

Supplementary Information

3D printed polymer objects with embedded electronics interconnected via conformally printed electrodes

Yejin Jo,^{a,b} Ju Young Kim,^a Sungmook Jung,^a Bok Yeop Ahn,^c Jennifer A. Lewis,^c
Youngmin Choi,^{a,b,*} Sunho Jeong^{a,b,*}

^aDivision of Advanced Materials, Korea Research Institute of Chemical Technology (KRICT), 19 Sinseongno, Yuseong-gu, Daejeon 305-600, Korea. E-mail: youngmin@kRICT.re.kr; sjeong@kRICT.re.kr

^bDepartment of Chemical Convergence Materials, Korea University of Science and Technology (UST), 217 Gajeongno, Yuseong-gu, Daejeon 305-350, Korea.

^cWyss Institute for Biologically Inspired Engineering, John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138, USA

KEYWORDS: 3D printing, electronics, conformal, conductive inks

Experimental Methods

Conductive Inks: We first synthesized amine-functionalized, multi-walled carbon nanotubes (NH₂-MWCNTs). A mixture composed of 1.4 g of MWCNT (97%, length: about 10 μm, Applied Carbon Nano Co. Ltd.), 0.35 g of perylene-3,4,9,10-tetracarboxylic dianhydride (PTDA, 97%, Aldrich), 350 mL of methylene chloride (99.5%, Samchun), 70 mL of triethylamine (99%, Samchun), and 14 mL of ethylenediamine (≥99%, Aldrich) is sonicated for 1 h and stirred vigorously for 24 h. The mixture is centrifuged and the precipitate is washed by methanol, methylene chloride and methanol (in that order) by centrifugation, followed by drying in a vacuum overnight. The poly(acrylic acid)-capped silver nanoparticles are synthesized by chemical reduction of Ag ions in DI water. To prevent agglomeration, polyvinylpyrrolidone (PVP, average MW ~10,000) and poly(acrylic acid) (PAA, sodium salt, average Mw ~15,000, 35 wt% in H₂O) are incorporated as surface-capping molecules and sodium borohydride is used as a reducing agent. In a typical procedure, 4.7 g of Ag nitrate (99.9%, Kojima Chemicals), 3.8 g of poly(acrylic acid), and 6.0 g of PVP were added to a three-necked, round-bottom flask containing 100 mL of DI water at a pH of 11. The resultant solution is heated to 60°C and stirred with a magnetic stirrer under a refluxing condition. When the temperature reaches 60°C, 9.7 g of aqueous sodium borohydride (98.5%, Kojima Chemicals) solution (pH = 11) is injected. After reacting for 60 min at 60°C, the synthesized Ag nanoparticles are selectively separated by centrifugation, followed by washing by DI water. To decorate the NH₂-MWCNTs with the PAA-capped Ag nanoparticles, 50 g of an aqueous NH₂-MWCNT solution with a concentration of 3 mg/ml is mixed with 6.75 g of an aqueous poly(acrylic acid) capped-Ag NP solution at a concentration of 20 wt%. After a subsequent sonication/homogenization process, the mixture is centrifuged to collect the PAA-Ag/NH₂-MWCNT hybrid material. The precipitates are then dispersed in DI water, followed by

adjusting the pH to 4. After the centrifugation process, precipitates are re-dispersed in ethyl alcohol, followed by centrifugation. The resultant precipitates are then mixed with a proper amount of Ag flakes (SF120, Ames Advanced Materials Corporation) and 50 g of toluene. After centrifugation, the precipitates are mixed manually with a proper amount of polystyrene-polyisoprene-polystyrene (SIS, styrene 22%, 12 poise @ 25 wt% in toluene, Aldrich) and 1,3-dichlorobenzene ($\geq 99.0\%$, Aldrich) in an agate mortar for 3 min. The weight fraction of conductive fillers to SIS is kept constant at 0.94 and the total solid loading is varied from 65 – 84 wt% .

Ink Rheology: The ink rheology was measured using a controlled-stress rheometer (MCR 101, Anton Paar). The elastic shear (G') and viscous loss (G'') moduli were measured in oscillatory mode as a function of controlled shear stress (1 – 10,000 Pa) at a frequency of 1 Hz with increasing amplitude sweep.

3D Polymer Objects with Embedded Electronics: Stereolithography (SLA) is used to print 3D polymer objects (Form2, Formlabs). A layer thickness is 50 μm , and a spot size of laser (with an intensity of 250 mW) is 140 μm . All conductive inks are printed using a programmable dispenser (Image Master 350PC Smart, Musashi) equipped with a nozzle with an inner diameter of 350 μm . We carried out all printing processes at room temperature without heating the stage. The printing speed and air pressure are 0.2-5 mm/sec and 100-200 kPa, respectively. The printed features are annealed at 80 $^{\circ}\text{C}$ for 1 h prior to carrying out electrical conductivity measurements, while features printed conformally and within the 3D polymer objects are dried for longer time (> 1 h) at room temperature. All electrical components are placed in surface and internal cavities within the SLA-printed polymer objects.

