

Nucleation and growth of superlattices of metallic nanoparticles using microfluidic evaporation

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1. Introduction

The response of materials to electromagnetic radiation is characterized by Maxwell's equations and the constitutive relations involve the permittivity ϵ and the permeability μ . All familiar materials have positive values for both ϵ and μ , but it is not unusual for some materials to have a negative permittivity. A negative permeability at optical frequencies however does not occur in natural materials.

Veselago [1] investigated materials with negative ϵ and μ and predicted that such a medium would exhibit exotic properties as for instance a negative index of refraction and inverse Doppler and Cerenkov effects. His analysis of materials has remained unnoticed in electromagnetic theory for more than thirty years but of course reemerged with the current and active field of metamaterials.

Now, it is possible to work with artificial materials that can produce negative ϵ and μ . To fabricate them, basic structures are positioned in space in order to manipulate the incident waves: for instance, *local resonators* must be designed and spaced at a scale much smaller than the electromagnetic wavelengths of interest, so that the incident radiation cannot distinguish the collection of elements as compared to an homogeneous material [2]. If we want these metamaterials to operate at optical frequencies, then the overall structure size of the individual components shall be scaled to the order of $\lambda/10 \approx 50$ nm with λ the typical wavelength of visible light.

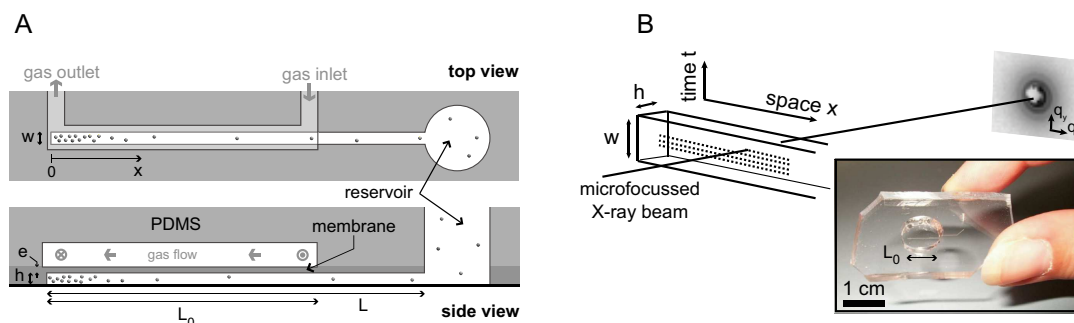


Fig. 1: Typical setup used for microevaporation: (A) top and side views showing the gas and liquid layers and the thin membrane in between (typical dimensions: $e = 10 \mu\text{m}$, $h = 20 \mu\text{m}$, $w = 200 \mu\text{m}$, $L_0 = 10$ mm); (B) a sketch of the similar microdevice mounted on a microfocused X-ray beam and repeatedly probed in space and time using a microfocused beam of size $1 \times 1 \mu\text{m}^2$.

The goal of present work is to assemble metallic nanoparticles (NPs) that can act as locally resonant structures (for their plasmonic response) on a lattice in order to create superlattices; such a superstructure is believed to be a possible candidate for metamaterials working in the visible range. We thus work with aqueous dispersions of tailor-made metallic (gold, silver) NPs that we try to self-assemble by removing the solvent in order to increase their concentration.

To do so, we use a specific *microfluidic device* which can handle extremely small volumes of solution (of order of the nanoliter) and which is dedicated to remove solvent at a very precise pace via *controlled evaporation*, see Fig. 1. Coupled to this *microevaporation* device, we used microscopy, spectroscopy, and X-ray scattering in order to unveil the structures that appear during the concentration process. We evidence that the evaporation process indeed permits to increase the concentration of NPs up to a point where dense structures appear which the latter are quite organized, probably crystalline.

2. Experimental tools for growing and characterizing crystals of NPs

Microfluidic device for controlled evaporation

We use a tool based on evaporation at the micron scale to study the nucleation and growth of crystals of NPs, Fig. 1A. This technique allows the concentration of *any* solute in a microfluidic device, starting from dilute solutions up to the formation of dense states; the experimental device is made of a microchannel (volume of a few microliters) molded in an elastomer (polydimethylsiloxane, PDMS) in contact with a thin PDMS membrane which is permeable to water but retains solutes. As the solvent evaporates, the solutes are thus continuously concentrated and when exceeding their solubility, they may crystallize and hopefully form superlattices in the specific case of NPs.

