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DEVELOPMENT OF DIRECT INK WRITING TECHNOLOGY FOR MICRO-STRUCTURES

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Abstract. Titania sol-gel ink was synthesized for the fabrication of fine structures using direct ink writing technology. Planar micro-structures such as micro-patterned lines were created using the sol-gel ink with uniform feature sizes and more complex structures such as foil bearing were also fabricated by precise motion control of three-axis robocaster and fine dispensing nozzle. The titania sol-gel ink was characterized using thermogravimetric analysis (TGA) and the micro-structures generated by direct ink writing technology was observed using scanning electron microscopy (SEM) and optical vision system to confirm that the CAD design of complex morphologies was successfully replicated into the real microstructures using the robocasting equipment.

1. INTRODUCTION

Direct ink writing technology has attracted much attention for the creation of functional micro-structures such as planar electrodes, photonic crystals, filters, scaffolds for tissue engineering, and self-healing systems [1-5]. This technology has been used for the design and fabrication of functional materials with arbitrary shapes. Expensive tooling, dies, or lithographic masks are not required for the shaping process by direct ink writing system, thus enabling the generation of tailed micro-structures with various ink materials.

For direct ink writing process, three kinds of inks such as nanoparticle inks, polyelectrolyte inks, and sol-gel inks have been widely utilized to fabricate functional complex micro-structures [1,2,5]. Though these three types of inks possess advantageous features, sol-gel inks can be adopted the writing technique since it is easy to handle and synthesize with various precursor materials.

In this study, we have developed direct ink writing apparatus for the fabrication of planar micro-structures with fine feature sizes using titania sol-gel ink. More complicated planar structures such as foil bearing were also generated using 3-D robocaster attached with dispensing nozzle for fine motion control of the micro-tips with the aid of CAD (computer aided design) data for shaping desired structures.

2. EXPERIMENTAL

Titania sol-gel ink was synthesized by mixing 0.62 g of binding material, polyvinyl-pyrrolidone (PVP, M_w = 55,000, Sigma-Aldrich) in 8 ml of ethanol and 6.25 g of titanium diisopropoxide bis(acetylacetonate) (TIP, 75% in 2-propanol, Sigma-Aldrich) using magnetic stirring bar. 8 ml of ethanol, 0.565 ml of distilled water, and 2.02 ml of ammonium hydroxide (28%, Aldrich) were added into the TIP and PVP mixture in ethanol, followed by the aging at 80 °C for 14 hours. The aged ink was concentrated by the

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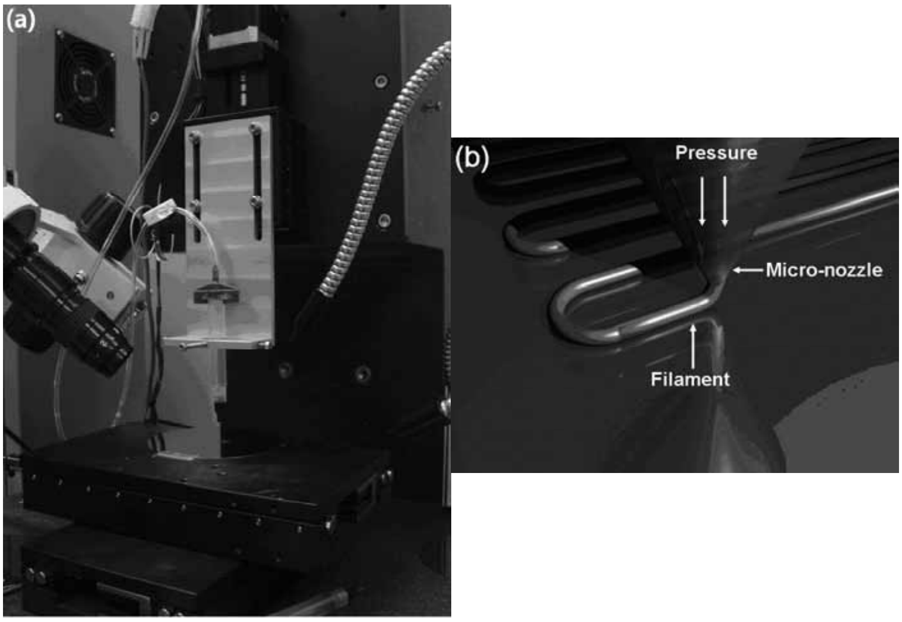


Fig. 1. (a) Experimental set-up for the direct ink writing process. (b) Schematic figure for the direct ink writing of nano-ink for microstructures on suitable substrate.

evaporation of solvent drying at room temperature for one week before the direct ink writing process. The sol-gel ink was characterized by using thermogravimetric analysis (TGA, SDT2960, TA Instruments).

