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# Spontaneous and dense assemblies of nanoparticles within micro-channels by the bubble deposition method

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ABSTRACT

We explore the potential of the bubble deposition method (BDM) for the specific monolayer organization of spherical and anisotropic NPs onto microstructured surfaces. These structurations cannot be only explained by the classical interactions between nano-objects and substrates but mainly by a combination of the drying front peculiar to the BDM with lithographically patterned substrates. Extended up to the integration of SWNT, this approach represents a simple, efficient, nano-object independent and potentially useful route for nanometric device realization.



## 1. Introduction

Self-assembly process of spherical or anisotropic nanoparticles (NPs) is one of the routes sustained for nanostructure realization and results from interactions of the nano-objects between themselves and with the surface. Nevertheless, the physical constraints imposed by a specific deposition method are far from being negligible. Several studies devoted to self-organization of nanoparticles have been carried out by classical techniques: Langmuir–Blodgett, spin coating and dip coating [1–5]; however, nanometric system realization cannot be envisaged without a compound saving method enabling homogeneous depositions on large scale. These two requirements are satisfied using the bubble deposition method (BDM). Developed in our group, this original approach has been first described for the deposition of pure surfactant films [6–8]. By confining the nanoparticles within the surfactant bilayer, the BDM has been proven to be efficient for ordering various nano-object films such as gold and silica spherical nanoparticles [9,10], mixed oxide nanowires [11], carbon nanotubes [12] and graphene oxide flakes [13]. Until now we focused our attention on the formation of monolayer, dense and homogeneous films on flat substrates. In the present study, we explore the feasibility to perform nanoparticle deposition onto lithographically microstructured surfaces. This synergetic combination of bottom-up and top-down approaches should generate integrable large-scale patterned arrays of nanoparticles in nanoscale devices. As the material processability is a critical step toward the integration of nano-objects into practical applications ranging from nanoelectronics [14,15] (e.g., transistors or photovoltaic cells based on carboned materials) to nanobiology (e.g., biosensors based on nanoparticles and biomolecules) [16,17] we propose, in this work, to highlight the specific organization of NPs within templates resulting from a spontaneous and non selective phenomenon whose origin will be discussed.

## 2. Experimental

### 2.1. Materials and substrate surface modification

Sodium dodecyl benzene sulphonate (SDBS) surfactant and colloidal silica nanoparticles (LUDOX LS colloidal silica, 30 wt% suspension in $H_2O$, 16 nm diameter reported by manufacturer) were provided by Sigma Aldrich and used as received. The solution of silica nanoparticles (0.30 wt%) was prepared in aqueous solution of the SDBS surfactant at 5 CMC (1 CMC = 0.556 mg/ml). SWNTs (Carbon Nanotechnologies Inc.) with an average diameter of 1 nm and a length of about 0.5–1 μm were used without further purifications. In order to prepare the SWNT solution, 10 mg of SWNT were suspended in 10 ml of an aqueous solution of SDBS surfactant at 5 CMC using sonication. The solution was then ultracentrifuged during 2 h at 21,000 × *g*. $CeVO_4$ nanowires (about 50–200 nm long and 5 nm tick) were selectively synthesized by hydrothermal process and were dissolved in aqueous solution of SDBS at 5 CMC.

Before the deposition stage, silicon and glass substrates underwent lithographic processes. Trenches are first designed by e-beam

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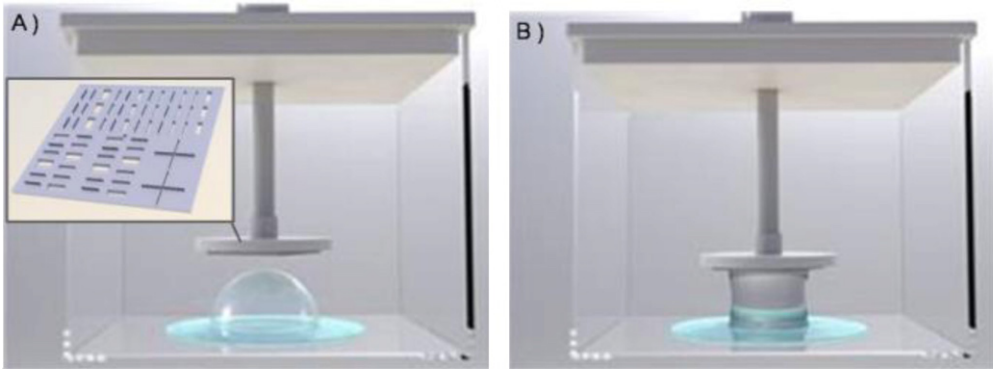


