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DELIVERABLE REPORT

WP15 - JA5 - Correlative Nano-Spectroscopy and Nano-Diffraction

D15.3
Fabrication of nanoparticle pattern templates

Due date

M29

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Dr. Thomas F. Keller (DESY)

DELIVERABLE DETAILS

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D – D15.3	Fabrication of nanoparticle pattern templates

DELIVERABLE DESCRIPTION

Design and fabrication of nanoparticle pattern templates for correlated nano-characterization including 1) the design and the creation of the templates, 2) the development and establishment of nanocrystal synthesis and 3) the wet chemical deposition protocols on the functional substrates.

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NATURE

☐ R - Report

☒ P - Prototype, Demonstrator

☐ DEC - Websites, Patent filing, Press & media actions, Videos, etc

☐ O - Other

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4	29/06/2023	Dr Athanasia Kostopoulou	Forth draft	Revision and approval

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INTRODUCTION

The working package WP15 of NFFA-Europe PILOT on Correlative Nano-Spectroscopy and Nano-Diffraction - Joint Action 5 (JA5) - aims to establish a user platform for routine experiments at Nanolabs and analytical large-scale facilities (ALSFs) permitting to collect structural and chemical information from a statistically relevant number of distinct nanoscale objects. Importantly, one prerequisite for an optimal determination of one-to-one size-structure-property correlations is that the probes like e.g., electrons or X-rays are illuminating individual nanoparticles. For experiments with a focused X-ray beam the foot-print is typically in the range of a few 10 nm × 10 nm up to a few 10 µm × 10 µm depending on the setup and the angle of incidence on the sample surface. Isolation of the nano-objects is required to ensure that signals are collected from only single nanoparticles. According to this prerequisite, the design and the creation of the proper templates for this type of experiments and the careful selection of protocols for the individual nanocrystal arrangement on the templates are essential (Task 15.2).

The purpose of the deliverable D15.3 which is a part of the Task 15.2 is to summarize the different protocols for the fabrication of the templates and those of the individual arrangement of the nanocrystals on them by their colloidal dispersions. Optimization of the templates and arrangement protocols is included in this report ensuring a successful correlative experiment.

Templates for correlative nano-spectroscopy and nano-diffraction

Two different types of templates have been fabricated for the isolation of the nanocrystals. First, Si patterned templates fabricated at Foundation for Research & Technology - Hellas (FORTH) have been evaluated in order to find out the optimum parameters for the isolation of the nanocrystals. Then, Si_3N_4 membranes structured by electron beam lithography (EBL) have been fabricated at Paul Scherrer Institute (PSI) for the planned X-ray scanning experiments in transmission mode. Although a careful handling is needed for these templates, they are necessary to decrease the X-ray footprint on the sample as it permits a transmission experiment and as such, an easier assignment of the X-ray data to the selected nanocrystals.

1. Si substrates

Structured substrates are known to permit a controlled attachment and in turn isolation of single nano-particulates. Here, different patterned Si templates were fabricated in order to find out the optimum structures for the single nanocrystal arrangement. Representative SEM images of patterned Si substrates are presented in Figure 1. These arrangement protocols were described also in the Milestone MS9 report submitted on 12/05/2022.

Specifically, for the formation of silicon truncated cones and lines to identify optimal structures for the single nanocrystal arrangement, ultrafast laser processing of silicon is employed in combination with subsequent wet chemical etching. In particular, an Yb:KGW Pharos – SP solid state laser is utilized, emitting at λ = 1024 nm central wavelength, with a repetition rate of 1 kHz and a pulse width of 170 fs. The substrates employed are [100]-silicon wafers with 250 µm thickness. Initially,

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a bare Si-substrate is treated with fs laser pulses below the ablation threshold in order to induce a phase transition of crystalline to amorphous silicon. Then, the induced thin layer of amorphous silicon is used as an etch stop in a following wet chemical etching step in KOH solution. The etching time in KOH solution was 15 min.

