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Multiscale Structuring of Materials - A Hybrid Additive, Subtractive and Directed Assembly Approach

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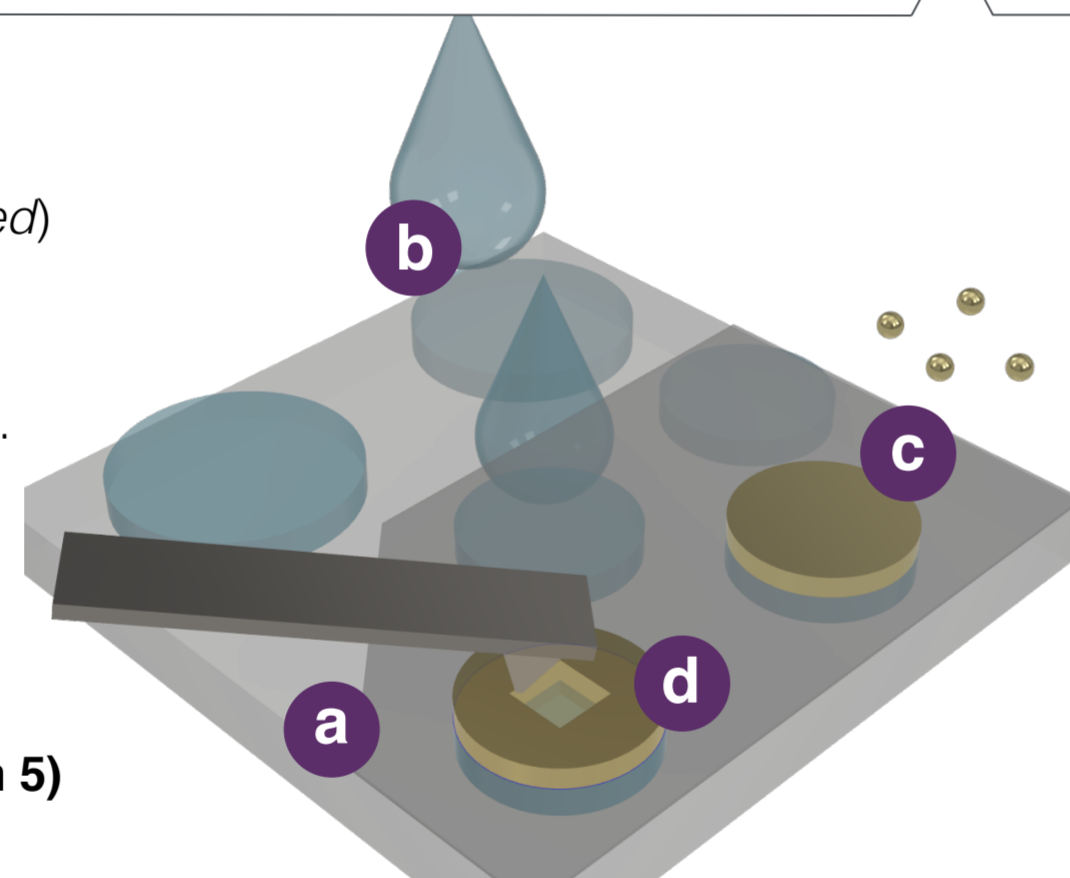
1. Introduction

Inkjet printing falls into an expanding class of rapid fabrication and additive manufacturing technologies [1] where novel advanced and functional materials can be rapidly formed into functional structures and devices [2]. For instance IJP technology is utilised in macro-scale additive manufacturing to carry out the selective build-up of complex 3D structures [3]. Often however, the process is limited by achievable resolution. The work presented explores inkjet printing of a cationic polyelectrolyte onto treated surfaces to increase process resolution. The polyelectrolyte droplets act as a template to direct the assembly of charged gold nanoparticles to the surface. The sharp tip of an Atomic Force Microscope (AFM) is then used to define smaller features within the nanocomposite structures. The work presents a novel combination of additive, subtractive and directed-assembly methodologies to create structured nanocomposite films as a potential route for the rapid evolution of functional surfaces and biological assays based on hierarchically structured films of new materials.

