Printed Origami Structures

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Origami, the traditional paper art, is a folding technique in which elegant and complex three-dimensional (3D) objects are produced from planar sheets.[1] Significant scientific and technological interest in origami assembly methods have emerged due to the recognition that nature utilizes controlled folding and unfolding schemes to produce intricate architectures ranging from proteins[2] to plants.[3] To date, novel folding pathways have been harnessed to fabricate nanoscale DNA-based objects[4,5] as well as nano- and mesoscale structures, such as 3D metallic objects[6–9] and silicon solar cells[10] that are lithographically patterned and spontaneously folded via surface tension effects.[11,12] However, the ability to assemble printed structures of arbitrary 3D form, composition, and functionality with the ease, low cost, and versatility of paper origami has not yet been demonstrated. Here, we combine direct-write assembly[13–15] with a wet-folding origami technique[16] to create 3D shapes that range from simple polyhedrons to intricate origami forms, which are then transformed to metallic and ceramic structures by thermal annealing.

Direct ink writing provides an attractive, non-lithographic approach for meeting the demanding design rules and form factors required for origami-based assembly. In this filament-based printing method, a concentrated ink is extruded through a tapered cylindrical nozzle that is translated using a three-axis (*x*-*y*-*z*), motion-controlled stage (Fig. 1a). Although this method is capable of printing simple planar and 3D structures from myriad materials, including metallic,[17] ceramic,[18] or polymeric inks,[19,20] it is difficult to pattern high aspect ratio structures without deformation (or slumping) and nearly impossible to directly pattern complex structures with large unsupported regions, such as overhanging features. By combining printing and origami methods, we demonstrate a powerful new approach to overcome such limitations.

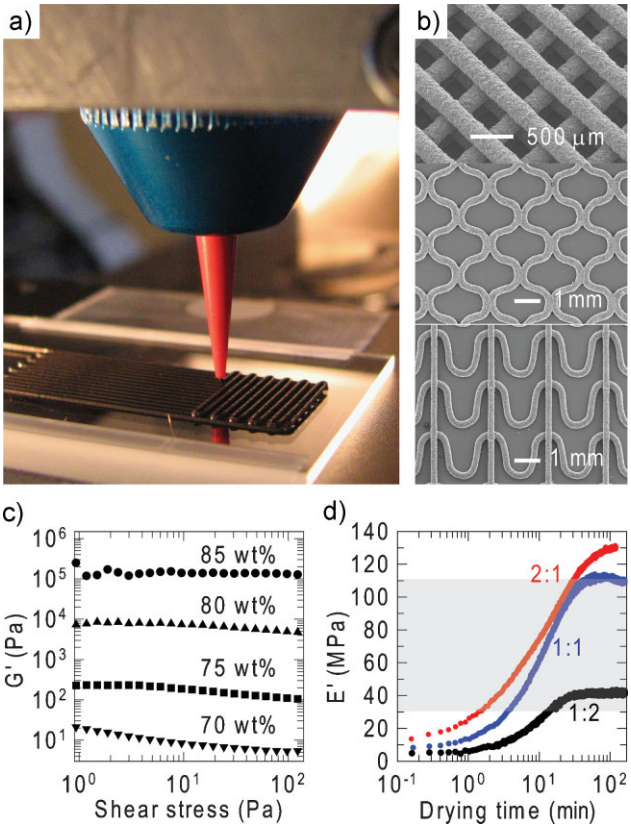

Figure 1. a) Optical image of direct ink writing of a concentrated TiH_2 ink. b) SEM images of printed square lattice and wavy patterns. c) Shear elastic modulus (G') of TiH_2 inks as a function of solids loading. d) Storage modulus (E') of printed filaments of varying 2-butoxyethanol:DBP ratio as a function of drying time, where the shaded region denotes optimal E' values for origami-based assembly.