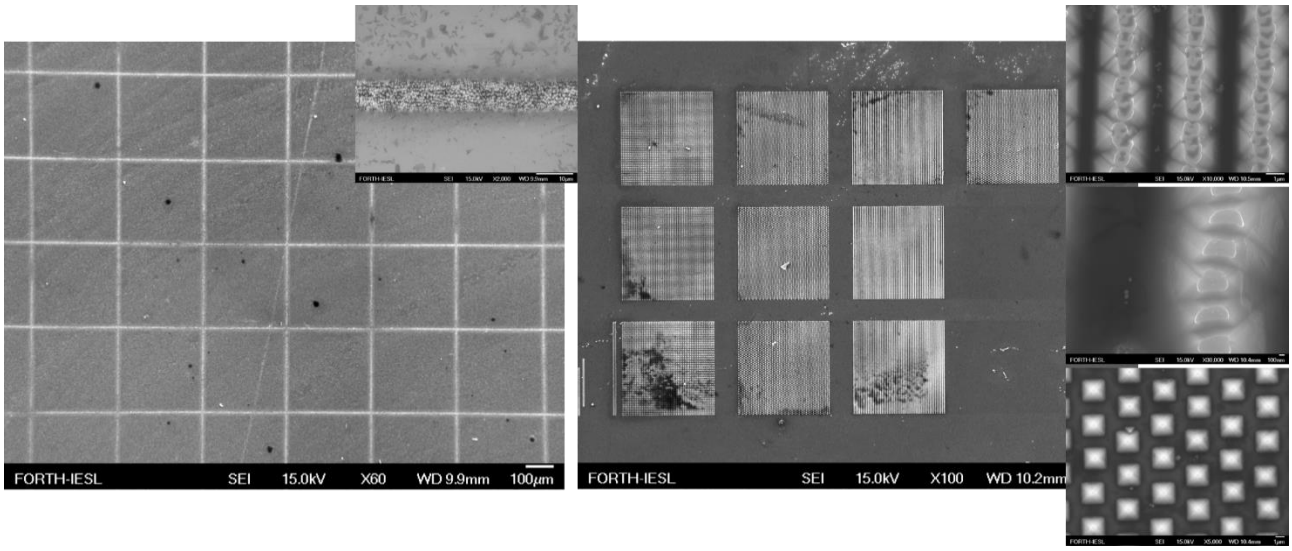

Figure 1. Representative SEM images of different patterned Si substrates.

2. Si_3N_4 membranes

9x9 mm² sized Si chips of 250 µm thickness containing a centred, 3x3 mm² e-beam structured Si_3N_4 membrane of same thickness have been fabricated by PSI (Figure 2a). The fabrication process is described in Figure 2b. The Si_3N_4 membrane contains many patterned areas of 100x100 µm² containing line gratings, arrays of circles and arrays of donuts (Figure 3).

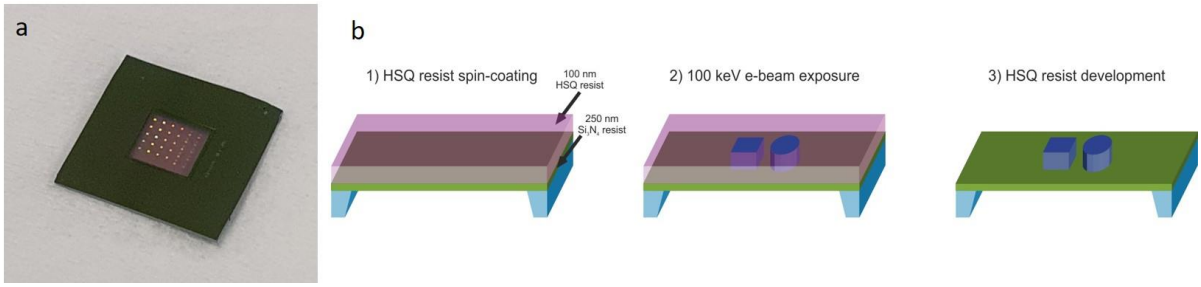

Figure 2. Si chip with Si_3N_4 membrane (a) and fabrication of the patterned Si_3N_4 membranes with e-beam lithography (b).