2. Methodology

Four key process steps were undertaken;

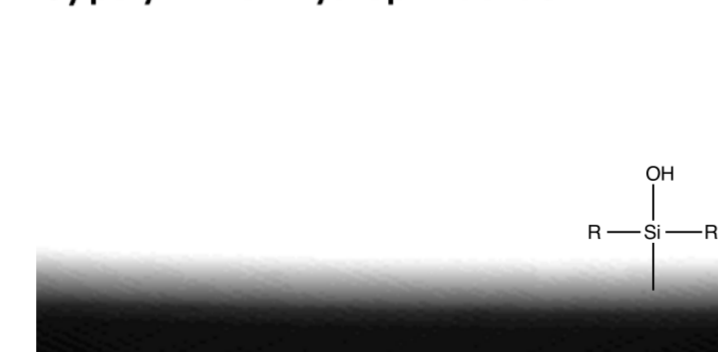
- Glass surface preparation to yield hydrophilic (*cleaned glass*) and hydrophobic (*CF₃ silane coated*) surfaces. (Section 3)
- Inkjet printing of cationic polyelectrolyte poly(diallyldimethylammonium chloride) (*polyDDA*). (Section 4)
- Directed assembly of negatively charged gold nanoparticles to polyDDA regions. (Section 4)
- Scratching of polyelectrolyte/nanoparticle regions using (AFM) to yield micro-scale features. (Section 5)



3. Surface Treatment

- On a consumer inkjet system, modification of the droplet size is difficult, however surface modification of substrates to control droplet spreading can be carried out.
- Immersion in a solution of trifluoropropylsilane (TFPS) for 2 h was used to render glass slides hydrophobic. After the TFPS deposition process, spectroscopic ellipsometry confirmed the presence of a 7.4 nm film on the surface of a section of silicon wafer.
- The static contact angle of a 2 μL droplet of a NaCl solution of polyDDA on a hydrophilic glass microscope slide and on a TFPS terminated, hydrophobic glass slide was observed, as expected, to be higher (~80°) on the TFPS surfaces compared to the untreated surface (<5°).

a) polyDDA on Hydrophilic Slide



b) polyDDA on Hydrophobic Slide

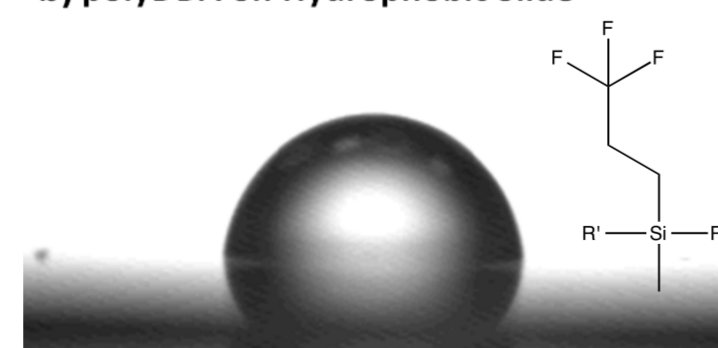


Fig 1 (right). Digital photographs (with inset structures of underlying surface chemistry) showing the contact angle of a polyDDA solution droplet on (a) a hydrophilic glass substrate and (b) a hydrophobised (CF₃ terminated) glass substrate.

4. Inkjet Printing and Directed Assembly

- Inkjet printing was carried out by cleaning and refilling the yellow print cartridge of a Canon IP5300 printer with the polyDDA solution. Varying the amount of polyDDA deposited per unit area was achieved by printing 4 shades of yellow, termed 1Y, 2Y, 3Y and 4Y with 1Y referring to the least amount of material deposited per unit area.
- In order to further derivatise the polyDDA regions printed on the glass surfaces, the resultant substrates were immersed in a colloidal suspension of citrate-stabilised Au nanoparticles with an approximate diameter of 20 + 5 nm (Au-NP) at pH 4.5.
- Features were analysed using optical microscopy and interferometry. For the lowest print density (1Y), individual island domains were formed on both the hydrophilic and hydrophobised glass surfaces, however a difference in lateral size of the islands was observed between the two substrates (Fig 2 and Fig 3a and b). For the hydrophobised surfaces at 2Y, there were a greater number of individual domains but a reduction in droplet coalescence (Fig 3c and d). For the 3Y density, the hydrophilic glass surface exhibited nearly full film coverage. The hydrophobised surfaces at this print density begin to show some droplet coalescence (Fig 2e and f). At the highest print density (4Y), the hydrophilic glass surfaces exhibit full film coverage. The hydrophobised surfaces again exhibit increased coalescence (Fig 3g and h).
- Features printed on hydrophilic and hydrophobised surfaces exhibited a range of thicknesses, typically in the range 30–60 nm.

