no significant role in catalysis under our experimental conditions.

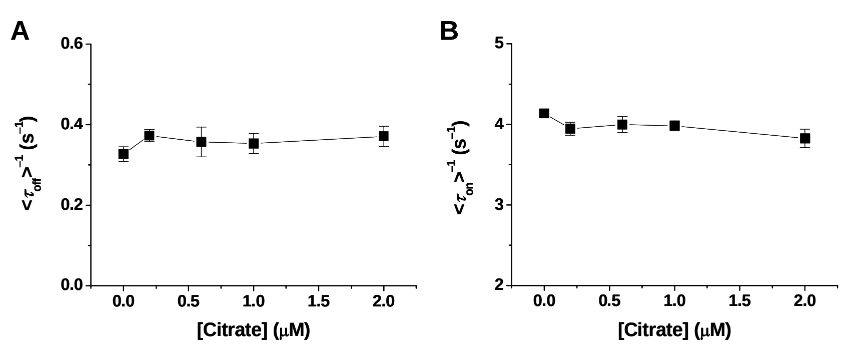


Figure S6. Titration of $\langle \tau_{off} \rangle^{-1}$ (A) and $\langle \tau_{on} \rangle^{-1}$ (B) of 13.7 nm individual Au-nanoparticles with increasing citrate concentration. Each data point is averaged over about 40-150 nanoparticles. [S] = 0.1 μM, [NH_2OH] = 1 mM, and pH = 7.3.

We further analyzed the possible effect of citrate on the surface restructuring dynamics. The activity fluctuation rates of both the τ_{off} and τ_{on} reactions do not show significant dependence on the citrate concentration (Figure S7). Therefore, citrate does not play significant roles in the dynamic surface restructuring of Au-nanoparticles.

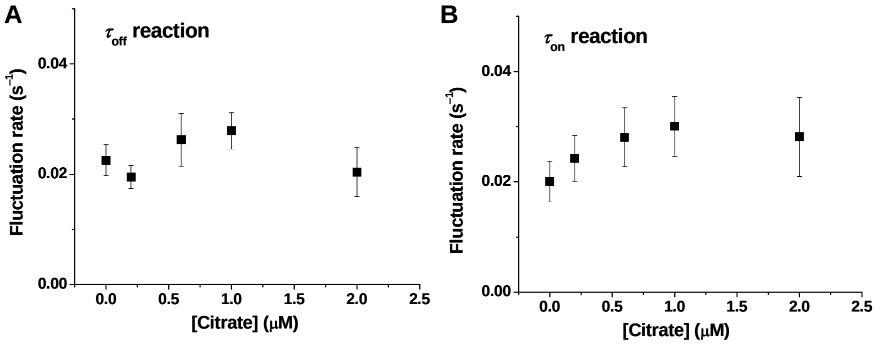


Figure S7. Effect of citrate concentration on the activity fluctuation rate (the inverse of the fluctuation correlation time) of the τ_{off} reaction (A) and the τ_{on} reaction (B) of 13.7 nm Au-nanoparticles. Each data point is an average from about 40-150 nanoparticles.

Supplementary Tables

Table S1. Fitting Parameters for Single-Particle [S] Titrations of $\langle\tau_{on}\rangle^{-1}$ in Figure 3.

	9.1 nm Nanoparticles			13.7 nm Nanoparticles		
	k_2 (s^{-1})	k_3 (s^{-1})	K_2 (μM^{-1})	k_2 (s^{-1})	k_3 (s^{-1})	K_2 (μM^{-1})
Type I	4.06±0.03	0.8±0.3	29±5	4.97±0.01	2.10±0.02	9.4±0.3
Type II	2.59±0.07	9.9±0.6	110±10	3.8±0.2	11±2	90±30
Type III	$k_2 = k_3$ = 3.0±0.2		-	$k_2 = k_3$ = 4.0±0.1		-

Table S2. Linear fit parameters for Figures 4C and D.

	Fluctuation rates of τ_{off} reaction			Fluctuation rates of τ_{on} reaction		
	6.0 nm	9.1 nm	13.7 nm	6.0 nm	9.1 nm	13.7 nm
Slope	0.23±0.03	0.25±0.02	0.23±0.01	0.64±0.04	0.34±0.04	0.24±0.03
Intercept	0.023±0.003	0.000±0.005	0.000±0.003	0.007±0.004	0.001±0.004	0.002±0.003
Intercept/Slope	0.10±0.04	0.00±0.02	0.00±0.01	0.01±0.01	0.00±0.01	0.01±0.01