

Research Article

Novel Patterning of Silicon-Substituted Hydroxyapatite

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Abstract Template-assisted electrohydrodynamic atomisation (TAEA) spraying of nanometer-sized silicon-substituted hydroxyapatite (nanoSiHA) was used to pattern implant surfaces for guided cell growth to improve the repair and regeneration of medical implants. A suspension of nanoSiHA was prepared and characterized. Patterns of pillars and tracks of various dimensions were prepared using the suspension. It was found that the resolution of the pattern was affected by TAEA processing parameters, such as applied voltage, flow rate, distance between needle and substrate, and spray time. Fifteen minutes spraying time provided the most clear and uniform patterned topography with a distance between nozzle and substrate of 50 mm and a flow rate of 4 $\mu\text{l}/\text{min}$. Therefore, well-defined nanoSiHA patterns can be achieved by TAEA deposition, it thus offers great potential for patterning the surface of medical implants.

Keywords surface topography; silicon-substituted hydroxyapatite; template; pattern; electrohydrodynamic atomization

1 Introduction

The osteoconductive and osseointegrative nature of hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, has made it a popular coating material for metallic orthopaedic implants for over two decades [3]. Carlisle demonstrated that silicon is an essential mineral for growth and skeletal development as chicks raised with a Si-deficient diet were significantly under developed, with diminished weight gain, cartilage, and bone development [7]. Silicon has also been found to promote the synthesis of collagen type 1, which constitutes 90% of extracellular matrix and enhance osteoblast differentiation [4] as well as preventing poor host bone metabolism in defect repair [1]. More recently, it has been demonstrated that the *in vivo* bioactivity of HA was significantly improved with the incorporation of silicate into

the HA structure, making silicon-substituted hydroxyapatite (SiHA) an attractive alternative to conventional HA in bone replacement [1,8]. The next task is to direct or guide cell attachment in a controlled way to further improve bone tissue integration and regeneration.

Topography has been found to provide a powerful set of signals for cells [2], inferring enhanced adhesion, accelerated cell movement, and orientation. Controlling cell direction, orientation, and proliferation rates is of paramount importance as it enables not only decreasing implant fixation time but also designating cells to be grown more in one area, so the fixation is stronger in desired areas. Therefore, in order to achieve more rapid bone apposition, patterning of the implant surface with highly bioactive nanoSiHA is the sensible approach to achieve a desired surface topography for “contact guidance”. In this study, nano-sized SiHA (nanoSiHA) was synthesized and deposited in a well-controlled manner with an aim of modifying the implant surface to guide and improve bone integration.

2 Materials and methods

Nano-sized HA and 1 wt% SiHA were synthesized based on the reaction between calcium hydroxide and orthophosphoric acid, where tetraethoxysilane was used for the incorporation of Si. Template-assisted electrohydrodynamic atomisation (TAEA) spraying deposition [5,6] was used for surface patterning of nanoSiHA. The TAEA process setup is shown in Figure 1(a). Freshly prepared nanoSiHA suspension was syringed to the needle at a controlled flow rate up to 25 $\mu\text{L}/\text{min}$, the applied voltage between the nozzle and substrate (ground electrode) was varied (up to 6 kV) to obtain stable cone-jet mode patterning. A high speed camera was connected to monitor the jet. Copper templates with different shapes and dimensions were placed on the substrate silicon surface. The distances between the substrates and nozzle were varied from 10 to 60 mm, spraying time was varied between 5 to 20 minutes.

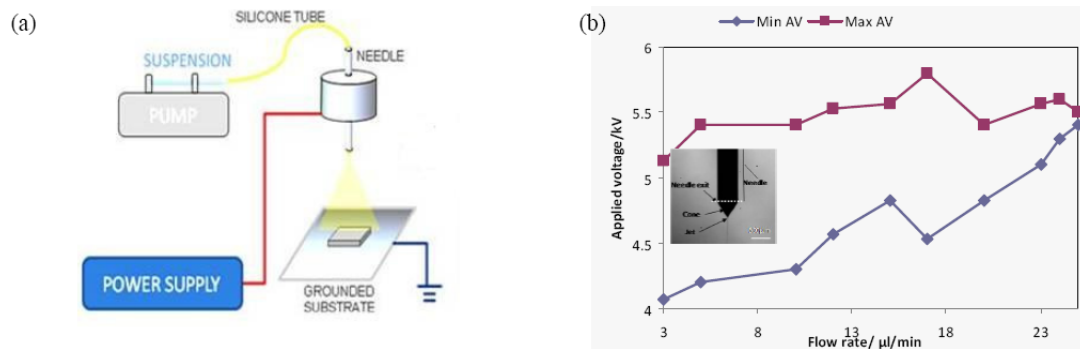


Figure 1: (a) Schematic diagram illustrating the TAEA patterning set up and (b) the relationship between the applied voltage (between the nozzle and substrate) and flow rate of nanoSiHA suspension, insert is an example of the stable cone-jet mode.

