Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Surface mobility and impact of precursor dosing during atomic layer deposition of platinum: in situ monitoring of nucleation and island growth - Supporting Information

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######################################
GISAXS SIMULATIONS : INPUT PARAMETERS
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#######################################  Framework and beam parameters  #############################################
# Framework     Diffuse,        Multilayer,     Number of index slices
  DWBA          LMA             1               25
# Beam Wavelength :     Lambda (nm),    W1_distribution
                        0.0972          none
# Beam Alpha_i    :     Alpha_i (deg),  Ai_distribution
                        0.516           none
# Beam 2Theta_i   :     2Theta_i (deg), Ti_distribution
                        0.              none
# Substrate       :     n-delta_S,      n-beta_S
                        3.e-6           2.8e-8
# Particle        :     n-delta_I,      n-beta_I
                        2.e-5           2.5e-6

##############################################  Grid parameters  #####################################################
# Ewald mode
  F
# Output q(nm-1)  :     Qx min-max,     Qy min-max,     Qz min-max,     n(1),   n(2),   n(3)
                        -2      0       0.1     2.5     0.6     3.5     1       80      100

##############################################  Particle parameters  ################################################
# Number of different particle types
  2
# Particle type,        Probability
  spheroid              0.5
  spheroid              0.5
# Geometrical parameters :      Flattening
                                0.83
                                1.66
# H_uncoupled
        T
        T
# Size of particle  :   Radius (nm),    R_distribution, SigmaR/R,       Rmin (nm),      Rmax(nm),       nR,     xR
                        3.8             log_normal      1.15            1               7               25      -2
                        3.8             log_normal      1.15            1               7               25      -2
# Height aspect ratio  :        Height/R,       H_distribution, SigmaH/H,       Hmin/R, Hmax/R, nH,     xH,     rho_H
                                1.66            gaussian        0.05            0.83    1.66    25      -2      0
                                1.66            gaussian        0.05            0.83    1.66    25      -2      0

##############################################  Lattice parameters  #################################################
# Particle distribution  :      type
                                1DDL
# Interference function  :      Peak position D (nm),   w (nm), Statistics,     Cut-off
                                9.51                    3.804   gau             100000
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Figure 1: Input parameters used for the IsGISAXS simulations.

Geometrical model for fast analysis

In order to quickly analyse the 2D GISAXS patterns, a simplified geometrical model was developed to determine changes in the morphology of the Pt particles that are deposited during the ALD process. The model assumes that the Pt particles consist of full spheroids without a size distribution and are placed on a regular 2D lattice. The average particle height and radius are obtained from a fast analysis of line profiles taken from the *in situ* 2D GISAXS patterns, respectively, using the relations $H = 2\pi / < \Delta q_{\mathrm{z}} >$ and $R = 4.4/q_{\mathrm{y,min}}$. The most common approach to estimate the center-to-center distance is by using the approximation $D = 2\pi/q_{y,max}$.[1] However, using this approach leads to a significant underestimation of the Pt loading on the surface, as measured by *in situ* XRF. The reason is that the GISAXS intensity is governed by the interplay between the interference function and form factor of the particles that are present on the sample. While the center-to-center distance can be obtained from the interference function, in a GISAXS pattern the peak position originating from the interference function is shifted from its actual value by the influence of the particle form factor and as a result estimating the distance from the peak position of the first scattering lobe can lead to significant deviations from the actual center-to-center distance.[1] Therefore, we propose another approach, in which the GISAXS measurements are combined with *in situ* XRF measurements to estimate the center-to-center distance by using Equation 1. The Pt loading, obtained from the additional XRF data, can be used as an input value for the model to obtain a value for the center-to-center distance. The validity of this approach is verified by using the input values to perform full-scale, detailed, simulations of selected patterns using the IsGISAXS software. A first optimization of the H, R, and D values does not cause significant change to the initial input values, illustrating that the fast analysis method combined with the XRF data can be used to obtain reliable values for the average particle properties. Further optimization by including other particle shapes, and particle size distributions leads to an even better fit to the experimentally obtained 2D GISAXS patterns. However, typically fully simulating such patterns requires some computational time and it is generally not feasible to perform such calculations fast enough to provide accurate feedback during the ALD process. The important aspect is that the simulation-free geometrical model combined with the fast analysis approach provides sufficiently accurate information about the properties of the particles without resorting to time consuming full-scale 2D simulations of the experimentally obtained GISAXS patterns.