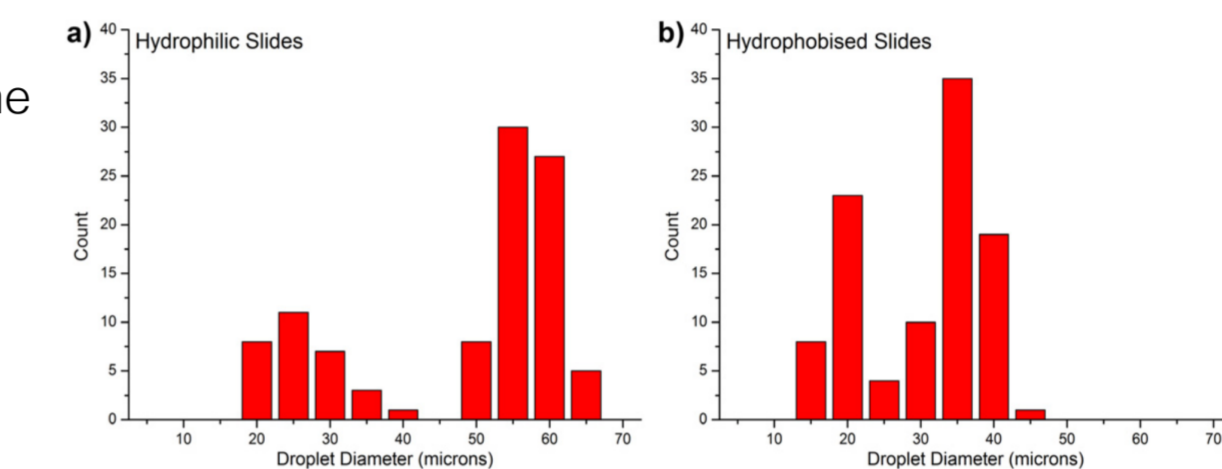


Fig 2 (above). Lateral size distributions of 1Y printed features on (a) hydrophilic glass and (b) hydrophobised glass, after immersion in Au-NP solution.

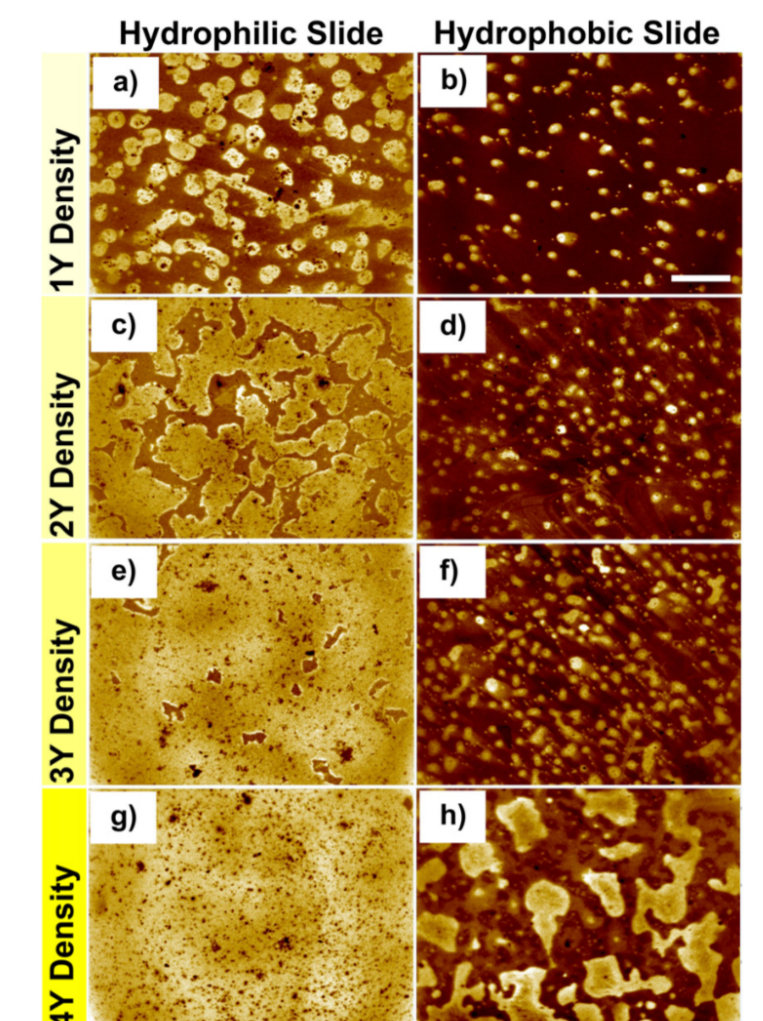


Fig 3 (above). Resultant interferometry images of the hydrophilic and hydrophobised glass substrates after printing and immersion in Au-NPs. Scale bar = 0.25 mm.

