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In situ electron microscopy observation of the redox process in plasmonic heterogeneous-photo-sensitive nanoparticles†

Diego Muraca,^a Lucia B. Scaffardi,^{bc} Jesica M. J. Santillán,^b David Muñeton Arboleda,^b Daniel C. Schinca^{bc} and Jefferson Bettini^d

Observation of relevant phenomena related with dynamical redox process in a plasmonic heterogeneous-photocatalyst system composed by silver nanoparticles (NPs) around and in contact with amorphous silver chloride NPs are reported by *in situ* transmission electron microscopy. During this process, nanobubbles are initially produced inside the silver chloride NPs, which immediately begin to move within the amorphous phase. Besides, silver atoms inside the silver chloride NPs start to migrate out the occupied volume leaving a space behind, which is filled by crystalline regions of silver chloride located between the pre-existing silver NPs. During the observation time, fast-nucleation, movement, growth, and fast-dissolution of silver NPs take place. Specific space correlation with silver mass loss (or gain) when a new NP is formed (or dissolved), was detected in different regions during the reaction. This mass loss (or gain) takes place on certain places of pre-existing silver NPs. All these phenomena were observed for a configuration comprising at least two silver NPs separated few nanometers apart by a silver chloride NP.

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Introduction

Understanding the catalytic properties of nanosystems requires extensive investigation by multidisciplinary techniques to collect information at different scales of their chemical, structural and electronic properties.^{1–3} During the last years, nanoplasmonic probes with catalytic materials used as an efficient plasmonic photocatalyst have gained relevant interest due to the improvement of their photocatalytic properties as well as their stability by the coupling between the material and plasmonic NPs.^{4–6} Several examples of the enhancement of photocatalytic activity by plasmonic NPs suggest that they are the critical point for developing an efficient plasmonic photocatalyst as well as a photovoltaic nanostructure.^{5,7–12}

Catalytic reactions observed by *in situ* transmission electron microscopy may provide a unique understanding of the involved processes due to the resolution attained with this technique.³ This understanding is essential for the

development of catalysts, which in turn are of fundamental importance for energy and environmental technologies.^{13–15} Effects of intense electron probes, such as material accumulation and hole formation, that depend on the induced surface diffusion or sputtering mechanisms, were reported using field-emission transmission electron microscope.^{16,17} However, when *in situ* transmission electron microscopy is performed on a nanosystem composed by NPs with a specific configuration and an electron-beam sensitive material (as the previously mentioned), the resulting interaction gives rise to new phenomena. Herein, we report the experimental and direct observation of redox-driven reaction ($\text{AgCl} + 1\text{e}^- \rightleftharpoons \text{Ag}_\text{s} + \text{Cl}^-$) of photo-sensitive and catalytic material composed of metallic silver NPs (Ag-NPs) and silver chloride nanoparticle (AgCl-NP). The electron dose used during all processes was about 2000 $\text{e}^- \text{Å}^{-2} \text{s}$ during movie acquisition (five movies) with a vacuum environment of $1.5 \times 10^{-5} \text{ Pa}$.

Two articles were published recently regarding *in situ* electron microscopy studies on Ag–AgCl NPs systems.^{13,14} The first one, published by Wu *et al.*,¹³ reported on the oxidation dynamics of an Ag/AgCl heterostructure using *in situ* environmental TEM microscopy in combination with DFT theory, working with a temperature controlled flow nanoreactor to independently change temperature and oxygen pressure. Their results show that sputtering of Cl atoms under the impact of incident electrons is much more likely than that of Ag atoms, thus leaving behind Ag atoms which oxidize to Ag_2O or AgO depending on the low or high (atmospheric) O_2 pressure in the

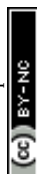
^aInstituto de Física ‘Gleb Wataghin’, Universidade Estadual de Campinas, Campinas, Brazil. E-mail: dmuraca@ifi.unicamp.br

^bCentro de Investigaciones Ópticas (CIOp) (CONICET La Plata-CIC-UNLP), Gonnet, La Plata, Buenos Aires, Argentina

^cFacultad de Ingeniería, UNLP, La Plata, Buenos Aires, Argentina

^dElectron Microscopy Laboratory, Brazilian National Nanotechnology Laboratory/CNPEM, Brazil. E-mail: jefferson.bettini@lnnano.cnpe.br