Structural and Electrical Characterization: The morphology of the printed features is measured by scanning electron microscopy (SEM, JSM-6700, JEOL) and optical microscopy (OM, BX

51, Olympus). The electrical resistance of the printed features is determined using an interactive digital source meter (2450, Keithley).

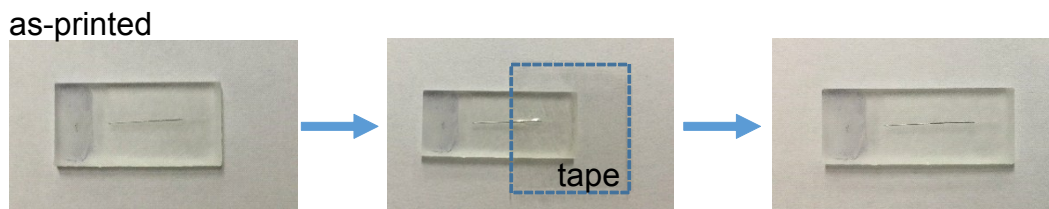


Figure S1. Photographs showing an adhesion tape-test for the electrode formed on SLA-printed polymer structure.

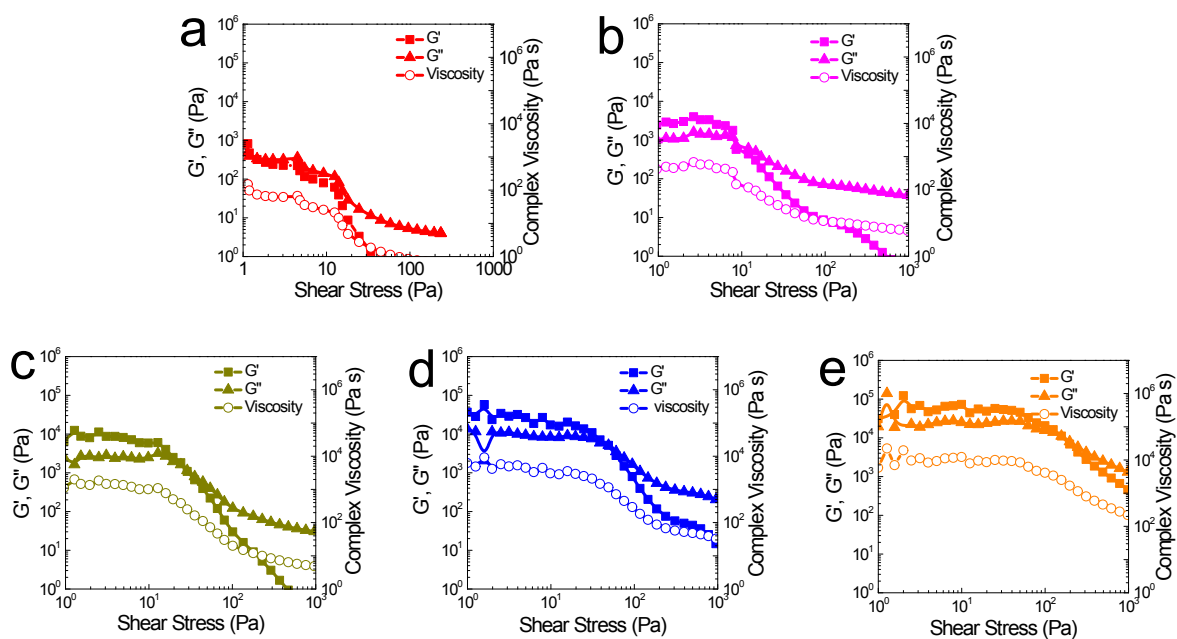


Figure S2. Rheological properties of conductive inks with different solids loadings of (a) 60 wt%, (b) 65 wt%, (c) 70 wt%, (d) 77 wt%, and (e) 84 wt%.

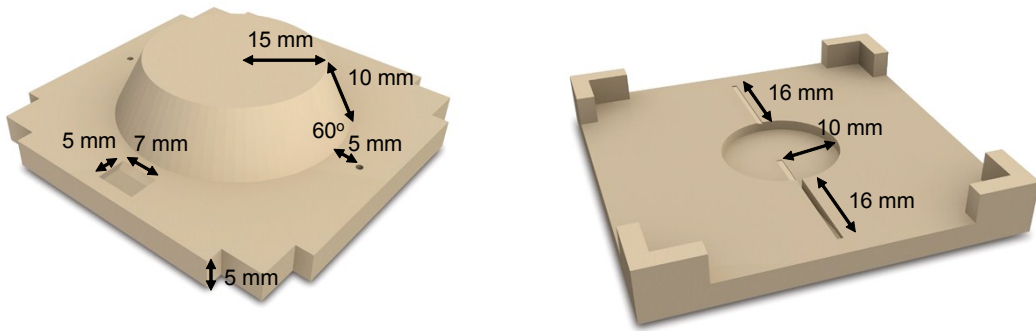


Figure S3. Schematics showing the actual dimensions of the 3D-printed embedded circuit

