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Assisted-assembly of coordination materials into advanced nanoarchitectures by Dip Pen nanolithography†

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Femtolitre droplets deposited on surfaces assisted by an AFM tip are used as reactor vessels to fabricate arrays of nanoarchitectures ranging from single-crystals of metal–organic frameworks to hollow capsules of magnetic polyoxometalates.

The controlled engineering of molecular-based nanoarchitectures on surfaces is a challenging area of growing interest and technological relevance in chemistry and materials science.¹ A major objective is to spontaneously induce the self-assembly of stable primary building blocks into highly defined and controllable structures by manipulating the local environment of the solution.² For instance, organization of molecular assemblies on surfaces using a combination of lithography and self-assembly techniques has already been described.³ In this sense, one of the most active topics deals with the controlled fabrication of oriented nanocrystal arrays of metal–organic frameworks (MOFs).⁴ Previous studies have reported that the well-known [Zn₄O(BDC)₃] (BDC = 1,4-benzenedicarboxylate; MOF-5) and [Cu₃(BTC)₂] (BTC = 1,3,5-benzenetricarboxylate; HKUST-1) can be grown as crystalline thin-films on SAM functionalized surfaces with well-defined orientations.⁵ It has even been shown how the formation of the crystals can be controlled *via* solvent effects and/or physical boundaries imposed by the use of soft lithographic techniques.⁶

In this communication, Dip Pen nanolithography⁷ (DPN) is used to fabricate MOF crystals confined in specific surface regions. DPN allows the direct transferring of the organic ligands and/or inorganic metal ion building blocks onto specific regions of a surface through an AFM tip that dispenses less than femtolitre droplets of the solution. Therefore, each droplet can act as a reactor vessel confined at the nanoscale, where the coordination polymerization takes place. Moreover, we have extended the capability of DPN to fabricate not only MOF nanostructures but also nanostructures

formed by hollow capsules of polyoxometalates (POMs) molecular clusters. The obtaining of such structures in bulk has already been described though the fabrication of controlled surface arrays remains so far elusive.⁸

First studies were focussed on the controlled growth of HKUST-1 crystals.⁹ In a typical experiment, the ink was obtained from the addition of a solution of Cu(NO₃)₂·3H₂O (0.209 g) in 3 mL of pure dimethylformamide (DMF) to a solution of 1,3,5-benzenetricarboxylic acid (H₃BTC) (0.105 g) in 3 mL of DMF under continuous stirring. The resulting blue mixture was stirred further for 1 h at 50 °C and immediately filtered at room temperature. Droplet arrays of this solution were obtained by traversing a coated AFM tip over two different self-assembled monolayers (SAMs) made of 16-mercaptohexadecanoic acid (MHA) and 1-octadecanethiol (ODT) on gold, at room temperature and a constant humidity of 35%. In both cases, fast evaporation of the droplets at room temperature resulted in a non-consistent growth of HKUST-1. For this reason, the substrates were incubated for 5 days in an air-tight chamber saturated with DMF vapours immediately after its fabrication. Such an incubation process ensures a reduction of the droplet evaporation rate, thus optimizing the crystal growth. The resulting crystals were cleaned of unreacted metal salts and organic ligands by carefully washing with ethanol and studied by field-emission scanning electron microscopy (FE-SEM). FE-SEM images of a representative HKUST-1 nanoarray generated on a CH₃-terminated SAM are shown in Fig. 1. As can be seen from the figure, well-defined HKUST-1 nanocrystals were grown specifically on each dot-like feature of the nanoarray (Fig. 1b). The size dispersion of the nanocrystals varies from “rounded” octahedra of approximately 150 nm in diameter to well-shaped crystals of 650 nm. Unexpectedly, we have even observed the growth of a single crystal per each dot-like feature (Fig. 1c and 1d).

Even though the obtaining of a single crystal per each dot-like feature is still not controllable, these experiments allowed us to show the potentiality of this technique to fabricate single crystal arrays of only 350–400 nm in size. Such control may be feasible since the formation of the crystals takes place on the surface, after incubation of the DPN deposited droplets. This fact was confirmed by reproducing the experiments on a COOH-terminated SAM. In this case, as shown in Fig. 2 and corroborated by X-ray diffraction experiments, the [111] face of the octahedral dominated the crystal growth.¹⁰

