



Arrays of copper rings with tunable dimensions via electro-colloidal lithography



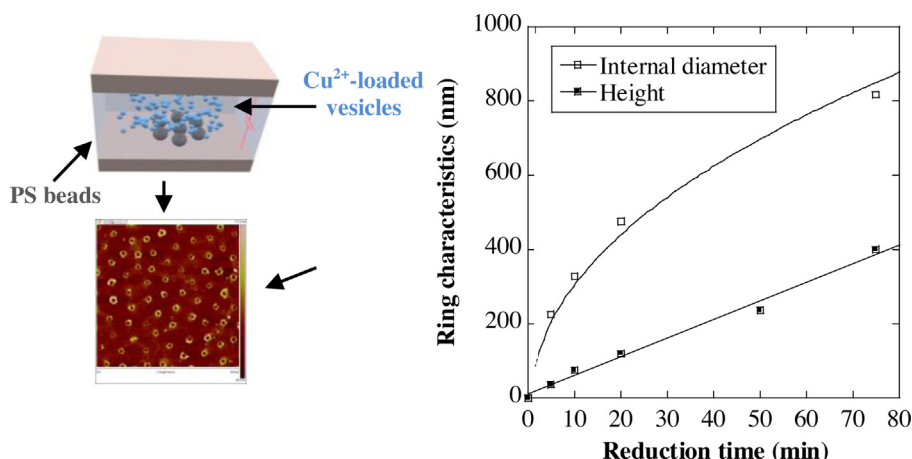
Damien Bazin, Hassan Saadaoui, Chrystel Faure*

Université de Bordeaux—Centre de Recherche Paul Pascal, Avenue du Dr Schweitzer, 33600 Pessac, France

HIGHLIGHTS

- Electro-colloidal lithography allows finely controlling patterned metal geometry.
- Copper film thickness and height depend linearly on DC field time application.
- Copper rings separation is controlled by AC field frequency and/or amplitude.
- Copper rings diameter is predictable and controlled by DC field time application.
- Polystyrene microbeads are shown to act as template for rings growth.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 8 July 2015

Received in revised form 12 October 2015

Accepted 13 October 2015

Available online 17 October 2015

Keywords:

Multi-lamellar vesicles

Self-assembling

2D colloidal crystals

Electric fields

Metallic coatings

Lithography

ABSTRACT

Electro-colloidal lithography (ECL) is an easy, fast, straightforward and cheap patterning process that has been used here to design patterned copper film. ECL consists in assembling polystyrene (PS) micro-beads in 2D hexagonal crystals onto an electrode using AC (Alternative Current) electric field, in sticking them onto the electrode surface where copper is then deposited using Cu²⁺-containing multi-lamellar vesicles (MLVs) submitted to a DC (Direct Current) electric field. Copper rings are then formed; their separation, ranging from 2 to 4.2 μm, could be varied playing on either PS beads size or on AC electric field parameters (frequency and amplitude). The ring internal diameter (100–880 nm range), the ring height (28–400 nm range) as well as the copper film thickness (6–102 nm range) were controlled through the time of DC field application. AFM, SEM, microscopic imaging as well as mathematical modeling show that PS beads behave as a template for copper ring growth, and that this patterning is due to an accumulation of MLVs around the dielectric PS spheres on the electrode.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Electro-colloidal lithography (ECL) has been developed recently to propose an alternative to colloidal lithography that are multi-step processes, associating the fabrication of a colloidal mask with

* Corresponding author. Present address: Laboratoire de Chimie et Biologie des membranes et nano-objets, Univ. Bordeaux, CBMN, UMR 5248, Allée Geoffroy St Hilaire, F-33600 Pessac, France. Fax: +33 54008496.

E-mail address: chrystel.faure@enscbp.fr (C. Faure).

traditional lithography techniques such as evaporation, [1–2] etching, [3–4] or even photolithographic processes [5]. In a previous paper, we described ECL and showed that it is a mono-technique process that allows patterning planar surfaces easily, rapidly and with large throughput [6–8]. Since magnetic, [9] optical, [10] electrocatalytic, [11] optoelectronic [12] and data storage [13] are properties influenced by the shape, size and inter-feature spacing, controlling the geometrical characteristics of patterns is crucial. The optical resonance properties in metal nanorings, for instance, can be tuned dramatically by varying their diameter and wall thickness, [12,14] which make metal nanorings promising for applications as ultrasensitive bio- and chemical sensors. Playing on inter-feature spacing as well as on their height will also influence the substrate roughness and then its wettability. Hence, the interest of a lithographic technique lies also on its ability to perfectly control the geometry of the patterned features. In that study, we will then apply ECL to the fabrication of two-dimensional arrays of copper rings in that objective.

Several examples can be found in the literature reporting the fabrication of metallic rings arrays, however, as already mentioned the reported processes are multi-steps, multi-techniques and not so easy to handle. These include electron-beam lithography, [15–17] molecular-beam epitaxy, [18] nano-imprint lithography, [19] etching and sputtering, [20,21] edge spreading lithography, [22] chemical modification, [23] and structure template techniques [24]. One of the easiest and fastest reported processes is colloidal lithography in combination with capillary lithography [25–27]. As an example, Bayati et al. [27] produced copper nanorings arrays by organizing 500 nm PS spheres (3D crystals by evaporation) onto highly oriented pyrolytic graphite (HOPG) and Si(100) substrates, impregnating the colloidal crystals with the template metal salt followed by its reduction by NaBH_4 . However, the limitation came from a lack of control of geometrical parameters since e.g., the ring height could not be controlled and was fixed to 5 nm.