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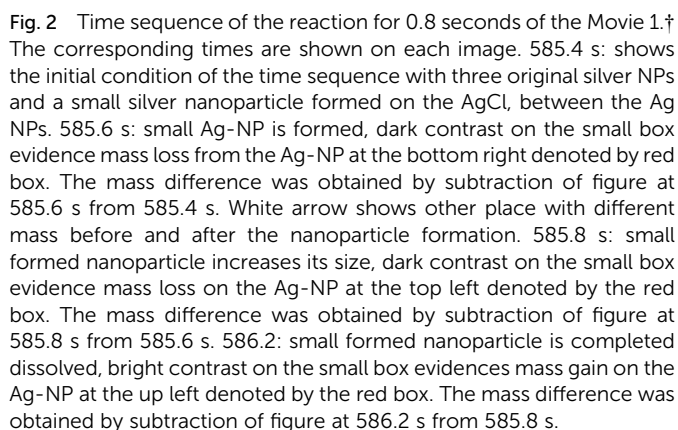


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The assumption of nanobubbles existence (initially with a spherical shape) is based on the lower contrast observed in some parts of the AgCl-NP (see also Movie 2, Fig. S1 and S2 on ESI[†]). Images of scanning transmission electron microscopy (STEM) acquired during the *in situ* energy dispersive spectroscopy corroborated the presence of nanobubbles during the reaction of the analogous system (ESI, Fig. S2[†]). Comparing the size of AgCl-NPs at the beginning and the end of the reaction, the initial thickness of AgCl-NP is estimated to be 14.2 nm,

B Nucleation and dissolution of silver nanoparticles

When the thickness of AgCl-NP reaches a critical value (see ESI: Movie 1 from 486.6 s, Movie 2 from 897.6 and Movie 3 from 0 s and Fig. S3†), the region with the darkest contrasts (Movie 1, ESI†) in the AgCl-NP starts to decrease in size from the top-right edge, although not uniformly. Then, “nucleation” and “dissolution” of small silver NPs occur very fast during the changes of the AgCl-NP crystalline regions, and undoubtedly, silver NPs nucleation and AgCl-NP crystalline structure are both interconnected with each other. While the reaction proceeds, new Ag-NP with a diameter smaller than 5 nm “nucleates” in between the other pre-existing Ag-NPs. This “nucleation” happened more than once at different places and at different times (see ESI: Movie 1 from 486.6 s, Fig. S4 to S6†). Each nucleated NP also dissolves, sometimes very fast, with a typical time <0.2 s. Making accurate analyses in the positions where the NPs were formed. It was possible to correlate their formation with the existence of AgCl crystalline phase. We noticed that the atoms that are forming this new NP have a correlation with at least two different and specific places (apart from the ones that could come from the AgCl-NP), denoted by an arrow and the red box of Fig. 2, 585.6 s. A difference in the number of atoms can be evidenced by the dark contrast shown in the inserted image, which corresponds to atoms correlation from the corner of bottom-right NPs surface (see Experimental section for more details of the images analysis). After 0.2 s, the size of the new NP increases. It was possible to show that a certain amount of the atoms responsible for the NP size increase is related with mass loss from the upper left part of the larger pre-existing Ag-NP, as shown in the inset of Fig. 2 (585.8 s), which was obtained by image subtraction. Hence, in the first part of nucleation, the atoms at the upper left corner are allowed to “diffuse”. Then, the new NP increases again mainly by mass loss from the left side corner of the large Ag-NP, confirming again the correlation between some parts on the edge of larger Ag-NP and the new NPs formed on AgCl. It is appropriate to point out here that our


$$(DT)^{1/2} = d, \quad (3)$$

As shown in Fig. 2, at an elapsed time of 0.4 s (from 585.8 s to 586.2 s), the small nanoparticle is completely dissolved and a mass gain was recorded at the original place on the outer surface of the pre-existing NP (shown as white contrast in the box on Fig. 2, 586.2 s). From these facts, it can be stated that the formed NPs are in a metastable state. This usually does not happen in particles of the same composition and size isolated on the same experimental conditions. In general, after NP nucleation, it should grow due to diffusion or coalescence