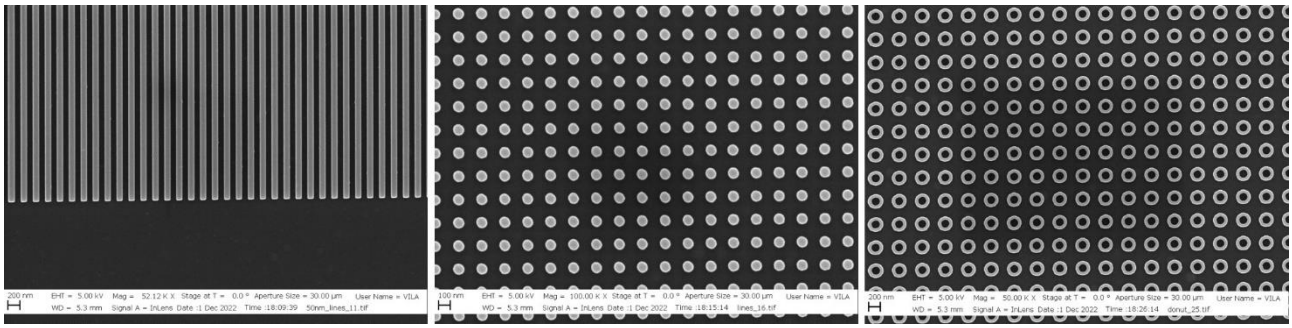

Figure 3. SEM images of different patterned Si_3N_4 membranes.

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Nanocrystal protocols and selection

Two different types of nanocrystals have been investigated as model systems for a generic attachment protocol to be adequately dispersed and isolated on the Si substrate. Fe_2O_3 cluster-like (~ 40 nm) and Cs_4PbBr_6 hexagonal-shaped metal halide perovskite (~ 90 nm) nanocrystals were synthesized at FORTH. The first nanocrystals were covered with a polymer (polyacrylic acid) and were dispersed in water while the second ones were capped with oleic acid and oleylamine and dispersed in toluene. Oleic acid and oleylamine are among the most frequently used capping ligands for the stabilization of nanocrystals produced by wet chemical approaches. The nanocrystals with the optimum arrangement in Si substrates (described in the Milestone MS9 report) will be used for the arrangement on the Si_3N_4 membranes.

1. Synthesis of Fe_2O_3 nanoclusters: The γ-Fe_2O_3 nanoclusters were synthesized by our previously reported protocol (Kostopoulou et al., Nanoscale, 2014, 6, 3764–3776). In a typical synthesis, $FeCl_3$ (0.8 mmol) and PAA (8 mmol) were dissolved in 40 mL of diethylene glycol (DEG) in a flask under anaerobic conditions in a glove-box. A yellowish solution was obtained under vigorous magnetic stirring (600 rpm) at room temperature. The mixture was heated to 220 °C and annealed at this temperature for 1 h under argon flow. Then, 3.8 mL of NaOH in DEG hot solution (70 °C) was injected in this mixture in a single shot. After reacting for 1 h the reaction was stopped by removing the heating mantle and the solution cooled down at room temperature. The γ-Fe_2O_3 nanoclusters were collected by centrifugation and then dispersed in water. Further purification was accomplished by performing successive magnetic separations and re-dispersions in water. The stock solution, which was added at 220 °C in the starting mixture of reagents was prepared separately from 50 mmol NaOH in 20 mL DEG and heated at 120 °C for 1 h. It was cooled to 70 °C and kept at this temperature until its injection into the starting reagent mixture.
2. Synthesis of metal halide perovskite nanocrystals. These nanocrystals have been synthesized through a re-precipitation-based colloidal protocol at low temperature (Kostopoulou et al., Nanoscale, 2019, 11, 882-889). Initially, $PbBr_2$ (0.4 mmole) and CsBr (0.4 mmole) precursors have been dissolved in 10 ml of anhydrous DMF in a sealed vial closed under Ar in a protective atmosphere of a glovebox. This solution was maintained under stirring for 3 hours until the complete dissolution of the precursors. Then, 1 ml oleic acid and 0.5 ml oleylamine were added in the above solution. Afterwards, 0.9 ml of this solution was rapidly added in 10 ml of anhydrous toluene in a sealed vial under vigorous stirring (1000 RPM). This vial was placed in ice before the addition of the stock solution and sustained under stirring for 30 minutes. Subsequently, it was retained on the bench for a day under ambient conditions. Then, the perovskite nanocrystals were separated upon centrifugation at 1000 RPM for 5 min and finally re-dispersed in toluene.

The γ-Fe_2O_3 nanoclusters are hydrophilic while the perovskite ones hydrophobic. Representative TEM images are presented in Figure 4.

