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SUPPLEMENTARY INFORMATION

Galvanic Reactions at the Single-Nanoparticle Level: Tuning Between Mechanistic Extremes

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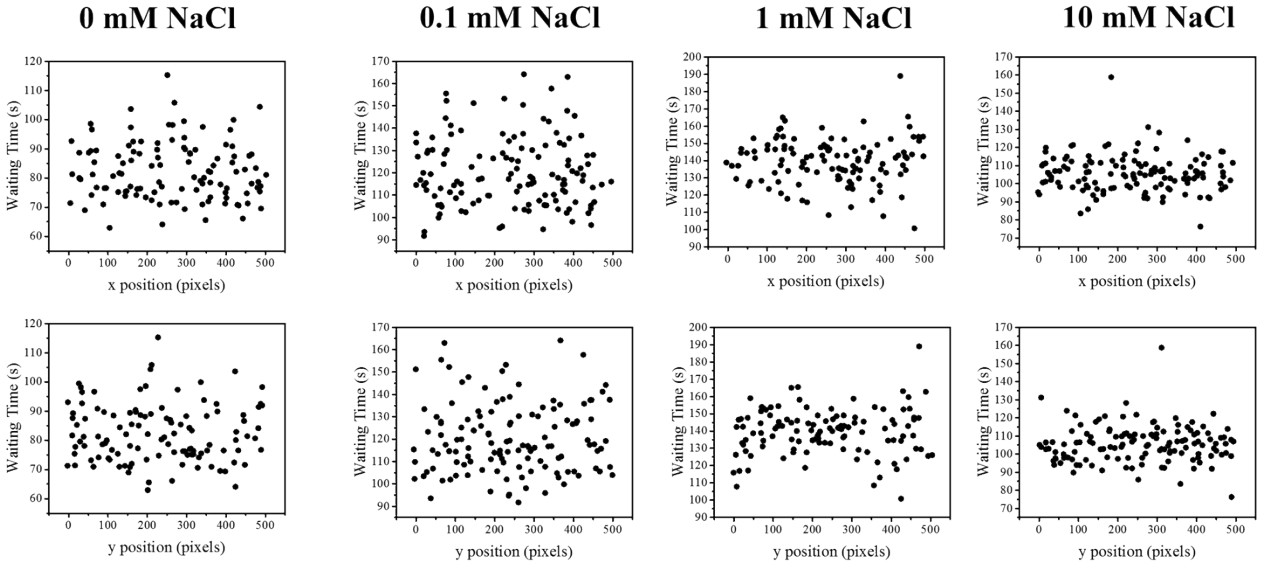

Figure S1. Plots show the lack of position bias in waiting times of individual NPs for the 0, 0.1, 1 and 10 mM NaCl cases (from left to right, respectively) shown in Fig. 1**.** For all NPs in each experiment, the waiting time is plotted versus the location of the NP in the field of view, in the form of *x* (top) and y (bottom) pixel positions.