**Scheme 1.** Schematic representations of the deposition cell just after the bubble formation (A) (insert: typical lithographically patterned substrate) and after the bubble adhesion on the substrate (B).

lithography using PMMA as resist. After development in MIBK/IPA, the sample is dry-etched by reactive ion etching (RIE) at a speed of $\sim$1 nm $s^{-1}$ with $SF_6$ as reactive gas. The etching times were set to obtain depths of 35 and 15 nm for silicon and glass substrates respectively. Following the lift-off of the PMMA, the sample is cleaned from potential resist residues by RIE using oxygen as the reactive gas. The etching of glass substrate is similar to that on the silicon, except that a thin film of aluminum is deposited on top of the PMMA before e-beam lithography to avoid charging effects. This process enables the fine tuning of the geometric template parameters (width and length) on the micrometer scale (from 1 to 10 μm wide and 20 μm long).

### 2.2. Deposition of nano-object monolayers

The deposition of nano-objects thin films is realized with the bubble deposition method that has already been described in our previous reports [8,12]. Briefly, this method enables the formation of diameter controlled hemispherical soap films (Scheme 1A) using really low volume of solution (<1 μl for a surface of 1 $cm^2$-large deposit). These soap films are composed of a surfactant bilayer that delineates a water core where NPs are in suspension. Drainage parameter enables the fine-control of the soap film thickness. These films are then transferred to every type of substrate (Scheme 1B). In this study it is essential to emphasize that (i) the microstructured surface does not induce any perturbation on the surfactant film during the bubble deposition process and (ii) the nano-object ordering occurs while enabling the deposition of a monolayer film.

The use of an ethanol vigourous rinsing in order to remove the surfactant while preserving the nano-object film morphology has already proven its efficiency and is then reproduce in the same way here [11].

### 2.3. Characterization

Topographical imaging of the deposited films was performed at room temperature with a 5500LS Atomic Force Microscope (Agilent Technologies) in tapping mode using Si tips. Images were systematically taken from all the lithographically patterned areas. The PicoImage software was used for the imaging treatment. XPS studies were performed with a KRATOS Axis Ultra DLD spectrometer, using the monochromatized Al Kα line at 1486.6 eV. The detector was calibrated at 84 eV for the $Au(4f)_{7/2}$ signal. SEM images were obtained with a Hitachi S4500 microscope.

## 3. Results and discussion

### 3.1. Deposition of isotropic model system

We have first investigated a simple assembly of spherical silica nanoparticles as an isotropic model system.

As shown in Fig. 1 an unexpected arrangement appears to be localized within the trenches independent of their geometric characteristics with: (i) a marked depletion area and (ii) a specific NP localization inside the micro-channels.

Such an organization behavior had never been observed when the depositions were achieved by the BDM on flat substrates, and thus shows the strong effect of microstructures. The depletion region is well-defined (≈4 μm around the channel) with no influence of the trenches sizes. The NP density inside the patterns is confirmed to be twice higher than in the nonetched areas by calculation from AFM profile extractions.

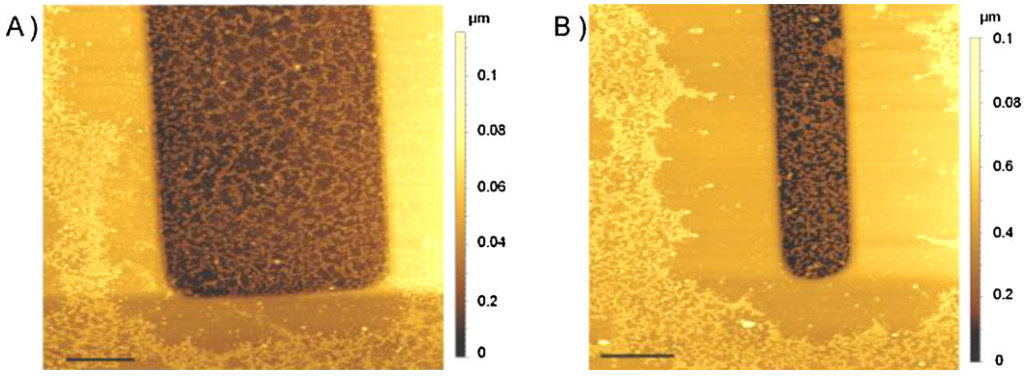


**Fig. 1.** AFM images of silica NP films on 15 μm (A) and 5 μm width (B) structures (scale bar: 5 μm).