Our challenge was then to propose an advantageous process in terms of simplicity, cost and throughput that also allows controlling the geometrical parameters of the patterned surface. We will then show how the spacing between copper rings, the ring internal diameter and the ring height can be tuned using ECL and, how to understand the geometrical characteristics of the rings.

2. Experimental section

2.1. 2D planar electrochemical cell fabrication

The fabrication of the electrochemical cell (Fig. 1) was detailed elsewhere [7,28]. ITO electrodes (Delta Technologies Limited, 70–100 Ω) were first treated to decrease surface roughness by plunging them into a KOH-saturated isopropanol solution for 24 hr. Then, electrodes were sonicated in a bath containing a Hellmanex® solution (Sigma, dilution 1:50 v:v) for 1 h before rinsing with distilled water, ethanol and acetone. After drying, both electrodes were separated by a 250 μm circular silicon spacer (Goodfellow, Lille, France), delimiting a 2 cm^2 working surface. The silicon joint was cut to let two apertures by which particles dispersions are introduced.

2.2. 2D assembling of functionalized PS beads under AC field

PS beads (Polysciences, Eppenheim, Germany) dispersions were introduced into the cell and let to rest under an AC field (5 kHz, 120 V/cm) to allow particle sedimentation (c.a. 30 min depending on their size). Then, the frequency was continuously decreased down to 2 kHz by 1 kHz step every 2 min, then down to a low frequency (LF) at which particles are attracted forming either compact

or distended aggregates. LF value depends on beads nature and size. From 1 kHz to LF, the frequency is decreased by 0.2 kHz step every 2 min.

For amine-modified PS beads, LF was 600 and 800 Hz for 3 μm -sized and 1 μm -sized beads, respectively. For those beads, LF corresponds to a close-compact hexagonal organization and further changes in AC field parameters (frequency or amplitude) cannot modify particles assembling.

For sulfate-modified PS beads (2 μm), LF was 800 Hz. Here, particles are forming distended aggregates (no contact between particles). Then, in this case the frequency was increased to a final frequency of 1200 Hz by 200 Hz step every 2 min. This step led to a separation of the particles that form “disordered” hexagonal arrays. The organization is drastically improved by a rise in AC field amplitude from 120 V/cm to 290 V/cm by 10 V/cm step every 2 min. For these particles, experiments were also performed at a final frequency of 400 Hz. In this case, AC frequency was decreased from 1200 Hz by 200 Hz step every 2 min.

Eventually, for carboxylate-modified PS beads, AC field amplitude was fixed at 80 V/cm for sedimentation, and the frequency was decreased down to 500 Hz. Then the amplitude was rise to a final one ranging from 80 to 380 V/cm.

Organized particles were stuck onto the electrode using a DC generator connected in parallel to the AC power supply (Hewlett Packard, 3324A). The sticking electric field value was 90 V/cm for all types of particles and was applied during a variable time called the “Sticking Time” (ST).

2.3. Cu^{2+} -loaded MLVs production

Cu^{2+} -loaded MLVs preparation was detailed elsewhere [28–29]. Briefly, it consists in mixing an equal amount of a 0.68 mol L^{-1} $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Aldrich) solution with GenaminT020 (GT020, Hoechst, Frankfurt, Germany). GT020 is a surfactant that self-organizes into a lamellar phase in the cupric aqueous solution. Under shear, the lamellar phase turns into a dense multi-lamellar vesicle phase. Cupric ions are trapped inside MLVs by chemical affinity to the GT020 polar headgroup. Here, shearing was produced by a simple mixing of the GT020- CuSO_4 mixture using a spatula. After c.a. 5 min. mixing, the paste was centrifuged for 5 min at 3000 rpm and both steps were repeated until the sample color was homogeneously blue. Dispersions of MLVs in distilled water were prepared by gentle mixing with a mechanical stirrer (500 rpm). Two MLVs concentrations were studied: 500 and 50 mg of MLVs/mL water. Whatever dispersion, the same value of electric field (–90 V/cm) was applied to induce MLVs transport and Cu^{2+} reduction: this value was chosen to avoid H_2 formation and to allow the copper film formation in a shortest time.

2.4. Surface characterization

The morphology of the metal deposits was examined by a SEM (HITACHI S4500, $V=5$ kV) microscope. Atomic Force Microscopy (AFM) (Nanoscope III, Digital Experiment) imaging was performed in tapping mode with a silicon tip.

2.5. Image treatment

Radial profiles were performed using Image-J software (<http://rsb.info.nih.gov/ij/>). AFM and optical images were first binarized using a threshold intensity to remove the noise. An autocorrelation of the treated images was applied before performing the radial profile.

Download English Version:

<https://daneshyari.com/en/article/591853>

Download Persian Version:

<https://daneshyari.com/article/591853>

[Daneshyari.com](https://daneshyari.com)