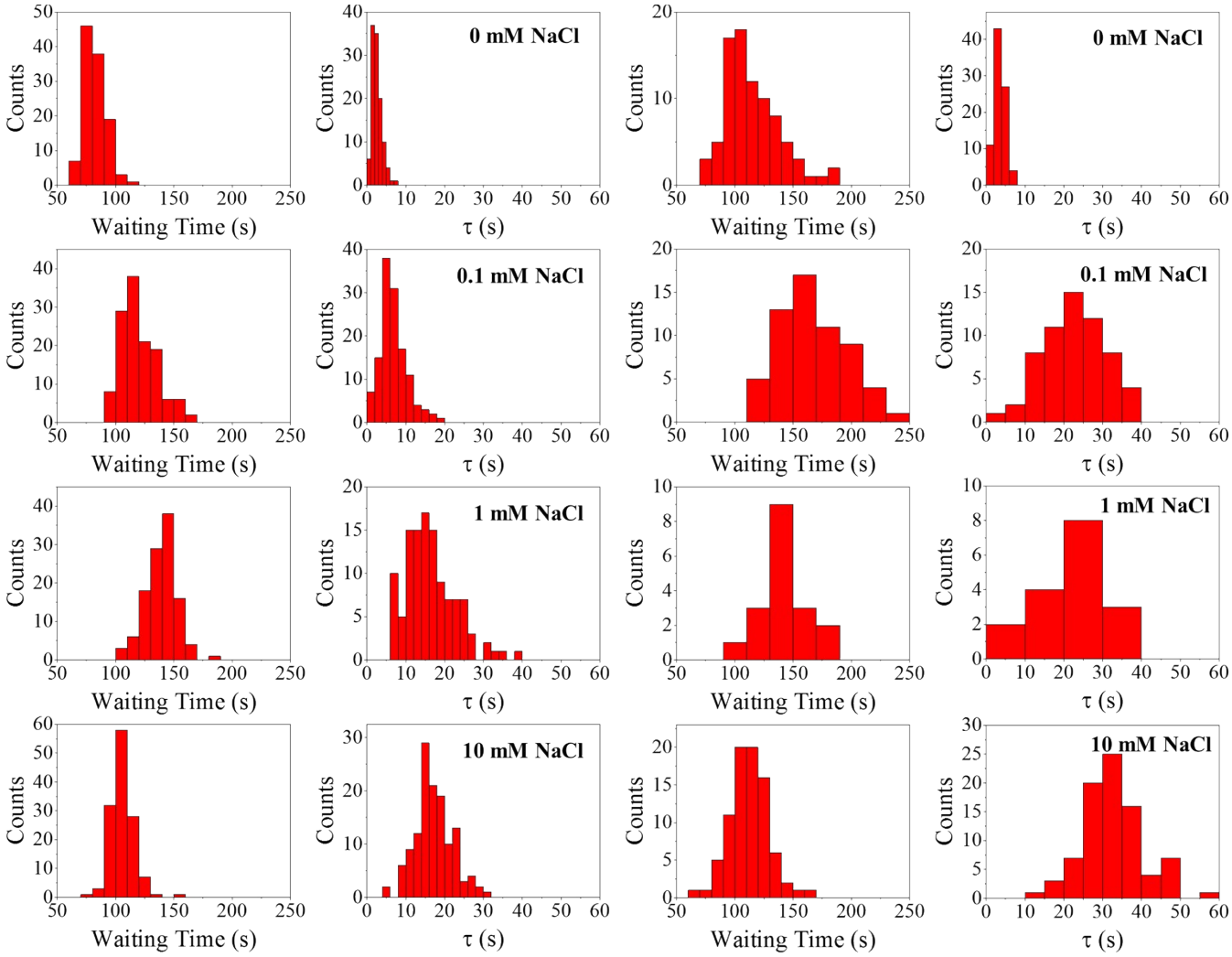

Figure S2. Histograms of waiting times and τ values for two separate trials (left and right) of NaCl concentration dependence experiments performed on 34 nm Ag nanospheres. The bin-width for each histogram was chosen to best reflect the distribution. The bin-width shown here also corresponds to the value used in the fitting.