One more evidence of Ag-NP dissolution on the AgCl-NP phase is shown in Fig. 3, which corresponds to time composition variation of the system followed by energy dispersive spectroscopy (EDS) in equal sample and with similar nanoparticle configuration. During the STEM experiment (see Movie 4, Fig. S2 and S3, ESI[†]) the movement of a nanobubble in the AgCl-NP, detected by dark contrast, was acquired at different times. Also, after some time (Movie 4,[†] 1858 s), a dark contrast begins to increase on the upper right edge with a square shape,

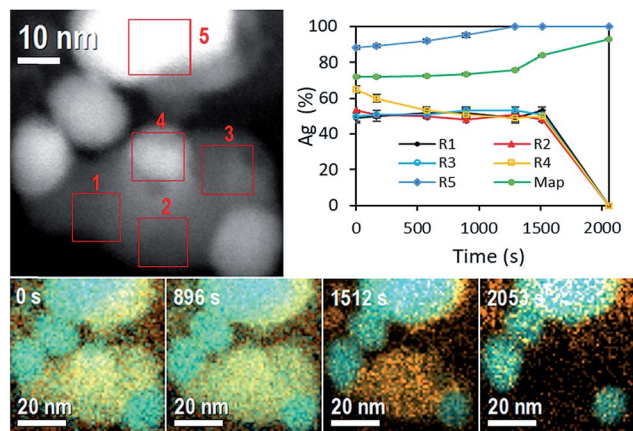


Fig. 3 Top left: STEM image of *in situ* energy dispersive spectroscopy showing different regions (R1 to R5) where the atomic composition spectrum was acquired. Top right: atomic composition evolution obtained by means of different regions R1 to R5 and the full map composition. Bottom: *in situ* energy dispersive spectroscopy showing composition variation for 2053 s. Cyan color corresponds to silver atoms and orange color corresponds to chlorine atom.

related to the AgCl crystalline shell structure of the AgCl NP and in accordance with results described and observed on Movie 1 (ESI†).

On EDS experiment, seven temporal and accumulative composition mapping were obtained from the full image shown in at the top left of Fig. 3, in five different selected regions (R). Regions R1, R2 and R3 correspond only to the mapping of AgCl-NP, and the average of Ag atomic content oscillates around $50\% \pm 1\%$, pointing out the Cl_2 gas is not trapped significantly inside those regions of the AgCl-NP (the obtained compositions are reported in Tables 1 and 2).

However, in R2 a reduction of Ag atomic content was observed twice (from 49.2 to 46.6%, and 50.8 to 45.7%) from 576 s to 896 s and from 1295 s to 1512 s, some amount of Cl_2 gas can be trapped inside of AgCl-NP during the acquisitions, see Movie 4 (ESI: Fig. S2 and S3†); the R2 also shows a darkening closely at the same time variation, from 1170 s to 1502 s. Initially, the R4 shows a silver NP on the AgCl-NP surface and Ag composition of 65%. The Ag content decreases to 50% at 576 s due to the dissolution of Ag-NP (during all experiments, Ag-NPs were utterly dissolved when they were entirely on the AgCl-NP surface). No enrichment of Ag content was observed in R1,

R2, and R3, indicating no absorption of Ag atoms by the AgCl-NP, supporting the hypothesis that Ag atoms migrate to other Ag-NP, preferably to the large one. The R5 shows enrichment of Ag content over the time due to the redox process of AgCl-NP, where the final measured content was 98% at. of Ag. For the full sample mapping, the silver content increases slightly (72.1% at. to 76.1% at.) from 0 to 1295 s and rate of Ag content (76.1% at. to 92.7% at.) increases from 1295 s to 2053 s (see Table 2). This time corresponds roughly to the moment at which the white contrast of AgCl-NP starts to reduce in size in Movie 4.† Other EDS experiments are reported on ESI (Fig. S10 and Table S1†).

D Silver chloride defects as preferential nucleation's points

The reasons for specific places on the preexisting NPs showed mass loss/gain when the new NPs are formed/dissolved, and what guides the NP movement after its formation, could be due to different causes. It was mentioned before that silver NPs nucleation and AgCl-NP crystalline structure should be linked by a certain interrelationship. Recently J. S. Du *et al.*, observed lattice oscillation on AgCl during a redox reaction on electron microscopy experiments on equal Ag–AgCl system.¹⁴ We also observed this lattice oscillation during our experiments (not shown here). These lattice dynamics could locally stretch or stress favoring a specific place for nanoparticle nucleation. Hence, to prove the possible relation between AgCl phase and Ag nucleation and dissolution, the AgCl phase was analyzed before and after each nucleation event during the experiment. Fig. 4 shows in more detail the analysis of the nucleation process shown previously in Fig. 2. The FFT (Fig. 4(b)) from the red box shows some regions marked with orange circles with higher intensity than the background of the FFT in the same radial distance, and corresponds to (220) AgCl planes distance (0.20 nm).