We first created periodic structures of varying lattice geometry and number of layers by direct-write assembly (Fig. 1b). As one example, we fabricated a 3-layer square lattice (15.4 mm × 12.1 mm) composed of stacked linear arrays of ink filaments (diameter, $D = 235$ μm) aligned with the *x*- or *y*-axis, such that their orientation is orthogonal to the previous layer. The square lattices have a center-to-center spacing that varies between 0.5–3 mm, with a typical value of 0.55 mm (top image in Fig. 1b). We also produced two wavy patterns. The first lattice (1-layer, 11 mm × 17 mm) consists of a planar array of sinusoidal patterned filaments ($D = 258$ μm) with a wavelength (λ) of

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2.2 mm and a height (h) of 0.6 mm with alternating arc centers (middle image in Fig. 1b). The second lattice (2-layers, 15 mm × 17 mm) is constructed by first printing an array of sinusoidal-like filaments ($D = 252\,\mu m$) with $\lambda = 2.2$ mm, $h = 0.9$ mm, and a center-to-center spacing of 1.9 mm. This is followed by the deposition of a linear array of ink filaments with a center-to-center spacing of 2.2 mm (bottom image in Fig. 1b). The total build times required are 12 min (3-layer square lattice), 6 min (1-layer wavy structure), and 8 min (2-layer wavy structure) at a printing speed of 1 mm s^{-1}. Each printed lattice is dried for 10 min under ambient conditions and then removed from the substrate to be folded, twisted, or rolled into the desired 3D form.

To produce printed structures suitable for wet-folding origami, we designed a highly concentrated ink composed of titanium hydride (TiH_2) particles, an acrylate-based triblock copolymer, and a graded volatility solvent system composed of 2-butoxyethanol (b.p. 171 °C) and dibutyl phthalate, DBP (b.p. 340 °C). This colloidal chemistry is chosen because TiH_2 particles can be readily transformed to titanium (Ti), titanium oxide (TiO_2), or other titanium-based phases by controlling the atmosphere in which the structures are annealed.[21–23] The inks are formulated at high solids loading, such that they possess the appropriate viscoelastic response to facilitate patterning of spanning structures (Fig. 1c).[18] In addition, they contain a graded volatility solvent system, whose composition can be precisely tailored to control the storage modulus evolution of the patterned features during drying (Fig. 1d).

Using this new ink design, the initial shear elastic modulus (G') can be varied over a broad range from 10^1 to 10^5 Pa by increasing the total solids loading (TiH_2 + copolymer) from 70 to 85 wt%, respectively (Fig. 1c). The most concentrated ink is capable of spanning gaps as wide as several millimeters at a maximum allowable deflection of $\sim 0.05D$.[14] More importantly, the wet-folding window is governed by the storage modulus (E') of the printed filaments, which can be adjusted by varying the 2-butoxyethanol:DBP ratio. Figure 1d shows the drying time-dependent storage modulus of the printed ink filaments as a function of solvent composition. Immediately after printing, ink filaments composed of 2-butoxyethanol:DBP ratios of 1:2 to 2:1 possess an E' of 4.5 to 13.5 MPa, respectively. Upon drying for 2 hr, these E' values increase to approximately 40–130 MPa. Analogous to wet-folding origami, in which paper is precisely wetted to enhance its pliability, while still retaining sufficient handling strength, we find that the partially dried, printed features must exhibit an $E' \sim 30$–110 MPa to facilitate their folding (or rolling). Their characteristic assembly time can be increased from roughly 30 min to several hours by reducing the 2-butoxyethanol:DBP ratio from 2:1 to 1:1. Under these conditions, the patterned scaffolds can be readily manipulated to create 3D objects of nearly arbitrary shape.

To demonstrate our printed origami approach, we begin by creating simple polyhedral structures. Figure 2a shows a folding scheme for a representative structure, in which a rectangular pattern (2-layer, 15.4 mm × 12.1 mm, filament diameter 250 μm, center-to-center filament spacing of 550 μm) is printed, removed from the substrate, and cut to the desired pre-folding shape. Next, the printed structure is placed on an apparatus consisting of metal sheets (100 μm thick) with bendable polymer hinges that guide the folding process. Each square feature (3 mm × 3 mm) is folded to create a cube, which is dried for 3 h at room temperature. Freestanding origami cubes are obtained upon removal of the structure from the folding apparatus. Finally, the folded edges are bonded together by locally depositing an isopropyl alcohol:xylene solution (7:3 by mass). As shown in Figure 2b, many polyhedral geometries, including a tetrahedron and a square pyramid structure can be produced in a similar manner. Additionally, objects such as the curved hemisphere shown in Fig. 2b can be readily molded. Figure 2c shows SEM images of an as-printed TiH_2 origami cube (left), a cube annealed at 1050 °C for 10 h in vacuum (middle), and one annealed at 1050 °C for 2 h in air (right). During vacuum annealing, decomposition of the hydride particles to metallic titanium followed by their densification, leads to a Ti cube with little distortion despite a volumetric shrinkage of 52% ± 1%. By contrast, densification and oxidation occur simultaneously when annealed in air, resulting in a TiO_2 cube with a net volumetric expansion of 7.5% ± 0.6%.