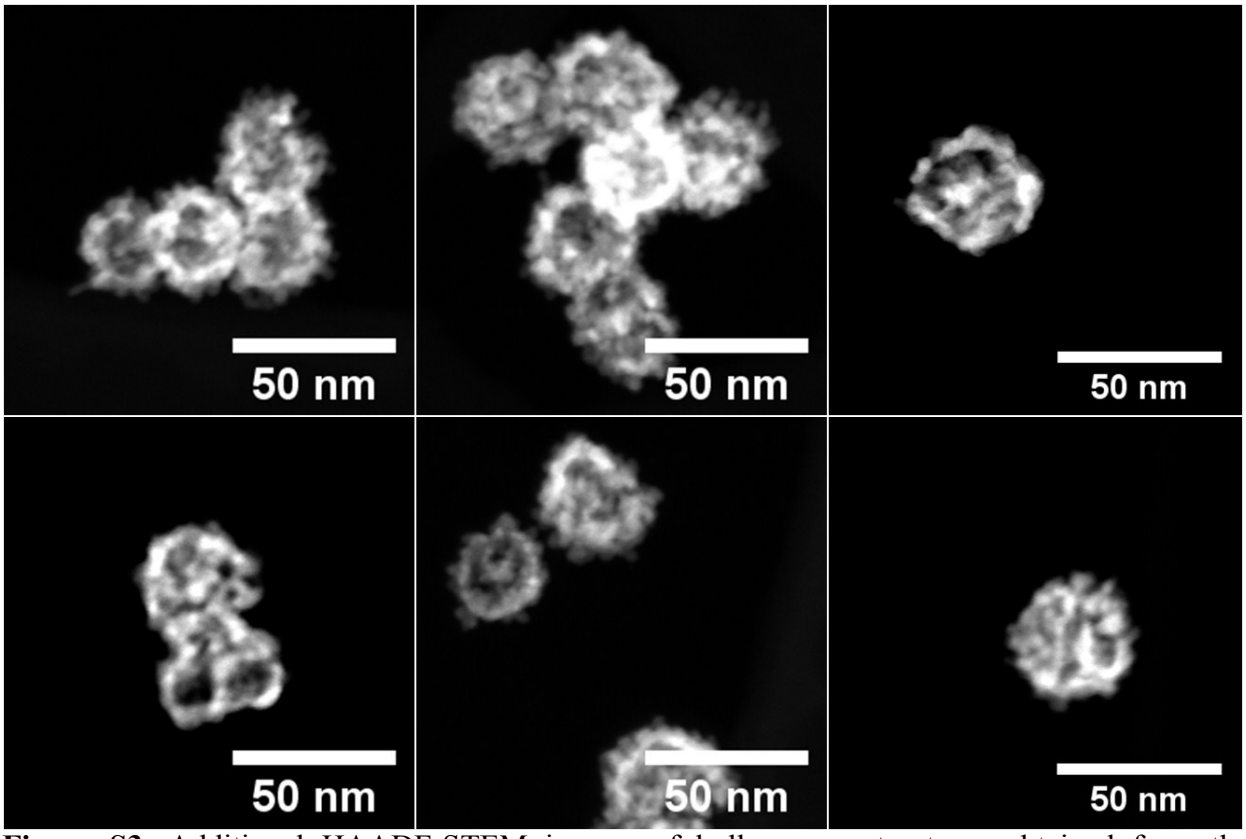

Figure S3. Additional HAADF-STEM images of hollow nanostructures obtained from the treatment of initially ~ 34 nm Ag nanospheres with 20 μM $Au(III)Cl_3$ in the absence NaCl.