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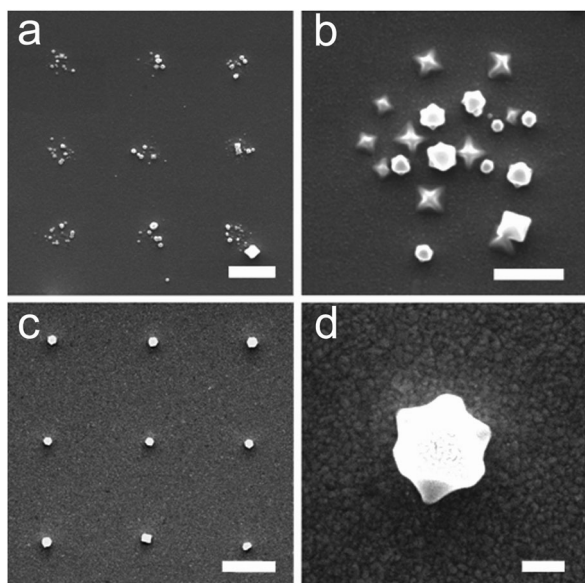


Fig. 1 FE-SEM images of the HKUST-1 nanocrystals grown inside the confined solution droplets deposited by DPN on a CH₃-terminated SAM. (a) Nanoarray; scale bar 2 μm. (b) Details of the nanocrystals grown inside each dot-like feature; scale bar 1 μm. Growth of a single crystal per dot nanoarray viewed from above (c) and at a 45° tilt angle (d); scale bars 2 μm and 200 nm respectively.

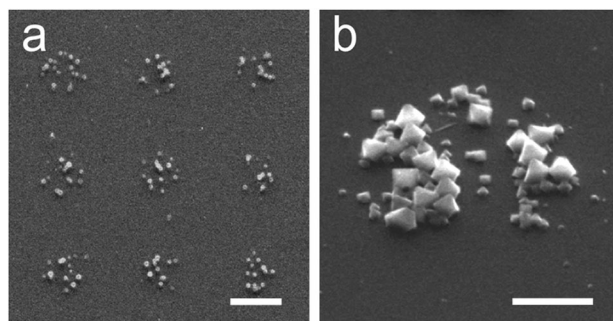


Fig. 2 FE-SEM images of oriented HKUST-1 nanocrystals grown on a COOH-terminated SAM surface assisted by DPN. (a) Nanoarray; scale bar 2 μm. (b) Details of the nanocrystals grown inside each dot-like feature viewed at a 45° tilt angle; scale bar 1 μm.

Polyoxometalates (POMs) experiments were done with two different magnetic polyanions: [ErW₁₀O₃₆]⁹⁻ and [GdP₅W₃₀O₁₁₀]¹²⁻. In a first step, aqueous solutions containing these POMs in bulk were sealed and kept at room temperature without any disturbance for 5 days. It is well-known that this procedure favours the POMs self-assembly, giving rise in some cases to the formation of hollow capsules in solution.¹¹ After such period, a droplet of the incubated solution was placed on a TEM grid for its study. TEM images confirmed the formation of the spherical capsules. Magnification of one of the areas (Fig. 3a) reveals the hollow nature of the POM nanostructures. Each particle consists of a darker ring formed by a shell of POM building blocks surrounding an empty core. It is important to emphasize that the nanostructures are stable even upon vacuum treatment in the electron microscopes.

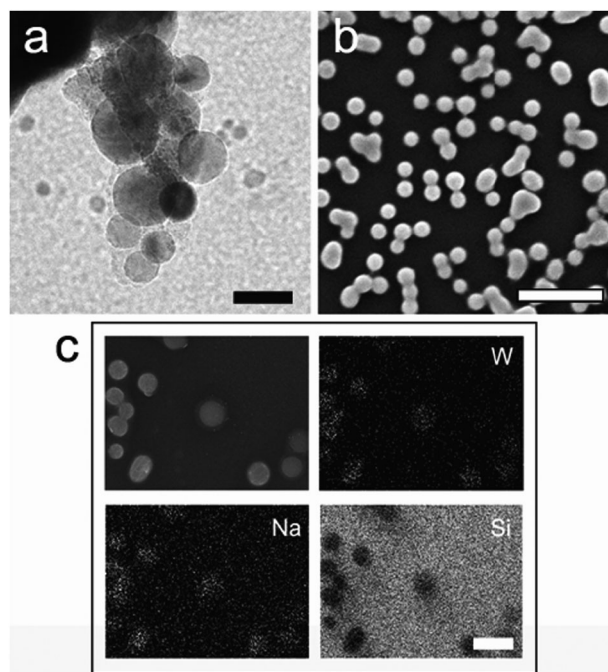


Fig. 3 (a) HR-TEM image of the spherical capsules obtained from a bulk solution of the [GdP₅W₃₀O₁₁₀]¹²⁻ polyanion after 5 days; scale bar 20 nm. (b) SEM image of the capsules obtained on the surface by drop casting a solution of the [ErW₁₀O₃₆]⁹⁻ polyanion and incubation for 5 days under high humidity conditions; scale bar 5 μm. (c) Energy dispersive X-ray spectroscopy (EDS) obtained for the [ErW₁₀O₃₆]⁹⁻ drop-casted sample; scale bar 2 μm.

