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Communications

Lipid vesicle adsorption on micropore arrays prepared by colloidal lithography-based deposition approaches

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(1) Lengthy experimental details

ZnO-based substrates preparation

For the deposition of ZnO patterned layers, a thin ZnO seed layer was firstly deposited by Metal Organic Chemical Vapor Deposition (MOCVD). Deposition temperature and time were fixed at 500°C and 1 hr, respectively, in Ar/O_2 reduced pressure (5 Torr) atmosphere. Polystyrene (PS) colloids (Polybead® Carboxylate Microspheres 0.35µm, Polysciences, Inc.), were deposited by drop casting of a 1% wt aqueous dispersion and left overnight under controlled atmosphere to allow the self-assembling assisted by slow solvent evaporation in close packed mono- and multi-layers. Afterwards, ZnO nanorods were grown onto seeded ZnO substrates by Chemical Bath Deposition (CBD) in a 1:1 $Zn(CH_3COO)_2•2H_2O$/(N,N,N′,N′-tetramethylethylenediamine (TMEDA)) nutrient bath aqueous solution at 70°C for 2 hrs. [16].

Lipid preparation

Small unilamellar vesicles were prepared from chloroform solutions of 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine (POPC) and 1-palmitoyl-2-oleoyl-sn-glycero-3-ethylphosphocholine (chloride salt) (POEPC) in a molar ratio of 3:1, respectively. In order to obtain fluorescent vesicles 1% Rhodamine-labeled PE lipids was added. All lipids were purchased from Avanti Polar Lipids, Alabaster, AL. The chloroform was removed firstly under a gentle argon stream and then under vacuum by using a rotary. The resulting thin lipid film was hydrated with phosphate buffer saline (PBS) solution (0.010 M phosphate buffer with 0.140 M NaCl and 0.0027M KCl, Aldrich, pH 7.4) to a concentration of 5 mg/mL. The lipid mixture was extruded using a mini extruder (Avanti Mini-Extruder, Avanti polar lipids, Alabaster, AL) utilizing polycarbonate membranes having pore sizes of 100 and 30 nm. An average diameter of about 80-100 nm of the extruded lipid micelles was measured by light scattering measurements.

(2) SEM cross section micrographs displaying ZnO seeding layer

Figure S1 shows the SEM images of patterned regions and reveals the coexistence of hybrid ZnO nanorods/PS 3D (ROI 1 and 2 Figure S1a) and 2D arrays (ROI 3 Figure S1b). More in details, ROI 1 and 2 are characterised by the presence of nanospheres multilayers, whilst in ROI 3 less densely packed nanosphere areas characterised by monolayers and/or extended region of ZnO nanorods lead to a less porous topography.

The ZnO seed layer, having a thickness of~70 nm, deposited by MOCVD, is clearly visible (red line) under the nanorods arrangement.

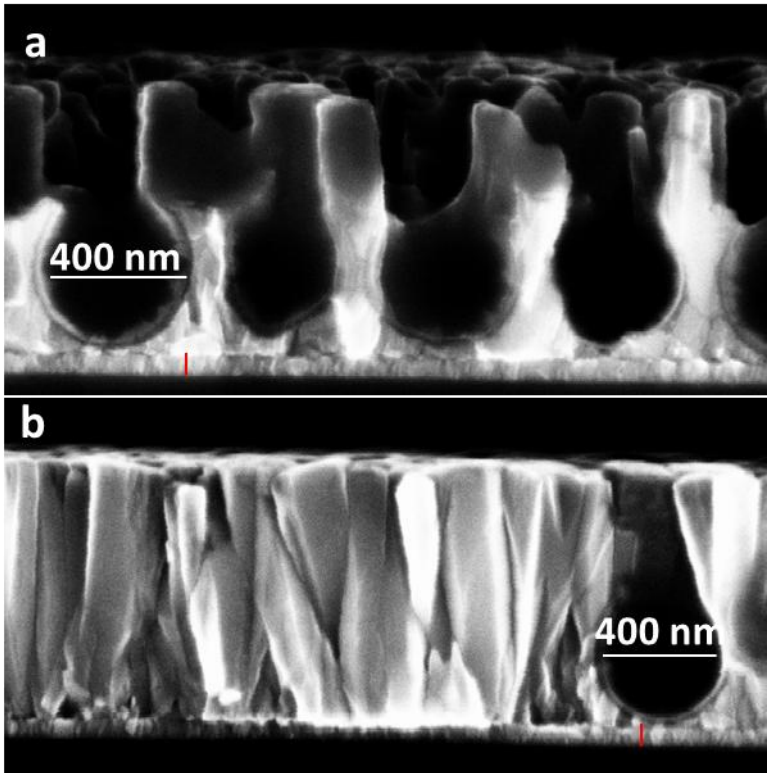

Figure S1:a) SEM high magnification (Scale bar 400 nm) cross section view of ZnO patterned region characterised by nanospheres multilayer arrangment (ROIs 1 and 2); b) and of ZnO patterned region characterised by isolated areas of nanosphere monolayer (ROI 3). The red lines are drawn to highlight the presence of a conformal ZnO seed layer under the nanostructure arrays