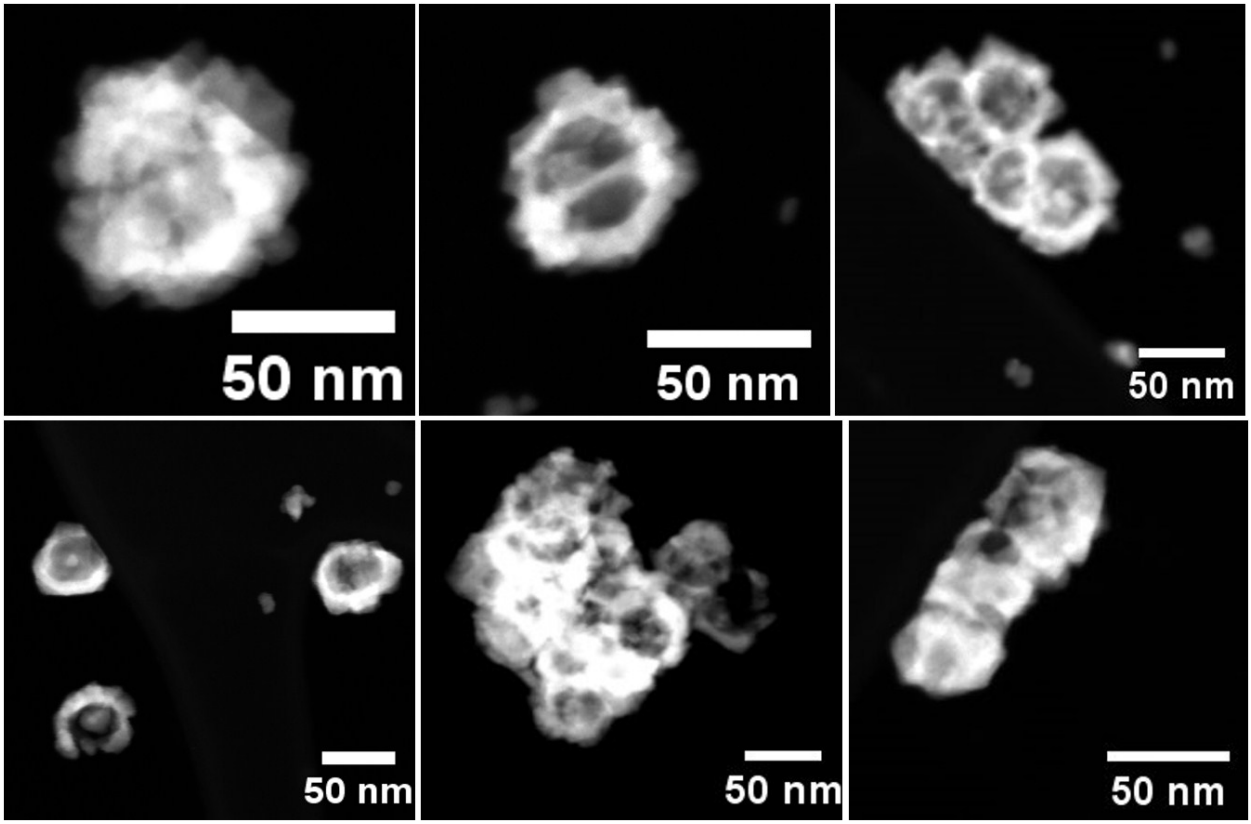

Figure S4. Additional HAADF-STEM images of hollow nanostructures obtained from the treatment of initially ~ 34 nm Ag nanospheres with 20 μM $Au(III)Cl_3$ in the presence of 10 mM NaCl. Nanostructures obtained from exchange have a peak size of 46.5 nm, considerably larger than the starting template.