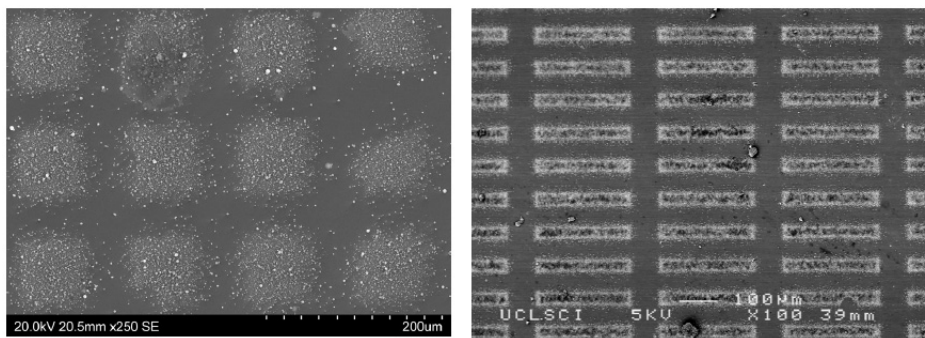


Figure 2: Scanning electron micrographs of nanoSiHA patterns on silicon.

3 Results and discussion

The phase purity of nanoHA and nanoSiHA was confirmed by XRD analysis. NanoSiHA suspension was then subjected to TAEA. A strong electric field is built up at the capillary nozzle, where the liquid forms a meniscus. This meniscus elongates in the electric field and beaks up into droplets in various modes. Cone-jet mode provides smooth and regular spraying. A stable cone-jet mode can be achieved under various processing conditions, as shown in Figure 1(b), thus, enabling even spray deposition to occur.

The stable cone-jet mode was maintained over the largest range of applied voltage, when the flow rate was up to $17 \mu\text{L}/\text{min}^{-1}$ for nanoSiHA, slightly lower than that of HA ($20 \mu\text{L}/\text{min}^{-1}$). Within this optimized range, well-defined nanoSiHA patterns were successfully achieved (Figure 2).

The resolution of the patterned nanoSiHA was related to the processing parameters. The flow rates employed above $7.5 \mu\text{L}/\text{min}$ were ineffective in producing clear patterning. This is supported by other studies [9]. The droplet (and relics) size decreased with decreasing flow rate, thus allowing slow patterning and height generation and a reduction in scattering. The scattering was significantly reduced when the flow rate decreased from $10 \mu\text{L}/\text{min}^{-1}$ to $4 \mu\text{L}/\text{min}^{-1}$.

The size of width and window of templates and the corresponding pattern dimensions were measured by image analysis. The correlation between the pattern and template to flow rate is shown in Figure 3. Lowering the flow rate to $4 \mu\text{L}/\text{min}^{-1}$ provides a linear relationship between template and pattern dimension as well as the coverage of template. A flow rate of $4 \mu\text{L}/\text{min}^{-1}$ provided 80% coverage of template area, whereas 5 and $6 \mu\text{L}/\text{min}^{-1}$ covered 67% and 62% coverage, respectively.

The resolution of nanoSiHA patterns was also affected by the spray time. The optimized spraying time was 15 minutes, as scattering was observed when spray time was over 20 minutes. Fifteen minutes provide an adequate amount of time for particles to form the pattern of the template on to the substrate, the structure was incomplete below this time period.

Increasing the distance of the nozzle to the substrate resulted in the decrease of the intensity of SiHA spray deposition on the substrate. The distance which allowed for the most significant build up was 50 mm (Figure 5). Clear pattern topography was not established with a substrate distance below 30 mm. The distance of 40 mm could be utilized when low density pattern topography on the substrate is required. The patterning was ineffective when the distance was over 60 mm due to severe scattering.