The titania sol-gel ink was applied for the direct ink writing process with the combined system of 3-axis robocaster (ALS130XY-100, ALS130Z, Aerotech Inc.) for the precise motion control and dispensing system (Ultimus^{TM}, EFD Inc.). The titania sol-gel ink was housed in a 3 ml barrel (EFD inc.) and the ink was dispensed from the commercial nozzle (100 mm in inner diameter, EFD inc.) attached with the barrel. For more fine writing lines, borosilicate glass micro-nozzle was also fabricated using laser based micropipette puller (P-2000, Sutter Instrument Co.) for use. The CAD data of foil bearing was transformed into g-code for the automated motion control of the robocaster with the aid of commercial software (A3200, Aerotech).

3. RESULTS AND DISCUSSIONS

Fig. 1a contains the photograph of the experimental set-up for the direct ink writing process composed of 3-axis robocaster, dispenser with dispensing nozzle, illuminator, and optical vision system for the observation of writing process on a substrate. By precise control of *x*, *y*, and *z*-axis using robocaster, any special morphologies can be deposited on a suitable substrates using computer aided design (CAD). CAD data can be transformed into g-codes to control the precise motion of the robocaster, and adequate pressure can be applied to the dispensing nozzle during the writing process. Through this approach, the ink filaments can be deposited with special shapes to create micro-structures with desirable materials, as shown in the schematic figure in Fig. 1b. Since the solid loading and viscosity are higher than those of conventional ink-jet inks, the ink materials like pastes can be deposited onto the substrate following the motion of the dispensing tip attached to the 3-axis stages of the robocaster, as depicted in Fig. 1b [6].

In this study, we have adopted the titania sol-gel ink to fabricate the microstructures with special morphologies such as line patterns and foil bearings. During the concentration step of the so-gel ink, the color of the ink turned to deep purple and the viscosity was increased, as shown in the photograph of Fig. 2a. Slow evaporation and hydrolysis of the ink materials resulted in the generation of adequate solid loading during the aging process for the direct ink writing process [7]. The weight loss of the ink was confirmed by thermogravimetric analysis (TGA), and 21% of solid was maintained by heating at temperature higher than around 580 °C under air atmosphere, as shown in the TGA result of Fig. 2b. Since the ink materials in this study are composed of titania sol-gel precursors, the possible volume shrinkage at high temperatures over 580 °C

