Nano- and microscale apertures in metal films fabricated by colloidal lithography with perovskite nanocrystals

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Abstract

We demonstrate patterning of metal surfaces based on lift-off of perovskite nanocrystals that enables the fabrication of nanometer-size features without the use of resist-based nanolithography. The perovskite nanocrystals act as templates for defining the shape of the apertures in metal layers, and we exploit the variety of sizes and shapes that can be controlled in the colloidal synthesis to demonstrate the fabrication of nanoholes, nanogaps and guides with size smaller than the wavelength of light in the visible spectrum. The process can be readily integrated with standard lithography and etching techniques for the creation of more complex structures.

Supplementary material for this article is available online

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(Some figures may appear in colour only in the online journal)

Introduction

Colloidal lithography has emerged as a viable low-cost alternative to electron-beam lithography (EBL) for the fabrication of nanostructures [1–3]. Its usual implementation employs micro- and nanospheres, made of polymers (e.g. polystyrene, poly(methyl methacrylate)) or inorganic materials (e.g. silica). After deposition on a target substrate, further processing (metal deposition, wet or dry etching) results in the formation of a variety of shapes on the substrate: circles, triangles, disks, rings, as well as 3D structures such as pillars and bowls. The resulting nanostructures and patterns have demonstrated peculiar optical [4], plasmonic [5, 6], and magnetic [7] properties, and these processes can modify surface properties such as wettability. These features have found application in many different fields, for example in optics, energy harvesting [8] and storage [9], sensors [10], and biology [11]. However, the set of shapes that can be obtained from micro/nanospheres is limited by the circular projection of a sphere onto a plane, or by the projection of their packed arrays, and a more complex, multiple-step fabrication is required for more elaborate patterns [12]. Expanding the library of shapes that can be obtained in a simple, one-step fabrication process would strongly enhance the versatility of colloidal lithography. For example, shapes such as long guides [13–15], or rectangular slots, or gaps in metal conductors [16] are not possible with spheres, yet these features would be highly appealing for nanophotonic or plasmonic applications [17], electronics, and nanofluidics [18].
Hydroxide (TMAH)-based solution (ma-D 533 from Micro Resist Technology GmbH). The lift-off can take from several minutes to hours, and can be assisted by ultrasonication, but typically we obtained the best results with duration of 15–30 min under sonication. This colloidal lithography process leads to a metal film with holes, whose size and shape are determined by the NCs. Figure 2 shows scanning electron microscopy (SEM) images of the different apertures in the metal film that we obtained: a square hole with few tens of nm edge length defined by CsPbBr3 nanocubes (see figure S2 for a statistical analysis), a hexagonal aperture with around 2.2 μm diameter by perovskite platelets, different rectangular shapes that are produced by nanosheets, and stripe-like apertures that result from nanowires. Nanowires are particularly appealing as templates because they can lead to straight or curved apertures, to crossings, and to loops [23]. A statistical analysis on the looped waveguides like the one depicted in figure 2(f) is presented in figure S3.

Instead of CsPbBr3 perovskite nanowires, we also prepared PbBrOH nanowires by simply heating up PbBr2 in oleyamine at 200 °C for one hour in air. Such PbBrOH nanowires should be robust to organic solvents, while perovskite nanowires are known to dissolve in acetone, chloroform, methanol or isopropanol [24]. We tested the lift-off process using both nanowires made of PbBrOH, and from CsPbBr3, to assess if our colloidal lithography process is due to mechanical lifting of the NC, or caused by a dissolution of the NC itself. As shown in figure S4, we did not observe any lift-off with the PbBrOH wires, even for extended sonication up to 90 min. On the contrary, the CsPbBr3 perovskite nanowires were removed after 5 min of sonication. Therefore, we conclude that the perovskite NCs are dissolved by the solvent, and the metal layer is removed in a similar fashion as in resist-based lithography.

Since nanoscale apertures are particularly appealing in plasmonics, we explored different plasmonic metals for the process, namely Au and Ag. In both cases we used a thin (few nm) Ti layer for better adhesion of the metal layer to the substrate. In principle, the lift-off works for both Au and Ag; however, while for Au the apertures reflect precisely the nanocrystal shape, for Ag the edges appear corrugated and consequently the obtained aperture is larger and its shape is less defined (figure S5). Cracks in CsPbI3 sheets coated with Ti/Ag further support that the Ag in the metal layer reacts with the perovskite nanocrystal.

Nanosite holes in metal films are an interesting system with appealing optical properties [6, 25–27]. To this end, the most promising NC templates in our approach are CsPbBr3 nanocubes that have an edge length of ~14 nm (see supplementary figure S1). We deposited these NCs from diluted dispersions in toluene by drop-casting, and applied the additional rinsing step in hexane or isopropanol to remove larger clusters of NCs from the surface. After metal deposition, we obtained holes with a diameter of around 22 nm that have a relatively narrow size distribution, as can be observed in figures 3(a), (b). Without the washing step, the holes were defined by the larger NC clusters, which resulted in diameters around 60 nm and a broader size distribution (figures 3(c),

Results and discussion

We employed nanocrystals of different shapes from the family of organic-lead halide perovskites, in particular CsPbBr3 nanocubes [19], CsPbBr3 nanowires [22], and CsPbBr3 and CsPbI3 nanosheets [21]. Figure S1 (available online at stacks.iop.org/NANO/31/185304/mmedia in the supporting information) shows transmission-electron-microscopy images of nanocubes and nanowires used in these experiments. In a typical colloidal lithography process, we deposit diluted colloidal solutions of the nanocrystals (NCs) (dispersed in toluene) to obtain individual NC structures on the surface. SEM inspection of the substrates revealed that drop-casting of diluted NC dispersions led to populations of individual NC and small NC clusters. With an additional rinsing step (in hexane or isopropanol) it was possible to remove the larger NC clusters from the surface, and the surface was also cleaned from other residues.