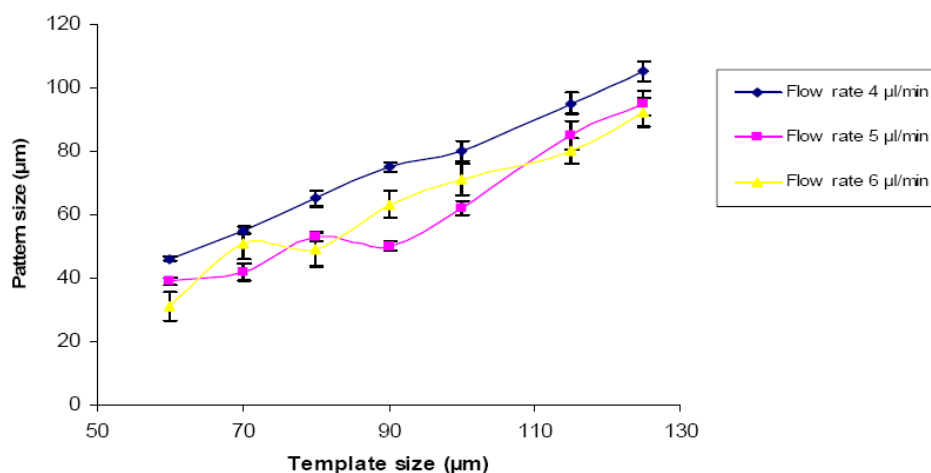


Figure 3: The relationship between template and actual pattern dimensions with varying flow rates.

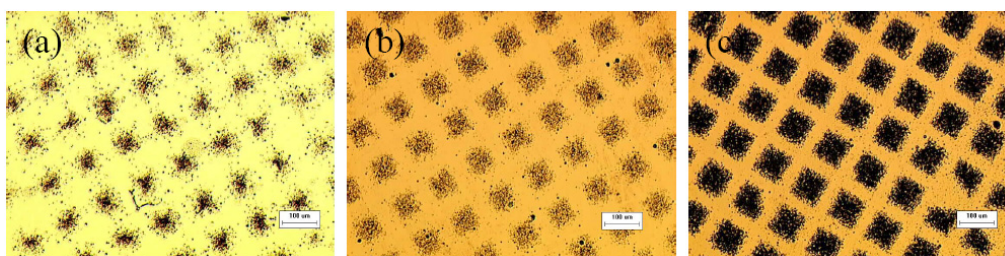


Figure 4: Optical micrographs for nanoSiHA pillars for varying spray time sets at (a) 5 minutes, (b) 10 minutes, and (c) 15 minutes.

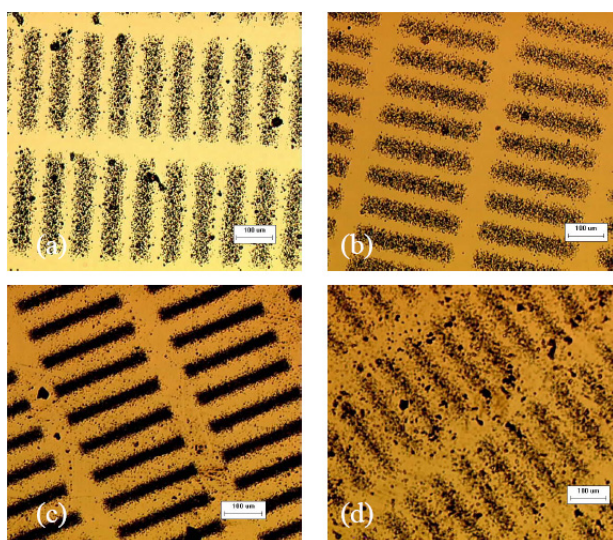


Figure 5: Optical micrographs for the track pattern obtained by varying distances between needle and substrate of (a) 30 mm, (b) 40 mm, and (c) 50 mm (d) 60 mm.

4 Conclusions

Nano-sized silicon-substituted HA has been synthesized and subjected to TAEA patterning. The resolutions of nanoSiHA patterns have been improved by controlling parameters of

the TAEA process, such as the flow rate, spray time, and distance between needle and substrate. Reducing the flow rate to $4 \mu\text{Lmin}^{-1}$ increased the template coverage with 50 mm being the optimum distance between the nozzle and substrate. Spray time of 15 minutes resulting in clear and even pattern formation (Figure 4). Therefore, well-defined nanoSiHA patterns can be achieved by TAEA patterning, it, thus, offers a great potential for patterning the surface of medical implants to enable desired biological responses.

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