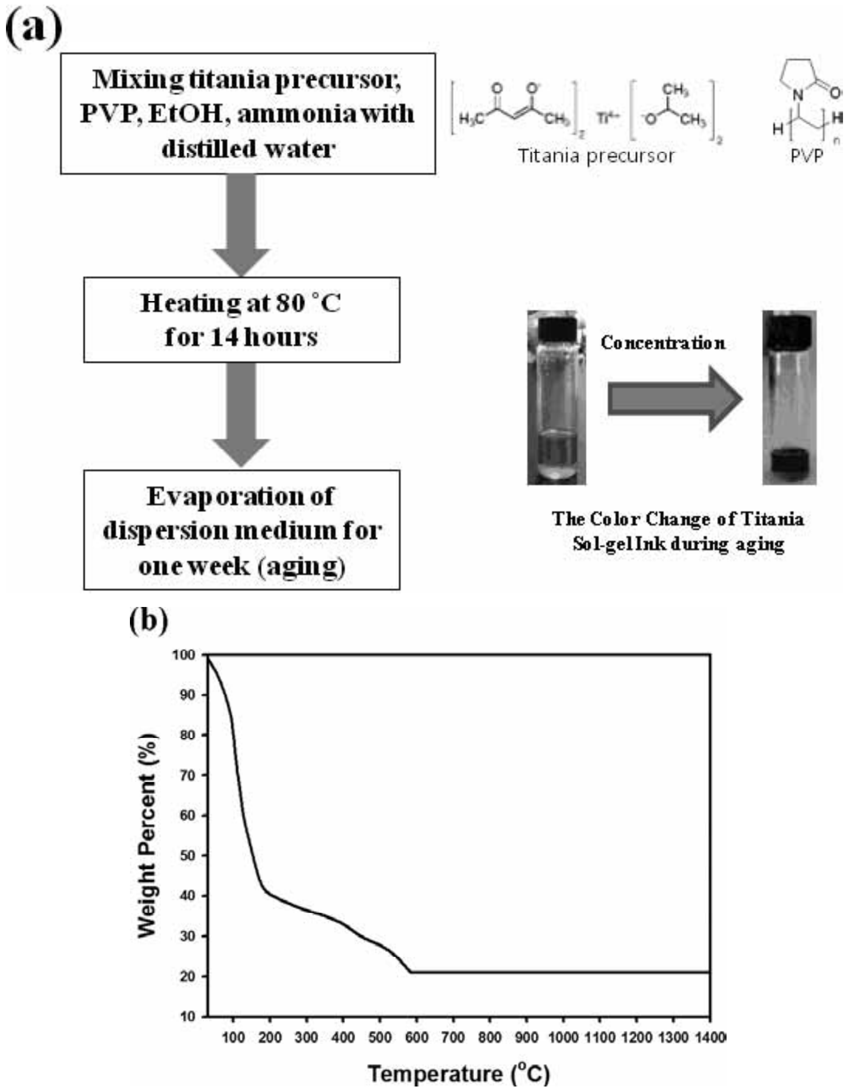


Fig. 2. (a) Work flow chart for the fabrication of titania sol-gel ink using the main component of titania sol-gel ink, titanium diisopropoxide bis(acetylacetonate) and the color change of resultant titania sol-gel ink. (b) thermogravimetric analysis (TGA) result of titania sol-gel ink.

can be anticipated if the high temperature calcinations process will be employed [7].

To test the writability of the titania sol-gel ink, some line patterns were fabricated using the sol-gel ink by direct ink writing process. The motion of the robocaster was controlled with the speed of 1 mm/sec and the dispenser was operated at the pressure of 3 to 4 psi. Fig. 3a contains the optical microscope image of the line pattern of the ink and dispensing tip with 100 μm in inner diameter during the writing process, and Fig. 3b displays the scanning electron microscope (SEM) image of the same pattern. Since the distance between dispensing tip and substrate, namely *z* is important factor to guarantee good adhesion of printed filament and the substrate, we have employed the optical vision system to observe and adjust the distance *z* as 0.8*d* before direct ink writing process (*d* indicates the inner diameter of the nozzle.) [5].

As displayed in the SEM image of Fig. 3b, the lines on the substrate possess uniform width with about 150 μm, and this pattern width can be reduced using more sharper nozzle such as 30 μm in inner diameter, as shown in the optical microscope image in Fig. 3c. The SEM image of the line pattern fabricated using 30 μm sodium borosilicate tip is also included in Fig. 3d, displaying the uniform line width of about 100 μm. The corner parts of the same line pattern are shown in the SEM image of Fig. 3e, displaying the smooth change of the writing direction according to the CAD data and g-code during the direct ink writing process.

Fig. 4a contains the optical microscope image of the rectangular line pattern generated by direct

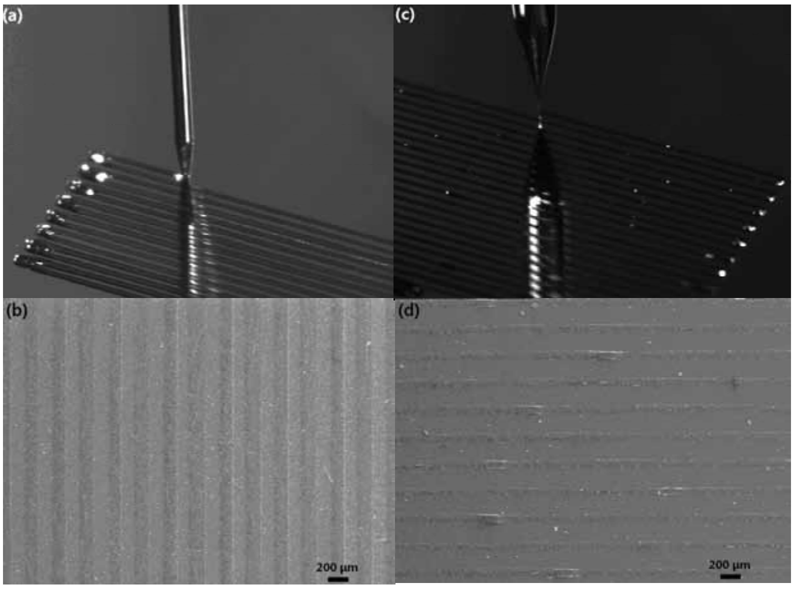


Fig. 3. (a) and (b) Optical and scanning electron microscope (SEM) images of line patterns generated by titania sol-gel ink using dispensing nozzle with 100 μm in inner diameter. (c) to (e) Optical and scanning electron microscope images of line patterns generated by titania sol-gel ink using dispensing nozzle with 30 μm in inner diameter.