Once the formation of these nanostructures was shown to take place in bulk, the next step was to confirm their formation on a drop-casted surface. For this, crystals of both compounds were first dissolved in Milli-Q water at 50 °C to give 0.5 mg mL⁻¹ solutions. The homogeneous solutions were then filtered and initially deposited on the Si/SiO_x surface by drop casting. Rapidly, the substrate was placed in an air-tight chamber that was saturated with water vapours at room temperature, and incubated without any disturbance for 5 days to favour the formation of the hollow spherical nanostructures. After incubation, bulk supramolecular nanostructures of POMs are consistently formed (Fig. 3b and 3c). Relatively mono-dispersed nanostructures with sizes varying from 700 nm to 1 μm were observed along the majority of the drop-casted sample, as confirmed by FE-SEM (Fig. 3b). By contrast, samples studied right after its deposition showed the formation of an amorphous material, confirming the relevance of the incubation time.

Finally, the hollow capsules were grown in localized DPN droplets. For this purpose, a 30 mg mL⁻¹ solution of [ErW₁₀O₃₆]⁹⁻ in Milli-Q water was prepared and filtered right before its use as ink for the AFM tip. Then, the coated tip was brought into contact with the Si/SiO_x surface to fabricate the POM-based arrays. All DPN patterns were fabricated at room temperature and a constant humidity of 60%, in order to avoid fast evaporation of the ink solution during the fabrication process. Nice arrays consisting of droplets of the [ErW₁₀O₃₆]⁹⁻ solution were formed before the incubation process and studied by FE-SEM (Fig. 4a). At this point, no presence of

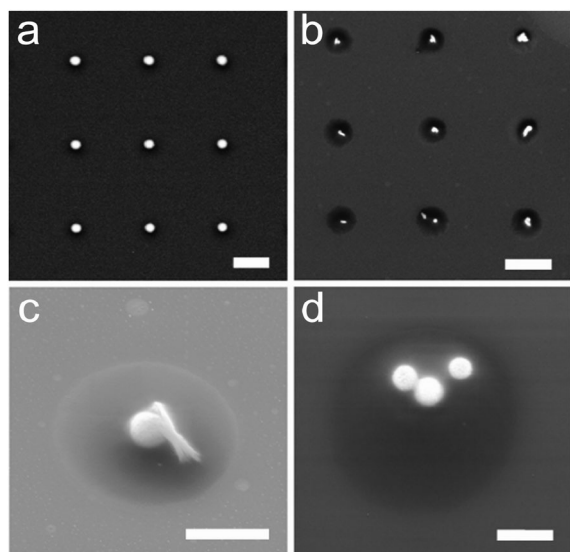


Fig. 4 FE-SEM images of POM-based arrays assisted by DPN. (a) Original array immediately after its formation and before the incubation process; scale bar 2 μm . (b) Well-defined POM capsules obtained in each dot after incubation for 5 days; scale bar 2 μm . Details of the spherical nanostructures grown inside each dot-like feature viewed at a 45° tilt angle (c) and from above (d); scale bars 1 μm .

spherical capsules was detected. When the same arrays were subjected to the incubation process for 5 days, water evaporates in a controlled manner leading to the formation of hollow capsules (Fig. 4b). Magnification of these dots showed the growth of the capsules more clearly with well-defined diameters ranging from 300 to 500 nm (Fig. 4c and d).

The evaporation rate of the solvent and spatial confinement also appear to significantly influence the POM self-assembly. For instance, when the samples are prepared by incubating solution droplets already deposited on the surfaces, sizes may vary from 700–1000 nm and from 300–500 nm, for droplets obtained by the drop-casting methodology and DPN, respectively.

In summary, DPN allowed us to fabricate molecular-based coordination nanoarchitectures using tip-induced droplets as reactor vessels. Since this is a direct deposition technique, such nanoarchitectures can be formed at will on a given surface position, almost on any surface of interest, without the need of a previous surface functionalization. Moreover, by controlling the tip–substrate contact time, we can have control over the dot size¹² allowing the obtaining of nanoarchitectures ranging well within the nanometric regime. Interestingly, these results can be extrapolated to any other coordination material opening a wide range of structures and applications to be studied. Among such studies, main efforts to simultaneously control the density, pattern of nucleation, sizes and orientations of the growing nanostructures must be made.

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