After NC deposition, the sample is coated with a metal layer by electron-beam evaporation, followed by a lift-off in acetone, chloroform, methanol, or a Tetramethylammonium...
We also tested NC deposition by spin-coating, but this typically led to areas with closely packed NCs that did not work well for the lift-off process (see figure S6).

Nanoholes in metal films can be used to concentrate analytes exploiting the different hydrophobicity of the metal and the substrate, and nanoscale apertures in a metal films can act as an optical cavity [28]. We spin-coated a solution of CdSe/ZnS core–shell quantum dots with 3.4 nm diameter and emission centered at a wavelength of 560 nm (purchased from Sigma Aldrich, Lumidot™ CdSe/ZnS 560) onto a metal film with apertures that were defined by clusters of perovskite nanocubes, leading to holes of around 60 nm diameter. Confocal fluorescence microscopy imaging (figure 3(e)) revealed a fluorescence signal in the green spectral band from

Figure 2. SEM images of the different kinds of apertures that were obtained by colloidal lithography using CsPbBr3 NCs as templates: (a) nanosized rectangle, (b) submicron hexagon, (c) micron-size combination of rectangles, (d) straight line with few tens of nm width, (e) curved line, (f) loops, (g) line crossing. Scale bar is 500 nm in all images. The metal layer consisted of Ti/Au with the following thickness: (a) 3/10 nm, (b), (c) 4/40 nm, (d) 3/30 nm, (e) 3/10 nm, (f), (g) 5/20 nm.

Figure 3. (a), (c) SEM images of Ti/Au metal films films with nano-apertures produced by mostly single NCs (a), and NC clusters (c). Scale bar is 500 nm, and the metal layer was Ti/Au with 3/10 nm thickness. The corresponding size distribution of the edge length of the apertures is given in (b), (d) and figure S2(b), (c), respectively. (e) Confocal microscope image from a metal film with nanoholes after spin-coating with a solution of CdSe/ZnS quantum dots emitting at 560 nm. The image shows an overlay of the reflectance of the surface (in gray scale) with the CdSe QD luminescence that appears in red color. Scale bar is 10 μm.
the holes, confirming the positioning of the luminescent quantum dots into the apertures of the metal film. Figure S7 shows a relatively large aperture in the metal film where the PL intensity is concentrated in the center.

The colloidal lithography can be readily integrated with electron- or photoresist-based lithography to combine the apertures defined by the colloidal lithography with deterministic patterning of the metal film. One interesting combination is to use the colloidal lithography with nanowire templates to create nanosized gaps in electrodes that were defined by optical or EBL. To this aim, we first spin the resist and define the desired pattern (i.e. the electrode in this case) by exposure and resist development. Then, a solution of the nanowires (in hexane) is drop-cast onto the poly(methyl methacrylate) (PMMA)/substrate sample, followed by metal deposition and lift-off in acetone. A second lift-off step in TMAH-based solution is performed to efficiently remove the nanowires. This process scheme is sketched in figure 4(a).

Figure 4(b) shows an Au electrode with a gap of 70 nm that was obtained by the combination of electron-beam and colloidal lithography. We note that the fabrication of such narrow gaps in electrodes with large width (exceeding 1 μm) is highly challenging in the fabrication by EBL alone.

Conclusions

We demonstrated how perovskite nanocrystals can be used as templates for the creation of nanoscale apertures in metal films. This functionality is driven by the dissolution of the perovskite material during the lift-off process in organic solvents. The diversity of the possible shapes of the perovskite nanocrystals enables the fabrication of a variety of aperture shapes such as rectangles, hexagons, and straight and bend lines as well as loops. Such complex apertures in metallic films are highly appealing for far- and near-field optical studies. Further improvement of our colloidal lithography process could be achieved by elaborate self-ordering of the template NCs, or by controlled deposition, for example by electrophoresis. Combination with other processes such as standard resist-based lithography and dry etching can pave the way to more elaborate 3D structures.

Experimental section

Lift-off without PMMA patterning: substrates (Si, SiO2, glass) were cleaned in an ultrasonic bath with acetone, followed by isopropanol, and then dried under nitrogen flow. The colloidal solution of the NCs (typically 10 μl of toluene dispersion) was drop-cast onto the poly(methyl methacrylate) (PMMA)/substrate sample, followed by metal deposition and lift-off in acetone. A second lift-off step in TMAH-based solution is performed to efficiently remove the nanowires. This process scheme is sketched in figure 4(a).

Figure 4(b) shows an Au electrode with a gap of 70 nm that was obtained by the combination of electron-beam and colloidal lithography. We note that the fabrication of such narrow gaps in electrodes with large width (exceeding 1 μm) is highly challenging in the fabrication by EBL alone.

Lift-off with PMMA patterning

For experiments with deposition of NCs on pre-patterned PMMA-coated substrates, we used Si/SiO2 samples, cleaned as described above. PMMA was spin-coated onto them, and the pattern was exposed with a Raith 150-II EBL system. After the resist development, the NCs dispersed in hexane were drop-cast onto the substrate. We choose hexane as solvent as it does not degrade the PMMA. Then the metal layer is deposited as described above, and a first lift-off in acetone (ultrasound-assisted) is performed to remove the PMMA. However, this step is not sufficient to remove the NCs, and therefore a second lift-off step in TMAH-based solution is applied.

Metal film imaging

SEM images were acquired with the Raith 150-II system used for EBL or with a FEI Helios NanoLab DualBeam 650. Analysis of the SEM images for the determination of the nanohole size was performed with Gwyddion.
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Author contributions

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