## Capillary Forces Assembly in microfluidic cell: Faster assembly by accelerating the particles convective flux and integration into complex pattern.

T. Pinedo, O. Lecarme, E. Rossito, K. Berton and D. Peyrade\*

CNRS-LTM, CEA Grenoble, 17 avenue des Martyrs, 38054 Grenoble CEDEX 9, France

Key words: capillary forces assembly, colloid, evaporative cooling convection, plasmons

Recent progresses made in chemical synthesis of colloids open the way to new functional materials based on the assembly of colloidal building blocks onto complex structure<sup>1</sup>. Nevertheless, low-cost, high throughput and precise assembly techniques are required to fully exploit the potentialities of "supra-colloidal" nanostructures. Most of promising assembly methods developed in the past are principally define or derivate from Capillary Force Assembly (CFA) techniques<sup>2</sup>. CFA is a two-stage process based on *convective transport of particles* towards the solid-liquid-vapor contact-line during the evaporation of a colloidal dispersion coupled with *attractive capillary force* that allows the formation of colloidal lattices or the pattern filling,<sup>3,4,5</sup>.

In this work, we present a new CFA approach which results from the combination of classical CFA combine with evaporative cooling convection assistance (to inhibit Brownian motion) in order to achieve a faster colloidal accumulation at the triple contact line. The microfluidic cell built for this purpose comprises an air-suction-driven convection flow and a sample temperature controller (Fig.1A): Firstly, the saturated air-suction inside the confined system creates a convection flow inside the colloidal solution (Fig.1B) pushing and concentrating the colloids towards the contact line (Fig.1C). Secondly, the contact angle is slightly reduced as the evaporation temperature is increased slightly above room temperature (Fig.1C, 1B) raising the capillary forces at the contact line.

The introduction of those two independent and controllable parameters (air-suction flow and temperature) improves the efficiency of the assembly process and accelerates the contact line speed to values as high as  $100\text{-}200~\mu\text{m/min}$ .

This technique allows large scale assembly of polystyrene beads (1  $\mu$ m – 200 nm and 50 nm ) and gold colloids (100 nm) (Fig. 2). Various gold colloidal assembly into lithographic patterns were obtained (binary object- line – triangle) and spectroscopic studies show plasmon spectra evolution of those colloidal clusters (Fig.3).

This presentation will highlight microfluidic cell CFA approach and present dynamically the effect of air-suction and temperature on colloids motion. Finally, we will show our results in the assembly of complex nanostructures and discuss plasmonic properties of gold colloidal assemblies.

<sup>\*</sup> To whom correspondence should be addressed. E-mail: david.peyrade@cea.fr

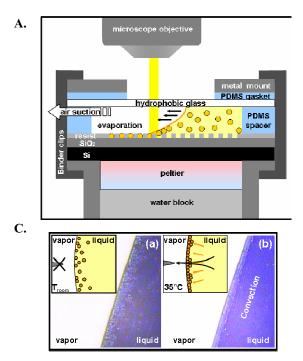
<sup>&</sup>lt;sup>1</sup> S.C. Glotzer. et al., Nature Materials , 557 (6), (2007)

<sup>&</sup>lt;sup>2</sup> N.D. Denkov et al. Langmuir, 3183 (8) (1992)

<sup>&</sup>lt;sup>3</sup> Xia Y. et al, J. Am. Chem. Soc., 123, 8718, (2001)

<sup>&</sup>lt;sup>4</sup> Alivisatos A. P. et al., Nano Lett., 4(6), 1093, (2004)

<sup>&</sup>lt;sup>5</sup> Peyrade et al., Microelec. Eng., 83, 1521, (2006)- M.J. Gordon et al. Appl. Phys. Lett. 89,053112 (2006)



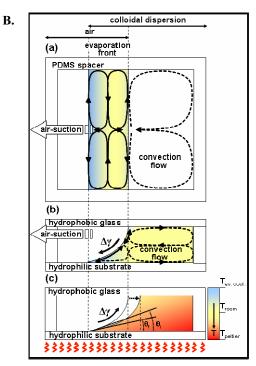
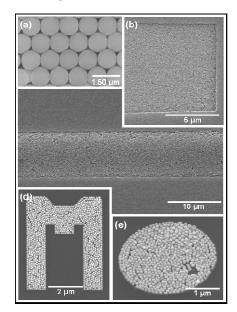
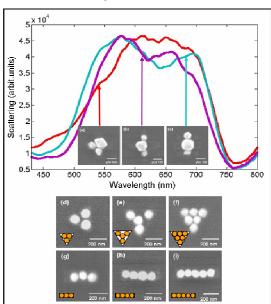


Figure 1. A. Schematic description of the experimental device that consists of a microfluidic cell, an air-suction system and a temperature control system via a peltier. B. (a) and (b) Schematic description of convection flow driven by evaporative cooling effect due to forced-evaporation by air-suction in a microfluidic cell.  $\gamma$  is the surface tension at the front of the colloidal dispersion and  $T_{\text{ev. cool}}$  is the evaporative cooling temperature at the contact-line. (a) Top view. (b). Lateral view (c) Schematic description of the effect of temperature on contact-angle at the triple contact-line (the temperature decreases from the bottom to the top of the cell). After heating, the evaporation front is stretched and the contact-line remains pinned. C. Optical micrographs of polystyrene colloids ( $1\mu m$  in diameter) motion at the triple contact-line. (a) In the absence of air suction, the colloids are not closely packed against the contact-line. (b) In the presence of air suction, Brownian motion is completely inhibited and the colloids are pushed further towards the contact-line.



**Figure 2.** SEM micrographs of large-scale assembly of polystyrene and gold colloids (a) close-packed 1-μm polystyrene colloids (b) 100-μm² area of 50-nm polystyrene colloids (c) 400-μm² area of 200-nm polystyrene colloids (d) and (e) 100-nm gold colloids assembled into large patterns.



**Figure 3.** Dark field reflectance measurements of binary objects (a), (b) and (c) fabricated from 250-nm and 150-nm gold colloids. SEM pictures: (d) (e) (f) assembly of 100-nm gold colloids into triangular objects. (g) (h) (i) Assembly of 100-nm gold colloids into linear objects with three, four and five colloids.