Next, we demonstrate the assembly of high aspect ratio, cylindrical coils using a rolling scheme shown in Figure 3a. First, a printed 2-layer rectangular pattern (3 cm × 2 cm, filament

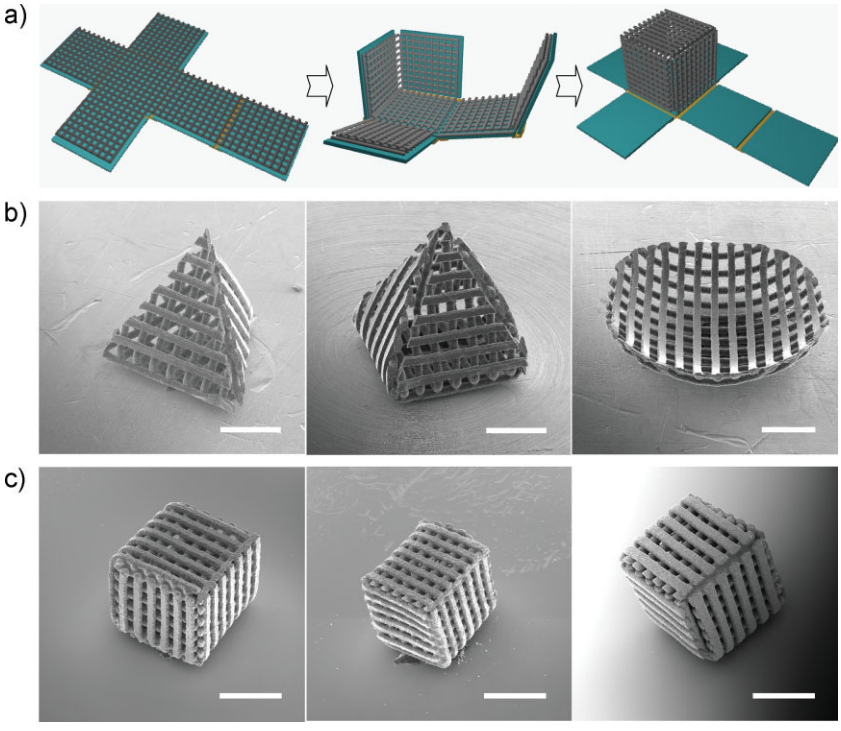

Figure 2. a) Schematic illustration of folding procedure for an origami cube. b) SEM images of a printed origami TiH_2 tetrahedron (left) and square pyramid (middle) as well as a printed and molded TiH_2 hemisphere (right). c) SEM images of a printed origami cube before (left, TiH_2) and after annealing in a vacuum (middle, Ti) or air (right, TiO_2) at 1050 °C. Scale bar = 2 mm.

diameter 250 μm, center-to-center filament spacing of 0.7 mm) is printed and then placed on a rolling apparatus. Upon rolling, a concentric cylindrical coil is produced, either without or with a central titanium tubular insert (Fig. 3b, top left and middle). In a similar manner, spirally coiled helices, stents, and hollow cylindrical structures are readily produced by rolling planar patterns onto an alumina tube, which is subsequently removed upon drying (Fig. 3b, top right and bottom row).

To further demonstrate the versatility of our approach, we create a TiO_2 crane, the most common paper origami structure. Figure 4a shows the folding scheme, in which a 2-layer square pattern (4.8 cm × 2.6 cm, filament diameter 250 μm, center-to-center filament spacing 900 μm) is printed and then manually folded using a complex folding and unfolding sequence. The printed TiH_2 sheets are sufficiently robust to enable the assembly of this intricate design, which requires fifteen steps, including mountain, valley, and inside-reverse folds. The TiH_2 folded structure (Fig. 4b) is then dried for 12 h at room temperature, followed by annealing at 1050 °C for 2 h in air to yield the desired TiO_2 structure (Fig. 4d). Upon heating to 400 °C, the structure loses approximately 13 wt% due to polymer pyrolysis. However, upon heating to 1000 °C, a net weight gain of nearly 38% is observed due to oxidation (Fig. 4c). Given the presence of large overhang regions in each wing, this complex 3D structure could not be produced solely by printing.

