

Electronic Supplementary Information

Revealing the sub-50ms electrochemical conversion of silver halide nanocolloids by stochastic electrochemistry and optical microscopy

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1. High frequency recording of AgX NPs EC collisions on Au UME

Examples of other nanoimpacts recorded at 100 kHz with a current amplifier are shown below to evidence the multistep collisions of single AgX NPs within an interval of 10ms maximum.

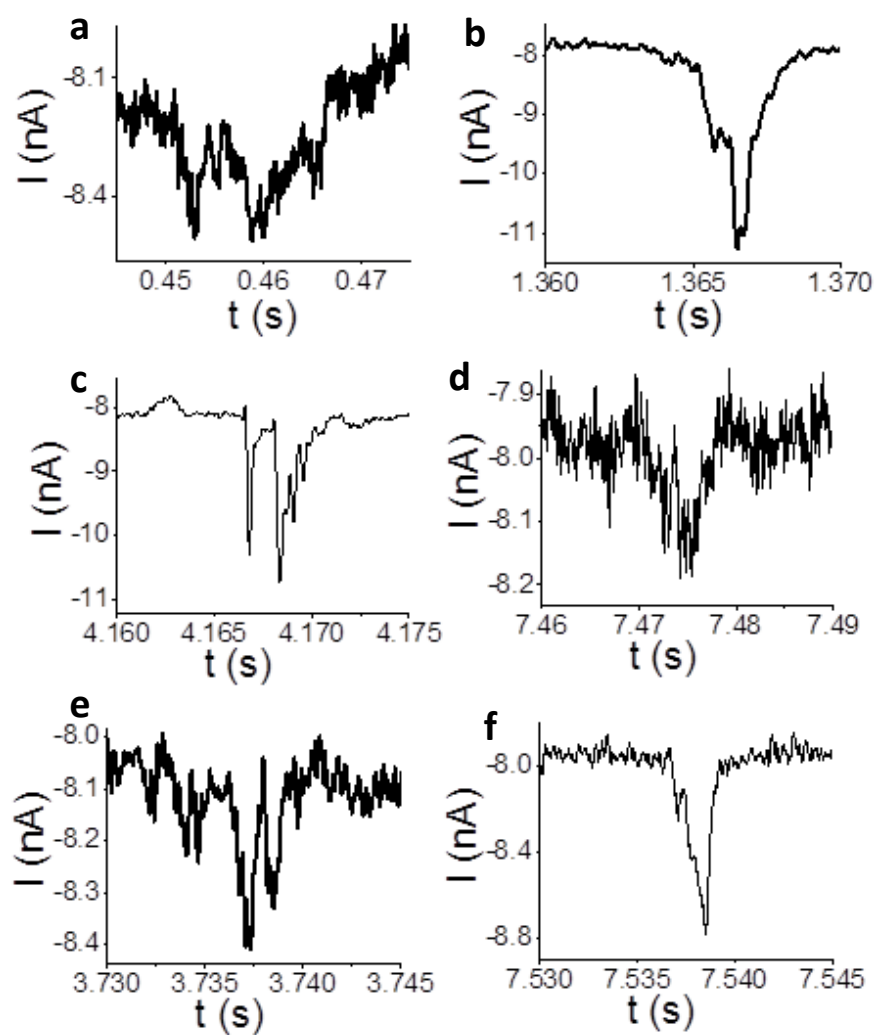


Figure ESI 1. Electrochemical impact experiments performed at a 25 μ m diameter gold UME in a colloidal solution of AgX NPs by applying -0.7V vs Pt and at an acquisition frequency of 100 kHz.

2. Optical monitoring of AgX NP EC collisions on BALM electrode

Example of larger surface area ($12.5 \times 15.6 \mu\text{m}^2$) image recorded during the optical monitoring of the same electrochemical experiment presented in Figures 4b and c: individual AgX NPs (dark features in red circles) from a colloidal solution are electrochemically transformed into Ag NPs (bright features in blue circles). The NP density, $0.1 \text{ NP}/\mu\text{m}^2$, from such image is comparable to the estimate from Figures 4b and c, as well as the proportion of Ag NPs (25%). The same analysis over the largest image area, $2100 \mu\text{m}^2$ (not shown), presents a similar density of NPs, $0.1 \pm 0.02 \text{ NP}/\mu\text{m}^2$, within the total experiment duration.