$$D = \sqrt{\frac{2}{3}\pi R^2 H \frac{66.24\ \text{atoms}\,/\,\text{nm}^3}{S_{Pt}}} \quad (1)$$

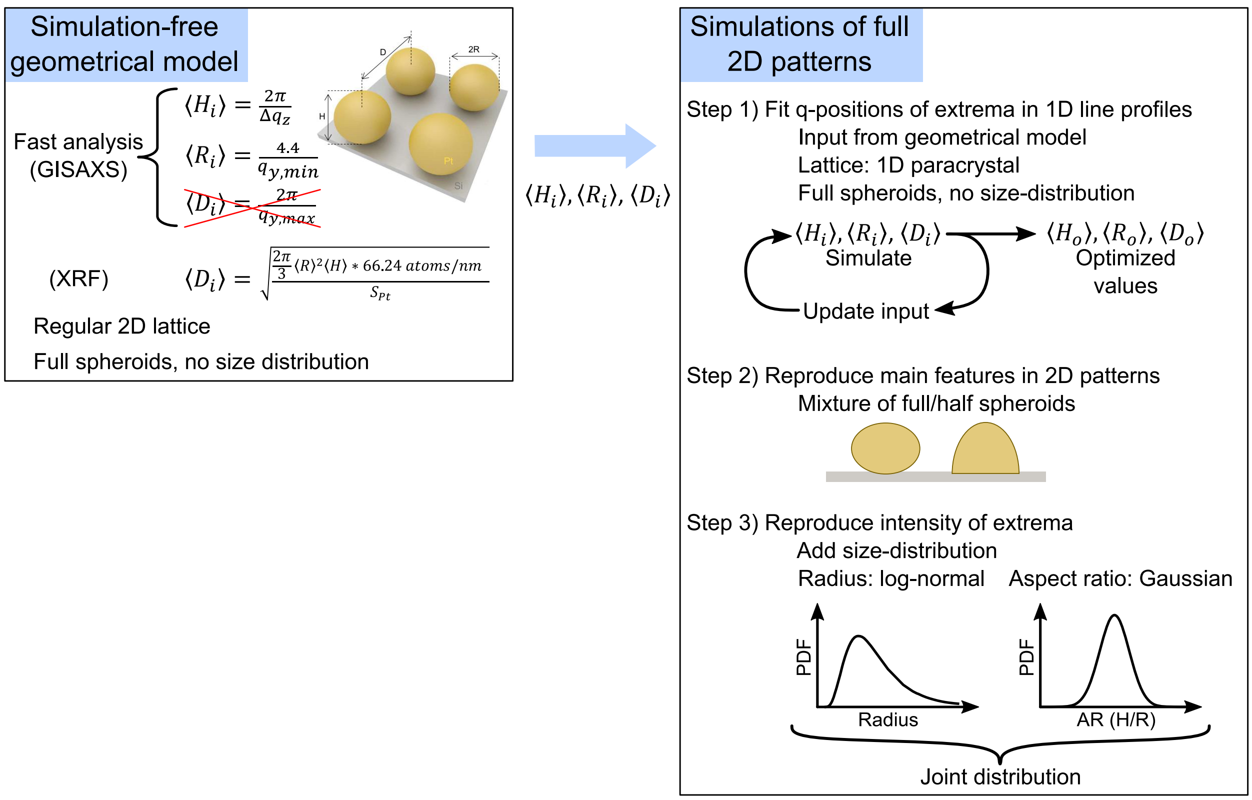

Figure 2: The three steps involved in the GISAXS analysis approach to obtain a full simulation of the measured GISAXS patterns, starting from a simplified geometrical model.