The four spots with the highest intensities correspond to (200) AgCl planes distance (0.28 nm) and the weakest one corresponds to (220) AgCl planes distance (0.20 nm), making 45 degrees with the (200) AgCl planes distance. Therefore, the AgCl planes are oriented in the [001] zone axis. However, the (220) planes distance denoted by orange circles are at 60, 70 and 90 degrees with the (200) AgCl planes respectively (white box denotes 2× zoom of region marked with orange circles), note also the complementary side in the FFT to better observe these regions. The (200) and (220) at 90 degrees correspond to [011] zone axis orientation, and in this orientation, the (111) planes can appear and have 0.32 nm distance and produce some strain in this region. In fact, the Fig. 4(d) shows some (200) AgCl planes stretched and stressed with 0.32 nm and 0.24 nm distance ($0.32 + 0.24 = 2 \times 0.28$) inside the white circle. (111) plane is stretching the (200) AgCl plane and as a compensation some planes are stressed and showing 0.24 nm distance. Red lines for stressed planes (0.24 nm) and green lines for stretched planes (0.32 nm) mark these regions. This defect could create a region with some charge or field gradient, attracting Ag ions to nucleate in this region, as was observed in other materials.^{33,34} However, more studies need to be done to fully support this

Table 1 Global atomic composition evolution obtained by means of EDS of two different samples on Fig. 3. The error is one sigma

Ag (% at.)	Cl (% at.)	Time (s)
72 ± 0.6	28 ± 1.2	0
72 ± 0.5	28 ± 1.0	169
73 ± 0.4	27 ± 0.8	576
74 ± 0.4	26 ± 0.9	896
76 ± 0.3	24 ± 0.9	1295
84 ± 0.2	16 ± 1.2	1512
93 ± 0.1	7 ± 2.2	2053



Table 2 Atomic composition evolution obtained by means of EDS at different regions (R1 to R5) of the sample shown in Fig. 3. The error is one sigma

Time (s)	R1 (% at.)		R2 (% at.)		R3 (% at.)		R4 (% at.)		R5 (% at.)	
	Ag	Cl	Ag	Cl	Ag	Cl	Ag	Cl	Ag	Cl
0	49 ± 3	51 ± 5	53 ± 3	47 ± 5	50 ± 3	50 ± 4	65 ± 2	35 ± 4	89 ± 1	11 ± 4
169	50 ± 3	49 ± 4	51 ± 2	49 ± 3	51 ± 2	48 ± 3	60 ± 2	40 ± 3	88 ± 1	11 ± 3
576	52 ± 2	48 ± 3	50 ± 2	50 ± 3	51 ± 2	49 ± 3	53 ± 2	47 ± 2	92 ± 1	8 ± 3
896	52 ± 2	48 ± 3	48 ± 3	52 ± 3	53 ± 2	47 ± 3	51 ± 2	49 ± 3	95 ± 1	4 ± 3
1295	49 ± 3	51 ± 4	51 ± 3	49 ± 3	53 ± 2	47 ± 3	49 ± 2	51 ± 3	100 ± 1	0 ± 3
1512	53 ± 2	49 ± 4	48 ± 3	52 ± 4	51 ± 4	49 ± 5	50 ± 3	50 ± 4	100 ± 0	0 ± 4
2053	00 ± 0	00 ± 0	00 ± 0	00 ± 0	00 ± 0	00 ± 0	00 ± 0	00 ± 0	100 ± 0	0 ± 5