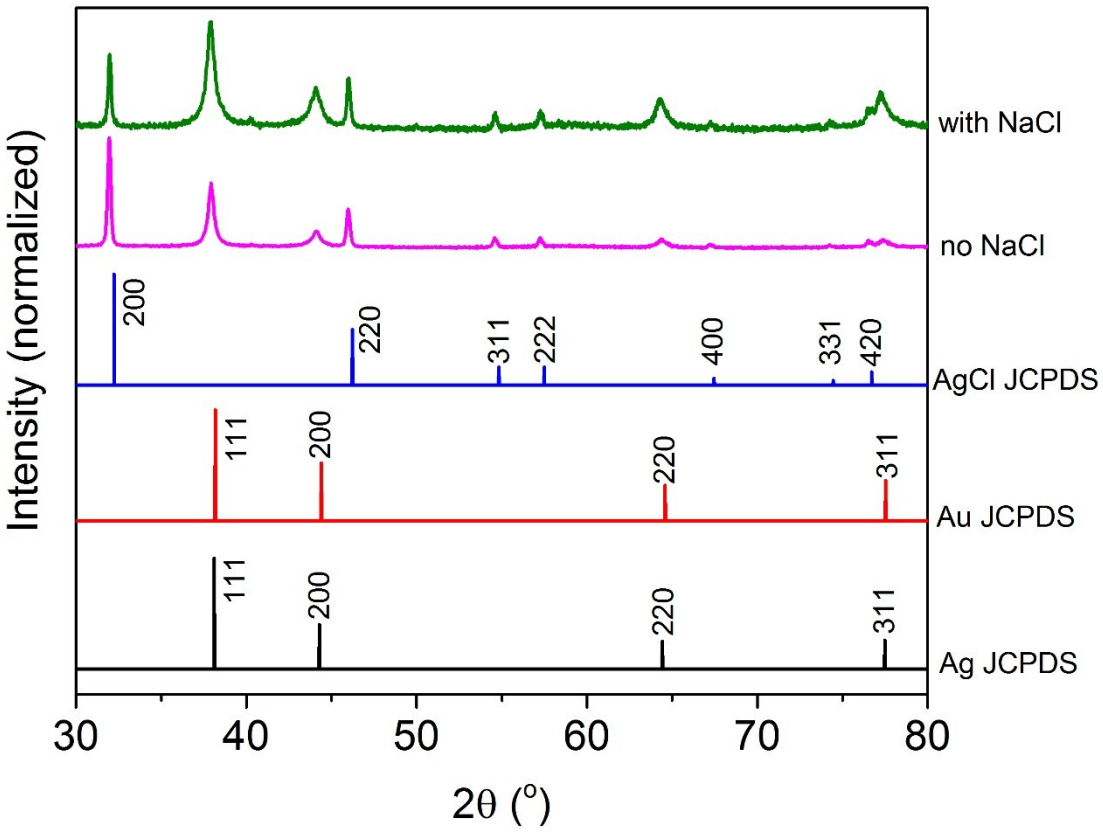

Figure S5. Powder X-ray diffraction (PXRD) patterns of Au/Ag nanocages produced by galvanic exchange of Ag NPs with 5 μM Au(III)Cl_3 in the absence of NaCl (pink curve) and with 10 mM NaCl present (green curve). Reference diffraction peaks for Ag (JCPDS # 04-0783), Au (JCPDS# 04-0784), and AgCl (JCPDS# 06-0480) are also shown. PXRD patterns were normalized to their respective maximum intensities and were offset in the y-axis direction for presentation purposes. As per PXRD, nanocages from both procedures contain Au and Ag. However, it is difficult to determine whether the two metals are present as an alloy or a mixture because Au and Ag have close reflections and because the observed diffraction peaks are broad due to the polycrystalline nature of the porous nanocage products. In addition, both samples contain AgCl, consistent with findings from EDS.