By merging direct-write assembly with a wet-folding origami technique, we have demonstrated a facile pathway for assembling metallic and ceramic materials in myriad shapes. These 3D mesoscale objects may find potential applications as tissue engineering scaffolds, biomedical devices, or catalyst supports.

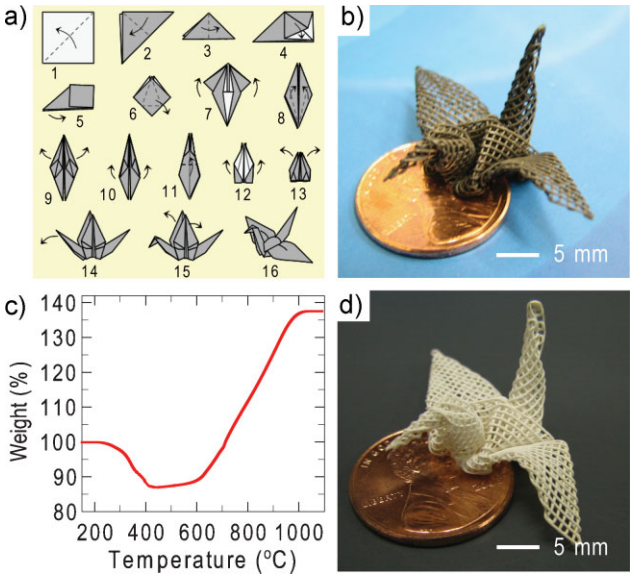

Figure 4. a) Schematic illustration of folding sequence for an origami crane. b) Optical image of printed origami TiH_2 crane. c) Thermogravimetric analysis of a dried ink filament. d) Optical image of a TiO_2 crane produced by annealing a printed origami TiH_2 crane at 1050 °C in air.

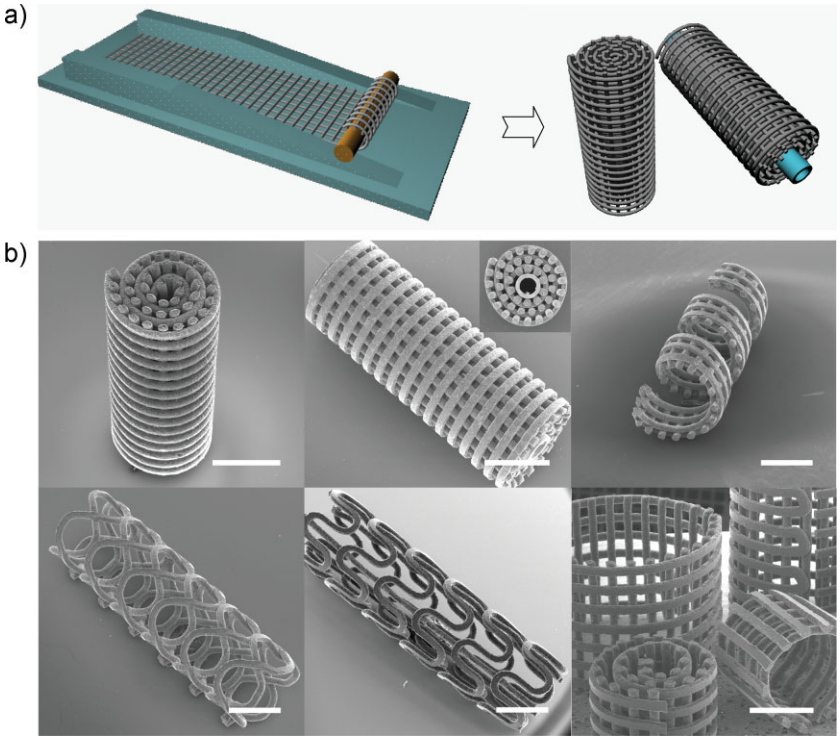

Figure 3. a) Schematic illustration of rolling procedure for high aspect ratio, cylindrical coils. b) SEM images of concentric cylindrical TiH_2 coils without and with a titanium tubular insert (top left and middle), helix (top right), stents (bottom left and right), and square latticed hollow cylinders (bottom right). Scale bar = 2 mm.