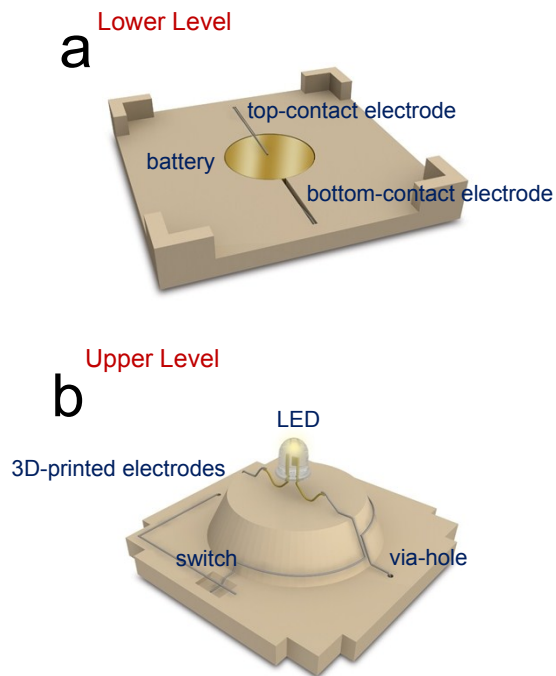


Figure S4. Schematics showing the lower and upper levels of the 3D-printed embedded circuit.

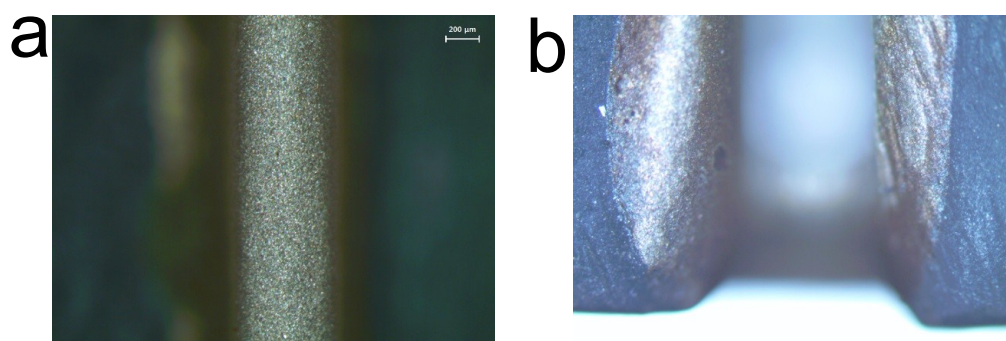


Figure S5. Optical images of electrodes printed within trenches: (a) bottom and (b) top surfaces, respectively.



Figure S6. Photograph of a well-formed interconnection between the lower and upper levels showing the voltage output of the battery embedded on the lower level.

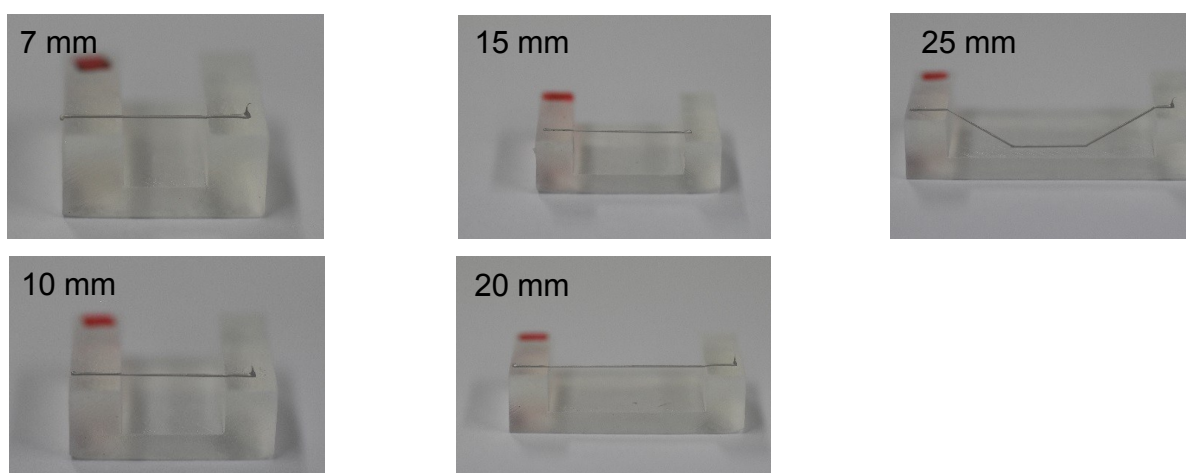


Figure S7. Photographs of electrodes suspended on the wells with different length.

Movie S1. Video of conformal printing of conductive electrodes on the upper level of a 3D polymer object.

Movie S2. Video of conformal printing of conductive electrodes on the upper level of a 3D polymer object.

Movie S3. Video of the printing process for fabricating the pressure-sensitive switch with an air gap.

Movie S4. Video of the operation of a 3D polymer object with embedded electrical components.

Movie S5. Video of the operation of a 3D polymer object with embedded printed circuit board.