5. Atomic Force Microscopy Scratching

- AFM scratching was investigated as a route for creating well-defined structures within the inkjet templated features. To carry out this process, 25 μm × 25 μm square AFM images were scanned at compressive loads of 0.65, 1.30, 1.95 and 2.60 μN (corresponding to tip deflections of -0.25 V, -0.5 V, -0.75 V and -1.0 V respectively). The durability of a polyDDA/Au-NP film printed at 4Y density was tested (Fig 4a).
- Compressive loads of 1.95 and 2.60 μN gave rise to the most complete material displacement. Loads in the μN range agree with those observed previously for scratching-based removal of soft materials from hard substrates [4].
- The scratched regions show a build-up of material in the top right hand corner and down the right hand side of the square features (Fig 4b).
- After determination of the force required to carry out the removal of material, the circular droplet features printed at 1Y density on hydrophilic (Fig 5a and b) and hydrophobic (Fig 5c) surfaces and immersed in Au-NPs, were subjected to AFM imaging at a load of 1.95 μN. After the scratching process, the droplets were imaged with the camera system of the AFM (Fig 5d and e). As expected, the removal of material with the AFM tip had been replicated in the centre of the droplets, showing that it was possible to further modify fabricated features after IJP. The image recorded by the AFM during the scratching process is presented inset in Fig 5d and shows the build-up of material towards the side of the scratched area.
- Beyond simple squares, it was possible to create other features without the use of a dedicated lithography interface, by simply manipulating scan direction, aspect ratio and position Fig 5f.