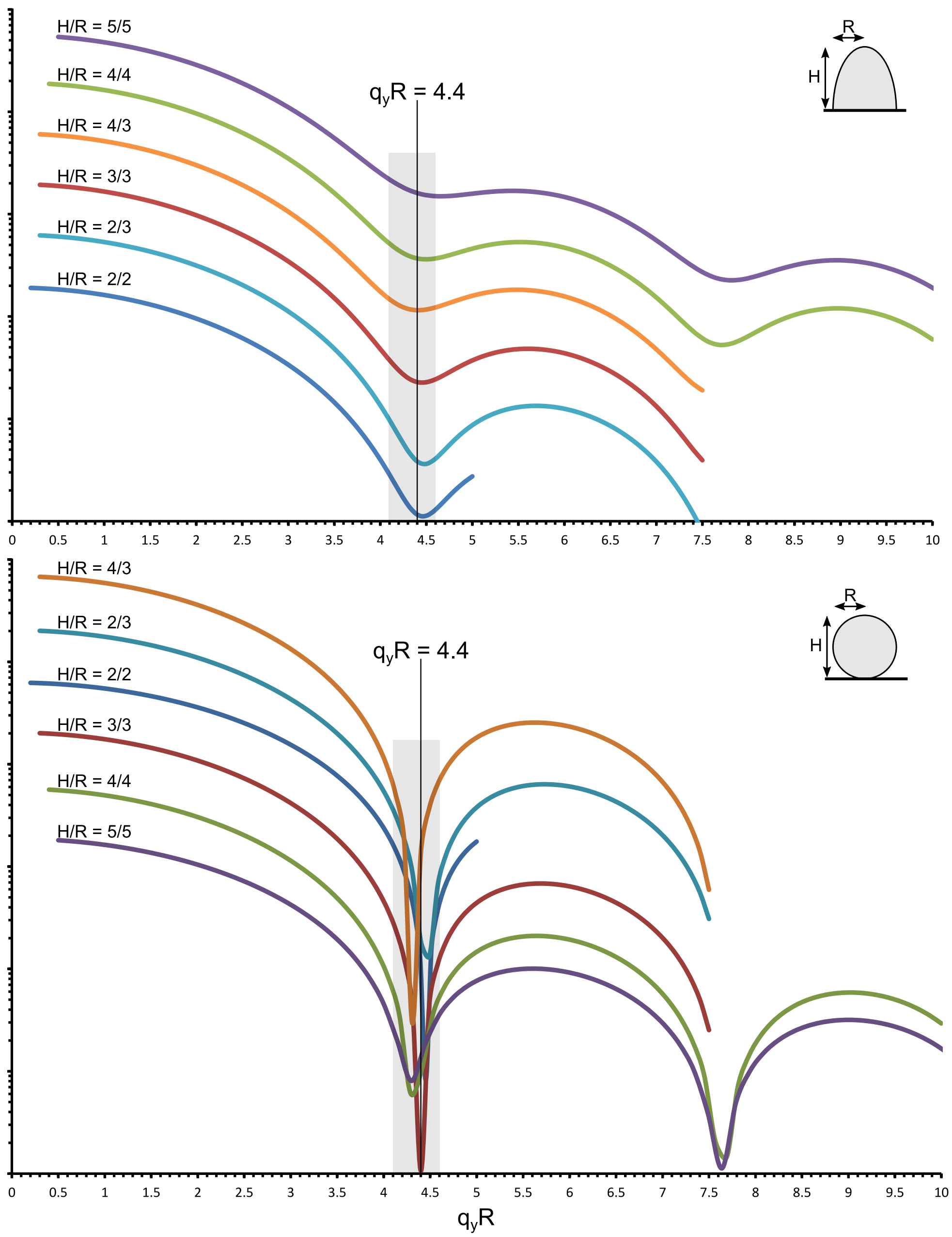

Figure 3: Form factor contribution for hemi-ellipsoids and full ellipsoids with H and R values between 2-5 nm. The scattering contribution is expressed as a function of q_yR. The position of the first minimum lies close to the q_yR value of 4.4 for every line profile, which means that the particle radius can be estimated by determining the q_y position of the first minimum along the q_y direction in the GISAXS pattern and applying the formula: $R = 4.4/q_y$.