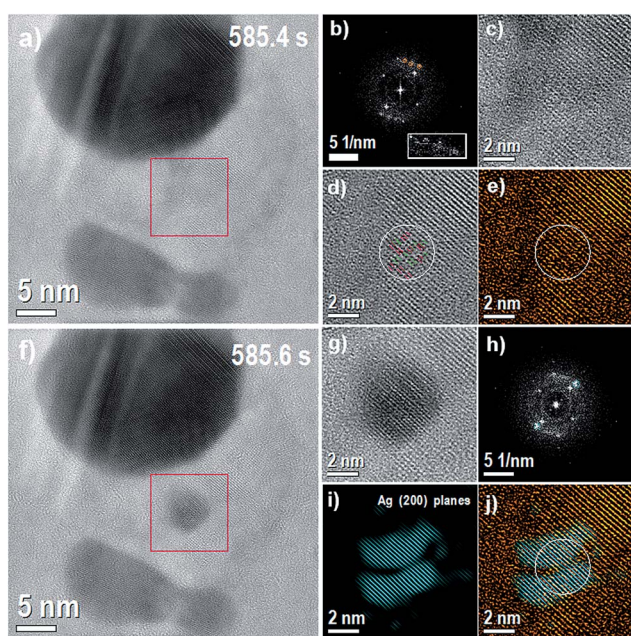


Fig. 4 (a) Image before the nucleation. Red box denotes the region where nucleation occurs (585.4 s), (b) FFT of the region denoted by red box; inset white box denotes 2× zoom of region marked with orange circles. (c) Inverse FFT of the same region (2× zoom in), see also ESI Fig. S11† (d) inverse FFT with the background removed (2× zoom in) with red lines showing stressed planes (0.24 nm) and green lines showing stretched planes (0.32 nm), (e) inverse FFT with the background removed and coloured with orange colour, (f) image with the nucleated particle and same region marked by red box, (g) image of the marked red box in panel (f) with 2× zoom in (585.6 s), (h) FFT of the region denoted by red box (585.6 s) with the (200) Ag planes marked with a blue mask on (h), (i) inverse FFT from the points marked with a blue mask, (200) Ag planes and (j) composite image with coloured orange and blue images.

claim. Fig. 4(g) shows the region of the nucleated Ag-NP and Fig. 4(h) the corresponding FFT. In order to see the matching of the nucleated particle and the (200) defects regions, Ag spots were selected by a mask and the inverse FFT shown in Fig. 4(i) was colored blue. The Fig. 4(j) shows the composite image obtained from Fig. 4(e) and (i).

The sequential images on Fig. 5(a) to (f) correspond to the growth of nucleated Ag-NP, *i.e.*, in this specific case we are not

analysing the nucleation (shown previously in Fig. 4). The FFT from the red box, Fig. 5(b) shows regions with the intensity higher than the background of the FFT denoted by orange circles. The plane distance of these regions is 0.255 nm, and the average angle between them is 57 degrees. The (111) Ag planes have 0.236 nm (fcc-structure), and two (111) Ag planes are only observable when the NP is oriented in the [110] zone axis. However, the angle between the (111) Ag planes in the [110]

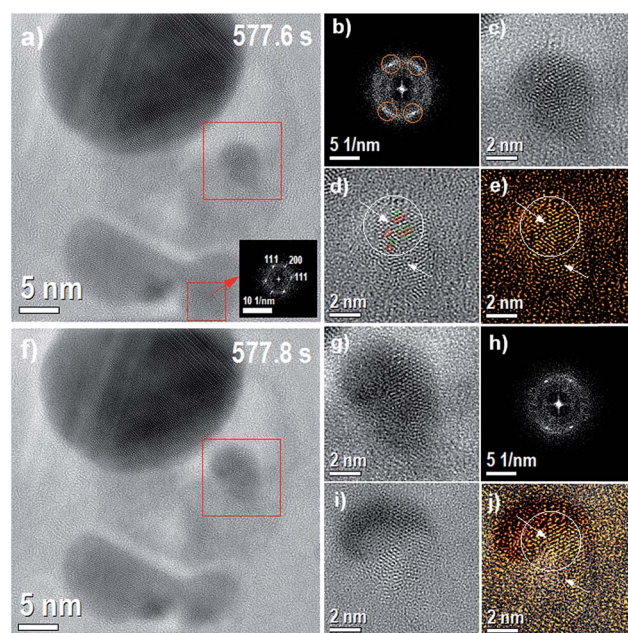


Fig. 5 This figure corresponds to the growth of nucleated Ag-NP showed during the Movie 1 (ESI†). From left to right, from up to down, (a) image before the growth of nucleated Ag-NP with the region where the growth occurs denoted by a red box (577.6 s), the inset image correspond to the FFT of the region also marked with a red box and indicated by the red arrow, (b) the FFT of the region denoted by red box, (c) the inverse FFT of the same region (2× zoom in), (d) the inverse FFT with the background removed (2× zoom in); see also ESI Fig. S11† (e) the inverse FFT with the background removed and colored with orange color, (f) the image with the Ag-NP grown and same region marked by red box, (g) the image marked by red box with 2× zoom in (577.8 s), (h) the FFT of the region denoted by red box (577.8 s), (i) the image obtained from the subtraction of images (g) and (c) and (j) the composite image with image (i) and colored orange image.