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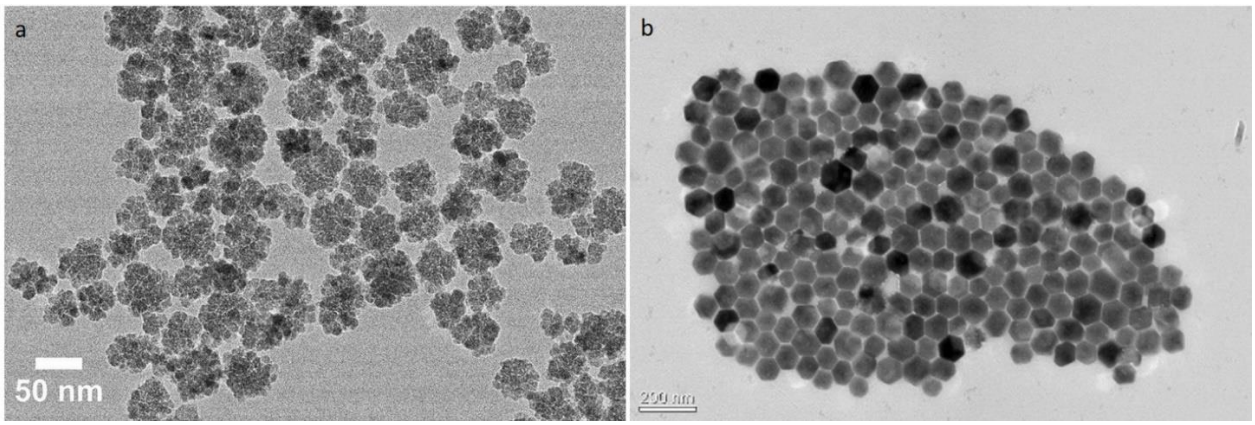

Figure 4. TEM images of γ-Fe_2O_3 cluster-like (a) hexagonally-shaped Cs_4PbBr_6 perovskite (b) nanocrystals.

Strategies to induce isolated nanocrystals attachment on Si templates - Optimum parameters

Firstly, direct deposition of nanocrystals from their colloidal dispersions through a drop casting approach on the Si substrate has been performed, but the nanocrystals seemed to be aggregated and not on the patterned areas (lines and cones) of the Si templates (Figure 5).

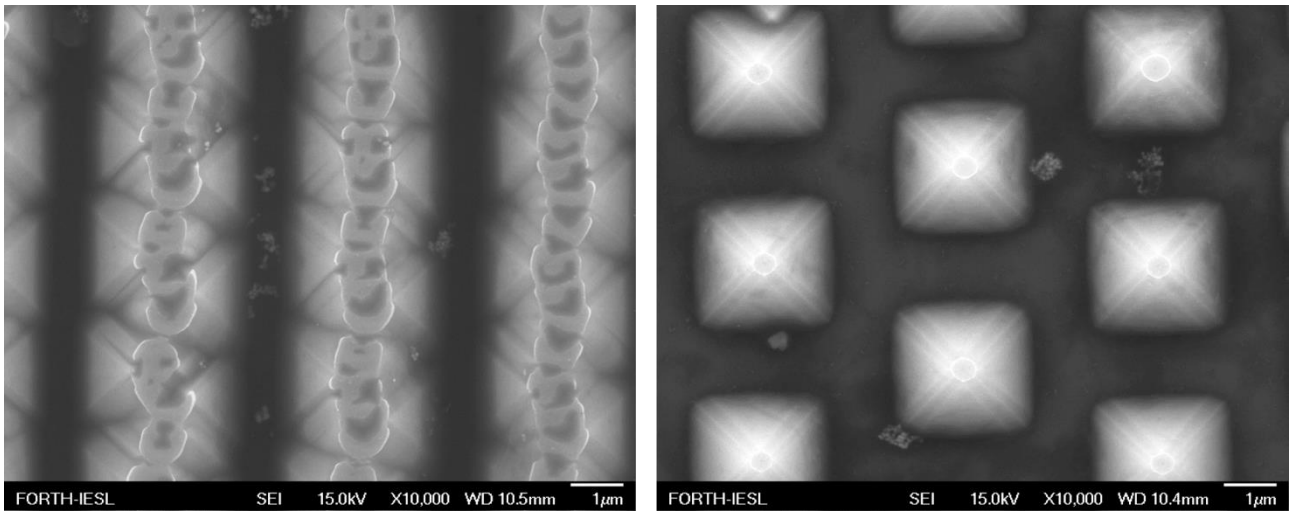

Figure 5. SEM images of the lines and cones with NPs deposited directly on them.