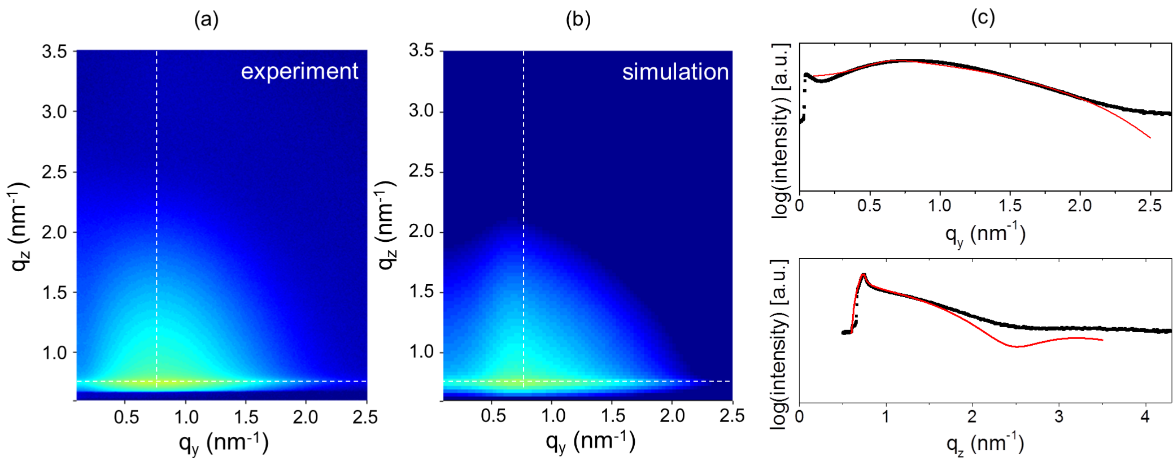

Figure 4: Experimental (a) and calculated (b) 2D GISAXS pattern obtained at 12 ALD cycles. (c) Experimental (black data points) and calculated (red curves) horizontal (top) and vertical (bottom) line profiles of the GISAXS patterns obtained at 12 ALD cycles.

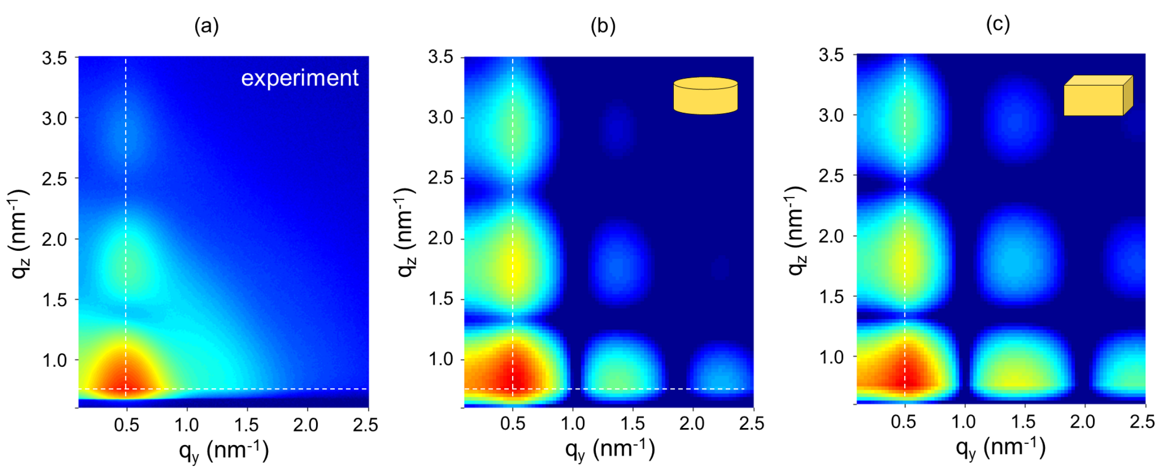

Figure 5: Experimental (a) and calculated (b,c) 2D GISAXS patterns obtained at 32 ALD cycles. The particle shapes assumed for the calculations are schematically represented in the top right corner of the images.