These AgCl defects can explain the possible existence of preferential space regions for the new NP nucleation and growth. However, they would not explain the correlation of Ag atoms loss/gain mass places when the NPs are formed/dissolved. Even more, it was observed (and can be clearly observed on Movie 1 of ESI†), that the new formed NPs can show an unexpected behavior after its formation, “moving” between the other metallic NPs for several seconds (see ESI Movie 1† from 551.8 s to 559.8 s, for example). This ion cluster or NP moves at a higher velocity than the bubbles at the initial stage of the reaction and seems to be attracted by the metallic NPs. In the experiments, we never observed similar phenomena for preexisting Ag-NPs smaller than 7 nm, or the distance among them smaller than 2–3 nm.

In summary, we report by *in situ* electron microscopy observation different stages and new phenomena of the dynamical redox process in plasmonic heterogeneous-photo-sensitive NPs. Initially with nanobubbles formation, growth and movement. Then we register nucleation and dissolution of small silver NPs. Was verify that silver chloride NP is the key for the silver NPs dissolution, *i.e.*, the presence of silver chloride matrix is a necessary condition for silver NP dissolution. Also, it was corroborated that defects on silver chloride NP acts as nucleation points to new silver NPs, during the reaction. We verify, as well, space correlations places, between the Ag and AgCl NPs,

during this dynamical process, when a NP is nucleated or dissolved.

The nucleation, dissolution, growth and reduction events observed in our experiments, together with the previous discussion leads us to think that plasmons and the electric field configuration between small metallic NPs are influencing the reaction.

These discoveries could contribute to improving the design of materials with photocatalytic properties, not necessarily restricted to AgCl material.

Experimental section

A Materials synthesis

Silver colloidal suspensions were generated using a 120 fs pulse width Ti:Sapphire chirped pulse amplification system from Spectra Physics, centred at 800 nm wavelength, 1 kHz repetition rate and a maximum output pulse energy of 1 mJ. A solid silver disk (99.99%) placed at the bottom of a 4 mL beaker filled with Dihydrated Sodium Citrate (DSC) aqueous stabilizer solution at a concentration of 1 mM and containing 30 mg kg⁻¹ of ion chloride, was used as ablation target. Ablation was performed by focusing the laser beam using a 5 cm focal length lens on the Ag disk producing a fluence of 5.9 J cm⁻². An XYZ motorized micrometric stage was used to move the target to ablate always on a fresh surface of the Ag sample. After about 10 minutes, a typical yellowish colour suspension indicating the presence of silver NPs was obtained.

B Electron microscopy equipment, settings and methods

In situ TEM analysis was performed on a JEOL JEM 2100F with a field emission gun (FEG) operating at 200 kV. The samples were prepared by a simple colloid dropping of the as-prepared colloids on amorphous carbon film supported on copper grids. *In situ* energy dispersive spectroscopy (EDS) was also acquired during the reaction using an Oxford SDD 100 mm², X-MAX model and AZTEC software for EDS data acquisition and processing. High-angle annular dark-field imaging (HAADF) JEOL SIOD digital scanning system with HAADF detector was used. All the experiments were performed at room temperature. The images were acquired using an SC600 CCD camera (Gatan) in camera view mode (live mode). Each image was constructed with a time frame of 0.2 s and binning 2 to increase the intensity (contrast) of the image. The movies were acquired using Auto-ScreenRecorder software (screen capture software) with an acquisition time of 0.2 s.

For EDS analysis, we assume the whole AgCl NP area in Fig. 3 (isolated from the part with that Ag-NP is in contact or on AgCl) as our standard sample (50–50%). We also used the first three measures of whole AgCl NP to obtain an average standard sample with Ag 50% and Cl 50%. Therefore, we calculated the EDX quantifications with their respective errors. They were obtained from Poisson error, and two sigma error bars was considered to describe the uncertainty for any measurement. The mass gain/loss image analysis process is detailed in ESI Fig. S15.†

Conflicts of interest

There are no conflicts to declare.

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