In order to prevent the aggregation of the particles, the Si substrates were functionalized with amino-silane in order to have only covalently-bonded nanocrystals on them. Specifically, the patterned substrates were treated in an UV ozone cleaner for 10 min in order to be cleaned. Then, they were dipped into a solution of 9 ml of ethanol with 1 ml (3-Aminopropyl)trimethoxysilane (APTMS). After 18 h of reaction at 60 °C, the substrates were washed thoroughly with methanol, ethanol and deionised water.

The arrangement of the particles on the functionalized templates was improved only for the hydrophobic nanocrystals, the perovskite ones. The perovskite nanocrystals seem to be individually arranged on the templates, while the γ-Fe_2O_3 nanoclusters still remained aggregated. Furthermore, different concentrations of nanocrystal solutions have been investigated (Figure 6). The total volume

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of the solution that is deposited on the Si substrates is 20 µl. The same volume was used for the Si_3N_4 membranes of the same size.

Some individual arranged nanocrystals were found on the cones when a concentrated solution was utilized. These separated particles could be easily inspected by SEM.

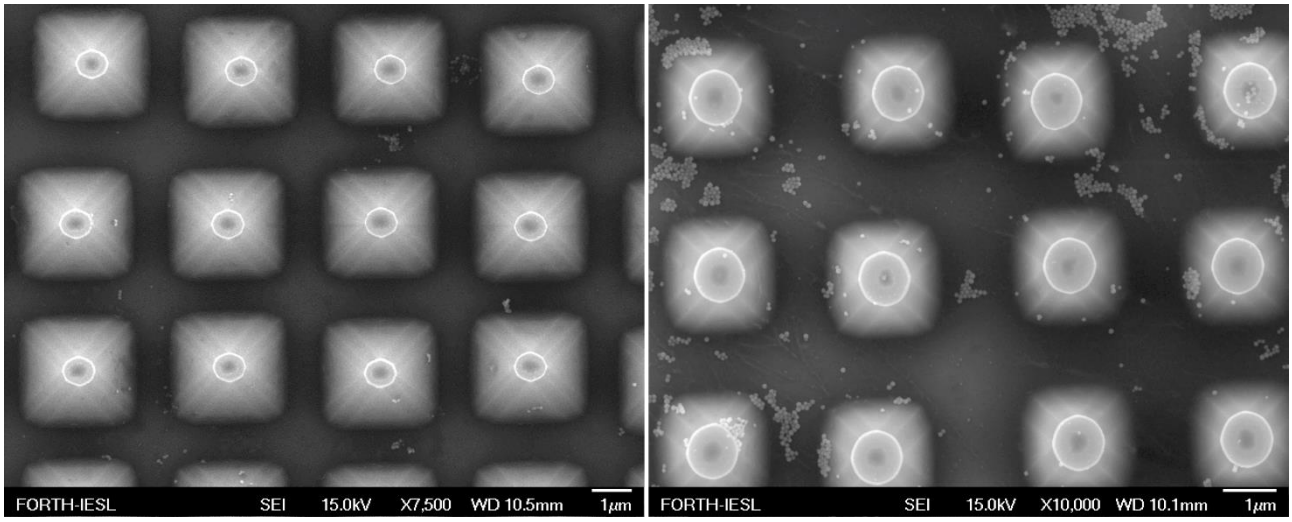

Figure 6. SEM images of the deposited perovskite nanocrystals with low (left) and high (right) concentration onto Si patterned templates with cones.

Strategies to induce isolated nanocrystals attachment on Si_3N_4 structured membranes

The optimum parameters from the attachment of the nanocrystals on the Si patterned templates were used as initial parameters for the attachment on the patterned Si_3N_4 membranes structured by EBL. The handling of these templates is challenging because they were fragile, but they are the optimum substates for the planned X-ray scanning experiments in transmission mode to decrease the footprint of the sample and to permit an easier assignment of the X-ray data to the selected nanocrystals.