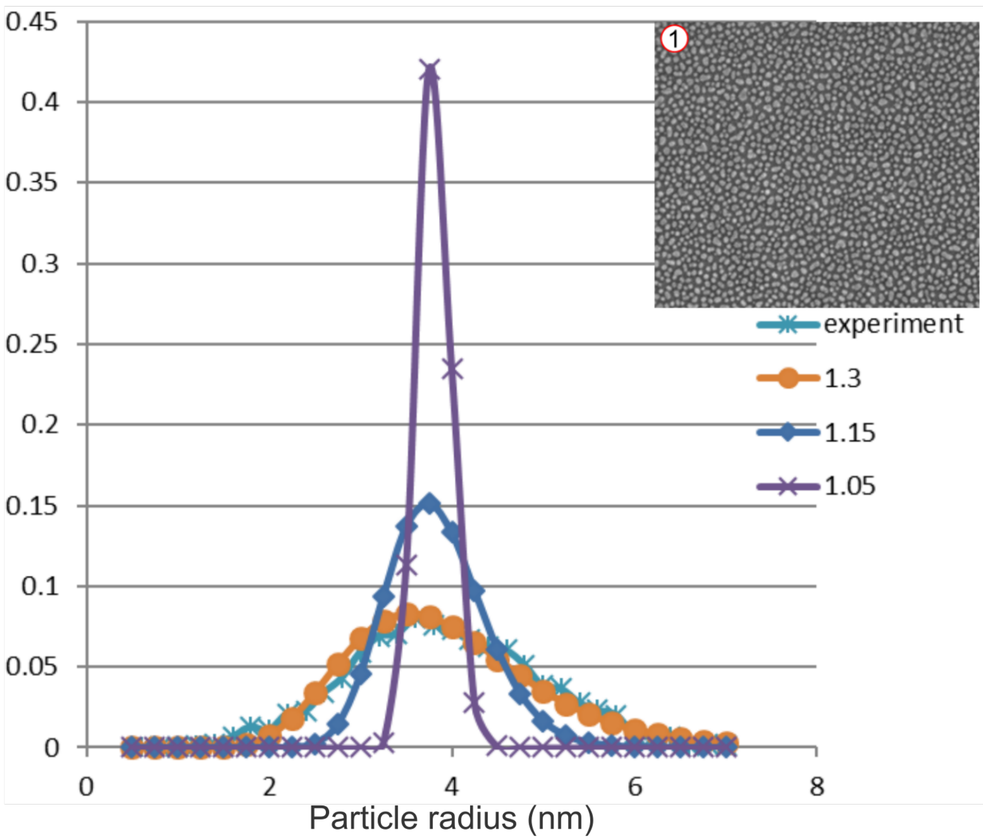

Figure 6: Particle size distributions, for the particle radius, obtained from the sample of a sample with 32 Pt ALD cycles and simulated particle size distribution with varying widths ($\sigma = 1.05/1.15/1.30$) of the log-normal size distribution. The best match between the size distribution from SEM and simulation is obtained for $\sigma = 1.30$.