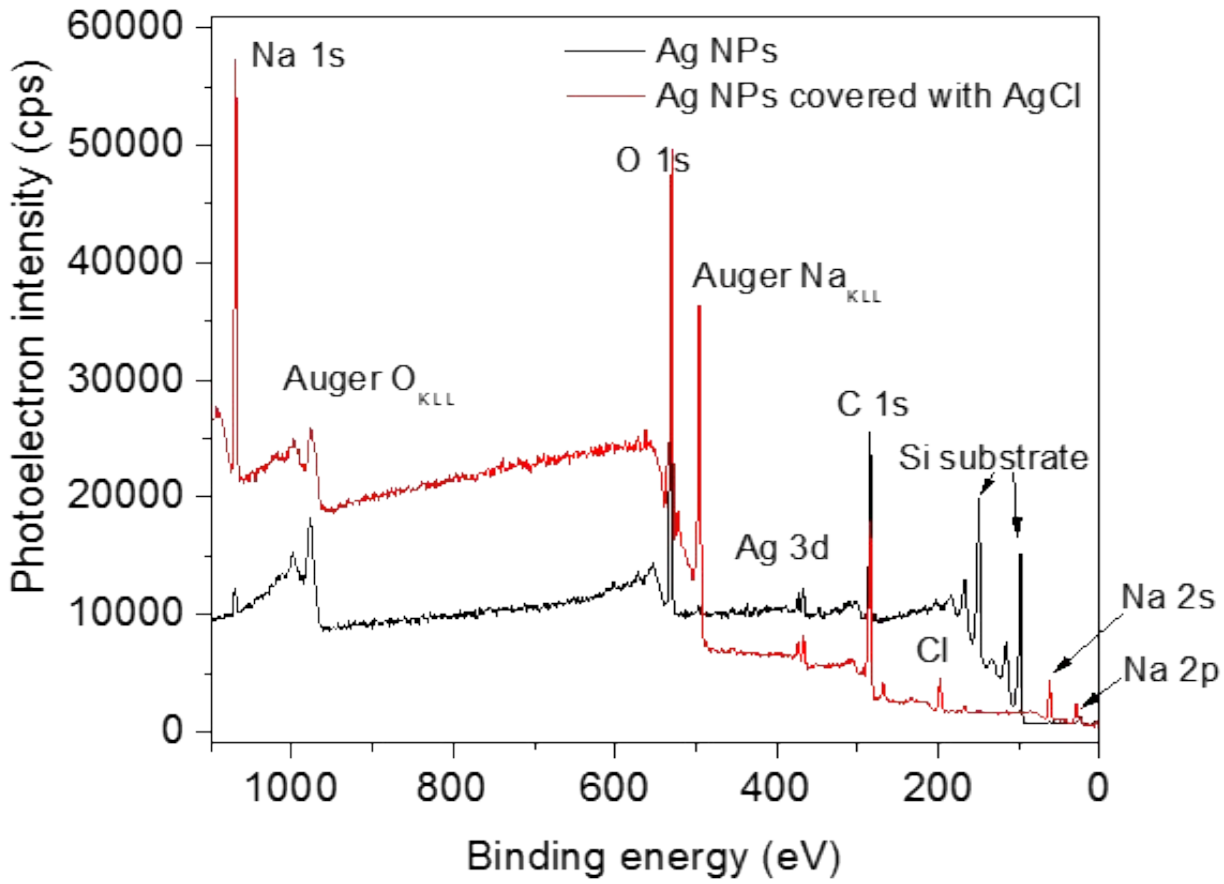

Figure S6. Survey XPS spectrum of Ag NPs with (red) and without (black) NaCl treatment. Spectra were plotted with appropriate offset in the y-axis direction for presentation purposes. Corresponding high-resolution photoemission spectra of Ag 3d and Cl 2p transitions are shown in Fig. 4.

Table 1. Summary of kinetic parameters measured from single-nanoparticle trajectories. This data was obtained from an analysis of histograms presented in Fig. S2. Values shown are averages over two separate trials performed under identical conditions.

Cl^- concentration (mM)	Avg. Waiting Time (s)	FWHM (s)	Peak τ (s)	FWHM/τ
0	94.8	35.8	3.1	11.6
0.1	141.2	53.2	15.2	3.5
1	138.7	28.9	19.7	1.5
10	110.8	27.5	24.4	1.1

Supporting Movie Captions

Movie M1. Movie showing the time-evolution of plasmonic scattering intensity of a wide-field of individual Ag NPs undergoing galvanic exchange with 5 μM $Au(III)Cl_3$ in the absence of NaCl. This movie corresponds to trajectories shown in Fig. 1 A. The $Au(III)Cl_3$/NaCl solution entered the flow cell at t = 39 s and the flow rate was maintained at 1.5 mL/hr.

Movie M2. Movie showing the time-evolution of plasmonic scattering intensity for a wide-field of individual Ag NPs undergoing galvanic exchange with 5 μM $Au(III)Cl_3$ and 10 mM NaCl. This movie corresponds to trajectories shown in Fig. 1 B. The $Au(III)Cl_3$/NaCl solution entered the flow cell at t = 32 s and the flow rate was maintained at 1.5 mL/hr.