Si_3N_4 membranes containing many patterned areas of 100x100 µm² including line gratings, array of circles and array of donuts have been used as templates for the attachment of the nanocrystals in order to find out the optimum structure for the individual nanocrystal arrangement. The Si_3N_4 membranes were covered with Cr in order to inspect them on SEM.

By careful inspection of the SEM images of the different patterned areas on the same Si_3N_4 membrane (Figure 7) we concluded that the optimum patterns for the individual nanocrystal's arrangement were the lines with gap/line width of 200/200 nm (Figure 7a) and those of 50/50 nm (Figure 7c). In the first case some individual nanocrystals were bonded on the lines while in the second pattern they were trapped between the lines.

These experiments revealed the best features of the patterned templates but the nanocrystal arrangement protocol had to be improved further as the density of the nanocrystals is still high.

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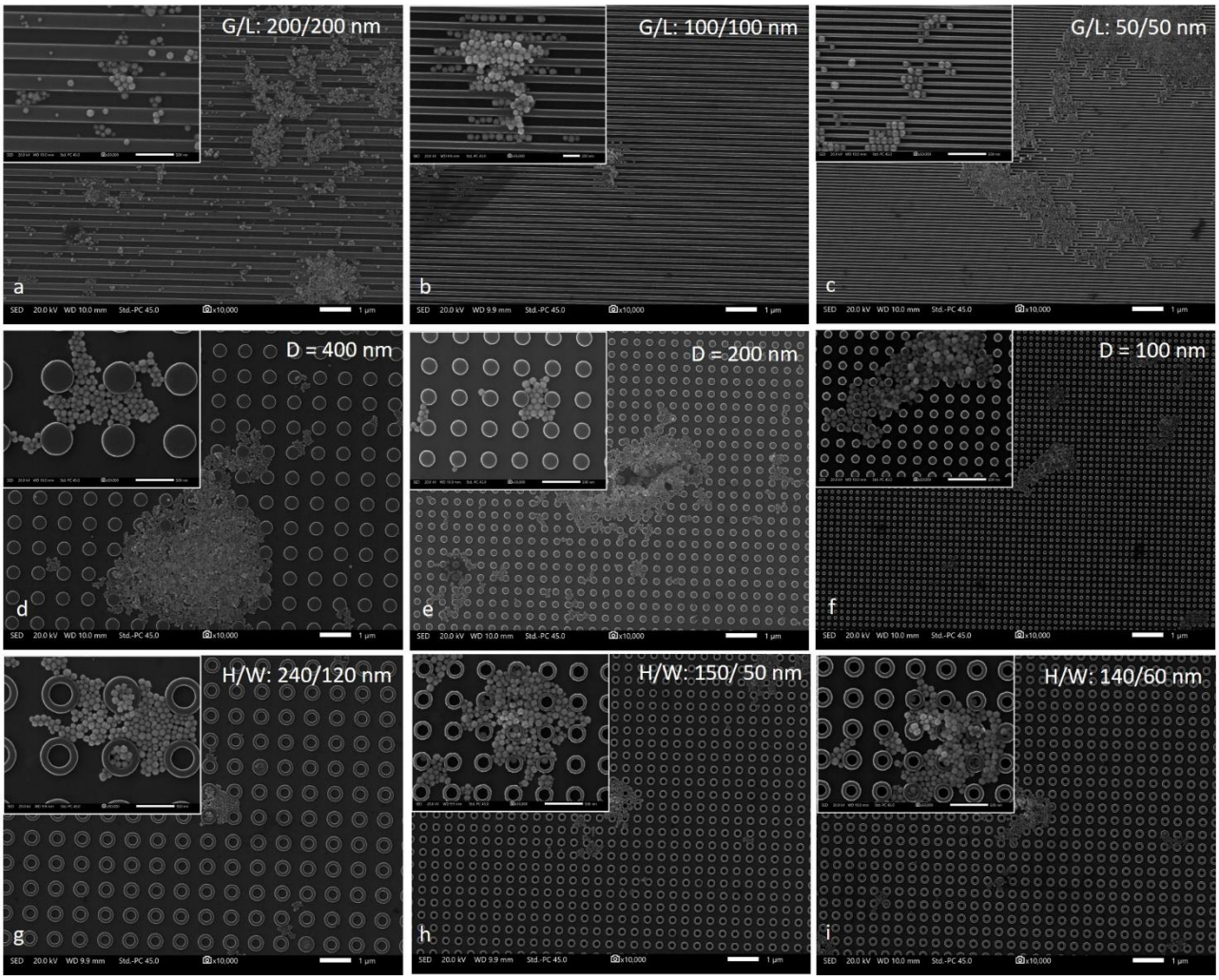