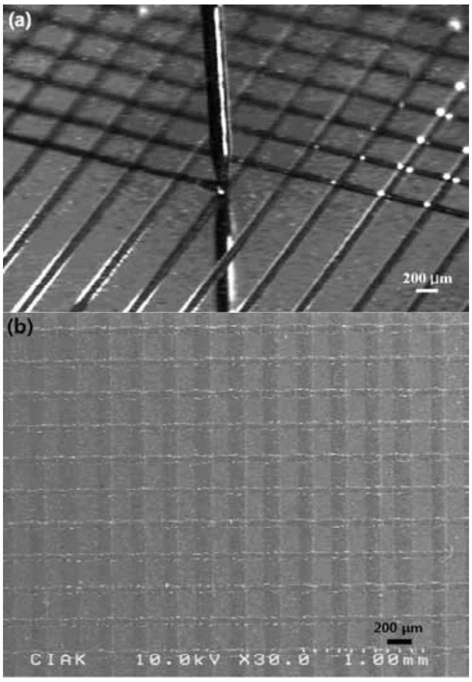
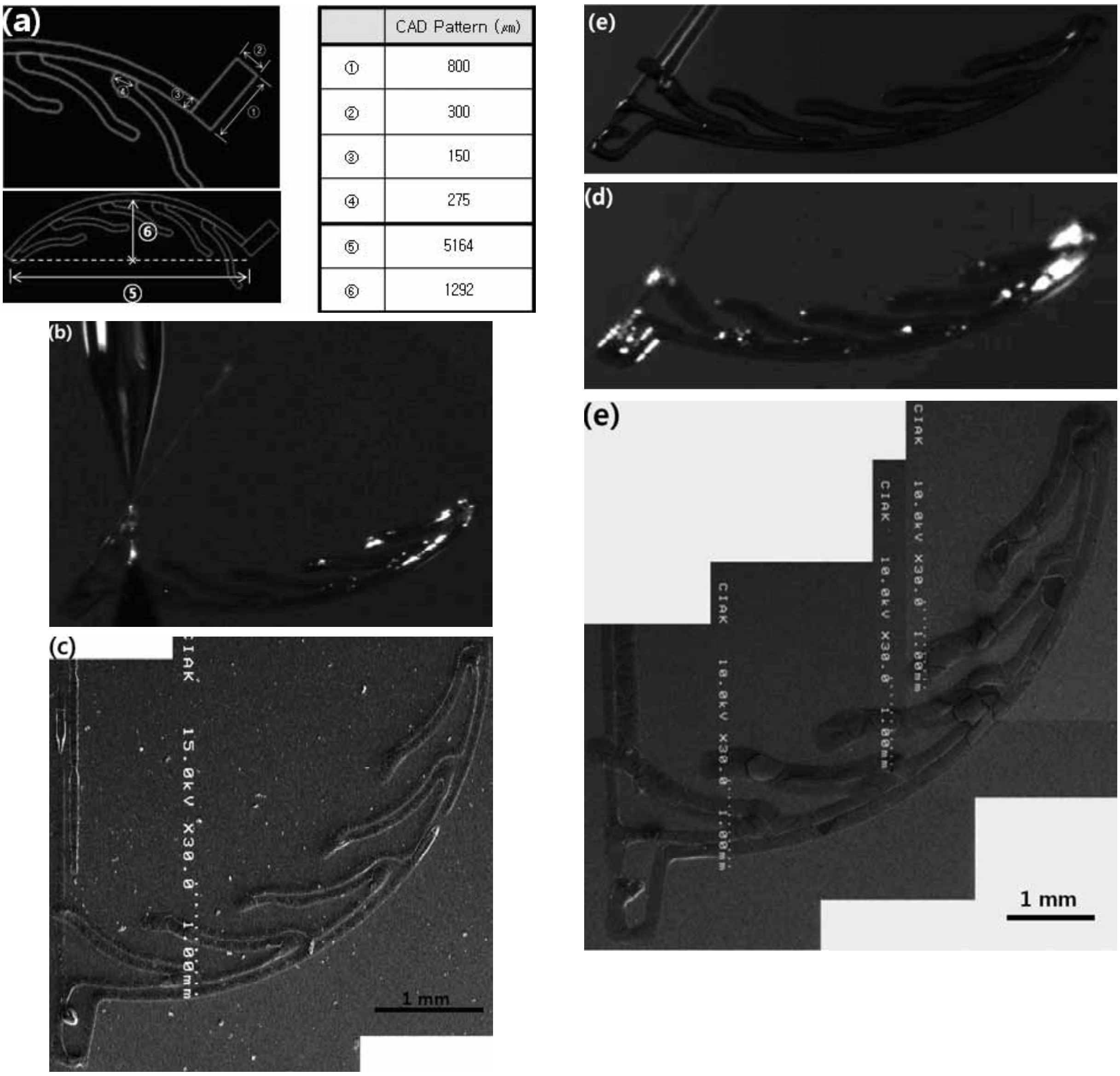