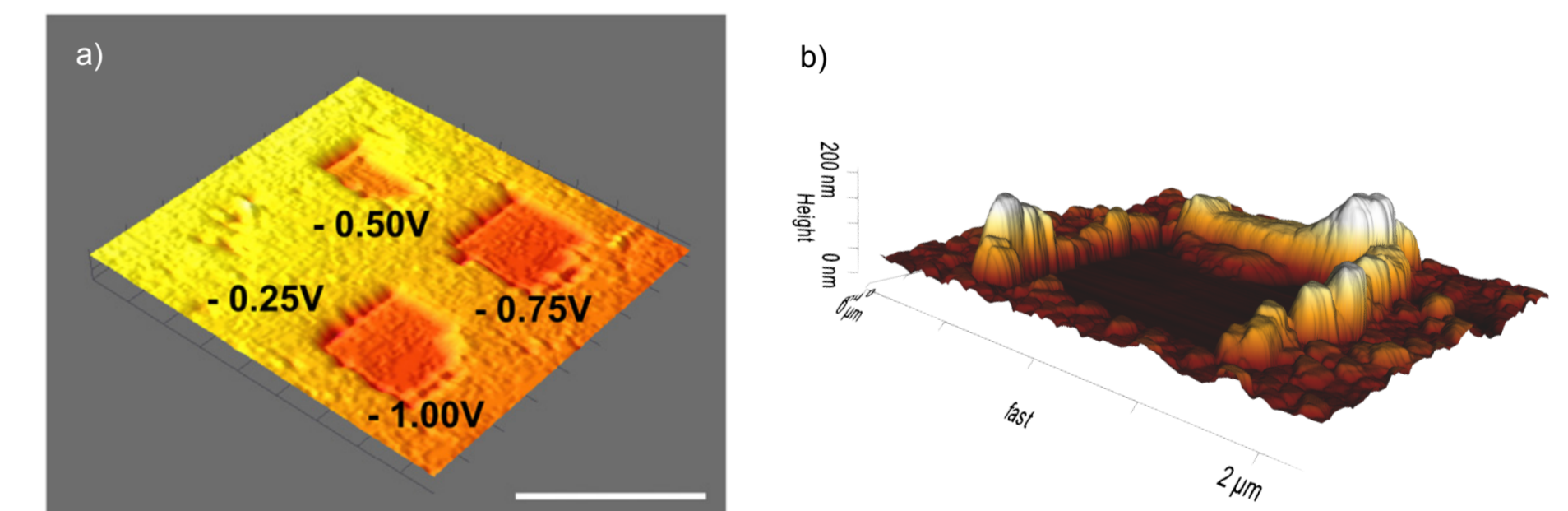


Fig 4 (above). 3D rendered optical microscopy image of 4Y printed film after imaging 4 regions under increasing loads with AFM. Scale bar = 50 μm (a) and representative AFM image of film after scratching process (b).

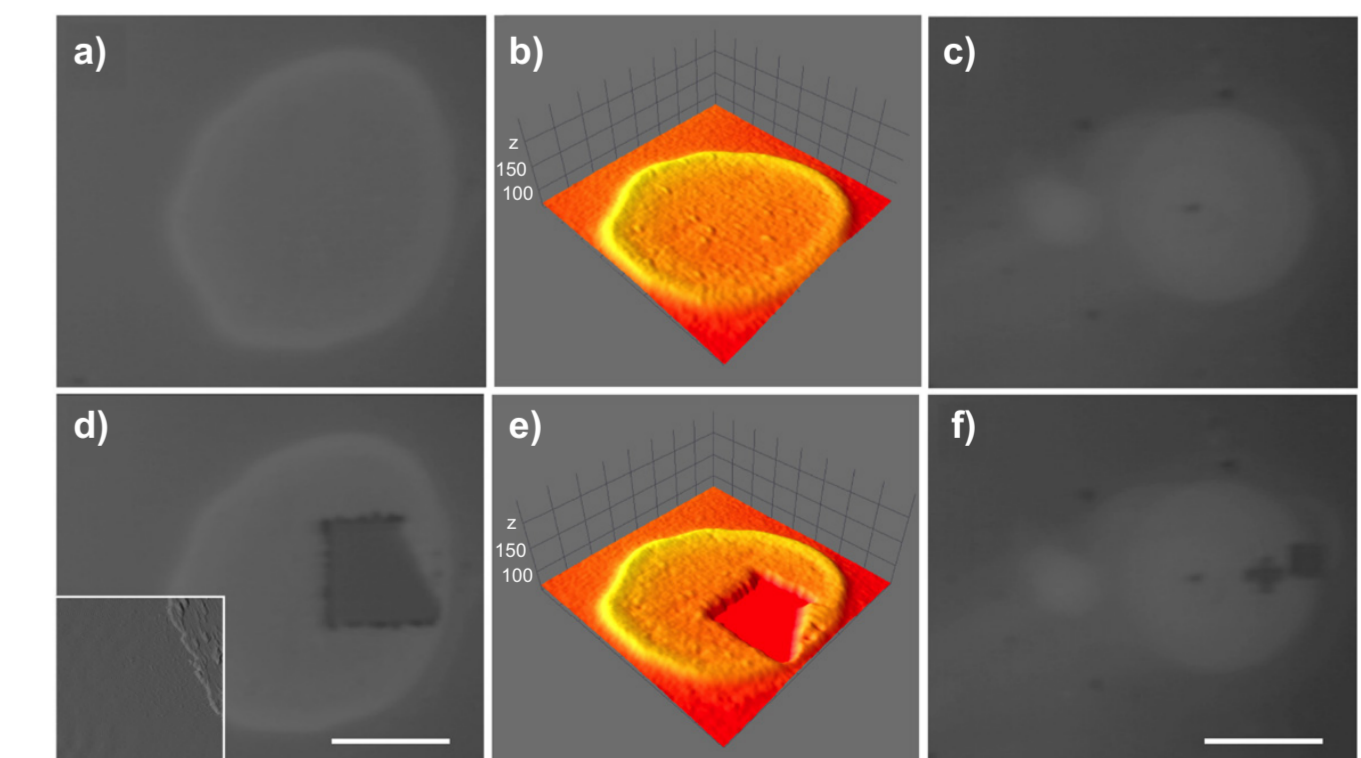


Fig 5 (above). Optical microscopy images of a printed and immersed feature on (a) and (b) hydrophilic glass, (c) hydrophobised glass before, during (d, inset) and after scratching under increased load, (e) and (f). Scale bars = 20 μm.

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