The rate at which the device extracts solvent has been quantified in details [3] and depends chiefly on the membrane efficiency, the channel length (L_0) and height (h), and the concentration of NPs in the reservoir. As the latter is usually very small (volume fraction $\phi \approx 10^{-6}$), we developed a very shallow chip which is able to concentrate the dilute solution a million times (up to a dense state at $\phi \approx 0.5$) in a matter of a few hours only.

Characterization

We use optical microscopy and colorimetry to characterize the growth of a dense state of NPs. Fig. 2 shows how a microevaporator gets filled with a suspension of gold NPs during the concentration process. Colorimetry yields an approximate estimate of the concentration in the capillary along with a automated detection of the moving front.

Besides, we performed in-situ Small-Angle X-ray Scattering (SAXS) measurements with a high brilliance microfocused beam (at ID13 beamline, ESRF, Grenoble, France). The incoming synchrotron X-Ray beam ($\lambda \approx 0.1$ nm, focal spot $\approx 1.5 \times 1.5 \mu\text{m}^2$) is focused on the PDMS chip mounted on a xy stage, and 2D SAXS patterns are collected with a CCD detector covering the $0.15 - 6 \text{ nm}^{-1}$ q -range. To monitor in space and time the NPs concentration profile, measurements are done on x -lines with small displacements in the y -direction between each line to avoid significant beam damage (see Fig. 1B). We also checked carefully using electronic microscopy and Raman confocal spectroscopy that our thin PDMS membranes were neither punched nor significantly chemically affected by successive shots of such an intense focused X-ray beam.

3. Evidence of crystals of NPs: toward 3D superlattices?

The general scenario we obtain and which holds for all the systems we studied (15 nm gold NPs with polymer ligands, 50 nm silver NPs capped with a silica shell, and 13 nm nanosilica) is the following:

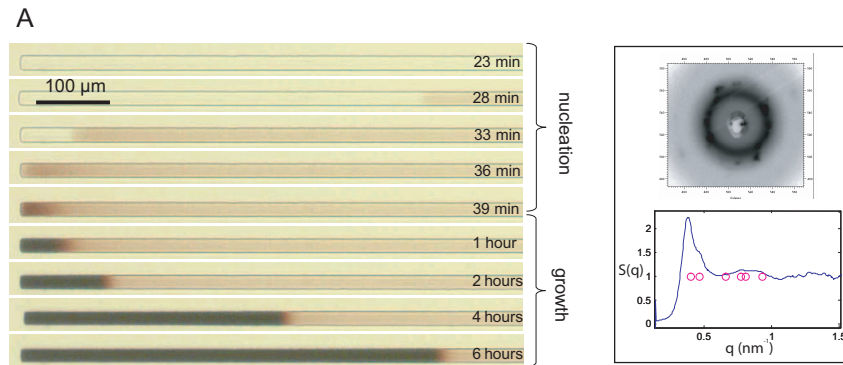


Fig. 2: (A) Time-lapsed optical microscopy of the nucleation and growth of a suspension of gold NPs initially dilute and then growing at a volume fraction $\phi \approx 0.4$. (B) X-ray patterns and analysis showing evidences of crystals of NPs, i.e., superlattices.

after a given induction time, a dense state nucleates, grows, and invades the channel as continuously fed by a fresh suspension.

The growth rate of the dense phase observed in Fig. 2A can be tracked by image analysis using a simple threshold on the color; mass conservation between the incoming and known flux of NPs and the growing dark front leads to an estimate of the concentration of the latter. In the case of gold NPs capped with polymers, we obtain a volume fraction $\phi \approx 0.4$ which is compatible with crystallization.

To go a step further, we analyzed the structure of the dense state using microfocused X-ray scattering. We managed to evidence that there are zones in the dense region where the NPs are particularly well ordered as witnessed by the numerous Bragg spots. While the exact nature of the corresponding structures are still being analyzed, we can assess that there is a reasonable degree of crystallinity in the sample with grains that sometimes have a micron-sized spatial extent.

4. Conclusion

We managed to grow dense states of several types of plasmonic NPs starting from very dilute solution, thanks to a dedicated microfluidic device. *In-situ* X-ray analysis suggests that the dense states we observed are made of compact grains of NPs crystallized of lattices (whose nature is still to be established). This opens up an interesting route for the genesis of 3D superlattices of NPs.

References

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