Fig. 4. (a) and (b) Optical and SEM images of rectangular line patterns generated by titania sol-gel ink using dispensing tip with 100 μm in inner diameter. Scanning bars indicate 200 μm.

ink writing process using 100 μm dispensing tip under the operating pressure of 3 to 4 psi and 1 mm/sec of writing speed. After the deposition of the bottom lines, the upper lines were fabricated along the perpendicular direction to the bottom lines. As shown in Fig. 4a, the line patterns with 100 to 150 μm width have been successfully fabricated with uniform inter-pattern distances over large pattern area. Since high pressure can induce the *flooding* of ink material through the nozzle, the mild dispensing pressure such as 3 to 4 psi was maintained during the writing process to create uniform line patterns. The *independent* motion of the x-y stages of the robocaster resulted in the successful generation of the patterned microstructure as shown in Fig. 4a [8]. Fig. 4b displays the SEM image of the same rectangular pattern with well-defined shapes having uniform pattern width and line thickness.

Besides simple line patterns, we have also fabricated more complicated micro-structures using direct ink writing technology. Foil bearing shown in the picture of CAD design in Fig. 5a was chosen as model system for the writing process to assess the writability of the titania sol-gel ink into complex structures. At first, we have tried to use 30 μm tip for the writing process with the writing speed of 1 mm/sec. As displayed in Fig. 5b, the foil bearing was successfully deposited onto silicon wafer, following the CAD data and g-code for the precise motion control of the robocaster. However, the inner part of the foil bearing generated by the writing process was not completely filled with the titania ink materials since the width of the line filament from the dispensing tip was small, as shown in the SEM image of Fig. 5c. Thus, we have replaced the dispensing nozzle with more bigger one, the 100 μm tip, and the resultant structure of the foil bearing is displayed in the opti-



	CAD Pattern (μm)
①	800
②	300
③	150
④	275
⑤	5164
⑥	1292

Fig. 5. (a) The CAD design of foil bearing. (b) and (c) Optical and SEM images of foil bearing fabricated by direct ink writing process using titania sol-gel ink with dispensing tip having 30 μm in inner diameter according to the original CAD design. Scale bar indicates 1 mm. (d) Optical microscope image of foil bearing fabricated by direct ink writing process using titania sol-gel ink with dispensing tip having 100 μm in inner diameter in inner diameter according to the original CAD design. (e) and (f) Optical and SEM images of foil bearing fabricated by direct ink writing process using titania sol-gel ink with dispensing tip having 100 μm in inner diameter. The g-code for the writing process was based on the 1.5 times of the original CAD design. Scale bar indicates 1 mm.

cal microscope image of Fig. 5d. As shown in the Fig. 5d, the inside of the foil bearing is completely filled with ink materials due to the increase of the line width of the deposited structure. Fixing the size of the dispensing nozzle, the CAD data was increased 1.5 times to the original morphologies shown in Fig. 5a, and the resultant foil bearing structure is shown in the optical microscope image in Fig. 5e. Only the edge part with rectangular shape of the foil bearing is not completely filled with the ink materials, and most part of the bearing structure is successfully fabricated as displayed in the SEM image of Fig. 5e. Further researches are under way to reduce the cracks of the deposited micro-structures and increase the height of the foil bearings by repetitive deposition of the ink materials.

4. SUMMARY AND CONCLUSIONS

Titania sol-gel ink was utilized for the direct ink writing process to fabricate micro-structures with complex morphologies. The sol-gel precursors of titania were formulated with polymeric material such as PVP to fabricate the sol-gel ink with adequate properties for dispensing process. The ink was characterized with TGA to assess the thermal stability of the ink, indicating that 21 wt.% of solid material remains at higher temperature over 580 °C. To test the writability of the ink material, the line patterns were fabricated with uniform line widths and more complex morphology such as foil bearing was also generated using direct ink writing technology. The minimal feature size of 100 μm in line width was accomplished using 30 μm borosilicate dispensing tips. The CAD design of the micro-bearing was transformed into suitable g-code for active motion control of the robocasting apparatus to realize the complex micro-structures with titania sol-gel ink. The combination of the precise motion control of the robocaster and the optimization of the writing conditions such as dispensing pressure and writing speed resulted in the successful fabrication and deposition of the ink materials into usable objects, indicating the potential importance of the technology for the generation of micro-structured functional architectures.

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