Experimental

TiH_2 Ink Preparation: Titanium hydride powder (Alfa Aesar, mean particle size ~20 μm, 4.4 wt% H_2), a triblock copolymer composed of poly(methyl methacrylate)–poly(n-butylacrylate)–poly-(methyl methacrylate) (PMMA–PnBA–PMMA) with respective block molecular weights of 23000–31000–23000 g/mol (Kuraray Co. Ltd.), and a graded volatility solvent system composed of dichloromethane (CH_2Cl_2) (b.p. 40 °C), 2-butoxyethanol (b.p. 171 °C), and dibutyl phthalate (DBP) (b.p. 340 °C) (Aldrich) are used as received. Concentrated inks are typically prepared by first dispersing 4.5g TiH_2 powder in a solution composed of 2g CH_2Cl_2, 0.6g 2-butoxyethanol, and 0.3g DBP by sonication (Fisher Scientific, FS30) for 30 min under ambient conditions. A triblock copolymer solution (0.72g polymer in 3.6g CH_2Cl_2) is then added to the resultant suspension to yield a copolymer-to-TiH_2 weight ratio of ~0.16. This suspension is then homogenized (ARE-250, Thinky Co.) and simultaneously concentrated by evaporation of dichloromethane, yielding a final colloidal ink composed of a total solids loading of ~85 wt% (TiH_2 + copolymer) and a 2-butoxyethanol: DBP ratio of 2:1. All planar and origami structures presented are created using this ink composition. Following this same procedure, however, concentrated TiH_2 inks of varying 2-butoxyethanol:DBP ratio are also produced. The inks are stable for several months when stored in a sealed vial under ambient conditions.

Ink Rheology: The ink rheology is measured using a controlled-stress rheometer (C-VOR, Malvern Instruments, Malvern, UK) equipped with a cup and

bob (C14, 14 mm bob diameter, 0.4 mm gap width) geometry at 25 °C in the presence of solvent trap to prevent evaporation. The concentrated ink (85 wt% total solids, 2-butoxyethanol:DBP ratio of 2:1) used for printing exhibited a shear elastic modulus of 0.22 MPa, as measured by an oscillatory technique at a frequency of 1 Hz.

Elastic Modulus of Printed Filaments: Dynamic mechanical analysis (RSA III, TA Instruments-Waters LLC) is used to determine the effect of solvent evaporation on the rheological property evolution of the printed ink features. Printed cylindrical ink filaments (250 μm in diameter, 15 mm in length) of varying 2-butoxyethanol:DBP ratio are mounted on a fiber compression/tension fixture with a 10 mm gap. Dynamic mechanical data are recorded under a 10.0g load and 0.1% strain at constant temperature (22.5 ± 0.5 °C) for 2 h.

Direct-Write Assembly: Planar lattices are patterned using a 3-axis micropositioning stage (ABL 9000 *x-y-z* motion stage, Aerotech Inc., Pittsburgh, PA), whose motion is controlled by computer-aided design software (RoboCAD, 3D Inks, Stillwater, OK) under ambient conditions at a relative humidity of ~20–30%. The concentrated TiH_2 ink is housed in a syringe (3 mL barrel, EFD Inc., East Providence, RI) attached by a luer-lok to a smooth-flow tapered nozzle (250 μm in diameter, *d*). An air-powered fluid dispenser (800 ultra dispensing system, EFD Inc.) equipped with a high-pressure adapter (HP7X, EFD Inc.) is used to pressurize the barrel and control the ink flow rate. The required pressure depends upon ink rheology, nozzle diameter, and printing speed, but typical values range from 100–600 psi (1 psi ~ 0.0689 bar) at 0.5–2 mm s^{-1}. TiH_2 lattices are printed onto glass substrates, with a nozzle height (*z*) of ~0.8*d* to ensure moderate adhesion to the substrate and between printed layers.

Microscopy: The printed lattices and origami forms are imaged by optical (Canon PC 1130, Canon Inc.) and scanning electron microscopy (SEM, JOEL 6060LV, JEOL Ltd.) after sputtering with Au/Pd for 30 s (Emitech K575 Sputter Coater, Emitech Ltd.). From the SEM images obtained, the center-to-center spacing between multiple filaments is measured along the *x*- and *y*-directions for the annealed structures to determine the corresponding linear shrinkage or expansion (ΔL), where the volumetric change is given by ~3ΔL.

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