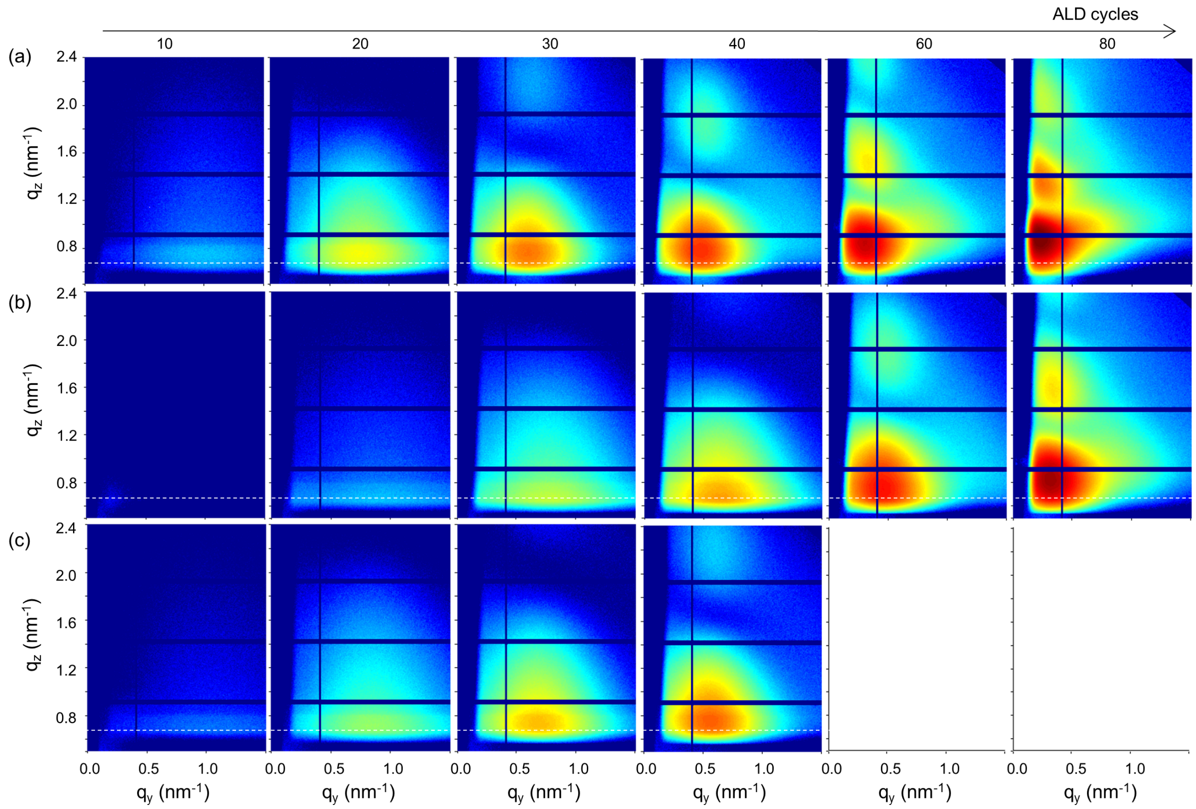

Figure 7: Experimental 2D GISAXS patterns obtained at 10, 20, 30, 40, 60 and 80 ALD cycles as measured in situ during three experiments using different Pt precursor dose modes: (a) static mode, (b) pump mode, and (c) static mode during 4 ALD cycles followed by pump mode.

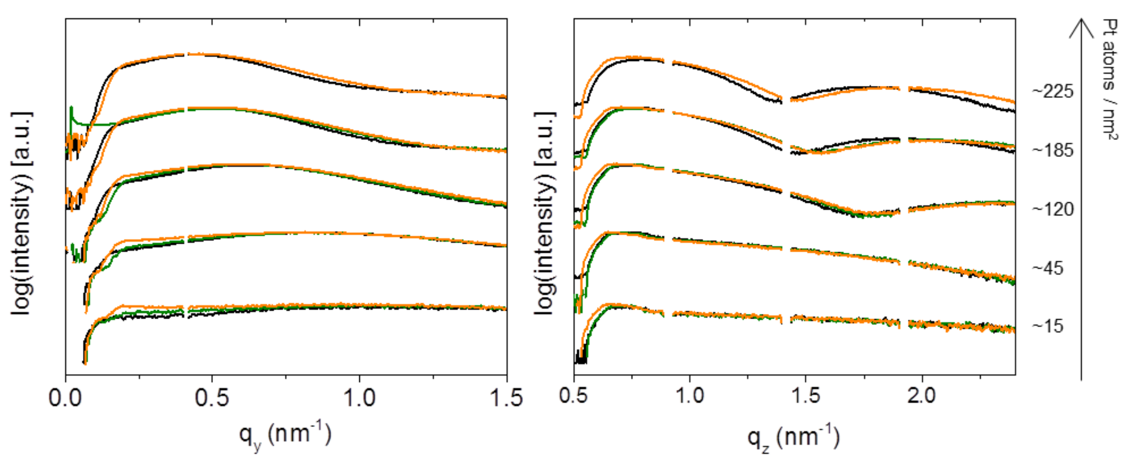

Figure 8: Experimental horizontal (left) and vertical (right) line profiles of the GISAXS patterns in Figure 14 obtained at surface densities of ∼15, ∼45, ∼120, ∼185 and ∼225 Pt atoms per nm^2 as measured in situ during three experiments using different Pt precursor dose modes: static mode (black curves), pump mode (green curves), and static mode during 4 ALD cycles followed by pump mode (orange).

References

1. Renaud, G.; Lazzari, R.; Revenant, C.; Barbier, A.; Noblet, M.; Ulrich, O.; Leroy, F.; Jupille, J.; Borensztein, Y.; Henry, C. R.; Deville, J.-P.; Scheurer, F.; Mane-Mane, J.; Fruchart, O. Real-Time Monitoring of Growing Nanoparticles. *Science* **2003**, *300*, 1416–1419.