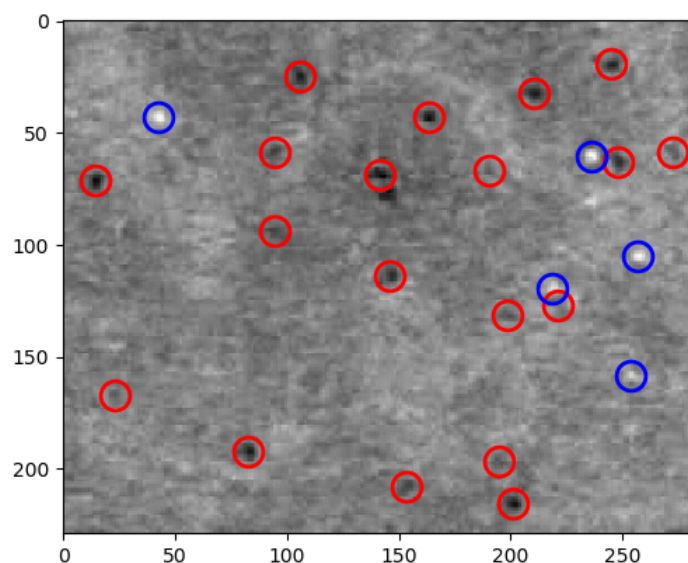
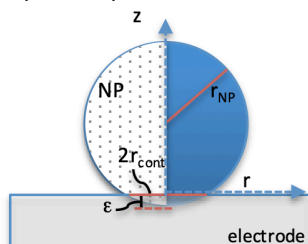


Figure ESI 2. Optical image ($12.5 \times 15.6 \mu\text{m}^2$) recorded during the EC of AgX NPs (dark features in red circles) into Ag NPs (bright features in blue circles) performed in a microdroplet of colloidal solution of AgX NPs deposited onto a BALM sampled polarized at -0.8 V vs Pt from the same experiment as that provided in Figure 4b in the manuscript.

3. Comsol model of the AgX to Ag NP conversion with electron hopping

The theoretical framework proposed by Compton et al.¹ for the diffusion controlled transport of an analyte inside a nanoparticle is complemented with an electron hopping mechanisms to accelerate the NP conversion inside the particle, as described earlier.²

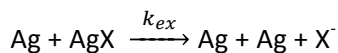
Briefly the transient situation is modeled in the 2D axisymmetric geometry. Only the transport reaction process is considered within a truncated sphere of radius $r_{NP}=d_{NP}/2$ filled with AgX at a concentration $[AgX]^* = 40 \text{ mol/dm}^3$. As depicted below, the truncated sphere is tangent to the electrode, the truncated part, of height ε , corresponds to region of the sphere that would be within tunneling distance from the electrode ($\varepsilon < 2\text{nm}$).



The $AgX \rightarrow Ag + X^-$ conversion is then initiated at the electrode-NP contact line, by imposing $[AgX]_{z=0, \text{electrode-NP}} = 0$. It proceeds by the apparent diffusive transport of AgX (formally Ag^+ and X^- , here limited by Ag^+ , $D = 10^{-11} \text{ cm}^2/\text{s}$) within the NP, while imposing a “no flux” condition at the NP outer interface. The model considers only one species, AgX, of concentration $[AgX]$, while:

$$[Ag] = [AgX]^* - [AgX].$$

The propagation of the reaction within the NPs through an electron hopping mechanism was considered as a first approximation model of a propagating interface. It was modeled through a homogeneous chemical reaction, of rate k_{ex} , for which the Ag material obtained by conversion of AgX serves as a support material to convert AgX:



The overall process is simulated by solving the diffusion equation for AgX assorted by this homogeneous transformation:

$$\frac{\partial [AgX]}{\partial t} = D \left(\frac{\partial^2 [AgX]}{\partial r^2} + \frac{1}{r} \frac{\partial [AgX]}{\partial r} + \frac{\partial^2 [AgX]}{\partial z^2} \right) - k_{ex} [AgX] \frac{[Ag]}{[AgX]^*}$$

To accommodate for the propagation of the AgX/Ag interface in the NP (large concentration gradient within a $< 2\text{nm}$ moving interface), the NP outer interface and NP-electrode contact interface are meshed with a maximum element size of 0.1nm propagated through a boundary layer mesh (20 layers with geometrical increment 1.02) allowing a dense element distribution along these interfaces normal direction. Overall it consists of up to 7×10^5 meshing elements in a 150nm NP.

The simulation was run by COMSOL 5.2 version on desktop computer equipped with a 3.6GHz core processor with 8 GB RAM operating under 64-bit Windows system.

References

¹ H. Le, C. Lin, E. Kätelhön, R.G. Compton, *Electrochim. Acta*, 2019, **298**, 778-787.

² J.-F. Lemineur, J.-M. Noël, A. Courty, D. Ausserré, C. Combellas, F. Kanoufi, *J. Am. Chem. Soc.*, 2020, **142**, 7937-7946.