(3) FRAP experiment of lipids adsorbed onto unpatterned ZnO

The confocal images of lipid adsorbed on unpatterned ZnO surfaces, deposited at the same MOCVD and CBD conditions than those used for the deposition of ZnO micropores but without the CL step, are shown in Figure S2.

The topography of the substrate is well evident (consistently with the root mean squared roughness of about 30 nm measured by AFM for dense ZnO nanorods), and this results in a non uniform emission intensity on the focal plane of the images, for both the green emission of the substrate and the red emission of the lipids

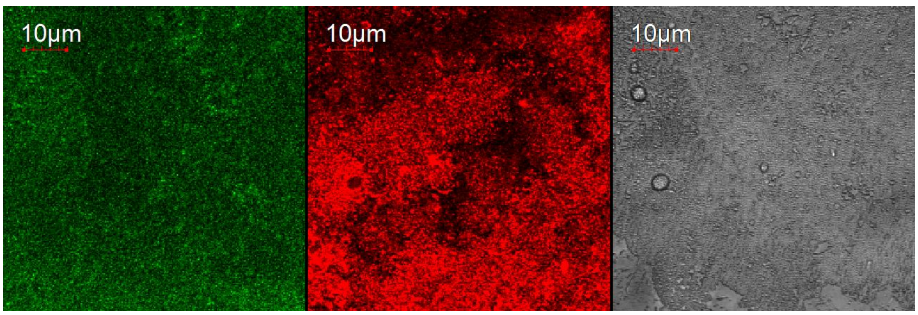

Figure S2 – LSM images (green: λex/λem=488/519 nm; red: λex/λem=543/591 nm) and bright field micrograph (in grey) of unpatterned ZnO sample prepared by MOCVD (500°C)-CBD.

FRAP experiments on on such unpatterned ZnO surfaces after lipid adsorption (Figure S3) indicate a negligible fluorescence recovery after photobleaching, thus point to the low lateral diffusion of the lipid molecules in the adlayer.

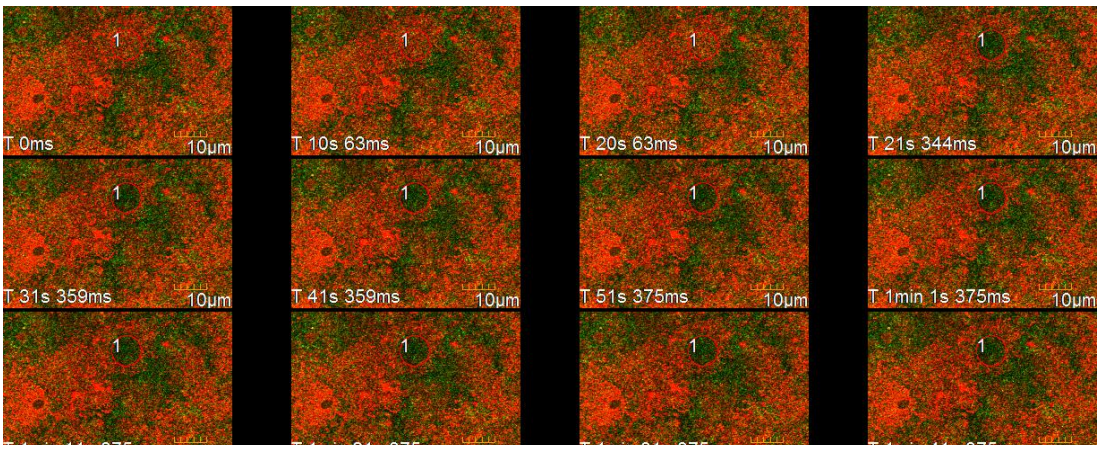

Figure S3 – Time lapse micrographs (merged green and red channels) for the FRAP experiment of lipid (red) adsorbed on unpatterned ZnO (green). The image sequence shows three frames before bleach, followed by bleach and eigth frames for the recovery after bleach.