Figure 7. SEM images of the deposited perovskite nanocrystals on Si_3N_4 patterned membranes including line gratings (a-c), array of circles (d-f) and array of donuts (g-i) covered with Cr.

Optimization of templates / protocols and optimum conditions

The deposition of the Cr on the membranes was necessary in order to examine by SEM but the arrangement was not the same with the uncovered membranes. New experiments with flat substrates had been done in order to find again the optimum concentration of the particles (Figure 8a) and then this to be used in the uncovered membranes (Figure 8b). For the SEM inspection, the templates decorated with the particles were covered with Au, but in this case the particles were attached directly onto the template.

The nanocrystals with this arrangement protocol and concentration (0.15 mmoles/L) were well separated and their density was accepted in order to use them for the correlative experiments.

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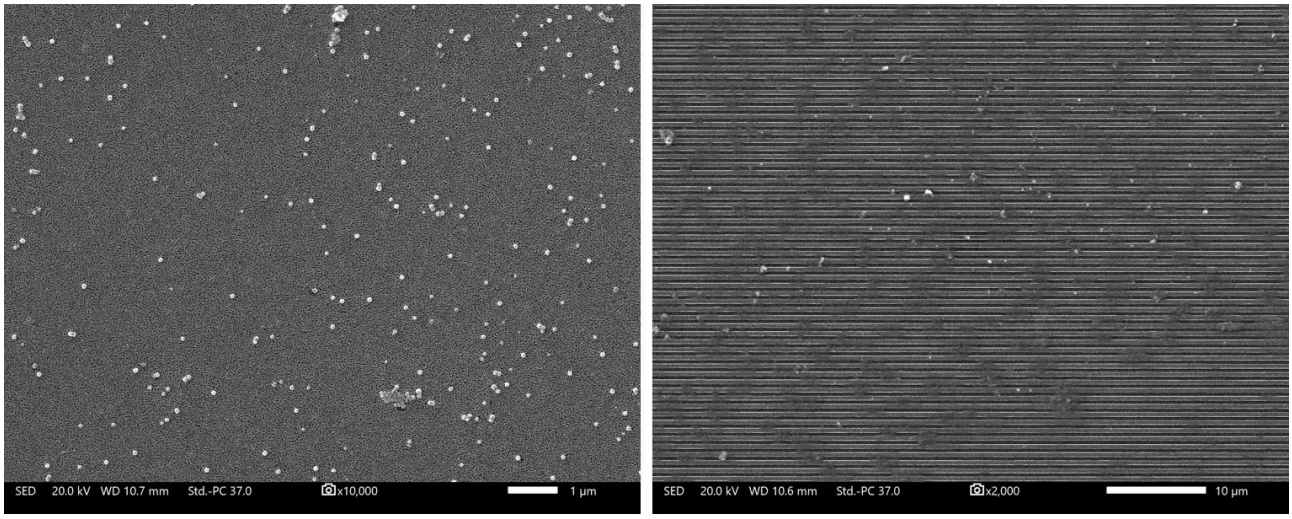

Figure 8. SEM images of the deposited perovskite nanocrystals on flat (left) and Si_3N_4 membranes patterned with lines (right).

Conclusions

The protocol established for the nanocrystal arrangement on functionalized patterned Si_3N_4 membranes seems suitable to serve as a general protocol for the nanocrystals of similar size and capped with hydrophobic ligands such as oleic acid and oleylamine that are the most common ligands for the stabilization of nanocrystals. Although a careful handling is needed for these templates because they are fragile, they are required for future X-ray scanning experiments to ensure a sufficient transmission and decrease the X-ray footprint on the sample in this geometry, permitting an easier assignment of the X-ray data to the selected nanocrystals. Patterned lines with lines width of (lines width / gap = 200 nm / 200 nm) facilitate the arrangement of separated nanocrystals.

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